Radical-Mediated Modification of Polyolefins: Investigation of the Synthesis of Graft Copolymers

by

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Abstract

A range of strategies exist for the production of polyolefin block copolymers with well-defined morphologies for the compatibilization of immiscible blends; however, high sensitivity to impurities and use of expensive transition-metal catalysts limit their economic viability. An alternative method is the solvent-free coupling of dislike polymers using peroxides and multifunctional coagents. This technique, however, does not distinguish between a blend of gelled homopolymers and the intended copolymer. The use of a solution-based approach, like the one described in this report, for the radical-mediated coupling of polyolefins with dislike polymers allows for the full characterization of the copolymer without the formation of gel.

A one- and two-step synthesis for the coupling of two homopolymers in solution is demonstrated using triallyl trimesate. The one-step approach produced a copolymer in low yields due to the differences in reactivity between the homopolymers. The two-step synthesis consisted of the solvent-free grafting of the coagent to the less reactive polymer, followed by coupling in solution with the other polymer. Though this technique demonstrated improved yields over that of the one-step approach, the overall yields were limited due to the dilution effects of the high solvent levels needed for comiscibility. The coupling of polyethylene with poly(ethylene oxide) had

a maximum graft yield of 9.5%, whereas the coupling between polypropylene and a thermoplastic polyolefin elastomer was negligible.

It was found that the grafting of allylic ester coagents to polyethylene results in an uneven graft distribution. Given enough peroxide and coagent, the material will reach its gel point where there is a small, high molecular weight population with a disproportionately high graft content, while the remaining chains contained a modest concentration of bound coagent. Furthermore, a survey of the effectiveness of several common coagents in the radical-mediated crosslinking of polyethylene was investigated where it was found that allylic coagents had a greater contribution to the crosslink density of the resin than vinyl coagents.

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Chapter 1

Introduction

1.1 Motivation

The production of compatible polymer blends is motivated by the economic advantages in producing a material that meets the customers' specifications at a lower cost. This can be achieved by diluting expensive engineering plastics with less expensive resins, by generating high performance blends whose components have synergistic properties, and by the recycling of plastic waste [1]. However, when blended, most polymers are immiscible and the resulting blend will have physical properties that are worse than their components.

When two immiscible polymers are blended, a heterogenous product is formed whose morphology will depend on interfacial tensions and accompanying interfacial adhesion. High interfacial tension leads to a lack of stability at the interface and gross separation during processing or use, while poor adhesion leads to brittle mechanical

behavior in the blend, whose mechanical properties become worse than that of the individual components [2]. Block copolymers that are miscible, but not necessarily of similar composition, with each phase in the blend are known to mitigate interfacial instability and improve the mechanical properties of the blend. This property of copolymers is due to their propensity to segregate completely into the two phases and thereby lowering the interfacial tension and improving adhesion between the two phases [3, 4].

1.2 Polyolefin Block Copolymer Synthesis

Polyolefins, which include the different grades of polyethylene and polypropylene have great commercial value. In 2006, polyethylene and polypropylene made up for 69% of the tonnage of thermoplastics produced in the United States and Canada [5]. Polyolefins are inexpensive materials that combine excellent chemical resistance with good mechanical properties and ease of processability [6]. However, they lack reactive or polar functionality which limits their potential for adhesion, dyeability, paintability or compatibility with other polymers. Blending polyolefins with polymers that contain these desired properties is a possible route to improving the end properties of the polyolefin resins; however, most blends of polyolefins and polar polymers are completely immiscible. Therefore a block copolymer is needed to stabilize the desired blend and allow for the production of polyolefin blends possessing these additional desired properties.

1.3 Block Copolymer Synthesis

Many different methods of producing block copolymers have been reported in the literature, but most of them fall into one of three categories: The sequential living polymerization of the component monomers, the polymerization of a new block onto a previously produced polymer and coupling of two post-production homopolymers.

The most common method for the synthesis of block copolymers involves living polymerization. Living polymers are defined as those that retain their ability to propagate in the absence of additional monomer by virtue of their negligible rates of termination and chain transfer [7]. This limited degree of termination allows for the sequential addition of monomers to form multiblock copolymers with well defined molecular structures. Several different methods of producing living diblock copolymers include anionic [8], cationic [9], group transfer [10], ring-opening metathesis [11] and controlled radical based approaches. Despite the exceptional control over the macromolecular structures of the block copolymers produced by these methods, they are limited by their incompatibility with olefinic monomers and their high sensitivity towards impurities.

1.4 Living Olefin Block Copolymers

Notwithstanding the availability of block copolymerization techniques, only recently has living techniques been developed for the synthesis of copolymers containing

olefinic blocks. Olefinic monomers are incompatible with most living systems, limiting their polymerization to metallocene catalysis. The first AB block copolymer that contained an olefinic and a polar block was a propylene-*b*-tetrahydrofuran copolymer synthesized by Doi et al. [12] in 1983. This was accomplished using a soluble Ziegler vanadium catalyst with $Al(C_2H_5)_2Cl$ in toluene at -78°C. Progress in the synthesis of polyolefin block copolymers containing polar blocks has been recently reviewed by Domski et al. [13]. The catalysts used in the living insertion polymerization techniques are derived from group 3, 5, 10 or lanthanide transition metals. These catalysts for the living polymerization of olefins have yielded a wide range of block copolymers with polar groups. However, the economic feasibility of this technology is limited by the stoichiometric formation of one polymer chain per metal complex, many of which are quite complex and expensive, and the low operating temperatures of the reactions [14].

Recently, another approach to the production of olefin block copolymers was chain shuttling polymerization. Arriola et al. [15] used this technique to produce an ethylene-octene multiblock copolymer with a narrow molecular weight distribution. The process uses two catalysts, which show high selectivity for each of the monomers and a chain shuttling agent (CSA) such as, diethylzinc. In the beginning of the reaction, each monomer polymerizes on its respective catalyst. After some period of time, one of the chains will transfer to the CSA. The polymer chain that is dormant on the CSA is then transferred to the other catalyst thereby adding onto the other polymer chain. This exchange of oligomers between the catalysts is responsible for the formation of the block configuration and is controlled by the CSA concentration in the reaction. By increasing the concentration of the CSA, the number of blocks on the

copolymer chain can be increased. This process has been demonstrated to produce multiblock copolymers with a statistical distribution of block lengths and number of blocks per chain. Furthermore this process has been demonstrated to possess greater efficiency as a continuous process, whereas living olefin polymerizations have only been demonstrated as batch processes. Despite the catalytic nature of the system, the reaction is stoichiometric with respect to the CSA. Though this process demonstrated the successful production of olefin multiblock copolymers, this process has yet to be demonstrated, and is most likely incompatible, for producing polar blocks. In order to accommodate the incorporation of polar monomers, the diethylzinc CSA needs to be replaced due to its electrophilic nature and the tendency for polar monomers to bind to the zinc center.

1.5 Two-Step Block Copolymer Syntheses

Given the limitations of the synthesis of pololefin block copolymers via living polymerization techniques, alternative approaches have been investigated. In the following sections, the formation of diblock copolymers containing polar blocks shall be discussed where the two blocks were polymerized using different mechanisms.

1.5.1 Use of Terminal Borane Groups for the Synthesis of Polyolefin Block Copolymers

Chung [16] has developed a versatile method for the production of diblock copolymers by introducing a terminal 9-borabicyclo-nonane functional group in the metallocene

polymerization of polyolefins. The reaction scheme for the introduction and use of the borane functionality can be seen in figure 1.1. The terminal borane group can
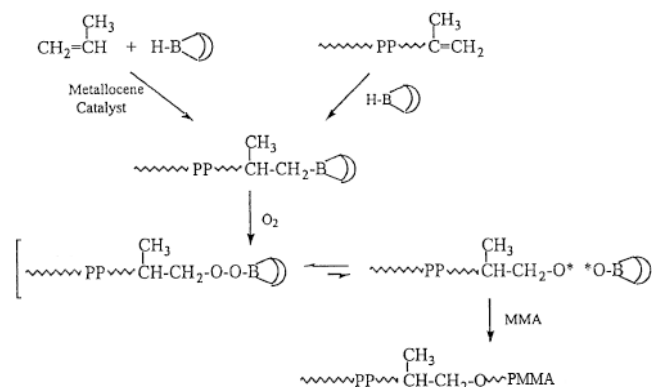
Figure 1.1: Reaction scheme for the use of terminal borane groups for the production of polyolefin block copolymers with polar blocks [16]

either be introduced to the polyolefin through an *in situ* chain transfer reaction to the B-H group during metallocene polymerization, or by hydroboration of chain-end unsaturation in the polymer. The attached borane group is spontaneously oxidized to form peroxyborane. The attached peroxyborane then decomposes at ambient temperatures to produce an alkoxy and a more stable borinate radical. The dissociation of the borinate radical followed by addition of monomer is believed to follow a reaction mechanism similar to that of nitroxide-mediated controlled radical polymerization. This approach has proved to be an effective means of synthesizing diblock copolymers containing both polyolefin and polar blocks with narrow molecular weight distributions [17]. This approach to copolymer synthesis has been extended to other functional blocks including ethyl methacrylate, vinyl acrylate, butyl acrylate, styrene [18] and ethylene oxide [19].

1.5.2 Alternative Two-Step Block Copolymer Syntheses

Similar to the diblock copolymer formation presented in section 1.5, Allgaier et al. [20] has introduced a method of producing polyolefin block copolymers with narrow molecular weight distributions and containing polar blocks. Isoprene was initially polymerized via anionic polymerization and terminated with an excess of ethylene oxide to form polyisoprene-OH with a predominantly 1,4-structure. The hydroxyl group was then deprotonated to form a macroinitiator for the polymerization of ethylene oxide. The polyisoprene macroinitiator was also hydrogenated to produce poly(ethylene-*co*-propylene) and then further polymerized with ethylene oxide. Despite the formation of a polyolefin diblock copolymer with a very narrow molecular weight distribution (PDI = 1.02), this technique is limited to monomers that polymerize via anionic techniques. Furthermore, due to the use of anionic techniques, the system is highly intolerant to impurities and oxygen.

Matyjaszewski et al. [21] polymerized atactic polypropylene to low molecular weight with nearly stoichiometric vinyl termination of each chain using a zirconocene/methyl aluminoxane cocatalyst system. 2-Bromoisobutyrate was attached to the terminal vinyl groups of the polypropylene via hydrosilation reactions. This functionalized PP then served as a macroinitiator for the block copolymerization of methyl methacrylate and *n*-butyl acrylate via atom transfer radical polymerization (ATRP). Though this technique successfully demonstrates the synthesis of polyolefin block copolymers with acrylic blocks, the copolymers produced were of a low molecular weight. In order to produce a polypropylene with high vinyl content, a "poor" catalyst that favors β-methyl over β-hydride termination is needed, however the latter impedes the catalyst

from polymerizing propylene to high molecular weights or crystallinity. Furthermore, the conversion of the polypropylene into a macroinitiator for ATRP polymerization required several synthetic steps, most of which were sensitive to moisture and oxygen.

A technique similar to Mahajan et al. [22] was used by Jankova et al. [23] where a commercial poly(ethylene-*co*-butylene) resin with hydroxyl functionality was used as a macroinitiator in the copolymerization with styrene and 4-acetoxystyrene. The hydroxyl group was esterified with 2-bromopropionic chloride and polymerized with styrene and 4-acetoxystyrene by ATRP. The block copolymer was also hydrolyzed to form poly(ethylene-*co*-butylene)-*block*-poly(hydroxystyrene). The commercial starting material was not completely characterized and it is unclear if all the hydroxyl groups are terminal or not. The possible presence of internal hydroxyl groups would give the copolymer a graft configuration over that of a block, thereby significantly altering its mechanical properties. De Brouwer et al. [24] used the same commercial resin to produce polyolefin block copolymers with polystyrene and poly(styrene-*co*-maleic anhydride) blocks via reversible addition-fragmentation chain transfer polymerization (RAFT). In this case, RAFT was used over ATRP due its greater tolerance for functional monomers.

Controlled/living radical and anionic polymerization techniques offer a wide range of polymers with great control over their macromolecular structures. However, many of these techniques are highly sensitive to impurities thereby requiring rigorous experimental procedures. Furthermore, most of these approaches are conducted in solution which requires expensive purification and disposal. Due to these economic constraints, the above methods for production of block copolymers are not economically viable at

the present time.

1.6 Coupling of Graft Copolymers

An alternative to the direct synthesis of block copolymers is the coupling of two post-polymerization polymers. Datta and Lohse [25] coupled a commercial grade of succinic anhydride functionalized polypropylene with a primary amine functionalized ethylene-propylene copolymer. The polypropylene resin was produced by the free-radical grafting of maleic anhydride to polypropylene resulting in a polymer with an average of 5 succinic anhydride groups per chain. The ethylene-propylene copolymer was made by incorporating 5-(methylamino)-2-norbornene during polymerization. This resulted in a polymer with an average of 3-5 amine groups per chain. These two polymers were then coupled in a batch mixer and then successfully used as a blend compatibilizer. This technique is limited to systems where the amine can be incorporated during polymerization and does not allow for the modification of post-polymerization resins, like the grafting of maleic anhydride. Furthermore, this technique did not allow for strict control over the number of grafts per chain or the copolymer morphology.

Hallden and Wesslen [26] coupled commercial grades of poly(ethylene-*co*-acrylic acid) with poly(ethylene oxide) monomethyl ether via an esterification reaction. The poly(ethylene-*g*-ethylene oxide) copolymer was used as an effective compatibilizing agent in LDPE and polyamide-6 blends [27]. Though this technique proved to be experimentally simple, this approach is limited in its applicability to other polymers. As well, due to the random location of the acrylic acid groups along the polymer

backbone, there is little control over the morphology or the number of grafts per chain in the copolymer.

In order to broaden the range of materials amenable to block copolymer synthesis, a free-radical grafting approach is necessary wherein the choice of polymer blocks are only limited by their reactivity towards hydrogen abstraction. As well, most free-radical coupling reactions can be conducted in the melt phase, thereby eliminating the costly and toxic effects of organic solvents. This idea forms the basis for the field of reactive blend compatibilization.

1.7   Reactive Blend Compatibilization

Despite the significant progress in the synthesis of block copolymers containing olefin and polar blocks, there remains a lack of economically viable routes for the synthesis of copolymers for commercial use as compatiblizers. Furthermore, the use of pre-formed compatibilizers is limited due to long diffusion times in the blend and micelle formation, thus requiring large amounts of compatibilizers [28]. An alternative to the synthesis of well-defined block copolymers is the *in situ* formation of copolymers within solvent-free blends. This technique is believed to produce copolymers that during formation locate preferentially at the interface between the two phases of the blend, thereby reducing the size of the dispersed phase and improving the interfacial adhesion between phases [29]. This is reported to have been accomplished simply by the addition of peroxides to a blend of polypropylene and low density polyethylene [30, 31].

Yu et al. [31] started with a high molecular weight polypropylene and a low molecular weight polyethylene in an attempt to bring the materials to comparable viscosities, thereby improving dispersability. There is a suggestion that covalent bonding between the two macroradicals across the interface occurs and the formation of graft copolymers is responsible for improved blend dispersion, yet there is no direct evidence of this occurring. This is demonstrative of the lack of commercial single-step compatibilization processes due to the tendency of the dispersed agent to act within the individual phases and not act across the interface. Due to the incompatibility of the two polymers, the dispersed phase tends to have large droplet sizes. These large droplets decrease the surface area between the two phases and decrease the statistical likelihood that the two macroradicals would encounter each other at the interface as opposed to in their individual phases.

