INVESTIGATION OF RADIATION CROSSLINKING STYRENIC BLOCK COPOLYMERS AND MALEIMIDE-TERMINATED IMIDE OLIGOMERS

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INVESTIGATION OF RADIATION CROSSLINKING STYRENIC BLOCK COPOLYMERS AND MALEIMIDE-TERMINATED IMIDE OLIGOMERS

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ABSTRACT

This dissertation consists of two research projects. In the first part of the dissertation, the effect of electron beam (e-beam) radiation on styrenic block copolymers (SBCs), including poly (styrene-block-butadiene-block-styrene) (SBS), poly (styrene-block-isoprene-block-styrene) (SIS) and a newly developed poly (styrene-block-isoprene/butadiene-block-styrene) (SIBS), were investigated as functions of radiation dose and concentration of pro-rads. The second part of the dissertation is about synthesis and characterization of ultraviolet (UV)-curable maleimide-terminated imide oligomers for high temperature coating application.

The effect of e-beam radiation on properties of SBCs was studied by investigating the structure and mechanical properties of SBCs at four radiation doses (60, 120, 190 and 240 kGy). The effect of pro-rads on promoting radiation induced crosslinking reaction of SIBS was also studied. Tensile properties of SBCs were investigated. The crosslink density was compared based on dynamic mechanical analysis (DMA) and equilibrium swelling method. The stress relaxation behavior was studied as function of temperature and radiation dose. Molecular weight characterization of soluble portion of the SBCs after crosslinking was analyzed by size exclusion chromatography (SEC). Furthermore, the gel content was calculated and the structure of the gel portion was investigated by solid state nuclear magnetic resonance ($^{13}$C NMR). Last, the morphologies were observed by both small angle X-ray scattering (SAXS) and atomic force microscopy (AFM).
It was found that the crosslink density and tensile moduli of e-beam irradiated SBCs increased as the e-beam radiation dose increased. The tensile strengths of SBCs highly depended on the crosslink density and network regularity. The tensile strength of SIBS and SIS decreased at low e-beam radiation doses (< 120 kGy) and then increased at high radiation doses (> 190 kGy), while the tensile strength of SBS significantly decreased at high e-beam radiation doses (> 190 kGy). Both crosslinking and chain scission reactions took place during the e-beam exposure. The crosslinking reaction was predominant. Cylindrical morphologies were observed for the SBCs studied. Pro-rads significantly improved the tensile properties and crosslink density of the SIBS at radiation dose below 190 kGy. Trimethylolpropane trimethacrylate (TMPTMA) and 517HP increased the tensile strength of SIBS by ~50 % without significantly sacrificing the elongation-at-break.

In the second section of the dissertation, UV-curable maleimide-terminated imide oligomers were synthesized and characterized. The UV radiation induced photopolymerization of imide oligomers with two reactive diluents, $N,N$-dimethylacrylamide (DMAA) and $N$-vinylpyrrolidone (NVP), were investigated by real-time FTIR and photo-differential scanning calorimetry (DSC). Crosslinked films were characterized by thermo gravimetric analysis (TGA), DMA and DSC. The glass transition temperature of UV-cured film was greater than 100 °C. And the film was thermally stable up to 400 °C, which was due to the high performance of imide oligomers.
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CHAPTER I
INTRODUCTION

Radiation technology has been used in crosslinking and modifying polymers, monomers and oligomers.\textsuperscript{1-5} The advantages of applying radiation technology in industrials include high energy efficiency, low processing temperature, low or zero volatile organic compounds (VOCs), high productivity, improved physical and chemical properties of materials, etc.\textsuperscript{1, 3, 5-7} Commercial interests led to extensive research on studying the radiation effect in polymers and developing radiation curable materials. Radiation technologies are used on a variety of products worldwide each day. The applications of radiation technology include coatings, inks and adhesives on various products, such as military and aerospace applications, pipes and tubings, automotives, pressure sensitive labels, electronic thin films, photovoltaics, lithograph, and encapsulation of electronic components, etc.\textsuperscript{3, 7-10} Using radiation energy to crosslink plastics and elastomers is another important application of radiation technology.\textsuperscript{10-16} The radiation crosslinked polymers have improved mechanical and barrier properties, thermal stability as well as chemical resistance.\textsuperscript{17-19}

Ultraviolet (UV) and electron beam (e-beam) are two radiation sources widely applied in industry.\textsuperscript{3, 6-7} E-beam radiation has much shorter wavelength and higher frequency than UV radiation.\textsuperscript{3} UV and e-beam curing process are typically described as using UV or e-beam radiation energy to polymerize a liquid formulation of monomers,
oligomers and other additives into a crosslinked solid film on the substrates. Radiation energy is also capable of crosslinking and degradation of high molecular weight polymeric materials, such as plastics and elastomers.\textsuperscript{2, 20-23} The difference between UV and e-beam radiation is that the UV radiation is photon from high intensity ultraviolet lamps. The e-beam radiation is accelerated electrons that can penetrate into solid materials. On the other hand, UV-curing process usually requires addition of photoinitiator that may cause some undesirable effects for the products in the long term use as well as healthy and safety concerns. However, in most cases the e-beam radiation crosslinking process does not require the addition of initiators. E-beam radiation is an alternative way to vulcanize elastomers and crosslink plastics. The investigation of effect of e-beam radiation on polymeric materials started as early as the 1940s.\textsuperscript{24} Compared to conventional vulcanization methods, it is more energy efficient and has advantages of short residence time. The important commercial applications involve improving the properties of plastics and rubbers. The properties of materials are subjected to change due to a series of chemical reactions subsequent to the ionization and excitation by high-energy e-beam radiation.\textsuperscript{2, 21-23}

