CHAPTER ONE: INTRODUCTION
1.1 Grafting as a tool for polymer fabrications

Graft copolymers are polymers whose main back bone chains consist of one type of monomer units and branches are made up of other monomer units [1]. A typical graft copolymer is represented in Figure 1.1 below.

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A A A A A A A A A
B B B B B B B B B
B B B B B B B B B
B B B B B B B B
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**Figure 1.1:** A typical graft copolymer; A: main chain unit; B: branch unit.

Grafting process, by definition, involves chemical attachments of monomer branches to the backbone structures of polymer substrates [1]. Attachments are made possible by the creation of grafting sites on the host polymer chains, followed by continuous additions of monomers to grafting sites [1,2]. In other words, grafting sites initiate polymerization of monomers and the final products are graft copolymers.

Grafting is an important method of polymer fabrications because different monomers can be grafted to the polymer substrates. Grafting has been used to improve chemical and mechanical properties of cellulose fibers [2], increase water absorbency of cellulose [3], make polypropylene (PPE) more dye-receptive [4], and improve solubility [5] and plasticity [6] of chitosan. Grafting has found applications in improving dispersibility of ultrafine silica particles [7], and weathering resistance of organic materials [8]. Grafting is also a common method for synthesizing pH sensitive membranes [9,10], blood compatible membranes [11,12] and cation captured membranes [13,14]. In coating formulations, grafting is an important process since extensive monomer grafting promotes good adherence of coated layers to base substrates [8]. Thus, for coating formulation, good grafting is always desired.
1.2 Free radical grafting

The route leading to graft copolymers generally involves the reaction of fresh monomers with a previously prepared parent homopolymer or copolymer [1]. While some graft copolymers were reported to form by ionic mechanisms [1,2], free radical grafting has been the most popular process to efficiently produce commercial quantities of graft copolymers [1,2].

The mechanism of the free radical grafting process mainly involves creations of free radical sites (or reactive sites) on parent polymer substrates [1,2]. These sites can be formed by high-energy irradiation (gamma, electron beam) [1-3,11-14], by initiators [1,2,4,8,10], or by chemical reactions [2,7,9]. In the high-energy irradiation method [1], radiation rays have sufficient energy to induce bond scissions of polymer chains or monomer molecules, leading to the production of free radicals. Free radical formation by gamma irradiation is represented in Scheme 1.1. Free radicals can be generated as products of chemical reactions, such as oxidation or reduction of suitable chemical species [1,2,7,9]. In the initiator method, free radicals are formed by the decompositions of initiators under heat [1] or ultraviolet (UV) irradiation [1,2,4,8]. These free radicals then react with polymer chains by abstracting labile hydrogen atoms. As a result, radical sites are created on the structures of substrates. Once radical sites are formed, they can initiate polymerization of adjacent monomers, producing graft copolymers. Grafted chains stop growing when being terminated by other nearby free radicals. The UV grafting process of a monomer to a polymer substrate in the presence of a photoinitiator is presented in Scheme 1.2.
Scheme 1.1: Free radical formation by gamma irradiation.

Scheme 1.2: UV grafting of a monomer to a polymer substrate with the presence of photoinitiators where PI' is the free radical formed upon photoinitiator photolysis.

In the scope of this project, most of experiments carried out were based on the initiator technique in which the initiators were photoinitiators in the presence of a UV source. However, in certain sections of the project, high-energy irradiation technique was also utilized for comparative studies. Parent polymers or substrates used were PPE and cellulose. When the monomers and substrates are present together initially and subjected to irradiation, the process is known as mutual or simultaneous method [1-7, 10]. In a preirradiation process, the polymer is first exposed to the radiation to produce long-lived or trapped radicals [1, 2, 9, 12-14] which lead to grafting when they are in contact with monomers. Although high grafting efficiencies can be achieved in this process, it is
difficult to generate and maintain an adequate concentration of radicals in solid polymer [1], and thus in this project, only the spontaneous method was employed.

1.3 Factors that influence free radical grafting process

There are a large number of factors which can influence the outcomes of the grafting process. The main factors are listed and discussed below.

1.3.1 Irradiation methods

There are two irradiation methods often employed for grafting namely high-energy irradiation from an electron beam, plasma or gamma source, and a low-energy ultraviolet (UV) irradiation from a high pressure mercury vapor lamp. In this project, UV and the high-energy gamma irradiations are used and these two sources of radiation will be the main concern for discussions in this section.

1.3.1.1 UV irradiation

In the UV irradiation method, the presence of photoinitiators and or sensitizers is crucial to ensure good and efficient grafting because UV light alone is not sufficient in energy to lead to bond scissions [2,15]. Photoinitiators absorb UV light and undergo photolysis, process to generate free radicals [1,2]. However, photosensitizers are totally different from photoinitiators since they do not undergo the photolysis but merely absorb the energy from a UV source and transfer that energy to another molecule that forms primary reactive species. Furthermore, a sensitizer compound is neither consumed nor changed structurally.

As previously mentioned, in this project, most experiments are based on the simultaneous method. However, due to its design in which substrates are submerged in monomer solutions, two competing processes are expected [2,3,16,17,18]. When UV light passes through a solution, it is likely to trigger the homopolymerization of the monomer in the solution as well as the grafting process, leading to a number of possible effects. Firstly, the homopolymerization reduces the amount of monomer molecules available for grafting [2,3]. Secondly, it increases the viscosity of the solution, and thus, limiting movements of
free radicals and the monomer or reducing exposure time [16-18]. Furthermore, the homopolymer formed may be opaque and thus partially block the passage of UV light, resulting in smaller amounts of radicals generated [18]. As a result, supply of monomer and free radical to grafting process will be reduced, leading to poor grafting. Several methods can be employed to address the problem caused by homopolymerization. In several publications [16-18], the presence of styrene as a comonomer has been reported to enhance the grafting of MMA to PPE substrates by reducing the formation of the homopolymer and thus, allowing longer UV exposure time. In another method [19], inorganic salts of Cu$^{2+}$, Fe$^{2+}$ and Mohr’s salt are reported as effective homopolymer suppressors due to the scavenging of monomer radicals by the inorganic ions.

1.3.1.2 Gamma irradiation

Grafting by gamma irradiation is more efficient because high penetration of gamma rays ensures quick formations of radical sites in the substrate structures [1,2,12-15,17-21]. With fewer steps involved, the grafting is faster and can compete directly with the homopolymerization for monomers. Both simultaneous [2,3,15,17-21] and preirradiation [12-14] methods were successfully employed to produce various graft copolymers. Since high-energy radiation is not selective, efficient grafting can be obtained only if the polymeric substrate can interact stronger with gamma radiation than the monomer can [1]. In this way active sites will be primarily generated on the polymeric substrate backbone. One way to indicate efficiencies of grafting is to compare the G values (the number of radicals formed per 100 eV absorbed) for the monomer and polymeric substrate [1,2]. However, the simultaneous gamma irradiation method has a similar problem with homopolymer formation as in the UV irradiation method. Technique involving styrene as a comonomer [17,18,22] or inorganic salts as homopolymer suppressors [19,23] can be similarly employed to enhance grafting.

1.3.2 Substrates

Since the grafting process involves the polymerization of monomers at reactive sites on a parent polymeric substrate, the ability of free radicals to react with polymer chains in the substrate to generate grafting sites and the ability of monomers to access to such sites is
of paramount importance. One of the factors that partially control the monomer and free radical accessibility is crystallinity of the parent polymer which can be defined as the degree of the orderly fashion polymer chains packed in their solid state [1,24]. It has been widely accepted that crystalline polymers are not 100% crystalline but contain crystalline (ordered) as well as amorphous (disordered) regions [1,2,24] and most grafting occurs in the amorphous regions [2,15]. With cellulose as an example, in its crystalline regions, cellulose chains are tightly packed, making it impossible for monomers or free radicals to squeeze in [2]. On the other hand, in its amorphous regions, irregularities of cellulose chains such as irregular branching, atacticity, chain ends and chain folding prevent complete crystallization, thus allowing significant spaces to accommodate relatively large molecules of monomers, radicals or solvents [2,24].

Using UV irradiation and photosensitizers, Hon [25] demonstrated that photochemical reactions occurred exclusively at the amorphous regions of cellulose and the amount of free radical species formed were linked to the degree of crystallinity of the polymer. Arthur and coworkers [26] used the high-energy gamma irradiation to generate free radicals on cellulose and reported that free radicals located in amorphous regions reacted readily with water and were terminated. However, in the crystalline regions, even after long periods of time in solvents which caused large dimensional changes in the cellulose structure, the trapped free radical were not terminated by reaction with solvents or water.

The effect of water on cellulose structure was also reported by Hatakeyama [27] in which he found the crystalline regions changed to the disorder structure in the presence of water, causing the increase in the amorphous region. At the same time, the amorphous region reorganized in different ways and thus irreversible structural changes in the amorphous region occurred.

Beside crystallinity, the presence of functional groups in polymer chains can greatly influence the grafting process. Polymer substrates are generally classified into two types: polar substrates (e.g., cellulose and cellulose derivatives) and non-polar substrates (e.g., PPE and polyethylene), based on the presence of polar functional groups in the
substrates. Grafting of monomers such as styrene [2,28-47], acrylonitrile (AN) [2,30,31,40,42,48-51] and methyl methacrylate (MMA) [2,16-18,22,31,35,36,40,42,52,53] to polar materials like cellulose and cellulose derivatives has been found to be dependent on the presence of solvents such as alcohols, dimethyl formamide or water which can wet or swell the cellulose structure. On the other hand, the grafting of the same vinyl monomers to non-polar substrates like PPE and polyethylene can occur in the presence or absence of solvents since the monomers themselves swell the polymer substrates [15-19,21-23,54-59].

Beside cellulose, its derivatives and polyolefins, grafting of monomers to a number of materials such as chitosan [4,5], rubber [60], poly(vinyl chloride) [15,61] and polyethylene terephthalate [15] has been successfully attempted.

Substrate thickness also plays an important role in determining the degree of grafting. In separate studies of styrene grafting to PPE using gamma irradiation, Yen [15], and Krassig and Stannet [20] reported that the grafting yield increased with decreasing film thickness. This property was explained to be due to more ready access of monomers into the PPE structure. For thick PPE or cellulose films, graft was thought to be mostly distributed on the surface, while for thin films, graft can penetrate more deeply into the substrate. Krassig and Stannett [20] also found that the grafting of styrene to cellulose acetate in pyridine by high energy radiation varied according to substrate thickness and was attributed to the combination effect of cellulose acetate swelling and styrene diffusion.

1.3.3 Monomers

A number of monomers have been successfully grafted to various materials by free radical grafting methods. As previously discussed, styrene [2,28-47], AN [2,30,31,40,42,48-51] and MMA [2,16-18, 22,31,40,42,52,53] have often been used in grafting studies. Other common monomers are methacrylic acid [62,63], 2-hydroxyethyl methacrylate [64,65], acrylamide [65], acrylic acid (AA) [66], methyl-, ethyl-, butyl acrylates [67,68] and maleic anhydride (MA) [69-71]. However, for a certain substrate,
different monomers have different reactivity towards grafting to the substrate when exposed to the same condition. For example, Abdel-Razik [67] reported that ethyl acrylate photografted to ethyl cellulose better than MMA and methyl acrylate did in the presence of photoinitiators. However, a study by Yen [15] showed acrylic acid, ethyl acrylate, n-butyl acrylate and acrylonitrile did not graft to PPE by gamma or UV irradiations while grafting yields were obtained for styrene and MMA. The indication of all these studies is that there is no general assumption regarding the grafting performance of a monomer as its grafting property varies from case to case.

The presence of two monomers can result in good grafting of both monomers. But the grafting of a binary monomer mixture is very complex because it can be considered as a copolymerization process of two monomers on the surface of the polymer substrate. The kinetics of copolymerization between two monomers in the solution is itself complicated and generally presented by the terminal model in Scheme 1.3 [1,2]. However, there are copolymerizations which do not conform to the terminal model, resulting in deviations. Some examples of causes leading to deviations include:

a) Penultimate unit effects[2,72-75]: occur when the rate constant for propagation is a function not only of the monomer and the chain end unit but also of units preceding chain end;

b) Non-steady-state behavior [2]: occurs when equation A (Scheme 1.3) of the terminal model is not satisfied;

c) Complex formation [2,74]: between chain ends and monomers or between monomers.

The presence of a solvent in the binary monomer mixture may further affect the propagation rate and reactive ratios of the copolymerization of monomers. Solvent effects have been discussed in a number of publications [76-88] and the effects are attributed to various factors such as: a) electrostatic repulsion of charge monomers and radicals, b) changes in monomer polarity, c) participation of monomer complexes, d) hydrogen-bonding of monomers with the solvents and e) solvent dielectric effects. The most important model to explain solvent effects in radical copolymerization was the “bootstrap” model proposed by Harwood [82] in which he stated that copolymers having
\[
\begin{align*}
M_1^+ + M_1 & \xrightarrow{k_{11}} M_1M_1^+ \\
M_1^+ + M_2 & \xrightarrow{k_{12}} M_1M_2^+ \\
M_2^+ + M_1 & \xrightarrow{k_{21}} M_2M_1^+ \\
M_2^+ + M_2 & \xrightarrow{k_{22}} M_2M_2^+ \\
\end{align*}
\]

\[k_{12}[M_1][M_2] = k_{21} [M_2'][M_1] \quad (A)\]

**Scheme 1.3:** Terminal model of the copolymerization kinetic of comonomers \(M_1\) and \(M_2\) with \(k_{11}\) and \(k_{22}\) as propagation rate constants of the homopolymerization of \(M_1\) or \(M_2\); \(k_{12}\) or \(k_{21}\) are the propagation rate constants of the copolymerization

These compositions have the same sequence distribution regardless of the solvent employed for their preparation and that a growing copolymer radical seems to control its own environment during copolymerization. He proposed that solvent effects in copolymerization are not manifested in the chain-end reactivity but rather in a solvent partitioning, whereby an equilibrium may exist in which monomers are distributed between free solvent and the domains of growing polymer radicals.

The kinetics of copolymerization is relevant in providing clues to what is happening in the grafting of the binary monomer mixture to a polymer substrate. Previous studies [15, 56] demonstrated grafting characteristic of binary monomer systems is different from that of a single monomer. However, there is a great difference between the two processes since the latter is strongly diffusion controlled and influenced by other factors, such as irradiation methods, parent polymers and additives, thus limiting the straight application of copolymerization models.
Using preirradiation method, Choi and Nho [89] obtained good grafting of binary monomer mixture of AN with acrylic acid, methacrylic acid or glycidyl methacrylate to polyethylene films. Furthermore, the presence of sulfuric acid was found to be beneficial in enhancing grafting yields. However, they found composition of grafted chains varied with types and concentrations of the comonomers in the feed.

Gupta and Sahoo [90] investigated ceric ion initiated grafting to cellulose from binary mixture of AN and methyl acrylate and found that grafting yields and compositions were dependent on monomers concentrations. They suggested the presence of methyl acrylate allowed AN monomer to participate effectively in the graft copolymerization to cellulose and the system showed tendency to form monomer blocks.

Ang et al [56] studied gamma grafting of AN to PPE using simultaneous method in the presence of methanol as the solvent and found that grafting yields were greatly improved when styrene was used as a comonomer. Grafting yields and the monomer compositions of grafted chains were reported to change with methanol and monomer concentrations.

By using gamma irradiation, Beddows et al [91] showed that the grafting of styrene and maleic anhydride or vinyl acetate and maleic anhydride to cellulose was not non-steady state in character and grafting yields as well as grafted chain compositions were influenced by monomer concentrations and solvents used.

1.3.4 Solvents

Solvents play an important role in the grafting process and their effects vary according to circumstances. As previously discussed in Section 1.3.2, for substrates such as cellulose and its derivatives, the presence of suitable solvents in the monomer solution has been found to be essential in ensuring good grafting yields.

Again, with cellulose as an example, Usmanov et al [31] grafted AN to cellulose by gamma irradiation using simultaneous method and found water and alcohols to be the most suitable solvents for obtaining high grafting yields while benzene was not suitable.
Dilli and Garnett [35] investigated the grafting of the monomers, styrene, MMA, vinyl acetate, 2- and 4-vinylpyridine, to cellulose by gamma irradiation and reported poor grafting yields when benzene, hexane, cyclohexane and ethyl acetate were present as solvents. On the other hand, good grafting was achieved when DMF, acetone and alcohols were used as solvents. They also reported that short chain alcohols were more effective in enhancing grafting than the long chain ones.

The dependence of the grafting process on solvents is commonly explained on the basis of the wetting and swelling theory [15]. According to the swelling theory [38], the swelling of cellulose by the solvents such as water, alcohols and DMF leads to the opening of the cellulose structure for easy access of the monomer and free radical to the grafting sites, thus allowing the grafting to proceed. The swelling of a solid is defined by its ability to take up a liquid while at the same time it does not lose its apparent homogeneity, i.e., its dimensions are enlarged and its cohesion is diminished [2]. Solvents such as benzene, hexane, cyclohexane and ethyl acetate did not swell cellulose, and thus, low grafting was resulted. In the wetting theory, the penetration of the monomer into the molecular space of cellulose is facilitated by the ability of the solvent to wet the cellulose structure. Failure of the solvent to do so will lead to poor grafting. For example, in the grafting study by Usmanov et al [31], poor grafting yields of AN to cellulose in benzene was explained by the author for being due to solvent’s inability to wet cellulose.

The same swelling and wetting mechanisms can be used to explain the solvent effects on the grafting of monomers to non-polar substrates such as polyolefins. However, it is very common for the non-polar substrate to be swollen by the monomers and thus the grafting process can proceed in the absence of solvents [57-59]. On the other hand, it has been observed by a number of researchers [15,54-59] that the presence of some solvents such as short chain alcohols, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) greatly enhance the grafting of monomers such as styrene, MMA to polyolefins by both gamma and UV irradiations despite poor substrate swelling. This phenomenon is explained by Odian et al [54] to be due to the Trommsdorff-type effect in which poor solubility of grafted polymers in such solvents leads to the tight coiling of growing
grafted polymer chains. Chances of grafted chains to be terminated by adjacent chain radicals are therefore reduced, resulting in the lower termination rate compared to the propagation rate and thus, leading to the acceleration of chains’ growth.

Degrees of monomers grafted to substrates are also dependent on concentrations of the monomers and solvents used. There is usually an optimum concentration of the monomer at which the grafting yield is highest and is called Trommsdorff peak [56,58]. The effect is referred to in this way because of Trommsdorff effect at that concentration where the high viscosity of the medium inhibits the termination rate, while at the same time does not significantly change the propagation rate of the grafting [56,58].

In their study of gamma grafting of styrene to polyethylene with methanol as a solvent, Machi et al [92] proposed a mechanism in which grafting rates were said to vary according to the viscosity of areas adjacent to grafting sites. According to their proposal, methanol reduces the concentration of the occluded styrene in polyethylene, hence, the swelling of polyethylene decreases and the viscosity of the grafting medium increases (styrene swells polyethylene while methanol does not). At low styrene concentrations, the initiation rate and the propagation rate are low but the termination rate is also low due to restrictions of radical movements at high viscosity. As styrene concentration increases, the viscosity is lower, leading to higher propagation and termination rates. However, rises in both rates are not equal and there is a point where the difference between the propagation and termination rates is the highest and the maximum styrene grafting is achieved.

Consideration of solvent effects can be extended to their influence on the kinetics of free radical polymerization, directly or indirectly. While reviewing kinetic relationships in radical polymerization, Scott and Senogles [93] listed possible effects of solvents on initiation (cage effect), propagation (monomer-solvent complexation) and termination (chain transfer and diffusion effects) steps which are resulted from their complex interactions with free radicals, monomers and their influence on the viscosity of the reacting medium. The discussion is relevant especially in the simultaneous method where
free radical polymerization competing with grafting, which itself is a similar process. Furthermore, Hermans [94] investigated the grafting of styrene and MMA to cellulose and found solvents such as ethanol and carbon tetrachloride played important role as chain transfer agents. On the other hand, in Section 1.3.3, the discussion of solvent effects on the grafting of binary monomer mixture has further illustrated their important role in the process.

1.3.5 Photoinitiators

In the UV grafting process, the presence of photoinitiators is to generate free radicals for creating grafting sites. The efficiency of the process is dependent on factors such as the ability of the photoinitiator to undergo photolysis when exposed to a UV source, the number of free radicals produced per photoinitiator molecule, the ability of those radicals to diffuse into the polymer structure and their reactivity towards the polymer in order to abstract hydrogen atoms and create grafting sites. These factors vary according to photoinitiator types and thus, different grafting performance is expected for each type used.

Recent studies by Garnett et al [16-18, 46,47] and Viengkhou et al [53] showed that the presence of photoinitiators was very effective in accelerating grafting reaction of MMA to cellulose and polyolefins by UV irradiation. However, they reported the variation of grafting yields according to photoinitiators used despite of the same experimental condition. By using different photoinitiators, Garnett et al [16,17] demonstrated the relation between the efficiency of photoinitiators with the degree of grafting by showing that Irgacure 1700 and 1800 photoinitiators performed better than Irgacure 184 and benzoin ethyl ether. Irgacure 1700 and 1800 photoinitiators contained bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide (DMBAPO) which could produce four radicals per molecule upon photolysis while Irgacure 184 and benzoin ethyl ether could produce two. However, they revealed that Darocur 1173 gave equivalent or better results than those obtained with both Irgacure 1700 and 1800 photoinitiators despite the fact that the previous generated only two radicals per molecule, and thus, stressing the importance of the reactivity of radicals.
The grafting process is also influenced by the concentration of photoinitiators in the solution. Using xanthone, 2-chloroantraquinone and phenylisulfide as photoinitiators, Kubota et al [66] studied the effect of photoinitiator concentrations on grafting yield of acrylic acid to cellulose by UV irradiation and found that there was an optimum concentration at which the grafting yield was the highest. The grafting was reported to decline rapidly when the photoinitiator concentration exceeded that value. This effect was attributed to the higher formation of homopolymer which directly compete for the monomer with the grafting process.

The presence of photoinitiators in the solution is not only beneficial for UV irradiation method but also for gamma irradiation method. Garnett et al [17,22] and Viengkhon et al [53] investigated the effect of photoinitiators on grafting of MMA or MMA/styrene to cellulose and polypropylene respectively by gamma irradiation and found photoinitiators markedly enhanced grafting yields and the effect was due to the generation of additional free radicals by the photoinitiators.

1.3.6 Oxygen

Oxygen can react with free radicals of reactive sites to form peroxy and hydroperoxy radicals. These species can continue reacting with other radicals or abstracting hydrogen atoms from the polymer to produce diperoxides and hydroperoxides which, in turn are very unstable and subsequently decompose, releasing PO\(^\cdot\) and OH radicals [23]. The whole process is presented in Scheme 1.4.

Oxygen presence is very important for some grafting methods especially the preirradiation method where the hydroperoxides and diperoxides can serve as the source of free radicals [12-14,23].
\[ \gamma \]
\[ \text{PH} \rightarrow \text{P}^\prime + \text{H}^\prime \]
\[ \text{P}^\prime + \text{O}_2 \rightarrow \text{POO}' \]
\[ \text{POO}' + \text{PH} \rightarrow \text{POOH} + \text{P}' \]
\[ \text{POO}' + \text{P}' \rightarrow \text{POOP} \]
\[ \text{POO}' + \text{POO}' \rightarrow \text{POOP} + \text{O}_2 \]
\[ \text{P}^\prime + \text{P}' \rightarrow \text{P-P} \]
\[ \text{POOP} \rightarrow \text{PO}^\prime + \cdot \text{OP} \]
\[ \text{POOH} \rightarrow \text{PO}^\prime + \cdot \text{OH} \]

**Scheme 1.4:** Reactions of radicals with oxygen in which PH represented polymer substrate.

Using the inclusion technique which involves the absorption of the monomer to the substrate before the irradiation, Huang *et al* [32] grafted styrene to cellulose by gamma irradiation and found the presence of oxygen enhanced rather than inhibited the grafting reaction at high doses above 2 Mrad. However, for low radiation dose range below 2 Mrad, grafting was more effective in vacuum. The phenomenon was attributed to the important role oxygen played in the intermediate radical mechanism.

For simultaneous irradiation methods, oxygen generally hinders the grafting process. Studies by Guthrie *et al* [38,39] reported the presence of oxygen caused a decrease in the grafting rate of styrene to cellulose by gamma irradiation in the initial stages and this effect seemed to decrease with increasing exposure to radiation. The observation was thought to be due to the quenching of reactive cellulose radicals by oxygen before grafting could occur.

Garnett *et al* [17] demonstrated that the gamma grafting of MMA to cellulose and PPE could be substantially enhanced by purging the monomer solution with nitrogen gas to remove oxygen. According to the authors, the method restricted the formation of less
reactive peroxy radicals, leaving a pool of the more reactive species [R'] for grafting. In similar studies, Garnett et al. [16,17] showed that the nitrogen purging technique was also effective for MMA grafting to cellulose by UV radiation in the absence of photoinitiators.

However, the oxygen effect on grafting should be treated carefully because it varies according to oxygen concentrations. Using simultaneous UV irradiation method with anthraquinone as the photosensitizer, Geacintov et al. [42] found that with very long UV exposure, grafting was higher in the presence of air than in vacuum. On the other hand, when air was bubbled through the reaction mixture, both grafting and homopolymerization were inhibited. The effect was attributed to complex reactions of cellulose radicals with oxygen and hydroperoxy radicals to produce hydrogen peroxide as presented in Scheme 1.5 below.

![Scheme 1.5: Reactions of cellulose radicals with oxygen and hydroperoxy radical.](image)

1.3.7 Additives

Additives may be present in small percentages in monomer solutions but they often have profound impacts on the grafting process. The most common additives are multifunctional monomers, inorganic salts and acids and the effect of each additive type on the grafting process is discussed as below.

1.3.7.1 Multifunctional monomers

Multifunctional monomers are often high molecular weight monomers which contain more than one double bond in their structures, and thus, can act as cross-linking agents in
free radical polymerization. Studies by various researchers [17-19,62-64,95] have shown that the presence of multifunctional monomers significantly enhances the grafting process.

The enhancement effect of multifunctional monomers has been mainly attributed to the branching of the growing grafted chains in which double bonds of the introduced polyfunctional component act as new sites for the grafting initiation [19,62]. Furthermore, it has been pointed out by several researchers [62,63] that this effect is favored by the number of double bonds as well as molecular weights of multifunctional monomers.

Kubota and Koyama [62] showed that trimethylolpropane triacrylate (TMPTA) which contains three double bonds per molecule was more effective than N,N'-methylenebisacrylamide (MBAAm) which has two double bonds per molecule in enhancing the grafting of methacrylic acid to polyethylene by UV irradiation with xanthone photoinitiator. The different performances between the two monomers were probably due to more branching of grafted chains in the case of TMPTA.

On the other hand, Kondo et al [63] found that the grafting yield of methacrylic acid to polyethylene increased with the number of ethylene glycol units when different ethylene glycol dimethacrylate (EGDMA) derivatives were used as additives. The effect was attributed to higher accessibility of double bonds for further grafting in the long chain monomers.

High concentrations of multifunctional monomers are also beneficial for the grafting process. In the same study, Kubota and Koyama [62] reported that the presence of more MBAAm caused a marked increase in the grafting which was a result of higher content of the multifunctional monomer in grafted chains. A similar trend between EGDMA concentrations and grafting yields were also found by Kondo et al [63].
1.3.7.2 Inorganic salts

Inorganic salts can affect the grafting process via chemical interactions with the grafting system. As previously discussed in Section 1.3.1, inorganic salts of Cu$^{2+}$, Fe$^{2+}$ and ammonium ferrous sulfate hexahydrate can be used to suppress homopolymerization of monomer by scavenging radicals and thus, leaving more monomer for grafting [19,23].

Suzuki and Ogawa [96] studied simultaneous gamma grafting of styrene to rayon in the presence of oxygen and found the process was enhanced in the presence of reducing cations such as Ti$^{3+}$, Sn$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Cr$^{3+}$. According to the authors, the acceleration was mainly caused by the decrease of the induction period caused by the oxygen in polymer phase.

However, inorganic salts can strongly influence the grafting by interfering in the diffusion of monomers to the substrate and the process is called the partitioning effect [19,21,58]. Inclusion of salts in the monomer solution leads to an increase in the concentration of monomer in the solution absorbed within the backbone polymer when compared with the original bulk grafting monomer solution. The effect is attributed to the reduced solubility of the monomer in the bulk solution because of the presence of dissolved electrolyte and thus, permitting higher concentration of monomer to be available for grafting. Garnett et al [58] investigated the swelling of polyethylene by styrene and reported that the amount of absorbed styrene increased with increasing concentrations of LiClO$_4$ in the monomer solution. Using simultaneous gamma irradiation, they showed the inclusion of LiClO$_4$ accelerated the grafting of styrene in methanol. However, by comparing different added lithium salts, the authors found the enhancement of grafting yield dramatically changed with the nature of anions.

Depending on the nature of the substrate, the partitioning can also occur to the added salts [19,58]. For non-polar substrates, the inorganic salt will partition in the more polar bulk monomer solution and thus, accelerating the partitioning of the monomer into the backbone polymer, resulting in good grafting. For polar substrates, the electrolytes can access the polymer structure and the enhancement effect can only occur later in the
grafting process when the grafted chains reduce the polarity of the substrates compared to that of the bulk monomer solution.

1.3.7.3 Mineral acids

The partitioning effect has also been observed with mineral acids. Several studies [19,21,58] have shown that the presence of acids such as sulfuric acid lead to the enhancement of grafting yields. On the other hand, acid effects can be beyond the physical process illustrated by their interactions with solvents such as methanol and ionizing radiation to produce additional free radicals, leading to acceleration of grafting [18]. However, a study by Garnett et al [58] showed that not all acids have the enhancement effect, with HCl strongly inhibit grafting of styrene to cellulose by gamma irradiation. The inhibition is proposed to be due to the termination of the propagating chain by chlorine species.

1.4 Characterization of graft copolymers

Several techniques have been utilized to prove the presence of chemical bonding between the grafted chains and parent polymer substrates. However, these techniques can only prove the presence of monomer units in the grafted substrate. The following are the techniques commonly used to show that grafting has occurred.

1.4.1 FT-IR spectroscopy

This method is the most convenient one because the characterization can be quickly carried out with little preparation. The principle of the technique involves detecting the IR absorption signatures of the grafted monomers by comparing FT-IR spectra of graft copolymer with the one of the original substrate. There have been a number of studies [12,14,97-102] which successfully utilizing the method to implicate the presence of grafted chains.

For example, Imrisova and Maryska [97] compared the spectrum of the cotton substrate with the one of the AN-grafted cotton copolymer and found the presence of an intense absorption band at 2249 cm\(^{-1}\) due to valency vibration of the nitrile group.
Kwon et al [12] examined spectra of polyethylene glycol methacrylate-grafted polyethylene films and reported the stretching peaks of the carbonyl group at 1730 cm\(^{-1}\) due to the grafted monomer units.

However, it should be noted that the method is only indicative and its successful application very much depends on the thorough extraction of homopolymer from grafted substrate. Failure to do so will lead to spectra displaying absorption peaks of the homopolymer and grafted chains and thus resulting in incorrect analysis.

1.4.2 SEM

The grafting of a monomer to a polymer substrate often leads to the alteration of the polymer morphology which can be observed by SEM. Guthrie and Tune [100] applied the method to examine MMA grafted cellulose substrates and found that the grafting was evidenced by the reduction of cellulose fiber lengths and orientations. However, the coverage of grafted poly(MMA) seemed to vary with initiation methods in which the photochemically-initiated graft copolymer showed good surface coverage by poly(MMA) while it was localized and dense in places for the Ce (IV)-initiated one.

Using SEM, Kwon et al [12] showed that the grafting of polyethylene glycol methacrylate to polyethylene changed its physical properties. This was evidenced by the decrease of absorbed protein and platelet adhesion to the substrate surface with the grafting yield in human plasma protein absorption test.

1.4.3 Thermal analysis

Incorporation of grafted chains to a parent polymer may change its thermal characteristics. Guthrie and Tune [100] studied thermal behavior of cellulose-MMA graft copolymers and the original cellulose substrate by differential scanning calorimetry (DSC) and found that the endothermic decomposition peak emphasis shifted from that of cellulose (350 °C) to that of poly(MMA) (375 °C) as the MMA grafting level increase. In the same study, based on the activation energy of decomposition (\(E_a\)) values which were calculated from weight loss/temperature data using Broido method of analysis, they
found that those values decreased with increasing grafting yields and were lower than that of the cellulose substrate.

1.4.4 Water contact angle
This method utilizes changes in water contact angle to indirectly implicate the presence of grafting. Kwon et al [12] showed that the contact angle of polyethylene glycol methacrylate-grafted polyethylene was lower than that of polyethylene and decreased with the increasing extent of grafting due to the hydrophilicity of grafted polyethylene.

Using the critical surface tension values of wetting which was calculated from contact angle measurement on cellulose-MMA graft copolymer carbanilate films, Guthrie and Tune [100] found that those values decreased with increasing grafting yields because of the high hydrophobicity of poly(MMA) compared to cellulose.

1.5 Charge transfer (CT) complex polymerization
The complex formation concept between electron poor acceptor (A) and electron rich donor (D) is a common concept in organic chemistry. However, recent discoveries of spontaneous polymerization of complexes formed between electron poor acceptor and electron rich acceptor have sparked interests worldwide. These discoveries were very important since they promised a new coating and curing technology in which usage of photoinitiators was no longer necessary. Complete removals of photoinitiators from coating formulas are desirable because they are potentially toxic and expensive [103]. They may remain as impurities embedded in the polymer coating if not completely used up in the polymerization process. The coating products will be more stable and can be employed in outdoor application with no or minimal discoloration if photoinitiators are not present in the coating formulations.

1.5.1 Charge transfer complex polymerization mechanisms
By definition, a charge transfer complex is resulted from interactions between electron poor acceptor (A) and electron rich donor (D) [18,103-105] under the influence of a radiation source. Electron poor acceptors are called as such because of the presence of
electron withdrawing groups such as anhydrides, esters, imides, amides adjacent to double bonds in the molecules [18,103]. These groups withdraw electrons away from double bonds, making them electron poor in properties. Similarly, electron rich donors are referred to as such because of the presence of electron rich functional groups such as ethers, phenyl groups located near double bonds of the molecules[18,103]. These electron rich functional groups tend to increase the electron density in double bonds, making them comfortable in accommodating positive charge. Strong interactions between donors and acceptors may lead to the coloring of the monomer solution which fades as the polymerization proceeds.

When these complexes are exposed to UV lights, spontaneous polymerization occurs. The exact mechanism of charge transfer complex polymerization is unknown. However, many reaction models have been proposed and the most convincing one is the theory of the polymerization initiated by tetramethylene intermediates [104,105]. According to this theory, strong interactions between donors and acceptors under UV lights produce tetramethylene intermediates which can be a pure ionic Zwitterion nature or a 1,4 biradical nature. These intermediate species can initiate free radical or ionic polymerization. Jönsson and coworkers [104] also proposed the presence of fused radical ionic pairs as the products of CT interacted. These pairs can be either ionic or radical in nature and their dissociation can initiate both free radical as well as ionic polymerization. The mechanism is represented in Scheme 1.6.

Hall and Padias [105] further expanded the tetramethylene theory to explain spontaneous polymerization beyond CT interaction. They proposed that the rates of tetramethylene formation and of spontaneous polymerization are enhanced when there are forces to bring donor and acceptor monomers together. Possible spontaneous polymerization has been observed from interaction modes such as protic acid/base, Coloumbic attraction, Lewis acid/base and hydrophobic and hydrophilic interactions [105].
Radicals + Monomer → Polymer
Ions + Monomer → Polymer

Scheme 1.6: Tetramethylene intermediates and formation of radical ions mechanism.
Other mechanisms of polymerization involving donors (D) and acceptors (A) that should also be considered are as follows:

**i) Charge transfer complex acts as monomer (Scheme 1.7)**

In this mechanism, CT complex is thought to act as one monomer [105]. It polymerizes in a certain order, forming an alternating polymer

\[
\begin{align*}
\text{D}^+ + \text{A} \rightarrow \text{DAD}^- \\
\text{A}^- + \text{D} \rightarrow \text{ADA}^-
\end{align*}
\]

**Scheme 1.7:** Charge Transfer complex act as monomer.

**ii) Matrix polymerization (Scheme 1.8)**

In this mechanism, donors and acceptors are thought to realign in an alternative order in the monomer solution [105]. Thus, the polymerization process follows the same order, producing an alternating polymer.

\[
\begin{align*}
\text{D} \text{A} \text{A} \text{D} \text{A} \text{A} \rightarrow \text{DADADA}^-
\end{align*}
\]

**Scheme 1.8:** Matrix polymerization.

However, the two above mechanisms are not sufficient to explain spontaneous polymerization of CT complexes.

**iii) Electron transfer (Scheme 1.9)**

Interactions between electron donors and acceptors are thought to lead to the complete electron transfer from donors to acceptors [105]. A cation-radical/anion-radical pair is a product of the electron transfer process. The ion radicals are able to induce spontaneous
polymerization. However, this mechanism is found to be true in reactions of extremely rich electron donors and extremely poor electron acceptors.

\[ D \rightarrow^{e^-} A \rightarrow D \cdot A^- \]

**Scheme 1.9:** Radical ions formed in Electron Transfer.

### 1.5.2 Factors that influence CT complex polymerization

#### 1.5.2.1 Strengths of electron donors and acceptors

Polymerization rate of CT complex is strongly determined by the donating and accepting strengths of their components. Polymerization of different electron donors and acceptor systems was studied by Jönsson and coworkers [104]. They found that the strengths of complex formations were dependent on both electron poor and rich characteristics of acceptors and donors respectively in which the stronger these characteristics were, the faster the polymerization occurred. They also ranked various donors and acceptors according to their strengths as shown in Table 1.1.

**Table 1.1:** Typical donors and acceptors which are listed according to their corresponding electron donating or withdrawing strengths.

<table>
<thead>
<tr>
<th>Acceptor strengths</th>
<th>Donor strengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maleic anhydride (MA)</td>
<td>N-Vinyl pyrrolidone (NVP)</td>
</tr>
<tr>
<td>Maleimide</td>
<td>IsoEugenol (IEU)</td>
</tr>
<tr>
<td>N-Methyl maleimide</td>
<td>4-Propenylxymethyl-1,3,2-dioxolanone</td>
</tr>
<tr>
<td>p-Carboxethoxy phenyl maleimide</td>
<td>Paramethoxystyrene (p-MOS)</td>
</tr>
<tr>
<td>N-Phenyl maleimide</td>
<td>Paraglycidoyxystyrene (p-GOS)</td>
</tr>
<tr>
<td>4,4-Diamaleimidobisphenol F</td>
<td>Triethyleneglycol divinyl ether (DVE-3)</td>
</tr>
<tr>
<td>Dimethyl fumarate (DMFA)</td>
<td>Tetrahydrofurfuryl vinyl ether</td>
</tr>
<tr>
<td>Diallyl maleate</td>
<td></td>
</tr>
<tr>
<td>Dimethyl maleate (DMMA)</td>
<td></td>
</tr>
</tbody>
</table>

The direction of the arrows indicates the increase of the strengths.
1.5.2.2 Presence of free radicals

The presence of free radicals can significantly accelerate the polymerization rate of CT complex. Lee et al [106] investigated the photopolymerization of three bifunctional N-phenylmaleimide derivatives consisting of a maleimide and a methacrylate or a styryl moiety as electron acceptors with N-vinyl-2-pyrrolidone and styrene as electron donors and with maleic anhydride (MA) as an electron acceptor. They found that self-initiated photopolymerization was possible but a higher polymerization rate was obtained using benzoin methyl ether as a photoinitiator.

Using real-time infrared spectroscopy, Decker et al [107] monitored the high-speed copolymerization of N-substituted alkyl maleimide and vinyl ether mixtures upon UV exposures with or without photoinitiator and reported higher polymerization rates obtained when photoinitiator was present.

Zhang et al [108] studied UV copolymerization of difunctional vinyl ether and unsaturated polyester containing maleate in the presence of photoinitiator by differential photocolorimetry method and found increasing concentration of the photoinitiator significantly accelerated the copolymerization in initial stages.

1.5.2.3 Composition of monomer feed

The polymerization of CT complex is a copolymerization process, and thus, the concentration ratio between the donor and acceptor directly affects the kinetics of the polymerization. According to a study by Decker et al [107], the monomer feed composition of N-substituted alkyl maleimide and vinyl ether CT complexes greatly influence the UV polymerization kinetics of each monomer with or without photoinitiator. When the vinyl ether was in excess, the two monomers disappeared at similar rates to yield an alternating copolymer. When the maleimide was in excess the copolymerization and the maleimide homopolymerization occurred simultaneously to produce a polymer with isolated vinyl ether units and thus the author proposed a reaction scheme in which vinyl ether radicals were the main propagating species.
Using thermal initiator \( \alpha, \alpha' \)-azobis(isobutyronitrile) (AIBN), Erceg et al [109] prepared different copolymers from the copolymerization of 2-chlorostyrene, 4-chlorostyrene and 2,6-dichlorostyrene as electron donors with MA as an electron acceptor in toluene at 65 °C. They reported that all copolymers had alternating composition despite different monomer to monomer ratios in the feed. Furthermore, the initial rate of copolymerization increases with increasing electron donor concentrations and the highest rates were obtained at the equimolar ratios of comonomers in the feed.

Solvents also interfere in the free radical copolymerization process between electron donor monomers and acceptor monomers. Matsumoto and Mohri [110] investigated homopolymerization and copolymerization of styrene and vinyl benzoate as electron donors and diisopropyl furamate and MMA as electron acceptors in the presence of AIBN as initiator and found that the polymerization rate was enhanced in the polar electron-pair accepting solvents such as 2,2,2-trifluoroethanol. The rate was also linked to the electron-pair-accepting solvent used rather than the polarity.

1.5.2.4 Presence of Lewis acids
The spontaneous polymerization of CT complexes can be initiated by Lewis acids. In the review of CT complex polymerization mechanism, Hall and Padasia [105] listed a number of CT complexes with styrene/AN, styrene/MMA, isobutene/AN as examples which could undergo polymerization in the presence of Lewis acids such as ZnCl₂ and SnCl₄.

Garnett and Zilic [111] studied CT polymerization of MA, maleate and imide monomers as acceptors with DVE-3 as a donor and found that the presence of SbCl₃ considerably enhanced the polymerization rate.

1.5.2.5 Presence of hydrogen donors
Recent studies by Decker et al [107] and Jönsson et al [113] showed that the polymerization initiated by vinyl ether/maleimide CT complexes can rapidly occur in the absence of photoinitiators when exposed to UV radiation. High polymerization rates have been attributed to the presence of abstractable labile hydrogen atoms in the alfa-ether
position in the vinyl ether donor monomers which lead to the generation of more radicals during the interaction of excited state maleimides with the vinyl ethers. The mechanism of the radical formation is presented in Scheme 1.10.

\[
\begin{align*}
&\text{O} \quad \text{N} \quad \text{O} \quad \text{hv} \quad [\text{R1}] \quad [\text{R1}]^+ \\
&\text{O} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{R2}  \\
\end{align*}
\]

**Scheme 1.10:** Radical formation by hydrogen abstraction from a vinyl ether during its interaction with an excited state maleimides upon UV radiation exposure.

### 1.5.3 Grafting of charge transfer complexes to substrates

A great deal of effort has been invested in discovering new charge transfer complex systems and ways to control their polymerization, and at the same time, interests on their grafting properties to substrates have been pursued.

Ng et al [112] studied UV grafting of MA/DVE-3 CT complex system to wool, cellulose and polypropylene with and without photoinitiators, and found that grafting yields varied with the complex concentrations and solvents used. The presence of photoinitiator was very beneficial with the grafting yield increased by many folds.

Good grafting of different charge transfer complex systems such as DVE-3 with MA and maleates to cellulose substrates was reported by Garnett and Zillic [111]. In their studies, it was found that grafting yields varied according to charge transfer complex systems. It was also reported that additions of photoinitiators and additives such as Lewis acids significantly enhanced the grafting of these systems to cellulose substrates.
However, the grafting of charge transfer complexes to PPE by UV irradiation was found to be difficult. In their early works, Garnett et al [18] reported that CT systems of MA/n-vinyl-2-pyrrolidone (NVP) and MA/DVE-3 did not give good grafting to PPE substrates. But when these complex systems were used as additives for the grafting of MMA to PPE substrates, they significantly improved grafting yields.

1.6 Aims of this project
At the beginning of this project, Irgacure 819, a new photoinitiator on the market, was used for grafting studies. Irgacure 819 is a very efficient photoinitiator in term of free radical generation. However, its effects on grafting of monomers on polar and non-polar substrates were unknown at the time, and thus, the first task was to examine effects of Irgacure 819 photoinitiator on grafting of MMA and styrene to cellulose and PPE substrates under different conditions.

Influences of vinyl ethers of different functionality on the grafting of MMA and styrene to cellulose or PPE substrates was another area of interest in this study since vinyl ethers have been widely used as reactive diluents in coating formulations. However, some vinyl ethers were reported to retard monomer homopolymerization [114,115]. Therefore, it would be of interest to study the effect of vinyl ethers on the grafting of MMA and styrene to cellulose or PPE substrates.

Another major part of this research was to examine complex formation between weak electron acceptors such as methyl methacrylate (MMA), acrylic acid (AA), methyl acrylate (MAC), dimethyl maleate (DMMA), butyl methacrylate (BMA), acrylonitrile (AN) with weak electron donors such as vinyl ethers and styrene. The carbonyl or nitrile group present in these vinyl monomers exerts a pulling force of electron on adjacent double bonds, making them electron deficient. However, their role as electron acceptors in CT complex polymerization was not strong and thus it was interesting to see if polymerization could occur at all. In the process, grafting properties of vinyl monomers/vinyl ethers or styrene to PPE substrates were studied.
Finally, effects of various additives such as charge transfer complexes and acids on the grafting of styrene to PPE substrate were also examined. Throughout the project, the FT-IR spectroscopy technique was used to determine the presence of graft and the composition of any grafted chains.

1.7 References


CHAPTER TWO: EXPERIMENTAL
2.1 Materials

2.1.1 Monomers

Vinyl monomers of AR grade, styrene, methyl methacrylate (MMA), butyl methacrylate (BMA), methyl acrylate (MAC), acrylic acid (AA), acrylonitrile (AN), maleic anhydride (MA), dimethyl maleate (DMMA), dimethyl furamate (DMFA), ethyl maleimide (EMI) were obtained from Sigma Aldrich Co. Tri(ethylene glycol)divinyl ether (DVE-3) (AR grade) was donated by ISP Technologies. Other vinyl ethers of AR grade, ethyl vinyl ether (EVE), n-propyl vinyl ether (PVE), n-butyl vinyl ether (NBVE), iso-butyl vinyl ether (IBVE), tert-butyl vinyl ether (TBVE), ethylene glycol divinyl ether (DVE), hexanediol divinyl ether (HDVE), tetra(ethylene glycol) divinyl ether (DVE-4), trimethylolpropane trivinyl ether (TMPTVE), 2-ethylhexyl vinyl ether (EHVE) and 2-(diethylamino)ethanol vinyl ether (DEAEVE) were donated by BASF. Figure 2.1 presents the chemical structures and molar masses of vinyl monomers which functioned as acceptors and Figure 2.2 gives both the structure and molar masses of styrene and vinyl ethers which were donors used in this project.

i) Methacrylates

![Methyl methacrylate (100)](image1)

![Butyl methacrylate (142)](image2)

ii) Acrylic acid and methyl acrylate

![Acrylic acid (72)](image3)

![Methyl acrylate (86)](image4)
iii) **Acrylonitrile**

\[
\begin{align*}
&\text{N} \\
&\text{Acrylonitrile (53)}
\end{align*}
\]

iv) **Dimethyl maleate & dimethyl furamate**

\[
\begin{align*}
\text{MeO} &-\text{C} &\text{MeO} \\
\text{O} & & \text{O} \\
\text{O} & & \text{O} \\
\text{MeO} &-\text{C} &\text{MeO}
\end{align*}
\]

Dimethyl maleate (144)  \hspace{1cm}  \text{Dimethyl fumarate (144)}

v) **Maleic anhydride & ethyl maleimide**

\[
\begin{align*}
\text{O} &-\text{O} \\
\text{O} &-\text{O}
\end{align*}
\]

Maleic anhydride (98)  \hspace{1cm}  \text{Ethyl maleimide (125)}

**Figure 2.1:** Chemical structures of electron poor (EP) vinyl monomers used in this study with their corresponding molar masses (gmol\(^{-1}\)) within parenthesis.
Chapter two: Experimental

i) Electron rich vinyl monomer

\[
\begin{align*}
\text{Styrene (104)}
\end{align*}
\]

ii) Monofunctional vinyl ether

\[
\begin{align*}
\text{Ethyl vinyl ether (72) } & \quad \text{Propyl vinyl ether (86) } & \quad \text{n-butyl vinyl ether (100)} \\
\text{tert-butyl vinyl ether (100) } & \quad \text{iso-butyl vinyl ether (100) } & \quad \text{2-Ethylhexyl vinyl ether (156)} \\
\text{2-(Diethylamino)ethanol vinyl ether (143)}
\end{align*}
\]

iii) Difunctional vinyl ether

\[
\begin{align*}
\text{Ethylene glycol divinyl ether (114)} \\
\text{Tri(ethylene glycol)divinyl ether (202)}
\end{align*}
\]
iv) Trifunctional vinyl ether

Figure 2.2: Chemical structures of styrene and vinyl ethers used in this study with their corresponding molar masses (g mol\(^{-1}\)) within parenthesis.