Another common industrial approach is the functionalization of one polymer such that it is reactive toward functionality present in the other blend component. A leading example is the free-radical grafting of maleic anhydride (MAH) onto polyolefins for toughening polyamide blends. Polyamides (PA) are valued for their high strength and modulus, good chemical and abrasion resistance, high melting point, low coefficient of friction and toughness. However at low temperatures, PAs can be brittle [32]. As early as 1965 [33], it was reported that blending ethylene-methacrylic acid copolymers with PA-6.6 improved the toughness of the resin.

Lambla and Seadan [32] looked at the single-step reactive blending of low density polyethylene with polyamide-11 in the presence of maleic anhydride and organic peroxides. They found that 44% of the 80:20 blend of LDPE and PA that was reacted with MAH and peroxide was insoluble in refluxing xylenes and dimethyl formamide

(DMF). By extracting with xylenes and DMF, the copolymer would remain insoluble due to the combined solubilities of the two polymers. The method of grafting and crosslinking is believed to occur via two routes: the combination of the two macroradicals due to hydrogen abstraction at the interface and the reaction of terminal amine groups in the PA with the LDPE-g-MAH. The former mechanism is similar to that of Yu et al. [31] where the copolymer formation is reliant on encounters of the two macroradicals at the interface. As previously argued, this is an inefficient method of copolymer formation due to the limited surface area between the two phases. The latter mechanism relies on the grafting of MAH and the subsequent coupling with the terminal amine or internal imide of the polyamide. This is believed to be inefficient as well due to the poor solubility of MAH in LDPE and the likelihood that the unbound MAH would accumulate in the PA phase during blending due to its greater polarity.

Though Lambla and Seadan [32] report the formation of copolymer, the study does not distinguish between the formation of copolymer and the formation of gel. Due to the crosslinking in the individual phases of the blend, a significant amount of crosslinked material would have reached its gel point and remain insoluble during extraction. This gel formation would give false evidence of copolymer formation due to the presence of both polymers after extraction. Despite the economic benefits of grafting MAH and forming copolymers *in situ*, a more efficient use of the valuable reagents would be accomplished in a two-step approach.

1.7.1 Free-Radical Grafting of Maleic Anhydride for Subsequent Use as a Blend Compatibilizer

Free-radical grafting of maleic anhydride to polyolefins for subsequent use in blend compatibilization has been widely reported. As opposed to the *in situ* compatibilization as attempted by Lambla and Seadan [32], the more common route to the compatibilization of polyolefin/polyamide blends is by modifying the polyolefin prior to its introduction in the blend [34–36]. Van Duin and Borggreve [28] have reviewed the chemistry of the interaction between the grafted MAH and the amine and imide functionalities of polyamides, and demonstrated the complexity of the products formed in the coupling of the two polymers. Despite the success of this approach, the polyolefin-*g*-MAH system has been plagued with poor solubility of the MAH in the substrate and the formation of MAH oligomers on the polymer backbone. As well, this approach is limited to the compatibilization of polyolefin blends with polymers containing amine functionality. Due to these restrictions, it is necessary to move towards a grafting system that is independent of the functionality in the polymer backbone and only dependent on its reactivity towards free-radical grafting.

1.8 Use of Coupling Agents in the Graft Copolymerization of Polyolefins with Dislike Polymers

Based on the *in situ* reactive compatibilization presented by Lambla and Seadan [32], van Ballegooie and Rudin [37] extruded polystyrene and polyethylene in the presence of dicumyl peroxide and triallyl isocyanurate. The intent of the study was to use

the triallyl isocyanurate as a coupling agent at the blend interface. The extent of coupling was determined by extracting the unbound polystyrene in hot toluene. Under the forcing conditions applied in this study (0.5 wt% peroxide and 2.0 wt% triallyl isocyanurate) the insoluble resin contained 16% of the original polystyrene. Rather than forming copolymer it is believed that the unextracted polystyrene reached the gel point and was no longer capable of being removed by hot toluene. Due to the incompatibility of polystyrene and polyethylene, the dispersed phase would have large droplets limiting the interaction at the interface. Given the reactivity of polystyrene and polyethylene towards hydrogen abstraction and the low likelihood of interaction between the two phases, the retained polystyrene is most likely due to gel formation rather than coupling with the polyethylene.

Al-Malaika and Artus [38] looked at using triallyl isocyanurate and divinyl benzene for the *in situ* graft copolymerization of polystyrene and an ethylene-propylene-ethylidene norbornene terpolymer (EPDM). Similar to van Ballegooie and Rudin [37], there is little distinction between the crosslinking of the individual phases and the presence of grafted polystyrene in the polyolefin gel. Both studies lack the control experiments needed to see if the addition of coupling agent and peroxide to the homopolymers results in gel formation. The presence of polystyrene in the polyolefin retentate is most likely the result of crosslinking inside the individual phases of the blend rather than any coupling reaction. This *in situ* approach to copolymer formation is inadequate due to the lack of direct evidence for the formation of copolymer rather than the crosslinking of the the individual phases. Similar studies using N,N'-*m*-phenylene-*bis*-maleimide [39], trimethylolpropane triacrylate [40] and hexa(allylamino)cyclotriphosphonitrile [41] coupling agents have been reported

in the literature, yet there is very little evidence for the synthesis of copolymer rather than the formation of crosslinked, insoluble gel containing the components of the blends.

1.9   Objectives

The objective of this research project was to investigate the potential for using a trifunctional allylic coagent for the coupling of post-production resins. The use of free-radical grafting techniques shall be investigated due to their robust nature and insensitivity towards impurities. The *in situ* copolymer synthesis shall be compared with a two-step approach with the advantages and challenges of both approaches being explored. Care shall be taken to prevent the formation of gel in the coupling reaction in order to distinguish between the synthesized copolymer and a crosslinked gel. Furthermore, the challenges and side-reactions of this coupling reaction will be investigated, focusing on the effect of the radical-mediated grafting process on the molecular weight distribution of the polymer. In Chapter 2, the background behind the free-radical grafting of functional monomers onto polymers shall be discussed. The synthesis of graft copolymers of polyethylene/poly(ethylene oxide) and polypropylene/thermoplastic polyolefin elastomer shall be the focus of Chapter 3. In Chapter 4, the effect of the coupling reaction on the molecular weight distribution of polyethylene shall be explored. The results of this study shall be summarized and future work presented in Chapter 5.

Chapter 2

Background

2.1 Radical-Mediated Graft Modification of Polyolefins

Of the many potential methods for producing copolymers, a radical-mediated approach is a cost-effective method of introducing functionality onto polyolefins. This technique is practiced on industrial scale as many polymer modification reactions can be conducted in conventional polymer processing equipment [42]. The advantageous economics of the radical-mediated grafting approach is due to its robust nature as the reactions can take place in solution, melt phase or as a solid state process. Furthermore, radical-mediated grafting reactions are relatively insensitive to the presence of moisture or air, and in certain cases the reaction is even enhanced in the presence of oxygen [43]. There are several reviews that discuss the chemistry of the grafting process, most notably those by Moad [36], Russell [44] and Hu et al. [45].

2.2   Mechanism of Grafting

The main reaction steps involved in the radical-mediated grafting of functional co-agents are outlined in figures 2.1 and 2.3. Figure 2.1 illustrates the initiation and propagation steps for the grafting of allylic monomers, in this case allyl benzoate, onto a saturated polymer backbone. The modes of termination for the macroradical are shown in figure 2.3.

2.2.1   Initiation

The most common initiators for polyolefin modification are dialkyl peroxides, as they provide low volatility and reasonable decomposition half-lives at melt-grafting temperatures, which range between 150 - 200°C. Although the overall extent of grafting can be insensitive to temperature in the range under consideration [46], temperature is an important operational parameter in controlling the selectivity of the radicals formed. Furthermore, optimization of the process temperature is needed as long half-lives are economically prohibitive. Another factor to consider is the dependence of melt viscosity on temperature as lower temperatures increase the viscosity and limit good dispersion of both the initiator and coagent.

Initiation
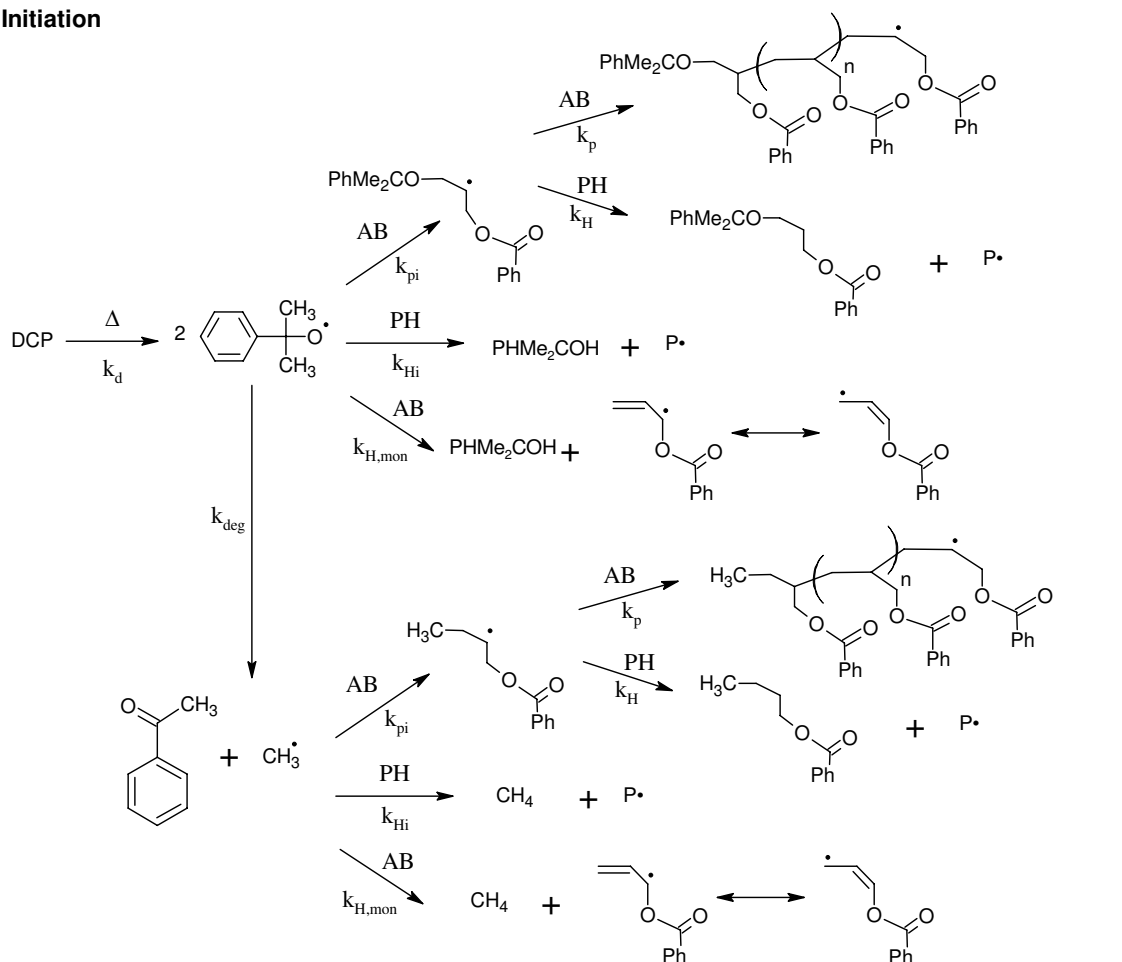
Propagation
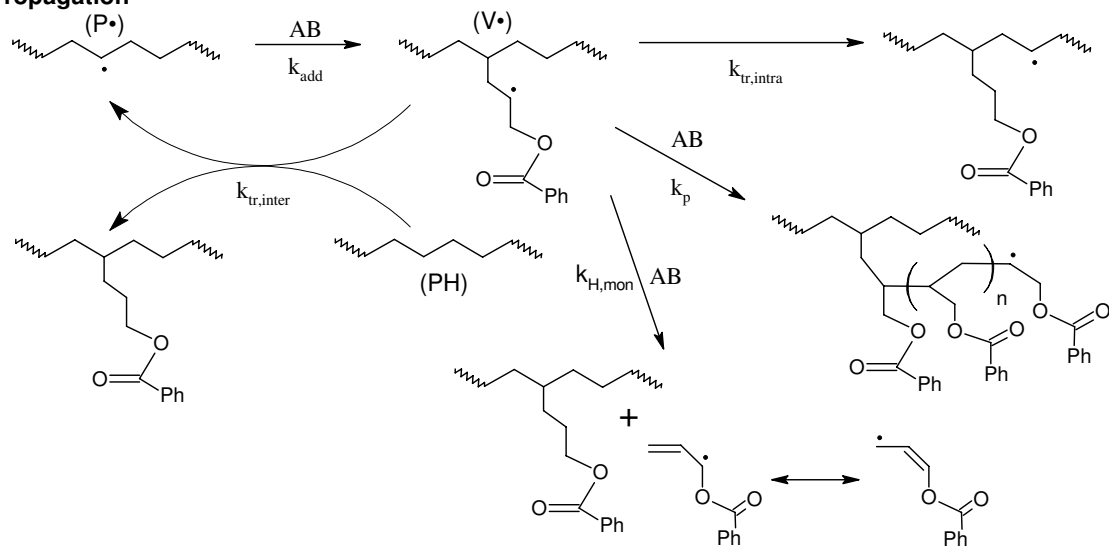
Figure 2.1: Reaction mechanism for the radical-mediated grafting of allyl benzoate onto saturated polyolefins. Adapted from Parent et al. [46].

Figure 2.1 illustrates the main decomposition routes for dicumyl peroxide and the resulting cumyloxy radical. Upon exposure of dicumyl peroxide to heat, the peroxide bond will homolytically cleave to form two cumyloxy radicals, whose efficiencies are governed by the cage effect for that radical pair. The extent of the cage effect, which is the competition between rate of recombination of the radical pair and the rate at which the newly formed radicals can diffuse apart, is dependent on the temperature and the lability of neighboring hydrogens [47, 48]. Temperature is an important factor in controlling the cage effect as the diffusion of the radical through the reaction medium is directly proportional to temperature and inversely proportional to medium viscosity. Increasing temperature lowers the apparent viscosity of the polymer melt, thereby improving the rate of radical diffusion. The lability of the neighboring hydrogens is discussed in the next section.

Dicumyl peroxide will homolytically cleave to form two cumyloxy radicals [43]. In absence of cage effects, the cumyloxy radical will either abstract a hydrogen to form cumyl alcohol, decompose via β-scission to form acetophenone and a methyl radical, or add to monomer. In a solution containing cyclohexane, by comparing the ratio of cumyl alcohol to acetophenone, the relative rates for hydrogen abstraction over β-scission can be determined. Avila et al. [49] demonstrated that at 30℃, the rate of hydrogen abstraction from an alkane is independent of solvent polarity, yet the rate of β-scission increases with increasing solvent polarity. Chodak and Bakos [50] demonstrated that for dicumyl peroxide, decomposition of the cumyloxy radical is favored at higher temperatures. Whereas at 30℃ only 4% of the cumyloxy radicals will decompose, approximately 30% of them will form acetophenone and methyl radicals at 160℃ [44].