Styrene was purified by column chromatography on alumina. Other liquid monomers were freed from inhibitors and trace polymers by conventional distillation under nitrogen and reduced pressure. Purified monomers were used immediately or were stored at \(-2\) °C for no longer than one week prior to use. Solid monomers, maleic anhydride (MA), dimethyl furamate (DMFA) and ethyl maleimide (EMI) were used as received.

2.1.2 Photoinitiators
Photoinitiators, Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one), Irgacure 2959 (4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-methylpropyl)ketone), Irgacure 184 (1-hydroxycyclohexyl phenyl ketone), Irgacure 1800 (25% bis(2,6-dimethoxybenzoyl)-
2,4,4-trimethylpentyl phosphine oxide and 75% Irgacure 184), Irgacure 1700 (25% bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide and 75% Darocur 1173), Irgacure 1000 (80% Darocur 1173 and 20% Irgacure 184), Irgacure 819 (bis(2,4,6-trimethyl benzoyl)-phenyl phosphine oxide) and Irgacure 369 (2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone) were donated by Ciba Geigy [1] and were used as received.

The cationic photoinitiator, KI85 (50% bis{4-(diphenylsulfonio)-phenyl}-sulphide-bis-hexafluoro phosphate and 50% propylene carbonate), was obtained from Ciba Geigy and was used as received.

2.1.3 Solvents
Solvents of AR grade, methanol, acetone, dimethylformamide (DMF), chloroform, dichloro methane, carbon tetrachloride, tetrahydrofuran (THF), ethyl acetate and acetonitrile were purchased from Sigma Aldrich and used as received.

2.1.4 Substrates
All substrates were cut to the size of 2.5 cm x 3 cm. Cellulose substrate which was Whatman 41 filter paper did not receive any chemical treatment prior to use. Polypropylene substrates which were isotactic doubly oriented polypropylene films of different thickness (0.10 mm and 17 µm) were supplied by the courtesy of ICI Australia. The 0.10 mm thick film was used in most cases. All polypropylene substrates were rinsed with acetone to remove grease and dirt.

All substrates were kept in a desiccator for at least 24 hours to stabilize their weights. They were weighed and used immediately after removing from the desiccator.

As discussed in Section 1.3.2 of Chapter 1, all substrates, PPE and cellulose, are not homogenous, with the percentage of crystalline and amorphous regions varied from one substrate sample to another. Therefore, it is impossible to obtain reproducible grafting yield results for the same substrate even under identical experimental conditions. Consequently, for each experiment, only grafting yield of one substrate was recorded.
However, for results that were contradictory to the observed trend, these experiments were repeated.

2.2 Radiation facilities

2.2.1 Ultraviolet light source

The UV light source was a mercury vapor-filled lamp of 90 watt made by Phillips (Holland). The lamp was in the center of an enclosed drum which also contained a circular rack which held 36 Pyrex sample tubes placed at a distance of 30cm from the lamp.

The energy absorbed per tube was determined by uranyl oxalate actinometer using the average quantum yield for oxalate as 0.57 [2]. Since the effective radiation lies between 320 nm, the absorption limit of Pyrex, and 440 nm, the absorption limit of uranyl ion, the average wavelength absorbed was taken as 350 nm. Detailed description of the UV lamp calibration can be obtained in Section 2.7. The dose rate was determined to be $1.02 \times 10^{-2}$ J/s or 36.7 J/hour and this dose rate was used to calculate the total exposure dose of the tested sample by timing it with the sample exposure time.

2.2.2 Gamma radiation source

The gamma source was the spent fuel facility at the Australia Institute of Nuclear Science and Technology Organization (ANSTO), Sydney. Samples in Pyrex test tubes were contained in a cardboard container. This container was then encased in a stainless steel canister which was then lowered into the gamma pond for a required time.

The gamma radiation dose was calibrated using ferrous sulfate dosimetry technique in which a small tube containing ferrous sulfate was positioned at the center of the cardboard container. The calibration of the gamma source was carried out by the technical staff at ANSTO and in all experiment the dose rate was quoted to be 2.6 kGy per hour.
2.3 Preparations of samples
Immediately after being weighed, all substrates were marked and positioned in the Pyrex test tubes. Solvents were always added first, followed by monomers, additives and then finally photoinitiators. Mixtures were swirled thoroughly to form homogenous solutions. For most experiments, volumes of solutions were 10 ml. Concentrations of monomers and solvents were measured in % v/v whilst additives and photoinitiators were added to solutions as % w/v. For CT polymerization experiments using solutions of MA with DVE-3 or with styrene as in Chapters 9 and 10, predetermined amount of MA was dissolved in 10 ml of acetone. DVE-3 or styrene monomers were added to the MA solution according to the desired double bond molar ratios. Finally, sample tubes were enclosed by rubber stoppers, and were quickly placed in the rack inside the UV drum.

For gamma radiation experiment, samples were prepared one night before and were refrigerated. They were allowed to warm up to room temperature before being exposed to gamma radiation.

After exposures, substrates were quickly removed from the tubes and immersed in appropriate solvents in order to dissolve homopolymers attached to their surfaces as well as to stop the polymerization process. In cases when large quantities of polymers formed and substrates were unable to be removed, solvents were added directly to the tubes and left overnight to dissolve the polymers. Finally, the grafted substrates were transferred to an soxhlet extractor for extraction to remove any polymer that might still adhere to the substrates.

2.4 Extractions
Polymers adhered to the surfaces of substrates were removed by extraction using appropriate solvents. The extraction was carried out in a large soxhlet extractor. Chloroform was used as a solvent for the following homopolymers and copolymers: poly(methyl methacrylate), poly(methyl acrylate), polyacrylonitrile, poly(butyl methacrylate) and polystyrene. For poly(acrylic acid) and its copolymers, water was used first and then chloroform was subsequently employed to extract
lymers. Other exceptions were copolymers of maleic anhydride with styrene and DVE-n which acetone was used as the extracting solvent.

The extraction was allowed to run for at least 72 hours to ensure the removal of all hered polymers. After the extraction, grafted substrates were air-dried for one hour to ve all the solvents evaporated. They were then kept for at least 24 hours in a desiccator ith anhydrous sodium sulfate as the drying agent.

5 Weighing and grafting yields calculations

Substrates were removed from the desiccator and their weights measured with readings to four decimal places. After weighing, samples were kept in commercial PPE bags, til analysed by FT-IR.

rafting yield calculations were performed using Excel Spread Sheet program with the mula for the calculation as in Equation 2.1:

\[ \text{Grafting yield (\%) = (} W_a - W_b \text{)} \times 100 / W_b \]  

(2.1)

\( W_a \): weight of a grafted substrate

\( W_b \): weight of an original substrate before grafting experiment

6 Characterizations of grafted substrates by FT-IR spectroscopy

T-IR characterizations of grafted substrates were performed on a Perkin Elmer pectrum One FT-IR Spectrometer. The software used was Spectrum v3.02, version 0.02.01 from the same company. The sampling range was from 450 cm\(^{-1}\) to 4000 cm\(^{-1}\).

ach sample was averaged over 9 scans at 4 cm\(^{-1}\) resolution.

PE substrates were analyzed as they were, without any physical or chemical treatment.

or cellulose substrates, only small pieces of samples were used. They were finely cut nd then ground to form cellulose powder. Due to the KBr press equipment not being
available during the course of this project, cellulose powder was examined as a mull between two flat KBr plates. Nujol was the mulling agent used.

FT-IR spectra of grafted PPE substrates showed complex absorption peaks of PPE as well as of grafted monomers. Therefore, in order to analyze FT-IR of such PPE samples, comparison with the spectrum of a PPE substrate was necessary.

FT-IR spectra of grafted cellulose substrates were more problematic to obtain. Despite all effort of grinding, grafted cellulose samples were sometimes too big, resulting in blocking the light transmission through the sample. Consequently, spectra of grafted cellulose substrates lacked details. In addition, cellulose has a complicated structure with most of their absorption peaks overlapped with peaks of grafted monomers. Also, a comparison between spectra of cellulose substrates with that of Nujol and an original cellulose substrate was necessary to identify the peaks that belonged to grafted monomers.

2.7 Calibration of UV source
Solutions of 0.02 M oxalic acid, uranyl nitrate and 0.01 M of potassium permanganate were prepared. Potassium permanganate was standardized by titration with hot acidified oxalic acid at 60-90 °C until a color change from a colorless solution to pink was detected. To each Pyrex test tube containing 25 ml of oxalic acid, 25 ml of uranyl nitrate was added and thoroughly mixed. The light source was equilibrated for 5 minutes. Four Pyrex tubes were placed in the rack around the UV lamp and irradiated for an allocated time with the tubes rotating constantly around the UV source. This actinometer depends on the uranyl-ion photosensitive decomposition of oxalic acid according to Reactions 2.7.1-2.7.2:

\[
\text{UO}_2^{2+} + \text{HO}_2\text{CCO}_2\text{H} \rightarrow \text{UO}_2^{2+} + \text{CO}_2 + \text{CO} + \text{H}_2\text{O} \tag{2.7.1}
\]

\[
\text{UO}_2^{2+} + \text{HO}_2\text{CCO}_2\text{H} \rightarrow \text{UO}_2\text{H}^+ + \text{H}^+ + 2\text{CO}_2 \tag{2.7.2}
\]
The solutions were then heated, acidified with 2 M sulfuric acid and titrated against the standardized potassium permanganate solution. Oxalic acid that was not decomposed by UO$_2^{2+}$ reacted with MnO$_4^-$ according to Reaction 2.7.3. The calibration was carried in duplicate at 10 minute time intervals up to 50 minutes.

\[
2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \quad (2.7.3)
\]

### 2.7.1 Calculations for UV dose rate

#### i) Standardization of KMnO$_4$ with oxalic acid

The KMnO$_4$ solution was standardized against 25 ml of 0.0199 M oxalic acid. The standardization procedure was carried out in triplicates and the average titre value was 14.40 ml. Titration values for the determination of decomposed oxalic acid are given in Table 2.1.

**Table 2.1: Determination of decomposed oxalic acid.**

<table>
<thead>
<tr>
<th>Sample (sec)</th>
<th>Time (second)</th>
<th>Titre of KMnO$_4$ (ml)</th>
<th>Mole of oxalic acid ($10^{-4}$)</th>
<th>Mole of decomposed oxalic acid ($10^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>14.4</td>
<td>4.98</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1800</td>
<td>13.5</td>
<td>4.66</td>
<td>0.320</td>
</tr>
<tr>
<td>3</td>
<td>1800</td>
<td>13.55</td>
<td>4.68</td>
<td>0.300</td>
</tr>
<tr>
<td>4</td>
<td>1800</td>
<td>13.55</td>
<td>4.68</td>
<td>0.300</td>
</tr>
</tbody>
</table>

Average = 0.306

Mole of oxalic acid = 0.0199 molL$^{-1} \times 25 \times 10^{-3}$ L = 4.98$\times 10^{-4}$ mole

Mole of KMnO$_4$ = 2/5 $\times$ 4.98$\times 10^{-4}$ mole = 1.99$\times 10^{-4}$ mole

Concentration of KMnO$_4$ = 1.99$\times 10^{-4}$ mole/ 14.40 $\times$ 10$^{-3}$ L = 13.81 $\times$ 10$^{-3}$ M

#### ii) Mole of oxalic acid at time ($t_x$)

\[
(\text{Concentration of KMnO}_4) \times (\text{titre of KMnO}_4) \times 5/2 = \text{mole of oxalic acid}
\]

\[
(13.81 \times 10^{-3}) \text{molL}^{-1} \times (13.50 \times 10^{-3}) \text{L} \times 5/2 = 4.66 \times 10^{-4} \text{mole}
\]
iii) Moles of decomposed oxalic acid

\[(\text{Mole of oxalic acid})_{t_0} - (\text{mole of oxalic acid})_{t_x}\]

\[[(4.98 \times 10^{-4}) - (4.66 \times 10^{-4})] \text{ mole} = 3.20 \times 10^{-5} \text{ mole of decomposed oxalic acid}\]

Where \(t_0\) = non-irradiated sample; \(t_x\) = irradiated sample at a certain time

iv) Number of Einsteins.s\(^{-1}\) required

\[= (\text{Moles of decomposed oxalic acid})/[(\text{time of exposure (s)}) \times \Phi]\]

Where \(\Phi = 0.57\) (Quantum yield of oxalic acid)

\[= 3.06 \times 10^{-5} \text{ mole/[(30 \times 60)s \times 0.57]} = 2.98 \times 10^{-8} \text{ Einsteins.s}^{-1}\]

v) Energy

\[E = (hc)/\lambda\]

Where \(\lambda = 350\) nm (average energy quanta between 245-435 nm); \(h = \text{Planks constant (6.626 x 10}^{-34}\) Js\); \(c = \text{speed of light (2.998 x 10}^{8}\) ms\(^{-1}\))

\[E = (6.626 \times 10^{-34}\text{Js} \times 2.998 \times 10^{8} \text{ ms}^{-1})/ 3.50 \times 10^{-7} \text{m} = 5.68 \times 10^{-19} \text{ J}\]

vi) Dose rate

Dose rate = (Einsteins.s\(^{-1}\)) \times (avagadro's number) \times (energy)

\[= (2.98 \times 10^{-8} \text{Einsteins.s}^{-1}) \times (6.022 \times 10^{23}) \times (5.68 \times 10^{-19} \text{ J})\]

Dose rate = 1.02 \times 10^{-2} \text{ Js}^{-1}

Dose rate (J/hour) = 1.02 \times 10^{-2} \text{ Js}^{-1} \times 3600 \text{ s/hr} = 36.7 \text{ J/hr}

2.8 References


CHAPTER THREE: UV GRAFTING OF METHYL METHACRYLATE TO CELLULOSE IN THE PRESENCE OF IRGACURE 819
3.1 Introduction

Cellulose forms the structural material for the greater part of plant cell walls, and is one of the most common natural polymer materials which are used extensively in textiles, papers and constructions [1,2]. Besides being present in abundance, it has a useful range of properties including low cost, durability and high thermal stability, good mechanical properties, and the ability to absorb moisture. However, it has a number of drawbacks [2]. Cellulose is not easily dissolved in solvents, and unlike thermoplastic, it cannot be melted and processed by heat setting. It also has poor dimensional stability.

Grafting monomers onto cellulose using UV irradiation in the presence of photoinitiators is one of the many techniques used to improve the properties of cellulose [2]. The grafting process is dependent on many factors such as the monomer types [3-5], concentration of monomers [2,3,5-7,9-11,13,14], types of photoinitiators [3,5,6,8,12-14] and concentrations of photoinitiators used [5,8,9], solvent types [2,5] and solvent concentrations [2,5,11,13,14], length of irradiation [3,5,8,9] and the presence of additives [10-14]. In this chapter, the grafting of MMA to cellulose under the influence of UV was performed. Irgacure 819, a newly available photoinitiator on the market during the time when this project was carried out, was used throughout this study.

3.1.1 Cellulose structure

Cellulose is a plant cell material which composed of thousands of anhydroglucose units linked by 1,4-β-glucosidic bonds to form long, linear, chain-like molecules [1,2]. Figure 3.1 presents the structure of one cellulose section.

![Figure 3.1: 1,4-β-glucosidic bonds of one cellulose fiber section](image-url)
Interactions between hydrogen and oxygen atoms in close vicinity lead to intramolecular and intermolecular hydrogen bonds holding the cellulose structure together [2]. Figure 3.2 shows typical formation of hydrogen bonds in one molecule section. Consequently, \(\beta\)-glucosidic bonds and intramolecular hydrogen bonds renders the cellulose molecule straight and stiff.

![Hydrogen bonds in cellulose molecule](image)

**Figure 3.2:** Hydrogen bonds in one cellulose molecule section

X-ray studies of cellulose suggest that it consists of amorphous (disordered) and crystalline (ordered) regions and these regions are arranged in a regular and repeated manner [2]. The same molecule runs through these regions creating an irregular flexible network. The crystalline regions are thought to be impenetrable to monomers and solvents. As a result, the grafting of monomers on cellulose must start in the amorphous regions first. As more monomers are grafted, structures of adjacent regular regions are loosened, becoming more open and grafting proceeds from this region [2].

### 3.1.2 Factors that influence the grafting of monomers on cellulose

The grafting of monomers on cellulose has been well studied. A. Hebeish and J. T. Guthrie [2] listed factors that influence the grafting process as follow:

- Solution containing the monomer in the solvent and the diffusion of the monomer from the solution phase to the cellulose;
- Adsorption of the monomer on the cellulose;
- Initiation of the active sites on the cellulose backbone;
• Formation and propagation of graft on the cellulose;
• Termination of the active sites on the cellulose backbone;
• Homopolymerization in solution.

The first four factors improve grafting while the last two reduce it. The first two factors involve physical process while the last four concerning chemical process. These factors generally are favored by higher monomer concentrations, longer reaction times and higher temperatures. Combination of these factors may result in optimal conditions exist for maximum grafting.

While chemical factors are very important, physical factors also play an equal part. It was found that swelling behavior of the cellulose in solvents and monomers determine the ability of monomers to graft to the cellulose backbone [2]. This is because when the cellulose was swollen in either solvents or monomers, monomers could gain access to the grafting sites with greater ease and thus the grafting process was favored.

3.1.3 UV grafting of MMA onto cellulose

MMA is a vinyl monomer which can easily undergo radical polymerization to form hard and transparent poly(methyl methacrylate) (PMMA) [1]. In the UV curing system, photoinitiators (PIs) are usually needed and radicals are formed from the photolysis of PIs to initiate the polymerization process. These radicals react with MMA monomer to form PMMA. The homopolymerization process is presented in Scheme 3.1.
**Initiation**

\[
\text{hv} \\
\text{PI} \rightarrow \text{R}^* \\
\text{MMA} + \text{R}^* \rightarrow \text{R(MMA)}^*
\]

**Propagation**

\[
\text{R(MMA)}^* + n\text{MMA} \rightarrow \text{R(MMA)}_{n+1}^*
\]

**Termination**

\[
\text{R(MMA)}_{n+1}^* + \text{R(MMA)}_{m+1}^* \rightarrow \text{PMMA}
\]

**Scheme 3.1:** Homopolymerization of MMA in the presence of a photoinitiator in which PI: photoinitiator; R*: radical.

In the grafting process, radicals formed from the photolysis of PI attack cellulose backbone, abstracting hydrogen atoms to create grafting sites [2,3,5,9]. These sites, in turn, react with MMA monomers to form polymer chains attaching to the cellulose [3,5,9,10,12,13,14]. The grafting process of MMA on the cellulose is presented in Scheme 3.2 below.

**Initiation**

\[
\text{Cel-H} + \text{R}^* \rightarrow \text{Cel'} + \text{RH} \\
\text{Cel'} + \text{MMA} \rightarrow \text{Cel-(MMA)}'
\]

**Propagation**

\[
\text{Cel-(MMA)}' + n\text{MMA} \rightarrow \text{Cel-(MMA)}_{n+1}'
\]

**Termination**

\[
\text{Cel-(MMA)}_{n+1}' + \text{Cel-(MMA)}_{n+1}' \rightarrow \text{Cel-PMMA}
\]

**Scheme 3.2:** Free radical grafting of MMA to cellulose. R' represents a free radical obtained from the photolysis of a PI.
As mentioned above, the ability of monomers and radicals to gain access to the backbone of the cellulose is a crucial factor deciding the degree of grafting. Accessibility is favored by solvents or monomers that can swell the cellulose [2,5,6,7]. Therefore, it is predictable that different reaction solutions made of different MMA-solvents combinations give different grafting yields. In this chapter, the solvent influence on grafting of MMA to cellulose is reconfirmed.

3.1.4 Irgacure 819 photoinitiator

Irgacure 819 photoinitiator has a chemical name of bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, which is a phosphine based photoinitiator. It is a very efficient photoinitiator because it can undergo subsequent photolysis to form four radicals. The photolysis process is presented in Scheme 3.3.

![Scheme 3.3: Photolysis of Irgacure 819 photoinitiator](image-url)
At the time of this study, Irgacure 819 was a new photoinitiator and was widely promoted by CIBA for UV curing and coating. None of the grafting studies involving this photoinitiator were reported elsewhere. This chapter presents the grafting behavior of MMA on the cellulose in the presence of Irgacure 819 and under the influence of UV radiation.

3.2 Results

3.2.1 Effects of solvents and photoinitiator concentrations on grafting of MMA to cellulose

Results in Table 3.1 and Figure 3.1 show the importance of methanol in enhancing the grafting process of MMA to cellulose. When methanol was absent, negligible grafting yields were observed even in the presence of high Irgacure 819 concentration. However, the presence of methanol led to significant increases of grafting yields.

Results in Table 3.2 and Figure 3.2 show grafting yields of MMA to cellulose in different solvents. As shown, significant grafting yields were observed only for methanol and DMF. These yields varied according to MMA concentrations. Nil or negligible grafting yields were achieved in cases of other solvents used.

Results in Table 3.1 represent the effect of the photoinitiator concentration on grafting yields. As shown, there was an optimum concentration of Irgacure 819 at which grafting yield was highest. In the solution containing 60% v/v MMA and 40% v/v methanol, the presence of 0.5% w/v Irgacure 819 resulted in the highest grafting yield.

3.2.2 Effect of UV doses

As shown in Table 3.3 and Figure 3.3, the increase of UV doses increased grafting yields.

3.2.3 Comparison between Irgacure 819 with other photoinitiators

Comparison between the performance of Irgacure 819 with other photoinitiators in enhancing grafting is presented in Table 3.4 and Figure 3.4. According to Table 3.4,
Irgacure 819 did not significantly enhance grafting yields despite being an efficient photoinitiator.

**Table 3.1:** Grafting of MMA to cellulose with different Irgacure 819 concentrations, with or without methanol as a solvent.

<table>
<thead>
<tr>
<th>Irgacure 819 conc. (% w/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA conc. (% v/v)</td>
</tr>
<tr>
<td></td>
<td>100⁴</td>
</tr>
<tr>
<td></td>
<td>60⁵</td>
</tr>
<tr>
<td>0.2</td>
<td>2%</td>
</tr>
<tr>
<td>0.5</td>
<td>1%</td>
</tr>
<tr>
<td>1</td>
<td>2%</td>
</tr>
<tr>
<td>1.5</td>
<td>1%</td>
</tr>
<tr>
<td>2</td>
<td>2%</td>
</tr>
</tbody>
</table>

⁴ Total dose: 55 J  
⁵ Total dose: 110 J  
Solvent: methanol  
Dose rate: 36.7 J/hr  
Temperature: 29 °C

**Figure 3.1:** Grafting of MMA to cellulose with different Irgacure 819 concentrations, with or without methanol as a solvent.
Table 3.2: Grafting of MMA on the cellulose with Irgacure 819 and with different solvents.

<table>
<thead>
<tr>
<th>MMA conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol</td>
</tr>
<tr>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>20</td>
<td>9</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1 % w/v  
Dose rate: 36.7 J/hr  
Total doses: 73 J  
Temperature: 29 °C

Figure 3.2: Effect of solvents on grafting of MMA to cellulose with 1% w/v Irgacure 819 photoinitiator.
Table 3.3: Grafting of MMA to cellulose with 1% w/v Irgacure 819 photoinitiator with different UV doses.

<table>
<thead>
<tr>
<th>Total dose (J)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA conc. (% v/v)</td>
</tr>
<tr>
<td></td>
<td>80</td>
</tr>
<tr>
<td>36.7</td>
<td>2</td>
</tr>
<tr>
<td>73</td>
<td>10</td>
</tr>
<tr>
<td>110</td>
<td>8</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1 % w/v
Solvent: methanol
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 3.3: Grafting of MMA to cellulose with 1% w/v Irgacure 819 photoinitiator with different UV doses.
Table 3.4: Grafting of MMA to cellulose with different photoinitiators.

<table>
<thead>
<tr>
<th>Photoinitiator</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA conc. (%v/v)</td>
</tr>
<tr>
<td></td>
<td>80</td>
</tr>
<tr>
<td>Irgacure 2959</td>
<td>5</td>
</tr>
<tr>
<td>Irgacure 1700</td>
<td>-</td>
</tr>
<tr>
<td>Darocur 1173</td>
<td>-</td>
</tr>
<tr>
<td>Irgacure 1000</td>
<td>17</td>
</tr>
<tr>
<td>Irgacure 819</td>
<td>10</td>
</tr>
<tr>
<td>Irgacure 369</td>
<td>0</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>-</td>
</tr>
</tbody>
</table>

Photoinitiator concentrations: 1 % w/v
Solvent: methanol
Total dose: 53 J
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 3.4: Grafting of MMA to cellulose with 1% w/v of different photoinitiator, with methanol as a solvent.
3.3 Discussion

3.3.1 Effect of solvents on UV grafting of MMA to cellulose

Table 3.1 and Figure 3.1 represent the grafting yields of MMA to cellulose in the presence of different Irgacure 819 concentration with and without methanol as a solvent. In the absence of methanol, the grafting yields were very low and close to zero. The increase in Irgacure 819 concentration in reacting solutions had no effect on grafting yield. However, it was observed that a large quantity of homopolymer was formed in each case. Consequently, only a maximum radiation dose of 55 J could be applied to all reacting solutions before gelation starts to occur.

The situation was reversed when 40% v/v of MMA was replaced by methanol. It was noticed that less homopolymer was formed thus allowing a higher exposure dose of 110J to be applied before gelation took place. At 0.2% w/v of Irgacure 819 photoinitiator, the grafting yield increased significantly from 2% to 13% when methanol was present. Similar situations of increased grafting yields were observed at other Irgacure 819 concentrations.

Table 3.2 and Figure 3.2 showed grafting yields of MMA to cellulose with different solvents. In all these experiments, Irgacure 819 photoinitiator concentration was fixed at 1% w/v. As shown, grafting yields significantly varied with types of solvents and theirs concentrations. The only two solvents which gave high grafting yields were methanol and DMF. The other solvents, acetonitrile, THF, ethyl acetate, dichloromethane, chloroform and carbon tetrachloride, resulted in low grafting yields close to zero. It was also noted that grafting yields changed with concentrations of MMA. For DMF, the grafting yield peaked when MMA concentration was 40% v/v, following the parabolic trend. In the case of methanol as solvent, no specific trend was observed. There was no significant variation in the grafting yields with varying MMA concentrations. Large quantity of white homopolymer precipitate was observed for each MMA-methanol solution. Generally, grafting yields in the presence of DMF were much higher than in methanol.
Variations of grafting yields with respect to MMA concentrations could be due to a combination of different factors. For DMF (Figure 3.2), at a high MMA concentration of 80% v/v, DMF was not sufficient to efficiently swell cellulose. Also, due to the design of the experiment, UV rays had to pass through solution before striking the cellulose surface. Radicals from the photolysis of PI that were formed in regions far from the cellulose surface were likely to react with MMA than diffusing to the surface area of the substrate to create reactive sites for grafting. Due to the abundance of MMA in the solution, homopolymer was quickly formed, thereby suppressing the grafting process. At a low MMA concentration of 20% v/v, there was sufficient DMF to swell cellulose but not enough MMA in the solution to graft, leading to low grafting yield. At MMA concentrations of 60% v/v and 40% v/v, the combination of monomer and solvent was in the right proportion and there was sufficient DMF to swell cellulose. By the same token, higher solvent concentrations reduced the viscosity of the solution, making it easier for radicals to emigrate to the cellulose surface. Hence, the homopolymerisation process was slower due to diluted MMA, leading to high grafting yields. For methanol, at higher irradiation dose of 110 J (Table 3.3, Figure 3.3), the grafting yields also followed a parabolic pattern as for DMF and thus the same explanations also applied. However, the precipitation of PMMA in methanol may have produced more complex grafting environments leading to mixed grafting results when UV exposure dose was at 70 J. Similar observations were reported by Garnett et al [14] in which precipitation of PMMA in methanol led to low transmission of UV lights, resulting in early termination of the grafting process.

The maximum yield observed for DMF and methanol could also be explained by Trommsdorff-type effect [15]. According to this effect, as viscosity of the solution increases due to homopolymerization, mutual termination between two growing radical chains is hindered more than the propagation reactions. It is because termination involves two long slowly moving chains which can become entangled while the propagation involves only one such long chain and mobile monomer molecules. As a result, the growth of polymer chains is accelerated. With reference to the results shown in Tables 3.2 and 3.3, towards the end of UV exposures, viscosity of solutions containing 80% v/v
MMA was too high and thus grafted chains could not grow due to monomer movement inhibition. However, viscosity of solutions with 60% v/v and 40% v/v of MMA was just high enough for the growth accelerations of grafted chains to occur but not too high to restrict monomer diffusions to grafting sites. As MMA concentration decreased to 20% v/v, viscosity of the solution decreased, resulting in high termination rates. On the other hand, both homopolymerization and grafting processes competed for a small amount of monomers. As a result, grafting yields were low in the presence of both solvents, methanol and DMF. However, acceleration effect on grafting yields was more likely to occur in methanol because PMMA was not soluble in methanol. This led to tightly coiled grafted PMMA chains whose radical was deeply hidden from other radicals, resulting in low termination rates. Trommsdorff effect was used to explain maximum grafting yields of styrene to cellulose by gamma irradiation [2,15].

Dependence of grafting yields on solvent types (Table 3.2) reconfirmed the necessity of having appropriate solvents to swell cellulose in order to obtain good grafting. The grafting process was favored by solvents such as methanol and DMF which were good penetrating solvents for cellulose [16,17,18]. Once they penetrated and swelled the fibrous structure of cellulose, molecules of greater molecular volume could access the swollen structure. These solvents were not only good for MMA grafting to cellulose but also for the grafting to cellulose of other monomers such as styrene and vinyl pyridine [16,17,18].

Apart from the ability to swell, the ability of methanol and DMF to wet cellulose backbone may have also played important part. This theory was first proposed by Dili and Garnett [19] in which significant grafting could be achieved only when solvents were able to wet the surface of cellulose. In the case of other solvents such as acetonitrile, THF, ethyl acetate and chloro hydrocarbon solvents, the low grafting yields (Table 3.2) could be explained by their inability to efficiently wet or swell cellulose.
3.3.2 Effects of Irgacure 819 concentrations on grafting of MMA to cellulose

Results in Table 3.1 and Figure 3.1 show grafting yield variations with respect to increase of Irgacure 819 concentrations in tested solutions. As shown, significant grafting was only achieved when methanol was used as a solvent. Grafting yield peaked at an Irgacure 819 concentration of 0.5% w/v and declined as its concentration increased. It proved that high concentration of the photoinitiator does not always enhance the grafting process. This could be due to the fact that with high PI concentration, although more reactive sites at the substrate are created for grafting, more radicals are produced which readily to react with diluted MMA in the solution. As a result, MMA is quickly depleted, leading to lower grafting yields. Kubota et al [8] reported similar grafting variations of acrylic acid (AA) to cellulose with respect to PIs concentrations. According to them, excessive photoinitiators had a negative effect on the grafting process since the homopolymerization was strongly promoted.

3.3.3 Effects of irradiation dose on grafting of MMA to cellulose

Table 3.3 and Figure 3.3 represent the grafting of MMA onto cellulose with different UV doses and with methanol as a solvent. A general trend was that grafting yield increased with the exposure dose. It was simply because more monomer molecules could be added to growing grafting chains and in addition more grafting sites could be created as the exposure time increased.

3.3.4 Comparison between Irgacure 819 and other photoinitiators

Results in Table 3.4 and Figure 3.4 show the grafting of MMA to cellulose with different PIs. For comparative purposes, Table 3.5 presents the chemical formulas of PIs used in this study with their corresponding free radicals upon photolysis [20]. At 60% w/v of MMA, the grafting yield was highest with Darocur 1173 and Irgacure 184, while lowest with Irgacure 369. When Tables 3.4 and 3.5 were cross-referenced, one observation was that the grafting yield was higher when radicals formed were small with no bulky groups present or contained hydroxyl group. For example, Darocur 1173 and Irgacure 184 formed small radicals with no steric hindrance, one of which contained a hydroxyl group and high grafting yields were resulted from using these 2 PIs. Under photolysis, Irgacure
produced large radicals and no grafting was resulted. Other photoinitiators formed mixtures of large and small radicals and corresponding yields were lower compared to Darocur 1173 and Irgacure 184. It is interesting in the case of Irgacure 1000 because it is a mixture of 80% Darocur 1173 and 20% Irgacure 184 but the grafting yield using this PI was lower than from each individual photoinitiator. In a similar study, Garnett et al [14] investigated the grafting of MMA to cellulose with methanol in the presence of 1% w/v PIs such as benzoin ethyl ether, Irgacure 184, Irgacure 1700, Irgacure 1800 and Darocur 1173 and found that the highest grafting yield of MMA to cellulose was achieved when Irgacure 184 and Darocur 1173 were present. However, the authors offered no explanation for different performances of these photoinitiators.

The dependence of grafting yields on free radical sizes and their functional groups is logical. To create grafting sites on cellulose backbone, radicals must get close to the amorphous regions of cellulose fibers and thus, smaller radicals are more efficient compared to large ones. Also, the hydroxyl group present on the radicals brings about the compatibility between cellulose and the free radicals thus allowing the radicals to come close to the fiber and create grafting sites.

Another observation was that the grafting yield was not dependent on the number of radicals formed. Take for instance, Irgacure 819 and other phosphine based photoinitiators such as Irgacure 1800 and Irgacure 1700 efficiently form at minimum 4 radicals (Table 3.5) under photolysis. However, grafting yields using these photoinitiators were not as good as of the two-radical forming photoinitiators such as Darocur 1173 and Irgacure 184 (Table 3.4). Possible contributing factors to the low grafting yields are the large size radicals formed by these PIs and also the incompatibility between the radicals and cellulose. Another possible explanation was the different reactivity of free radicals towards cellulose, or in other words the radical ability to abstract hydrogen atoms from cellulose structure to create grafting sites. For phosphine based PIs, free radicals could be efficiently produced but not all of them were sufficiently reactive towards cellulose and thus the homopolymerization of the monomer could more effectively compete with the grafting process.
### Table 3.5: Photoinitiators and their radicals.

<table>
<thead>
<tr>
<th>Photoinitiator</th>
<th>Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgacure 2959</td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td>Irgacure 1800</td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>Irgacure 1700</td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>Darocur 1173</td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>Irgacure 1000</td>
<td><img src="image5" alt="Image" /></td>
</tr>
<tr>
<td>75%</td>
<td>25%</td>
</tr>
<tr>
<td>Irgacure 819</td>
<td><img src="image6" alt="Image" /></td>
</tr>
</tbody>
</table>
Table 3.5: Photoinitiators and their radicals (continued).

<table>
<thead>
<tr>
<th>Irgacure 369</th>
<th>Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Irgacure 369 structure" /></td>
<td><img src="image" alt="Radicals structure" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Irgacure 184</th>
<th>Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Irgacure 184 structure" /></td>
<td><img src="image" alt="Radicals structure" /></td>
</tr>
</tbody>
</table>

3.4 Conclusions

In this chapter, the grafting of MMA onto cellulose has been studied. The grafting yields were found to vary with types of solvents, MMA concentrations, irradiation doses, photoinitiators and their concentrations. Among tested solvents, methanol and DMF were very effective for the grafting. The preferred MMA concentrations resulting in high grafting yields were 60% v/v and 40% v/v. Finally, it was found that while Irgacure 819 was a very efficient radical forming photoinitiator, it did not enhance MMA grafting to cellulose for the reasons stated in the discussions Section 3.3.4.
3.5 References

CHAPTER FOUR: UV GRAFTING OF MMA TO POLYPROPYLENE IN THE PRESENCE OF IRGACURE 819
4.1 Introduction
Polypropylene (PPE) is a very common synthetic polymer which has good mechanical strength (elasticity, tensile strength, elongation, impact strength), good physical properties (good thermal expansion, low conductivity), and good chemical properties (inert to most chemical)[1-3]. It is widely used in household products such as chairs, handles, food containers, plastic sheets and fibers, and industrial products including machine parts, tubes and electrical isolations. However, as a polyolefin, it has some drawbacks such as being hydrophobic and lack of polar sites resulting in poor water absorption and poor dyeability. Grafting is a technique to introduce polar functional groups to PPE chains in order to impart desired properties such as hydrophilicity and dyeability onto the polymer. Various monomers such as 2-hydroxyethyl methacrylate [3], 4-vinyl pyridine [4], acrylonitrile [2,5], styrene [4-12], MMA [4,10-12], butyl acrylate [13], succinic anhydride [14], maleic anhydride [15] and 2-methoxyethylacrylate [16] were successfully grafted to PPE substrates by either gamma or UV irradiation. This chapter concerns mainly the evaluation of the grafting properties of MMA to PPE substrates in the presence of the new Irgacure 819 photoinitiator.

4.1.1 PPE structure
PPE is a simple polyolefin consisting of a long hydrocarbon chain with methyl groups attached to it. There are three arrangement manners of the methyl groups around the hydrocarbon chain [1] i.e. isotactic, syndiotactic and atactic. In isotactic arrangement (Figure 4.1), all methyl groups appear on the same side of the polymer chain. In syndiotactic arrangements (Figure 4.2), methyl groups can be alternating on both sides of the hydrocarbon chain. Methyl groups can appear randomly along the length of the chain, giving an atactic arrangement (Figure 4.3). Isotactic and syndiotactic PPE are crystalline while atactic PPE is amorphous due to its disordered structure [1]. However, in this project, only the grafting of MMA to isotactic PPE was studied.

Although isotactic PPE is considered to be crystalline but, unlike metals or ceramics, it is not 100% crystalline. In isotactic PPE, irregularities due to defects along the chain (irregular branching, atacticity) or chain ends and chain folding prevent the polymer from
being completely crystallized [1]. Therefore, between crystalline regions, there are amorphous regions which are more likely and easily to be penetrated by monomers and solvents.

Figure 4.1: Isotactic arrangement of PPE.

Figure 4.2: Syndiotactic arrangement of PPE.

Figure 4.3: Atactic arrangement of PPE

4.1.2 **UV grafting of MMA to PPE**

The mechanism of MMA grafting to PPE under the influence of UV is similar to that of MMA grafting to cellulose in which free radicals formed from the photolysis of photoinitiators diffuse to PPE chains, and subsequently abstract hydrogen atoms from the polymer structure to produce reactive sites. These reactive sites can initiate the polymerization of nearby MMA molecules to form PMMA chains which are chemically bonded to the main PPE chain. The growth of a grafted PMMA chain is terminated by an adjacent chain carrying a radical or by a free radical present in the solution.

MMA has been shown to be a suitable monomer for UV grafting to PPE substrates [4,10,11]. According to these studies, grafting yields of MMA to PPE were dependent on MMA concentrations, types of solvents, photoinitiators and their concentration, lengths
of UV exposure and the presence of additives. However, grafting properties of MMA to PPE substrates in the presence of Irgacure 819 photoinitiator under the influence of UV radiation have not been studied at the time of this project and thus setting the aim for this chapter.

4.2 Results

4.2.1 Effects of solvents and Irgacure 819 concentrations on MMA grafting to PPE film of thickness 0.12 mm

Table 4.1 presents grafting yields of MMA to PPE with or without methanol as a solvent and in the presence of Irgacure 819 at different concentrations. As shown, the presence of methanol reduced grafting yields. Figure 4.1 depicts grafting yields versus the concentration of Irgacure 819. A variation of grafting yields with different photoinitiator concentration was observed. The highest grafting yield of 60% was achieved at 0.2% w/v Irgacure 819 followed by 57% grafting yield at 1% w/v Irgacure 819. At the end of UV exposure, solutions containing 1% w/v Irgacure 819 or above remained yellow due to unreacted PI whilst solutions containing 0.2% w/v and 0.5% w/v photoinitiator turned colorless and thus indicating a more efficient photolysis of the added Irgacure 819 in these solutions.

Results in Table 4.2 and Figure 4.2 show grafting yields of MMA to PPE in different solvents. Grafting yields were found to decrease with decreasing MMA concentration. They also varied according to the solvent types with good grafting yields being achieved in the presence of methanol, DMF, THF, ethyl acetate, methylene dichloride, chloroform and carbon tetrachloride. The exception was when acetone was the solvent. The MMA solution was exposed to a higher UV dose of 92 J in order to achieve full polymerization.

4.2.2 UV grafting of MMA to PPE (0.015 mm) with different solvents and 1% w/v Irgacure 819

Results in Table 4.3 and Figure 4.3 show that grafting yields to a thinner PPE substrate also changed with solvent types. These results can be compared with the ones in Table 4.2 to deduce the effect of film thickness on grafting.
4.2.3 UV grafting of MMA to PPE (0.015 mm) with different solvents and UV doses in the presence of 1% w/v Irgacure 819

The effect of UV doses was clearly demonstrated in Table 4.4 and Figure 4.4 with grafting yields increased with increasing UV exposure, except in cases of DMF and acetonitrile as solvents where grafting yields were low.

4.2.4 UV grafting of MMA to PPE (0.12 mm) with different photoinitiators

The performance of Irgacure 819 in enhancing grafting was compared with other photoinitiators in Table 4.5 and Figure 4.5. As shown, a significant grafting yield was achieved in the case of Irgacure 819. But Irgacure 184 led to the highest grafting, followed by Darocur 1173.
Table 4.1: UV grafting of MMA to PPE substrates (0.12 mm) with and without methanol, with different Irgacure 819 photoinitiator concentrations.

<table>
<thead>
<tr>
<th>Irgacure 819 conc. (% w/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA conc. (% v/v)</td>
</tr>
<tr>
<td></td>
<td>100&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>80&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.2</td>
<td>60%</td>
</tr>
<tr>
<td>0.5</td>
<td>50%</td>
</tr>
<tr>
<td>1</td>
<td>57%</td>
</tr>
<tr>
<td>1.5</td>
<td>23%</td>
</tr>
<tr>
<td>2</td>
<td>31%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Total dose: 46 J
<sup>b</sup> Total dose: 55 J
Solvent: methanol
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 4.1: UV grafting of MMA to PPE substrates (0.12 mm) with and without methanol, with different Irgacure 819 photoinitiator concentrations.
Table 4.2: UV grafting of MMA to PPE substrates (0.12 mm) with Irgacure 819 photoinitiator and different solvents.

<table>
<thead>
<tr>
<th>MMA conc. (% v/v)</th>
<th>Methanol</th>
<th>DMF</th>
<th>Acetonitrile</th>
<th>THF</th>
<th>Ethyl Acetate</th>
<th>Dichloromethane</th>
<th>Chloroform</th>
<th>Carbon tetrachloride</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>44</td>
<td>1</td>
<td>1</td>
<td>27</td>
<td>26</td>
<td>37</td>
<td>40</td>
<td>34</td>
<td>13</td>
</tr>
<tr>
<td>60</td>
<td>29</td>
<td>0</td>
<td>0</td>
<td>21</td>
<td>10</td>
<td>9</td>
<td>6</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1 % w/v
Dose rate: 36.7 J/hr
Total doses: 55 J
Temperature: 29 °C

Total doses: 92 J

Figure 4.2: UV grafting of MMA to PPE substrates (0.12 mm) with Irgacure 819 photoinitiator and different solvents.
Table 4.3: UV grafting of MMA to PPE substrates (0.015 mm) with different solvents and with Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>MMA conc. (% v/v)</th>
<th>MeOH</th>
<th>DMF</th>
<th>Acetonitrile</th>
<th>THF</th>
<th>Ethyl Acetate</th>
<th>Dichloromethane</th>
<th>Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>30</td>
<td>44</td>
<td>15</td>
<td>42</td>
<td>39</td>
<td>83</td>
<td>99</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1 % w/v
Dose rate: 36.7 J/hr
Total doses: 55 J
Temperature: 29 °C

Figure 4.3: UV grafting of MMA to PPE substrates (0.015 mm) with different solvents and with Irgacure 819 photoinitiator.
Table 4.4: UV grafting of MMA to PPE (0.015 mm) with different solvents and UV doses.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55 J</td>
</tr>
<tr>
<td>Methanol</td>
<td>30</td>
</tr>
<tr>
<td>THF</td>
<td>42</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>39</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>83</td>
</tr>
<tr>
<td>Chloroform</td>
<td>99</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1 % w/v  
Dose rate: 36.7 J/hr  
Temperature: 29 ºC

Figure 4.4: UV grafting of MMA to PPE (0.015 mm) with different solvents and UV doses.
Table 4.5: UV grafting of MMA to PPE (0.12 mm) with different photoinitiators, with methanol as a solvent.

<table>
<thead>
<tr>
<th>Photoinitiator</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgacure 2959</td>
<td>0</td>
</tr>
<tr>
<td>Irgacure 1800</td>
<td>23</td>
</tr>
<tr>
<td>Irgacure 1700</td>
<td>26</td>
</tr>
<tr>
<td>Darocur 1173</td>
<td>54</td>
</tr>
<tr>
<td>Irgacure 1000</td>
<td>43</td>
</tr>
<tr>
<td>Irgacure 819</td>
<td>32</td>
</tr>
<tr>
<td>Irgacure 369</td>
<td>37</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>60</td>
</tr>
</tbody>
</table>

Photoinitiators' concentration: 1 % w/v  
MMA concentration: 80 % v/v  
Solvent: methanol  
UV dose: 55 J  
Dose rate: 36.7 J/hr  
Temperature: 29 °C

Figure 4.5: UV grafting of MMA to PPE (0.12 mm) with different photoinitiators, with methanol as a solvent.
4.3 Discussion

4.3.1 Effect of solvents on UV grafting of MMA to PPE (0.12 mm)

Results in Table 4.1 and Figure 4.1 show MMA grafting to PPE in the presence of Irgacure 819 photoinitiator with and without methanol. Grafting yields were higher in neat MMA than with the presence of methanol despite the fact that the irradiation dose for neat MMA was lower than for solutions with methanol. Table 4.2 and Figure 4.2 present the grafting yields of MMA to PPE with different solvents. As in the case with methanol, grafting yields in these solvents were lower as compared to neat MMA. This set of results thus show that, unlike cellulose, PPE does not need solvents to facilitate grafting. In fact, DMF, while very effective for MMA grafting to cellulose, was not suitable for PPE. One important observation in this study was that the grafting was greatest with the highest MMA concentration of 80% v/v in all solvents but declining with decreasing in MMA concentration. This was because, unlike in the case with cellulose, MMA did slightly swell and wet PPE fibers [4]. It could swell the PPE structure, and thus aid in transporting free radicals formed from photoinitiator photolysis to the PPE surface. As a result, the grafting process was dependent to a large extent on MMA concentration. Thus, the addition of solvents diluted MMA, leading to lower grafting yields. In most cases, when the concentration of MMA was 40% v/v, the grafting yields declined rapidly, getting to almost zero when the concentration was 20% v/v.

The grafting of MMA to PPE does not require the presence of solvents. However, the presence of solvents could greatly interfere with the grafting process. As shown in Table 4.2 and Figure 4.2, grafting yields varied accordingly to the type of solvents. Non-polar solvents such as dichloromethane, chloroform and carbon tetrachloride enhanced the grafting of MMA to PPE. These solvents have the dual function of swelling PPE for grafting and dissolving the homopolymer PMMA formed [17]. The dissolution of PMMA was very important because it reduced the viscosity of the reaction solutions, resulting in decreasing gel effect. It also helped to maintain the transportation of the monomer to growing grafting chains. More polar solvents, including THF, ethyl acetate and acetone, also gave good grafting, however no grafting was observed for DMF and
acetonitrile. This could be due to the inability of these solvents to efficiently wet and swell PPE or dissolve PMMA [17].

One unique solvent was methanol. As a polar solvent, it was not expected to efficiently wet and swell PPE and additionally PMMA was observed to precipitate in its presence. Despite this, methanol gave grafting yields higher than halogenated hydrocarbon solvents. This phenomenon was probably due to Trommsdorff-type effect which was also thought to be responsible for good MMA grafting to cellulose substrates when methanol was used as a solvent (Section 3.2.1 of Chapter 3). The main cause of this effect was that termination rate was very slow due to the precipitation and tight coiling of grafted PMMA chains in methanol. Propagation rate was higher than termination rate, leading to the growth of grafted chains [17,18].

4.3.2 Substrate thickness effect on the grafting of MMA to PPE
The results of grafting yields of MMA to thin PPE substrates (0.015mm) were given in Table 4.3 and shown in Figure 4.3. As compared to Table 4.2, grafting yields generally were higher with thin substrates in most solvents. The only exception was methanol which produced a lower result. Since all substrates were exposed to the same conditions of UV doses, monomer concentrations, substrate dimension and temperature, it was concluded that the increase in grafting yields was mainly due to the decrease of films' thickness. This phenomenon could be explained due to the ability of MMA to thoroughly swell thin PPE substrates. MMA could access to the bulk of thin PPE films a great deal quicker, leading to high grafting yields. For the thicker PPE films, MMA could access only to limited regions near the surface. Therefore MMA grafting to thick PPE films was more of surface phenomenon.