2.2.2 Bond Dissociation Energies

The propensity for a radical to abstract a hydrogen atom over adding to the monomer is controlled by lability of available hydrogen donors and the nature of the radical species. In figure 2.1, the abstraction of hydrogen from the polymer $(k_H, k_{Hi}, k_{H,mon})$ leads to the formation of the polymeric macroradical. The energy needed to dissociate the bond between the hydrogen and the carbon atom of the polymer is usually discussed in relation to the Evans-Polanyi equation, which gives an expression for the energy needed to homolytically cleave a C-H bond. The hydrogen bond dissociation energies for several relevant molecules are shown in table 2.1. Bond dissociation

Table 2.1: Bond dissociation energies for common C-H bonds in radical-mediated grafting reactions [51]

Bond	Dissociation Energy (kJ/mol)
CH_3-H	439
$(CH_3)_2CH$-H	413
Cyclohexyl-H	400
$(CH_3)_3C$-H	404
CH_2=$CH(CH_3)CH$-H	345
Tetrahydrofuran-2-yl-H	385
$CH_3CH(OH)$-H	389
C_6H_5-H	465

energies provide some insight into the hydrogen abstraction step of a coagent graft propagation sequence. The bond dissociation energy for cyclohexane is representative of hydrogen abstraction from a polyethylene molecule as the internal methylene groups of the polymer are all equivalent. Tetrahydrofuran is a model compound for poly(ethylene oxide) and its lower bond dissociation energy than that for the model of polyethylene is responsible for the difference in reactivities towards grafting between

the two polymers. The low bond dissociation energy of 1-butene is demonstrative of the resonance stabilized radical that can be formed in the grafting of allylic monomers, which will be discussed in section 2.2.6. Furthermore, the bond dissociation energy for benzene justifies the use of aromatic solvents in radical reactions as it is relatively inert towards hydrogen abstraction.

2.2.3 Cumyloxy Radicals

The abstraction of hydrogen from a polymer by the cumyloxy radical is exothermic. Bertrand and Surzur [52] described the trend between the rate of abstraction over that of monomer addition for several substituted oxygen-centered radicals, with t-butoxide proving to be most reactive in hydrogen atom transfer. Following this trend, the cumyloxy radical should favor abstraction even more due to its improved electrophilicity derived from the greater donation of electron density from the phenyl substituent.

Cumyloxy radicals do not tend to add to electron deficient monomers (i.e. maleic anhydride) owing to their electrophilic character. If a suitable hydrogen atom donor is not available, a cumyloxy radical is likely to decompose to form acetophenone and a methyl radical. Given the concentration of monomer in the grafting system and their probability of interaction, the addition of the cumyloxy radical to monomer is believed to be negligible.

2.2.4 Methyl Radicals

Based on bond dissociation energies, the methyl radical should be equally capable of abstracting hydrogen from the polymer as that of the cumyloxy radical. However, due to its highly nucleophilic nature, the methyl radical prefers to add to the electron deficient monomer, even at the low monomer concentrations in the grafting reaction [44, 53, 54]. The methyl radical has a high propensity to add to monomer rather than abstract hydrogen from the electron-rich polyolefin backbone. Therefore the nucleophilic methyl radical is even less likely to abstract a hydrogen from the electron poor environment of the methylene adjacent to the ester group in allyl benzoate. In the grafting reaction, the methyl radicals are most likely to add to the monomer over abstracting a hydrogen.

2.2.5 Addition of Monomer

The abstraction of hydrogen from the polymer forms the macroradical $(P\cdot)$, which can engage in the propagation sequence illustrated in figure 2.1. The polymeric macroradicals tend to add to the less substituted end of the carbon-carbon bond due to steric effects. The adduct radical undergoes two possible reactions: hydrogen abstraction or oligomerization (k_p). The adduct radical can either abstract a hydrogen intermolecularly $(k_{tr,inter})$, intramolecularly $(k_{tr,intra})$ or from the monomer $(k_{H,mon})$.

The intermolecular abstraction of a hydrogen atom from a different polymer chain allows for the production of a graft modified chain without consuming the radical by closing the reaction sequence. This ability to consume C=C bonds without a loss in

radical population is known as the kinetic chain length of grafting. Intermolecular abstraction by the adduct radical and long kinetic chain lengths are the favored outcomes in the production of uniformly grafted polymer chains. Intramolecular abstraction is less favored as it produces multiple grafts on a single chain which is not advantageous for either copolymer synthesis or coagent-assisted crosslinking.

The macroradical can also abstract hydrogen from the monomer or undergo oligomerization, which leads to the consumption of monomer without donating any additional functionality to the polymer chain. Though oligomerization does not decrease the radical population, it should be avoided as it unnecessarily consumes monomer. Hydrogen atom abstraction from allylic monomers in the graft modification of polyolefins shall be discussed in section 2.2.6.

2.2.6   Degradative Chain Transfer

Allylic monomers are commonly used for the graft-modification of polyolefins due to their low propensity towards homopolymerization. The abstraction of a hydrogen to form a stabilized allylic radical is referred to as degradative chain transfer. A generalized scheme for the degradative chain transfer of allylic monomers is shown in figure 2.2. For allyl benzoate, where $X = CO_2Ph$, resonance effects contribute to the stability of the allylic radical, thereby limiting its reactivity towards further addition. In the event that the cumyloxy radical encounters a monomer unit, due to the tendency of the cumyloxy radical to abstract hydrogen rather than add to monomer, the cumyloxy radical will preferentially abstract hydrogen from the monomer. This
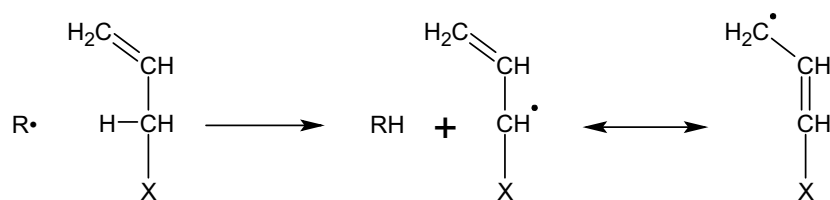
Figure 2.2: Generalized mechanism for the degradative chain transfer in allylic monomers

abstraction of hydrogen leads to degradative chain transfer which suppresses the polymerization of monomer.

2.2.7 Termination

The radical-mediated graft modification of polyolefins leads to the formation of a wide variety of radical species which are subject to termination. Radical-radical termination is a bimolecular process that is limited by the frequency of encounters between a radical pair. As termination requires the interaction of two radical species, the rate of radical termination is a diffusion-controlled process [43]. However, despite the dependence of termination on the rate of diffusion, the interacting radicals will have a preferred mode of termination.

Upon interaction with each other, the radical intermediates may terminate via combination and disproportionation. A generalized scheme for the radical-radical termination of the macroradical is shown in figure 2.3. Radical-radical combination results in the formation of a covalent bond. The formation of crosslinks in a grafting reaction should be avoided due to its effect on the molecular weight of the resin and its consumption of two radical species without contributing to graft content.
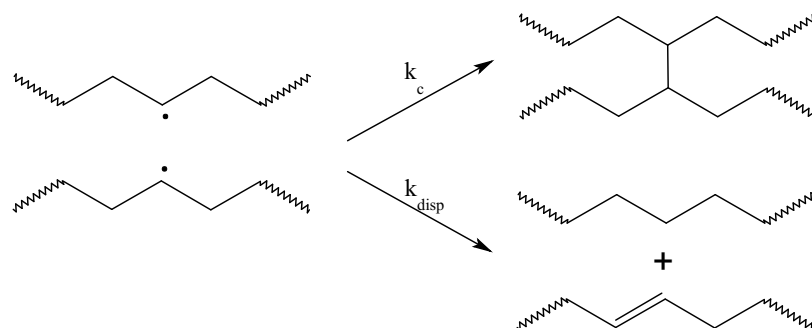
Figure 2.3: Radical-radical termination of the macroradical in the absence of monomer (top: combination; bottom: disproportionation)

Disproportionation involves the abstraction of a hydrogen on the carbon β to one of the approaching radicals. The abstraction of hydrogen leads to consumption of the two interacting radicals due to the formation of a vinyl group. Though disproportionation does not affect the molecular weight distribution of the resin, it does, however, consume two radicals and introduces unsaturation in one of the interacting species.

The relative rates of combination over disproportionation (k_{disp}/k_c) have been widely reported in the literature for the termination of alkyl and allyl radicals [55]. The ratios of rate constants for disproportionation over combination for several radicals of interest in solution at 30°C, are listed in table 2.2. The tendency for a radical

Table 2.2: Disproportionation-combination ratios in solution [55]

Radical	Type	k_{disp}/k_c
$2\,CH_3CH_2\cdot$	1°	0.15
$2\,(CH_3)_2CH\cdot$	2°	1.2
$2\,C_6H_{11}\cdot$	2°	1.1
$2\,(CH_3)_3C\cdot$	3°	4.5
$2\,CH_2{=}CHC\cdot(CH_3)_2$	allylic	0

pair to terminate via disproportionation over combination is highly dependent on the structure of the radical species. The availability of a labile hydrogen in the β position to the radical favors disproportionation.

The introduction of a coagent, as is the case in figure 2.1, complicates the products formed due to termination. Little data has been reported in the literature on the selectivity of the termination modes for radical-mediated grafting reactions, especially at the temperatures used in this study. Though the macroradical and its adduct radical may terminate by either combination and disproportionation, the allylic radical formed due to degradative chain transfer will terminate almost exclusively via combination.

2.2.8   Effect of Termination on Homopolymers

Despite the economic benefits of melt grafting to polyolefins, there are several challenges that still need to be addressed in the use of this technique for the synthesis of graft copolymers. The most significant challenge is the effect of radical formation on the molecular weight distribution of the resin. In the case of polyethylene, in the absence of monomer, the polymeric macroradical will tend to crosslink [56]. Polypropylene, on the other hand, will tend to degrade via β-scission of the polymer backbone at the macroradical site [57]. Poly(ethylene oxide) has been shown to both crosslink and degrade in the presence of organic peroxides [58]. This effect requires a balance between graft yields and control of the molecular weight of the resin. It is important for those polymers that crosslink to avoid the growth of molecular weight beyond the gel point in the coupling reaction. The formation of gel should be avoided

as it introduces difficulty in the fractionation step and limits the polymer's solubility in the coupling reaction. The effect of degradation on the molecular weight of the polymer is discussed in section 3.4.1.

2.3   Graft Copolymer Formation

Using the grafting chemistry as described in section 2.2, dislike polymers can be coupled to form graft copolymers. The synthesis of polyethylene-g-poly(ethylene oxide) and polypropylene-g-thermoplastic polyolefin elastomer shall be described in Chapter 3, where triallyl trimesate is used as the coupling agent and dicumyl peroxide as the initiator. As opposed to the *in situ* reactive compatibilization reactions discussed in section 1.8, a solution based approach was used for the coupling of the immiscible polymers. In the reactions described in section 1.8, the peroxide and the coupling agents were evenly dispersed throughout the blend. During the blending of a polyolefin with a dislike polymer, due to the immiscibility of the system, one polymer would be present as a dispersed phase within the other. This dispersed phase would have a large droplet size and a very small surface area at the interface. Due to this limited contact between the phases, the majority of the grafting reactions would occur within the individual phases, thereby crosslinking the homopolymer rather than coupling across the interface. By dissolving the two polymers in solution, this dispersed phase would be eliminated and better interactions between the two polymers would occur. The solvation of the two polymers would allow for greater interaction between the two polymeric macroradicals and the coupling agent, thereby encouraging the formation of copolymer.

Chapter 3

Copolymer Synthesis

3.1 Introduction

Solvent-free reactive coupling between a polyolefin and a second immiscible polymer has been widely claimed in the literature [29–32, 37, 38], but without convincing evidence of the copolymer yields or structure. An alternative approach is a solution-borne coupling process wherein miscibility allows for greater interaction between polymers. In this phase of the project, the syntheses of a polyethylene/poly(ethylene oxide) and an isotactic polypropylene/thermoplastic elastomer graft copolymer were investigated.

3.2   Objectives

The objective of this phase of the project was to generate a graft copolymer with an equal distribution of two different homopolymers. Initially, the reactivity of each homopolymer towards the radical-mediated grafting of an allylic ester coagent was assessed. A single- and multi-step graft copolymerization approach was then attempted through allylic coagent assisted cross-coupling.

3.3   Experimental

3.3.1   Materials

An unstabilized grade of isotactic polypropylene (i-PP, M_n = 40,000, Dow Chemical Company) was used without purification. Triallyl trimesate (TAM, >98.0%, TCI), allyl benzoate (AB, >98%, TCI) and dicumyl peroxide (DCP, 98%, Sigma-Aldrich) were stored under refrigeration. Poly(ethylene oxide) (PEO, M_n = 100,000, Scientific Polymer Products) was purified by dissolution-precipitation (methanol-ether) prior to use. Polyethylene (PE, M_n = 1400, Scientific Polymer Products) and a thermoplastic polyolefin elastomer (TPE, MFI = 30, DuPont-Dow Elastomers) were purified by dissolution-precipitation (chlorobenzene-methanol) prior to use. The following solvents were used as received from Fisher Scientific: methanol (ACS grade), ethyl ether anhydrous (ACS grade), chlorobenzene (certified mono), xylenes (ACS grade) and hexane (ACS grade). 1,2,4-Trichlorobenzene (TCB, 99%+ spectrophotometric grade, Sigma-Aldrich) and 2,6-di-*tert*-butyl-*p*-cresol (BHT, 99%, Alfa Aesar) were used as

received. Calcium stearate, Irganox 1010 and Irgafox were used as received from Dow Chemical.

3.3.2 Grafting of Allyl Benzoate onto PE, PEO and *i*-PP in Solution

Polymer (1 g), AB (0.05 g, 308 μmol) and TCB (6.5) were charged to a round-bottom flask and flushed with nitrogen for 10 minutes. The reaction mixture was submerged in an oil bath at 160℃ for 15 minutes under a nitrogen atmosphere to form a homogenous solution, after which a solution of various DCP loadings and TCB (1 g) were added. The concentrations of DCP can be seen in figure 3.2. After 35 minutes, the resulting mixture was precipitated from solution using methanol (200 mL) and dried under vacuum. The resulting products were pressed into thin films and analyzed using FT-IR. The bound AB content was determined from the ratio of the integration area of the carbonyl resonance relative to an internal standard resonance for the polymer. The regions used for the analysis of the bound AB content can be seen in table 3.1.

Table 3.1: FT-IR regions used for the measurement of grafted allyl benzoate content

Polymer	Carbonyl Resonance (cm^{-1})	Internal Standard Resonance (cm^{-1})
i-PP	1761–1701	492–422
PEO	1745–1695	2287–2119
PE	1761–1668	2093–1996

3.3.3   One-Step Synthesis of PE-*g*-PEO

PE (1 g), PEO (1 g), TAM (0.05 g, 151 μmol) and TCB (14 g) were heated to 160°C under a nitrogen atmosphere. After 10 minutes, a solution of DCP (6.0 mg, 22 μmol) and TCB (1 g) was added to the round-bottom flask. After 35 minutes, the resulting yellow solution was precipitated using ether (200 mL) and dried *in vacuo*. A sample of the dried material was analyzed by ^{1}H-NMR to measure the residual allylic content of the grafted TAM. FT-IR was used to measure the TAM graft content of the crude product. Separation of unbound PEO was accomplished by charging a cellulose extraction thimble with the crude product and submerging it in refluxing methanol for 3 hours. The extraction solution was stabilized with BHT (~10 mg) and the methanol wash was recycled to the thimble every 15 minutes. The thimble was allowed to drain overnight and dried *in vacuo*; the methanol wash was reduced via rotational evaporation. The retained product and the methanol wash extract were analyzed by ^{1}H-NMR for indications of copolymer formation. The TAM content of the separated products was determined using FT-IR by comparing the ratio of the areas of the bound carbonyl resonance to that of an internal standard for the polymer.

3.3.4   Bulk Reactivity of PE Towards Grafting of Triallyl Trimesate

PE (1 g), TAM (0.05 g, 151 μmol) and DCP were degassed by three pump-fill cycles and put under a nitrogen atmosphere before stirring in an oil bath at 120°C for 10 minutes. The DCP loadings used can be seen in figure 3.5. Following the pre-mixing

of the reagents, the round-bottom flask was heated to 160°C for 35 minutes while under a nitrogen atmosphere. The crude product was then dissolved in xylenes (15 mL) at 120°C and precipitated from solution using methanol (200 mL) and dried *in vacuo*. The purified product was pressed into thin films and analyzed using FT-IR. The TAM graft content was determined by comparing the ratio of the area of the bound carbonyl resonance (1830-1668 cm^{-1}) to an internal standard resonance for PE (2093-1996 cm^{-1}). Residual allyl content of the bound TAM was measured using ^{1}H-NMR.

3.3.5 Bulk Reactivity of *i*-PP Towards Grafting of Trially Trimesate

TAM (0.175 g, 530μmol/g) and DCP were solution cast onto *i*-PP (3.5 g) in a 100 mL beaker and dried under blowing air for 30 minutes. The DCP loadings used can be seen in figure 3.6. The contents of the beaker were then charged to a DSM Xplore 5 mL twin-screw micro-compounder at 180°C with a co-rotating screw speed of 60 rpm under a nitrogen atmosphere. After 8 minutes, the polmer was extruded from the micro-compounder and allowed to cool before being pressed into thin sheets at 180°C. The thin film sheets were dissolved in chlorobenzene (20 mL) and precipitated from solution using methanol (200 mL) and dried *in vacuo*. The purified product was pressed again into thin films and analyzed using FT-IR. The TAM graft content was determined by comparing the ratio of the area of the bound carbonyl resonance (1801-1659 cm^{-1}) to an internal standard resonance for *i*-PP (492-422 cm^{-1}).

3.3.6   Rheological Properties of PE-*g*-TAM

PE (3.5 g) was charged to a 50 mL round bottom flask where TAM and DCP (see table 3.3) were added by solution casting in hexanes. The contents of the flask were dried for 30 minutes under blowing air and then degassed by three pump-fill cycles and put under a nitrogen atmosphere. While under a blanket of nitrogen, the round-bottom flask was heated to 180°C for 6 minute. The cooled PE products were pressed into thin sheets at 120°C and mixed with a masterbatch of calcium stearate (500 ppm), Irganox 1010 (500 ppm) and Irgafos (1000 ppm) before being charged to the rheometer for creep-recovery analysis. A 1 g aliquot was analyzed for gel content by submerging in a stainless steel mesh bag (120 mesh) in refluxing xylenes for 6 hours. The gel extraction was stabilized with BHT (~10 mg).

3.3.7   Synthesis of PE-*g*-PEO: Macrocoagent Approach

The first stage of the macrocoagent approach was the same as that of the bulk grafting of TAM in section 3.3.4, except chlorobenzene was used to dissolve the crude product for the removal of unbound TAM. The concentrations of reagents used are reported in table 3.2. The copolymer synthesis and PEO separation used a similar procedure to the one-step synthesis in section 3.3.3.

Table 3.2: Reagents used for copolymer synthesis using macrocoagent approach

Macrocoagent			Copolymer			
PE	TAM	DCP	Macro-coagent	PEO	DCP	TCB
(g)	(g)	(mg)	(g)	(g)	(mg)	(g)
1.5	0.075	4.5	1.0	1.0	6.0	15.0
1.5	0.075	1.5	1.0	1.0	6.0	15.0

3.3.8   Synthesis of *i*-PP-*g*-TPE: Macrocoagent Approach

The macrocoagent was formed using the steps outlined in section 3.3.5. The purified macrocoagent was analyzed for gel content by submerging a 1 g aliqout in a stainless steel mesh bag (120 mesh) in refluxing xylenes for 6 hours. Macrocoagent (1.0 g), TPE (1.0 g) and trichlorobenzene (14 g) were charged to a 50 mL round-bottom flask and flushed with nitrogen for 10 minutes. The flask was then submerged in an oil bath at 160°C under a nitrogen atmosphere for 10 minutes to form a homogeneous solution. DCP (6.0 mg, 22 μmol) was dissolved in 0.5 g of TCB and added to the reaction mixture. After 35 minutes, the yellow reaction mixture was precipitated from solution using 200 mL of methanol and dried *in vacuo*. The crude product (0.5 g) was charged to a stainless steel mesh bag and submerged in refluxing toluene for 3 hours. Toluene was used to selectively dissolve the TPE from the *i*-PP products. The toluene extract was precipitated from solution using methanol (100 mL) and the fractionated products were dried *in vacuo* and analyzed using FT-IR. A 0.5 g aliquot of the crude product was also analyzed for gel content by submerging in a stainless steel mesh bag in refluxing xylenes for 6 hours. All extractions were stabilized with BHT (~10 mg).

3.3.9   Analysis

NMR spectra were recorded with a Bruker AVANCE-600 spectrometer (600.17 MHz ^{1}H) in toluene-d$_8$ at 353K with chemical shifts referenced to tetramethylsilane. For quantitative integrations of allylic proton resonances, a d1 relaxation time of 20 seconds was used. FT-IR spectra were acquired from thin films or pressed KBr disks

using a Nicolet Avatar 360 FT-IR ESP spectrometer.

3.3.10 Rheology

Creep-recovery measurements were conducted under a nitrogen atmosphere using a Reologica ViscoTech stress-controlled rheometer with 48 mm diameter parallel plates at a gap of 0.5 mm. The creep-recovery measurements were conducted at 120°C using a stress of 1.0 Pa.

3.4 Results

3.4.1 Justification for Material Selection

It has been shown that allylic esters can be grafted to polyolefins using radical-mediated techniques [59]. A detailed discussion regarding the selection of coagents can be found in section 4.4.2. Maximizing copolymer yields requires an average of one TAM molecule per polymer chain. The TAM concentration needed to activate each chain at least once has an inversely-proportional relationship to the initial molecular weight of the polymer, as illustrated in figure 3.1.

These molecular weight calculations are based on the initial molecular weight of the polymer. However, radical-mediated modification results in changes to the polymers' molecular weight, requiring careful consideration of starting materials. For example, polymers that undergo radical degradation must start with a high molecular weight so as to stay above the threshold where bound TAM contents are too low to activate
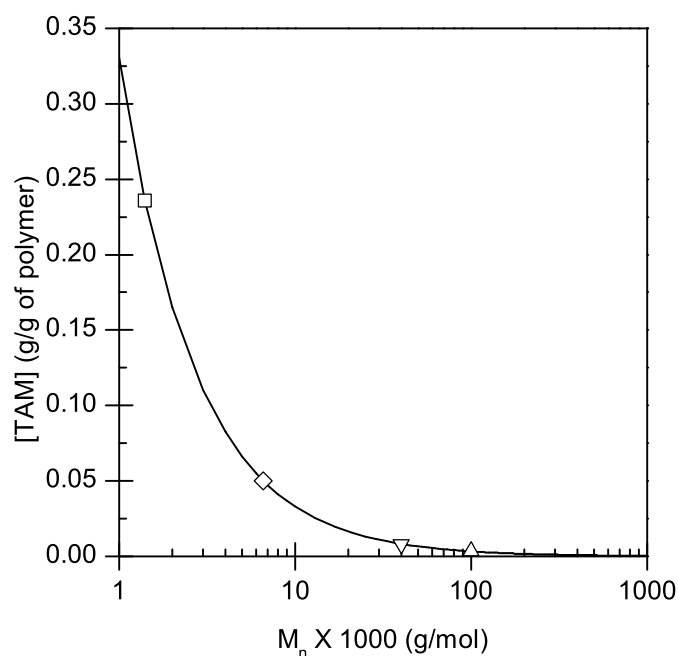
Figure 3.1: TAM concentration dependence on the molecular weight of the resin
in order to achieve uniform graft distributions. (Initial M_n of □ PE;
▽ *i*-PP; △ PEO; ◇ $[TAM]_0$ of the macrocoagent)

every chain. In contrast, resins that crosslink under the action of peroxide must be
chosen with sufficiently low molecular weight so as to surpass the threshold for uniform
single grafts without reaching the gel point. The theoretical final molecular weight
(◇) where the moles of chains equals the moles of TAM (151μmol/g of polymer) input
into the system is 6600 g/mol, assuming all of the TAM has been grafted. Below this
molecular weight, the moles of chains outnumbers the moles of TAM and regardless
of graft yields, a significant number of chains would remain unactivated.

The poly(ethylene oxide) resin used in this study (△) was chosen to have a high
enough molecular weight, so that after degradation its molecular weight would be
above the TAM concentration threshold for chain activation. An ultra-high molecular
weight PEO (M_n = 5,000,000 g/mol) was investigated for use in copolymer synthesis,

however more than twice the TCB loading was needed in order for it to codissolve with PE. The polypropylene used in this study ($\triangledown$) was chosen due to its molecular weight being sufficient to withstand chain scission and allow for a uniform graft distribution. The thermoplastic elastomer was chosen due its lack of gel formation under the conditions used in the copolymer synthesis.

The polyethylene used in this study ($\square$) had a sufficiently low molecular weight that under all grafting reaction conditions in the copolymer study, the resin did not reach the gel point. When a PE resin with an order of magnitude higher molecular weight (M_n = 21,500 g/mol) under significantly milder conditions ([TAM] = 91 μmol/g; [DCP] = 3.7 μmol/g) was reacted with TAM, the material reached the gel point and was no longer soluble for use in copolymer syntheses.

3.4.2 Homopolymer-*g*-AB Graft Yield Study

Candidate polymers for radical-mediated copolymer syntheses differ in terms of ability to form a macroradical, and by extension, their reactivity toward coagent addition. During this phase of the project a model coagent, allyl benzoate, was used to investigate each polymer's propensity to add to allylic esters without suffering from complications associated with molecular weight variation and multiple allyl group activation. PE, *i*-PP and PEO were reacted with allyl benzoate in a trichlorobenzene solution using the same solvent loadings and temperature as the copolymer syntheses that follow.

As demonstrated in figure 3.2, there is a significant difference in the reactivity of the three homopolymers studied, which are directly related to the propensity of each
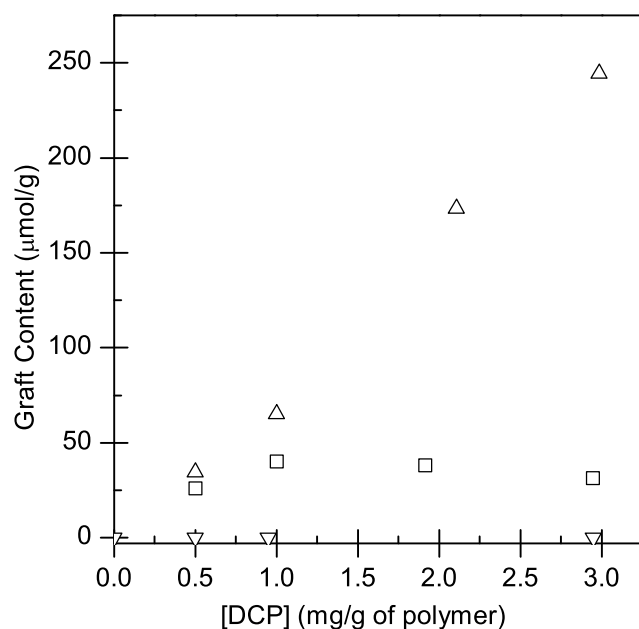
Figure 3.2: Effect of DCP on allyl benzoate graft content in TCB. T = 160°C, $[AB]_0 = 308$ μmol/g. □ PE, △ PEO, ▽ i-PP

homopolymer to donate hydrogen and add to coagent. The relative rates of hydrogen abstraction and macroradical formation have been quantified using nitroxide radical traps. Busfield et al. [60] used 1,4-dioxane and cyclohexane as model compounds for PEO and PE respectively. An equimolar amount of the two compounds were reacted in the presence of di-*tert*-butyl diperoxyoxalate and an excess of 1,1,3,3-tetramethylisoindoline-2-oxy at 60°C to observe a relative hydrogen abstraction yield of 1.4. The greater reactivity of 1,4-dioxane towards hydrogen donation is explained to be due to the donation of electron density from the oxygen lone pair into the antibonding orbital of the adjacent C-H bond [60, 61]. This donation of electron density lowers the activation energy for hydrogen abstraction and increases the rate of PEO macroradical formation.

The greater reactivity of PE over i-PP was explained by Dokolas et al. [62] using 3-methylpentane and 2,4-dimethylpentane as model compounds for linear low-density polyethylene and polypropylene, respectively. Using the same initiator and nitroxide radical trap as Busfield et al. [60], differences in reactivity towards hydrogen abstraction between LLDPE and PP were quantified by comparing the ratios of the rate constants of hydrogen abstraction (k_H) over t-butoxy radical degradation (k_{deg}). Dokolas et al. [62] found that k_H/k_{deg} for LLDPE was 7.3 times higher than that for polypropylene in a benzene solution. Dokolas et al. [63] attributed the differences in reactivity to differences in the C-H bond strength and steric effects of the two polymers.

Based on these graft yield measurements, i-PP was not considered for single-step copolymer syntheses owing to its poor reactivity in solution. Polyethylene and poly(ethylene oxide) showed reasonable reactivity towards the radical-mediated grafting of allylic esters in solution and were investigated further.

3.4.3 One-Step Copolymer Synthesis

The one-step copolymer synthesis allows for the *in situ* formation of graft copolymer by dispersing the coupling agent, the initiator and both homopolymers in solution. This procedure differs from that of the *in situ* reactive compatibilization, due to the solvation of the two polymers which increases the potential for chain interaction. The likelihood of encounter between the two polymers is no longer dependent on the size of the dispersed phase and its corresponding interfacial surface area, allowing for potentially greater interaction. The coupling of PE and PEO was attempted because

of their greater reactivity towards radical-mediated modification in chlorinated aromatic solvents. The TCB solution concentration was determined by dissolving equal masses of each homopolymer at various TCB concentrations in order to determine the lowest TCB loading needed for cosolubility. The synthesis and fractionation of the copolymer products is summarized in figure 3.3.
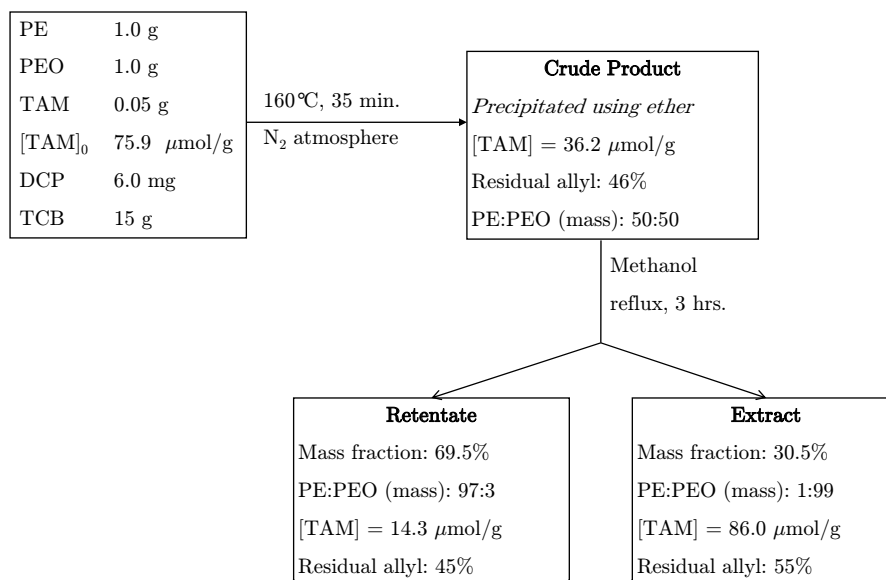
Figure 3.3: Synthesis and fractionation of single-pot copolymer synthesis

PE and PEO were reacted with triallyl trimesate in the presence of DCP in a trichlorobenzene solution. Following the decomposition of 99% of the initiator, the reaction volume remained a homogenous solution, indicating that no gel had formed. The reaction volume was precipitated from solution using ether to extract ungrafted TAM without solvating either polymer. The crude product was analyzed for TAM conversion and graft content, giving a bound TAM content of 36.2 μmol/g, which is equivalent to a graft yield of 48%. Furthermore, the TAM in the crude product had a 46% residual allylic content; indicating that in spite of a relatively high DCP loading,

almost half of the pendent allylic groups remained unactivated.