The grafting process to thin films was especially enhanced by using solvents of methylene dichloride and chloroform. The grafting yields were more than double compared to thick films at the same MMA concentrations. This was because these solvents were more effective at swelling PPE than the others. As a result, radicals and monomers could penetrate deeper into thin film structure, leading to higher yields.
Effect of PPE film thickness on grafting yields was previously reported by Yen [17]. When studying the grafting of styrene to PPE films with different thickness using gamma irradiation, this author found that thin substrates gave higher grafting yields than thick substrates.

4.3.3 Effect of irradiation dose on the grafting of MMA to PPE (0.015mm)

Table 4.4 and Figure 4.4 show the results of the grafting of MMA to thin PPE films with different solvents and different UV doses. As in the case of cellulose, the grafting yield increased with UV doses. For methanol, no significant grafting increase was observed at the higher dose. For other solvents, considerable grafting increases were observed. Specifically, the grafting yield increased three times for THF, twice for ethyl acetate, two and half times for dichloromethane, one and half times for chloroform. These increases were probably due to Trommsdorff-type effect in which, towards the end of the exposure, grafted PMMA chains kept growing because high solution viscosity limited the possible termination of the growth of polymer chains. Different solvents gave different effects depending on their compatibility with the homopolymer. For solvents such as dichloromethane and chloroform which could well dissolve PMMA, the effect was less pronounced. For others, the effect was increased, leading to high grafting yields.

In the case of using methanol as the solvent, because methanol had the ability to precipitate PMMA, the homopolymer partially blocked UV lights from reaching the PPE surface. Therefore, the longer the reacting solution and substrate are exposed to UV radiation, precipitates would form instead. Ultimately, PMMA precipitate totally prevented the formation of new grafting sites. The Trommsdorff effect would still occur but more pronounced in the bulk of the solution than at the vicinity of the grafting sites. As the dose was further increased, more homopolymer was formed to a point when it was impossible to separate homopolymer from substrates.
4.3.4 Effect of Irgacure 819 photoinitiator concentrations on the grafting of MMA to PPE (0.12 mm)

Effect of Irgacure 819 concentration on grafting yields of MMA to PPE is given in Table 4.1 and Figure 4.1. As shown, grafting yields peaked at the PI concentrations of 0.2% w/v and 1% w/v, then declined as the concentration increased. At low Irgacure 819 concentration of 0.2% w/v, the homopolymerisation and grafting processes each competed for a small available amount of radicals. Although not many grafting sites were created because of the abundance of MMA with a small number of free radicals present, grafted chains were long leading to high grafting yields. As Irgacure 819 concentration increased, more radicals were formed and since the homopolymerisation was easier to achieve, a large quantity of homopolymers were produced, thereby suppressing the grafting process. At the Irgacure 819 concentration of 1% w/v, it can be expected that a large amount of radicals were generated, thus increasing the termination rates of both homopolymerisation and grafting processes, resulting in short polymer chains. However, due to a high number of radicals formed at the same time, more grafting sites were also created. The grafting process was expected to compete with the homopolymerisation of MMA monomer, and therefore, grafting yields were high. Also at a higher Irgacure 819 concentration, more radicals were formed and it can be envisaged that as soon as one radical initiated grafting or homopolymerisation, there were radicals nearby ready to terminate the growing polymer chain. As a result, grafted chains and homopolymer chains were expected to be very short.

Similar effect of varying photoinitiator concentrations on UV grafting of 2-hydroxyethyl methacrylate to PPE was reported by Shukla and Athyle [3]. According to their observations, there was an optimum concentration of a photoinitiator at which grafting yield was the highest. Similar explanations were offered by these authors for their observations.

4.3.5 Comparison between Irgacure 819 and other photoinitiator

Comparisons between the grafting yields using Irgacure 819 and other photoinitiators were presented in Table 4.5 and Figure 4.5. As in the case of using cellulose as the
substrate, Darocur 1173 and Irgacure 184 again were the best photoinitiators for the PPE system, and so was Irgacure 1000 (a mixture of the two photoinitiators). While very effective for cellulose, Irgacure 2959 did not perform as expected for PPE. Irgacure 369 had the opposite effect on PPE in which a high grafting yield was obtained. Compared to other photoinitiators, Irgacure 819 had an average performance.

When grafting yields were related to the structures of free radicals formed (Table 3.5, Chapter 3), it was observed that efficient photoinitiators (Irgacure 1800, Irgacure 1700 and Irgacure 819) did not guarantee good grafting. For example, Irgacure 1800, Irgacure 1700 and Irgacure 819 could generate several free radicals per molecule (Table 3.5) but their corresponding grafting yields were low compared to those of Darocur 1173. Once again, reactivity of free radicals and their sizes may have played important roles [19]. Grafting could be initiated only when free radicals could access into the PPE structure and be reactive enough to abstract hydrogen atoms from PPE chains in order to create grafting sites. If free radicals generated were not able to penetrate into the PPE structure or to abstract hydrogen atoms from PPE, low grafting yield resulted.

However, effect of photoinitiator types on MMA grafting to PPE was found to vary with irradiation techniques. In similar MMA grafting to PPE experiments but by gamma irradiation, Garnett and coworkers [11] reported that Darocur 1173 did not perform as well as Irgacure 1700 and 1800. Comparison with our data led to the conclusions that photoinitiator types had a significant effect on grafting process but that effect also varied according to irradiation techniques.

4.4 Conclusions
In this chapter, grafting of MMA to PPE substrates has been studied. The grafting process was found to depend on solvents, substrates’ thickness, exposure doses, photoinitiators and their concentrations. With reference to the previous chapter, grafting of MMA to PPE was influenced by similar conditions as with cellulose. However, the main difference between the two materials was that solvents had more pronounced effects on cellulose than on PPE.
4.5 References


CHAPTER FIVE: MMA GRAFTING TO PPE WITH VINYL ETHERS AS COMONOMERS USING UV RADIATION
5.1 Introduction

Vinyl ethers are extremely reactive monomers which are known to undergo polymerization by a cationic mechanism and are useful in applications which require a high speed curing of a resin formulation [1-3]. Besides having high reactivity, they also possess another appealing property of low toxicity which is essential for consumer goods applications [3]. While a lot of efforts have been concentrated on studying the homopolymerization [3-8] and copolymerization [2,3,9-17] of vinyl ethers, not many studies of their effects on grafting to substrates such as cellulose and PPE have been carried out. The purpose of this and the following chapters is to examine the effects of vinyl ethers on MMA grafting to PPE and cellulose substrates under the influence of UV radiation.

5.1.1 Vinyl ethers

Vinyl ethers are very reactive monomers depending on their structures. Vinyl ethers can contain from one to many vinyl ether functional groups. The general formula of a monofunctional vinyl ether is presented in Figure 5.1.

\[ \overset{\text{O}}{\text{R}} \]

**Figure 5.1:** formula of a monofunctional vinyl ether.

Due to the effect of oxygen atom in the vinyl ether group, double bonds present in vinyl ethers are slightly polar in character and therefore cationic polymerization is favored [1]. Vinyl ethers can undergo rapid cationic polymerization in the presence of protonic and Lewis acids such as hydrogen iodide, hydrogen chloride and zinc halides [1-17]. Scheme 5.1 shows the cationic polymerization mechanism of vinyl ether with protonic and Lewis acid.
Scheme 5.1: The mechanism of the cationic polymerization of vinyl ethers with protonic and Lewis acid.

5.1.2 Copolymerization of vinyl ethers with other vinyl monomers

While very reactive towards cationic polymerization, neat vinyl ethers are known not to undergo free radical polymerization [1]. That means grafting of neat vinyl ethers to substrates by free radical mechanism is impossible. Since the grafting by cationic growth is very inefficient due to extensive chain transfer [18], no literature on grafting of neat vinyl ethers to cellulose or PPE substrates have been reported.

However, vinyl ethers were reported to readily copolymerize with other vinyl comonomers in the presence of free radicals [1-3,17]. Decker and co-workers [11-13] reported that multifunctional vinyl ethers such as triethylene glycol divinylether (DVE-3) and diethylene glycol divinylether (DVE-2) were extremely reactive towards both cationic and radical polymerization in the presence of multifunctional acrylates such as polyether tetracrylate (Ebecryl 80) or trimethylol propane triacrylate (TMPTA). In fact, their presence greatly enhances the polymerization rates as well as the overall cure extent of the above multifunctional acrylate monomers. The enhancement of polymerization rates was thought to be due to a copolymerization mechanism involving a cross-propagation by the vinyl ether and acrylate radicals to give copolymers with isolated vinyl ether units [11]. Vinyl ethers were also reported to undergo copolymerization with a range of vinyl monomers, such as maleic anhydride [10] and maleates [12], in the presence of free radicals. Since vinyl ethers can undergo free radical copolymerization with acrylates, it is therefore possible that vinyl ethers can be incorporated into grafted chains on substrates. The ability of vinyl ethers to accelerate copolymerization may influence the grafting process as well.

Not all vinyl ethers were found to readily participate in free radical copolymerization with other vinyl monomers. Bevington and coworkers [16,17] reported that monofunctional
vinyl ethers, such as n-propyl vinyl ether (NPVE), ter-butyl vinyl ether (TBVE) and dodecyl vinyl ether (DDVE), retarded polymerization of MMA and styrene induced by radicals generated from AIBN. Since there are similarities in the homopolymerization and grafting processes, such monofunctional vinyl ethers are expected to have similar effects of hindering grafting of MMA to PPE or cellulose substrates. Thus, one objective of the study in this chapter was to examine the effect of vinyl ether on MMA grafting to PPE substrates by UV irradiation.

5.1.3 Vinyl ethers as electron donors in Charge Transfer complexes
As electron donors, vinyl ethers can spontaneously polymerize with electron poor vinyl monomers such as maleic anhydride, maleimides, maleates and furamates under the influence of a UV source without the inclusion of PIs [19-22,24,25]. As discussed in Section 1.5 of Chapter 1, the polymerization mechanism is called Charge Transfer Complex polymerization in which complexes are formed via the interaction between electron rich monomers (donors) and electron poor monomers (acceptors) [19-25]. Under the influence of a UV source, such complexes get excited and the subsequent decay of these excited CT complexes to their lower energy states lead to the generation of radicals as well as ionic species, resulting in the polymerization of vinyl monomers [20,23]. The concept of CT complexes is relevant when considering monomer mixtures such as vinyl ethers and MMA. Despite MMA being a very weak acceptor, there is a possibility that vinyl ethers (as electron donors) may form CT complexes with MMA and thus, can have influence on grafting yields.

In this chapter, the ability of different vinyl ethers to form CT complexes with MMA will be under investigation, and the effect of vinyl ethers on grafting yields will be considered.

5.2 Results
5.2.1 Grafting of vinyl ethers to PPE with and without Irgacure 819 photoinitiator
The purpose of these experiments was to confirm that the vinyl ethers of interest could not undergo homopolymerization under the influence of a UV source with or without the presence of free radicals. Results in Table 5.1 show that in the absence of PI all the neat vinyl ethers did not show any sign of polymerization or grafting to PPE despite long
exposure to UV radiation. The experiments were repeated but with the inclusion of 1% w/v of Irgacure 819 and the reacting solutions were again exposed to UV radiation for long periods of time exceeding 16 hours. Again, no polymerization and grafting were observed. These results were in accordance with the above understanding that vinyl ethers do not homopolymerize under the influence of UV radiation even in the presence of free radicals.

However, the situation was different when neat MMA was exposed to UV radiation in the absence of PI for a long period of time. The polymerization commenced at the radiation dose of 367 J and a clear polymer was formed at the dose of 593 J. The polymer formed was so excessive that it was impossible to separate the substrate from the homopolymer.

5.2.2 Grafting of MMA and vinyl ethers to PPE without Irgacure 819 photoinitiator

Results of MMA grafting to PPE with vinyl ethers in the absence of Irgacure 819 photoinitiator are presented in Table 5.3-Figure 5.3 and Table 5.4-Figure 5.4. MMA/vinyl ethers ratio in Table 5.3 is 80/20 and in Table 5.4 is 60/40. The solution compositions were varied in order to investigate the possibility of CT complex formation.

As shown in Table 5.3, high exposure doses were required for the polymerization of reacting solutions. UV dose for each solution to polymerize also varied with the type of vinyl ethers. DVE required the lowest dose of 232 J to form a white polymer. Solutions of MMA with other vinyl ethers except PVE and IBVE also polymerized but to a lower extent. Generally, solutions which polymerized to a larger extent also resulted in high grafting yields. One exception was with MMA/TMPTVE where excessive polymer was formed, leading to the loss of the substrate.

As shown in Table 5.4, for the grafting of various vinyl ethers and MMA onto PPE in the absence of Irgacure 819, the grafting yield does depend on the concentration of MMA in solutions. At MMA concentration of 60% v/v, except for DVE, TMPTVE and DEAEVE, no grafting was observed. On the same token, only solutions which contained the mentioned vinyl ethers polymerized to form clear polymers under the same conditions.
Experiments involving a further decrease of MMA concentration to 40% v/v were conducted to investigate the possibility of CT complex formation at lower MMA concentration. Results in Table 5.5 indicated that MMA solutions containing DVE and TMPTVE polymerized to form clear polymers. However, grafting was observed in MMA solutions containing DVE, HDVE, DVE-4 and TMPTVE with the solution containing DVE achieving the highest grafting yield of 200%.

5.2.3 Grafting of MMA to PPE with vinyl ethers as comonomers, with 1% w/v Irgacure 819 photoinitiator.
Results in Table 5.6 and Figure 5.6 present the grafting of MMA to PPE in which MMA/vinyl ethers was 80/20 and with the inclusion 1% w/v of Irgacure 819. In the presence of the photoinitiator, only a small irradiation dose of 37 J was required to polymerize all solutions. Polymers resulted were clear and yellow due to the unreacted photoinitiator. Grafting yields were also high, increasing with the increase in the number of vinyl ether functional groups as well as the increase in molecular weight of vinyl ethers.

5.2.4 Characterization of grafted substrates by FT-IR
FT-IR spectra in Figure 5.7 show the composition of MMA/vinyl ether grafted substrate. The presence of MMA units in grafted chains is apparent with their large absorption peak at 1732 cm\(^{-1}\). The spectrum of the ungrafted PPE substrate at the bottom of Figure 5.7 is displayed for comparison purposes.
Table 5.1: UV grafting of vinyl ethers or MMA to PPE substrates without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Monomers</th>
<th>0% Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>PVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>TBVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>NBVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>DVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>HDVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>DVE-4</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>DEA EVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>EHVE</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>DVE-3</td>
<td>0</td>
<td>593</td>
</tr>
<tr>
<td>MMA</td>
<td>Excessive</td>
<td>593</td>
</tr>
<tr>
<td>MMA</td>
<td>69</td>
<td>367</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr  
Temperature: 29 °C
Table 5.2: UV grafting of vinyl ethers to PPE substrates with 1% w/v Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers</th>
<th>1% w/v Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>PVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>TBVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>NBVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>DVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>HDVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>DVE-4</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>EHVE</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>DVE-3</td>
<td>0</td>
<td>440</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C
Table 5.3: UV grafting of MMA to PPE with vinyl ethers as comonomers, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers (20% v/v)</th>
<th>80% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>88</td>
<td>862</td>
</tr>
<tr>
<td>PVE</td>
<td>0</td>
<td>896</td>
</tr>
<tr>
<td>TBVE</td>
<td>563</td>
<td>832</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>896</td>
</tr>
<tr>
<td>NBVE</td>
<td>41</td>
<td>896</td>
</tr>
<tr>
<td>DVE</td>
<td>200</td>
<td>232</td>
</tr>
<tr>
<td>HDVE</td>
<td>20</td>
<td>896</td>
</tr>
<tr>
<td>DVE-4</td>
<td>343</td>
<td>896</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>Excessive</td>
<td>832</td>
</tr>
<tr>
<td>DEAEEVE</td>
<td>18</td>
<td>896</td>
</tr>
<tr>
<td>EHVE</td>
<td>39</td>
<td>896</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr  
Temperature: 29 °C

Figure 5.3: UV grafting of MMA to PPE with vinyl ethers as comonomers, without Irgacure 819 photoinitiator. All solutions contained 80% v/v MMA, 20% v/v vinyl ethers.
Table 5.4: UV grafting of MMA to PPE with vinyl ethers as comonomers, without Irgacure 819 photoinitiator. Solutions contained 60% v/v MMA, 40% v/v vinyl ethers.

<table>
<thead>
<tr>
<th>Vinyl ethers (40% v/v)</th>
<th>60% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>PVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>TBVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>NBVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>DVE</td>
<td>197</td>
<td>734</td>
</tr>
<tr>
<td>HDVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>DVE-4</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>91</td>
<td>734</td>
</tr>
<tr>
<td>DEAEEVE</td>
<td>5</td>
<td>881</td>
</tr>
<tr>
<td>EHVE</td>
<td>0</td>
<td>881</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 5.4: UV grafting of MMA to PPE with vinyl ethers as comonomers, without Irgacure 819 photoinitiator. Solutions contained 60% v/v MMA, 40% v/v vinyl ethers.
Table 5.5: UV grafting of MMA to PPE with vinyl ethers and without Irgacure 819 photoinitiator. Solutions contained 40% v/v MMA, 60% v/v vinyl ethers.

<table>
<thead>
<tr>
<th>Vinyl ethers (60% v/v)</th>
<th>40% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>PVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>TBVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>NBVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>DVE</td>
<td>200</td>
<td>618</td>
</tr>
<tr>
<td>HDVE</td>
<td>6</td>
<td>881</td>
</tr>
<tr>
<td>DVE-4</td>
<td>17</td>
<td>881</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>95</td>
<td>618</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>0</td>
<td>881</td>
</tr>
<tr>
<td>EHVE</td>
<td>0</td>
<td>881</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 5.5: UV grafting of MMA to PPE with vinyl ethers as comonomers, without Irgacure 819 photoinitiator. Solutions contained 40% v/v MMA, 60% v/v vinyl ethers.
Table 5.6: Grafting of MMA to PPE with vinyl ethers and 1% w/v of Irgacure 819 photoinitiator. Solutions contained 80% v/v MMA, 20% v/v vinyl ethers.

<table>
<thead>
<tr>
<th>Vinyl ethers</th>
<th>80% w/v MMA - 1% w/v Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>53</td>
<td>37</td>
</tr>
<tr>
<td>PVE</td>
<td>61</td>
<td>37</td>
</tr>
<tr>
<td>TBVE</td>
<td>39</td>
<td>37</td>
</tr>
<tr>
<td>IBVE</td>
<td>67</td>
<td>37</td>
</tr>
<tr>
<td>NBVE</td>
<td>90</td>
<td>37</td>
</tr>
<tr>
<td>DVE</td>
<td>386</td>
<td>37</td>
</tr>
<tr>
<td>HDVE</td>
<td>312</td>
<td>37</td>
</tr>
<tr>
<td>DVE-4</td>
<td>506</td>
<td>37</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>900</td>
<td>37</td>
</tr>
<tr>
<td>DEAEEVE</td>
<td>8</td>
<td>37</td>
</tr>
<tr>
<td>EHVE</td>
<td>172</td>
<td>37</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 5.6: Grafting of MMA to PPE with vinyl ethers and 1% w/v of Irgacure 819 photoinitiator. Solutions contained 80% v/v MMA, 20% v/v vinyl ethers.
Figure 5.7: UV grafting of MMA/vinyl ether grafted PPF substrates using UV radiation with 1% Irgacure 819.
5.3 Discussion

5.3.1 Solutions’ polymerization without Irgacure 819 photoinitiator

Without any photoinitiator present in the reacting solutions there are two types of radicals formed upon UV irradiation. One type is formed on the PPE substrates and another is in the reacting solutions. Since Pyrex tubes were used, most of the UV light of wavelengths shorter than 320 nm was cut off [26]. The UV light which reached the bulk of the solution and the substrate has wavelengths longer than 320 nm, too weak to excite and break bonds in pure PPE. However, commercial PPE may be able to absorb such wavelength to produce radicals. An excellent review of UV light absorption of PPE was done by Yen [26]. The absorption of the UV light of such long wavelengths is thought to be due to impurities present in PPE. Impurities are likely to be aromatic compounds because single carbonyl bonds or double bonds only absorb at wavelengths shorter than 300 nm. These impurities become excited by UV lights through a biphotonic mechanism to an upper excited triplet state followed by energy transfer from the second excited state to the unsaturated bonds in the polymer. As a result, the allyl hydrogens of the unsaturated bonds are released, producing radicals. The mechanism is presented in Scheme 5.2.

\[
\begin{align*}
\left[ \text{Aromatic} \right] & \xrightarrow{hv} \left[ \text{Aromatic} \right]^* \\
\left[ \text{Aromatic} \right]^* + \text{PH} & \rightarrow \left[ \text{Aromatic} \right] + \left[ \text{PH} \right]^* \\
\left[ \text{PH} \right]^* & \rightarrow \text{H}^* + \text{P}^*
\end{align*}
\]

Scheme 5.2: Radical formation upon PPE’s UV absorption. PH represents a polymer.

The formation of polymers in solutions is mainly thought to be due to impurities in solutions which act as sensitizers at wavelengths greater than 320 nm [26]. Upon UV light absorption, energy of impurities’ excited state may be transferred to MMA to form radicals. These radicals then react with other monomers leading to grafting. Long
exposure of vinyl ethers to UV radiation can also generate free radicals in the solutions. It is well known that ethers, when exposed to UV lights for a long period of time, produce free radicals which, in the presence of air, react with oxygen to form peroxy radicals or hydroperoxides [1]. These species can decompose to form radicals which are capable of initiating polymerization. The mechanism of the formation of peroxy radicals and hydroperoxides by the interaction between a vinyl ether and UV radiation is presented in Scheme 5.3.

\[
\begin{align*}
\text{hv} & \quad \text{R} - \text{O} - \text{O} \quad \rightarrow \quad \text{R} - \text{O} - \text{O} - \cdot \\
\text{O}_2 & \quad \text{R} - \text{O} - \text{O} \quad \rightarrow \quad \text{R} - \text{O} - \text{O} - \cdot \\
\text{OO} - & \quad \text{R} - \text{O} - \text{O} \quad \rightarrow \quad \text{R} - \text{O} - \text{O} - \cdot \\
\text{OOH} & \quad \text{R} - \text{O} - \text{O} \quad \rightarrow \quad \text{R} - \text{O} - \text{O} + \cdot \text{OH}
\end{align*}
\]

**Scheme 5.3:** Radical formation from the interaction of vinyl ether with UV radiation.

Radicals on the surface of PPE can also participate in the chain transfer process in which radical is transferred from growing grafted chains to MMA molecules in the bulk of solutions [26]. These newly formed radicals, with other radicals formed from the decomposition of hydroperoxides, continue to react with other monomers to form polymers in solutions. The chain transfer process is presented in Scheme 5.4.

\[
PPE-(\text{MMA})_n^- + \text{MMA} \rightarrow PPE-(\text{MMA})_n + [\text{MMA}]^-
\]

**Scheme 5.4:** Radical formation due to chain transfer process with MMA monomer

The above possibilities are useful to explain the polymer formation in the neat MMA solution. According to results in Table 5.1, MMA appeared to commence polymerization at the dose of 367 J and a large amount of homopolymer was produced when the UV dose reached 593 J. Despite the fact that MMA was purified before usage, it was
unavoidable that it still contained traces of impurities which could promote the formation of radicals. PPE substrate was used as purchased, again impurities and irregular bonds may have played a part in producing reactive sites for grafting on its surface. This was proved by the grafting yield of 69% when neat MMA was exposed to UV light with the dose of 367 J. This is impressive considering that the grafting yield of neat MMA with 1% w/v of Irgacure 819 photoinitiator at 46 J dose was only 57% (Table 4.1, Chapter 4). With such a high grafting yield achieved while the solution was only slightly polymerized, it thus indicated that more activities were occurring at the surface of PPE rather than in the bulk of solutions.

Tables 5.1 and 5.2 reconfirm the inability of vinyl ethers to undergo radical polymerization despite a large amount of Irgacure 819 photoinitiator was used and very long UV exposures were applied. This is originated from the fact that the double bond of vinyl ether functional groups is slightly polar and can only participate in the cationic polymerization [1]. Without the presence of cations, neat vinyl ethers did not polymerize and hence no grafting was observed.

From Table 5.3, it was observed that, for MMA/vinyl ether comonomer systems, very long UV exposures were required in order for polymerization to occur. These doses were significantly higher than the dose of 593 J required for neat MMA. Despite of large radiation doses, solutions containing PVE and IBVE did not polymerize at all. This indicates that these vinyl ethers did not actively participate as comonomers with MMA in the polymerization process. To some extent, some vinyl ethers such as PVE and IBVE appeared to have hindered the process. One exception is the polymerization of MMA/DVE (Table 5.3). The UV dose of 232 J was very low compared to the dose of 593 J for neat MMA. This showed DVE was an active component in enhancing the polymerization of the MMA/DVE system.

The extent of polymerization also differed between vinyl ethers (Table 5.3). Based on the appearance of viscosity of the solutions, MMA solutions containing multifunctional vinyl ethers, DVE, HDVE, DVE-4 and TMPTVE, polymerized more than solutions containing
monofunctional vinyl ethers. First of all, this may be due to the number of vinyl ether
groups present in the multifunctional vinyl ethers. While vinyl ether radicals were not
reactive towards the double bond present in vinyl ethers, they may have been reactive
towards MMA monomer. Due to the presence of multifunctional vinyl ethers, cross-
linking between different MMA polymer chains was possible. This led to limited
movements of the growing chains, hence reducing termination rates brought about by the
Trommsdorff effect. This was more apparent in the case of TMPTVE which produced
excessive polymer. Secondly, this may be due to the higher viscosity of multifunctional
vinyl ethers. The increase in viscosity of solutions may have hindered the diffusion of
radicals, thus reducing the chances of termination. As polymer grew, the viscosity of the
solution increased, leading to gelation.

Also, there is a possibility of CT complex formation between vinyl ethers and MMA. As
vinyl ethers are electron rich they are electron donors. The presence of carboxyl group in
MMA molecule may withdraw electrons from the double bond and therefore it can be
classified as an electron acceptor although it may not be as a strong acceptor as maleic
anhydride, maleates and maleimides. According to the CT complex polymerization
mechanism, if such complexes are formed under UV exposure they should be able to
undergo a spontaneous polymerization reaction. From Table 5.3, the system of
MMA/DVE strongly suggested the possible formation of a CT complex because the
required UV dose (232 J) for this solution to polymerize was very low compared to that
(367 J – Table 5.1) of the neat MMA monomer.

As the concentration of MMA decreased, the ability of the reacting solutions to
polymerize also decreased. In Table 5.4, with MMA concentration of 60% w/v, only two
reacting solutions which contained DVE and TMPTVE polymerized whilst the others
remained in a liquid state. In Table 5.5, MMA concentration was decreased further to
40% w/v. Again, only two solutions containing DVE and TMPTVE formed polymers at a
comparatively lower UV dose (618 J). This strongly suggested DVE and TMPTVE could
have interacted with MMA upon UV exposures and formed CT complexes.
Chapter Five: MMA Grafting To PPE With Vinyl Ethers As Comonomers Using UV Radiation

The results in Tables 5.3 and 5.4 are consistent with a previous study by Bevington and co-workers [16]. In their experiments of MMA with a number of monofunctional and multifunctional vinyl ethers, they found that monofunctional vinyl ethers, such as PVE, TBVE, 2-chloroethyl vinyl ether and dodecyl vinyl ether, showed little tendency to undergo radical polymerization with MMA. It was also found that divinyl ethers of polyethylene glycols could lead to cross-linking when used as comonomers with MMA. In another study [17], they also found that the radical polymerization of MMA in benzene were retarded by vinyl ethers such as n-propyl, t-butyl and n-dodecyl compounds and the chain lengths of the resulting copolymers were less than those of the corresponding homopolymer.

The data in these two tables suggests that most vinyl ethers (especially low molecular weight monofunctional vinyl ethers) not only did not enhance grafting but also appeared to have retarded MMA polymerization process. This explains the liquid appearance of the reacting solutions even after being exposed to a high UV dose of 881 J as compared to neat MMA which polymerized after an UV dose of 367 J was applied.

5.3.2 Grafting of MMA to PPE with vinyl ethers without Irgacure 819 photoinitiator

In studying grafting process, it is important to know what processes are taking place in the bulk of solutions. This is because any process that is occurring in solutions may directly or indirectly influence grafting.

As mentioned above (Tables 5.1 and 5.2), no grafting was observed when only neat vinyl ethers were used. It was because vinyl ethers could not react with reactive sites on the PPE surface. However, when vinyl ethers were mixed with MMA in the ratio of vinyl ether: MMA = 20/80, some grafting was achieved as shown in Table 5.3 and Figure 5.3. But the degree of grafting greatly varied with the type of vinyl ethers. The grafting yields were from as low as zero for reaction solutions contain PVE and IBVE to as high as 563% for TBVE. The grafting yields did not follow any particular trend with respect to the number of vinyl ether groups or molecular weights. Very high grafting yields in the MMA/TBVE, MMA/DVE and MMA/DVE-4 systems together with the excessive
grafting in the case of TMPTVE may have been due to very rapid polymerization of the monomers, resulting in the whole block of grafted polymer chains being bonded onto the PPE surfaces.

It was observed that the grafting yields were related to the extent of polymerization, as all solutions which polymerized also gave high grafting yields. This could be due to the similarity in the grafting process and the polymerization process that was taking place in the bulk of solution. It also may have been caused by the Trommsdoff effect which accelerated the growth of grafted chains when the increase in the viscosity of the solutions severely limited chances of termination.

As the concentration of vinyl ethers increased to 40% v/v (Table 5.4) and 60% v/v (Table 5.5), the MMA concentration in the systems were diluted further. As shown in the two tables, increasing vinyl ether concentrations appeared to retard MMA homopolymerization [16,17] in the solutions as well as growth of the grafted chains resulting in low or zero grafting yields in most cases.

Again, DVE and TMPTVE were the exceptions with high grafting yields achieved at both MMA concentrations of 60% v/v and 40% v/v, despite the lower UV exposure doses used compared to the other systems. High grafting yields may have been due to Trommsdoff effect caused by the polymerization of the solutions containing these two vinyl ethers. Another reason was that DVE and TMPTVE can function as cross-linking agents which led to the branching of grafted chains. Other multifunctional vinyl ethers, HDVE and DVE-4, could not function as such since the polymerization of their solutions did not take place. Since no PI was present in these systems, this strongly suggests that both polymerization and grafting processes were initiated by CT complexes in these systems.
5.3.3 Polymerization of MMA/vinyl ethers in the presence of Irgacure 819 photoinitiator

The presence of abundant radicals generated from the photolysis of Irgacure 819 photoinitiator was expected to have accelerated the polymerization of solutions. According to results in Table 5.6, the required dose was only 37 J in all systems and this was a significantly lower dose used compared to the UV dose used in the absence of the photoinitiator (Tables 5.3-5.4-5.5). All solutions polymerized, producing clear polymers.

5.3.4 Grafting of MMA/vinyl ethers to PPE in the presence of Irgacure 819 photoinitiator

As all MMA/vinyl ether systems were exposed to the same experimental conditions, comparison of grafting yields could therefore be made. As shown in Table 5.6 and Figure 5.6, grafting yields increased with the increase in the number of vinyl ether groups. The highest grafting yield was achieved for the system containing MMA/TMPTVE, a trifunctional vinyl ether. Other systems containing divinyl ethers, such as DVE-4, DVE and HDVE, had obtained very high grafting yields but considerably lower than in the case of MMA/TMPTVE. The order of declining grafting yields follows the order of declining molecular weights. DVE-4 with the highest molecular weight had the highest grafting yield of 506%.

For systems containing monofunctional vinyl ethers, grafting yields were significantly lower compared to those containing multifunctional vinyl ethers. The grafting yields increased with increasing molecular weight of vinyl ethers with EHVE attaining the highest grafting yield of 172%. One exception was DEAEVE which had a high molecular weight but had the lowest grafting yield.

TBVE, IBVE and NBVE are structural isomers as shown in Figure 2.2 of Chapter 2. It was observed that solutions containing MMA in the presence of these vinyl ethers gave different grafting yields, and similar observations were found in Table 5.3 where Irgacure 819 was not present. Results in Table 5.3 and Table 5.6 show that the grafting yield depends on chemical structure of the vinyl ethers. However, in the absence of Irgacure
819 (Table 5.3), NBVE was better at enhancing MMA grafting than IBVE and TBVE did. The opposite was observed when Irgacure 819 was present (Table 5.6), thus indicating no concrete trend relating the structures of vinyl ethers to the grafting yields can be drawn.

High grafting yields achieved for solutions containing multifunctional vinyl ethers compared to those of monofunctional vinyl ethers were mainly due to the ability of the former vinyl ethers which act as crosslinking agents [16]. As mentioned in Section 5.3.2, multifunctional vinyl ethers could enhance grafting by causing the branching of grafted chains and the extra double bonds on the vinyl ethers could serve as new grafting center. The degree of branching possibly increased with the number of double bonds as being evidenced by the highest grafting yield obtained for MMA solutions containing TMPTVE. Another possible effect of multifunctional vinyl ethers as crosslinking agents was that they aided the gelling of reaction solutions, leading to high viscosity which may have caused Trommsdorff effect on both polymerization and grafting processes. Furthermore, their presence may have accelerated the growth of grafted chains since studies by Decker [11] and Decker et al [13] found that DVE-3 participated in rapid copolymerization with trimethylol propane triacrylate under the influence of a UV source.

Besides the branching effect, higher molecular weight multifunctional vinyl ethers may have been more compatible with PPE. As PPE is a non-polar material of long hydrocarbon chains, the presence of long chain vinyl ethers may have served as a useful wetting and swelling agent for PPE, making it easier for the MMA monomer to access into the PPE structure. The incorporation of high molecular weight multifunctional vinyl ethers into grafted chains also resulted in the larger increase in grafting yields as compared to the incorporation of low molecular weight monofunctional vinyl ethers.

With reference to grafting yield value of 32% for neat MMA in the presence of 1% w/v Irgacure 819 in Chapter 4 (Table 4.5), the addition of multifunctional and high molecular weight vinyl ethers to MMA certainly have improved the grafting to PPE, despite of
shorter UV radiation exposures. While effect of low molecular weight monofunctional vinyl ethers on grafting yields was less profound, they also played an active part in the polymerization process.

5.3.5 Characterizations of grafted substrates by FT-IR

FT-IR is a useful technique for analyzing components present in the grafted chains. Figure 5.7 shows the spectra of grafted substrates. All spectra show large absorption peaks at the frequency of 1732 cm\(^{-1}\) which is due to C=O stretch of MMA units in grafted chains.

Unfortunately, when comparing spectra of various MMA/vinyl ether grafted substrates with that of neat MMA grafted substrate (Figure 4.7 of Chapter 4) in an attempt to find the presence of vinyl ether units in grafted chains, no conclusive evidence could be obtained. It is because C-O-C absorption range of vinyl ether units lies in the range of 1070-1240 cm\(^{-1}\) which is the same as that of C-O-C absorption range of the ester functional group of MMA units [27].

Solid state NMR would be a relevant technique applied for this valuation. However, this facility was not available when this work was carried out and a study should be investigated in the future to correctly address the question of grafted components.

5.4 Conclusions

In this chapter, a study on the effect of vinyl ether on the concurrent grafting and curing of MMA to PPE has been carried out. In the absence of Irgacure 819 photoinitiator, solutions of MMA in the presence of vinyl ethers except PVE and IBVE were found to be able to polymerize but only at high MMA concentrations. At lower concentrations of MMA, only two solutions with DVE and TMPTVE polymerized. Thus, the polymerization process was possibly initiated by the interaction between electron poor MMA and the two electron rich vinyl ethers upon UV exposure. With the presence of Irgacure 819, grafting yields were found to be dependent on the number of vinyl ether
groups, molecular weight and molecular structure of vinyl ethers. In all grafted samples, MMA was confirmed by FT-IR as the main component of the grafted chains.

5.5 References


CHAPTER SIX: MMA GRAFTING TO PPE WITH VINYL ETHERS AS COMONOMERS USING GAMMA RADIATION
6.1 Introduction

The use of gamma irradiation is an efficient technique to graft monomers to a variety of substrates. Good grafting results are often achieved because under the influence of gamma irradiation, reactive sites are created on polymer chains of substrates, reducing the number of steps in the grafting process [1-3]. Grafting of a number of vinyl monomers such as styrene, acrylic monomers and 4-vinyl pyridine to PPE and cellulose substrates has been successfully carried out using gamma irradiation [1-3]. In this chapter, our interest in gamma grafting technique is due to the possibility of cation formation from the interaction between substrates [2] or monomers [3,4] with gamma radiation. The presence of cations in reacting solutions has an important implication since vinyl ethers have been reported to undergo cationic homopolymerization [5]. Thus, the aim of this chapter is to investigate the ability of the vinyl ethers of interest to undergo polymerization under the influence of gamma irradiation as well as the effect of these vinyl ethers on gamma grafting of MMA to PPE substrate.

6.1.1 Radical and cation formations by gamma irradiation

In the concurrent curing and grafting technique, the PPE substrate is in direct contact with monomer solution and thus upon gamma exposure there are two potential sources of free radicals, from PPE as well as the monomer [1]. As discussed in Section 1.3.1.2 of Chapter 1, free radicals are formed in PPE structure due to bond scissions under the influence of gamma radiation [1,3]. Most of bond scissions occur at bonds between carbon and hydrogen atoms and most of hydrogen atoms are released as hydrogen gas [1]. The mechanism of radical formations in PPE under gamma exposure is similar to the one presented in Scheme 1.1 of Section 1.2, Chapter 1. Generated radicals may initiate the polymerization of the monomer which subsequently lead to grafting. On the other hand, these radicals may react with oxygen in the solution, resulting in the formation of peroxy radicals, peroxide or hydroperoxide species [1]. Further decompositions of peroxides and hydroperoxides under the influence of temperature generate free radicals which are useful in inducing the polymerization of the monomer in the solution [1]. The mechanism of radical reacting with oxygen is described in Scheme 1.4 of Section 1.3.6, Chapter 1.
Under the influence of gamma radiation, C-H bonds in MMA and vinyl ethers can be broken up, forming radicals which can either induce the homopolymerization of MMA in the solution or react with PPE to create grafting sites [3-5]. Further reactions of such free radicals with oxygen may lead to the formation of hydroxy and peroxide radicals and the process is similar to the mechanism previously described in Scheme 5.4 of Section 5.3.1, Chapter 5. The radical formation in MMA under the influence of gamma radiation is presented in Scheme 6.1 below.

\[
\begin{align*}
\text{MMA} & \xrightarrow{\text{Gamma Radiation}} [\text{MMA}]^* + \text{H}^* \\
\end{align*}
\]

**Scheme 6.1:** Radical formation in MMA by gamma radiation.

Gamma radiation is an ionizing radiation and thus its interaction with monomers can produce cationic and anionic species [3]. As vinyl ethers undergo cationic polymerization, the generation of cationic species could potentially lead to the homopolymerization of vinyl ethers in solutions and thus influencing the grafting process. The mechanism of cation formation from MMA under the influence of gamma radiation is represented in Scheme 6.3.

\[
\begin{align*}
\text{MMA} & \xrightarrow{\text{Gamma Radiation}} [\text{MMA}]^+ + \text{e}^- \\
\end{align*}
\]

**Scheme 6.3:** Cation formation from a vinyl monomer under the influence of gamma radiation.
6.2 Results

6.2.1 Grafting of neat vinyl ethers to PPE by gamma irradiation

PPE films in neat vinyl ethers, PVE, TBVE, IBVE, DVE, HDVE, DVE-4, TMPTVE, DEAEVE, EHVE and DVE-3, were exposed to gamma radiation to evaluate their ability to polymerize as well as to graft, and no grafting was achieved. However, except TMPTVE, all the other vinyl ethers under study did not polymerize. TMPTVE appeared to have polymerized to form a clear polymer.

6.2.2 Grafting of MMA to PPE with vinyl ethers as comonomers by gamma irradiation

The vinyl ethers as given in the above section were mixed with MMA in the volume ratio of 80% MMA: 20% vinyl ether, and all solutions were exposed to gamma radiation. Grafting yields are summarized in Table 6.2. Figure 6.2 shows comparison of grafting yields in the presence of different vinyl ethers. Polymerization was observed in most solutions at a dose of 4.9 kGy.

6.2.3 Gamma grafting of MMA to PPE with vinyl ethers as comonomers and chloroform as solvent

Chloroform was chosen as the solvent in this study due to its ability to swell PPE substrate and above all it was shown to have enhanced grafting yields of MMA to PPE in the case of UV radiation as in Chapter 4. It was added to solutions containing MMA and vinyl ethers in the volume ratio of chloroform:vinyl ethers:MMA=20:16:64 in order to study the effect of this solvent on grafting yield. By comparing data in Table 6.3 and Figure 6.2, the addition of this solvent led to significant changes in grafting yields and polymerization behavior. Grafting yields were significantly lower in solutions containing EVE, PVE, TBVE, IBVE, NBVE and DEAEVE but higher in solutions containing DVE, HDVE, DVE-4, TMPTVE and EHVE. A slightly higher gamma dose of 5.2 kGy was also required for the polymerization of all reacting solutions.
6.2.4 Effect of vinyl ether concentration on grafting of MMA to PPE by gamma irradiation

The effect of vinyl ether concentrations on grafting yields was evaluated using DVE-3 as a comonomer. DVE-3 was chosen because this vinyl ether is widely used in coating formulas as a reactive diluent. Results in Table 6.4 and Figure 6.4.1 show grafting yields of solutions of different MMA/DVE-3 ratios. Suitable doses were applied to allow polymerization to take place. Figure 6.4.2 represents gamma doses used versus MMA concentrations in solutions. The solution containing 20% v/v MMA required the lowest dose for polymerization to occur.

6.2.5 Gamma grafting of MMA to PPE with DVE-3 as a comonomer and with different solvent

The results on the effect of solvents on the grafting of MMA and DVE-3 to PPE are presented in Table 6.5 – Figure 6.5. Grafting yields were found to be dependent on the type of solvents used as in the case of UV radiation described in Chapter 4.

6.2.6 FT-IR spectra of MMA/vinyl ether grafted PPE substrates

Figure 6.6 depicts the spectra of PPE substrates grafted with MMA and various vinyl ethers. FT-IR spectra in this figure exhibit a large absorption peak at 1732 cm\(^{-1}\) due to C=O stretch, indicating the presence of MMA units in the grafted chains.

FT-IR spectra in Figure 6.7 belong to grafted PPE substrates with solutions containing MMA and DVE-3 in various MMA concentrations. Again, a large absorption peak at 1732 cm\(^{-1}\) due to C=O stretch of MMA units in the grafted substrates is present in all spectra. It appeared that the size of the peak decreased with increasing DVE-3 concentrations.

In both Figures 6.6 and 6.7, the spectrum of ungrafted PPE film is displayed for comparison purpose.
Table 6.1: Grafting of neat vinyl ethers to PPE by gamma irradiation.

<table>
<thead>
<tr>
<th>Vinyl ethers</th>
<th>Grafting yield (%)</th>
<th>Dose (kGy)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVE</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>TBVE</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>DVE</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>HDVE</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>DVE-4</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>0</td>
<td>3.5</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>DEAEE</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>EHVE</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>DVE-3</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
</tbody>
</table>

Dose rate: 2.6 kGy/hr
Table 6.2: Grafting of MMA to PPE with vinyl ethers by gamma irradiation.

<table>
<thead>
<tr>
<th>Vinyl ethers (20% v/v)</th>
<th>80% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (kGy)</td>
</tr>
<tr>
<td>EVE</td>
<td>37</td>
<td>4.9</td>
</tr>
<tr>
<td>PVE</td>
<td>56</td>
<td>4.9</td>
</tr>
<tr>
<td>TBVE</td>
<td>56</td>
<td>4.9</td>
</tr>
<tr>
<td>IBVE</td>
<td>117</td>
<td>4.9</td>
</tr>
<tr>
<td>NBVE</td>
<td>118</td>
<td>4.9</td>
</tr>
<tr>
<td>DVE</td>
<td>89</td>
<td>4.9</td>
</tr>
<tr>
<td>HDVE</td>
<td>151</td>
<td>4.9</td>
</tr>
<tr>
<td>DVE-4</td>
<td>92</td>
<td>4.9</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>67</td>
<td>4.9</td>
</tr>
<tr>
<td>DEAEV</td>
<td>145</td>
<td>4.9</td>
</tr>
<tr>
<td>EHVE</td>
<td>588</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Dose rate: 2.6 kGy/hr

Figure 6.2: Grafting of MMA to PPE with different vinyl ethers by gamma irradiation.
Table 6.3: Gamma grafting of MMA to PPE with different vinyl ethers, with chloroform as the solvent.

<table>
<thead>
<tr>
<th>Vinyl ethers (16% v/v)</th>
<th>64% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (kGy)</td>
</tr>
<tr>
<td>EVE</td>
<td>31</td>
<td>5.2</td>
</tr>
<tr>
<td>PVE</td>
<td>45</td>
<td>5.2</td>
</tr>
<tr>
<td>TBVE</td>
<td>5</td>
<td>5.2</td>
</tr>
<tr>
<td>IBVE</td>
<td>38</td>
<td>5.2</td>
</tr>
<tr>
<td>NBVE</td>
<td>27</td>
<td>5.2</td>
</tr>
<tr>
<td>DVE</td>
<td>Excessive</td>
<td>5.2</td>
</tr>
<tr>
<td>HDVE</td>
<td>162</td>
<td>5.2</td>
</tr>
<tr>
<td>DVE-4</td>
<td>125</td>
<td>5.2</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>198</td>
<td>5.2</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>46</td>
<td>5.2</td>
</tr>
<tr>
<td>EHVE</td>
<td>198</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Solvent: chloroform (20% v/v)
Dose rate: 2.6 kGy/hr

Figure 6.3: Gamma grafting of MMA to PPE with different vinyl ethers, with chloroform as the solvent.
Table 6.4: Grafting of MMA to PPE with DVE-3 by gamma irradiation.

<table>
<thead>
<tr>
<th>MMA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th>Dose (kGy)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>85</td>
<td>4.9</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>92</td>
<td>4.8</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>55</td>
<td>4.8</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>45</td>
<td>4.8</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>8</td>
<td>3.5</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Dose rate: 2.6 kGy/hr

Figure 6.4.1: Grafting of MMA to PPE with DVE-3 by gamma irradiation.

Figure 6.4.2: Gamma doses versus MMA concentrations.
Table 6.5: Gamma grafting of MMA to PPE with DVE-3 as a comonomer in the presence of different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>64 % v/v MMA - 16 % v/v DVE-3</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (kGy)</td>
</tr>
<tr>
<td>Chloroform</td>
<td>61</td>
<td>5.2</td>
</tr>
<tr>
<td>Methanol</td>
<td>61</td>
<td>5.2</td>
</tr>
<tr>
<td>THF</td>
<td>123</td>
<td>5.2</td>
</tr>
<tr>
<td>DMF</td>
<td>73</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Dose rate: 2.6 kGy/hr

Figure 6.5: Gamma grafting of MMA to PPE with DVE-3 as a comonomer, with different solvents.
Figure 6.6: FT-IR spectra of MMA/vinyl ether grafted PPE substrates using gamma radiation.
Figure 6.7: FT-IR spectra of MMA/DVE-3 grafted PPE substrates using gamma radiation.
6.3 Discussion

6.3.1 Grafting of neat vinyl ethers to PPE by gamma irradiation

When neat vinyl ethers were exposed to gamma radiation, similar results were obtained as with UV exposure in the absence or presence of PI. As shown in Table 6.1, no grafting was observed and with the exception of TMPTVE, no polymerization occurred. The explanation rendered with UV as the radiation source (Section 5.3.1, Chapter 5) is also relevant with gamma radiation.

The ability of TMPTVE to undergo polymerization under gamma irradiation may have been due to two possibilities. One was due to the initiation of cationic homo-polymerization by cations formed on the vinyl ether when exposed to gamma irradiation. TMPTVE has three vinyl ether functional groups and therefore this monomer has the ability to form more carbocations necessary for homo-polymerization compared to the bifunctional or monofunctional vinyl ethers. The second possibility was that it may have participated in homopolymerization due to the recombination of free radicals formed in the vinyl ether carbon chain structure during the irradiation process. As TMPTVE contains three vinyl ether groups, when under the influence of gamma irradiation, more radical sites could have resulted for each TMPTVE molecule compared to other vinyl ethers under study. However, no grafting of TMPTVE was observed on the PPE substrate. This implied the difficulty of TMPTVE radicals in approaching and reacting with the reactive sites on PPE. It is understandable since TMPTVE molecules were very large in size and in addition, it did not swell PPE. Therefore, even if some TMPTVE molecules were successfully bonded to PPE, there were still problems for those active sites to grow.

6.3.2 Grafting of MMA to PPE with vinyl ethers as comonomers using gamma irradiation

In the presence of MMA, most solutions polymerized with the exception of those with low molecular weight monofunctional vinyl ethers (Table 6.2). The radical polymerization of MMA in solutions must have been predominant due to the presence of free radicals generated from gamma irradiation. However, it appeared that the
polymerization was retarded by low molecular weight monofunctional vinyl ethers, but was enhanced by high molecular weight or multifunctional vinyl ethers [5,6]. As previously discussed in Section 5.3.4 of Chapter 5, high molecular weight monofunctional vinyl ethers may aid MMA/vinyl ether solutions to reach gel point quicker while multifunctional vinyl ethers enhance the polymerization by acting as crosslinking agents.