The upfield ^{1}H-NMR spectrum of the crude PE-g-PEO copolymer (top) can be seen in figure 3.4, whereas the bottom spectrum is that of pure TAM. The broad peak at
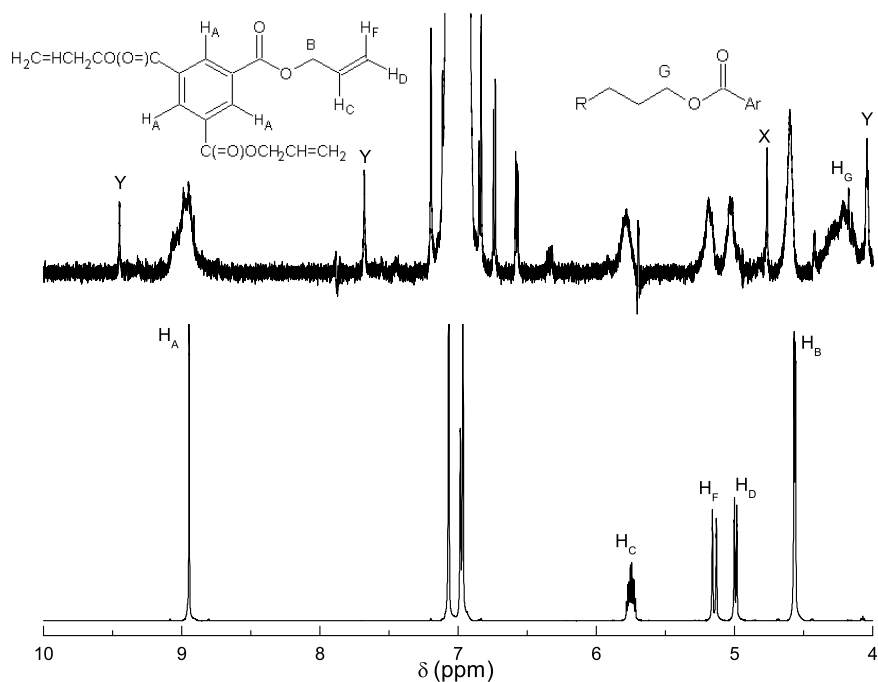
Figure 3.4: ^{1}H-NMR spectra (toluene-d$_8$, 353 K) of downfield region of crude PE-g-PEO (top) and pure TAM (bottom); (X = PE, Y = PEO)

4.2 ppm in figure 3.4 is consistent with the proton resonance for a methylene proton adjacent to an ester group (H$_G$) [64]. A broad aromatic peak at 8.9 ppm is indicative of multiple grafts per TAM molecule. Resonances between 7.2 and 6.5 ppm are due to residual TCB.

Following the isolation of the crude product in ether, the polymer was placed in a cellulose thimble under refluxing methanol for three hours. The thimble retentate and methanol extract were analyzed, the results of which were summarized in figure 3.3. From the ^{1}H-NMR analysis of the thimble retentate, the copolymer had a

poor distribution between the two homopolymers. The copolymer that was retained in the thimble contained only 2% of the PEO input into the system. Seeing as the retentate is composed primarily of PE and the extract wash of PEO, there is a significant difference in reactivity towards the grafting of TAM between the two polymers. This difference in reactivity prevented the success of the single-step approach due to the greater consumption of TAM by the more reactive polymer, in this case, PEO. A two-step synthesis where the less reactive polymer, PE, is grafted with TAM and then coupled with the more reactive polymer in a subsequent reaction is the basis for the macrocoagent approach. By pre-grafting PE with TAM, the differences in reactivity between the two homopolymers can be decoupled.

3.4.4   Homopolymer-*g*-TAM Graft Yield Study

Section 3.4.3 demonstrated the need to decouple the reactivities of the homopolymers in the copolymer synthesis, therefore the feasibility of a macrocoagent approach was investigated. The macrocoagent approach pre-grafts the coupling agent, in this case TAM, to the less reactive polymer in bulk. The polymer-*g*-TAM is then codissolved with the other homopolymer and the reaction is re-initiated to form a copolymer. In this case, the grafting of TAM to PE was conducted solvent-free to investigate its potential as a macrocoagent for producing a PE-*g*-PEO copolymer. As can be seen in figure 3.5, PE showed good reactivity towards TAM under solvent-free conditions and is a good candidate for use as a macrocoagent. Furthermore, even at high graft yields, there is a significant concentration of the residual allylic groups within polymer-bound TAM that are needed for copolymer synthesis. When choosing a DCP loading for the formation of the macrocoagent, the amount of free allylic groups bound to the
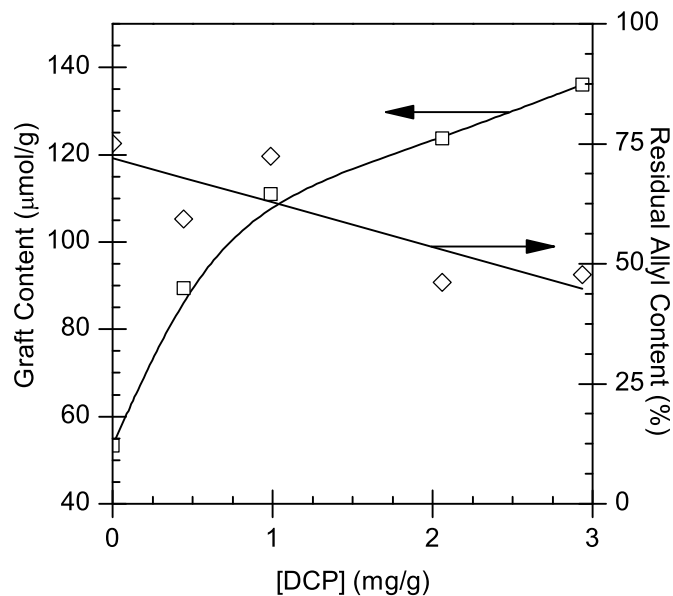
Figure 3.5: Effect of DCP on the bulk reactivity of PE and TAM (T = 160°C, $[\text{TAM}]_0 = 151 \ \mu\text{mol/g}$)

polymer needs to be balanced against TAM graft content.

The use of i-PP as a macrocoagent was also investigated. i-PP was reacted solvent-free with TAM at various DCP loadings to investigate its potential as a macrocoagent in the production of an i-PP-g-TPE copolymer. As is illustrated in figure 3.6, i-PP shows good reactivity in the solvent-free radical-mediated grafting of TAM. However, due to the insolubility of i-PP in NMR solvents, the extent of conversion of the grafted allylic functionality remains unknown. Though i-PP shows good reactivity towards the grafting of TAM, it is unclear how effective i-PP-g-TAM would be as a macrocoagent in copolymer syntheses without knowledge of the residual allylic content.
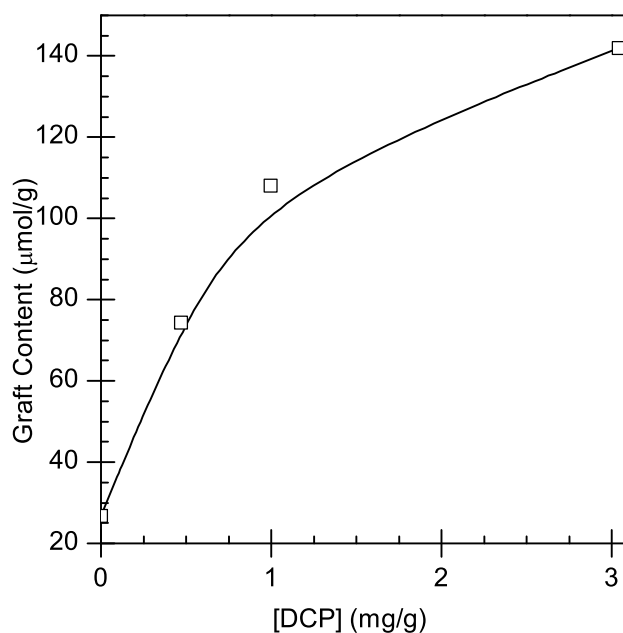
Figure 3.6: Effect of DCP on the bulk reactivity of *i*-PP and TAM (T = 180°C,
[TAM]$_0$ = 151 μmol/g)

3.4.5   Rheological Properties of PE-*g*-TAM

The activation of peroxides within polyethylene leads to an increase in the crosslink
density of the resin [56, 65] as polyethylene macoradicals do not fragment, and prefer
to terminate via combination. The addition of a multifunctional coagent will further
enhance this crosslink density, and given enough peroxide and coagent, the resin
will eventually reach its gel point. The formation of gel should be avoided in the
production of the macrocoagent as the polymer would no longer be soluble for use in
subsequent coupling reactions. The effect of grafting TAM on the molecular weight
of the polymer was investigated by measuring the zero-shear viscosity (η_0) and gel
content of the modified resin. Unpurified resins were used to avoid the effects of
residual solvent on the rheology of the polymers. For linear polymers, η_0 is fairly

independent of the molecular weight distribution and directly proportional to the average molecular weight of the polymer. This direct proportionality is true below the critical molecular weight for chain entanglement as above this point, the viscosity increases with the 3.4-power of M_w [66]. The zero shear viscosities and gel contents for PE-*g*-TAM can be seen in table 3.3.

Table 3.3: Effect of DCP on the zero shear viscosity and gel content of PE-*g*-TAM[a]

[DCP] (mg/g)	[TAM] (μmol/g)	η_0 (Pa s)	Gel content (%)
0	0	0.747	0
0.50	91	0.789	0
1.0	91	0.810	0
3.0	0	0.869	0
3.0	91	1.12	0
3.0	151	1.78^b	0

a. modified at T = 180°C

b. purified resin

Over the range of conditions used to produce PE-*g*-TAM, there was only a slight increase in the zero-shear viscosity of the resin. This slight increase in η_0 indicates that the grafting of TAM, under the conditions used for the macrocoagent, had only a slight effect on the molecular weight of the polymer. Furthermore, the lack of gel formation indicates that the conditions used for the macrorcoagent synthesis are appropriate as all of the chains remain soluble in trichlorobenzene.

3.4.6 Macrocoagent Approach to Copolymer Synthesis: PE-*g*-PEO

In an effort to decouple the reactivity differences between PE and PEO, a copolymer synthesis was attempted using the macrocoagent approach. Two copolymer syntheses were attempted using the reagent loadings reported in table 3.2. The results for the first macrocoagent synthesis are summarized in figure 3.7. For the copolymer
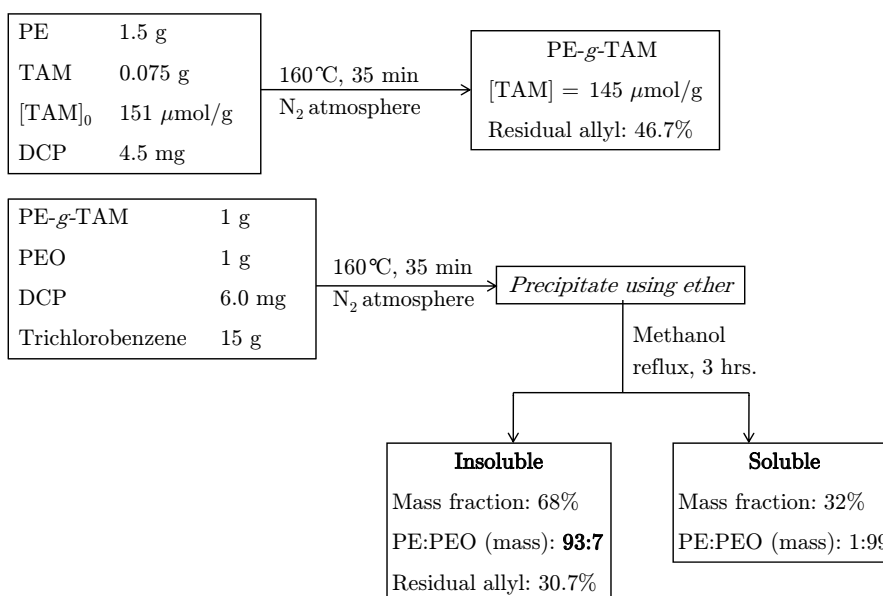
Figure 3.7: Results for macrocoagent approach to copolymer synthesis ([DCP] = 3.0 mg/g for the macrocoagent step)

synthesis, an equal mass of PE-*g*-TAM and PEO were dissolved in a 15:1:1 mass ratio of TCB:PE:PEO and initiated with 3.0 mg/g of DCP. The product was precipitated from the reaction mixture using ether to remove ungrafted TAM and the DCP decomposition by-products. The crude product was charged to a cellulose thimble and extacted with methanol for 3 hours. The insoluble component of the methanol

extraction contained 9.5% of the PEO charged to the system. The residual allyl content of the copolymer was 30.7% indicating that nearly one third of the pendent allyl groups remained unmodified.

The synthesis of the macrocoagent resulted in a residual allyl content of 46.7% and a doubling of the zero-shear viscosity of the polymer. Therefore, less forcing conditions were investigated to allow for decreased consumption of allyl groups in the grafting of TAM. The results of this milder macrocoagent synthesis are summarized in figure 3.8.

Figure 3.8: Results for macrocoagent approach using milder conditions for the synthesis of copolymer ([DCP] = 1.0 mg/g for the macrocoagent step)

As can be seen for the milder macrocoagent synthesis, approximately 2/3 of the allylic functionality in the macrocoagent remained unconverted. However, when reacted in the presence of PEO and DCP in solution, the milder macrocoagent produced a

copolymer with only 2% of the PEO charged to the system. Despite the higher uncon-verted allylic content, due to the low concentration of bound TAM, there were fewer sites available for PE-g-TAM/PEO coupling. Only 8.5% of the residual allyl groups were converted in the copolymer synthesis indicating that due to the fewer moles of bound coagent, the statistical likelihood of a PEO macroradical encountering a pen-dent allyl group was too small to produce an appreciable amount of copolymer.

From figures 3.7 and 3.8, the more forcing conditions produced the more equally distributed copolymer. This is believed to be due to the greater TAM graft content of the macrocoagent, which allowed for greater coupling opportunities with PEO. Despite the greater consumption of allylic ester groups in the macrocoagent synthesis step in figure 3.7, the concentration of residual unsaturation was sufficient to allow for coupling with the PEO macroradical.

Though a high DCP concentration in the macrocoagent step improved the copoly-mer distribution, a further increase in DCP loading would not result in significant improvements. In figure 3.7, the TAM graft yield was 96%; therefore any increase in initiator concentration in the macrocoagent step would further consume free allyl groups without contributing to graft content, thereby limiting the opportunities for coupling with PEO. For the use of TAM in the macrocoagent synthesis, a balance needs to be achieved between high graft yields and residual allyl content.

3.4.7 Macrocoagent Approach to Copolymer Synthesis: *i*-PP-*g*-TPE

A copolymer synthesis was attempted using the macrocoagent produced in section 3.4.4. The results of the copolymer synthesis are summarized in figure 3.9. The *i*-PP-*g*-TAM
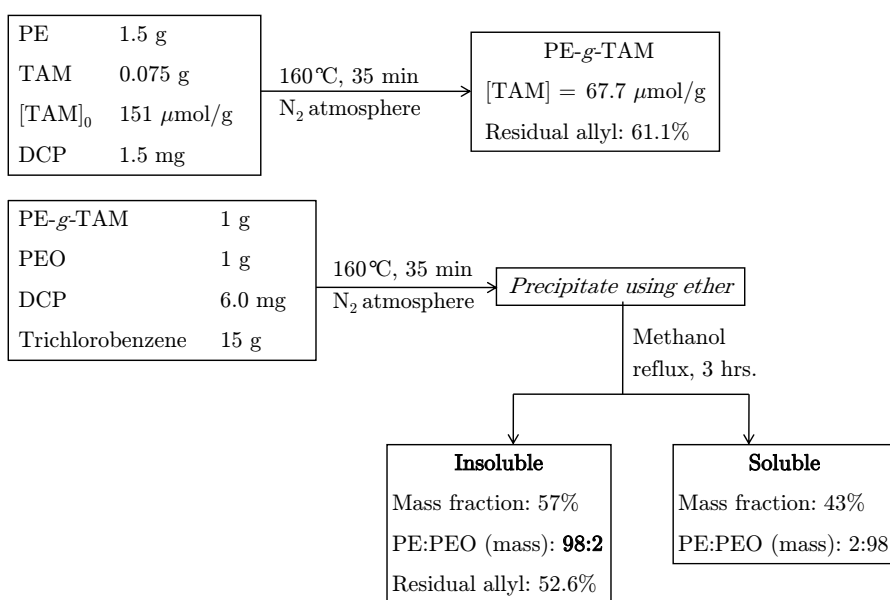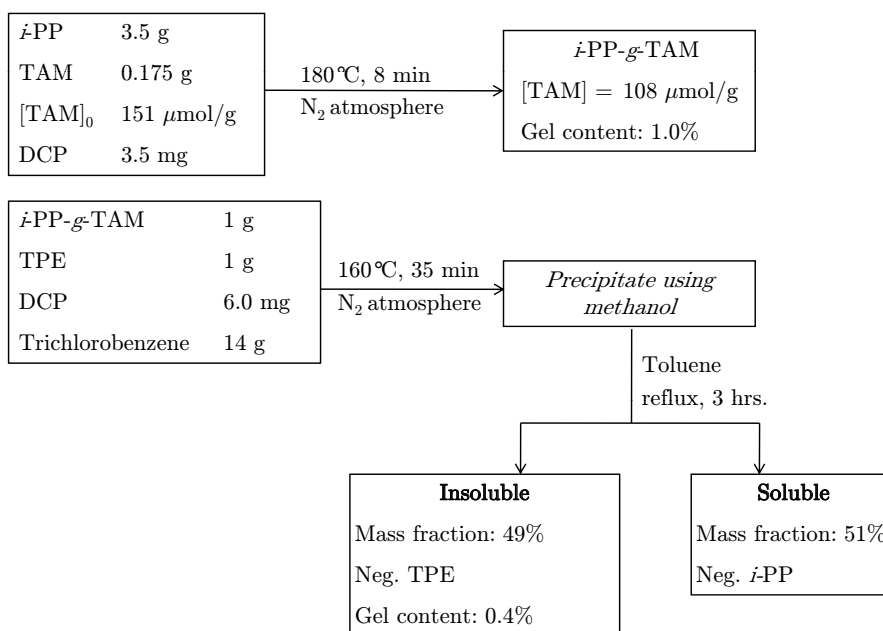
Figure 3.9: Results for the macrocoagent approach synthesis of *i*-PP-*g*-TPE

macrocoagent was codissolved with TPE in the presence of DCP. After the decomposition of 99% of the initiator, the homogeneous reaction mixture was precipitated from solution using methanol. The crude product was then fractionated by submerging in a stainless steel mesh bag in refluxing toluene. From the fractionation products, it was concluded that the grafting of TPE onto *i*-PP in solution produced a copolymer in negligible yield. The toluene fractionation products of the crude copolymer yielded an insoluble material consisting entirely of PP products and an extract that consisted

almost entirely of the TPE. The FT-IR spectra for the toluene fractionation products are illustrated in figure 3.10.
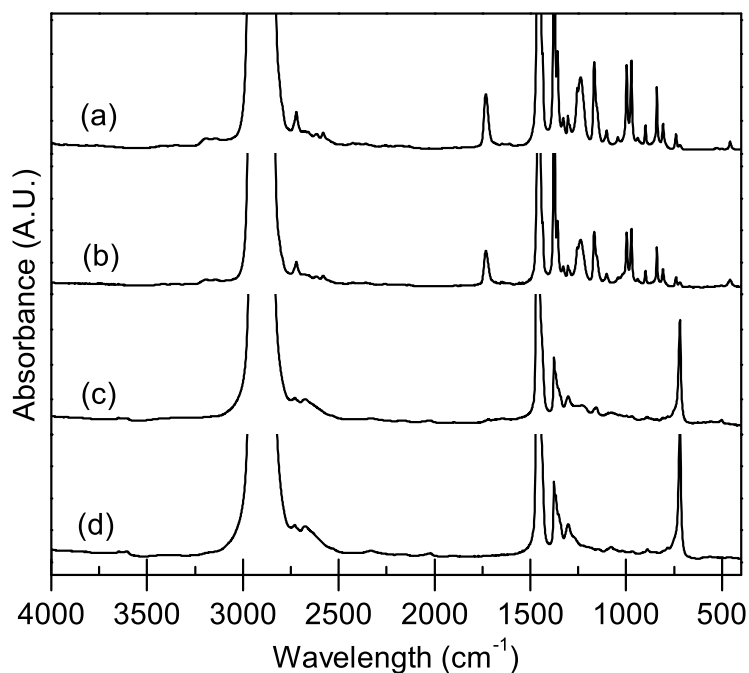
Figure 3.10: FT-IR spectra of the toluene fractions of the i-PP-g-TPE copolymer (a. i-PP-g-TAM macrocoagent; b. toluene retentate; c. toluene soluble fraction; d. TPE)

The fractionation procedure was effective at separating the PP products from ungrafted TPE, and the procedure was confirmed using a blend of i-PP and TPE where the homopolymers were separated in quantitative yields. The toluene retentate (b) shows only evidence of PP and PP-g-TAM with no absorption due to TPE, as the spectrum lacks the characteristic TPE peak between 790-675 cm^{-1}. Furthermore, the toluene extract spectrum (c) does not show evidence of the characteristic PP doublet at 1025-950 cm^{-1} indicating that all of the PP products were retained in the mesh bag. These results indicate that under the conditions presented in figure 3.9, a negligible

amount of copolymer was produced. A similar copolymer synthesis was attempted using an i-PP-g-TAM macrocoagent with a high TAM graft content ([TAM] = 142 μmol/g), but the copolymer fractionation yielded results similar to those described above.

3.4.8   Limitations to the Macrocoagent Approach

Trichlorobenzene was selected for this study due to its high boiling point (214°C) and stability towards hydrogen abstraction. However, PEO is poorly soluble in TCB and in order to achieve miscibility, high levels of solvent were used. The level of dilution in the copolymer synthesis is believed to be greater than the critical concentration for chain entanglement, where the polymer chains no longer overlap [67]. Beyond the critical concentration, the polymer chains are widely separated and do not encounter each other. The separation between polymer chains leads to a significant decrease in the frequency of PEO macroradical encounters with PE-g-TAM chains.

Despite the more similar polarity of PP and TPE, a high TCB loading was also needed to codissolve these two polymers. Due to this high TCB loading, there was little chain entanglement and interaction between the TPE macroradicals and the macrocoagent. The solution-based copolymer synthesis is limited by the lack of solvents that can codissolve the two homopolymers and be inert towards hydrogen abstraction. Even for somewhat similar polymers, such as i-PP and TPE, the solvent concentrations needed are well beyond the critical concentration resulting in little interaction between chains.

Another factor to consider is PEO's poor solubility in trichlorobenzene and its effect

on the conformation of the polymer in solution. PE is quite soluble in TCB and when solvated, the chains are well dispersed throughout the solution volume. Due to its poor solubility, PEO polymer chains take on a coil-like conformation thereby decreasing their hydrodynamic volume. The coil-like conformation of PEO lowers the chain entanglement between the two polymers and thereby limits the interactions between the PE-g-TAM and PEO macroradicals. This lack of chain entanglement between the two polymers is believed to further limit the distribution of PEO in the retained copolymer. Dilution beyond the critical concentration and the presence of polymer in a contracted coil conformation is characteristic of a low solution viscosity.

Furthermore, it is believed that the grafting of TAM in the macrocoagent step does not result in a product with an even distribution of grafted adducts. Assuming the polymer has a normal molecular weight distribution, when peroxides are evenly distributed within the polymer, the radicals that form have a higher statistical likelihood to attack the larger chains. Therefore TAM will preferentially graft to the larger chains resulting in an uneven graft distribution across the molecular weight distribution of the polymer. This occurrence of an uneven graft distribution in the macrocoagent is the focus of Chapter 4.

3.5   Conclusions

A coagent grafting approach for preparing graft copolymers does not give products with an equal distributions of the two homopolymers. It is believed that the results observed in the one-step approach are due to the differences in grafting reactivities between PE and PEO. Using the macrocoagent approach, the reactivities of the two

copolymers were decoupled, however, the low yields are believed to be due to a lack of chain entanglements in solution. The radical-mediated coupling of polymers in solution is limited by the availability of solvents that codissolve the two homopolymers below the critical concentration for chain entanglements and are inert to hydrogen abstraction reactions.

Chapter 4

Effect of Coagent on the Molecular Weight Distribution of Polyethylene

4.1 Introduction

Organic peroxides have been widely used for the production of thermoset polyethylene resins. Dicumyl peroxide homolytically cleaves to produce two cumyloxy radicals that are theoretically capable of abstracting two hydrogen atoms from the polymer to give a pair of macroradicals. Termination of these intermediates by combination can generate one crosslink, meaning that dialkyl peroxide-only cures have a maximum yield of one crosslink per mole of peroxide. However, inefficiencies in the abstraction of hydrogen from the polymer and the tendency for some radicals to terminate via

disproportionation, means that the crosslink yield falls short of this limit. For example, twenty-three percent of alkyl radicals generated from n-pentadecane and dicumyl peroxide terminated by disproportionation [65].

In order to improve the efficiency of peroxide cures, multifunctional unsaturated co-agents can be employed. By using either trivinylic or triallylic coagents, an improvement in the crosslink density can be achieved without an increase in initiator concentration. This improvement is due to a closed propagation sequence involving macroradical attack on C=C bonds and hydrogen atom donation to the resulting coagent-derived radical. Since crosslinks can be created without terminating radical intermediates, coagent-assisted cures can achieve high crosslink densities using comparatively little initiator.

The radical-mediated crosslinking of polyethylene is not a selective process and the product distribution is based on the probability of radical encounters. Assuming that the probability of abstracting a hydrogen atom is the same for all -CH$_2$- groups in a polyethylene melt, larger polymer chains are statistically more likely to donate hydrogens than smaller chains. These larger macroradicals will, in turn, combine to form even larger chains. As the material reaches the gel point, a small population of chains would be highly crosslinked while the majority of the matrix would remain mostly unmodified.

Tobita [68] and Gloor et al. [69] have demonstrated these principles for a random molecular weight distribution, showing that the introduction of random crosslinks causes a small chain population to grow in size while the rest of the matrix remains mostly unmodified. Multifunctional coagents, like triallyl trimesate should amplify

this non-uniform crosslinking distribution. Larger chains will be statistically more likely to undergo coagent addition, and the resulting macrocoagent will have a more efficient means of building molecular weight than other chains in the population. The formation of a small population of crosslinked chains containing high graft contents and the enhancement of bimodality in the molecular weight distribution of polyethylene due to the coagent is the focus of this phase of the study.

4.2   Objectives

The objective of this phase of the project was to investigate the graft distributions in a highly graft-modified polyethylene system. Furthermore, the effect of grafting several common coagents on the molecular weight distribution of polyethylene was studied. The coagents used in this study were triallyl trimesate (TAM), triallyl phosphate (TAP) and trimethylolpropane triacrylate (TMPTA), the structures of which are illustrated in figure 4.1. The effect on the molecular weight distribution was de-
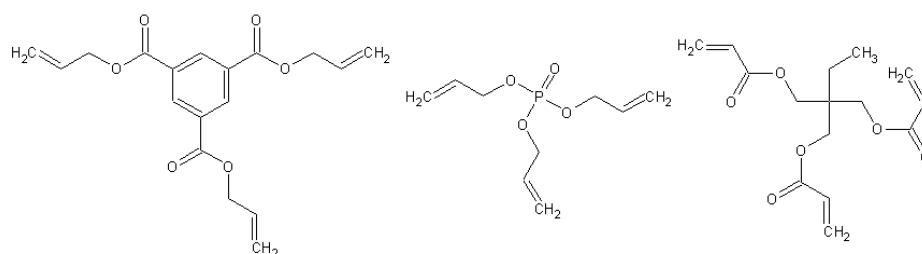

Figure 4.1: Coagents used for the radical-mediated crosslinking of polyethylene (left-to-right: TAM, TAP, TMPTA)

termined by measuring the rheological properties and the gel contents of the modified resins.

4.3 Experimental

4.3.1 Materials

Polyethylene (PE, M_n = 1400, Scientific Polymer Products) was purified by dissolution-precipitation (chlorobenzene-methanol) prior to use. Dicumyl peroxide (DCP, 98%, Sigma-Aldrich), triallyl trimesate (TAM, Monomer-Polymer), triallyl phosphate (TAP, > 94%(GC), TCI) and trimethylolpropane triacrylate (TMPTA, technical grade, Sigma-Aldrich) were all stored under refrigeration. An ethylene-octene copolymer (LLDPE, MFI = 1.0, DuPont-Dow Elastomers) was used without purification. The following solvents were used as received from Fisher Scientific: methanol (ACS grade), ethyl ether anhydrous (ACS grade), chloroform (ACS grade), chlorobenzene (certified mono), xylenes (ACS grade) and toluene (ACS grade). 2,6-Di-*tert*-butyl-*p*-cresol (BHT, 99%, Alfa Aesar) was used as received.

4.3.2 Gel Formation in Radical-Mediated Crosslinking of a Low-Molecular Weight Polyethylene

TAM (0.149 g, 0.45 mmol) and DCP (0.0541 g, 0.2 mmol) were solution cast in ether onto PE (5 g) in a 50 mL round-bottom flask and allowed to dry for 30 minutes under blowing air. The polymer was then degassed by three pump-fill cycles and put under a nitrogen atmosphere before stirring in a oil bath at 120°C for 10 minutes. Following the homogenous mixing of the reagents, the flask was submerged in oil at 180°C for 9 minutes. The flask was then removed and allowed to cool under nitrogen. A 1 g aliquot was analyzed for gel content by submerging in a stainless steel mesh bag (120

mesh) in refluxing xylenes for 6 hours. The gel extraction was stabilized with BHT (~10 mg). The sol was precipitated from xylenes using methanol (200 mL) and both the gel and precipitated sol were dried *in vacuo*. The graft content was determined by comparing the ratio of the area of the bound carbonyl resonance (1830-1668 cm^{-1}) to an internal standard resonance for PE (2093-1996 cm^{-1}). The residual unsaturation of the coagent was analyzed by ^{1}H-NMR using a 50 mg sample dissolved in toluene-d$_8$ at 80°C.