High grafting yields were achieved for all solutions containing 80% v/v MMA and 20% v/v vinyl ether (Table 6.2 and Figure 6.2). Such high yields were probably due to the abundance of reactive sites created on substrates by gamma irradiation. However, grafting yields varied according to the type of vinyl ethers. While low molecular weight monofunctional vinyl ethers such as IBVE and NBVE were thought to impede the homopolymerization of MMA in the presence of the thermal initiator 2,2'-azobisisobutyronitrile (AIBN) [7], it was not the case for grafting by gamma irradiation. In fact, grafting yields of solutions containing IBVE and NBVE were higher than those of DVE and TMPTVE. This may have been due to the high concentration of MMA in reacting solutions compared to those of vinyl ethers, thus, reducing the vinyl ether effect. Poor performances of multifunctional vinyl ethers in enhancing the grafting of MMA to PPE compared to monofunctional vinyl ethers may have been due to excessive polymers formed in the presence of multifunctional vinyl ethers leading to lower MMA monomer available for the grafting process.

High molecular weight monofunctional vinyl ethers, EHVE and DEAEVE, proved to be useful comonomers with MMA for grafting. In particular, the solution containing EHVE gave a significantly high grafting yield of 588%. This was probably because these vinyl ethers, while promoting the polymerization of MMA/vinyl ether mixtures, did not lead to the total depletion of MMA and there was still sufficient MMA available for grafted chain growth. Also, the increase in viscosity towards the end of the exposures may have led to Trommsdorff effect resulted in long grafted chains.
6.3.3 Gamma grafting of MMA to PPE with vinyl ethers as comonomers, in the presence of chloroform as a solvent

The presence of chloroform had a number of effects on grafting. In the reacting solutions, its presence proportionally reduced the concentrations of both MMA and vinyl ethers. Chloroform has the ability to dissolve PMMA, and therefore, solutions took longer to reach the gel point. As a result, a higher irradiation dose (5.2 kGy) was required for polymerization to occur. Chloroform was found to be very effective in swelling the PPE substrate [1] and this leads to the ease of access for both MMA and vinyl ethers to the reactive sites.

Results in Table 6.3 clearly display the difference in effect between low molecular weight monofunctional vinyl ethers and other vinyl ethers towards grafting in chloroform, with MMA solutions containing low molecular weight monofunctional vinyl ethers, EVE, PVE, TBVE, IBVE, NBVE and DEAEVE, achieving low grafting yields. Better penetration of the smaller size monofunctional vinyl ethers into the PPE substrate in the presence of chloroform may have led to the more profound hindering influence of such vinyl ethers on MMA grafting compared with the case where the solvent was absent. For other high molecular weight vinyl ethers such as EHVE and multifunctional vinyl ethers, HDVE, DVE-4 and TMPTVE, grafting yields remained high. This phenomenon was due to the fact that chloroform had retarded the homopolymerization of MMA (by dissolving the homopolymer, taking solutions longer to reach gel points), resulting in more MMA available for grafting. The increase in grafting yield can also be brought about by swollen substrates which permit vinyl ethers and MMA to access the grafting sites with ease. Also, the presence of multifunctional vinyl ethers promoted crosslinkings, leading to higher grafting yields. These results were in line with the findings of Garnett and coworkers [8] in which they reported the small presence of multifunctional vinyl ethers, 1,4-cyclohexanediolmethanol divinyl ether (CHVE), DVE-3 or a high molecular weight monofunctional vinyl ether, 4-hydroxybutyl vinyl ether (HBVE), improved UV grafting of MMA to PPE with methanol as a solvent.
6.3.4 Effect of vinyl ethers' molecular structures on the gamma grafting of MMA to PPE
As in the case of UV irradiation (Section 5.3.4, Chapter 5), gamma grafting of MMA to PPE was proved to be dependent on the structures of vinyl ethers. As shown in Tables 6.2 and 6.3, solutions containing MMA and vinyl ethers, such as NBVE, TBVE and IBVE, which are structural isomers gave different grafting yields. The variation in grafting yields could be attributed to different arrangements of butyl group attaching to the vinyl ether functional group.

6.3.5 Gamma grafting of MMA to PPE with DVE-3 as a comonomer
Gamma irradiation of MMA with DVE-3 as the comonomer in various concentration ratios resulted in grafting yields which were dependent on the concentration of the comonomer present. As shown in Table 6.4 and in Figure 6.4.1, grafting yields increased with increasing MMA concentrations. When grafting yields of neat MMA was compared with that of the solution containing 80% v/v MMA and 20% v/v DVE-3, it was observed that the presence of DVE-3 improved grafting. This observation was similar to the results reported by Garnett and coworkers [8] in which 1% w/v DVE-3 enhanced UV grafting of MMA to PPE substrates in the presence of methanol and a photoinitiator.

However, the decline of the grafting yields with respect to MMA concentrations indicates that DVE-3 did not participate as an active monomer for the grafting. This means that MMA was the main component in the grafted chains and this was further ascertained when FT-IR spectra of grafted substrates were examined in a later section.

The most interesting observation was that while grafting yields declined with decreasing MMA concentration, solutions containing high DVE-3 concentration required smaller doses to polymerize compared to that of neat MMA (Table 6.4-Figure 6.4.2). This phenomenon implied DVE-3 actively participated in polymerization. At DVE-3 concentration of 80% v/v, the smallest dose of 3.5 kGy was sufficient to promote polymerization. Tacky characteristics of polymers from MMA/DVE-3 mixtures of 20/80 and 40/60 ratios were possibly due to the high content of DVE-3 in the polymers, and
thus, further indicating DVE-3’s involvement in polymerization. With the fact that neat DVE-3 did not undergo polymerization under gamma irradiation (Table 6.1), it was strongly suggested that MMA interacted with DVE-3 as a donor-acceptor pair which, under gamma irradiation, produced radicals and ionic species. These species were able to initiate both free radical polymerization of MMA and cationic polymerization of DVE-3. Lower doses required for solutions with high DVE-3 concentrations to polymerize gave an indication of higher cationic polymerization rate of DVE-3 compared to that of the radical polymerization of MMA. However, cationic polymerization process did not lead to any grafting which was evidenced by the decrease of grafting yields with increasing DVE-3 concentrations.

6.3.6 Solvent effect on gamma grafting of MMA to PPE with DVE-3 as a comonomer
Table 6.5 shows solvent effect on gamma grafting of MMA to PPE with DVE-3 as a comonomer. Among the solvents used, THF was proved to be the best performer in enhancing grafting. This was followed by DMF, then chloroform and methanol. High grafting yields in the case of THF, DMF and methanol were possibly due to their ability to function as hydrogen donors. Hydrogen donors are compounds which contain abstractable hydrogens located adjacent to heteroatoms such as O, N and S. Grafting yield is significantly higher in the presence of THF shows that it is a stronger hydrogen donor, resulting in the generation of more free radicals for grafting and polymerization reactions.

6.3.7 Characterization of grafted substrates by FT-IR
6.3.7.1 Grafted substrates from solutions containing MMA and vinyl ethers other than DVE-3
Figure 6.6 shows FT-IR spectra of grafted substrates from solutions containing MMA and vinyl ethers other than DVE-3. All spectra have a large absorption peak at 1732 cm⁻¹ which belongs to C=O stretch of grafted MMA units, indicating the dominant presence of MMA units in grafted chains.
However, the FT-IR method is not adequate to study the possible vinyl ether incorporation in grafted chains due to the overlapping between absorption bands of vinyl ether units and those of MMA units as discussed in Section 5.3.5 of Chapter 5.

6.3.7.2 Grafted substrate from solutions containing MMA and DVE-3
Spectra in Figure 6.7 also indicate the presence of MMA. However as the grafting yields decrease so does the absorption peak at 1730 cm\(^{-1}\). This shows the diminishing of MMA in the grafted chains with increasing DVE-3 concentrations, and this is in line with the discussions in Section 6.2.5.

The presence of DVE-3 in grafted chains cannot be confirmed due to the same reason of overlapping between absorption bands of vinyl ether units and those of MMA units.

6.4 Conclusions
Experiments using gamma irradiation again confirmed that vinyl ethers under study with the exception of TMPTVE could not undergo free radical polymerization. Gamma polymerization of TMPTVE was possible, probably due to the presence of more radicals per molecule which could combine with radicals from carbon chains adjacent molecules to form the polymer or due to cationic species formed in the vinyl ether molecules. Without the presence of chloroform, there was no significant difference in grafting yields between vinyl ethers. However, with the addition of 20% v/v chloroform, grafting yields of solutions containing high molecular weight and multifunctional vinyl ethers were clearly higher than the yields of low molecular weight vinyl ethers.

There was a possible donor-acceptor (DA) type interaction between DVE-3 and MMA under the influence of gamma radiation leading to the polymerisation. The mechanism generating both radicals and cations were proposed. Electron spin resonance is the best way to confirm the free radical mechanism and can be carried out in the future work. Grafting yields were found to depend on MMA concentrations and the solvents used.
Attempts to characterize grafted substrates were made using the FT-IR method and MMA was proved to be the main component of the grafted chains. However, other techniques such as solid state NMR can be a technique utilized in the future to determine the presence of vinyl ethers in the grafted substrate.

6.5 References
CHAPTER SEVEN: MMA GRAFTING TO CELLULOSE WITH VINYL ETHERS AS COMONOMERS USING UV RADIATION
7.1 Introduction
Following the study of MMA and vinyl ethers grafting to PPE in Chapter 5, this chapter is a continuation in which the grafting of MMA to cellulose substrate with various vinyl ethers as comonomers will be studied, in order that the comparison in grafting between polar and non-polar substrates can be made. Cellulose is a polar polymer and, as discussed in Chapter 3, the grafting of MMA to cellulose is very much dependent on the presence of suitable solvents which can swell and wet the cellulose structure. In this chapter, the important role of solvents in the grafting process will be once again evaluated. However, the main objective is to investigate the influence of vinyl ethers have on the grafting of MMA to cellulose.

7.1.1 Radical generation by UV irradiation without photoinitiators
Although pure cellulose can weakly absorb UV radiation, the energy absorbed is believed to lead to localization of energy within the molecule, with consequent degradation[1]. Products of cellulose degradation are radicals which can initiate a series of reactions including depolymerization, dehydrogenation, dehydroxylation and dehydroxymethylation with the production of hydrogen, carbon monoxide, carbon dioxide and radicals [1]. Radical formation rate may be small but a large number of radicals can be produced under continuous exposure of the cellulose substrate to a UV source. As discussed in Section 1.3.6 and presented in Scheme 1.4 of Chapter 1, further reactions of these radicals with oxygen in monomer lead to the generation of peroxyl and hydroxy radicals that are useful for initiating both grafting and homopolymerization processes. The radical formation in cellulose under the influence of UV irradiation is described in Scheme 7.1 below.

\[
[\text{Cellulose}] \xrightarrow{hv} [\text{Cellulose}]^* \\
[\text{Cellulose}]^* \rightarrow [\text{Cel}_1]^* + [\text{Cel}_2]^*
\]

Scheme 7.1: Radical due the degradation of cellulose under the influence of UV irradiation.
Another source of free radicals is from vinyl ethers in the reacting solutions under exposure to a UV source. As discussed in Section 5.3.1 and presented in Scheme 5.4 of Chapter 5, radicals can be formed from the interaction of the vinyl ether with UV radiation. Such radicals can initiate polymerization as well as grafting or continue to react with oxygen in the solution to generate peroxy and hydroxy radicals.

7.1.2 Vinyl ethers and MMA copolymerization

As pointed out in Chapter 5, interactions between vinyl ethers and MMA in solutions had large influence on the grafting process. The change of substrate type (from PPE to cellulose) should not have changed the nature of reactions in monomer mixtures because most of the components in test samples were kept the same as the ones described in Chapter 5 (except DMF was introduced as a swelling agent). Once again, the work carried out by Bevington and coworkers [3,4] serve as good references for the analysis of results. According to their studies, monofunctional vinyl ethers (such as PVE, TBVE) did not actively participate in radical copolymerization with MMA while divinyl ethers of polyethylene glycols can lead to crosslinking when used as comonomers with MMA [3]. They also found MMA polymerization in benzene was retarded by monofunctional vinyl ethers of PVE, TBVE and n-dodecyl vinyl ether and the resulting copolymers' chainlengths were shorter than the corresponding homopolymer [4]. These findings were in line with observations by Garnett and coworkers in which they reported vinyl ethers reduced homopolymerization of MMA [5]. On the other hand, multifunctional vinyl ethers such as DVE, DVE-3 were found by other researchers to readily polymerize with multifunctional acrylates in the presence of radicals [6-8]. With possible complex formation with MMA, vinyl ethers as comonomers have proven in Chapter 5 to have greatly influenced polymerization of MMA.

7.1.3 Grafting of MMA to cellulose with vinyl ethers as comonomers

The presence of multifunctional vinyl ethers has been reported to be beneficial for MMA grafting to cellulose. Garnett and coworkers [5] found that small amounts of multifunctional vinyl ethers such as DVE-3, 1,4-cyclohexanediethanol divinyl ether (CHVE), or 4-hydroxybutyl vinyl ether (HBVE) improved MMA grafting to cellulose by gamma and UV irradiation without any PIs, in the presence of methanol as a solvent.
[5,9]. However, in another work, Garnett and Zilic [10] found that only poor grafting to cellulose was observed when DVE-3 was used as a comonomer with MMA despite the presence of a photoinitiator. As most vinyl ethers studied so far were multifunctional, therefore in this chapter, the effect of both multifunctional and monofunctional vinyl ethers on grafting will be investigated and compared.

7.2 Results

7.2.1 UV grafting of neat vinyl ethers to cellulose

7.2.1.1 Without Irgacure 819 photoinitiator
Table 7.1 shows the grafting of neat vinyl ethers to cellulose without Irgacure 819 photoinitiator. Only very low grafting yields were achieved whilst no polymerization was observed in all vinyl ethers.

7.2.2.2 With 1% w/v Irgacure 819 photoinitiator
Table 7.2 shows the grafting yields of neat vinyl ethers to cellulose with 1% w/v Irgacure 819 photoinitiator. Again, very low grafting yields were achieved and no polymerization was observed in all systems.

7.2.2 UV grafting of MMA to cellulose with vinyl ethers as comonomers, without Irgacure 819 photoinitiator

7.2.2.1 In the absence of solvents
Table 7.3 shows the grafting yields of MMA to cellulose with vinyl ethers as comonomers in the absence of solvents. With the exception of MMA/EVE system, all the other MMA/vinyl ether systems polymerized to form solid polymers. However, very low grafting yields were achieved.

7.2.2.2 With DMF as a solvent
In Chapter 3, excellent MMA grafting to cellulose substrate was achieved in the presence of DMF and thus in this part of experiment it was chosen as the solvent for all grafting systems. DMF was mixed with MMA and vinyl ethers in two ratios. The first ratio comprised of MMA/vinyl ethers/DMF = 64/16/20 and the results are summarized in
Table 7.4. The second ratio consisted of MMA/vinyl ethers/DMF=48/12/40 and the results are reported in Table 7.5. The purpose of changing the concentration of DMF in solutions was to study the effect of DMF on the grafting process. According to the two tables, slight increases of grafting yields were observed when DMF was used as a solvent. Figure 7.3 depicts the effect of DMF on grafting based on results taken from Tables 7.3, 7.4 and 7.5.

7.2.3 UV grafting of MMA to cellulose with vinyl ethers as comonomers, with 1% w/v Irgacure 819 photoinitiator

7.2.3.1 In the absence of solvents
Results in Table 7.6 show grafting yields of MMA to cellulose with vinyl ethers as comonomers (MMA: vinyl ethers = 80: 20) in the absence of solvents. Again, very low grafting yields were observed in all systems but showing a significant increase in comparison with the results in Table 7.3 where no Irgacure 819 was present.

7.2.3.2 With DMF as a solvent
Table 7.7 shows grafting yields of MMA to cellulose with vinyl ethers as comonomers with DMF added to MMA vinyl ethers in the following ratio: MMA/vinyl ethers/DMF=48/12/40. Significant increases of grafting yields were observed in the presence of this solvent. Figure 7.5 based on results from Tables 7.6 and 7.7 evidently shows the importance of DMF in enhancing grafting yields.

7.2.3.3 Grafting of MMA to cellulose with EVE as a comonomer, with different solvents, with 1% w/v Irgacure 819 photoinitiator
This experiment was performed to compare the enhancing effect of DMF with other solvents including methanol, chloroform and dichloromethane on the grafting of MMA to cellulose in the presence of a vinyl ether as a the comonomer. The vinyl ether EVE was chosen as the comonomer due to only a small amount of homopolymer was observed being formed in its presence. Results in Table 7.8 show the solvent effect on grafting in the presence of EVE and 1% w/v Irgacure 819 photoinitiator. Grafting yield of 36% was the highest with DMF as the solvent followed by methanol as the solvent with a grafting
yield of 24%. Grafting yield of 1% in the presence of dichloromethane suggested that this 
solvent had inhibited the grafting process as compared with the grafting yield of 
MMA/EVE in the absence of solvent (Table 7.6).

7.2.4 FT-IR characterization of MMA/vinyl ether grafted cellulose substrates
Grafted substrates from the solutions containing MMA and EVE, NBVE or HDVE with 
the inclusion of 40% v/v DMF and 1% v/v Irgacure 819 were chosen for the FT-IR 
characterization due to the difficulty of making fine powders from the other grafted 
substrates. FT-IR spectra of samples containing EVE and HDVE as comonomers in 
Figure 7.6 show a small absorption peak at 1732 cm\(^{-1}\) due to C=O stretch of grafted 
MMA units. As Nujol was added during the characterization process, the spectra of Nujol 
and ungrafted cellulose powder in Nujol are displayed in Figure 7.6 for comparison 
purposes.
Table 7.1: UV grafting of neat vinyl ethers to cellulose without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers</th>
<th>0% w/v Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVE</td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>593</td>
</tr>
<tr>
<td>PVE</td>
<td>2</td>
<td>593</td>
</tr>
<tr>
<td>TBVE</td>
<td>1</td>
<td>593</td>
</tr>
<tr>
<td>IBVE</td>
<td>2</td>
<td>593</td>
</tr>
<tr>
<td>NBVE</td>
<td>2</td>
<td>593</td>
</tr>
<tr>
<td>DVE</td>
<td>2</td>
<td>593</td>
</tr>
<tr>
<td>HDVE</td>
<td>3</td>
<td>593</td>
</tr>
<tr>
<td>DVE-4</td>
<td>2</td>
<td>593</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>3</td>
<td>593</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>2</td>
<td>593</td>
</tr>
<tr>
<td>EHVE</td>
<td>1</td>
<td>593</td>
</tr>
<tr>
<td>DVE-3</td>
<td>1</td>
<td>593</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C
Table 7.2: UV grafting of neat vinyl ethers to cellulose with 1% w/v Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers</th>
<th>1% w/v Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>5</td>
<td>440</td>
</tr>
<tr>
<td>PVE</td>
<td>4</td>
<td>440</td>
</tr>
<tr>
<td>TBVE</td>
<td>5</td>
<td>440</td>
</tr>
<tr>
<td>IBVE</td>
<td>4</td>
<td>440</td>
</tr>
<tr>
<td>NBVE</td>
<td>5</td>
<td>440</td>
</tr>
<tr>
<td>DVE</td>
<td>4</td>
<td>440</td>
</tr>
<tr>
<td>HDVE</td>
<td>5</td>
<td>440</td>
</tr>
<tr>
<td>DVE-4</td>
<td>2</td>
<td>440</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>6</td>
<td>440</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>6</td>
<td>440</td>
</tr>
<tr>
<td>EHVE</td>
<td>5</td>
<td>440</td>
</tr>
<tr>
<td>DVE-3</td>
<td>0</td>
<td>440</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C
Table 7.3: UV grafting of MMA to cellulose with vinyl ethers as comonomers, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers (20% v/v)</th>
<th>80% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>1</td>
<td>807</td>
</tr>
<tr>
<td>PVE</td>
<td>1</td>
<td>807</td>
</tr>
<tr>
<td>TBVE</td>
<td>1</td>
<td>807</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>NBVE</td>
<td>1</td>
<td>807</td>
</tr>
<tr>
<td>DVE</td>
<td>0</td>
<td>367</td>
</tr>
<tr>
<td>HDVE</td>
<td>2</td>
<td>807</td>
</tr>
<tr>
<td>DVE-4</td>
<td>2</td>
<td>807</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>2</td>
<td>367</td>
</tr>
<tr>
<td>DEAEEVE</td>
<td>2</td>
<td>807</td>
</tr>
<tr>
<td>EHVE</td>
<td>1</td>
<td>807</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C
Table 7.4: UV grafting of MMA to cellulose with vinyl ethers as comonomers, with 20% v/v DMF as a solvent, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers (16v/v%)</th>
<th>64% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>4</td>
<td>627</td>
</tr>
<tr>
<td>PVE</td>
<td>6</td>
<td>627</td>
</tr>
<tr>
<td>TBVE</td>
<td>5</td>
<td>627</td>
</tr>
<tr>
<td>IBVE</td>
<td>6</td>
<td>627</td>
</tr>
<tr>
<td>NBVE</td>
<td>7</td>
<td>627</td>
</tr>
<tr>
<td>DVE</td>
<td>16</td>
<td>627</td>
</tr>
<tr>
<td>HDVE</td>
<td>5</td>
<td>627</td>
</tr>
<tr>
<td>DVE-4</td>
<td>5</td>
<td>627</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>26</td>
<td>627</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>6</td>
<td>627</td>
</tr>
<tr>
<td>EHVE</td>
<td>7</td>
<td>627</td>
</tr>
</tbody>
</table>

Solvent: DMF (20% v/v)

MMA concentration was 64% v/v in all solutions

Vinyl ethers concentrations were 16% v/v in all solutions

Dose rate: 36.7 J/hr

Temperature: 29 °C
Table 7.5: UV grafting of MMA to cellulose with vinyl ethers as comonomers, with 40% v/v DMF as a solvent, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers (12% v/v)</th>
<th>48% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>5</td>
<td>752</td>
</tr>
<tr>
<td>PVE</td>
<td>5</td>
<td>752</td>
</tr>
<tr>
<td>TBVE</td>
<td>6</td>
<td>752</td>
</tr>
<tr>
<td>IBVE</td>
<td>6</td>
<td>752</td>
</tr>
<tr>
<td>NBVE</td>
<td>5</td>
<td>752</td>
</tr>
<tr>
<td>DVE</td>
<td>11</td>
<td>752</td>
</tr>
<tr>
<td>HDVE</td>
<td>12</td>
<td>752</td>
</tr>
<tr>
<td>DVE-4</td>
<td>8</td>
<td>752</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>13</td>
<td>752</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>13</td>
<td>752</td>
</tr>
<tr>
<td>EHVE</td>
<td>6</td>
<td>752</td>
</tr>
</tbody>
</table>

**Solvent:** DMF (40% v/v)

**MMA concentration was 48% v/v in all solutions**

**Vinyl ethers concentrations were 12% v/v in all solutions**

**Dose rate:** 36.7 J/hr

**Temperature:** 29 °C
Figure 7.3: UV grafting of MMA to cellulose with vinyl ethers as comonomers, with or without DMF as a solvent, without Irgacure 819 photoinitiator.
Table 7.6: UV grafting of MMA to cellulose with vinyl ethers as comonomers, without solvents, with 1% w/v Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers (20% v/v)</th>
<th>80% v/v MMA – 1% w/v Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>7</td>
<td>52</td>
</tr>
<tr>
<td>PVE</td>
<td>6</td>
<td>52</td>
</tr>
<tr>
<td>TBVE</td>
<td>6</td>
<td>52</td>
</tr>
<tr>
<td>IBVE</td>
<td>3</td>
<td>52</td>
</tr>
<tr>
<td>NBVE</td>
<td>5</td>
<td>52</td>
</tr>
<tr>
<td>DVE</td>
<td>9</td>
<td>52</td>
</tr>
<tr>
<td>HDVE</td>
<td>11</td>
<td>52</td>
</tr>
<tr>
<td>DVE-4</td>
<td>41</td>
<td>52</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>5</td>
<td>52</td>
</tr>
<tr>
<td>EHVE</td>
<td>6</td>
<td>52</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C
Table 7.7: UV grafting of MMA to cellulose with vinyl ethers as comonomers, with 40% v/v DMF as a solvent, with 1% w/v Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers (12% v/v)</th>
<th>48% v/v MMA – 1% w/v Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>36</td>
<td>92</td>
</tr>
<tr>
<td>PVE</td>
<td>33</td>
<td>92</td>
</tr>
<tr>
<td>TBVE</td>
<td>18</td>
<td>92</td>
</tr>
<tr>
<td>IBVE</td>
<td>47</td>
<td>92</td>
</tr>
<tr>
<td>NBVE</td>
<td>41</td>
<td>92</td>
</tr>
<tr>
<td>DVE</td>
<td>117</td>
<td>92</td>
</tr>
<tr>
<td>HDVE</td>
<td>111</td>
<td>92</td>
</tr>
<tr>
<td>DVE-4</td>
<td>75</td>
<td>92</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>36</td>
<td>92</td>
</tr>
<tr>
<td>DEAEEVE</td>
<td>24</td>
<td>92</td>
</tr>
<tr>
<td>EHVE</td>
<td>68</td>
<td>92</td>
</tr>
</tbody>
</table>

Solvent: DMF (40% v/v)
MMA concentration was 48% v/v in all solutions
Vinyl ethers concentrations were 12% v/v in all solutions
Dose rate: 36.7 J/hr
Temperature: 29 °C
Figure 7.5: UV grafting of MMA to cellulose with vinyl ethers as comonomers, with or without DMF as a solvent, with 1% w/v Irgacure 819 photoinitiator.
Table 7.8: UV grafting of MMA to cellulose with EVE as a comonomer, with different solvents and 1% w/v Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Grafting yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>36</td>
</tr>
<tr>
<td>Methanol</td>
<td>24</td>
</tr>
<tr>
<td>Chloroform</td>
<td>3</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>1</td>
</tr>
</tbody>
</table>

Solvent concentration: 40% v/v  
MMA concentration was 48% v/v in all solutions  
EVE concentration was 12% v/v in all solutions  
Dose rate: 36.7 J/hr  
Total dose: 92J  
Temperature: 29 °C
Figure 7.7: FT-IR spectra of MMA/vinyl ether grafted cellulose substrates using UV radiation with 40% v/v DMF as the solvent and 1% w/v Irgacure
7.3 Discussion

7.3.1 UV grafting of neat vinyl ethers to cellulose with and without Irgacure 819

Results in Tables 7.1 (without Irgacure 819) and 7.2 (with Irgacure 819) reconfirmed the inability of vinyl ethers to undergo free radical polymerization, despite high UV doses were applied in the presence of Irgacure 819 photoinitiator. These results were attributed to the polarity of the double bonds in vinyl ethers which were ready to undergo cationic polymerization rather than free radical polymerization [2], as explained in Chapter 5.

As shown in Tables 7.1 and 7.2, very low grafting yields for all vinyl ethers under study were recorded. This was probably due to the inability of vinyl ethers to react with radicals formed on cellulose in the presence of Irgacure 819 to form grafted chains. These findings were in line with observations in Chapter 5 where no vinyl ethers grafting to PPE substrate were reported. The results in these two Tables serve as useful backgrounds for analyzing data in the following sections.

7.3.2 UV grafting of MMA to cellulose with vinyl ethers as comonomers, in the absence of solvents and Irgacure 819 photoinitiator

In the absence of PI, the grafting and polymerization processes were very inefficient. As shown in Table 7.3, long UV exposure dose (807 J) were required by all systems for polymerization to occur. However, MMA solutions containing DVE and TMPTVE needed only 367 J to polymerize. This UV dose was observed to be higher as compared to the corresponding dose of 232 J required for MMA/DVE mixture to polymerize in the case of PPE (Table 5.3, Chapter 5). The difference between the two doses used was attributed to the fact that PPE substrate was transparent while cellulose substrate was not. In the case of cellulose, the solution in a tested sample was divided into two areas by the cellulose substrate with one area being exposed to UV lights and the other was not. As a result, higher doses were required because free radicals could not be formed in the area shielded from the UV light. As was discussed in Section 5.3.1 of Chapter 5, the low dose required for MMA/DVE and MMA/TMPTVE mixtures to polymerize was explained by the possibility of DA interaction between the two vinyl ethers with MMA.
Unlike the grafting of MMA and vinyl ethers to PPE, negligible grafting yields to cellulose were observed although all solutions polymerized. Based on discussions in Section 3.2.1 of Chapter 3, which stressed the importance of wetting and swelling substrate in order to achieve high grafting, it thus appeared that MMA/vinyl ether solutions did not wet or swell cellulose. As a result, MMA monomer could not access to the grafting sites to form grafted chains. The results were in line with findings reported by Garnett and Zilic [10] in which poor UV grafting of MMA and DVE-3 to cellulose was obtained when no solvents were used, despite the presence of a PI.

7.3.3 UV grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent, without Irgacure 819 photoinitiator

From Chapter 3, DMF was found to be a good solvent for MMA grafting to cellulose and therefore the addition of DMF to MMA/vinyl ether solutions was expected to promote grafting. According to results in Table 7.4 and Figure 7.3, there were significant increases in grafting yields when 20% v/v DMF was added despite shorter exposures to UV radiation and a lower MMA concentration. Changes of grafting yields reconfirmed the important role of solvents in swelling in the grafting process of MMA. In this case, DMF swelled the cellulose structure, allowing MMA to access and react with the grafting sites, leading to the formation of grafted chains.

Again, solutions containing DVE and TMPTVE were two exceptions. Corresponding grafting yields of solutions containing these two vinyl ethers were much higher than the rest. The grafting enhancement by these two vinyl ethers may have been due to their ability to quickly polymerize with MMA and also their ability to form crosslinkings between grafted PMMA chains. Similar grafting results of MMA to PPE with these two vinyl ethers in the absence of solvents and PIs were observed and discussed in Section 5.3.2 of Chapter 5.

However, as shown in Table 7.4 and Figure 7.3, grafting yields for solutions containing multifunctional vinyl ethers such as HDVE and DVE-4 were even lower than those for solutions containing monofunctional vinyl ethers. One observation was that these two
divinyl ethers were more bulky than DVE and therefore their penetration into the cellulose structure was not as good as DVE. With cellulose substrates being only partially swollen by the small amount of DMF added and with the abundant presence of MMA monomer, HDVE and DVE-4 may have enhanced the polymerization of MMA in the solution rather than grafting to cellulose. On the other hand, TMPTVE, although was also bulky, could cause more branching of grafted chains than HDVE and DVE-4 would, thus explaining its good grafting performance.

When DMF concentration was increased further to 40% v/v, mixed results were observed. In comparison with the results in Table 7.3 where no DMF was present, grafting yields observed in Table 7.5, were still higher despite much lower concentration of MMA and vinyl ethers, thus reconfirming the enhancing effect of DMF on grafting. Different effects produced by monofunctional vinyl ethers and multifunctional vinyl ethers were clearer. Grafting yields of solutions containing the multifunctional vinyl ethers, DVE, HDVE, DVE-4 and TMPTVE, were higher than those of solutions containing monofunctional vinyl ethers, except DEAEVE. This difference may have been due to the branching of grafted chains caused by multifunctional vinyl ether as well as Trommsdorff effect caused by the high viscosity since the solutions containing multifunctional vinyl ethers were able to reach gel points more quickly than solutions containing monofunctional vinyl ethers. In comparison with Table 7.4, the enhancing effect on grafting of HDVE and DVE-4 in the presence of high DMF concentration was probably due to the thorough swelling of the cellulose substrate, therefore allowing these two vinyl ethers to access to the grafting sites to a greater extent. Good grafting achieved by the solution containing DEAEVE, a monofunctional vinyl ether, may have been attributed to the high molecular weight of the vinyl ether which may have led to the early gelation of the solution, thus creating the Trommsdorff effect. These explanations were reasonable since high molecular weight and multifunctional vinyl ethers have also proven to be beneficial for the grafting process of MMA to cellulose [9].
7.3.4 UV grafting of MMA to cellulose with vinyl ethers as comonomers, in the absence of solvents, with 1% w/v Irgacure 819 photoinitiator

In the presence of Irgacure 819, the MMA/vinyl ether solutions efficiently underwent polymerization, requiring only low UV dose of 52 J (Table 7.6). Despite excessive polymers formed at the end of UV exposure, low grafting yields were observed. As shown in Table 7.6, most systems had grafting yields of less than 10%. These observations were similar to the ones described in Section 7.3.2 (Table 7.3) and again the low grafting yields were attributed to the poor cellulose swelling abilities of vinyl ethers and MMA. These results were similar with findings by Garnett and Zilic [10] in which low UV grafting of MMA and DVE-3 were reported when no solvents were presence, despite the presence of a photoinitiator.

However, solutions containing HDVE and especially DVE-4 gave considerable high grafting yields (Table 7.6). These results are interesting since poor grafting yields were achieved for MMA with these vinyl ethers as comonomers in the absence of both PI and solvent (Table 7.3). The possibility was that the grafting reported was not true grafting but highly cross-linked PMMA polymer films physically and strongly adhered to cellulose surface. These layers were possibly the products of fast polymerization due to the presence of Irgacure 819 and these polymers were not soluble in chloroform during the extraction process. The solution containing TMPTVE, an efficient cross-linking agent, did not produce significant graft because a lower UV dose (37 J) was applied since MMA/TMPTVE formed a white polymer at this dose.

7.3.5 UV grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent, with 1% w/v Irgacure 819 photoinitiator

With the addition of 40% v/v DMF to MMA/vinyl ether solutions, high grafting yields were achieved in all systems studied (Table 7.7) despite at much lower MMA concentrations. Higher UV doses (92 J) than 52 J could be applied since MMA was diluted by DMF. However at the end of exposure, most solutions only slightly polymerized (solutions turned viscous) with the exception of the solution containing TMPTVE which polymerized to form a clear polymer. The ability of TMPTVE to form a
clear polymer with MMA in diluted condition may have been due to its efficiency in forming crosslinks as a multifunctional vinyl ether and also the possibility of its DA interaction with MMA. The possibility of TMPTVE to interact with MMA as shown by results in Table 7.3, enabled the polymerization rate to be enhanced due to the presence of radicals formed.

One factor which contributed to the high grafting yields in these systems was the presence of DMF. The role of DMF in enhancing MMA grafting to cellulose with vinyl ethers as comonomers in the absence of Irgacure 819 has been discussed in Section 7.3.3. Other factors contributing to the grafting improvement were low MMA concentration and higher UV doses. As the concentration of MMA was diluted by DMF, the rate of polymerization was retarded, leading to the supply of monomers to grafting sites being maintained. In other words, the grafting process could compete with the polymerization for monomers more efficiently. High UV doses used was an important factor for grafting as longer exposure in the presence of a photoinitiator would lead to more grafting sites being created on cellulose.

Results in Table 7.7 again show the effect of vinyl ethers on enhancing grafting yields. While high grafting yields were obtained for all systems, the solutions containing bifunctional vinyl ethers, such as DVE, HDVE and DVE-4, gave much higher grafting than solutions containing monofunctional vinyl ethers. Difference between grafting yields would again be contributed by vinyl ethers’ high viscosity and their ability to act as crosslinking agents as previously discussed. However, the solution containing TMPTVE did not give high grafting despite being a multifunctional vinyl ether, as it possibly polymerized quickly with MMA, leading to a reduced amount of monomer available for grafting.

While the effect of chemical structure of vinyl ethers on grafting yields was not clear based on results in Tables 7.3-7.6, however, the importance of chemical structure was manifested in Table 7.7. Although TBVE, IBVE and NBVE were vinyl ethers of the same empirical chemical formula, they resulted in different grafting yields. This indicated
that chemical structure influence on the grafting process and these results agree with the observations as discussed in Chapter 5 and 6.

7.3.6 Effect of solvents on grafting of MMA to cellulose with EVE as a comonomer, with 1% w/v Irgacure 819 photoinitiator
Solvent effect on grafting of MMA to cellulose with EVE as a comonomer is shown in Table 7.8. As discussed in Chapter 3, methanol and DMF were good solvents for enhancing the grafting of MMA to cellulose with EVE as a comonomer while chloroform and dichloromethane did not promote grafting. This was due to the inefficiency of chloroform and dichloromethane in swelling cellulose and therefore, MMA could not gain access to the grafting sites, resulting in low grafting. Also, DMF and methanol both possess abstractable H atoms. Free radicals which can enhance grafting are formed once these H atoms have been abstracted.

7.3.7 Characterization of grafted substrates using the FT-IR spectroscopy
As shown in Figure 7.7, spectra of grafted cellulose show absorption peaks at about 1732 cm\(^{-1}\) contributed by the C=O stretch of MMA in the cases of EVE and HDVE as comonomers. This confirms the presence of MMA unit in those grafted substrates. In the case of NBVE, no such absorption peak is observed despite a high grafting yield (41%) reported in Table 7.7. This shows that the FT-IR technique is not sensitive for cellulose characterization. A closer examination of the spectra in the range 800-1200 cm\(^{-1}\) reveals the lack of details in this section of the spectra, thus suggesting the need of using more sensitive characterization methods such as Solid-state NMR in a future study.

The presence of vinyl ether units in grafted chains could not be confirmed from the spectra due to the lack of details and above all the overlapping of their absorption peaks with those of cellulose and MMA.

7.4 Conclusions
Results in this chapter reconfirm the very important role of solvents play in the grafting of MMA to cellulose with vinyl ethers as comonomers. This study clearly demonstrated
that the presence of DMF improved grafting yields, either with or without Irgacure 819. As expected, very low grafting was obtained in the absence of Irgacure 819. Similar to the case of PPE as substrate, vinyl ethers also influenced the grafting process in cellulose. Grafting yields were found to be dependent on the type of vinyl ethers, their chemical structures and number of functional groups. FT-IR spectra of grafted substrates proved the presence of MMA as a component of grafted chains. However, further analysis using Solid-state NMR should be carried out to determine the presence of vinyl ethers.

7.5 References


CHAPTER EIGHT: MMA GRAFTING TO CELLULOSE WITH VINYL ETHERS AS COMONOMERS USING GAMMA RADIATION
8.1 Introduction

When monomers are irradiated with gamma rays, the energetic ionising radiation is capable of breaking bonds leading to formulation of free radicals which are essential for radical induced polymerization. In Chapter 6, MMA grafting to PPE substrates under the influence of gamma radiation has been discussed and there is a potential difference in the grafting process to cellulose since it is polar in characteristics. This chapter will examine the grafting of MMA to cellulose in the presence of gamma radiation with vinyl ethers as comonomers, and also the importance of solvents in grafting.

8.1.1 Radical generations in cellulose by gamma irradiation

The radical generation process by gamma irradiation in cellulose substrate is similar to that of PPE substrate as discussed in Chapter 6. Under the influence of gamma radiation, scissions of C-C and C-H bonds in cellulose occur, producing ionic species which are quickly converted to radicals in both amorphous and crystalline regions [1-4]. Due to the inaccessible nature of the crystalline regions, only radicals formed in amorphous regions are useful for grafting [1,2]. The formation of radicals in cellulose by gamma irradiation is represented in Scheme 8.1. In the simultaneous technique, newly formed radical sites on cellulose chain can immediately initiate grafting because monomers are in direct contact with the cellulose structure (Scheme 8.2) [1-4]. However, radical sites can react with oxygen molecules in solutions to produce peroxides and hydroperoxides, which in turn can decompose to generate other radicals [1-3]. Mechanisms for the formation of peroxides and hydroperoxides have been presented in Scheme 1.4 of Section 1.3.6, Chapter 1. These new radical species can either initiate grafting or homopolymerization of MMA. The radical formation in cellulose by gamma irradiation is very efficient but long exposures may lead to degradation of the substrate [2,3].

\[
\text{[Cel-H]} \xrightarrow{\text{gamma}} \text{[Cel]}^\cdot + \text{H}^\cdot
\]

Scheme 8.1: Radical generation in cellulose under the influence of gamma radiation.
\[
\text{[Cel]}^* + n\text{MMA} \rightarrow \text{[Cel]}-(\text{MMA})_n^*
\]

**Scheme 8.2:** Grafting of MMA to cellulose under the influence of gamma radiation.

### 8.1.2 Radical generation in monomers by gamma irradiation

As discussed in Chapter 6, radicals can be formed when monomers are exposed to gamma irradiation [5]. If stable, these radicals can react with monomers, leading to polymerization of monomers or may attack cellulose structure to create reactive grafting sites. Other products of interactions between monomers and gamma rays are ions which are capable of initiating ionic polymerization [2,5].

### 8.2 Results

#### 8.2.1 Grafting of neat vinyl ethers to cellulose by gamma irradiation

Table 8.1 shows the grafting results of different vinyl ethers to cellulose by gamma irradiation. Extremely low grafting yields were achieved and, as expected, no obvious gelling was observed in almost all system with the exception of TMPTVE which formed a clear polymer.

#### 8.2.2 Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, in the absence of solvents

MMA was mixed with vinyl ethers in the following ratio by volume: MMA/vinyl ether=80/20. Solutions were exposed to gamma radiation and, as shown in Table 8.2, grafting yields were insignificant. However, polymerization took place in all systems except MMA/EVE.

#### 8.2.3 Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as the solvent

DMF was chosen as the solvent for this experiment due to its graft enhancing property as discussed in Chapter 7. DMF was mixed with MMA and vinyl ethers in the following ratio by volume: MMA/vinyl ether/DMF= 48/12/40. Solutions were exposed to gamma rays and grafting yields are presented in Table 8.3 and Figure 8.3. As expected, high
grafting yields were achieved for all reacting solutions. Also, high degree of polymerization was observed in all systems under study.

8.2.4 Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, without any solvent

DVE-3 was chosen as a comonomer of MMA since the vinyl ether was widely used as a reactive diluent in coating formulas as discussed in Chapter 6. Its concentration in the solution was varied to examine the possible formations of CT complexes between MMA and DVE-3. The two monomers were mixed in different concentration ratios and the solutions were exposed to gamma radiation until polymerization had taken place. As shown in Table 8.4, polymerization of solutions containing DVE-3 was more rapid than the neat MMA solution. Significant polymerization was observed for all systems except the neat DVE-3 solution. However, only low grafting was achieved in all cases.

8.2.5 Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, with different solvents.

Effect of solvent types on the grafting of MMA to cellulose with DVE-3 as a comonomer was shown in Table 8.5 and Figure 8.5. Four different solvents, DMF, methanol, chloroform and THF were evaluated. As shown, very high grafting yields were achieved with DMF and methanol.

8.2.6 FT-IR characterization of a MMA/DVE-3 grafted substrate

A grafted substrate from the solution containing 48% MMA, 12% DVE-3 was chosen for the FT-IR characterization due to the difficulty in making fine cellulose powder from the other grafted substrate. As shown in Figure 8.6, the spectrum contained an absorption peak at 1732 cm\(^{-1}\) and this is attributed to C=O stretch of grafted MMA units. As in Chapter 7, spectra of Nujol and ungrafted cellulose powder with Nujol are displayed for comparison purpose.
Table 8.1: Grafting of neat vinyl ethers to cellulose by gamma irradiation.

<table>
<thead>
<tr>
<th>Vinyl ethers</th>
<th>Grafting yield (%)</th>
<th>Dose (kGy)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBVE</td>
<td>2</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>NBVE</td>
<td>2</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>DVE</td>
<td>2</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>HDVE</td>
<td>1</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>DVE-4</td>
<td>1</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>1</td>
<td>3.5</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>EHVE</td>
<td>1</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>DVE-3</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
</tbody>
</table>

Dose rate: 2.6 kGy/hr

Table 8.2: Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, without any solvent.

<table>
<thead>
<tr>
<th>Vinyl ethers (20% v/v)</th>
<th>80% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (kGy)</td>
</tr>
<tr>
<td>EVE</td>
<td>1</td>
<td>7.5</td>
</tr>
<tr>
<td>PVE</td>
<td>1</td>
<td>7.5</td>
</tr>
<tr>
<td>TBVE</td>
<td>1</td>
<td>7.5</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>7.5</td>
</tr>
<tr>
<td>NBVE</td>
<td>1</td>
<td>7.5</td>
</tr>
<tr>
<td>DVE</td>
<td>0</td>
<td>7.5</td>
</tr>
<tr>
<td>HDVE</td>
<td>1</td>
<td>7.5</td>
</tr>
<tr>
<td>DVE-4</td>
<td>1</td>
<td>7.5</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>7</td>
<td>7.5</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>0</td>
<td>7.5</td>
</tr>
<tr>
<td>EHVE</td>
<td>1</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Dose rate: 2.6 kGy/hr
Table 8.3: Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent.

<table>
<thead>
<tr>
<th>Vinyl ethers (12% v/v)</th>
<th>48% v/v MMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (kGy)</td>
</tr>
<tr>
<td>EVE</td>
<td>124</td>
<td>7.8</td>
</tr>
<tr>
<td>PVE</td>
<td>131</td>
<td>7.8</td>
</tr>
<tr>
<td>TBVE</td>
<td>80</td>
<td>7.8</td>
</tr>
<tr>
<td>IBVE</td>
<td>119</td>
<td>7.8</td>
</tr>
<tr>
<td>NBVE</td>
<td>112</td>
<td>7.8</td>
</tr>
<tr>
<td>DVE</td>
<td>130</td>
<td>7.8</td>
</tr>
<tr>
<td>HDVE</td>
<td>152</td>
<td>7.8</td>
</tr>
<tr>
<td>DVE-4</td>
<td>138</td>
<td>7.8</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>124</td>
<td>7.8</td>
</tr>
<tr>
<td>DEA EVE</td>
<td>172</td>
<td>7.8</td>
</tr>
<tr>
<td>EHVE</td>
<td>135</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Solvent: DMF (40% v/v)
Dose rate: 2.6 kGy/hr

Figure 8.3: Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent.
Table 8.4: Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, without any solvents.

<table>
<thead>
<tr>
<th>MMA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th>Dose (kGy)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>4.9</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>0</td>
<td>3.5</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0</td>
<td>3.5</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0</td>
<td>3.5</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>3</td>
<td>3.5</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>3.5</td>
<td>Remained liquid</td>
</tr>
</tbody>
</table>

Dose rate: 2.6 kGy/hr
Table 8.5: Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, with different solvents.

<table>
<thead>
<tr>
<th>Solvent (40% v/v)</th>
<th>48% v/v MMA – 12% v/v DVE-3</th>
<th>Grafting yield (%)</th>
<th>Dose (kGy)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>1</td>
<td>7.8</td>
<td></td>
<td>Turned viscous</td>
</tr>
<tr>
<td>THF</td>
<td>2</td>
<td>7.8</td>
<td></td>
<td>Turned viscous</td>
</tr>
<tr>
<td>Methanol</td>
<td>131</td>
<td>7.8</td>
<td></td>
<td>Turned viscous</td>
</tr>
<tr>
<td>DMF</td>
<td>125</td>
<td>7.8</td>
<td></td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Dose rate: 2.6 kGy/hr

Figure 8.5: Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, with different solvents.
Figure 8.6: FT-IR spectrum of MMA/DVE-3 grafted cellulose substrate using gamma irradiation with 40% DMF as a solvent
8.3 Discussion

8.3.1 Grafting of neat vinyl ethers to cellulose by gamma irradiation

Despite the presence of cations as products of interactions between gamma radiation and monomers or cellulose [2,5], results in Table 8.1 indicated that the brief appearance of the ionic species was not sufficient to initiate polymerization of vinyl ethers. Most of the vinyl ethers remained as liquid after irradiation. This once again demonstrated that vinyl ethers were not reactive towards radicals in the solutions. TMPTVE was again an exception with its neat solution being polymerized at the end of irradiation to a dose of 3.5 kGy. As discussed in Section 6.3.1 of Chapter 6, the possibility of multiple radical formation under the influence of gamma radiation in the TMPTVE molecule that contributed to polymerization. However, cations formed at the initial stage of irradiation could be of significance as TMPTVE may be more reactive in the presence of such ions than the other vinyl ethers under study, since it had three double bonds present in its structure.

Although polymerization was observed for TMPTVE, no grafting was observed with cellulose. If polymerization was induced by cations, the near zero grafting was understandable since grafting is predominantly a free radical process.

8.3.2 Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, without any solvents

As shown in Table 8.2, when solutions of MMA with vinyl ethers as comonomers were exposed to gamma radiation, low grafting yields were observed in the absence of solvents. Low yields indicated vinyl ethers did not sufficiently swell cellulose, rendering it impossible for MMA to access and graft to the cellulose structure.

One interesting observation was the difference in the extent of polymerization. MMA solution containing monofunctional vinyl ethers, such as EVE, PVE, TBVE and EHVE, did not fully polymerize, while all solutions containing multifunctional vinyl ethers such as DVE, HDVE, DVE-4 and TMPTVE, polymerized to form a clear polymer. The difference was attributed either to the ability of the multifunctional vinyl ethers to
promote polymerization by crosslinking or the possible retardation of polymerization by the monofunctional vinyl ethers. However, it should be noted that the solutions containing the two monofunctional vinyl ethers, NBVE and DEAEVE, also fully polymerized, thus, indicating the importance of the vinyl ether types in enhancing polymerization. These results were reasonable since a study by Bevington et al [7] found that monofunctional vinyl ethers such as PVE and TBVE hindered the polymerization of MMA while divinyl ethers of polyethylene glycols acted as crosslinking agents for MMA polymerization in the presence of the thermal initiator AIBN.

8.3.3 Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent

When DMF was used as a solvent in MMA/vinyl ether systems, very high grafting yields were achieved. As shown in Table 8.3, most of the grafting yields were in excess of 100% despite the low MMA concentrations of 48% v/v. The promotion of grafting by DMF could be explained due to the swelling of cellulose in the solvent which make MMA accessible to grafting sites. As explained in Section 7.3.3 of Chapter 7, DMF presence also reduced polymerization rate (by diluting MMA), thus allowing the monomer to be available for the grafting process.

Evaluation of varying vinyl ethers to grafting yields did not follow any clear trend. This could be attributed to the abundance of reactive sites formed by gamma irradiation on the cellulose structure or the relatively high concentrations of both DMF and MMA as compared to vinyl ethers. Based on results in Table 8.3 and Figure 8.1, it was observed that solutions containing high molecular weight monofunctional vinyl ethers such as DEAEVE and EHVE, or multifunctional vinyl ethers, such as DVE, HDVE, DVE-4 and TMPTVE, appeared to give higher grafting yield than solutions containing other low molecular weight monofunctional vinyl ether. This phenomenon, as explained in Section 7.3.3 of Chapter 7, was attributable to the ability of these vinyl ethers either to act as crosslinking agents or to influence the viscosity of reacting solutions.
8.3.4 Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, without any solvents

The polymerization of MMA/DVE-3 mixtures was a matter of interest since there was a possibility of CT complex formation. As only MMA and DVE-3 were used without any solvents, low grafting was achieved as shown in Table 8.4. This is in line with the similar observation in Table 8.2. While neat DVE-3 did not polymerize, the solution containing 20% v/v DVE-3 required a dose of 4.9 kGy to polymerize, but solutions with higher DVE-3 concentrations required only 3.5 kGy for polymerization to take place. This observation thus suggested the polymerization was initiated by the interaction of MMA and DVE-3 as a DA pair under the influence of gamma radiation. This is similar to what was observed with the systems studied in Section 6.2.5 of Chapter 6 and the mechanism of this process should have involved the formations of both cationic and radical species in order to successfully explain the decrease of required gamma doses for polymerization with increasing DVE-3 concentrations [8,9].

8.3.5 Solvent type effect to gamma grafting of MMA to cellulose with DVE-3 as a comonomer

As mentioned in Chapter 3, some solvents such as methanol and DMF promoted UV grafting of MMA to cellulose while others, such as chloroform and THF, did not. Results in Table 8.5 show that similar findings were observed for gamma grafting of MMA to cellulose with DVE-3 as a comonomer. Solutions containing chloroform and THF gave low grafting yields while solutions containing DMF and methanol produced very high grafting yields. Difference in grafting yields was due to the swelling of cellulose contributed by the polarity of solvents. DMF and methanol are more polar solvents than chloroform and THF, with THF being the least polar solvent.

8.3.6 Characterization of the grafted substrate using the FT-IR spectroscopy

Figure 8.6 shows the spectrum of a grafted substrate from the MMA/DVE-3 system in the presence of DMF as the solvent. As mentioned in Section 8.2.6, the presence of MMA as the main component of the grafted chains is apparent due to the absorption peak
at 1732 cm$^{-1}$ of C=O. However, for the same reasons discussed in Section 7.3.7, the presence of DVE-3 units could not be confirmed.

8.4 Conclusions
In this chapter, gamma grafting of MMA to cellulose with vinyl ethers as comonomers was examined. As with the case of UV grafting of MMA to cellulose with vinyl ethers as comonomers, the presence of solvents such as DMF which could swell cellulose was proved to be essential. With the inclusion of DMF, significantly high grafting yields were achieved for all systems under study. In addition, grafting yields were found to be dependent on vinyl ether types. The grafting process appeared to be favored by high molecular weight monofunctional vinyl ethers or multifunctional vinyl ethers. The polymerization behavior of MMA/DVE-3 mixtures suggested the possibility of DA pair interaction mechanism as discussed in Chapter 6.

8.5 References
CHAPTER NINE: GRAFTING OF DIFFERENT DONOR/ACCEPTOR PAIRS TO PPE USING UV RADIATION
9.1 Introduction

The concept and mechanisms of CT complex polymerization initiated by the interaction between electron donors and electron acceptors under the influence of UV radiation as well as the advantages associated with this polymerization process have been discussed to a certain depth in Section 1.5 of Chapter 1 [1-11]. It has been observed by researchers that the polymerization rate of CT complex is strongly influenced by the strengths of donors and acceptors [2,3,5], the presence of free radicals [5,6,8,9] and Lewis acids [3,5], the presence of hydrogen donors [4,6,11] and the composition of monomer feed [5,6]. Most spontaneous polymerization occurs in cases of CT complexes containing either strong electron acceptors such as maleic anhydride and maleimide or strong electron donors, N-vinylpyrrolidone and paramethoxystyrene [1-10]. On the other hand, the spontaneous polymerization of CT complexes consisting of weak electron acceptors such as acrylates and methacrylates and weak electron donors, such as vinyl ethers, have been rarely studied. Therefore, the main aim of this chapter is to investigate possible spontaneous polymerization under the influence of UV radiation of vinyl monomer/vinyl ether mixtures in which vinyl monomers, AA, MAC, AN, MMA and BMA, are weak electron acceptors whilst vinyl ethers, DVE-3, TMPTVE and NBVE, are weak electron donors. Such spontaneous polymerization is compared to polymerization of MA/vinyl ether and DMMA/vinyl ether systems under the influence of UV radiation. In the case of MA/vinyl ether system, MA was a solid and thus acetone was used as the solvent for dissolving the monomer. The grafting of such vinyl monomer/vinyl ether mixtures to PPE is also under investigation.

9.2 Results

9.2.1 UV grafting of vinyl monomers to PPE with or without Irgacure 819 photoinitiator

9.2.1.1 Without Irgacure 819 photoinitiator

Table 9.1 shows grafting results of different vinyl monomers to PPE substrates in the absence of Irgacure 819 photoinitiator. No grafting was achieved for most of the monomer solutions which still remained in a liquid state. However, 7% grafting yield was observed for MMA while a significant grafting yield of 69% was achieved for BMA.
9.2.1.2 With 1% w/v of Irgacure 819 photoinitiator
Results in Table 9.2 show that in the presence of Irgacure 819 photoinitiator, most of the monomers with the exceptions of MA and DVE-3 polymerized, but grafting was observed only for MAC, BMA and MMA.

9.2.2 UV grafting of different electron poor vinyl monomer/DVE-3 DA pairs to PPE
without Irgacure 819 photoinitiator
UV polymerization and grafting of different electron poor (EP) vinyl monomer/DVE-3 DA pairs are shown in Tables 9.3-9.9 in which vinyl monomers MA, DMMA, AN, AA, MAC, BMA and MMA were used as acceptors. Spontaneous polymerization was observed for most systems but the general trend was that solutions with high DVE-3 content (80% v/v and above) polymerized faster than solutions with low DVE-3 content. Figures 9.3-9.9 represent UV doses required in order for the EP vinyl monomer/DVE-3 solutions to polymerize versus double bond molar ratios between DVE-3 and EP vinyl monomers. The double bond molar ratios (DBMR) were calculated according to the double bond functionality of the monomers present in each system. Grafting yields were insignificant for most systems regardless of monomer concentration ratios. However, solutions containing high concentration in MMA (60% v/v and above) and BMA (40% v/v and above) (Tables 9.8-9.9) showed good grafting yields.

9.2.3 UV grafting of different EP vinyl monomer/DVE-3 systems to PPE with Irgacure 819 photoinitiator
With the presence of Irgacure 819 photoinitiator, UV polymerization of most EP vinyl monomer/DVE-3 DA pairs rapidly occurred, producing large quantities of polymers (Tables 9.10-9.16). Due to the low reactivity of BMA and MMA, solutions of these two vinyl monomers and DVE-3 contained 1% w/v Irgacure 819 while only 0.2% w/v Irgacure 819 was present in other EP vinyl monomer/DVE-3 systems. Results in these tables show a general trend in which solutions with high content of DVE-3 (60% v/v and above) polymerized to form tacky polymers as compared with solutions of low DVE-3 contents which formed polymers with no tacky texture. This suggested that not all DVE-3 was used up in the polymerization process. However, solutions containing lower
concentrations of DVE-3 and high concentrations of BMA and MMA (60% v/v and above) formed clear glassy polymers. It was also observed that when DVE-3 concentrations were high (80% v/v and above) and EP vinyl monomers' concentrations were low (20% v/v and below), the solutions merely turned viscous. These observations indicated that the free radical from the photolysis of Irgacure 819 had enhanced homopolymerization of the EP vinyl monomers when they were present in excess. Figures 9.10-9.16 depict graphs of UV exposure doses required for solutions to polymerize versus DBMR between DVE-3 and EP vinyl monomers. The relationship between these two variables will be discussed for each individual system in Section 9.3.1.3.

Results in Tables 9.10-9.14 show poor grafting of MA, DMMA, AN, AA, MAC and DVE-3 to PPE substrates despite extensive formation of polymers. Solutions containing high MMA or BMA concentrations (60% v/v and above) (Tables 9.15-9.16) were again the two exceptions, giving reasonable grafting yields.

9.2.4 UV grafting of MAC to PPE substrates with NBVE and TMPTVE as electron donors, with or without Irgacure 819 photoinitiator

9.2.4.1 Without Irgacure 819 photoinitiator

As shown in Table 9.17, with the exclusion of Irgacure 819, all solutions containing MAC with NBVE and TMPTVE did not polymerize or produce any grafting.

9.2.4.2 With 0.2% w/v of Irgacure 819 photoinitiator

Tables 9.19-9.20 show UV grafting and polymerization results of solutions containing MAC and the two vinyl ethers with varying concentrations in the presence of Irgacure 819 photoinitiator. All solutions polymerized, but it was observed that the required UV doses for MAC/NBVE solutions (Table 9.19) to polymerize increased with increasing NBVE concentrations. On the contrary, UV doses required for MAC/TMPTVE solutions (Table 9.20) to polymerize followed an opposite trend. These two trends are presented in Figure 9.20 in which UV doses are plotted against DBMR between the vinyl ethers and
MAC. Small grafting yields were observed for MAC/NBVE solutions but no significant grafting was achieved for MAC/TMPTVE solutions.

9.2.5 UV grafting of AN to PPE substrates with NBVE and TMPTVE as electron donors, with or without Irgacure 819 photoinitiator

9.2.5.1 Without Irgacure 819 photoinitiator

Table 9.18 presents results of UV grafting and polymerization of solutions containing AN and the vinyl ethers, NBVE and TMPTVE. As shown, no grafting was obtained while most solutions did not polymerize after extensive UV exposures. However, solutions containing AN and 60% v/v or 80% v/v TMPTVE did polymerize.

9.2.5.2 With 0.2% w/v of Irgacure 819 photoinitiator

Tables 9.21-9.22 show rapid polymerization in all solutions containing AN and the two vinyl ethers but the ones containing TMPTVE polymerized more rapidly than the ones containing NBVE. As in the case of MAC, UV exposure doses for AN/NBVE solutions (Table 9.21) increased with increasing NBVE concentrations while UV doses required for AN/TMPTVE decreased with increasing TMPTVE concentrations. Figure 9.21 shows the plots of DBMR between the two vinyl ethers and AN versus the UV doses. However, despite extensive polymerization, hardly any grafting was observed in these systems.

9.2.6 UV grafting of DMMA to PPE substrates with different vinyl ethers, without Irgacure 819 photoinitiator

Results in Table 9.23 show UV grafting and polymerization of different DMMA/vinyl ether systems in which DMMA concentrations were at 80% v/v. Only solution containing DVE polymerized while no grafting was observed for all systems.

Results in Table 9.24 present UV grafting and polymerization of different DMMA/vinyl ether systems in which DMMA concentrations for all systems were at 60% v/v. Again, only the solution containing DVE polymerized and all the other systems produced insignificant grafting despite extensive UV exposures.
Table 9.1: UV grafting of different vinyl monomers to PPE without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl monomers</th>
<th>0% w/v Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>MA*</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>DMMA</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>AN</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>AA</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>MAC</td>
<td>0</td>
<td>440</td>
</tr>
<tr>
<td>BMA</td>
<td>7</td>
<td>440</td>
</tr>
<tr>
<td>MMA</td>
<td>69</td>
<td>367</td>
</tr>
<tr>
<td>DVE-3</td>
<td>0</td>
<td>440</td>
</tr>
</tbody>
</table>

* Acetone was a solvent, 50% w/w

Dose rate: 36.7 J/hr

Temperature: 29 °C
Table 9.2: Grafting of different vinyl monomers to PPE with 1% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl monomer</th>
<th>1% w/v Irgacure 819</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>MA(^a)</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>DMMA</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>AN</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>AA</td>
<td>0</td>
<td>28</td>
</tr>
<tr>
<td>MAC</td>
<td>5</td>
<td>29</td>
</tr>
<tr>
<td>BMA</td>
<td>17</td>
<td>43</td>
</tr>
<tr>
<td>MMA</td>
<td>57</td>
<td>46</td>
</tr>
<tr>
<td>DVE-3</td>
<td>0</td>
<td>440</td>
</tr>
</tbody>
</table>

\(^a\): MA was dissolved in acetone, 50% w/w

Dose rate: 36.7 J/hr

Temperature: 29 °C
Table 9.3: UV grafting of MA to PPE with DVE-3 as a comonomer, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>DVE-3:MA conc. ratio (mole/mole)</th>
<th>Double bond molar ratios between DVE-3/MA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5:1</td>
<td>1:1</td>
<td>L</td>
<td>330</td>
<td>Formed a brittle black polymer</td>
</tr>
<tr>
<td>1:1</td>
<td>2:1</td>
<td>L</td>
<td>330</td>
<td>Formed a brittle black polymer</td>
</tr>
<tr>
<td>2:1</td>
<td>4:1</td>
<td>0</td>
<td>355</td>
<td>Formed a brittle, clear polymer</td>
</tr>
<tr>
<td>3:1</td>
<td>6:1</td>
<td>0</td>
<td>31</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>4:1</td>
<td>8:1</td>
<td>6</td>
<td>37</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

L: Lost due to the decomposition of substrate under excessive heat released from extremely exothermic polymerization.

Acetone was used as a solvent, 50% w/w.

Dose rate: 36.7 (J/hr)

Temperature: 29 (°C)

Figure 9.3: UV doses versus DBMR between MA/DVE-3 without Irgacure 819 photoinitiator.
Table 9.4: UV grafting of DMMA to PPE with DVE-3 as a comonomer, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>DMMA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/DMMA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.3:1</td>
<td>0</td>
<td>529</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.8:1</td>
<td>4</td>
<td>83</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.9:1</td>
<td>2</td>
<td>43</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>5:1</td>
<td>7</td>
<td>31</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>11.2:1</td>
<td>6</td>
<td>43</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>1</td>
<td>99</td>
<td>122.7:1</td>
<td>0</td>
<td>385</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.4: UV doses versus DBMR between DMMA/DVE-3 without Irgacure 819 photoinitiator.
Table 9.5: UV grafting of AN to PPE with DVE-3 as a comonomer without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>AN conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/AN</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.2:1</td>
<td>0</td>
<td>765</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.4:1</td>
<td>0</td>
<td>217</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1:1</td>
<td>2</td>
<td>110</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>2.6:1</td>
<td>2</td>
<td>55</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>5.9:1</td>
<td>0</td>
<td>43</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>1</td>
<td>99</td>
<td>64.9:1</td>
<td>3</td>
<td>37</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr  
Temperature: 29 °C

Figure 9.5: UV doses versus DBMR between AN/DVE-3 without the presence of Irgacure 819 photoinitiator.
Table 9.6: UV grafting of AA to PPE with DVE-3 as a comonomer without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>AA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/AA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.2:1</td>
<td>0</td>
<td>960</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.5:1</td>
<td>0</td>
<td>960</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.0:1</td>
<td>2</td>
<td>960</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>2.7:1</td>
<td>2</td>
<td>18</td>
<td>Formed a clear, tacky polymer; exothermic</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.6: UV doses versus DBMR between AA/DVE-3 without Irgacure 819 photoinitiator.
Table 9.7: UV grafting of MAC to PPE with DVE-3 as a comonomer without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>MAC conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/MAC</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.2:1</td>
<td>0</td>
<td>765</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.6:1</td>
<td>45</td>
<td>765</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.3:1</td>
<td>109</td>
<td>765</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>3.6:1</td>
<td>1</td>
<td>55</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>8.1:1</td>
<td>0</td>
<td>43</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>1</td>
<td>99</td>
<td>88.7:1</td>
<td>0</td>
<td>765</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.7: UV doses versus DBMR between MAC/DVE-3 without the presence of Irgacure 819 photoinitiator.
Table 9.8: UV grafting of BMA to PPE with DVE-3 as a comonomer without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>BMA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/BMA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.4:1</td>
<td>5</td>
<td>532</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>1.1:1</td>
<td>101</td>
<td>532</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>2.4:1</td>
<td>39</td>
<td>370</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>6.3:1</td>
<td>0</td>
<td>184</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>14.2:1</td>
<td>0</td>
<td>184</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>30.0:1</td>
<td>0</td>
<td>184</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>1</td>
<td>99</td>
<td>156.4:1</td>
<td>0</td>
<td>275</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr  
Temperature: 29 °C

Figure 9.8: UV doses versus DBMR between BMA/DVE-3 without the presence of Irgacure 819 photoinitiator.
Table 9.9: UV grafting of MMA to PPE with DVE-3 as a comonomer without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>MMA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/MMA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>1</td>
<td>0.0:1</td>
<td>203</td>
<td>278</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>95</td>
<td>5</td>
<td>0.1:1</td>
<td>77</td>
<td>278</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>0.1:1</td>
<td>166</td>
<td>278</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>0.3:1</td>
<td>42</td>
<td>278</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.7:1</td>
<td>273</td>
<td>177</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.6:1</td>
<td>20</td>
<td>156</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>4.3:1</td>
<td>13</td>
<td>156</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>9.6:1</td>
<td>3</td>
<td>141</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>20.2:1</td>
<td>0</td>
<td>141</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>1</td>
<td>99</td>
<td>105.4:1</td>
<td>0</td>
<td>141</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.9: UV doses versus DBMR between MMA/DVE-3 without Irgacure 819 photoinitiator.
Table 9.10: UV grafting of MA to PPE with DVE-3 as a comonomer with 0.2% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>DVE-3:MA conc. ratio (mole/mole)</th>
<th>Double bond molar ratios between DVE-3/MA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5:1</td>
<td>1:1</td>
<td>L</td>
<td>2</td>
<td>Formed a clear polymer; exothermic</td>
</tr>
<tr>
<td>1:1</td>
<td>2:1</td>
<td>L</td>
<td>2</td>
<td>Formed a clear polymer; exothermic</td>
</tr>
<tr>
<td>2:1</td>
<td>4:1</td>
<td>0</td>
<td>2</td>
<td>Formed a clear polymer; exothermic</td>
</tr>
<tr>
<td>3:1</td>
<td>6:1</td>
<td>3</td>
<td>1</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>4:1</td>
<td>8:1</td>
<td>0</td>
<td>1</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

L: Lost due to the decomposition of substrate under excessive heat released by the extreme exothermic polymerization

Acetone was used as a solvent

Irgacure 819 concentration: 0.2% w/v

Dose rate: 36.7 J/hr

Temperature: 29 °C

Figure 9.10: UV doses versus DBMR between MA/DVE-3 with 0.2% w/v of Irgacure 819 photoinitiator.
Table 9.11: UV grafting of DMMA to PPE with DVE-3 as a comonomer with 0.2% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>DMMA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/DMMA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.3:1</td>
<td>1</td>
<td>6</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.8:1</td>
<td>0</td>
<td>4</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.9:1</td>
<td>0</td>
<td>3</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>5:1</td>
<td>0</td>
<td>3</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% w/v
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.11: UV doses versus DBMR between DMMA/DVE-3 with 0.2% w/v of Irgacure 819 photoinitiator.
Table 9.12: UV grafting of AN to PPE with DVE-3 as a comonomer with 0.2% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>AN conc. (%) v/v</th>
<th>DVE-3 conc. (%) v/v</th>
<th>Double bond molar ratios between DVE-3/AN</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.2:1</td>
<td>0</td>
<td>9</td>
<td>Formed a white polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.4:1</td>
<td>3</td>
<td>5</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1:1</td>
<td>0</td>
<td>5</td>
<td>Formed a clear, tacky polymer; exothermic</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>2.6:1</td>
<td>0</td>
<td>4</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% w/v
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.12: UV doses versus DBMR between AN/DVE-3 with 0.2% w/v of Irgacure 819 photoinitiator.
Table 9.13: UV grafting of AA to PPE with DVE-3 as a comonomer, with 0.2% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>AA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/AA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.2:1</td>
<td>0</td>
<td>9</td>
<td>Formed a clear hard polymer; exothermic</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.5:1</td>
<td>L</td>
<td>4</td>
<td>Extremely exothermic; Polymer decomposed</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.0:1</td>
<td>L</td>
<td>2</td>
<td>Extremely exothermic; Polymer decomposed</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>2.7:1</td>
<td>L</td>
<td>2</td>
<td>Extremely exothermic; Polymer decomposed</td>
</tr>
</tbody>
</table>

L: Lost due to the decomposition of substrate under excessive heat released by the extreme exothermic polymerization
Irgacure 819 concentration: 0.2% w/v
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.13: UV doses versus DBMR between AA/DVE-3 with 0.2% w/v of Irgacure 819 photoinitiator.
Table 9.14: UV grafting of MAC to PPE with DVE-3 as a comonomer, with 0.2% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>MAC conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/MAC</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.2:1</td>
<td>0</td>
<td>9</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.6:1</td>
<td>0</td>
<td>4</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.3:1</td>
<td>0</td>
<td>4</td>
<td>Formed a clear, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>3.6:1</td>
<td>0</td>
<td>2</td>
<td>Formed a clear, tacky polymer</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% w/v
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.14: UV doses versus DBMR between MAC/DVE-3 with 0.2% w/v of Irgacure 819 photoinitiator.
Table 9.15: UV grafting of BMA to PPE with DVE-3 as a comonomer with 1% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>BMA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/BMA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.4:1</td>
<td>14</td>
<td>55</td>
<td>Formed a clear, yellow polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>1.1:1</td>
<td>35</td>
<td>73</td>
<td>Formed a clear, yellow polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>2.4:1</td>
<td>0</td>
<td>86</td>
<td>Formed a clear, yellow polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>6.3:1</td>
<td>0</td>
<td>135</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>14.2:1</td>
<td>0</td>
<td>165</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1</td>
<td>99</td>
<td>156.4:1</td>
<td>0</td>
<td>190</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 9.15: UV doses versus DBMR between BMA/DVE-3 with 1% w/v of Irgacure 819 photoinitiator.
Table 9.16: UV grafting of MMA to PPE with DVE-3 as a comonomer with 1% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>MMA conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Double bond molar ratios between DVE-3/MMA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.3:1</td>
<td>60</td>
<td>55</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.7:1</td>
<td>23</td>
<td>73</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.6:1</td>
<td>5</td>
<td>91</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>4.3:1</td>
<td>0</td>
<td>110</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v  
Dose rate: 36.5 J/hr  
Temperature: 29 °C

Figure 9.16: UV doses versus DBMR between MMA/DVE-3 with 1% w/v of Irgacure 819 photoinitiator.
Table 9.17: UV grafting of MAC to PPE with NBVE and TMPTVE as comonomers without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>MAC conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NBVE</td>
<td>TMPTVE</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Total dose: 832 J  
Dose rate: 36.7 J/hr  
Temperature: 29 °C

Table 9.18: UV grafting of AN to PPE with NBVE and TMPTVE as comonomers without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>AN conc. (% v/v)</th>
<th>NBVE</th>
<th>TMPTVE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting (%)</td>
<td>Solution Appearance</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>Remained liquid</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>Remained liquid</td>
</tr>
</tbody>
</table>

Total dose: 832 J  
Dose rate: 36.7 J/hr  
Temperature: 29 °C
Table 9.19: UV grafting of MAC to PPE with NBVE as a comonomer with 0.2% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>MAC conc. (% v/v)</th>
<th>NBVE conc. (% v/v)</th>
<th>Double bond molar ratio between NBVE/MAC</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.2:1</td>
<td>5</td>
<td>24</td>
<td>Formed a clear, tacky polymer; exothermic</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.5:1</td>
<td>7</td>
<td>26</td>
<td>Formed a clear, tacky polymer; exothermic</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.1:1</td>
<td>8</td>
<td>28</td>
<td>Formed a clear, tacky polymer; exothermic</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>2.8:1</td>
<td>7</td>
<td>32</td>
<td>Formed a clear, tacky polymer; exothermic</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% w/v  
Dose rate: 36.7 J/hr  
Temperature: 29 °C

Table 9.20: UV grafting of MAC to PPE with TMPTVE as a comonomer with 0.2% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>MAC conc. (v/v%)</th>
<th>TMPTVE conc. (v/v%)</th>
<th>Double bond molar ratio between TMPTVE/MAC</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.3:1</td>
<td>0</td>
<td>11</td>
<td>Formed a hard, clear polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.8:1</td>
<td>0</td>
<td>8</td>
<td>Formed a hard, clear polymer; exothermic</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.8:1</td>
<td>0</td>
<td>6</td>
<td>Formed a hard, clear polymer; exothermic</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>4.8:1</td>
<td>0</td>
<td>5</td>
<td>Formed a hard, clear polymer; exothermic</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% v/v  
Dose rate: 36.7 J/hr  
Temperature: 29 °C
Figure 9.20: UV doses versus DBMR between MAC/vinyl ether with 0.2% w/v of Irgacure 819 photoinitiator.
Table 9.21: UV grafting of AN to PPE with NBVE as a comonomer with 0.2% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>AN conc. (%) v/v</th>
<th>NBVE conc. (%) v/v</th>
<th>Double bond molar ratio between NBVE/AN</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.1:1</td>
<td>0</td>
<td>28</td>
<td>Formed a white, tacky polymer</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.3:1</td>
<td>1</td>
<td>46</td>
<td>Formed a white, tacky polymer</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0.8:1</td>
<td>0</td>
<td>53</td>
<td>Formed a white, tacky polymer</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>2.0:1</td>
<td>0</td>
<td>61</td>
<td>Formed a white, tacky polymer</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% v/v
Dose rate: 36.7 J/hr
Temperature: 29 °C

Table 9.22: UV grafting of AN to PPE with TMPTVE as a comonomer with 0.2% w/v of Irgacure 819 photoinitiator

<table>
<thead>
<tr>
<th>AN conc. (%) v/v</th>
<th>TMPTVE conc. (%) v/v</th>
<th>Double bond molar ratio between TMPTVE/AN</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.2:1</td>
<td>0</td>
<td>9</td>
<td>Formed a hard, clear polymer; exothermic</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.6:1</td>
<td>0</td>
<td>6</td>
<td>Formed a hard, clear polymer; exothermic</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1.3:1</td>
<td>0</td>
<td>5</td>
<td>Formed a brittle, clear polymer; exothermic</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>3.5:1</td>
<td>0</td>
<td>5</td>
<td>Formed a brittle, clear polymer; exothermic</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% v/v
Dose rate: 36.7 J/hr
Temperature: 29 °C
**Figure 9.21:** UV doses versus DBMR between AN/vinyl ether with 0.2% w/v of Irgacure 819 photoinitiator.
Table 9.23: UV grafting of DMMA to PPE with vinyl ethers as comonomers, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers (20% v/v)</th>
<th>80% v/v DMMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>PVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>TBVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>NBVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>DVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>HDVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>DVE-4</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>DEA-EVE</td>
<td>0</td>
<td>1077</td>
</tr>
<tr>
<td>EHVE</td>
<td>0</td>
<td>1077</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C
### Table 9.24: UV grafting of DMMA to PPE with vinyl ethers as comonomers, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ethers (40% v/v)</th>
<th>60% v/v DMMA</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grafting yield (%)</td>
<td>Dose (J)</td>
</tr>
<tr>
<td>EVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>PVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>TBVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>IBVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>NBVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>DVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>HDVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>DVE-4</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>0</td>
<td>807</td>
</tr>
<tr>
<td>EHVE</td>
<td>0</td>
<td>807</td>
</tr>
</tbody>
</table>

Dose rate: 36.7 J/hr
Temperature: 29 °C

### Table 9.25: DBMR between DVE/DMMA and DVE-4/DMMA.

<table>
<thead>
<tr>
<th>DMMA conc. (% v/v)</th>
<th>DVE Conc. (% v/v)</th>
<th>DBMR between DVE/DMMA</th>
<th>DVE-4 Conc. (% v/v)</th>
<th>DBMR between DVE-4/DMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0.5:1</td>
<td>20</td>
<td>0.3:1</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>1.3:1</td>
<td>40</td>
<td>0.7:1</td>
</tr>
</tbody>
</table>
9.3 Discussion

9.3.1 Polymerization of different DA pairs of vinyl monomers and DVE-3

9.3.1.1 Homopolymerizations of vinyl monomers by UV lights with and without Irgacure 819 photoinitiator

Results in Table 9.1 show most of the studied EP vinyl monomers did not polymerize after long UV exposures. The slow homopolymerization rates were mainly due to the lack of free radicals in the solutions. As discussed in Section 5.2.1 of Chapter 5, neat MMA undergoes polymerization at the UV dose of 367 J. DVE-3, however, does not undergo radical induced homopolymerization. Widely being used as reactive diluents in radiation curable coatings [12,13], neat vinyl ethers are known to participate mostly in cationic polymerization [13-19].

In the presence of Irgacure 819 photoinitiator (Table 9.2), the EP vinyl monomers undergo polymerization in acetone, producing homopolymers with the exceptions of MA and DMMA. Vinyl monomers, such as AN, AA and MAC, homopolymerized much faster than MMA and BMA while MA, DMMA and DVE-3 did not undergo polymerization even with long UV exposures.

9.3.1.2 DA pair polymerization by UV irradiation without Irgacure 819 photoinitiator

Existence of CT complexes between MA, DMMA, AN, AA, MAC, BMA, MMA and DVE-3 were possible from results in Tables 9.3 to 9.9. Most solutions of EP vinyl monomers and DVE-3 spontaneously polymerized when they were exposed to UV radiation despite much lower UV doses than the doses applied to neat EP vinyl monomers as shown in Table 9.1. Such spontaneous polymerization suggested that interactions between EP vinyl monomers and DVE-3 may have led to the formation of CT complexes since individual EP vinyl monomer was shown in Table 9.1 not to polymerize in the absence of PIs. However, reactivity of different systems was found to be different. Within each DA system, based on required UV doses, it was observed that reactivity was dependent on concentration ratios between donors and acceptors. In order to understand exactly what had taken place, it is necessary to analyze DA pairs based on each individual case.
9.3.1.2.1 MA and DVE-3
In recent studies [1-3,5,9], MA is listed as a very strong acceptor and DVE-3 is quoted as a moderate donor. MA is a solid and does not dissolve well in DVE-3. Consequently, in this study, acetone was added as a solvent. Since CT complex formation involved interactions between each double bond of the donor with each of the double bond of the acceptor, the polymerization was expected to be fastest when there was double bond ratio of 1 to 1 between DVE-3 and MA. However, as shown in Table 9.3 and Figure 9.3, UV exposure doses and the solution appearance indicated otherwise. Solutions with high DVE-3 content were found to polymerize first and the required UV exposure doses were also much lower than those solutions with high MA concentration. The increase of tackiness in polymers with increasing DVE-3 concentrations showed high content of DVE-3 in the polymer. With the understanding that neat DVE-3 did not homopolymerize when exposed to UV radiation (Table 9.1), polymerization of solutions with high DVE-3 content must have involved the homopolymerization of DVE-3 which was probably initiated by MA/DVE-3 complex. For solutions with high DVE-3 content, it was observed that once the polymerization was initiated it occurred very fast. Extreme heat was also released, evidenced by black polymers as products of decomposition.

9.3.1.2.2 DMMA and DVE-3
Similar to MA, DMMA is quoted as a strong acceptor [1,2,5] and thus, all DMMA/DVE-3 solutions polymerized under the influence of UV radiation (Table 9.4). However, the solution containing DVE-3 and DMMA with double bond molar ratio of 0.3:1 required a high UV dose of 532 J to polymerize and this was probably due to the inability of excess DMMA to polymerize (Table 9.1). As DMMA concentration decreased, lower UV doses were required (Figure 9.4), indicating an increase in polymerization rates. This observation was in line with the report of Garnett and Zilic [5]. The authors studied polymerization of DVE-3/DMMA systems in two double bond molar ratios of 1:1 and 0.5:1 and found that a longer UV dose was also required for the solution with a higher DMMA content to polymerize.
Polymerization of solutions with high DVE-3 concentration implied the homopolymerization of DVE-3. However, a significant increase of the exposure dose was required for polymerization to take place when DVE-3 concentration increased to 99% v/v (Figure 9.4). The increase of the required UV dose indicated that the presence of DMMA/DVE-3 complex in the solution was barely sufficient to initiate polymerization process.

9.3.1.2.3 AN and DVE-3

Spontaneous polymerization of AN/DVE-3 solutions has never been reported previously in literature. As shown in Table 9.5 and Figure 9.5, the solution with highest AN concentration of 80% v/v did not polymerize despite of very long UV exposure and this was again due to the inability of excess AN to polymerize (Table 9.1). All other solutions polymerized, forming clear, tacky polymers. Figure 9.5 shows that as the concentration of DVE-3 increased, the required UV exposure doses of the solutions rapidly decreased, indicating an increase of polymerization rate with decreasing UV doses. The ability of high DVE-3 content solutions to polymerize pointed to the possible homopolymerization of DVE-3. Unlike DMMA/DVE-3 system, the solution containing 99% v/v of DVE-3 did polymerize in the shortest UV exposure of 37 J. This could therefore be deduced that the interaction of AN/DVE-3 pair in the solution was sufficient to initiate the polymerization process.

9.3.1.2.4 AA and DVE-3

The AA/DVE-3 system is different from other systems because AA is an organic acid. As shown in Table 9.6 and Figure 9.6, when AA concentration in solutions was greater than 40% v/v, no polymerization was observed even after a long UV exposure (960 J). One possibility was that excess AA strongly hindered the polymerization initiated by the interaction of AA/DVE-3 DA pair. However, the solution containing DVE-3 of concentration 80% v/v underwent rapid polymerization (required UV dose of 18 J), releasing a great amount of heat. Again, polymerization that had taken place must be due to the homopolymerization of DVE-3.
9.3.1.2.5 MAC and DVE-3

Table 9.7 and Figure 9.7 show similarity between polymerization of MAC and DVE-3 solutions and the solutions containing DMMA/DVE-3. The solution containing 80% v/v of MAC did not polymerize despite a long UV exposure (765 J). As MAC concentrations decreased, all solutions polymerized and UV exposure doses were found to decrease with increasing DVE-3 concentrations (Figure 9.7). However, a long UV exposure of 765 J was required for the solution containing 99% v/v DVE-3 to polymerize, indicating the polymer was mainly the homopolymer of DVE-3.

9.3.1.2.6 BMA and DVE-3

Results of polymerization of BMA/DVE-3 in different ratios are shown in Table 9.8 in which solutions with BMA concentration of 80% v/v remained as a liquid and the 60% v/v solution slightly polymerized (viscous) after a long UV exposure (532 J). The UV doses required for polymerization decreased with increase in DVE-3 concentration (Figure 9.8), indicating an increase of polymerization rate with decrease in required UV dose. However, when compared to the lowest required UV doses for the systems containing MA, DMMA, AA, MAC, AN and DVE-3 (Tables 9.3 to 9.7), the lowest required UV dose of 184 J (Table 9.8) for the solution containing BMA/DVE-3 to polymerize was much higher and thus indicating the weakness of BMA/DVE-3 DA pair interaction. According to results in Table 9.1, neat BMA did homopolymerize but after a long UV exposure of 440 J. Since the BMA/DVE-3 interaction was weak, it was possible that homopolymerization of BMA along with BMA/DVE-3 DA pair polymerization as well as the formation of DVE-3 homopolymer could have all taken place at the same time.

9.3.1.2.7 MMA and DVE-3

MMA/DVE-3 systems were very much similar to BMA/DVE-3 systems. The lowest required UV dose of 141 J for solutions containing 1-10% v/v MMA in MMA/DVE-3 to polymerize (Table 9.9 and Figure 9.9) was very high compared with the lowest required UV doses for the systems containing MA, DMMA, AA, MAC, AN and DVE-3 (with these vinyl monomers also having the concentration of 1-10% v/v), implying the weak
interaction between MMA and DVE-3. On the other hand exposure doses also decreased with increasing DVE-3 concentrations, indicating increasing polymerization rates. The ability of solutions with high DVE-3 concentration to polymerize also meant the occurrence of DVE-3 homopolymerization. Compared to neat MMA polymerization (Table 9.1), exposure doses for MMA/DVE-3 solutions were much lower. This proved that MMA homopolymerization was much slower than DA pair polymerization. However, like BMA/DVE-3 system, at high MMA concentrations, homopolymerization of MMA along with DA pair polymerization as well as DVE-3 homopolymerization could have taken place at the same time.

In summary, all data showed high polymerization rate with high DVE-3 concentration in the solutions. The ability of solutions with high DVE-3 content to polymerize implied homopolymerization of the vinyl ether in conjunction with the polymerization initiated by DA interaction possibly in the form of CT complex. The increase of polymerization rates with increase in DVE-3 concentration also suggested that DVE-3 homopolymerization rate was faster than free radical polymerization of EP vinyl monomers or formations of CT complexes. The inability of solutions with high EP vinyl monomer contents to polymerize implied that while CT complexes could spontaneously polymerize, they could not initiate free radical polymerization of EP vinyl monomers.

9.3.1.3 Polymerization mechanisms of DA pairs of EP vinyl monomers and DVE-3

A number of mechanisms involving CT complex polymerization have been mentioned in Section 1.5.1 of Chapter 1. They are: a) tetramethylenes and dissociated radical ionic pair as initiators of spontaneous polymerization (Scheme 1.6), b) a CT complex which acts as a monomer (Scheme 1.7), c) matrix polymerization (Scheme 1.8) and d) electron transfer (Scheme 1.9) [2,3].

It is not feasible to use mechanisms b and c to explain the spontaneous polymerization of solutions containing high concentrations of DVE-3. With all evidences pointing to the homopolymerization of DVE-3 which was initiated by cationic species, mechanisms involving formation of cations in CT complexes are therefore supported. However,
complete electron transfer mechanism is not viable because this mechanism is only workable with very strong donors and acceptors [3]. With DVE-3 as a weak donor and most of EP vinyl monomers used were weak acceptors, the occurrence of polymerization following this type of mechanism is unlikely.

In this study, the mechanism in which tetramethylene was formed as an intermediate and dissociated radical ions (discussed in Section 1.5.1) which subsequently initiate spontaneous polymerization appeared to be a feasible explanation for the spontaneous homopolymerization of DVE-3. According to Scheme 1.6, both free radicals and ions are products of interactions between donors, acceptors and UV light. These species are able to initiate either free radical polymerization or ionic polymerization depending on the monomer types.

When applying the above mechanism to explain our experimental data, it can be said that, tetramethylene intermediates or radical ions were responsible for initiating the copolymerization of vinyl monomer/DVE-3 complexes and the homopolymerization of vinyl monomers (radical induced) and DVE-3 (cationic induced). Based on the exposure doses (Tables 9.3-9.9), the radical homopolymerization of EP vinyl monomers and their complexes was very slow while the cationic homopolymerization of DVE-3 was very fast. It was possibly the reason why solutions with high DVE-3 concentrations polymerized faster than solutions with high EP vinyl monomer concentrations. However, at very high concentrations of DVE-3 (for example 99% v/v), the low complex concentrations of were not sufficient to initiate the homopolymerization of DVE-3 and as a result, long UV exposures were required.

9.3.1.4 CT complex polymerization by UV irradiation with Irgacure 819 photoinitiator

A number of researchers [5,6,8,9] have found that the presence of photoinitiators significantly enhanced polymerization rate of CT complexes. Furthermore, in a number of studies, vinyl ethers have been shown to participate in free radical copolymerization with other vinyl monomers [20-25]. Therefore, with the addition of Irgacure 819
photoinitiator to EP vinyl monomer/DVE-3 solutions, polymerization of most solutions occurred almost immediately, as shown in Tables 9.10-9.16.

9.1.3.4.1 MA and DVE-3 with 0.2% w/v Irgacure 819

Results in Table 9.10 show that MA/DVE-3 solutions were very responsive to the presence of Irgacure 819 photoinitiator. Polymerization of solutions with various double bond ratios required only 1-2 J of UV radiation. Solutions with high MA concentrations underwent extremely exothermic polymerization, releasing a large quantity of heat, indicating strong spontaneous reactions between these two monomers. MA (dissolved in acetone) or neat DVE-3 do not undergo homopolymerization even in the presence of Irgacure 819 (Tables 9.1-9.2) and solutions of MA/DVE-3 with high MA concentration required long UV exposures to polymerize in the absence of photoinitiators (Table 9.3). Therefore fast polymerization of MA/DVE-3 solutions in the presence of Irgacure 819 was attributed to the abundance of free radicals from the photolysis of Irgacure 819.

9.1.3.4.2 DMMA and DVE-3 with 0.2% w/v Irgacure 819

Although DMMA/DVE-3 solutions (Table 9.11) polymerized very quickly, the rates were not as fast as solutions containing MA and DVE-3 under the same conditions. The difference gave an indication that the interaction between DVE-3 with DMMA as a CT complex was not as strong as with MA. Comparison with polymerization of DMMA/DVE-3 solutions without Irgacure 819 photoinitiator (Table 9.4) also indicated that the acceleration of DMMA/DVE-3 complex polymerization was caused by free radicals.

9.3.1.4.3 AN and DVE-3 with 0.2% w/v Irgacure 819

Similar to DMMA/DVE-3 solutions, AN/DVE-3 solutions underwent rapid radical induced polymerization, producing polymers with appearance depending on DVE-3 concentration. At high AN concentrations, polymers were white and hard (Table 9.12) and as DVE-3 concentration increased, polymers became clear and tacky, showing vinyl ether characteristics. Since AN undergoes polymerization in the presence of radicals (Table 9.2), it can be deduced that in this instance there were three possible polymerization processes taking place simultaneously, i.e., free radical
homopolymerization of AN, free radical polymerization of AN/DVE-3 complexes, and

cationic homopolymerization of DVE-3. As shown in Table 9.2, neat AN solution

required a much longer UV exposure than AN/DVE-3 solutions (Table 9.12), indicating

the preference polymerization of AN/DVE-3 systems to the homopolymerization of AN.

Figure 9.12 again shows that polymerization rates increased with increasing DVE-3

concentrations, implying the high homopolymerization rate of DVE-3 over the

copolymerization rate of AN/DVE-3 complexes. The solution containing 60% v/v of

DVE-3 (1.0:1 double bond ratio between DVE-3 and AN) was extremely exothermic

during polymerization (Table 9.12), indicating the polymerization of AN/DVE-3

complexes worked best at 1:1 double bond molar ratio.

9.3.1.4.4 AA and DVE-3 with 0.2% w/v Irgacure 819 photoinitiator

Solutions containing AA/DVE-3 were extremely reactive in the presence of radicals

formed from the photolysis of Irgacure 819, being evidenced by short UV exposures

required and the exothermic nature of polymerization (Table 9.13). With reference to

Table 9.2 in which AA did polymerize after a longer UV exposure, it again suggested

that AA/DVE-3 complex polymerization was initiated by free radicals from Irgacure 819.

Similar to the other EP vinyl monomer/DVE-3 systems, UV exposure doses decreased

with increasing DVE-3 concentrations, indicating increasing polymerization rate with

increasing DVE-3 concentration (Figure 9.13). This implied that the cationic

homopolymerization rate of DVE-3 was faster than free radical polymerization rate of

AA/DVE-3. Extreme heat released may have been mainly due to rapid polymerization of

DVE-3 initiated by AA/DVE-3 complex. The acidic nature of AA may have also played

a part in high reactivity of AA/DVE-3 solutions towards free radical induced

polymerization. In Chapter 11, the effect of acids on DVE-3 polymerization will be

discussed.

9.1.3.4.5 MAC and DVE-3 with 0.2% w/v Irgacure 819

High reactivity of MAC/DVE-3 solutions in the presence of radicals was similar to that

of AN/DVE-3 solutions. As shown in Table 9.14, all solutions polymerized quickly

producing polymers. As concentrations of DVE-3 increased, polymers formed became
tacky. Polymerization of MAC/DVE-3 mixtures appeared to have three polymerization processes occurring simultaneously as in the case of AN/DVE-3 mixtures, i.e., free radical homopolymerization of MAC; free radical copolymerization of MAC/DVE-3 complexes; and cationic homopolymerization of DVE-3. Figure 9.14 shows that UV exposure doses decreased with increasing DVE-3 concentration. This observation again indicated higher homopolymerization rate of DVE-3. Also, when compared to the AA/DVE-3 systems, the replacement of H with methyl group in MAC significantly reduced reactivity of MAC system as a whole, evidenced by less heat being released.

9.1.3.4.6 BMA, MMA and DVE-3 with 1% w/v Irgacure 819

In the presence of Irgacure 819 photoinitiators, solutions of BMA/DVE-3 and MMA/DVE-3 showed different characteristics. Solutions with high concentration of methacrylates polymerized more rapidly and to a greater extent than the ones with low methacrylate concentrations (Tables 9.15-9.16). These were in contrary to the observations in Tables 9.8 and 9.9. Figures 9.15-9.16 also show that required UV doses increased with increasing DVE-3 concentration in solutions, giving an indication of weak interactions between methacrylates and DVE-3. Instead of forming complexes with DVE-3, MMA and BMA possibly preferred to react with free radicals to produce homopolymers. DVE-3 could participate in the polymerization but only as a crosslinking agent as reported by Bevington and Huckerby [24]. Due to the weak interaction between these methacrylates and DVE-3, any CT complex formed was not able to initiate polymerization and DVE-3 homopolymerization. As a result, solutions with high DVE-3 concentrations only slightly polymerized despite extensive UV exposures.

In summary, the EP vinyl monomers under study could be classified into two groups. One group consists of MA, DMMA, AN, AA and MAC which strongly or moderately formed complexes with DVE-3. Experimental evidences suggested these complexes strongly react with free radicals to produce polymers and they were also found to initiate and enhance homopolymerization of DVE-3. Final products from the interaction between the monomers in this group and DVE-3 probably resulted in three polymers: homopolymers from EP vinyl monomers, copolymers from EP vinyl monomer/DVE-3
complexes and homopolymers from DVE-3. Another group of EP vinyl monomers includes BMA and MMA which prefer to react with free radicals from photolysis of Irgacure 819 photoinitiator with DVE-3 acted merely as a crosslinking agent.

From Tables 9.10-9.16 and Figures 9.10-9.16, it is possible to rank reactivity of vinyl monomers as acceptors in the presence of Irgacure 819 photoinitiators. Based on required doses for complexes with DVE-3 to polymerize and on solution appearances, vinyl monomers with decreasing acceptor strengths were arranged in the following order: MA>AA>DMMA=AN=MAC>MMA>BMA.

This ranking shows the influences of functional groups in relation to the electron withdrawing properties on the unsaturated double bonds present in these monomers. The double bond of MA is very electron poor because of the strong electron withdrawing property of the anhydride group. The carboxyl group of AA is weaker than the anhydride group in electron withdrawing and hence the double bond of AA is less comfortable to accommodate extra electrons. Since alkyl groups are electron releasing, the ability of the ester group to withdraw electrons is much less than the carboxylic group, thus the double bond in MAC less readily accepts electrons. AN is also a good acceptor because the nitrile group has a strong electron withdrawing property. MMA and BMA are weak acceptors because they both have the methyl group attaching to the carbon bearing the double bond adjacent to the carboxylate group. The methyl group is electron rich and can hinder to a certain degree the electron withdrawing property of the carboxylate group in the methacrylates. The electron withdrawing power of ester groups is also dependent on chainlengths. The electron withdrawing power of the ester group decreases with increase in the chain lengths (long chains can accommodate electron deficiency better than short chains) and therefore MMA is a better acceptor than BMA.
9.3.2 Grafting of EP vinyl monomers to PPE with DVE-3 as a comonomer

9.3.2.1 UV grafting of EP vinyl monomers to PPE with DVE-3 as a comonomer without Irgacure 819 photoinitiator

Polymerization and grafting are two separate but competing processes. The grafting process is slower since it involves firstly the creation of grafting sites and then the reaction of grafting sites with diffused monomers. As discussed in Chapters 5, 6, 7 and 8, events occur in solutions can greatly influence grafting outcomes.

From Table 9.3-9.9, there were four systems which gave nil or negligible grafting yield, and these including the systems containing DVE-3 and the four EP vinyl monomers, MA, DMMA, AN and AA. Low grafting yields for these systems are understandable since these EP vinyl monomers and DVE-3 interacted under the influence of a UV source to form polymers under certain conditions but these complexes may not have produced sufficient radicals to either initiate homopolymerization of EP vinyl monomers which were present in excess (evidenced by liquid appearances of some solutions with high EP vinyl monomer concentrations and large UV dose, Tables 9.5-9.6) or create reactive sites on PPE. In solutions with high DVE-3 concentrations, cationic homopolymerization of DVE-3 was dominant, and hence diminished the chance for grafting to take place.