4.3.3 Coagent-Assisted Crosslinking of Polyethylene

TMPTA (1.06 g, 3.6 mmol), TAM (1.19 g, 3.6 mmol) and DCP loadings of 0.216 g (0.8 mmol), 0.054 g (0.2 mmol) and 0.027 g (0.1 mmol) were solution cast in ether onto LLDPE (40 g) and allowed to dry for 30 minutes under blowing air. TAP (0.785 g, 3.6 mmol) was solution cast in chloroform due to its poor solubility in ether. The polymer was then blended for 5 minutes in a Haake Polylab R600 internal batch mixer at 60 rpm and a nominal block temperature of 70°C. Following blending, a 5 g aliquot was reacted in an Alpha Technologies Advanced Polymer Analyzer APA 2000 at 180°C for 9 minutes. A 1 g aliquot of the reacted blends was analyzed for gel content by submerging in a stainless steel mesh bag (120 mesh) in refluxing xylenes for 6 hours. The gel extraction was stabilized with BHT (~10 mg).

4.3.4 Analysis

NMR spectra were acquired with a Bruker AVANCE-600 spectrometer (^{1}H, 600.17 MHz) by dissolving samples in toluene-d$_8$ at 353K. For quantitative integrations of

allylic proton resonances, a d1 relaxation time of 20 seconds was used. FT-IR spectra were acquired with a Nicolet Avatar 360 FT-IR ESP spectrometer using either thin films or pressed KBr disks. Crosslinking reactions involving LLDPE were conducted in a Alpha Technologies Advanced Polymer Analyzer APA 2000 oscillating at a frequency of 100 cpm with a 3° arc.

4.4   Results

4.4.1   Gel Formation in the Radical-Mediated Crosslinking of a Low-Molecular Weight Polyethylene

The radical-mediated grafting of a coagent onto polyethylene produces resins that have exceeded their gel points (see section 4.4.2). These thermoset products demonstrate elasticity in the melt state and are insoluble in boiling xylenes. However, coagent grafting does not affect polymer chains equally, as only some chains reach a molecular weight higher than the gel point. In this study, xylene has been used to selectively fractionate those chains whose molecular weights exceed the gel point from the soluble matrix material. Those extracted chains with molecular weights below the gel point were precipitated from xylenes using methanol in order to isolate the polymer from any unbound TAM or DCP decomposition by-products. Furthermore, many of the chains that have not approached the gel point will remain soluble in toluene at 80°C and can be characterized by ^{1}H-NMR. In this phase of the study, a low molecular weight polyethylene/TAM blend was reacted with initiator loadings sufficient to form gel. The product was fractionated and analyzed for graft content

and residual coagent unsaturation.

Polyethylene and TAM were activated by DCP for 10 initiator half-lives at 180°C. The
reaction yields and the results of the xylene extractions are summarized in figure 4.2.
The graft content of the xylene extraction products were analyzed by FT-IR where
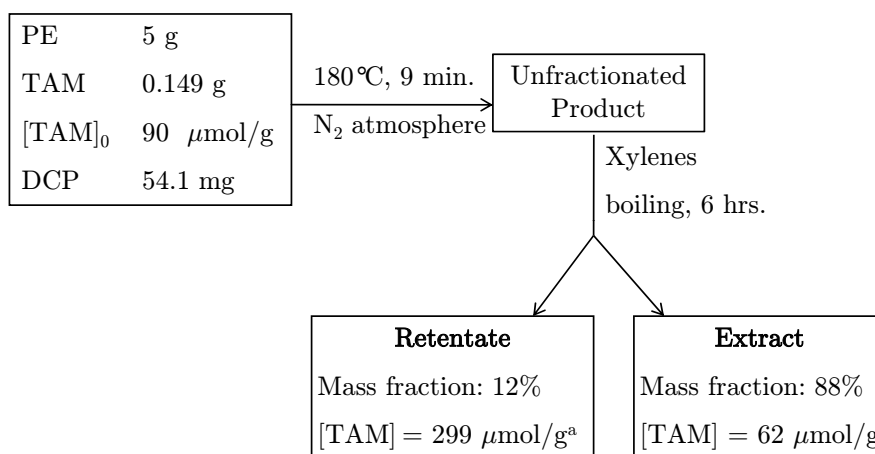
Figure 4.2: Summary of TAM-assisted crosslinking of low molecular weight
polyethylene (a. approximate value based on mass balance)

the graft content of the retentate was approximated based on the assumption that
TAM was grafted in quantitative yields. This assumption was confirmed by a similar
fractionation in toluene, where the graft contents for the sol and gel were within the
range of the calibration curve.

The relatively small amount of xylene-insoluble gel contained a disproportionate
amount of bound coagent, providing clear evidence of a non-uniform graft distribu-
tion in coagent-assisted polyethylene crosslinking. Furthermore, the sol was analyzed
by ^{1}H-NMR for residual allylic groups, and nearly all of the groups were converted as
the integrations for the resonances at 9.05 and 4.25 ppm, which corresponds to the
resonances for H_G and H_A from figure 3.4, were equivalent.

Figure 4.3 demonstrates FT-IR spectra of the fractions isolated from this PE-*g*-TAM sample. TAM and polyethylene were present in both the sol and gel, indicating that the gel is not just homopolymerized coagent, but a graft-modified chain population that has reached its gel point. The strong carbonyl resonance between 1760-1690 cm^{-1} is derived from bound TAM, whereas the strong resonances between 1520-1410 cm^{-1} and 755-670 cm^{-1} are characteristic of polyethylene.
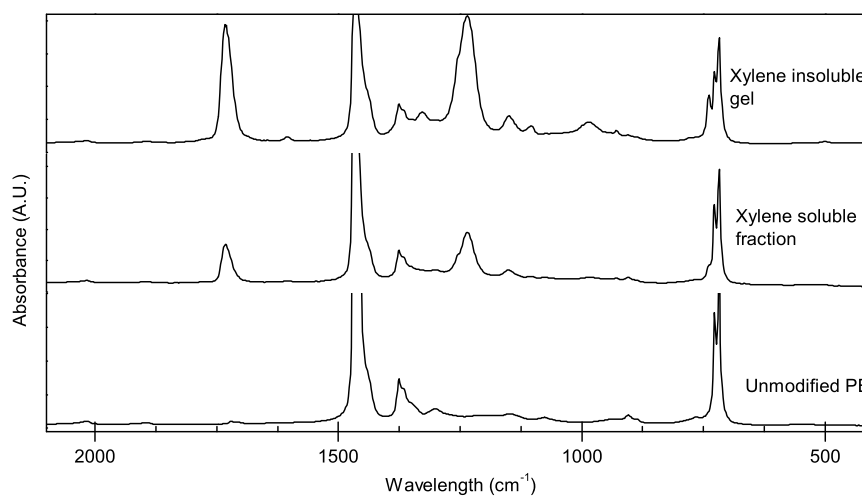
Figure 4.3: FT-IR spectra of fractionation products for PE-*g*-TAM (a: xylene insoluble gel; b: xylene soluble fraction; c: unmodified PE)

The uneven graft distribution within PE-*g*-TAM may have an adverse effect on the graft copolymer syntheses presented in Chapter 3, since only a small population of PE chains are capable of coupling with PEO. Though it has been demonstrated to occur in PE-*g*-TAM system, non-uniform graft distributions have been observed with other coagents, such as trimethylolpropane triacrylate (Appendix A).

4.4.2   Coagent-Assisted Crosslinking of Polyethylene

Studies of coagent-assisted PE curing were broadened to include other coagents. Oscillatory shear rheometry was used to investigate the extent of crosslinking as it can be measured up to and beyond the gel point of the matrix. Figure 4.4 demonstrates the effect of peroxide on the complex viscosity and the rate of change in the storage modulus (dG'/dt). Peroxide alone increased the complex viscosity (η^*) from 4.4 to a plateau of 9.4 kPa·s at 180°C. In figure 4.4, the initial decrease in complex viscosity was due to melting of sample in rheometer.
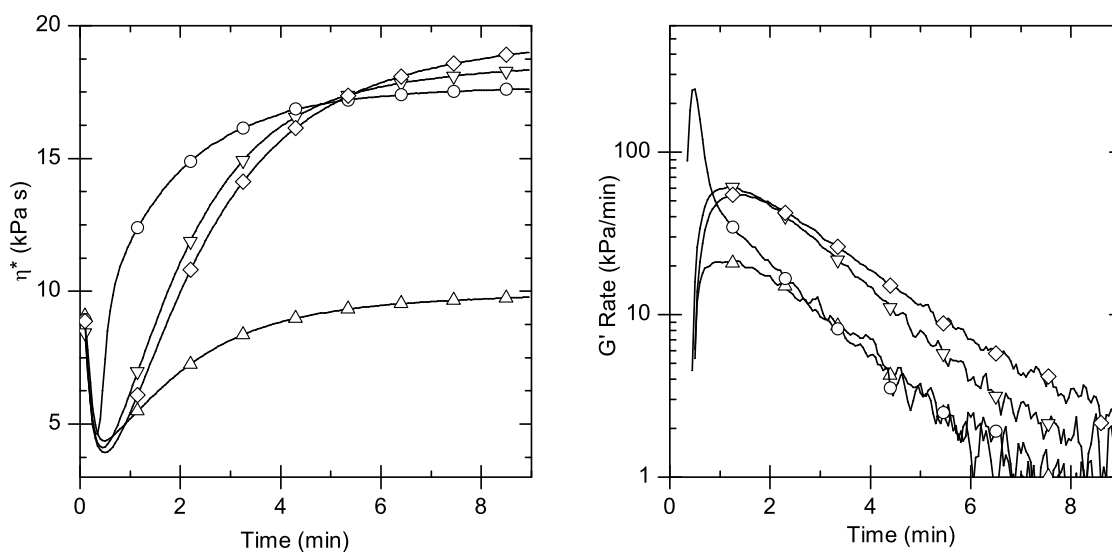
Figure 4.4: Effect of curing with coagent and peroxide on the complex viscosity of LLDPE. △ DCP, no coagent; ▽ TAP; ○ TMPTA; ◇ TAM. ([coagent] = 90 μmol/g, [DCP] = 5 μmol/g, T = 180°C)

The inclusion of coagent caused a significant increase in the complex viscosity. In a coagent-free reaction, the number of crosslinks formed is limited to one-half of the number of polymeric macroradicals generated by the peroxide. In the presence of an unsaturated monomer, such as the coagents in this study, when the polymeric

macroradical adds to the C=C bond, the adduct radical (V·) can abstract a hydrogen from an adjacent chain, thereby closing the grafting reaction sequence. The extent of crosslinking is no longer limited exclusively by the number of moles of initiator in the system and depends mainly on the kinetic chain length for grafting and the extent of oligomerization of the coagent. The kinetic chain length controls the extent of crosslinking by limiting the number of times a coagent can be added by a given radical before it terminates.

The kinetic chain length is dependent on the initiator loading, the decomposition rate of the peroxide (k_d), the concentration of the coagent and its reactivity towards grafting [46]. The extent of crosslinking is also controlled by the propensity of the coagent to oligomerize, due to the consumption of C=C bonds without contributing to the formation of crosslinks. Oligomerization is a significant concern in the grafting of vinyl monomers, but less so with allylic ones due to their lower rates of polymerization. In selecting a coagent for use in either crosslinking or the formation of graft copolymers, grafting should completely consume coagent unsaturation without engaging in oligomerization.

The gel content of the cured polymers was analyzed to further confirm the extent of crosslinking (Table 4.1). The extent of gelation clearly demonstrates the significant contribution of the coagent to the crosslink density of the system. However, in the absence of initiator, coagent has a negligible impact on the crosslink density of the LLDPE blend, which can be seen in Appendix B.

Table 4.1: Effect of coagent on the gel content of crosslinked LLDPE[a]

Coagent	Gel Content (%)
-	13
TMPTA	93
TAP	84
TAM	95

a. [Coagent] = 90 μmol/g, [DCP] = 5 μmol/g

4.4.3 Allylic Coagent-Assisted Crosslinking of Polyethylene

Allylic monomers, such as TAM and TAP do not form homopolymers of high molecular weight when activated by peroxides. Bartlett and Altschul [70] demonstrated that independent of the peroxide loading, the degree of polymerization for allyl acetate was found to be 13.7 ± 0.4 over a range of 1 - 10 wt% of benzoyl peroxide at 80°C. Rather than polymerize to a high degree, the propagating radical on an allylic monomer has a high tendency to undergo termination via chain transfer. The propagating radical for allyl acetate will abstract hydrogen from cyclohexane at 80°C with a transfer constant, which is defined as k_{tr}/k_p, of 5.6×10^{-3} [71].

Even the modest kinetic chain lengths provided by coagents such as TAM and TAP (figure 4.4) can impact crosslink densities. This is further confirmed by the G' rate of the TAP and TAM systems in figure 4.4, where G' descends at a much higher rate than observed in the absence of coagent. Note that the coagent grafting rate is responsible for the rate of complex viscosity growth, but the ultimate extent of crosslinking is a function of the propensity of a coagent to oligomerize.

4.4.4   Trimethylolpropane Triacrylate-Assisted Crosslinking of Polyethylene

TMPTA was also investigated for its use in the coagent-assisted crosslinking of polyethylene. Figure 4.4 shows that TMPTA produced a G' growth rate of 244.9 kPa/min, which declined after 2 minutes to that of the coagent-free reaction. This demonstrates how the grafting of TMPTA undergoes two phases; initially there is a rapid consumption of free acrylate that is grafted to the polymer causing the increase in complex viscosity and storage modulus. This period of rapid grafting is followed by a period where rate of crosslinking mirrors that of the coagent-free system.

The rapid crosslinking with TMPTA in the coagent-assisted reaction is consistent with the exceptional reactivity of acrylates with respect to radical addition. The degree of polymerization for ethyl acrylate at 80°C in benzene was found to be 12,800, almost three orders of magnitude higher than allyl acetate. However, the transfer constant to cyclohexane for ethyl acrylate is 1.22×10^{-4}, which is almost 50 times less than that for allyl acetate [72]. This is indicative of a monomer that tends to homopolymerize rapidly, with a low tendency to abstract hydrogen and close the grafting reaction sequence. This preference for oligomerization limits the efficacy of acrylic monomers in coagent-assisted PE crosslinking, since monomer is inefficiently consumed.