MAC systems were exceptional because grafting yields of 45% and 109% were achieved for solutions containing 60% and 40% v/v of MAC respectively (Table 9.7) whilst neat MAC did not homopolymerize even after a long UV exposure (Table 9.1). Grafting yields indicated that MAC/DVE-3 formed CT complex was able to initiate the grafting to PPE without the presence of any photoinitiator.

In previous Chapters (3-8), MMA is shown to be a good monomer for grafting to PPE substrates by UV irradiation. As BMA is also a methacrylate, similar performance in grafting by the two monomers would be expected. With reference to Table 9.1, no grafting was observed for neat MMA and BMA under the influence of a UV source in the absence of photoinitiator. However, for methacrylate/DVE-3 systems, according to results in Tables 9.8-9.9, grafting of methacrylates to PPE decreased with increasing
DVE-3 concentrations. This implied that cationic homopolymerization of DVE-3 in solutions did not lead to DVE-3 being grafted to PPE substrate. Compared to the grafting of neat methacrylates to PPE (Table 9.1), the presence of DVE-3 certainly improved grafting yields. For BMA, the highest grafting yield was achieved at the double bond molar ratio between DVE-3 and BMA of 1.1:1 (Table 9.8). As the ratio exceeded 2.4:1, no grafting yield was observed. In the case of MMA, grafting yield was highest at the DVE-3/MMA double bond molar ratio of 0.3:1 (Table 9.9), declining as this ratio increased. The decrease of grafting yields with increasing DVE-3 concentrations was mainly caused by the reduction of EP vinyl monomers available either for grafting or formation of CT complexes which led to radical generation. However, the presence of DVE-3 resulted in the grafting enhancement of these two EP vinyl monomers to PPE. This was attributed to: a) DVE-3 role as a crosslinking agent; b) higher reactivity of methacrylate/DVE-3 complexes to reactive sites; c) possible Trommsdorff's effect since high viscosity and fast solution polymerization reduced movements of radicals and hence termination rates.

9.3.2.2 UV grafting of EP vinyl monomers to PPE with DVE-3 as a comonomer, with Irgacure 819 photoinitiator

As discussed in Section 9.3.1.4, with the addition of Irgacure 819, solutions containing MA, DMMA, AN, AA and MAC with DVE-3 polymerized very rapidly (Tables 9.10-9.14) compared to the polymerization of neat EP vinyl monomers in the presence of photoinitiator or EP vinyl monomer/DVE-3 complexes. In cases of MA and AA (Tables 9.10-9.13), the polymerization process was so exothermic that both polymer products and substrates decomposed. Fast polymerization is not useful for grafting since it depletes the supply of monomers for grafting and in addition, high viscosity of solution prevents diffusion of monomers to the grafting sites. Since grafting is a slow process, it does not efficiently compete for monomers which undergo polymerization.

Tables 9.10-9.14 present the grafting results of MA, DMMA, AN, AA and MAC to PPE in the presence of DVE-3 and Irgacure 819 photoinitiator. All grafting yields (except the ones whose substrates were lost due to extreme reactions) were negligible and the rapid
polymerization process could have contributed to such poor results. Low grafting yields also implied that while these CT systems were very reactive in the presence of radicals, they did not react with reactive sites on substrate to graft. Besides CT complex polymerization, there were possibly radical induced homopolymerization of the EP vinyl monomers and cationic homopolymerization of DVE-3. With reference to Table 9.2, homopolymerization of the mentioned vinyl monomers did not give any significant grafting while cationic homopolymerization of DVE-3 could not lead to grafting either.

As shown in Tables 9.15-9.16, MMA and BMA once again proved to be monomers achieving efficient grafting and the highest grafting yields were observed when the methacrylate concentrations were at 80 and 60% v/v respectively. As concentrations of methacrylates decrease, grafting yields dropped rapidly to zero. This is in line with the discussions in Section 9.3.1.4 regarding the tendency of methacrylate monomers reacting with free radicals from the photoinitiator instead of forming complexes with DVE-3. DVE-3 would be a component in the grafted chains since it could act as a crosslinking agent in this instance. The ability of MMA and BMA in grafting was probably due to the slow polymerization rates as compared to other EP vinyl monomers (Table 9.2).

9.3.3 Polymerization of charge transfer complex systems of MAC, AN with NBVE and TMPTVE by UV irradiation

9.3.3.1 Polymerization of charge transfer complex systems of MAC with NBVE and TMPTVE without Irgacure 819 photoinitiator

In order to evaluate the ability of MAC to form CT complexes with NBVE and TMPTVE, solutions containing MAC with these vinyl ethers in different ratios were exposed to a UV source for a long period of time. Results shown in Table 9.17 indicate that interactions between NBVE or TMPTVE with MAC were very weak, evidenced by the fact that no polymerization was formed even after very long UV exposures. With the knowledge that MAC could form CT complex with DVE-3 (as discussed in Section 9.3.1), it is therefore possible to deduce that NBVE and TMPTVE are weaker electron donors than DVE-3.
9.3.3.2 Polymerization of charge transfer complex systems of AN with NBVE and TMPTVE without Irgacure 819 photoinitiator

From Table 9.18, it is observed that all AN/NBVE solutions did not polymerize even after very long UV exposures, indicating weak complex formation between AN and NBVE. However, spontaneous polymerization was observed for two solutions containing 60 and 80% v/v of TMPTVE, implying that AN/TMPTVE complexes were strong enough to undergo spontaneous polymerization at high TMPTVE concentrations. The polymers formed could be the result of the cationic homopolymerization of TMPTVE initiated by AN/TMPTVE complexes. In comparison to results in Table 9.17, it could be stated that AN was a stronger acceptor than MAC.

9.3.3.3 UV polymerization of charge transfer complex systems of MAC with NBVE and TMPTVE, with Irgacure 819 photoinitiator

To further evaluate the strength of interactions between MAC and the two vinyl ethers, small amounts of Irgacure 819 photoinitiator were added to the MAC/vinyl ether solutions to initiate free radical polymerization. Tables 9.19-9.20 show two opposite behaviors between MAC/NBVE and MAC/TMPTVE solutions. Figure 9.20 shows that, for MAC/NBVE solutions, the required UV dose for polymerization increased with increasing NBVE concentrations. This characteristic was very similar to those of MMA/DVE-3 (Figure 9.16) and BMA/DVE-3 (Figure 9.15) solutions, indicating very weak interaction between MAC and NBVE. From such an observation, it is possible to deduce that MAC prefers to react with free radicals rather than interacting with NBVE to form a CT complex. Exposure doses for polymerization were similar in values to the ones for neat MAC (Table 9.2) indicating NBVE did not enhance the polymerization rate of MAC.

According to Table 9.20 and Figure 9.20, polymerization of MAC/TMPTVE showed a similar trend to that of MA, DMMA, AN, AA and MAC with DVE-3 solutions (Figures 9.10-9.114) with required UV exposure doses for polymerization decreased with increasing TMPTVE concentrations, suggesting CT complex formation. The lower required UV exposure doses compared to the dose required for neat MAC (Table 9.2) is
another evidence supporting that suggestion. Since TMPTVE did not polymerize in the presence of free radicals (Table 5.2, Section 5.2.1 of Chapter 5), it was possible that cationic homopolymerization of TMPTVE was dominant in solutions with high vinyl ether concentrations since required doses were very low.

9.3.3.4 UV polymerization of charge transfer complex system of AN with NBVE and TMPTVE, with Irgacure 819 photoinitiator

Similar observations were made for AN/NBVE solutions as in MAC/NBVE solutions with Irgacure 819 photoinitiator (Table 9.21-Figure 9.21), suggesting that interactions between AN and NBVE were very weak and AN was likely to react alone with radicals from the photolysis of Irgacure 819. When comparison was made on required UV dose for AN/NBVE solutions (Table 9.21) and neat AN (Table 9.2) to polymerize, it appeared that NBVE retarded the polymerization of AN, evidenced by longer exposures required for polymerization.

Table 9.22-Figure 9.21 shows that the polymerization of AN/TMPTVE solutions was as fast as the polymerization of AN/DVE-3 solutions, indicating strong complex formations between AN and TMPTVE. As the required UV exposure doses were much lower than the dose for neat AN to polymerize (Table 9.2), it was possible to deduce that the CT complex polymerization of AN and TMPTVE was much faster than the homopolymerization of AN. Required UV doses were found to decrease with increasing TMPTVE concentrations, suggesting high cationic homopolymerization rate of TMPTVE.

9.3.3.5 Comparisons between NBVE, DVE-3 and TMPTVE as electron donors

Results from above experiments make it possible to compare reactivity of the three vinyl ethers as electron donor in CT transfer complexes. In an order of decreasing electron-rich characteristics, they can be arranged as followed: DVE-3>TMPTVE>NBVE.

Differences between the three vinyl ethers in the role of donor are stemmed from the difference in their structures. Vinyl ether functional groups are electron rich. Therefore,
the presence of more than one group in a structure can reinforce electron-rich characteristics of nearby vinyl ether groups. In the case of TMPTVE, it has three vinyl ether groups close to each other and so it is a good candidate as an electron donor. For DVE-3, it has a long chain and two vinyl groups at each end of the molecule. However, the main chain consists of triethylene glycol unit which is electron rich, and it can enhance electron rich characteristics of vinyl groups, leading to good performance of DVE-3 as an electron donor. For NBVE, it has only one vinyl ether group and the butyl is a comparatively weaker electron releasing group than ethylene glycol unit, thus this vinyl ether is not a strong electron donor as the other two.

9.3.3.6 Effect of chain lengths in vinyl ethers

From this study, chain lengths of vinyl ethers appeared to have interfered with their formation of CT complexes with EP vinyl monomers. This was evidenced from results in Tables 9.23 and 9.24 which show that DMMA solution containing DVE polymerized and the solution containing DVE-4 did not. This could be due to the fact that DVE has one ethylene glycol unit between the two vinyl groups whereas DVE-4 has a tetraethylene glycol unit between two vinyl groups and therefore it is bulkier than DVE. DVE being a smaller molecule is therefore comparatively more mobile than DVE-4.

Longer UV exposure doses for DMMA/DVE solutions to polymerize (Tables 9.23-9.24) proved that DVE was a weaker electron donor than DVE-3 (Table 9.4). All results pointed to the importance of the number of ethylene glycol units present in the main chains between the vinyl groups. For DVE, the two vinyl groups are close but one ethylene glycol unit is not as effective in enhancing electron rich characteristics to both vinyl groups. DVE-3 has a tri(ethylene glycol) unit linking its two vinyl groups and the tri(ethylene glycol) unit appeared to be more efficient in enhancing the electron rich characteristic of the double bonds in DVE-3 and also the molecule is not as bulky as DVE-4. This can be further illustrated by the polymerization results based on DBMR values as shown in Table 9.4 for solution containing DVE-3/DMMA and 9.25 for DVE/DMMA and DVE-4/DMMA systems. At the DBMR of 0.5:1, 0.8:1 and 0.7:1 between DVE:DMMA, DVE-3:DMME and DVE-4:DMMA respectively, only the DVE-
4:DMMA system showed no evidence that polymerization had taken place. More evidences of the chain length effects can be found in Table 5.4, Chapter 5 in which the solution containing MMA/DVE polymerized without the presence of PIs while the solution containing MMA/DVE-4 did not.

Evaluation of the possible complex formations between DMMA and different vinyl ethers were also carried out and reported in Tables 9.23-9.24. As shown, only DVE had strong complex formation with DMMA but these solutions polymerized after long UV exposures. On the other hand, other vinyl ethers did not seem to be good electron donors as their solutions did not polymerize even after extensive UV exposures. Most of these vinyl ethers are monofunctional with three exceptions including HDVE, DVE and DVE-4 which are divinyl ethers. Monofunctional vinyl ethers such as NBVE were poor electron donors probably for the same reason, i.e., attached alkyl groups were weak electron donating and only one vinyl ether group was present in the structures of these monofunctional vinyl ethers. For HDVE, hexyl group has a comparatively weak electron donating property. For DVE-4, the reason for it not forming a CT complex with DMMA was given above.

9.3.4 UV grafting of charge transfer complex systems of MAC, AN with NBVE, TMPTVE to PPE

9.3.4.1 UV grafting of MAC to PPE with NBVE and TMPTVE as comonomers without Irgacure 819 photoinitiator

Table 9.17 shows that no grafting was achieved which was probably due to the fact that no free radical polymerization of MAC or formation of MAC/NBVE complex occurred.

9.3.4.2 UV grafting of MAC to PPE with NBVE and TMPTVE as comonomers, with 0.2% w/v of Irgacure 819

Results in Table 9.19 show small grafting yields when Irgacure 819 photoinitiator was present in MAC/NBVE solutions. This proved that reactive sites on PPE were created and MAC did react with these sites to form grafted chains. Grafting yields increased with decreasing MAC concentration, reaching maximum at MAC concentration of 40% v/v.
The observed trend was probably due to very rapid homopolymerization of MAC at its high concentration and thus, depleting the available MAC monomer for grafting or slowing its diffusion towards grafting sites. As MAC concentration decreased, polymerization rate of MAC decreased, leaving more monomer available for grafting while solution viscosity was not too high to hinder the mobility of monomer. Hence, higher grafting yields were achieved. However, as MAC concentration decreased further, there was simply not enough MAC monomer for both grafting and homopolymerization and thus a lower grafting yield was obtained.

For MAC/TMPTVE solutions, the solution polymerization occurred so fast that all monomers for grafting were depleted and therefore, no significant grafting was achieved (Table 9.20).

### 9.3.4.3 UV grafting of AN to PPE with NBVE and TMPTVE as comonomers without Irgacure 819 photoinitiator

Without any photoinitiator, AN/NBVE solutions did not polymerize and hence no grafting was recorded (Table 9.18).

As shown in Table 9.18, no grafting was obtained when solutions of AN/TMPTVE were exposed to UV radiation despite solutions containing high TMPTVE concentrations of 60 and 80% v/v did polymerize, indicating at higher TMPTVE concentration, cationic homopolymerization of TMPTVE predominantly took place, resulting in poor grafting yield.

### 9.3.4.4 UV grafting of AN to PPE with NBVE and TMPTVE as comonomers, with 0.2% w/v of Irgacure 819 photoinitiator

Free radicals from the photolysis of Irgacure 819 initiated the polymerization of AN/NBVE (Table 9.21), but did not induce grafting to PPE substrate. However, this was in line with the expectation since polymerization of neat AN solution did not lead to any grafting to PPE (Table 9.2). This was probably due to the preference of AN reacting with free radicals in solutions rather than reactive sites on substrates.
Poor grafting was reported in Table 9.22 despite solutions of AN and TMPTVE polymerized very quickly in the presence of Irgacure 819. Fast polymerization reduced monomers available for grafting and retarded their diffusion rate towards reactive sites on the substrates. Neat AN did not graft to PPE (Table 9.2) and it was unlikely that the cationic polymerization of TMPTVE would lead to any grafting and thus no grafting was achieved.

**9.3.4.5 UV grafting of DMMA to PPE with different vinyl ethers as comonomers, without the presence of Irgacure 819 photoinitiator**

According to Table 9.1, DMMA did not homopolymerize or graft to PPE under UV irradiation. In Tables 9.23-9.24, all solutions of DMMA with the vinyl ethers under study did not polymerize even after very long UV exposures and therefore, zero grafting was understandable. An exception was the solution of DMMA and DVE which polymerized, with no grafting being observed, indicating DMMA/DVE complex was not reactive towards creating reactive sites on PPE substrate.

**9.4 Conclusions**

In this chapter, the ability of weak electron acceptors to interact with electron rich vinyl ethers as DA pairs was extensively investigated. Acceptors including MA, DMMA, AA, MAC, AN, BMA and MMA were shown to undergo spontaneous polymerization with DVE-3 under the influence of UV radiation thus indicating the formation of CT complexes between the above EP vinyl monomers and DVE-3. Required UV exposure doses for polymerization (indicators of polymerization rates) were mostly found to decrease with increasing DVE-3 concentrations, suggesting cationic homopolymerization of DVE-3 in solutions. The tetramethylenes and radical ions mechanism was applied to explain the observed spontaneous polymerization. The reactivity of each EP vinyl monomer/DVE-3 complex system was compared in order to rank the strength of each vinyl monomer as an electron acceptor. The difference between the EP vinyl monomers in accepting electrons was mainly due to different electron withdrawing powers of functional groups attaching to the double bonds. However, grafting yields to PPE substrate were very poor for most EP vinyl monomer/DVE-3 solutions, indicating
radicals generated in the DA interaction were not sufficiently reactive to abstract hydrogen atoms from PPE to create grafting sites. On the other hand, solutions containing MMA/DVE-3 and BMA/DVE-3 gave very high grafting yields due to the slow rate of polymerization.

The CT complex systems of EP vinyl monomer/DVE-3 were shown to undergo very rapid polymerization in the presence of Irgacure 819. However, UV exposure doses were found to mostly decrease with increasing DVE-3 concentrations, suggesting cationic homopolymerization of DVE-3 predominantly took place beside the copolymerization reaction with vinyl monomers. In the presence of Irgacure 819, most EP vinyl monomer/DVE-3 solutions produced no significant grafting to PPE due probably to rapid free radical and cationic induced polymerization reactions which quickly depleted monomers available for grafting or diffusion of monomers towards grafting sites was restricted. However, MMA and BMA were exceptional monomers achieving high grafting yields. This phenomenon was due to their preference in undergoing radical induced polymerization in the presence of Irgacure 819 rather than in CT complexes with DVE-3. This possibility was further supported by UV exposure doses which increased with increasing DVE-3 concentrations. The role of DVE-3 in polymerization and grafting in these systems was probably limited to as a crosslinking agent.

In this chapter, the ability of other vinyl ethers to act as electron donors was also investigated. DVE and TMPTVE were found as suitable electron donors but not as good as DVE-3. Other vinyl ethers, especially monofunctional vinyl ethers, did not undergo spontaneous polymerization with DMMA or with AN and MAC, and thus were considered to be very weak electron donors. Explanations for these different performances were based on their different molecular structures.

9.5 References
10.1 Introduction

Styrene is a common monomer which is mainly used in the production of polystyrene [1]. Styrene displays good grafting properties and it has been successfully grafted to various polymers, such as cellulose [2-14], modified cellulosics [14,15], polyolefins [16-24], polyvinyl chloride [24], nylon 66 [24] and polyethylene terephthalate [24], by different grafting methods. Furthermore, styrene also has been found to induce grafting of other vinyl monomers such as AN [18,24], MMA [23-26] and ethyl acrylate [24] to PPE and cellulose substrates. Due to its chemical structure which contains a benzene ring attaching to the double bond [1], styrene can be considered as a weak electron donor. With the recent discovery of charge transfer complex polymerization, it is possible for styrene, as a weak electron donor, to form CT complexes with suitable acceptors. In Chapter 9, spontaneous polymerization of weak acceptors such as DMMA, AN, AA, MAC and MMA with DVE-3 was explored. In this chapter, the possibility of these vinyl monomers to form CT complexes with styrene and undergo spontaneous polymerization is under thorough investigation.

10.1.1 Styrene as a weak electron donor

Phenyl group is a weak electron donating group due to high electron density in the benzene ring [1]. In styrene, the phenyl group directly attaches to the double bond and thus the double bond is slightly electron rich in characteristic. Interestingly, if one or two hydrogen atoms in the benzene ring are replaced by electron rich functional groups such as ethers, the strength of monomers as donors considerably increases. For example, the two derivatives of styrene, p-methoxy styrene (PMS) and p-glycidyloxy styrene (PGOS), are strong electron donors [27-30].

Styrene's role as an electron donor has been documented in a number of publications [29,31-33], but its copolymerization with strong acceptors such as MA [31], diisopropyl fumarate [32] and maleimides [33] has been carried out in the presence of initiators [32,33] or a Lewis acid [31]. Spontaneous polymerization of styrene with weak acceptors such as AN [29], MMA [29] has also been reported but only in the presence of Lewis acids such as zinc chloride or stannous chloride. Hence, it is a matter of interest to
investigate the possible spontaneous polymerization of styrene and electron poor (EP) vinyl monomers, MA, MMA, AA, MAC, AN and DMMA, by UV radiation in the absence of photoinitiator to elucidate the possible formation of CT complexes.

10.1.2 UV grafting of styrene to PPE substrates

Styrene is a suitable monomer for UV grafting to substrates because it undergoes slow radical polymerization, and thus, long UV doses can be applied [18,22,24]. It has been used as a comonomer with MMA in order to reduce homopolymerization of MMA and improve grafting to cellulose and PPE substrates [23,25,26]. Styrene had been successfully grafted to PPE substrates utilizing both gamma and UV irradiation methods [18-24] and the extent of grafting had been found to be mainly dependent on the factors already mentioned in Chapter 1 such as styrene concentrations, solvents, photoinitiators and their concentrations [18-24].

One important property of styrene is its ability to co-polymerize and co-graft with a number of comonomers such as acrylates, methacrylates and AN. In earlier grafting works, Ang et al [18] and Yen [24] reported good grafting yields of styrene/AN, styrene/MMA and styrene/ethyl acrylate to PPE substrates using gamma irradiation [18,24]. They also confirmed the presence of both styrene and the corresponding vinyl monomers in grafted chains [18,24]. However, they failed to draw any conclusion regarding the relationship between concentrations of styrene and the vinyl monomers, AN and MMA, in reacting solutions to that of the composition of each monomer in grafted chains. Thus, the task in this study is to address this question by characterizing grafted substrates using the FT-IR spectroscopy. However, UV irradiation rather than gamma irradiation was employed in the presence of Irgacure 819 photoinitiator.

In this chapter, grafting of MA/styrene CT complex to PPE was also under investigation in order to compare with grafting of MA/DVE-3 to the same substrates as in Chapter 9. Composition of MA/styrene grafted PPE substrate was also analyzed by the FT-IR spectroscopy and results were used to interpret the effect of monomer concentrations on grafting yields.
10.2 Results

10.2.1 UV grafting of neat styrene to PPE substrates with or without Irgacure 819 photoinitiator, with various solvents

10.2.1.1 Without photoinitiators

Table 10.1 and Figure 10.1 show UV grafting yields of styrene to PPE substrates in various solvents, without the inclusion of Irgacure 819. Since no photoinitiator was present, all solutions required a very long UV dose of 746 J. However, significant grafting was observed and the grafting yield generally increased with increasing styrene concentration and reached a maximum when no solvent was present. On the other hand, based on grafting yields, DMF and methanol were shown to be more suitable solvents in enhancing grafting than chloroform.

10.2.1.2 With 1% w/v Irgacure 819 photoinitiator

As shown in Table 10.2 and Figure 10.2.1, UV grafting of styrene to PPE was more efficient in the presence of Irgacure 819 photoinitiator, requiring a much shorter UV exposure dose of 147 J. However, high grafting yields were obtained only for solutions with high concentration of styrene. Again, DMF and methanol were the two solvents under study that enhanced grafting yields.

10.2.1.3 FT-IR characterization of styrene grafted substrates

Figure 10.2.2 shows FT-IR spectra of styrene grafted substrates from styrene in methanol with the inclusion of Irgacure 819.

10.2.2 UV grafting of MA/styrene CT complex to PPE substrates with or without Irgacure 819 photoinitiator

10.2.2.1 Without photoinitiators

Results in Table 10.3 show UV grafting and polymerization of MA/styrene CT complex in the absence of Irgacure 819 photoinitiator. All solutions spontaneously polymerized but with required UV exposure dose increased with increasing styrene concentration (Figure 10.3). However, no significant grafting was obtained, although extensive polymerization occurred.
10.2.2.2 With 0.2% w/v Irgacure 819 photoinitiator

Table 10.4 shows the results of photopolymerization of MA/styrene CT complex in the presence of Irgacure 819 photoinitiator and also the grafting of styrene onto PPE with MA as the comonomer. Figure 10.4.1 represents the required UV doses versus DBMR between styrene and MA in solutions. Polymerization process was observed to be very efficient with much shorter UV doses required, but small grafting yields were obtained only for solutions with high styrene concentrations, as shown in Figure 10.4.2. Again, required UV doses were found to increase with increasing styrene concentrations.

10.2.2.3 FT-IR characterization of MA/styrene grafted substrates

Figure 10.4.3 represents spectra of MA/styrene grafted substrates from solutions with acetone a solvent and in the presence of Irgacure 819.

10.2.3 UV grafting of styrene to PPE in the presence of electron poor (EP) vinyl monomers, MMA, MAC, AN, DMMA and AA, without photoinitiators

Results in Table 10.5 and Figure 10.5.1 show grafting yields of various EP vinyl monomer/styrene systems to PPE substrates in the absence of Irgacure 819 photoinitiator under the influence of UV irradiation. Grafting yields were shown to be dependent on the types of vinyl monomers and their concentrations. Grafted substrates were then characterized by FT-IR and the spectra as shown in Figures 10.5.2-10.5.6 are for the analysis of composition of grafted chains.

10.2.4 UV grafting of styrene to PPE in the presence of EP vinyl monomers and Irgacure 819 photoinitiator

Table 10.6 and Figure 10.6.1 summarize the required UV doses and grafting yields of various EP vinyl monomer/styrene systems to PPE substrates in the presence of Irgacure 819 photoinitiator. Again, grafting yields were dependent on the vinyl monomer types and their concentrations. However, grafting of AA/styrene system to PPE was an exception since required UV doses (Figure 10.6.2) increased with increasing styrene concentrations. FT-IR spectra are presented in Figures 10.6.3-10.6.7.
10.2.5 UV grafting of styrene to PPE in the presence of MMA and AN, with different solvents and in the absence of Irgacure 819 photoinitiator

Tables 10.7-10.8 and Figures 10.7-10.8 present the grafting results of MMA/styrene and AN/styrene to PPE substrates in solvents such as chloroform, DMF and methanol in the absence of photoinitiators. These solvents were used since chloroform swells PPE whilst the other two do not, thus a comparison between the two types of solvents can be drawn. Grafting yields were shown to depend on the monomer types, their concentrations and solvents used.

10.2.6 UV grafting of styrene to PPE in the presence of MMA, AN, MAC and AA and Irgacure 819 and with different solvents

Results of UV grafting of various EP vinyl monomer/styrene systems are presented in Tables 10.9-10.12 and Figures 10.9-10.12 in which grafting yields were found to vary according to monomer types, their concentrations and solvents used.
Table 10.1: UV grafting of styrene to PPE with different solvents, without Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chloroform</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>80</td>
<td>4</td>
</tr>
<tr>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Solvents: chloroform, DMF and methanol
Total dose: 748 J
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.1: UV grafting of styrene to PPE with different solvents, without Irgacure 819 photoinitiator.
Table 10.2: UV grafting of styrene to PPE with different solvents, in the presence of 1% w/v of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chloroform</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>80</td>
<td>7</td>
</tr>
<tr>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v
Solvents: chloroform, DMF and methanol
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.2.1: UV grafting of styrene to PPE with different solvents, with 1% w/v of Irgacure 819.
Figure 10.2.2: UV grafting of styrene to PPE with methanol as the solvent and with 1% w/v Irgacure 819.
Table 10.3: UV grafting of styrene to PPE with MA as a comonomer, with acetone as a solvent and in the absence of photoinitiator.

<table>
<thead>
<tr>
<th>Double bond molar ratio between styrene/MA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0</td>
<td>98</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>2:1</td>
<td>0</td>
<td>184</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>4:1</td>
<td>0</td>
<td>413</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>8:1</td>
<td>0</td>
<td>413</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>MA</td>
<td>0</td>
<td>413</td>
<td>Did not polymerize</td>
</tr>
<tr>
<td>Styrene</td>
<td>0</td>
<td>413</td>
<td>Liquid appearance</td>
</tr>
</tbody>
</table>

Solvent: acetone, 50% w/w
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.3: UV doses versus DBMR between MA/styrene without Irgacure 819 photoinitiator.
Table 10.4: UV grafting of styrene to PPE with MA as a comonomer, with 0.2% w/v of Irgacure 819 photoinitiator and acetone as a solvent.

<table>
<thead>
<tr>
<th>Double bond molar ratio between styrene/MA</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0</td>
<td>9</td>
<td>Formed a clear polymer; exothermic</td>
</tr>
<tr>
<td>2:1</td>
<td>6</td>
<td>12</td>
<td>Formed a clear polymer; exothermic</td>
</tr>
<tr>
<td>4:1</td>
<td>13</td>
<td>83</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>8:1</td>
<td>10</td>
<td>147</td>
<td>Formed a clear polymer</td>
</tr>
<tr>
<td>MA</td>
<td>0</td>
<td>147</td>
<td>Did not polymerize</td>
</tr>
<tr>
<td>Styrene</td>
<td>1</td>
<td>147</td>
<td>Liquid appearance</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% w/v
Solvent: acetone, 50% w/w
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.4.1: UV doses versus DBMR between MA/styrene with 0.2% w/v of Irgacure 819 photoinitiator.
Figure 10.4.2: UV grafting of styrene to PPE with MA as a comonomer, with 0.2% w/v of Irgacure 819 photoinitiator.
Figure 10.4.3: UV grafting of MA/styrene to PPE with 0.2% w/v Irgacure 819.
Chapter Ten: UV Grafting Of Styrene To PPE With Different Eleletron Poor (EP) Vinyl Monomers As Comonomers

Table 10.5: UV grafting of styrene to PPE with various EP vinyl monomers as comonomers, in the absence of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>Vinyl monomer conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
<td>MAC</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>66</td>
</tr>
<tr>
<td>40</td>
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<tr>
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<td>20</td>
<td>8</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Total dose: 746 J
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.5.1: UV grafting of styrene to PPE with various EP vinyl monomers as comonomers, in the absence of Irgacure 819 photoinitiator.
Figure 10.5.2: UV grafting of styrene to PPE with MMA as the comonomer, without Irgacure 819.
Figure 10.5.3: UV grafting of styrene to PPE with MAC as the comonomer, without Irgacure 819.
Figure 10.5.4: UV grafting of styrene to PPE with AN as the comonomer, without Irgacure 819.
Figure 10.5.5: UV grafting of styrene to PPE with DMMA as the comonomer, without Irgacure 819.
Figure 10.5.6: UV grafting of styrene to PPE with AA as the comonomer, without ligature 819.
Table 10.6: UV grafting of styrene to PPE with various EP vinyl monomers in the presence of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>Vinyl monomer conc. (% v/v)</th>
<th>MMA - 1 % 819 Dose (J)</th>
<th>MAC - 0.2 % 819 Dose (J)</th>
<th>AN - 0.2 % 819 Dose (J)</th>
<th>DMMA - 1 % 819 Dose (J)</th>
<th>AA - 0.2 % 819 Dose (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>80</td>
<td>89</td>
<td>147</td>
<td>53</td>
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<td>7</td>
<td></td>
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</tr>
</tbody>
</table>

*: with 1% w/v Irgacure 819
Dose rate: 36.7 J/hr
Temperature: 29 °C
Figure 10.6.1: UV grafting of styrene to PPE with different vinyl monomers and Irgacure 819 photoinitiator.

Figure 10.6.2: UV doses required for AA/styrene solutions to polymerize.
Figure 10.6.3: UV grafting of styrene to PPE with MMA as the comonomer and with 1% w/v Irgacure 819.
Figure 10.6.4: UV grafting of styrene to PPE with MAC as the comonomer and with 0.2% w/w Igacure 819.
Figure 10.6.6: UV grafting of styrene to PPE with DMMA as the comonomer and with 1% w/v Irgacure 819.
Figure 10.6.7: UV grafting of styrene to PPF with AA as the comonomer and with 0.2% Irgacure 819.
Table 10.7: UV grafting of MMA/styrene to PPE in different solvents, in the absence of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>MMA conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>Chloroform</td>
</tr>
<tr>
<td>16</td>
<td>64</td>
<td>54</td>
</tr>
<tr>
<td>32</td>
<td>48</td>
<td>30</td>
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<tr>
<td>48</td>
<td>32</td>
<td>17</td>
</tr>
<tr>
<td>64</td>
<td>16</td>
<td>7</td>
</tr>
</tbody>
</table>

Solvents: chloroform, DMF and methanol
Total dose: 746 J
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.7: UV grafting of MMA/styrene on PPE in different solvents, in the absence of Irgacure 819 photoinitiator.
Table 10.8: UV grafting of AN/styrene to PPE in different solvents, in the absence of Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>Acrylonitrile conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th></th>
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<tr>
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<td>Chloroform</td>
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<tr>
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<tr>
<td>64</td>
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<td>25</td>
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</tbody>
</table>

Solvents: chloroform, DMF and methanol
Total dose: 746 J
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.8: UV grafting of AN/styrene to PPE in different solvents, in the absence of Irgacure 819 photoinitiator.
Table 10.9: UV grafting of MMA/styrene to PPE with different solvents and Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>MMA conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
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<td>Chloroform</td>
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<td>7</td>
</tr>
<tr>
<td>64</td>
<td>16</td>
<td>6</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v
Solvents: chloroform, DMF and methanol
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.9: UV grafting of MMA/styrene to PPE with different solvents and Irgacure 819 photoinitiator
Table 10.10: UV grafting of AN/styrene to PPE with different solvents and Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>AN conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
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<tr>
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<td></td>
<td>Chloroform</td>
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</tr>
<tr>
<td>64</td>
<td>16</td>
<td>19</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% w/v  
Solvents: chloroform, DMF and methanol  
Total dose: 147 J  
Dose rate: 36.7 J/hr  
Temperature: 29 °C

Figure 10.10: UV grafting of AN and styrene to PPE with different solvents and Irgacure 819 photoinitiator.
Table 10.11: UV grafting of MAC and styrene to PPE with different solvents and Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>MAC conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Chloroform</td>
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<tr>
<td>64</td>
<td>16</td>
<td>8</td>
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</tbody>
</table>

Irgacure 819 concentration: 0.2 % w/v
Solvents: chloroform, DMF and methanol
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.11: UV grafting of MAC and styrene to PPE with different solvents and Irgacure 819 photoinitiator.
Table 10.12: UV grafting of AA and styrene to PPE with different solvents and Irgacure 819 photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>AA conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chloroform</td>
<td>DMF</td>
</tr>
<tr>
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<tr>
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<tr>
<td>64</td>
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<td>0</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 0.2% w/v
Solvents: chloroform, DMF and methanol
Dose rate: 36.7 J/hr
Temperature: 29 °C

Figure 10.12: UV grafting of AA and styrene to PPE with different solvents and Irgacure 819 photoinitiator.
10.3 Discussion

10.3.1 UV grafting of styrene to PPE

10.3.1.1 Without Irgacure 819 photoinitiator, in solvents, chloroform, DMF and methanol

Results of styrene grafting to PPE without the inclusion Irgacure 819 and in the solvents, chloroform, DMF and methanol are summarized in Table 10.1. In the absence of PI, the grafting of styrene to PPE required a very long UV exposure dose (746 J) because free radicals were not efficiently or sufficiently formed without the presence of photoinitiators [24]. Polymerization of styrene solutions was found to be a very slow process and even for the neat styrene solution, at the end of the UV exposure, no apparent polymer was formed. However, in most cases, slight occurrence of polymerization was evidenced by viscous appearance of the solutions.

Exposures of solutions to a UV source did indeed lead to grafting of styrene to PPE substrate. As shown in Table 10.1 and Figure 10.1, grafting yields increased with increasing styrene concentrations and varied according to solvents. Methanol and DMF seemed to be the efficient solvents than chloroform in enhancing grafting despite the latter did swell PPE and dissolve polystyrene formed in the process. This could be due to the fact that methanol and DMF contained abstractable hydrogen atoms which could have contributed to the enhancement of grafting as discussed in Section 6.3.6 of Chapter 6. As discussed in Section 1.3.4 of Chapter 1, grafting of styrene to polyolefins (such as polyethylene and polypropylene) in the presence of methanol and DMF is possibly due to Trommsdorff effect. The termination rate is slower than propagation rate because the precipitation of grafted polystyrene chains in the two solvents lead to tight coiling, thus, limiting chances for two adjacent chains to collide [17,18,20,24].

10.3.1.2 With Irgacure 819 photoinitiator, in solvents, chloroform, DMF and methanol

With the presence of Irgacure 819 photoinitiator, styrene monomer rapidly polymerized under an UV source, resulting in lower required UV doses. Results of UV grafting of styrene to PPE are presented in Table 10.2 and Figure 10.2.1 in which grafting yields were found to increase with increasing styrene concentration. Again, methanol and DMF
showed better performances in enhancing grafting over chloroform probably due to the same reason as discussed in Section 10.3.1.1.

However, it was observed that the presence of solvents aided the grafting process especially for solutions containing 80% v/v styrene. The grafting yields for all these solutions were at least equal or much higher than that for the neat styrene solution (Table 10.2). As discussed above, the presence of DMF and methanol enhanced styrene grafting to PPE probably due to Trommsdorff effect. On the other hand, the solvents may have diluted the monomer concentration, thus, reducing homopolymerization and leading to more styrene available for the grafting process. These factors coupled with the fact that both methanol and DMF possess abstractable H atoms could have contributed to the higher grafting yields.

10.3.1.3 Characterization of grafted substrates by FT-IR

Grafted substrates were analyzed by FT-IR to confirm that grafting had occurred. Figure 10.2.2 presents IR spectra of styrene grafted substrate from solutions containing various styrene concentrations, in the presence of methanol and 1% w/v Irgacure 819. The presence of styrene as a component of grafted chains are characterized by two absorption peaks at 1601 cm\(^{-1}\) and 1583 cm\(^{-1}\) which are due to benzene ring stretches. Two larger peaks observed at 758 cm\(^{-1}\) and 699 cm\(^{-1}\) are attributed to C-H out of plane deformation. Only spectra of substrates in solutions containing 60% v/v and 80% v/v of styrene exhibit absorption peaks at the above mentioned wave numbers indicating grafting took place in these two samples.

10.3.2 UV grafting of styrene to PPE with MA as a comonomer

10.3.2.1 UV polymerization of MA/styrene solutions

10.3.2.1.1 UV polymerization of MA/styrene solutions without photoinitiator

To demonstrate the ability of styrene to form CT complexes with MA, solutions containing styrene and MA were exposed to a UV source. Results in Table 10.3 show MA/styrene mixtures in acetone spontaneously polymerized under UV exposures. On the other hand, the solution of MA alone in acetone or neat styrene did not appear to fully
polymerize even after extensive UV exposure dose of 413 J (Table 10.3). The spontaneous polymerization of MA/styrene solutions gave an indication of CT complex formation between MA and styrene. As shown in Figure 10.3, required UV doses for polymerization were found to increase with increasing styrene concentrations. The required UV dose was the lowest when styrene/MA DBMR was 1:1 and the highest at the ratio of 8:1. As the UV exposure dose can be considered as an indicator for polymerization rate, it is therefore feasible to say that polymerization rates decreased with increasing styrene concentrations. This finding is opposite to the trend observed in MA/DVE-3 system as discussed in Section 9.3.1.2.1 of Chapter 9. The solutions containing high concentration of DVE-3 in MA/DVE-3 systems tended to polymerize first. The difference between MA/styrene and MA/DVE-3 systems may be attributed to the free radical induced polymerization of styrene was much slower than MA/styrene CT complex polymerization while the MA/DVE-3 CT complex polymerization was much slower than the cationic homopolymerization of DVE-3. The MA/DVE-3 CT complex can enhance the cationic homopolymerization of DVE-3 to a greater degree than the MA/styrene CT complex can in enhancing the polymerization of styrene.

A CT complex formed by the interaction between MA (acceptor) and styrene (donor) had enhanced the rate of polymerization of MA/styrene systems as well as the homopolymerization of styrene. These enhancements may possibly be due to two processes. Firstly, the CT complex polymerization may aid solutions to reach gel point faster due to a rise in viscosity of the solutions. Secondly, efficient free radicals were produced from the CT complex formations between MA and styrene, resulting in faster styrene homopolymerization.

10.3.2.1.2 UV polymerization of MA/styrene solutions with Irgacure 819 photoinitiator
As shown in Table 10.4, the presence of Irgacure 819 photoinitiator significantly accelerated the polymerization of MA/styrene mixtures, leading to significantly shorter required UV exposures. Again, rapid polymerization was observed in solutions containing styrene and MA in the DBMRs of 1:1 and 2:1, and the reactions were very exothermic, pointing to strong polymerization reactions. However, as the styrene
concentration increased, required UV doses were found to significantly increase as well (Figure 10.4.1), indicating decreasing in polymerization rates. The accelerations of solution polymerization in the presence of Irgacure 819 suggested MA/styrene CT complex also followed free radical polymerization. The two possible polymerization processes occurring at the same time in the solutions are the CT complex polymerization of MA and styrene, and the homopolymerization of styrene, with the CT polymerization rate significantly greater than the homopolymerization rate of styrene.

10.3.2.1.3 Mechanism of MA/styrene CT complex polymerization

Results from Table 10.3 and 10.4 supported the view that under a UV source, interaction between MA and styrene monomers produced an excited CT complex intermediates which photochemically decay to form radicals. The free radicals thus formed then initiated the polymerization of styrene. The polymerization mechanism is similar to the one presented in Scheme 1.6 of Section 1.5.1, Chapter 1.

10.3.2.2 UV grafting of MA/styrene complexes to PPE

10.3.2.2.1 UV grafting of MA/styrene complexes to PPE without Irgacure 819 photoinitiator

As shown in Table 10.3, in the presence of acetone as a solvent, no grafting of styrene to PPE substrate was observed even after very high UV dose of 413 J. On the other hand, polymerization occurred for the MA/styrene solutions, indicating that MA/styrene complexes were just strong enough to initiate polymerization but not grafting.

10.3.2.2.2 UV grafting of MA/styrene complexes to PPE with Irgacure 819 photoinitiator

Results from Table 10.4 and Figure 10.4.2 show that good grafting yields were achieved for MA/styrene solutions in the presence of Irgacure 819 photoinitiator and the grafting yield increased with increasing styrene concentrations. Low grafting yield was achieved at MA/styrene ratio of 1:1 possibly due to fast polymerization which reduced monomers available for grafting. As the styrene concentration increased, solutions could be exposed to UV radiation for longer periods since excessive styrene did not undergo
polymerization as rapid as styrene/MA complex did. This resulted in better grafting yields.

FT-IR spectra in Figure 10.4.3 show that both MA and styrene were the components of grafted chains. The presence of MA in grafted chains is evidenced by three absorption peaks at 1857 cm\(^{-1}\), 1780 cm\(^{-1}\) and 1709 cm\(^{-1}\). The first two peaks are due to anti-symmetric stretches of C=O bonds while the last peak is due to symmetric stretches of C=O. Absorption peaks of styrene are slightly shifted in which two absorption peaks at 1602 cm\(^{-1}\) and 1583 cm\(^{-1}\) are observed due to ring stretches while two peaks at 760 cm\(^{-1}\) and 702 cm\(^{-1}\) are the products of plane deformation of C-H bonds.

According to peak heights at 1780 cm\(^{-1}\) and 702 cm\(^{-1}\), the amount of grafted MA and styrene are proportional to grafting yields and even for the solution with the styrene/MA ratio of 8:1, MA was found to be a significant component of the grafted chains. As MA/styrene complexes are suggested in Section 10.3.2.1 to polymerize faster than the homopolymerization of styrene, the grafting of the complexes to reactive sites were probably faster than the grafting of styrene monomers. As a result, no significant increases in absorption peak heights for solutions with high styrene concentrations were observed. However, it should be noted that the comparison of absorption peak heights should only be relative because all substrates were slightly different in thickness and hence grafting was not even. As only small areas of substrates were examined, the resulted spectra only presented compositions of the grafted chains in those areas examined.

10.3.3 UV grafting of styrene to PPE in the presence of various EP vinyl monomers

10.3.3.1 UV grafting of styrene to PPE in the presence of various EP vinyl monomers as comonomers, without Irgacure 819 photoinitiator

As shown in Table 10.5, in the absence of Irgacure 819, polymerization of styrene with the above mentioned EP vinyl monomers was slow, thus, large UV doses (746 J) were required. According to the grafting results, grafting yields were found to vary according to the EP vinyl monomer types and their concentrations. Variation of grafting yields
versus styrene concentrations is demonstrated in Figure 10.5.1, in which two opposite trends were observed. Compositions of grafted substrates were analyzed by FT-IR spectroscopy and their spectra were presented in Figures 10.5.2-10.5.6. Since styrene was used in all reacting solutions, its presence in grafted chains could be identified based on absorption peaks at 1601 cm\(^{-1}\), 1583 cm\(^{-1}\), 758 cm\(^{-1}\) and 698 cm\(^{-1}\). The absorption peak height at 698 cm\(^{-1}\) can be employed to indicate the approximate quantity of polystyrene grafted to PPE substrate in solutions with different styrene concentrations. The presence of the other EP vinyl monomers in grafted chains could be shown based on absorption peaks at certain frequencies due to their functional groups. Again, the absorption peak height can be used to indicate the amount of grafted EP vinyl monomer in the sampling areas of the grafted substrates. In order to differentiate performance of each EP vinyl monomer in grafting, it is necessary to examine the grafting process of each EP vinyl monomer/styrene system onto PPE substrate.

10.3.3.1. I MMA and styrene

According to results in Table 10.5, grafting yields of MMA/styrene systems decreased with increasing styrene concentration. With reference to Table 5.1 of Chapter 5, in which MMA displayed good grafting property to PPE substrates in the absence of PI, the observed trend suggested that MMA polymerized and grafted to PPE faster than styrene. However, grafting yields from 8% up to 66% were achieved in solutions containing 80-20% v/v styrene concentrations respectively, indicating good grafting property of both monomers to PPE substrate based on monomers’ concentrations.

FT-IR spectra of the grafted substrates displayed in Figure 10.5.2 show the presence of both MMA and styrene as the components of grafted chains. The presence of MMA units was indicated by the absorption peak at 1723 cm\(^{-1}\) due to C=O stretches of the carbonyl group. The presence of styrene units in grafted chains was identified based on its absorption peaks at the previously mentioned frequencies. Based on absorption peak height at 1723 cm\(^{-1}\), the amount of grafted MMA is observed to decrease with decreasing MMA concentrations while grafted styrene seems to follow the opposite trend. Based on the absorption peak height at 698 cm\(^{-1}\), styrene composition in grafted chains is fairly
consistent despite its corresponding concentration in the solutions increased from 20% v/v to 60% v/v. However, the peak height appears to decline at the highest styrene concentration of 80% v/v, thus providing an evidence of the slowness of styrene grafting to PPE. From grafting results in Table 10.5 and FT-IR spectra in Figures 10.5.2, it is possible to conclude that MMA is the dominating monomer in the grafting process. On the other hand, the variation trend of styrene composition suggests a certain degree of interaction between the two monomers. As discussed in Section 9.3.1.2 of Chapter 9, MMA is a weak electron acceptor and therefore, CT complex formation between MMA and styrene is possible. While MMA/styrene interaction is not strong enough to lead to spontaneous polymerization, it may significantly influence the grafting outcomes.

10.3.3.1.2 MAC and styrene

Table 10.5 shows insignificant grafting yields obtained for solutions containing MAC/styrene, indicating MAC retarded the grafting of styrene to PPE. However, FT-IR spectra (Figure 10.5.3) of the grafted substrates revealed small amount of grafting of MAC and styrene. The presence of MAC as a grafted component is evidenced by the absorption peak at 1732 cm\(^{-1}\) due to C=O stretches. According to the spectra, the grafting is only observed when styrene concentrations are at or greater than 60% v/v. Based on absorption peak heights at 1732 cm\(^{-1}\) (MAC) and 698 cm\(^{-1}\) (styrene), the grafting of MAC/styrene is found to increase with increasing styrene concentrations, suggesting the dominating role of styrene in the grafting process. On the other hand, the trend also indicates the MAC's preference to co-graft with styrene rather than grafting on its own. This suggestion is feasible because if MAC was to be more reactive, then the grafted chains would mainly consist of MAC units, and its composition should then be very high for solutions with high MAC concentrations. Since MAC retarded the grafting process and preferred to co-graft with styrene, there was a possibility of weak CT complex formation between these two monomers and the CT complex could have played an important role in the grafting process.
10.3.3.1.3 AN and styrene

In the absence of PI, reasonable grafting yields of up to 37% were observed for AN/styrene system. Similar to the MAC/styrene, the yields were found to increase with increasing styrene concentrations (Table 10.5), indicating that styrene predominantly took part in the grafting process. With reference to Table 9.1 of Chapter 9, neat AN did not polymerize or graft to PPE without PI. These results thus imply that AN enhanced the grafting of styrene to PPE.

As shown in spectra presented in Figure 10.5.4, the presence of AN units in grafted chains is indicated by an absorption peak at 2229 cm⁻¹ due to CN bond stretch. The spectra also show styrene as the component of grafted chains. Absorption peak height of AN at 2229 cm⁻¹ indicates the increase of AN composition in grafted chains as styrene concentration in the solution increases. Based on absorption peak height at 698 cm⁻¹ of styrene, it can be seen that styrene composition in the grafted chain increased, following the same trend as AN. The two trends thus reconfirm that styrene was predominantly grafted to PPE whilst AN mainly reacted with the grafted polystyrene chains. The significant grafting yields shown in Table 10.5 also imply the preference of styrene to co-graft with AN, and this is being further supported by the fact that higher grafting yield was achieved in the presence of AN. Similar behavior of AN in the co-grafting process with styrene to PPE substrates by gamma irradiation was reported by Yen [24]. The co-grafting process was attributed to by the preferential absorption of AN to the growing grafted chains because of the higher polarity and the smaller molecular size of the AN molecules, as compared to those of styrene molecules. However, another possibility is the Ï•T complex formation between AN and styrene which could have governed the way in which both monomers are grafted to the PPE substrate.