4.4.5   Effect of Initiator Loading on Grafting of Coagents

In order to further clarify the behavior of the coagent-assisted crosslinking of LLDPE, reactions were conducted at two other DCP loadings, 20 and 2.5 μmol/g. As expected,
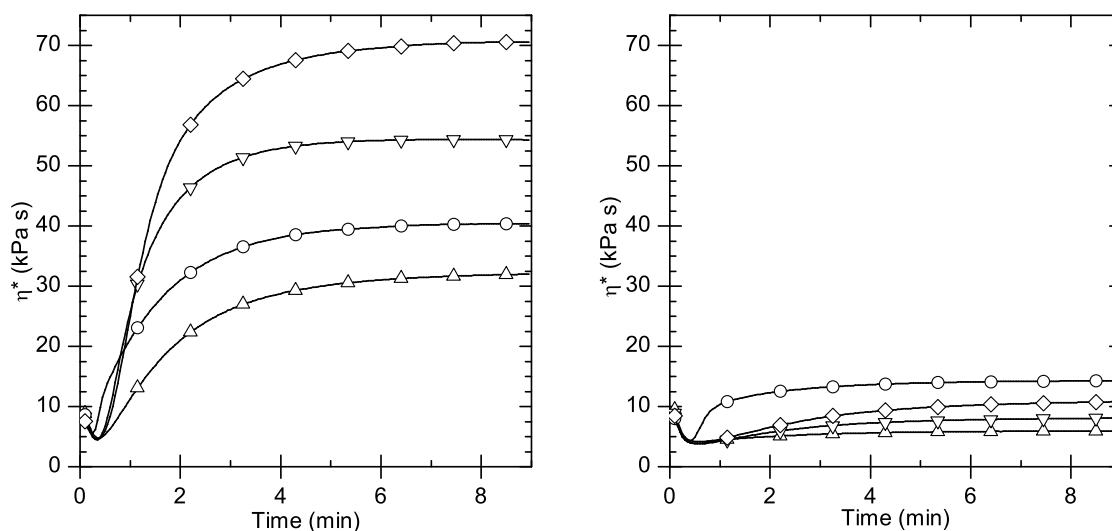
Figure 4.5: Cure measurements on LLDPE with coagent and peroxide. △ DCP, no coagent; ▽ TAP; ○ TMPTA; ◇ TAM. ([coagent] = 90 μmol/g, left: [DCP] = 20 μmol/g; right: [DCP] = 2.5 μmol/g)

for each coagent and the coagent-free system, there was an increase in the plateau η^* with increasing initiator loading; however, with increasing initiator loadings, the relative order of coagent performance changed. The plateau complex viscosities for the three coagents and the coagent-free system are summarized in table 4.2. The G' rate plots (figure B.2) for the crosslinking reactions in figure 4.5 are shown in Appendix B.

Table 4.2: Effect of DCP loading on the plateau complex viscosity of LLDPE-g-coagent[a]

[DCP] (μmol/g)	Coagent-free (kPa·s)	TMPTA (kPa·s)	TAM (kPa·s)	TAP (kPa·s)
0	4.35	4.02	4.14	4.12
2.5	5.94	14.3	10.8	8.09
5.0	9.77	17.6	19.0	18.3
20	32.0	40.4	70.6	54.3

a. [Coagent] = 90 μmol/g, T = 180°C

4.5   Conclusions

Statistical preference for grafting larger chains leads to non-uniform bound coagent distributions in the radical-mediated modification of polyethylene. This non-uniformity is expected to impact negatively on any subsequent attempts to generate copolymers through a macrocoagent approach. The inclusion of a multifunctional unsaturated coagent to a peroxide-initiated PE curing system improves the crosslink densities by creating crosslinks without consuming macroradicals. The higher plateau complex viscosity for TAP and TAM at intermediate to high DCP concentrations is due to their high transfer constant and their low propensity to oligomerize. On the other hand, TMPTA is kinetically more reactive, but has a much greater tendency to oligomerize, therefore reducing its crosslinking efficiency.

Chapter 5

Conclusions

5.1 Summary

5.1.1 Copolymer Synthesis

The one-step graft copolymer synthesis was shown to be inefficient in coupling polyethylene with poly(ethylene oxide) due to the differences in reactivities between the two polymers towards macroradical formation. By grafting triallyl trimesate to polyethylene in bulk, then coupling the grafted polymer with poly(ethylene oxide) in solution, a 9.5% graft yield of poly(ethylene oxide) was attained. However, when isotactic polypropylene was pre-grafted with TAM and then coupled with a thermoplastic polyolefin elastomer in solution, negligible copolymer was formed. Poor copolymer yields were experienced due to the lack of chain entanglements between the polymers in solution. The efficiency of the macrocoagent approach is limited by the lack of available solvents that can codissolve the two polymers, at low loadings, while

remaining unreactive towards hydrogen abstraction.

5.1.2 Effect of Coagent on the Molecular Weight Distribution of Polyethylene

The grafting of triallyl trimesate onto polyethylene results in the formation of two distinct chain populations. One is a small, high molecular weight population with a high graft content, whereas the remaining chains contained only a modest graft content. This uneven graft distribution is due to the higher statistical likelihood for the formation of macroradicals on the longer chains, which undergo further chain growth through the addition of triallyl trimesate. A survey of several common coagents was used to demonstrate their contribution to the crosslink density of polyethylene over that of the coagent-free system. At intermediate to high initiator loadings, allylic coagents had a greater contribution to the crosslink density of polyethylene over that of vinyl ones. This improved performance is due to the allylic coagents' low degree of oligomerization and their high tendency to terminate via chain transfer, thereby forming crosslinks without terminating radicals.

5.2 Future Work

Alternative solvents for the radical-mediated coupling of dislike polymers should be studied as to lower the solvent loading needed for comiscibility. For the radical-mediated grafting of coagents to polyethylene, the effect of grafting on the molecular weight distribution of the resin should be further investigated using triple-detector

gel permeation chromatography.

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Appendix A

Effect of Grafting TMPTA on the Molecular Weight Distribution of PE

A.1 Experimental

A.1.1 Materials

Polyethylene (PE, $M_n = 1400$, Scientific Polymer Products) was purified by dissolution-precipitation (chlorobenzene-methanol) prior to use. Dicumyl peroxide (DCP, 98%, Sigma-Aldrich), triallyl phosphate (TAP, > 94%(GC), TCI) and trimethylolpropane triacrylate (TMPTA, technical grade, Sigma-Aldrich) were all stored under refrigeration. The following solvents were used as received from Fisher Scientific: methanol

(ACS grade), ethyl ether anhydrous (ACS grade), chlorobenzene (certified mono) and xylenes (ACS grade). 2,6-Di-*tert*-butyl-*p*-cresol (BHT, 99%, Alfa Aesar) was used as received.

A.1.2 Gel Formation in the Radical-Mediated Crosslinking of a Low-Molecular Weight Polyethylene

TMPTA (0.133 g, 0.45 mmol) and DCP (0.0165 g, 50 μmol) were solution cast in ether onto PE (5 g) in a 50 mL round-bottom flask and allowed to dry for 30 minutes under blowing air. TAP (0.098 g, 0.45 mmol) was solution cast in chloroform. The reaction conditions and extraction procedures were the same as those presented in section 4.3.2. The graft content was determined by comparing the ratio of the area of the bound carbonyl resonance (1786-1660 cm^{-1}) to an internal standard resonance for PE (2093-1996 cm^{-1}). The residual unsaturation of the coagent was analyzed by ^{1}H-NMR using a 50 mg sample dissolved in toluene-d$_8$ at 80°C.

A.2 Results

A.2.1 PE-*g*-TMPTA

TMPTA and polyethylene were reacted in the presence of DCP for at least 10 half-lives at 180°C. The reaction scheme and the results of the xylene extractions are summarized in figure A.1. The soluble product from the xylene extraction had a TMPTA graft content of 43 μmol/g, whereas the insoluble material contained mostly
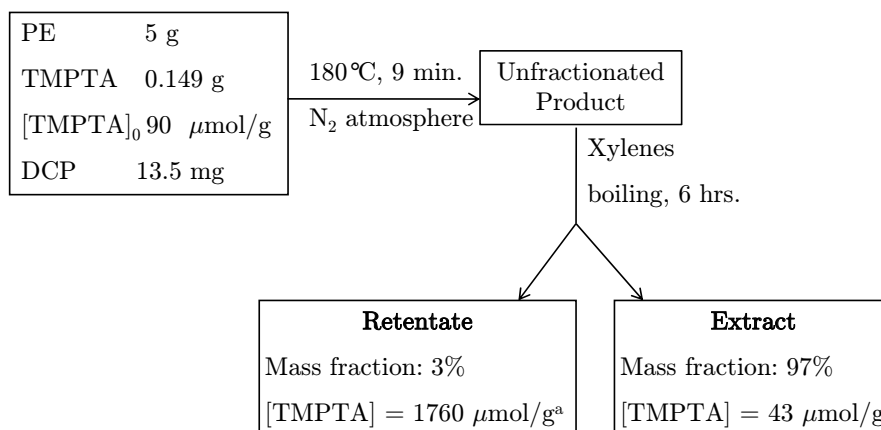
PE	5 g
TMPTA	0.149 g
$[\text{TMPTA}]_0$	90 μmol/g
DCP	13.5 mg

180℃, 9 min.
N_2 atmosphere

Unfractionated
Product

Xylenes
boiling, 6 hrs.

Retentate

Mass fraction: 3%

$[\text{TMPTA}] = 1760\ \mu\text{mol/g}^{\text{a}}$

Extract

Mass fraction: 97%

$[\text{TMPTA}] = 43\ \mu\text{mol/g}$

Figure A.1: Summary of TMPTA-assisted crosslinking of low molecular weight
polyethylene (a. approximate value based on mass balance)

oligomerized TMPTA. The graft content of the gel was approximated based on the
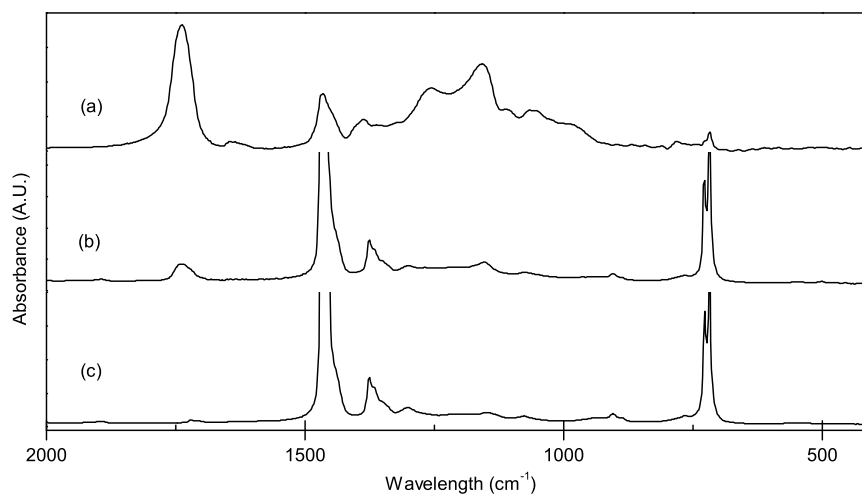complete consumption of TMPTA. The strong carbonyl resonance between 1860-1640

Figure A.2: FT-IR spectra of fractionation products for PE-*g*-TMPTA (a: xylene
insoluble gel; b: xylene soluble fraction; c: unmodified PE)

cm^{-1} is derived from bound TMPTA, whereas the strong resonances between 1520-
1410 cm^{-1} and 755-670 cm^{-1} are characteristic of polyethylene.

The disproportionately high graft content in the insoluble fractions is consistent with the high rate constant for polymerization of acrylic monomers. Upon the evolution of the first few macroradicals, the radical concentration was sufficient to polymerize the TMPTA to near completion, with minimal abstraction of hydrogen from adjacent chains. All subsequently formed macroradicals terminated in the absence of coagent. This resulted in a few PE chains grafted to long TMPTA oligomers, while the majority of the matrix resembled that of coagent-free crosslinked PE.

A.2.2 PE-g-TAP

Despite the forcing conditions used ([DCP] = 90 μmol/g, [TAP] = 90 μmol/g), the PE/TAP system never reached the gel point. The crude product was completely soluble in refluxing xylenes and contained a quantitative graft yield. The xylene soluble fraction was precipitated using methanol and the recovered product was characterized by ^{1}H-NMR to reveal the complete consumption of the unsaturation of the bound triallyl phosphate. Further study is needed of the bimodality in the PE-g-TAP system.

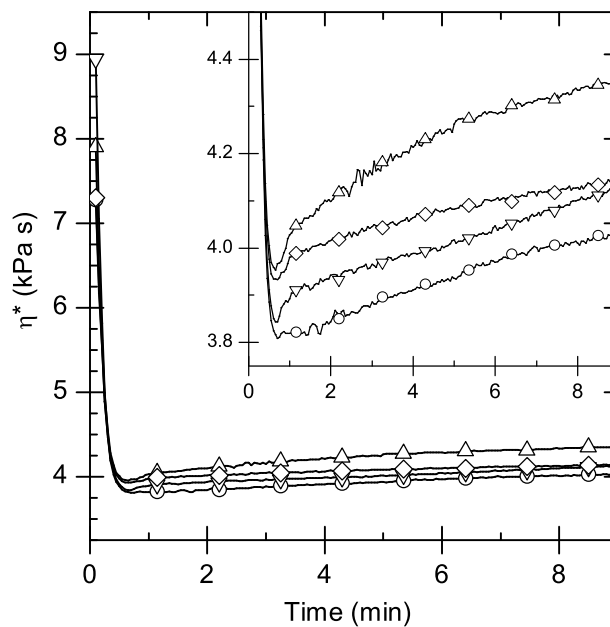# Appendix B

Steady-Shear Oscillatory Measurements of LLDPE

Figure B.1: Steady-shear oscillatory measurements of LLDPE with coagent the in absence of initiator. △ no coagent; ▽ TAP; ○ TMPTA; ◇ TAM ([coagent] = 90 μmol/g, T = 180°C)
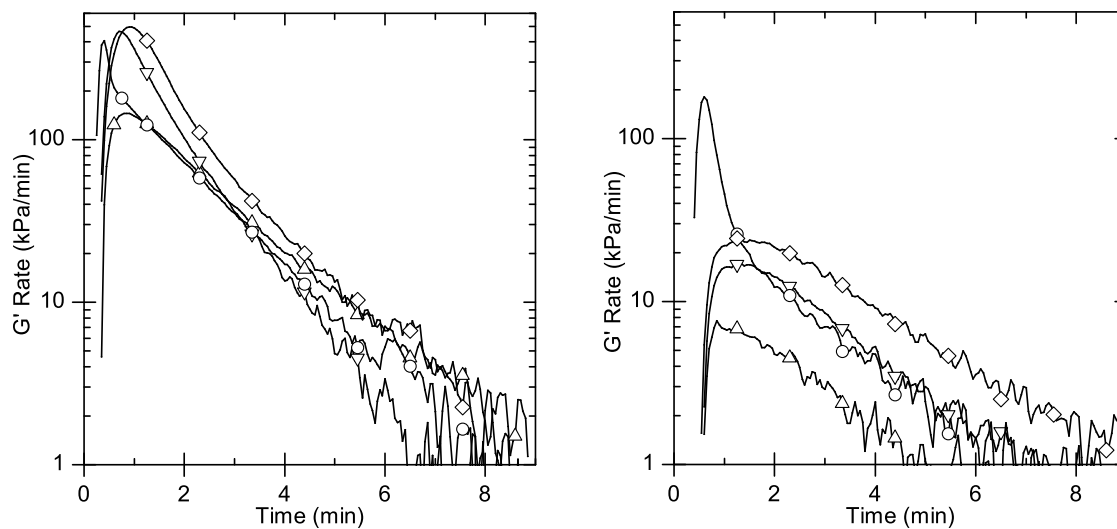
Figure B.2: G' rate measurements for LLDPE. △ DCP, no coagent; ▽ TAP; ○ TMPTA; ◇ TAM. ([coagent] = 90 μmol/g, left: [DCP] = 20 μmol/g; right: [DCP] = 2.5 μmol/g)