10.3.3.1.4 DMMA and styrene

Very little grafting was observed in solutions containing both DMMA and styrene even when a high UV dose of 746 J was used (Table 10.5). Because the grafting yields were much lower than in the case when neat styrene was used, it thus appeared that DMMA retarded the grafting of styrene to PPE.
FT-IR spectra of the grafted PPE substrate (Figure 10.5.5) reveal the presence of DMMA and styrene as components of the grafted chains. An absorption peak at 1738 cm\(^{-1}\) is due to C=O stretches of the carbonyl groups in DMMA units. Based on absorption peak heights, the compositions of both DMMA and styrene increase as the concentration of styrene increases. As DMMA does not homopolymerize even in the presence of PI (Table 9.1, Chapter 9), it is therefore likely that DMMA was incorporated into the grafted chains by reacting with the polystyrene chains which were predominantly grafted to PPE. Low grafting yields obtained from DMMA/styrene mixtures compared to that from the neat styrene solution indicate that styrene is not reactive towards grafted chains ended with DMMA units.

10.3.3.1.5 AA and styrene
In the absence of PI, all solutions containing both AA and styrene were not viscous at the end of the UV exposure. As shown in Table 10.5, no grafting was observed for all, implying that AA retarded the grafting of styrene to PPE. FT-IR spectra of the substrates (Figure 10-13) show that grafting of styrene and AA to PPE is so low that no absorption peak belonged to either monomers was observed.

10.3.3.2 UV grafting of styrene to PPE in the presence of various EP vinyl monomers and Irgacure 819 photoinitiator
The presence of Irgacure 819 photoinitiator induced fast polymerization and therefore much lower UV doses were applied. Results in Table 10.6 show that high grafting yields were obtained in all systems but varied according to EP vinyl monomers used. 0.2% w/v Irgacure 819 was used in solutions containing AN, MAC and AA. However, as discussed in Section 9.3.1.1 of Chapter 9, MMA required a higher PI concentration to initiate the polymerization process, thus, 1% w/v of Irgacure 819 was used. Similar to Section 10.3.3.1, the presence of styrene in the grafted chains of all EP vinyl monomer/styrene systems was based on the appearance of absorption peaks at 1601 cm\(^{-1}\), 1583 cm\(^{-1}\), 758 cm\(^{-1}\) and 698 cm\(^{-1}\) in FT-IR spectra of the grafted substrates. The presence of the other EP vinyl monomers in the grafted chains was also shown by absorption peaks of their functional groups. Again, absorption peak height was used to gauge the approximate
amount of the grafted monomers in the sampling areas of the grafted substrates under FT-IR study.

10.3.3.2.1 MMA and styrene

The presence of the PI significantly improved grafting yields with shorter UV doses required. According to results in Table 10.6 and Figure 10.6.1, grafting yields decreased with increasing styrene concentrations and this observation was in line with the finding in Section 10.3.3.1.1 when no PI was included in the same system (Table 10.5). High grafting yields obtained with increasing MMA concentrations were again attributed to the grafting ability of MMA to PPE. Again, the decreasing grafting yield as the styrene concentration increased possibly implies styrene did not graft as fast as MMA to PPE, and MMA was the main drive of the grafting process. Another possibility was that the inclusion of styrene reduced homopolymerization of MMA in solutions leading to more monomers available for the grafting. Using styrene as the comonomer at 20% v/v, Garnett et al [26] found that simultaneous grafting of MMA to PPE in methanol as a solvent using gamma and UV irradiation was significantly enhanced. The effect was attributed to the reduction of the propagation rate constant of MMA by styrene, thus resulting in a lower rate of homopolymerization of MMA. Retardation of the homopolymerization in the presence of styrene therefore allowed MMA to diffuse more readily into the polymer backbone to react with the grafting sites, thus enhancing grafting yield.

As in Section 10.3.3.1.1, both MMA and styrene are found as components in the grafted chains. In Figure 10.6.3, the presence of MMA is evidenced by absorption peaks at 1723 cm⁻¹ (C=O stretches) whilst the styrene presence is indicated by the appearance of absorption peaks at the frequencies already mentioned at the beginning of the section. Based on absorption peak height at 1723 cm⁻¹, MMA composition is found to decrease with decreasing MMA concentrations in the solutions. Interestingly, absorption peak height at 758 cm⁻¹ suggests styrene composition reaches maximum at the highest MMA concentration of 80% v/v, thus implying styrene preference to co-graft with MMA to
PPE. Since grafting yields increased with increasing MMA concentration, the results suggest that in this system, MMA was predominantly grafted to PPE substrate.

10.3.3.2.2 MAC and styrene

The presence of Irgacure 819 photoinitiator greatly enhanced grafting yields for the MAC/styrene system. As shown in Table 10.6 and Figure 10.6.1, the grafting yield had a maximum value of 53% at 80% v/v of MAC, reaching the minimum of 12% grafting yield at 40% v/v of MAC, and then increased again to 36% at 20% v/v of MAC. With reference to Table 9.2 of Chapter 9, neat MAC gave low grafting yield of 5% though it underwent rapid homopolymerization. The high grafting yields in Table 10.6 for the MAC/styrene system could be mainly attributed by the grafting of styrene. Similar to the MMA/styrene system, the presence of styrene was essential, probably because it retarded the homopolymerization of MAC by reducing its propagation rate, resulting in MAC monomer being more available to react with the reactive sites on PPE substrates to produce grafted chains.

Figure 10.6.4 presents FT-IR spectra of MAC/styrene grafted substrates in which both MAC and styrene are shown to be components of grafted chains. The absorption peak at 1732 cm\(^{-1}\) is due to the C=O stretch in MAC while other absorption peaks at 1602 cm\(^{-1}\), 1583 cm\(^{-1}\), 760 cm\(^{-1}\) and 702 cm\(^{-1}\) belong to styrene. Based on absorption peak height at 1732 cm\(^{-1}\), MAC composition appeared to decrease with increasing styrene concentrations, indicating MAC efficiently grafts to PPE in the presence of styrene and Irgacure 819. This trend is also opposite to the observation for the same system but with the exclusion of Irgacure 819 in Section 10.3.3.1.2, where MAC composition is found to increase with increasing styrene concentration. Based on absorption peak height at 760 cm\(^{-1}\), styrene composition appeared to decline with MAC concentration, reaching the minimum at 60% v/v of styrene, then increasing again. The observation implies styrene’s preference to react with grafted chains ended by MAC units. The results of grafting and FT-IR studies show that MAC predominantly grafted to PPE in the presence of styrene and Irgacure 819.
10.3.3.2.3 AN and styrene

In the presence of Irgacure 819 photoinitiator, good grafting yields were also obtained for the AN/styrene system. Styrene appeared to have retarded the polymerization rate (this was shown by longer required UV doses compared to that in Table 9.2 of Chapter 9), allowing more monomers to be available for grafting. In Table 10.6 and Figure 10.6.5, the grafting yield of 4% was the lowest at 80% v/v of AN, and the highest of 38% grafting yield at 40% v/v of AN. This trend was generally similar to the results in Table 10.5 where no PI was present, and thus indicated that styrene predominantly grafted to the substrate.

FT-IR spectra of grafted substrates are shown in Figure 10.6.5 in which AN is represented by an absorption peak at 2229 cm\(^{-1}\) (CN stretch). The spectra in Figure 10.6.5 reveal that grafted chains consisted of both monomers but their composition vary accordingly to their concentrations in the solutions. However, for the mixture containing 80% v/v AN, only a very small amount of styrene is detected in the spectrum, evidenced by a small absorption peak at 758 cm\(^{-1}\) while there is no evidence for the presence of AN. These spectra reveal that AN's composition in the graft increased with increasing styrene concentration. Its presence cannot be detected using FT-IR technique when its concentration in the solution is above 60% v/v. Similarly, comparison between absorption peaks of spectra reveals the styrene composition in grafted chains increased with increasing in styrene concentration, implying that styrene was predominantly grafted to PPE. Grafting yields and spectra's analyses reconfirmed suggestions of CT complex formation and preferential absorption of AN to the growing grafted chains made in Section 10.3.3.1.3 and in the two cases, the grafting behaviors of both AN and styrene are similar and the presence of AN enhanced the grafting process of styrene to the substrate.

10.3.3.2.4 DMMA and styrene

According to Table 10.6 and Figure 10.6.1, the grafting yield increases with decreasing DMMA concentrations. The observed trend implied that styrene was the active monomer in the grafting process. However, in the presence of Irgacure 819, DMMA was shown to
make a contribution to the grafting process. This was clearly evidenced by the high grafting yields of 24% with 60% v/v styrene in the solutions as compared to 7% yield of the neat styrene solution. The high grafting yields in the presence of PI were caused by an increase in radicals from the photolysis of the PI. This result is opposite to the finding in Section 10.3.3.1.4, where DMMA is reported to have hindered the grafting process in the absence of PI.

FT-IR spectra of grafted substrates as shown in Figure 10.6.6 reveal both DMMA and styrene as components in the grafted chains. The presence of DMMA is evidenced by an absorption peak at 1738 cm\(^{-1}\) which were due to C=O stretch. Based on absorption peak heights at 1738 cm\(^{-1}\) for DMMA and at 758 cm\(^{-1}\) for styrene, DMMA and styrene compositions in grafted chains are both found to increase with increasing styrene concentrations. This trend strongly suggests the important role styrene plays in the grafting process. In this instance DMMA appeared to enhance styrene grafting in the presence of PI as compared to the PI-free system. This difference may be due to the possible weak interactions between the two monomers in which DMMA is an electron acceptor and styrene, an electron donor. In the absence of PI, the CT complex formed was not sufficient to initiate grafting, thus low grafting was resulted.

10.3.3.2.5 AA and styrene
In the presence of Irgacure 819 photoinitiator (Table 10.6, Figure 10.6.1), polymerization of AA/styrene system was rapid. As shown in Figure 10.6.2, the solutions with high AA concentrations polymerized more rapidly than solutions with low AA concentrations. Very high grafting yields of 223% and 112% were observed for the two solutions containing styrene concentrations of 60% v/v and 80% v/v respectively. The results were significant since neat AA solution did not produce any grafting in the presence of the PI (Table 9.2). The findings were also contrary to observations in Section 10.3.3.1.5 in which AA was found to retard the grafting process in the absence of PI. However, the high concentration AA in the solution was shown not to be beneficial because, negligible grafting yields were recorded for the solutions containing AA concentrations of 60% v/v and 80% v/v. This was possibly due to very fast AA homopolymerization or
copolymization with styrene in the presence of Irgacure 819, leading to the depletion of both monomers and radicals, resulting in their less availability for the grafting process.

FT-IR spectra in Figure 10.6.7 show that both AA and styrene grafted to PPE. An absorption peak at 1702 cm⁻¹ is due to C=O stretch of AA. Absorption peak heights at 1702 cm⁻¹ (AA) and 758 cm⁻¹ (styrene) indicate that AA and styrene compositions increase with decreasing AA concentrations. The trend suggests that the presence of styrene enhanced the incorporation of AA into the grafted chains. Also, by comparing the very high grafting yields achieved to the low grafting yield from neat styrene solution, AA displayed an important role in the grafting process. The FT-IR analysis strongly suggests that grafting was predominantly from styrene since small peak heights of both monomer units were detected at high AA concentration.

It is interesting to compare grafting yields of AA/styrene systems to those of MAC/styrene systems. MAC is different from AA by only one methyl group attaching to the carboxyl group. However, in the presence of Irgacure 819 (Table 10.6), AA/styrene system required much lower UV doses than MAC/styrene system did. Furthermore, high grafting yields up to 223% was achieved for AA/styrene system. The difference between the two systems was possibly due to the stronger CT complex formation between AA and styrene compared to that of MAC and styrene. This was supported by observations in Section 9.3.1.4.4 where AA displayed a stronger electron withdrawing property over MAC in the presence of DVE-3 and Irgacure 819.

10.3.3 Effects of solvents on the grafting of styrene and vinyls to PPE

10.3.3.1 Without Irgacure 819 photoinitiator

In the absence of Irgacure 819 photoinitiator, only solutions of styrene with MMA and AN were shown to give significant grafting (Table 10.5). Therefore, the study of solvent effect on vinyl monomer/styrene systems grafting to PPE was carried out only for MMA and AN as the monomers. According to results in Tables 10.7 and 10.8, reasonable grafting yields were achieved for most solutions with the grafting yields being enhanced
by chloroform and methanol to a greater extent than by DMF in the MMA/styrene system.

i) **MMA/styrene with 20% v/v of chloroform, DMF and methanol**

Results in Table 10.7 and Figure 10.7 show the grafting yields of MMA/styrene system to PPE with different solvents without PI. Grafting yields were found to decrease with increasing styrene concentrations. This trend was similar with the findings in Section 10.3.3.1 where solvents were not used (Table 10.5). This observation once again suggests that MMA was predominantly grafted to the substrate. However, the variation of grafting yields according to solvents indicated that these solvents did play an important role in the co-grafting process. As shown in Figure 10.7, chloroform and methanol gave better grafting than DMF and these results were possibly due to the Trommsdorff effect as well as different swelling properties of PPE and grafted polymers in solvents as discussed in Section 4.3.1 of Chapter 4.

ii) **AN/styrene with 20% v/v of chloroform, DMF and methanol**

Good grafting yields of AN/styrene system to PPE in the presence of solvents are summarized in Table 10.8 and Figure 10.8. The grafting yields followed a similar trend as for AN/styrene grafting to PPE without solvents and PI (Table 10.5). Grafting yields increased with increasing styrene concentrations, maximizing at 48% v/v of styrene, thus, indicating that styrene was predominantly grafted and the explanations for such phenomenon could be due to the formation of CT complex and preferential absorption of AN to the growing grafted chains as previously discussed in Section 10.3.3.1.3. Results from Figure 10.8 also show the influence of solvents on grafting outcomes with chloroform and methanol as the more efficient solvents in enhancing grafting.

**10.3.3.3.2 With Irgacure 819 photoinitiator**

In the presence of Irgacure 819 photoinitiator, both polymerization and the grafting processes were enhanced due to the additional radicals from the photolysis of PI. Again, grafting yields (Tables 10.9-10.12) were dependent on solvents used.
i) **MMA/styrene with 20% v/v of chloroform, DMF and methanol**

Table 10.9 and Figure 10.9 show grafting yields decreased with increasing styrene concentrations. As the same trend was observed in Section 10.3.3.2, this reconfirms MMA as a main active grafting monomer. Grafting yields were also found to vary with solvents used but their influence was not consistent across the monomer concentrations. At MMA concentration of 64% v/v, methanol and chloroform were the most efficient solvents but as MMA concentration decreased to 48% v/v or less, DMF proved to be a better solvent than the other two.

ii) **AN and styrene with 20% v/v of chloroform, DMF and methanol**

Results of the grafting of AN/styrene to PPE in the presence of Irgacure 819 and chloroform, DMF and methanol are summarized in Table 10.10 and Figure 10.10. Significant grafting occurred when chloroform was the solvent used while very low grafting yields were recorded in the presence of methanol and DMF as solvents. The results were in total contradiction to the grafting of the same systems to PPE in the absence of Irgacure 819 as reported in Section 10.3.3.3.1 (Table 10.8). The difference between the two cases is obviously due to the presence of Irgacure 819 which led to the production of a large amount of polymers in the solutions. These polymers which were not soluble in either DMF or methanol, possibly formed a layer of polymer adhering to substrate’s surface. As a result, the supply of monomers and radicals essential for the grafting process was likely to be inhibited, leading to early termination of grafting. However, this phenomenon was not observed in the PI-free system (evidenced by the high UV doses of 746 J used, Table 10.8). Chloroform was found to be a good solvent for swelling PPE and dissolving polymers, and hence, grafting yields were improved in this solvent for the systems studied. With chloroform as the solvent, grafting of AN and styrene to PPE followed the same trend observed in Section 10.3.3.2 in which yields increased with increasing styrene concentrations. The trend suggests styrene was the main active monomer in the grafting process.
iii) MAC/styrene with 20% v/v of chloroform, DMF and methanol

According to Table 10.11 and Figure 10.11, two opposite trends were observed. For MAC/styrene solutions with chloroform as the solvent, a subtle decrease in grafting yields with decreasing MAC concentrations was observed. This followed the same trend as observed for the grafting of the same system to PPE in the absence of solvents. On the other hand, with DMF and methanol as solvents, grafting yields increased with decreasing MAC concentrations. A similar solvent influence occurred in the case of AN/styrene in which good grafting yields were achieved only when chloroform was used as the solvent.

iv) AA/styrene with 20% v/v of chloroform, DMF and methanol

Solutions of AA and styrene were very reactive even when they were diluted by solvents. In Table 10.12, styrene solutions with high AA concentrations underwent rapid polymerization process and thus required short UV exposures. Chloroform was proved to be the most efficient solvent for the grafting of AA/styrene to PPE with DMF and methanol as solvents leading to very low grafting. The difference between DMF, methanol and chloroform may be caused by their ability to wet and swell PPE or to dissolve polymers formed in the solutions. Chloroform has such properties while DMF and methanol do not, and thus leading to different influence on the grafting process. As shown in Table 10.12 and Figure 10.12, with chloroform as the solvent, grafting yields increased rather dramatically with increasing styrene concentration. A similar trend was also observed where methanol was a solvent, and thus, indicating styrene was the main reactive monomer in the grafting process.

10.3.3.3.3 Further discussion on the effect of solvents on the grafting of EP vinyl monomer/styrene systems to PPE substrates

In the previous section, the concept of CT complex as well as physical properties of solvents have been applied to explain the influence of solvents on the co-grafting of vinyl monomers and styrene to PPE substrates. As discussed in Section 1.3.3 of Chapter 1, solvents have been reported to strongly affect the kinetics of copolymerization in solutions, namely termination and propagation rates [38-49]. These effects have been
attributed to a) electrostatic repulsion of charged monomers and radicals, b) changes in monomer polarity, c) participation of monomer complexes, d) hydrogen-bonding of monomer with solvent and e) solvent dielectric effects, but there has been no universal model to successfully explain these effects [43,44]. Besides wetting and swelling effects caused by interactions of solvents with PPE, these factors may also be applied to explain the observed effects of solvents on grafting of vinyl monomer/styrene to PPE since the process can be considered as the copolymerization occurring on the surface of the polymer. However, it should be noted that because the method used was simultaneous grafting method, there are very complex interactions between substrates, radicals, monomers, polymers, the UV source and solvents, which make it impossible to get to a definite conclusion about the role of solvents in the grafting process.

As previously mentioned in Section 1.3.3 of Chapter 1, another important phenomenon was observed by Harwood [44], in which he reported that copolymers having the same composition have the same microstructure, independently of the solvent used during their preparation. He further proposed the “bootstrap effect”, stating solvent effects in copolymerization are not manifested in the chain-end reactivity but rather in a solvent partitioning, whereby an equilibrium may exist in which monomers are distributed between free solvent and the domains of growing polymer radicals [44]. If the “bootstrap effect” is true for the grafting process, solvents such as chloroform, DMF and methanol may influence grafting yields, but structurally, grafted chains should have the same sequence distribution of styrene and vinyl monomer units as long as monomers compositions in the feeds are the same. This will serve as an area for future investigation.

10.4 Conclusions
In this study, possible CT complex formation between the EP vinyl monomers, MA, MMA, MAC, DMMA, AN and AA, and styrene have been explored. Among these EP vinyl monomers, only MA initiated spontaneous polymerization with styrene under UV irradiation, but UV exposure doses required for the process increased with increasing styrene concentrations. The system was also shown to undergo rapid free radical induced polymerization. However, significant grafting was only reported in the presence of
Irgacure 819, with yields increased with increasing styrene concentrations. FT-IR study showed the presence of both MA and styrene in grafted chains with increase in peak height at 1601 cm⁻¹ which belongs to benzene ring stretching with increase in styrene concentration.

In the absence of PI, good grafting was achieved for most EP vinyl monomer/styrene systems except for MAC/styrene and AA/styrene. However, grafting yields were found to vary with EP vinyl monomer types and their concentrations. In the presence of Irgacure 819, the grafting process was induced in all systems and again, EP vinyl monomers and their concentrations played important roles in influencing grafting yields. For grafted substrates, both styrene and EP vinyl monomers were indicated by FT-IR spectra as components of grafted chains, but their compositions were dependent on their concentrations in the feeds and the presence of Irgacure 819.

The effect of solvents on the co-grafting process of EP vinyl monomer/styrene to PPE by UV irradiation have also been under examination. In the absence of PI, chloroform and methanol were found to be more efficient solvents for the grafting of MMA, AN with styrene as the comonomer. However, in the presence of Irgacure 819, solvents displayed large influences in which chloroform was shown as the best solvent for all systems while DMF and methanol retarded the grafting of AN/styrene or AA/styrene.

10.5 References


Chapter Ten: UV Grafting Of Styrene To PPE With Different Eleletron Poor (EP) Vinyl Monomers As Comonomers


CHAPTER ELEVEN: UV GRAFTING OF STYRENE TO PPE WITH ADDITIVES
Part A: Effect of cationic photoinitiator on UV grafting of styrene to PPE with vinyl ethers as comonomers

11.1 Introduction
In Chapters 5, 6, 7 and 8, various vinyl ethers were shown not to undergo free radical induced polymerization. However, their presence in monomer mixtures could dramatically change the ability of monomers to polymerize as well as influence the outcomes of the grafting process. Vinyl ethers are reported to actively participate in cationic polymerization [1-8] initiated by the presence of Lewis acids. Such Lewis acids can be formed from decomposition of cationic photoinitiators (CIs), such as thiobis(triphenyl sulfonium hexafluorophosphate) with 50 wt % solution in propylene carbonate (KI85), under UV exposure [7,8]. The initiation and propagation of cationic polymerization is presented in Scheme 11.1.

In the copolymerization of vinyl ethers with styrene, the presence of a cationic photoinitiator along with the free radical photoinitiator may further alter the polymerizing characteristics. This may influence the grafting process by reducing the available vinyl ether monomers or by changing the diffusion of monomers to the reactive sites. Therefore, the aim of this section is to examine the effects that the presence of KI85 cationic photoinitiator may have on the grafting of styrene to PPE substrate with vinyl ethers as comonomers under the influence of UV radiation.

\[
\text{S}[(\text{Ph})_3\text{S}^{+}\text{PF}_6^{-}]_2 \xrightarrow{\text{hv}} (\text{Ph})\text{S}(\text{Ph})\text{S}(\text{Ph})\text{S}(\text{Ph}) + 2 \text{PhH} + 4 \text{R} + 2 \text{HPF}_6
\]

\[
\text{H}_2\text{C} = \text{C} - \text{OR} \xrightarrow{\text{H}^+(\text{HPF}_6)} \text{H}_3\text{C} - \text{CHOR} \xrightarrow{\text{monomer}} \text{Polymer}
\]

Scheme 11.1: Cationic polymerization of a vinyl ether initiated by KI85 (thiobis(triphenyl sulfonium hexafluorophosphate) with 50 wt % solution in propylene carbonate) with Ph represents phenyl group and RH is hydrogen donor molecule such as vinyl ethers.
11.2 Results

11.2.1 UV grafting of vinyl ethers to PPE substrates with 1% w/v of KI85

The results of UV grafting of vinyl ethers to PPE in the presence of KI85 are presented in Table 11.1. Only DVE-3 and EVE gelled in relatively short UV exposures while other vinyl ethers did not gel despite high UV doses. Furthermore, poor grafting was observed for all vinyl ether solutions.

11.2.2 UV grafting of styrene to PPE with vinyl ethers as comonomers, with or without Irgacure 819 photoinitiator, with or without KI85

11.2.2.1 Styrene/DVE-3 system

Irgacure 819 and KI85 were added to styrene/DVE-3 solutions to initiate both free radical and cationic polymerization reactions. In Table 11.2 and Figure 11.2, reasonable grafting yields up to 14% was observed for the solutions with a high styrene concentration of 80% v/v. In the case of no photoinitiator present, the polymerization process was slow, and thus a longer UV dose of 832 J was required.

11.2.2.2 With other monofunctional or multifunctional vinyl ethers

Since reasonable grafting yield was obtained when the styrene concentration was 80% v/v in the divinyl ether DVE-3, subsequently all styrene/vinyl ether solutions were prepared to contain 80% v/v styrene. Table 11.3 and Figure 11.3 present the appearance and grafting results of different styrene/vinyl ether solutions to PPE substrates after UV exposures. Yields were shown to vary according to the vinyl ether types.
Table 11.1: UV grafting of styrene and vinyl ethers to PPE in the presence of KI85 cationic photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ether</th>
<th>Grafting yield (%)</th>
<th>Total dose (J)</th>
<th>Solution appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVE</td>
<td>0</td>
<td>32</td>
<td>Formed a clear polymer; exothermic</td>
</tr>
<tr>
<td>HDVE</td>
<td>0</td>
<td>55</td>
<td>Remained as liquid</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>0</td>
<td>55</td>
<td>Remained as liquid</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>0</td>
<td>55</td>
<td>Remained as liquid</td>
</tr>
<tr>
<td>DVE-3</td>
<td>0</td>
<td>14</td>
<td>Formed a clear, brittle polymer</td>
</tr>
<tr>
<td>Styrene</td>
<td>0</td>
<td>147</td>
<td>Remained as liquid</td>
</tr>
</tbody>
</table>

Cationic photoinitiator: 1% w/v
Dose rate: 36.7 J/hr
Temperature: 29 °C

Table 11.2: UV grafting of styrene to PPE with DVE-3 as a comonomer, with or without Irgacure 819 photoinitiator, and KI85 cationic photoinitiator.

<table>
<thead>
<tr>
<th>Styrene conc. (% v/v)</th>
<th>DVE-3 conc. (% v/v)</th>
<th>Grafting yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NA^a</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

NA: No photoinitiator
Irgacure 819 concentration: 1% w/v
Cationic photoinitiator: 1% w/v
Total dose a: 832 J
Total dose b: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C
Figure 11.2: UV grafting of styrene to PPE with DVE-3 as a comonomer, with or without Irgacure 819 photoinitiator, and KI85 cationic photoinitiator.
Table 11.3: UV grafting of styrene to PPE with 20% v/v of various vinyl ethers as comonomers, with Irgacure 819 photoinitiator, with or without KI85 cationic photoinitiator.

<table>
<thead>
<tr>
<th>Vinyl ether</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%819</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVE</td>
<td>3</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HDVE</td>
<td>11</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>18</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>2</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>DVE-3</td>
<td>14</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1%819 + 1%KI85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVE</td>
<td>3</td>
<td>Formed black precipitate</td>
</tr>
<tr>
<td>HDVE</td>
<td>11</td>
<td>Formed white precipitate; turned viscous</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>13</td>
<td>Formed white precipitate; turned viscous</td>
</tr>
<tr>
<td>DEAEVE</td>
<td>3</td>
<td>Formed white precipitate; turned viscous</td>
</tr>
<tr>
<td>DVE-3</td>
<td>14</td>
<td>Formed white precipitate; turned viscous</td>
</tr>
</tbody>
</table>

Styrene concentration: 80% v/v
Vinyl ether concentration: 20% v/v
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C
Figure 11.3: UV grafting of styrene to PPE with 20% v/v of various vinyl ethers as monomers, with Irgacure 819 photoinitiator, with or without KI85 cationic photoinitiator.
11.3 Discussion

11.3.1 UV polymerization and grafting of neat vinyl ethers to PPE with KI85 cationic photoinitiator

Table 11.1 shows that not all vinyl ethers underwent polymerization in the presence of KI85. Only EVE and DVE-3 did gel after fairly low UV exposures of 32 J and 14 J respectively and the EVE polymerization reaction was exothermic indicating a high reactivity of this vinyl ether towards the cationic photoinitiator. The product of DVE-3 polymerization exhibited very poor mechanical property, as it could be easily broken by a spatula. No polymerization was expected for DEAEVE because the monomer is basic, which reacted with the cations formed.

No grafting was observed for all the tested samples, even in the cases of EVE and DVE-3, implying the presence of KI85 did not initiate grafting of vinyl ethers or styrene to the PPE substrate. This finding can serve as a good reference to interpret the effect of vinyl ethers and the cationic photoinitiator on the grafting of styrene in later sections.

11.3.2 Effects of cationic photoinitiator and vinyl ethers on grafting of styrene by UV radiation

11.3.2.1 Effects of DVE-3 and KI85

As shown in Table 11.2, the grafting of styrene to PPE substrate was influenced by a number of factors which include the presence of PI, CI and as well as the concentration ratios between styrene and vinyl ethers. As the grafting environments changed with the compositions of solutions, it is therefore necessary to examine each system on individual basis.

11.3.2.1.1 Styrene and DVE-3, without PIs or CIs

Free radical formation in monomer solutions and the creating of grafting sites on substrates by UV irradiation were discussed in Section 5.3.1 of Chapter 5 and MMA was demonstrated to have undergone homopolymerization in the absence of a PI. However, results in Table 11.2 show that styrene in the presence of the comonomer DVE-3 undergoes very slow polymerization in the absence of PI and CI. Polymer formation was
indicated by the viscous appearance of the monomer solution at the end of a long UV exposure (832 J). A reasonable grafting yield of 20% was obtained when the styrene concentration reached 40% v/v but appeared to decrease beyond this styrene concentration.

11.3.2.1.2 Styrene and DVE-3 with Irgacure 819 photoinitiator
As shown in Table 11.2, in the presence of Irgacure 819, the grafting process was more efficient, being evidenced by a lower required UV exposure dose of 147 J. Grafting yields were found to increase with increasing styrene concentration, with the highest grafting yield of 14% at the styrene concentration of 80% v/v. However, no grafting yield was observed for solutions with styrene concentrations less than 40% v/v. Also, the presence of DVE-3 was shown to enhance the grafting of styrene to PPE as compared to the grafting result achieved with neat styrene. This observation is consistent with studies by other researchers [9-12] who have shown that DVE-3 is a good crosslinking agent due to the presence of two vinyl ether groups in its structure. It is capable of creating branch grafted chains and hence enhancing the solutions to gel points, leading to the acceleration of chain growths. These explanations were relevant since in recent publications, Garnett and coworkers [13,14] also reported multifunctional vinyl ethers such as DVE-3, 1,4-cyclohexane dimethanol divinyl ether and hydroxy butyl vinyl ether as additives in enhancing co-grafting of MMA and styrene to cellulose and PPE substrates by gamma or UV radiation. Other crosslinking agents such as multifunctional acrylates have been reported in a number of studies [15-18] to have the similar effect of inducing styrene grafting to polyolefins by gamma or UV radiation and similar explanations are offered for their observations.

11.3.2.1.3 Styrene and DVE-3 with Irgacure 819 and cationic photoinitiator
With reference to Table 11.1 on polymerization result, one observation from Table 11.2 and Figure 11.2 was that styrene seemed to retard the cationic polymerization of DVE-3, being evidenced by a longer UV dose of 147 J, even in the presence of both Irgacure 819 and KI85. In the presence of Irgacure 819 and KI85, there were possibly three processes occurring in the solutions. They were: a) the free radical polymerization of styrene, b) the
crosslinking of styrene units by DVE-3 by free radical process, and c) the cationic polymerization of DVE-3. The third process may have influenced the grafting by either depleting the amount of DVE-3 or by increasing the viscosity of the solution. In the presence of PI and Cl, poor grafting yields were obtained for solutions with DVE-3 concentration greater than 60% v/v.

11.3.2.2 UV grafting of styrene to PPE with vinyl ethers as comonomers, with Irgacure 819 photoinitiator, with or without KI85 cationic photoinitiator

As shown in Chapters 5-8, vinyl ethers such as EVE, HDVE, TMPTVE, DEAEVE and DVE-3, had large influences on the grafting of MMA to cellulose and PPE substrates by gamma or UV radiation. It was therefore anticipated that similar influences could be observed for the grafting of styrene to PPE by UV radiation. In this section, the effect of KI85 cationic photoinitiator is further explored.

11.3.2.2.1 Styrene and vinyl ethers with Irgacure 819 photoinitiator

Results in Table 11.3 show the dependence of grafting yields on vinyl ether types in which grafting yields were greatest for solutions containing TMPTVE and HDVE. On the other hand, solutions containing EVE and DEAEVE had very poor grafting yields. Differences in grafting yields between solutions containing different vinyl ethers were possibly due to the number of functional groups present in vinyl ethers and their corresponding molecular weights. As discussed in Section 11.3.2.1, multifunctional vinyl ethers were good cross-linking agents and they could influence the grafting process by branching grafted chains or by hastening the solutions to gel points. These suggestions are relevant since TMPTVE, a tri-functional vinyl ether, was shown to better enhance styrene grafting than HDVE, a bi-functional monomer (Figure 11.3). DVE-3, also a bifunctional vinyl ether, improved styrene grafting more than HDVE probably due to DVE-3 having a high molecular weight. On the other hand, a study by Bevington et al [19] showed that monofunctional vinyl ethers, such as n-propyl, tert-butyl and n-dodecyl vinyl ethers, retarded radical polymerization of styrene, and this may also be the case for EVE and DEAEVE in the current study.
11.3.2.2 Styrene and vinyl ethers with Irgacure 819 photoinitiator and KI85 cationic photoinitiator

A vigorous reaction between vinyl ethers and the cationic photoinitiator was clearly shown in the case of EVE where black precipitates were observed (Table 11.3). Styrene solutions containing EVE and DEAEVE again recorded the lowest grafting yields of 3% in both cases while grafting yields for the solutions containing TMPTVE, DVE-3 and HDVE were relatively higher with grafting yield of 13%, 14% and 11%, respectively. The effect of the number of vinyl ether functional groups on grafting, as discussed in the last section, is once again demonstrated that the presence of KI85 did not pose any significant influence on the grafting yields. This was probably due to low vinyl ethers concentrations with respect to that of styrene.

11.4 Conclusions

In this section of the chapter, potential enhancing grafting effect of vinyl ethers on UV grafting of styrene to PPE substrate was studied. KI85 cationic photoinitiator was found to induce homopolymerization of some vinyl ethers but did not lead to grafting. Furthermore, its effects on the grafting of styrene to PPE with vinyl ethers as comonomers were not clear. However, from the results obtained, it is apparent that the grafting of styrene to PPE substrates was shown to be influenced by the vinyl ether types and their concentrations. The results also demonstrated that multifunctional vinyl ethers, such as TMPTVE, DVE-3 or HDVE, promoted grafting while monofunctional monomers, such as EVE and DEAEVE, retarded it.
Part B: Effects of acids on UV grafting of styrene to PPE with vinyl ethers as comonomers

11.5 Introduction
During the course of experiment, it was observed that DVE-3 reacted violently with dilute sulfuric acid (2 M of methanol and water; ratio of methanol:water is 99%:1% by volume; water is added to assist the hydrolysis of the acid) to form chars. The reaction could spontaneously occur even without the UV exposure and was extremely exothermic. Consequently this aroused the interest to further investigate the reaction of other vinyl ethers and acids. As discussed in Part A, the presence of vinyl ethers is important in the grafting of styrene to PPE. Hence, their potential reactions with mineral acids may pose more influences on the grafting process. A number of publications [16,17,20-22] have reported that mineral acids also affect the grafting of styrene to polymer materials under the influence of gamma irradiation. It is therefore of interest to examine the potential interference mineral acids may have on the grafting of styrene to PPE in the presence of vinyl ethers under the influence of UV irradiation.

11.6 Results

11.6.1 UV polymerization of vinyl ethers and their grafting to PPE with acids as additives
Results in Table 11.4 show that DVE-3, EVE and HDVE reacted with 1% w/v dilute sulfuric acid (2 M) resulted in black polymer products. The additions of 1% w/v various dilute acids of 2 M concentration to other vinyl ethers did not produce any apparent change and in all cases, no significant grafting was observed.

11.6.2 UV grafting of styrene to PPE in the presence of 1% w/v Irgacure 819, with or without methanol as a solvent, with acids as additives
Various acids were tested for their effect on the grafting of styrene to PPE. These included $\text{H}_2\text{SO}_4$, HCl, HNO$_3$, H$_3$PO$_4$. These acids were all of 2 M concentration prepared as described above and were added to the solution as additives at 1% w/v concentration. Poor grafting results of styrene to PPE are presented in Table 11.5 and Figure 11.5, with
HCl giving the poorest yield. However, the presence of methanol as a solvent enhanced grafting yields and results in Table 11.6 and Figure 11.6 clearly show the grafting varied according to the acid types. Methanol was chosen as the solvent due to its ability to enhance grafting of styrene to PPE (as shown in Table 10.1 of Chapter 10) and it is more mixable with acids than other solvents previously used in this study.

11.6.3 UV grafting of styrene to PPE with vinyl ethers as comonomers, with 1% w/v Irgacure 819, with acids as additives

11.6.3.1 Styrene/vinyl ether with 1% w/v of 0.2 M H₂SO₄

0.2 M H₂SO₄ solution was used instead since reactions of vinyl ethers with 2 M H₂SO₄ solution were too violent (Table 11.4). Results in Table 11.7 show poor grafting yields of styrene/vinyl ether systems to PPE in the presence of H₂SO₄ with the exception of the solution containing TMPTVE. Again, only solutions containing DVE-3, EVE and HDVE showed signs of reactions in the presence of the acid by the change of color in solutions.

11.6.3.2 Styrene/vinyl ether in the presence of 1% w/v of 2 M HCl, HNO₃ and H₃PO₄

Results in UV grafting of styrene/vinyl ether systems to PPE in the presence of HCl, HNO₃ and H₃PO₄ as additives were presented in Tables 11.8-11.12 and Figures 11.8-11.12. Grafting yields were found to vary according to the acids and vinyl ether types as well as the vinyl ether concentrations.
Table 11.4: UV polymerization and grafting of vinyl ethers to PPE with acids as additives and no photoinitiators.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Vinyl ether</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% H₂SO₄ 2 M</td>
<td>DVE-3</td>
<td>0</td>
<td>Formed a black polymer; extremely exothermic</td>
</tr>
<tr>
<td></td>
<td>EVE</td>
<td>0</td>
<td>Turned black</td>
</tr>
<tr>
<td></td>
<td>HDVE</td>
<td>0</td>
<td>Turned black</td>
</tr>
<tr>
<td></td>
<td>TMPTVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>DEAEEVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td>1% HCl 2 M</td>
<td>DVE-3</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>EVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>HDVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>TMPTVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>DEADEVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td>1% HNO₃ 2 M</td>
<td>DVE-3</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>EVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>HDVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>TMPTVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>DEADEVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td>1% H₃PO₄ 2 M</td>
<td>DVE-3</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>EVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>HDVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>TMPTVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>DEADEVE</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
</tbody>
</table>

Acid concentration: 1% w/v
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C
Table 11.5: UV grafting of styrene to PPE with 1% w/v Irgacure 819 and acids as additives.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>6</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HCl</td>
<td>3</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HNO₃</td>
<td>6</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>6</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>No acid</td>
<td>7</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Styrene concentration: 100% w/v  
Irgacure 819 concentration: 1% w/v  
Acid concentrations: 1% w/v  
All stock acids had concentrations of 2 M (prepared in 1% water and 99% methanol)  
Dose rate: 36.7 J/hr  
Temperature: 29 °C

Figure 11.5: UV grafting of styrene to PPE with 1% w/v Irgacure 819 and acids as additives.
Table 11.6: UV grafting of styrene to PPE with methanol as a solvent, with 1% w/v Irgacure 819 photoinitiator and acids as additives.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>6</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HCl</td>
<td>4</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HNO₃</td>
<td>6</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>11</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>No acids</td>
<td>15</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Solvent: methanol

Styrene concentration: 80% v/v

Irgacure 819 concentration: 1% w/v

Acids concentrations: 1% w/v

All stock acids had concentrations of 2 M (prepared in 1% water and 99% methanol)

Dose rate: 36.7 J/hr

Temperature: 29 °C
Figure 11.6: UV grafting of styrene to PPE with methanol as a solvent, with 1% w/v Irgacure 819 photoinitiator and acids as additives.
<table>
<thead>
<tr>
<th>Vinyl ether</th>
<th>Styrene conc. (% v/v)</th>
<th>Vinyl ether conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVE-3</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>Dark orange with acid; exothermic; black at the end of irradiation</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>Dark orange with acid; exothermic; black at the end of irradiation</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>Dark orange with acid; exothermic; black at the end of irradiation</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>Dark orange with acid; exothermic; black at the end of irradiation</td>
</tr>
<tr>
<td>EVE</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>Turned dark orange</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>Turned dark red</td>
</tr>
<tr>
<td>HDVE</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>Turned dark orange; formed black precipitates</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>Turned dark orange; formed black precipitates</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>Turned dark red; formed black precipitates</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>Turned dark red; formed black precipitates</td>
</tr>
<tr>
<td>TMPTVE</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>16</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>24</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>12</td>
<td>No colour change; remained liquid</td>
</tr>
<tr>
<td>DEA EVE</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>Did not change in color; did not polymerize</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>Did not change in color; did not polymerize</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>Did not change in color; did not polymerize</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>3</td>
<td>Did not change in color; did not polymerize</td>
</tr>
</tbody>
</table>

**Irgacure 819 concentration:** 1% w/v  
**Sulfuric acid concentration:** 1% w/v  
**Stock sulfuric acid concentration:** 0.2 M (prepared in 1% water and 99% methanol)  
**Total dose:** 1.47 J  
**Dose rate:** 36.7 J/hr  
**Temperature:** 29 °C
Table 11.8: UV grafting of styrene to PPE with DVE-3 as a comonomer, with 1% w/v Irgacure 819 and acids as additives.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Styrene conc. (%) v/v</th>
<th>DVE-3 conc. (%) v/v</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>2</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>5</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HNO₃</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>3</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>14</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>8</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>17</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v
Acids concentrations: 1% w/v
All stock acids had concentrations of 2 M (prepared in 1% water and 99% methanol)
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C
Figure 11.8: UV grafting of styrene to PPE with DVE-3 as a comonomer, with 1% w/v Irgacure 819 and acids as additives.
Table 11.9: UV grafting of styrene to PPE with EVE as a comonomer, with 1% w/v Irgacure 819 and acids as additives.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Styrene conc. (% v/v)</th>
<th>EVE conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% HCl</td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% HNO₃</td>
<td>60</td>
<td>40</td>
<td>2</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% H₃PO₄</td>
<td>60</td>
<td>40</td>
<td>1</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>2</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v
Acids concentrations: 1% w/v
All stock acids had concentrations of 2 M (prepared in 1% water and 99% methanol)
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 ºC

Figure 11.9: UV grafting of styrene to PPE with EVE as a comonomer, with 1% w/v Irgacure 819 and acids as additives.
Table 11.10: UV grafting of styrene to PPE with HDVE as a comonomer, with 1% w/v Irgacure 819 and acids as additives.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Styrene conc. (% v/v)</th>
<th>HDVE conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>60</td>
<td>40</td>
<td>2</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>2</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HNO₃</td>
<td>60</td>
<td>40</td>
<td>11</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>8</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>60</td>
<td>40</td>
<td>13</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>9</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v
Acids concentrations: 1% w/v
All stock acids had concentrations of 2 M (prepared in 1% water and 99% methanol)
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C
**Figure 11.10:** UV grafting of styrene to PPE with HDVE as a comonomer, with 1% w/v Irgacure 819 and acids as additives.
Table 11.11: UV grafting of styrene to PPE with TMPTVE as a comonomer, with 1% w/v Irgacure 819 and acids as additives.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Styrene conc. (% v/v)</th>
<th>TMPTVE conc. (%v/v)</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>60</td>
<td>40</td>
<td>16</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>18</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HNO₃</td>
<td>60</td>
<td>40</td>
<td>22</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>12</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>60</td>
<td>40</td>
<td>26</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>16</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v
Acids concentrations: 1% w/v
All stock acids had concentrations of 2 M (prepared in 1% water and 99% methanol)
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C
Figure 11.11: UV grafting of styrene to PPE with TMPTVE as a comonomer, with 1% w/v Irgacure 819 and acids as additives.
Table 11.12: UV grafting of styrene to PPE with DEAEVE as a comonomer, with 1% w/v Irgacure 819 and acids as additives.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Styrene conc. (% v/v)</th>
<th>DEAEVE conc. (% v/v)</th>
<th>Grafting yield (%)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>3</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>HNO₃</td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Irgacure 819 concentration: 1% w/v
Acids concentrations: 1% w/v
All stock acids had concentrations of 2 M (prepared in 1% water and 99% methanol)
Total dose: 147 J
Dose rate: 36.7 J/hr
Temperature: 29 °C
11.7 Discussion

11.7.1 Polymerization of vinyl ethers in the presence of acids, in the absence of photoinitiators

According to the results in Table 11.4, only sulfuric acid showed strong interaction with the vinyl ethers, DVE-3, EVE and HDVE. It was a special case with DEAEVE which is an amine and it is likely that it reacts with an acid to produce an organic salt [1]. For other solutions, no obvious change in solutions color, indicating no interaction between the acids and vinyl ethers. The observed phenomena may have been originated from the tendency of vinyl ethers to participate in cationic polymerization. In other words, it was possible that the polymerization of the mentioned vinyl ethers followed the same mechanism as the one presented in Scheme 11.1 of part A. On the other hand, the polymerization of DVE-3 and EVE in the presence of dilute sulfuric acid was similar to the result in Table 11.1 in which only these two vinyl ethers participated in cationic polymerization initiated by KI85 cationic photoinitiator. However, cationic polymerization could not lead to any grafting, as evidenced by zero yields shown in Table 11.4.

11.7.2 Effects of acids on UV grafting of styrene to PPE in the presence of 1% w/v Irgacure 819

Results in Table 11.5 indicate that the presence of acids in styrene may have some effect on UV grafting of styrene to PPE substrates. Therefore, it is essential to determine what these effects are in order to single out the effects that influence the interaction between vinyl ethers and acids that lead to the enhancement of the grafting of styrene to PPE.

11.7.2.1 Without methanol as a solvent

In Table 11.5 and Figure 11.5, all styrene solutions in the presence of 1% w/v of 2 M H$_2$SO$_4$, HCl, HNO$_3$ and H$_3$PO$_4$ were exposed to the same UV doses and contained the same amounts of Irgacure 819. However, grafting yields were slightly lower for substrates in styrene solutions where acids were added. This suggested that acids, especially in the case of hydrochloric acid, hindered the grafting of styrene to PPE.
However, no concrete conclusions could be made due to very small differences between the yields obtained.

11.7.2.2 With 20% v/v of methanol as a solvent
The presence of methanol was obviously beneficial for the grafting process with significant increase in grafting yields. The effect exerted by methanol on grafting was discussed in Section 10.3.1.1 of Chapter 10 as Trommsdorff effect as well as the fact that methanol contains absorbable H atoms. Strong interference of acids on the grafting of styrene to PPE was clearly observed. As shown in Table 11.6 and Figure 11.6, strong acids namely sulfuric acid, nitric acid and especially hydrochloric acid, strongly hindered the grafting process while the weak phosphoric acid had the opposite effect, hence, the influence of acids can be suggested to depend on the nature of anions. In a publication concerning the effect of acids on the grafting of styrene to polymers by gamma irradiation, Garnett et al [21] also agreed that the nature of the acid was very important since its interactions with solvent molecules may vary with charge density on the acid anion. They also reported that hydrochloric acid displayed similar strong inhibiting behavior and attributed the effect to the depletion of methoxy radicals by chloride anions. The proposed mechanism is presented in the following Scheme 11.2.

\[
\text{CH}_3\text{O}^- + \text{Cl}^- \rightarrow \text{CH}_3\text{O}^- + \text{Cl}^-
\]

\[
\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2^-
\]

Scheme 11.2: Reactions of methoxy radicals with chloride anions.

However, it is not plausible to use this mechanism to explain the hindering effect of sulfuric acid and nitric acid on grafting and therefore, other explanations should be explored. A number of publications [16,20-22] reported that the presence of acids, such as sulfuric acid, leads to the enhancement of styrene grafting to polyolefins by gamma and UV irradiation but only under specific conditions. The grafting inducement by acids was popularly thought to due to the partitioning process in which the inclusion of mineral acids in the monomer solution leads to an increase in the concentration of monomer in
the solution absorbed within the backbone polymer. Furthermore, the extent of monomer partitioning depends on the polarities of monomers, substrates and solvents as well as the type and concentrations of acids. On the other hand, with nonpolar substrates such as PPE, the acid is also partitioned because of its polarity and thus becomes available for increasing the partitioning of styrene into the backbone polymer, thus further enhancing grafting. This, however, was not observed in Table 11.6, thus opening new rooms for a future investigation.

### 11.7.3 Effects of acids and vinyl ethers on UV grafting of styrene to PPE with 1% w/v Irgacure 819

#### 11.7.3.1 Effect of sulfuric acid and vinyl ethers on UV grafting of styrene to PPE with 1% w/v Irgacure 819

As shown in Table 11.7, the addition of the dilute sulfuric acid solution to systems of styrene/vinyl ethers initiated reactions in the systems containing DVE-3, EVE and HDVE. The system containing styrene/DVE-3 showed the strongest reaction, turning from colourless to dark orange as soon as sulfuric acid was added. Towards the end of experiment, the solutions turned completely black with black precipitates dispersing in the solution. Similar observations were noted for solutions containing EVE and HDVE. With reference to Section 11.8.1, changes in solution colours and formation of black precipitates were probably the product of the reactions between vinyl ethers with sulfuric acid in which extreme heat released led to the decomposition of polymers. No changes were recorded for solutions containing TMPTVE and DEAEVE, indicating no interaction between these vinyl ethers and the acid.

Significant grafting yields were only observed for substrates in the styrene/TMPTVE system and this was expected since TMPTVE did not react with sulfuric acid (Table 11.4) but was observed to enhance the grafting of styrene to PPE up to when the concentration of TMPTVE was 40% v/v. As discussed in Section 11.3.2 of Part A where KI85 cationic photoinitiator was present, the enhancing effect of TMPTVE on styrene grafting to PPE was due to the vinyl ether ability to act as a crosslinking agent, resulting
in the branching of grafted chains. Grafting yields were found to increase with rise in styrene concentrations and the observed trend was possibly due to Trommsdorff effect.

As DEAEVE was known to retard the grafting of styrene to PPE (Section 11.3.2 of Part A), it was understandable that substrates in solutions containing styrene/DEAEVE did not show any significant grafting (Table 11.7). On the other hand, as mentioned in Section 11.7.1, DEAEVE is also an amine which can react with the added sulfuric acid to form an organic salt. As the amount of DEAEVE used was many times greater than the amount of the added acid, all added acid was likely to be neutralized by DEAEVE, which was evidenced by pH 5 measured after the acid was added. However, poor grafting yields indicated either DEAEVE, or its organic salt with sulfuric strongly hinder the grafting of styrene to PPE.

All solutions containing styrene with the following vinyl ethers, EVE, DVE-3 or HDVE, showed very poor grafting results (Table 11.7). It is very interesting to compare these results with grafting values in Table 11.3 (Section 11.3.2 of Part A) where high grafting yields were reported for styrene solutions containing DVE-3 and HDVE with the inclusion of only Irgacure 819. The difference between these two sets of results suggested that the reactions of vinyl ethers with sulfuric acid together with acid interference on the grafting of styrene to PPE were likely the main reasons for low grafting yields.

11.7.3.2 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with DVE-3 as a comonomer, with 1% w/v Irgacure 819 photoinitiator

Results as shown in Table 11.4 indicate that HCl, HNO₃ and H₃PO₄ alone were not able to initiate polymerization of DVE-3. However, results in Table 11.8 show that all solutions containing styrene/DVE-3 in the presence of these three acids and 1% w/v Irgacure 819 only slightly polymerized at the end of the reaction time, as evidenced by their viscous appearances. However, small grafting yields were observed especially in solutions containing low DVE-3 concentrations, indicating the grafting process of styrene to PPE was not completely hindered by interactions between the monomer, the acids and DVE-3. Grafting was found to be proportional to the styrene concentration, thus implying
Trommsdorff effect had taken place. On the other hand, Figure 11.5 shows that grafting yields varied according to the acid strength with the weakest acid, H₃PO₄, giving the highest yield. Substrates in solutions where HCl was added had the lowest grafting yields, thus indicating the hindering effect of the acid on grafting of styrene to PPE as discussed in Section 11.8.2.

11.7.3.3 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with EVE as a comonomer, with 1% w/v Irgacure 819

Table 11.9 and Figure 11.9 show little grafting occurred when acids were added to solutions containing styrene/EVE. The poor grafting results were possibly due to the interference of the acids and EVE on the grafting of styrene to PPE (as discussed in Section 11.3.2.2 of Part A and Section 11.7.2 of Part B). However the effects of interaction between EVE and the acids upon grafting yields were not clear. No colour change was observed for the reacting solutions.

11.7.3.4 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with HDVE as a comonomer, with 1% w/v Irgacure 819

According to Table 11.10 and Figure 11.10, addition of HCl, HNO₃ or H₃PO₄ to solutions containing styrene/HDVE produced similar results to those of styrene/DVE-3 with the lowest grafting yields for HCl and highest for H₃PO₄, suggesting the dependence of grafting yields on acid strength. Grafting yields were also found to increase with rise in HDVE concentrations and the variation was likely due to Trommsdorff effect. There was no change of colour in the reacting solutions, thus indicating weak interaction between HDVE and the acids, resulting in no significant effect of the acids on the grafting yields.

11.7.3.5 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with TMPTVE as a comonomer, with 1% w/v Irgacure 819

As TMPTVE was shown not to react with HCl, HNO₃ and H₃PO₄ (even with sulfuric acid-Table 11.4), the presence of the vinyl ether together with one of the acids in the reacting solutions would not lead to significant interaction between the two. However, as shown in Table 11.11 and Figure 11.11, this vinyl ether enhanced grafting yields with the
highest yield of 26% obtained in the presence of H₃PO₄. Hence, the presence of TMPTVE appeared to have reduced the acid hindering effect on the grafting of styrene to PPE. Similar explanations of TMPTVE effect as a crosslinking agent was offered in Sections 11.3.2.2 (Part A) and 11.8.3.1 (Part B).

11.7.3.6 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with DEAEVE as a comonomer, with 1% w/v Irgacure 819

As discussed in Section 11.7.3.1, DEAEVE was an amine and it is supposed to have reacted with added acids to form organic salts. Table 11.12 shows very poor grafting yields which were possibly due to the interference of either DEAEVE or its organic salt with the acids or the acids themselves.

11.8 Conclusions

Results in this Part show that sulfuric acid initiated the polymerization of DVE-3, HDVE or EVE even in the absence of a cationic photoinitiator and the mechanism for the polymerization process was proposed. On the other hand the presence of acids such as sulfuric, nitric, hydrochloric and phosphoric acids, were demonstrated to hinder the grafting of styrene to PPE substrates by UV irradiation in the presence of Irgacure 819. Similar acid effects were observed when styrene was grafted to PPE with vinyl ethers as comonomers and in the presence of Irgacure 819. However, the extent of acid interference was largely dependent on the strength of the acids, vinyl ether types as well as their concentrations.
Part C: Effects of charge transfer complexes as additives on UV grafting of styrene to PPE in the presence of Irgacure 819

11.9 Introduction
Garnett and coworkers [14] reported the enhancement of MMA grafting to PPE in the presence of different CT complex systems which acted as additive and these CT complex systems included MA/DVE-3, MA/NVP and MA/CHVE. The result has a very important implication on coating formulations since it offers a potentially new technique to promote coating attachment to polymer materials. In this chapter, effects of a number of CT complexes on photografting of styrene to PPE will be investigated.

In Chapter 9, grafting of different CT complex systems to PPE was discussed. DVE-3 was found to be a good electron donor while MA, DMMA, MAC, AN and AA were electron acceptors which could form CT complexes with DVE-3. DVE-3 was able to spontaneously polymerize with these acceptors when exposed to a UV source. In Chapter 10, different electron poor (EP) vinyl monomers were shown to copolymerize and co-graft with styrene, especially at high styrene concentrations. It is therefore a matter of interest to study the effect of the CT complex formed between DVE-3 and EP vinyl monomers upon the grafting of styrene to PPE. In these instances, there are two possible competing processes, i.e., CT complex polymerization of vinyl monomers with DVE-3 as well as copolymerization of the EP vinyl monomers with styrene which potentially influence outcomes of the grafting processes.

11.10 Results
11.10.1 UV grafting of styrene to PPE substrates with different CT complexes as additives and Irgacure 819 photoinitiator
Grafting results of styrene in the presence of CT complexes formed between DVE-3 and EP vinyl monomers, MA, DMMA, DMFA, EMI, MAC, AN and AA, are presented in Table 11.13 and Figure 11.13.1 in which yields were found to vary with the EP vinyl monomers used. The CT complexes in general did not appear to contribute significantly to grafting yields, with the exceptions of the CT complexes formed between DVE-3 and
the two EP vinyl monomers AA and MA achieving grafting yields of 39% and 22% respectively.

**11.12.2 FT-IR characterization of grafted substrates**

Figures 11.13.2-11.13.9 are spectra of grafted substrates which clearly showed components of grafted chains.

**Table 11.13:** UV grafting of styrene to PPE with 1% w/v Irgacure 819 and various CT complex systems or their components as additives.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Grafting yield (%)</th>
<th>Dose (J)</th>
<th>Solution Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additives</td>
<td>7</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DVE-3</td>
<td>4</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% MA</td>
<td>10</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DVE-3 + 1% MA</td>
<td>22</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DMMA</td>
<td>5</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DVE-3 + 1% DMMA</td>
<td>6</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DMFA</td>
<td>4</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DVE-3 + 1% DMFA</td>
<td>3</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% EMI</td>
<td>5</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DVE-3 + 1% EMI</td>
<td>7</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% MAC</td>
<td>4</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DVE-3 + 1% MAC</td>
<td>6</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% AN</td>
<td>6</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DVE-3 + 1% AN</td>
<td>7</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% AA</td>
<td>36</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
<tr>
<td>1% DVE-3 + 1% AA</td>
<td>39</td>
<td>147</td>
<td>Turned viscous</td>
</tr>
</tbody>
</table>

Styrene concentration: 100% w/v  
Irgacure 819 concentration: 1% w/v  
Dose rate: 36.7 J/hr  
Temperature: 29 °C
Figure 11.13.1: UV grafting of styrene to PPE with 1% w/v Irgacure 819 and various CT complex systems or their components as additives.
Figure 11.13.2: UV grafting of styrene to PPE with DVE-3 as the additive, with 1% w/v Irgacure 819.
Figure 11.13.3: UV grafting of styrene to PPE with MA/DVE-3 CT complex as the additive, with 1% w/v Irgacure 819.
Figure 11.13.4: UV grafting of styrene to PPE with DMMA/DVE-3 CT complex as the additive, with 1% w/v Irgacure 819.
Figure 11.13.5: UV grafting of styrene to PPE with DMFA/DVE-3 CT complex as the additive, with 1% Irgacure 819.
Figure 11.13.6: UV grafting of styrene to PPE with EMI/DVE-3 CT complex as the additive, with 1% w/v Irgacure 819.
Figure 11.13.7: UV grafting of styrene to PPE with MAC/DVE-3 CI' complex as the additive, with 1% w/v Irgacure 819.
Figure 11.13.8: UV grafting of styrene to PPE with AN/DVE-3 CT complex as the additive, with 1% w/v Irgacure 819.
Figure 11.13.9: UV grafting of styrene to PPE with AA/DVE-3 CT complex as the additive, with 1% w/v Irgacure 819.
11 Discussion

11.1 Effects of CT complex systems as additives on UV grafting of styrene to PPE

h 1% w/v Irgacure 819

Addition to CT complexes studied in Chapter 9, CT complex systems of dimethyl amate (DMFA), ethyl maleimide (EMI) and DVE-3 were added to styrene to initiate grafting of styrene to PPE. These CT complexes are considered as strong CT complexes [23-24]. Thus, their effects on the grafting of styrene to PPE were also studied compared with other systems.

In order to study the effect of CT complex systems on the grafting of styrene to PPE, it is necessary to compare the results of grafting yields when separate components which needed the CT complexes were used in grafting. Table 11.13 and Figure 11.13.1 show the presence of individual EP vinyl monomers and DVE-3 did not enhance the grafting of styrene with yields less than 7% was obtained. Furthermore, the CT complexes formed between DVE-3 as the donor and various EP vinyl monomers as acceptors did not lead to any improvement in grafting yields. However, there were two exceptions in the cases of using MA and AA as acceptors, as considerable increase of grafting yields were resulted especially more significant with MA as the acceptor. The best increases were when AA or AA/DVE-3 complexes were used as the additives.

An increase of grafting yields indicated that the presence of the complexes formed between DVE-3 and EP monomers, AA and MA, enhanced the grafting of monomers to PPE.

1.2 Characterizations of grafted substrates

An individual electron acceptors and their corresponding donors were added to styrene solutions, there were potentially competing processes, especially when Irgacure 819 was present. In Chapter 9, it was shown that DVE-3 quickly polymerized with EP vinyl monomers with the inclusion of Irgacure 819. In Chapter 10, it was found that vinyl monomer compositions of the grafted chains generally increased with increasing styrene concentrations in reacting solutions. When CT complex systems comprising of both donors and acceptors were added to styrene, EP vinyl monomers, which functioned as
acceptors, could polymerize with either DVE-3 or styrene. As a small quantity of a CT complex was dispersed in a comparatively large volume of styrene under the influence of UV radiation, the chance for the intended donor/acceptor pair to form the CT complex was hampered as acceptors may have ended up reacting with styrene which is a weak donor. Events occurred in solutions always had strong influences on the outcome of the grafting process. To have a better understanding of what took place, grafted substrates were analyzed by the FT-IR technique.

Spectra in Figures 11.13.2-11.13.9 show the presence of styrene as the main component of grafted chains with its main absorption peaks at 1601 cm\(^{-1}\), 1583 cm\(^{-1}\), 758 cm\(^{-1}\), 698 cm\(^{-1}\). However, the presence of DVE-3 unit as the component of the grafted chains could not be identified in these spectra. The only way to identify DVE-3 was via absorption peaks in the range of 1070-1240 cm\(^{-1}\) due to stretch or antisymmetric stretch of C-O-C functional group [27]. Unfortunately, this absorption range is also overlapped by the absorption of grafted styrene, EP vinyl monomers and the PPE substrate. As shown in Figure 11.13.2, in the absorption range of 1000-1400 cm\(^{-1}\), the section of the spectrum of styrene grafted substrate in the absence of DVE-3 contains exactly the same peaks as the ones in the case when 1% w/v DVE-3 was added. Similar observations are noted when spectra of grafted substrates in the cases of the presence or absence of DVE-3 as the additive (Figures 11.13.3-11.13.9) are compared.

Spectra in Figures 11.13.3-11.13.9 show that EP vinyl monomers were the components of the grafted chains. The presence of MA was indicated by absorption peaks at 1781 cm\(^{-1}\), 1736 cm\(^{-1}\), 1706 cm\(^{-1}\) due to symmetric and antisymmetric stretch of the anhydride functional group. DMFA, EMI, MAC and AA are presented by the absorption peaks at 1738 cm\(^{-1}\) (DMFA), 1701 cm\(^{-1}\) (EMI, MAC and AA) due to C=O stretch in their carbonyl functional group. In the cases of MA and AA, the absorption peaks due to these two monomers were especially strong and this was in line with the grafting results (Table 11.13). In all cases, whether DVE-3 was included or excluded, absorption peaks due to grafted EP vinyl monomer units were similar in size, thus implying that the presence of DVE-3 in the reacting solutions did not significantly affect the incorporation of the EP
vinyl monomers into grafted chains. This strongly suggests that the EP vinyl monomers preferred to react with styrene rather than with the small amount of DVE-3 present in the reacting solutions.

However, there were two exceptions with DMMA and AN in which spectra (Figures 11.13.5 and 11.13.8) of the grafted substrates do not contain any absorption peaks to indicate their presence in grafted chains. This was possibly due to the reactions of these two EP vinyl monomers with DVE-3 instead of styrene.

11.12 Conclusions
In Part C, the presence of different CT complexes were not found to be beneficial to the grafting of styrene to PPE substrate in the presence of Irgacure 819 under the influence of UV irradiation. FT-IR studies showed that most of the EP vinyl monomers were present as components of grafted chains while no absorption peaks could be assigned to indicate the presence of DVE-3. However, there were two exceptions namely with MA and AA as acceptors and DVE-3 as the donor. These donor/acceptor pairs induced the grafting of styrene to PPE and the two vinyl monomers were analyzed to be present as component in grafted chains using FT-IR technique.

11.13 References


CHAPTER TWELVE: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH
The conclusions of this thesis can be summarized as follows:

1. MMA was successfully grafted onto both cellulose and PPE substrates in the presence of Irgacure 819 and under the influence of UV radiation. The performance of Irgacure 819 in enhancing grafting yields has been compared to that of other photoinitiators. Despite being very efficient in radical forming, Irgacure 819 did not enhance the grafting of MMA to cellulose and PPE substrate, as compared to other photoinitiators, such as Darocur1173 and Irgacure 184.

2. Vinyl ethers as comonomers have a profound influence on the grafting of MMA to cellulose and PPE substrates with or without the presence of Irgacure 819 under the influence of a UV source and gamma radiation.

3. Vinyl ether/EP vinyl monomer mixtures have been observed to undergo spontaneous polymerization under the influence of UV radiation. The polymerization mechanism has been proposed to follow the CT complex polymerization mechanism. Polymerization rates were found to vary with strengths of vinyl ethers as electron donors and EP vinyl monomers as electron acceptors. However, the polymerization of such mixtures did not lead to any significant enhancement of grafting yields.

4. EP vinyl monomers as comonomers have influenced the UV grafting of styrene to PPE substrate to a large extent. EP vinyl monomers and styrene were found as components of grafted chains but their composition vary with styrene as well as EP vinyl monomer concentrations in the reaction mixtures. The presence of Irgacure 819 and certain solvents, such as chloroform and methanol, were found to enhance the grafting process.

5. Vinyl ethers as comonomers have also influenced UV grafting of styrene to PPE in the presence of Irgacure 819 photoinitiator. Additives, such as KI85 cationic photoinitiator, acids and CT complexes, all have shown mixed effects on enhancing grafting of styrene to PPE.
As a result of this research, the following recommendation can be made for future research.

1. Characterization of grafted substrates for the grafting of hybrid systems, such as vinyl ether/EP vinyl monomer or EP vinyl monomer/styrene mixtures to cellulose and PPE substrates, can be carried out using the Solid State NMR. This technique may give a clearer picture of chemical composition as well as structure of the grafted chains. By relating the chemical structure of the grafted chains to the composition of the reacting feed, a better understanding of grafting mechanism, as well as influencing factors can be achieved.

2. Grafting studies of vinyl ether/MMA mixtures to cellulose and PPE substrates were carried out using DMF (cellulose) or chloroform (PPE) as the solvents. A future study should expand the number of solvents used to investigate solvent polarity on grafting yields.

3. Only grafting studies of vinyl ether/EP vinyl monomer, styrene/EP vinyl monomer and styrene/vinyl ether systems to PPE have been carried out. It will be of interest to investigate the grafting of such systems onto polar substrates such as cellulose or wool in order to evaluate the contribution of substrate on grafting.
EFFECTS OF SOLVENTS AND COMONOMERS ON RADIATION CURING AND GRAFTING PROCESSES

by

DUC NGOC NGUYEN

a candidate for the degree of

DOCTOR OF PHILOSOPHY

a thesis submitted in the School of Science, Foods and Horticulture

UNIVERSITY OF WESTERN SYDNEY

June 2002
PLEASE NOTE

The greatest amount of care has been taken while scanning this thesis,

and the best possible result has been obtained.
I, Duc Ngoc Nguyen, hereby declare that the work described in this thesis has been carried out by me in the School of Science, Food and Horticulture, The University of Western Sydney.

No part of it has been submitted previously to any University or Institution for an award or postgraduate degree.

........................

3/6/03
TABLE OF CONTENTS

ACKNOWLEDGEMENTS  
AWARDS & PUBLICATIONS  
ABSTRACT  
LIST OF ABBREVIATIONS

{| Chapter | Title | Page |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Grafting as a tool for polymer fabrications</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Free radical grafting</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>Factors that influence free radical grafting process</td>
<td>4</td>
</tr>
<tr>
<td>1.3.1</td>
<td>Irradiation methods</td>
<td>4</td>
</tr>
<tr>
<td>1.3.1.1</td>
<td>UV irradiation</td>
<td>4</td>
</tr>
<tr>
<td>1.3.1.2</td>
<td>Gamma irradiation</td>
<td>5</td>
</tr>
<tr>
<td>1.3.2</td>
<td>Substrates</td>
<td>5</td>
</tr>
<tr>
<td>1.3.3</td>
<td>Monomers</td>
<td>7</td>
</tr>
<tr>
<td>1.3.4</td>
<td>Solvents</td>
<td>10</td>
</tr>
<tr>
<td>1.3.5</td>
<td>Photoinitiators</td>
<td>13</td>
</tr>
<tr>
<td>1.3.6</td>
<td>Oxygen</td>
<td>14</td>
</tr>
<tr>
<td>1.3.7</td>
<td>Additives</td>
<td>16</td>
</tr>
<tr>
<td>1.4</td>
<td>Characterization of graft copolymers</td>
<td>19</td>
</tr>
<tr>
<td>1.4.1</td>
<td>FT-IR spectroscopy</td>
<td>19</td>
</tr>
<tr>
<td>1.4.2</td>
<td>SEM</td>
<td>20</td>
</tr>
<tr>
<td>1.4.3</td>
<td>Thermal analysis</td>
<td>20</td>
</tr>
<tr>
<td>1.4.4</td>
<td>Water contact angle</td>
<td>21</td>
</tr>
<tr>
<td>1.5</td>
<td>Charge transfer complex polymerization</td>
<td>21</td>
</tr>
<tr>
<td>1.5.1</td>
<td>Charge transfer complex polymerization mechanisms</td>
<td>21</td>
</tr>
<tr>
<td>1.5.2</td>
<td>Factors that influence CT complex polymerization</td>
<td>25</td>
</tr>
<tr>
<td>1.5.2.1</td>
<td>Strengths of electron donors and acceptors</td>
<td>25</td>
</tr>
</tbody>
</table>
1.5.2.2 Presence of free radicals 26
1.5.2.3 Composition of monomer feed 26
1.5.2.4 Presence of Lewis acids 27
1.5.2.5 Presence of hydrogen donors 27

1.5.3 Grafting of charge transfer complexes to substrates 28

1.6 Aims of this project 29
1.7 References 30

CHAPTER TWO  EXPERIMENTAL

2.1 Materials 36
  2.1.1 Monomers 36
  2.1.2 Photoinitiators 39
  2.1.3 Solvents 40
  2.1.4 Substrates 40

2.2 Radiation facilities 41
  2.2.1 Ultraviolet Light Source 41
  2.2.2 Gamma Radiation Source 41

2.3 Preparations of samples 42
2.4 Extractions 42
2.5 Weighing and grafting yields calculations 43
2.6 Characterizations of grafted substrates by FT-IR spectrocopy 43
2.7 Calibration of UV source 44
  2.7.1 Calculations for UV dose rate 45
2.8 References 46

CHAPTER THREE  UV GRAFTING OF MMA TO CELLULOSE IN THE
PRESENCE OF IRGACURE 819

3.1 Introduction 47
  3.1.1 Cellulose structure 47
  3.1.2 Factors that influence the grafting of monomers on cellulose 48
  3.1.3 UV grafting of MMA onto cellulose 49
  3.1.4 Irgacure 819 photoinitiator 51
3.2 Results

3.2.1 Effects of solvents and photoinitiator concentrations on grafting of MMA to the cellulose
3.2.2 Effect of UV doses
3.2.3 Comparison between Irgacure 819 with other photoinitiators

3.3 Discussion

3.3.1 Effect of solvents on UV grafting of MMA to cellulose
3.3.2 Effects of Irgacure 819 concentrations on grafting of MMA to cellulose
3.3.3 Effects of irradiation dose on grafting of MMA to cellulose
3.3.4 Comparison between Irgacure 819 and other photoinitiators

3.4 Conclusions
3.5 References

CHAPTER FOUR
UV GRAFTING OF MMA ONTO POLYPROPYLENE IN THE PRESENCE OF IRGACURE 819

4.1 Introduction

4.1.1 PPE structure
4.1.2 UV grafting of MMA to PPE

4.2 Results

4.2.1 Effects of solvents and Irgacure 819 concentrations on MMA grafting to PPE film of thickness 0.12 mm
4.2.2 UV grafting of MMA to PPE (0.015 mm) with different solvents and 1% w/v Irgacure 819
4.2.3 UV grafting of MMA to PPE (0.015 mm) with different solvents and UV doses in the presence of 1% w/v Irgacure 819
4.2.4 UV grafting of MMA to PPE (0.12 mm) with different photoinitiators

4.3 Discussion

4.3.1 Effect of solvents on UV grafting of MMA to PPE (0.12 mm)
4.3.2 Substrate thickness effect on the grafting of MMA to PPE
4.3.3 Effect of irradiation dose on the grafting of MMA to PPE (0.015 mm)
4.3.4 Effect of Irgacure 819 photoinitiator concentrations on the grafting of MMA to PPE (0.12 mm)
CHAPTER FIVE  MMA GRAFTING TO PPE WITH VINYL ETHERS AS COMONOMERS USING UV RADIATION

5.1 Introduction
  5.1.1 Vinyl ethers
  5.1.2 Copolymerization of vinyl ethers with other vinyl monomers
  5.1.3 Vinyl ethers as electron donors in Charge Transfer complexes

5.2 Results
  5.2.1 Grafting of vinyl ethers to PPE with and without Irgacure 819 photoinitiator
  5.2.2 Grafting of MMA and vinyl ethers to PPE without Irgacure 819 photoinitiator
  5.2.3 Grafting of MMA to PPE with vinyl ethers as comonomers, with 1% w/v Irgacure 819 photoinitiator
  5.2.4 Characterization of grafted substrates by FT-IR

5.3 Discussion
  5.3.1 Solutions' polymerization without Irgacure 819 photoinitiator
  5.3.2 Grafting of MMA to PPE with vinyl ethers without Irgacure 819 photoinitiator
  5.3.3 Polymerization of MMA/vinyl ethers in the presence of Irgacure 819 photoinitiator
  5.3.4 Grafting of MMA/vinyl ethers to PPE in the presence of Irgacure 819 photoinitiator
  5.3.5 Characterizations of grafted substrates by FT-IR

5.4 Conclusions
5.5 References
CHAPTER SIX      MMA GRAFTING TO PPE WITH VINYL ETHERS AS COMONOMERS
                     USING GAMMA RADIATION

6.1 Introduction
6.1.1 Radical and cation formations by gamma irradiation

6.2 Results
6.2.1 Grafting of neat vinyl ethers to PPE by gamma irradiation
6.2.2 Grafting of MMA to PPE with vinyl ethers as comonomers
    by gamma irradiation
6.2.3 Gamma grafting of MMA to PPE with vinyl ethers as comonomers
    and chloroform as solvent
6.2.4 Effect of vinyl ether concentration on grafting of MMA to PPE
    by gamma irradiation
6.2.5 Gamma grafting of MMA to PPE with DVE-3 as a comonomer and
    with different solvent
6.2.6 FT-IR spectra of MMA/vinyl ether grafted PPE substrates

6.3 Discussion
6.3.1 Grafting of neat vinyl ethers to PPE by gamma irradiation
6.3.2 Grafting of MMA to PPE with vinyl ethers as comonomers using
    gamma irradiation
6.3.3 Gamma grafting of MMA to PPE with vinyl ethers as comonomers,
    in the presence of chloroform as a solvent
6.3.4 Effect of vinyl ethers’ molecular structures on the gamma grafting
    of MMA to PPE
6.3.5 Gamma grafting of MMA to PPE with DVE-3 as a comonomer
6.3.6 Solvent effect on gamma grafting of MMA to PPE with DVE-3
    as a comonomer
6.3.7 Characterization of grafted substrates by FT-IR
    6.3.7.1 Grafted substrates from solutions containing MMA and
        vinyl ethers other than DVE-3
    6.3.7.2 Grafted substrate from solutions containing MMA and DVE-3

6.4 Conclusions
6.5 References
CHAPTER SEVEN MMA GRAFTING TO CELLULOSE WITH VINYL ETHERS AS COMONOMERS USING UV RADIATION

7.1 Introduction
  7.1.1 Radical generation by UV irradiation without photoinitiators 122
  7.1.2 Vinyl ethers and MMA copolymerization 123
  7.1.3 Grafting of MMA to cellulose with vinyl ethers as comonomers 123

7.2 Results
  7.2.1 UV grafting of neat vinyl ethers to cellulose 124
    7.2.1.1 Without Irgacure 819 photoinitiator 124
    7.2.2.2 With 1% w/v Irgacure 819 photoinitiator 124
  7.2.2 UV grafting of MMA to cellulose with vinyl ethers as comonomers, without Irgacure 819 photoinitiator 124
    7.2.2.1 In the absence of solvents 124
    7.2.2.2 With DMF as a solvent 124
  7.2.3 UV grafting of MMA to cellulose with vinyl ethers as comonomers, with 1% w/v Irgacure 819 photoinitiator 125
    7.2.3.1 In the absence of solvents 125
    7.2.3.2 With DMF as a solvent 125
    7.2.3.3 Grafting of MMA to cellulose with EVE as a comonomer, with different solvents, with 1% w/v Irgacure 819 photoinitiator 125
  7.2.4 FT-IR characterization of MMA/vinyl ether grafted cellulose substrates 126

7.3 Discussion
  7.3.1 UV grafting of neat vinyl ethers to cellulose with and without Irgacure 819 138
  7.3.2 UV grafting of MMA to cellulose with vinyl ethers as comonomers, in the absence of solvents and Irgacure 819 photoinitiator 138
  7.3.3 UV grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent, without Irgacure 819 photoinitiator 139
  7.3.4 UV grafting of MMA to cellulose with vinyl ethers as comonomers, in the absence of solvents, with 1% w/v Irgacure 819 photoinitiator 141
  7.3.5 UV grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent, with 1% w/v Irgacure 819 photoinitiator 141
7.3.6 Effect of solvents on grafting of MMA to cellulose with EVE as a comonomer, with 1% w/v Irgacure 819 photoinitiator
7.3.7 Characterization of grafted substrates using the FT-IR spectroscopy
7.4 Conclusions
7.5 References

CHAPTER EIGHT  MMA GRAFTING TO CELLULOSE WITH VINYL ETHERS AS COMONOMERS USING GAMMA RADIATION

8.1 Introduction
  8.1.1 Radical generations in cellulose by gamma irradiation
  8.1.2 Radical generation in monomers by gamma irradiation
8.2 Results
  8.2.1 Grafting of neat vinyl ethers to cellulose by gamma irradiation
  8.2.2 Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, in the absence of solvents
  8.2.3 Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent
  8.2.4 Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, without any solvent
  8.2.5 Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, with different solvents
  8.2.6 FT-IR characterization of a MMA/DVE-3 grafted substrate
8.3 Discussion
  8.3.1 Grafting of neat vinyl ethers to cellulose by gamma irradiation
  8.3.2 Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, without any solvents
  8.3.3 Gamma grafting of MMA to cellulose with vinyl ethers as comonomers, with DMF as a solvent
  8.3.4 Gamma grafting of MMA to cellulose with DVE-3 as a comonomer, without any solvents
  8.3.5 Solvent type effect to gamma grafting of MMA to cellulose with DVE-3 as a comonomer
8.3.6 Characterization of the grafted substrate using the FT-IR spectroscopy

8.4 Conclusions

8.5 References

CHAPTER NINE GRAFTING OF DIFFERENT DONOR/ACCEPTOR PAIRS TO PPE USING UV RADIATION

9.1 Introduction

9.2 Results

9.2.1 UV grafting of vinyl monomers to PPE with or without Irgacure 819 photoinitiator

9.2.1.1 Without Irgacure 819 photoinitiator

9.2.1.2 With 1% w/v of Irgacure 819 photoinitiator

9.2.2 UV grafting of different electron poor vinyl monomer/DVE-3 DA pairs to PPE without Irgacure 819 photoinitiator

9.2.3 UV grafting of different EP vinyl monomer/DVE-3 systems to PPE with Irgacure 819 photoinitiator

9.2.4 UV grafting of MAC to PPE substrates with NBVE and TMPTVE as electron donors, with or without Irgacure 819 photoinitiator

9.2.4.1 Without Irgacure 819 photoinitiator

9.2.4.2 With 0.2% w/v of Irgacure 819 photoinitiator

9.2.5 UV grafting of AN to PPE substrates with NBVE and TMPTVE as electron donors, with or without Irgacure 819 photoinitiator

9.2.5.1 Without Irgacure 819 photoinitiator

9.2.5.2 With 0.2% w/v of Irgacure 819 photoinitiator

9.2.6 UV grafting of DMMA to PPE substrates with different vinyl ethers, without Irgacure 819 photoinitiator

9.3 Discussion

9.3.1 Polymerization of different DA pairs of vinyl monomers and DVE-3

9.3.1.1 Homopolymerizations of vinyl monomers by UV lights with and without Irgacure 819 photoinitiator

9.3.1.2 DA pair polymerization by UV irradiation without Irgacure 819 photoinitiator
9.3.1.2.1 MA and DVE-3 185
9.3.1.2.2 DMMA and DVE-3 185
9.3.1.2.3 AN and DVE-3 186
9.3.1.2.4 AA and DVE-3 186
9.3.1.2.5 MAC and DVE-3 187
9.3.1.2.6 BMA and DVE-3 187
9.3.1.2.7 MMA and DVE-3 187
9.3.1.3 Polymerization mechanisms of DA pairs of EP vinyl monomers and DVE-3 188
9.3.1.4 CT complex polymerization by UV irradiation with Irgacure 819 photoinitiator 189
9.1.3.4.1 MA and DVE-3 with 0.2% w/v Irgacure 819 190
9.1.3.4.2 DMMA and DVE-3 with 0.2% w/v Irgacure 819 190
9.3.1.4.3 AN and DVE-3 with 0.2% w/v Irgacure 819 190
9.3.1.4.4 AA and DVE-3 with 0.2% w/v Irgacure 819 photoinitiator 191
9.1.3.4.5 MAC and DVE-3 with 0.2% w/v Irgacure 819 191
9.1.3.4.6 BMA, MMA and DVE-3 with 1% w/v Irgacure 819 192

9.3.2 Grafting of EP vinyl monomers to PPE with DVE-3 as a comonomer 194
9.3.2.1 UV grafting of EP vinyl monomers to PPE with DVE-3 as a comonomer without Irgacure 819 photoinitiator 194
9.3.2.2 UV grafting of EP vinyl monomers to PPE with DVE-3 as a comonomer, with Irgacure 819 photoinitiator 195

9.3.3 Polymerization of charge transfer complex systems of MAC, AN with NBVE and TMPTVE by UV irradiation 196
9.3.3.1 Polymerization of charge transfer complex systems of MAC with NBVE and TMPTVE without Irgacure 819 photoinitiator 196
9.3.3.2 Polymerization of charge transfer complex systems of AN with NBVE and TMPTVE without Irgacure 819 photoinitiator 197
9.3.3.3 UV polymerization of charge transfer complex systems of MAC with NBVE and TMPTVE, with Irgacure 819 photoinitiator 197
9.3.3.4 UV polymerization of charge transfer complex system of AN with NBVE and TMPTVE, with Irgacure 819 photoinitiator 198
9.3.3.5 Comparisons between NBVE, DVE-3 and TMPTVE as electron donors 198
9.3.3.6 Effect of chain lengths in vinyl ethers

9.3.4 UV grafting of charge transfer complex systems of MAC, AN with NBVE, TMPTVE to PPE

9.3.4.1 UV grafting of MAC to PPE with NBVE and TMPTVE as comonomers without Irgacure 819 photoinitiator

9.3.4.2 UV grafting of MAC to PPE with NBVE and TMPTVE as comonomers, with 0.2% w/v of Irgacure 819

9.3.4.3 UV grafting of AN to PPE with NBVE and TMPTVE as comonomers without Irgacure 819 photoinitiator

9.3.4.4 UV grafting of AN to PPE with NBVE and TMPTVE as comonomers, with 0.2% w/v of Irgacure 819 photoinitiator

9.3.4.5 UV grafting of DMMA to PPE with different vinyl ethers as comonomers, without the presence of Irgacure 819 photoinitiator

9.4 Conclusions

9.5 References

CHAPTER TEN

UV GRAFTING OF STYRENE TO PPE WITH DIFFERENT ELECTRON POOR (EP) VINYL MONOMERS AS COMONOMERS

10.1 Introduction

10.1.1 Styrene as a weak electron donor

10.1.2 UV grafting of styrene to PPE substrates

10.2 Results

10.2.1 UV grafting of neat styrene to PPE substrates with or without Irgacure 819 photoinitiator, with various solvents
  10.2.1.1 Without photoinitiators
  10.2.1.2 With 1% w/v Irgacure 819 photoinitiator
  10.2.1.3 FT-IR characterization of styrene grafted substrates

10.2.2 UV grafting of MA/styrene CT complex to PPE substrates with or without Irgacure 819 photoinitiator
  10.2.2.1 Without photoinitiators
  10.2.2.2 With 0.2% w/v Irgacure 819 photoinitiator
  10.2.2.3 FT-IR characterization of MA/styrene grafted substrates
10.2.3 UV grafting of styrene to PPE in the presence of electron poor (EP) vinyl monomers, MMA, MAC, AN, DMMA and AA, without photoinitiators

10.2.4 UV grafting of styrene to PPE in the presence of EP vinyl monomers and Irgacure 819 photoinitiator

10.2.5 UV grafting of styrene to PPE in the presence of MMA and AN, with different solvents and in the absence of Irgacure 819 photoinitiator

10.2.6 UV grafting of styrene to PPE in the presence of MMA, AN, MAC and AA and Irgacure 819 and with different solvents

10.3 Discussion

10.3.1 UV grafting of styrene to PPE
   10.3.1.1 Without Irgacure 819 photoinitiator, in solvents, chloroform, DMF and methanol

10.3.1.2 With Irgacure 819 photoinitiator, in solvents, chloroform, DMF and methanol

10.3.1.3 Characterization of grafted substrates by FT-IR

10.3.2 UV grafting of styrene to PPE with MA as a comonomer
   10.3.2.1 UV polymerization of MA/styrene solutions
      10.3.2.1.1 UV polymerization of MA/styrene solutions without photoinitiator
      10.3.2.1.2 UV polymerization of MA/styrene solutions with Irgacure 819 photoinitiator
      10.3.2.1.3 Mechanism of MA/styrene CT complex polymerization

10.3.2.2 UV grafting of MA/styrene complexes to PPE
   10.3.2.2.1 UV grafting of MA/styrene complexes to PPE without Irgacure 819 photoinitiator
   10.3.2.2.2 UV grafting of MA/styrene complexes to PPE with Irgacure 819 photoinitiator

10.3.3 UV grafting of styrene to PPE in the presence of various EP vinyl monomers
   10.3.3.1 UV grafting of styrene to PPE in the presence of various EP vinyl monomers as comonomers, without Irgacure 819 photoinitiator
      10.3.3.1.1 MMA and styrene
      10.3.3.1.2 MAC and styrene
      10.3.3.1.3 AN and styrene
10.3.3.2 UV grafting of styrene to PPE in the presence of various EP vinyl monomers and Irgacure 819 photoinitiator

10.3.3.2.1 MMA and styrene

10.3.3.2.2 MAC and styrene

10.3.3.2.3 AN and styrene

10.3.3.2.4 DMMA and styrene

10.3.3.2.5 AA and styrene

10.3.3.3 Effects of solvents on the grafting of styrene and vinyls to PPE

10.3.3.3.1 Without Irgacure 819 photoinitiator

i) MMA/styrene with 20% v/v of chloroform, DMF and methanol

ii) AN/styrene with 20% v/v of chloroform, DMF and methanol

10.3.3.3.2 With Irgacure 819 photoinitiator

i) MMA/styrene with 20% v/v of chloroform, DMF and methanol

ii) AN and styrene with 20% v/v of chloroform, DMF and methanol

iii) MAC/styrene with 20% v/v of chloroform, DMF and methanol

iv) AA/styrene with 20% v/v of chloroform, DMF and methanol

10.3.3.3.3 Further discussion on the effect of solvents on the grafting of EP vinyl monomer/styrene systems to PPE substrates

10.4 Conclusions

10.5 References

CHAPTER ELEVEN UV GRAFTING OF STYRENE TO PPE IN THE PRESENCE OF ADDITIVES

Part A: Effect of cationic photoinitiator on UV grafting of styrene to PPE with vinyl ethers as comonomers
11.1 Introduction

11.2 Results

11.2.1 UV grafting of vinyl ethers to PPE substrates with 1% w/v of KI85

11.2.2 UV grafting of styrene to PPE with vinyl ethers as comonomers, with or without Irgacure 819 photoinitiator, with or without KI85

11.2.2.1 Styrene/DVE-3 system

11.2.2.2 With other monofunctional or multifunctional vinyl ethers

11.3 Discussion

11.3.1 UV polymerization and grafting of neat vinyl ethers to PPE with KI85 cationic photoinitiator

11.3.2 Effects of cationic photoinitiator and vinyl ethers on grafting of styrene by UV radiation

11.3.2.1 Effects of DVE-3 and KI85

11.3.2.1.1 Styrene and DVE-3, without Pls or Cls

11.3.2.1.2 Styrene and DVE-3 with Irgacure 819 photoinitiator

11.3.2.1.3 Styrene and DVE-3 with Irgacure 819 and cationic photoinitiator

11.3.2.2 UV grafting of styrene to PPE with vinyl ethers as comonomers, with Irgacure 819 photoinitiator, with or without KI85 cationic photoinitiator

11.4 Conclusions

Part B: Effects of acids on UV grafting of styrene to PPE with vinyl ethers as comonomers

11.5 Introduction

11.6 Results

11.6.1 UV polymerization of vinyl ethers and their grafting to PPE with acids as additives

11.6.2 UV grafting of styrene to PPE in the presence of 1% w/v Irgacure 819, with or without methanol as a solvent, with acids as additives
11.6.3 UV grafting of styrene to PPE with vinyl ethers as comonomers, with 1% w/v Irgacure 819, with acids as additives

11.6.3.1 Styrene/vinyl ether with 1% w/v of 0.2 M H₂SO₄

11.6.3.2 Styrene/vinyl ether in the presence of 1% w/v of 2 M HCl, HNO₃ and H₃PO₄

11.7 Discussion

11.7.1 Polymerization of vinyl ethers in the presence of acids, in the absence of photoinitiators

11.7.2 Effects of acids on UV grafting of styrene to PPE in the presence of 1% w/v Irgacure 819

11.7.2.1 Without methanol as a solvent

11.7.2.2 With 20% v/v of methanol as a solvent

11.7.3 Effects of acids and vinyl ethers on UV grafting of styrene to PPE with 1% w/v Irgacure 819

11.7.3.1 Effect of sulfuric acid and vinyl ethers on UV grafting of styrene to PPE with 1% w/v Irgacure 819

11.7.3.2 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with DVE-3 as a comonomer, with 1% w/v Irgacure 819 photoinitiator

11.7.3.3 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with EVE as a comonomer, with 1% w/v Irgacure 819

11.7.3.4 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with HDVE as a comonomer, with 1% w/v Irgacure 819

11.7.3.5 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with TMPTVE as a comonomer, with 1% w/v Irgacure 819

11.7.3.6 Effects of HCl, HNO₃ and H₃PO₄ on UV grafting of styrene to PPE with DEAEVE as a comonomer, with 1% w/v Irgacure 819

11.8 Conclusions

Part C: Effects of charge transfer complexes as additives on UV grafting of styrene to PPE in the presence of Irgacure 819

11.9 Introduction

11.10 Results
11.10.1 UV grafting of styrene to PPE substrates with different CT complexes as additives and Irgacure 819 photoinitiator 290
11.12.2 FT-IR characterization of grafted substrates 291
11.11 Discussion 301
  11.11.1 Effects of CT complex systems as additives on UV grafting of styrene to PPE with 1% w/v Irgacure 819 301
  11.11.2 Characterizations of grafted substrates 301
11.12 Conclusions 303
11.13 References 303

CHAPTER TWELVE CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH 306
ACKNOWLEDGEMENTS

The author wishes to express his thanks to a long line of people who have helped him towards the completion of this work. Their advice and material help has made a tedious road bearable.

First of all, the author would like to thank Dr Loo-Teck Ng for her guidance, patience and invaluable help. He wishes to thank Associate Professor J. L. Garnett for his advice and some chemicals used in this project, and Professor S. Adelooju for his help in getting this excellent scholarship (OPRS).

To academic and technical staff for the setting up of equipment and purchasing of chemicals and fellow students for their encouragement.

Above all, the author is indebted to his mum, dad, brothers and sisters, and especially his loving wife for the love, encouragement and support that he has received.
AWARD
Overseas Postgraduate Research Scholarship (OPRS) 1998, The University of Western Sydney, Nepean, Australia

PUBLICATIONS
Duc Nguyen, Loo-Teck Ng, Samuel Adeloju, Effects of solvents and comonomers on grafting of MMA to polypropylene and cellulose in the presence of a UV source (in preparation).


CONFERENCE PRESENTATIONS

ABSTRACT

A study has been made on the irradiation induced grafting of MMA to PPE and cellulose substrates in the presence of various solvents and Irgacure 819 photoinitiator, a new photoinitiator on the market at the commencement of this project. UV is the main irradiation source used. The grafting yields have been found to vary with parameters such as the substrate types and thickness, MMA concentration, solvents used, Irgacure 819 concentration and UV doses. For the cellulose substrate, good grafting yields were obtained only when solvents such as methanol and DMF were used. On the contrary, MMA could graft to PPE with or without solvents, although high grafting yields were achieved in the presence of methanol, DMF and other chlorinated solvents. The solvent effects on the grafting process of MMA to PPE and cellulose substrates were attributed to the wetting and swelling effects by the solvents as well as the Trommsdorff effect. During the course of this study, a comparison in the performance between Irgacure 819 and other photoinitiators (PIs) was also carried out.

Effects of vinyl ethers as comonomers on MMA grafting to PPE and cellulose substrates under the influence of UV or gamma radiation were investigated with or without the presence of Irgacure 819. In all cases, neat vinyl ethers were found not to undergo free radical polymerization irrespective of irradiation methods. However, when being used as comonomers with MMA, they have profound effect on polymerization and grafting processes. The inclusion of di-vinyl ethers such as ethylene glycol divinyl ether (DVE), tri(ethylene glycol) divinyl ether (DVE-3), tetra(ethylene glycol) divinyl ether and hexanediol divinyl ether (HDVE) or a tri-functional vinyl ether, trimethylolpropane trivinyl ether (TMPTVE) led to more rapid polymerization rates and higher grafting yields than the other monofunctional vinyl ethers such as ethyl vinyl ether (EVE), propyl vinyl ether (PVE), n-, iso-, tert-butyl vinyl ethers (NBVE, IBVE and NBVE), 2-(diethylamino) ethanol vinyl ether (DEAEVE) and 2-ethyl hexyl vinyl ether (EHVE) under study. The difference in performance between multifunctional vinyl ethers and monofunctional vinyl ethers on grafting was mainly attributed to the ability of the multifunctional ones forming cross-linking thus causing branching of grafted chains.
However, in some cases, polymerization of solutions containing multifunction vinyl ethers rapidly occurred, resulting in lower grafting yields. Analysis of the grafted substrates using the FT-IR spectroscopy technique showed that MMA was the main component present in the grafted substrates.

The spontaneous polymerization initiated by Charge-Transfer (CT) complex systems containing vinyl ethers as electron donors and electron poor (EP) vinyl monomers including maleic anhydride (MA), dimethyl maleate (DMMA), acrylonitrile (AN), acrylic acid (AA), methyl acrylate (MAC), butyl methacrylate (BMA) and methyl methacrylate (MMA), as acceptors under the influence of UV radiation was investigated with or without Irgacure 819 photoinitiator. Based on the required UV doses for vinyl ether/EP vinyl monomer mixtures to polymerize, strengths of vinyl ethers as electron donors and vinyl monomers as electron acceptors were deduced. A mechanism was also proposed which relates the spontaneous polymerization of vinyl ether/EP vinyl monomer mixtures to the formation of radicals and cationic species under the influence of UV radiation. However, in most cases, only low grafting yields of such systems to PPE substrate were achieved with or without the presence of Irgacure 819 photoinitiator. The exceptions were in the cases of BMA and MMA which resulted in good grafting yields especially with the presence of Irgacure 819. The phenomenon was attributed to the reactivity of these two EP vinyl monomers and their corresponding CT complexes formed with vinyl ethers towards free radicals.

A study was made of the UV radiation induced grafting of styrene to PPE substrate with EP vinyl monomers and vinyl ethers as comonomers. The possibility of spontaneous polymerization of styrene/EP vinyl monomer mixtures under the influence of UV radiation was also investigated. Grafting yields were found to vary with the comonomer types and their concentrations, the presence or absence of solvents and additives such as Irgacure 819 photoinitiator, KI85 cationic photoinitiator, mineral acids and CT complexes. In addition, the composition of grafted substrates was studied by using the FT-IR spectroscopy technique.
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AA</td>
<td>Acrylic acid</td>
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<tr>
<td>AN</td>
<td>Acrylonitrile</td>
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<td>BMA</td>
<td>Butyl methacrylate</td>
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<tr>
<td>DMFA</td>
<td>Dimethyl fumarate</td>
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<td>DMMA</td>
<td>Dimethyl maleate</td>
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<tr>
<td>EMI</td>
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<td>MA</td>
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<td>MMA</td>
<td>Methyl methacrylate</td>
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<td>CHVE</td>
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<tr>
<td>TMPTVE</td>
<td>Trimethylolpropane trivinyl ether</td>
</tr>
<tr>
<td>TBVE</td>
<td>Tert-butyl vinyl ether</td>
</tr>
<tr>
<td>CI</td>
<td>Cationic photoinitiator</td>
</tr>
<tr>
<td>DBMR</td>
<td>Double bond molar ratio</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>EP</td>
<td>Electron poor</td>
</tr>
<tr>
<td>PI</td>
<td>Free radical photoinitiator</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>PPE</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
</tbody>
</table>