Two types of high performance materials are focused in this work. One is styrenic block copolymers (SBCs) and the other is thermosetting polyimide. Part of the research covers investigation of the effect of e-beam radiation on properties of SBCs and influence of pro-rads on properties of a particular elastomer, poly (styrene-block-isoprene/butadiene-block-styrene) (SIBS). Pro-rads, also called electron beam sensitizers, which can increase the amount of reactive species of the materials irradiate under E-beam. SBCs are class of thermoplastic elastomers which contain polystyrene as end block and
rubbery segment as mid-block.\textsuperscript{25-27} Due to the phase separation, they are capable of forming physically crosslinked network at ambient temperature.\textsuperscript{28-29} Like other thermoplastic elastomers, SBCs possess the mechanical properties of vulcanized rubbers, as well as the processing characteristics of thermoplastics.\textsuperscript{26-27} The crosslinking process provides a method to improve the chemical resistance, high temperature stability, tensile properties and barrier properties of SBCs in an efficient way.\textsuperscript{12, 14, 30-32}

The main challenge has been to find out what type of chain reaction occurred in each block of SBCs and which reaction was predominant in the block copolymers at a given radiation dose. Another challenge is to improve the overall crosslinking efficiency and tensile strength of elastomers at a low e-beam radiation dose. The chain reaction for SBCs under e-beam radiation was reported to be chain scission and crosslinking.\textsuperscript{2, 21-23} Adding pro-rads may achieve the goal of increasing the crosslinking efficiency. Therefore, an additive approach was proposed. A series of difunctional and trifunctional monomers and oligomers were used in this study to promote the crosslinking reaction of SBCs. As controls, the SIBS without pro-rad was irradiated under e-beam. After e-beam radiation curing the tensile properties under uniaxial stretch, gel content, crosslink density, equilibrium swelling, molecular weight and morphology were characterized.

The effect of e-beam radiation on tensile properties and viscoelastic properties were investigated in Chapter III. The change of tensile strength, elongation-at-break and modulus of copolymer as a function of radiation dose was studied. The optimum radiation dose for increasing the tensile strength of SBCs was discussed. Stress relaxation behavior of SBCs was studied as functions of temperature and e-beam radiation dose. Chain reaction of SBCs initiated by e-beam radiation was discussed in Chapter IV. The
comparison of molecular weight, gel content, equilibrium swelling behavior, and morphology of SBCs were made to elucidate what was the predominant chain reaction in SBCs at a given radiation dose. The effect of pro-rads in SIBS was investigated in Chapter V. Ten types of pro-rads were investigated, including trifunctional acrylate, methacrylate oligomers and monomers, triallyl cyanurate and trifunctional thiols. Both effects of pro-rads concentration and e-beam radiation dose on properties of SIBS were studied.

Another part of this work is about the synthesis and characterization of UV-curable maleimide terminated imide oligomers. Polyimide was originally developed in 1955 by DuPont.\textsuperscript{33-35} Since then, it has been widely used in electric and space engineering due to its excellent thermal oxidative stability, chemical resistance, and low dielectric constant.\textsuperscript{20} The rigid aromatic chain provides a high glass transition temperature and good mechanical strength. However, linear high molecular weight aromatic polyimide in fully imidized state is usually insoluble and infusible, which makes it impossible for processing.\textsuperscript{42-44} Therefore, polyimide is processed in the form of poly (amic acid) (PAA) precursor. PAA solution was cast or coated on substrate and after that the film or coating was subsequently heated up to fully imidized state at elevated temperature. High imidization temperature (300 °C) limits its applications. Another problem with this system is that the PAA solution is sensitive to humidity, which may result in the hydrolysis induced chain scission during the storage period. In addition, the water released from imidization process may cause voids in the products, especially for the relatively high molecular weight polyimide and thick films or composites. Even though the polyimide with good solubility in common solvents was developed to solve these
problems, the drawback with soluble polyimide is poor chemical resistance. In order to overcome those drawbacks of linear thermoplastic polyimide, thermosetting polyimide was developed by NASA in the 1960s. However, the high crosslinking temperature is still a major concern for their applications in heat sensitive substrates.

The challenge of expanding the application area of polyimide is to lower the curing temperature of thermosetting polyimide. Our approach is to use UV radiation curing technology to crosslink the imide oligomers. The UV-curing process is performed at ambient temperature and is widely used in coating and printing industries. UV-curable imide oligomers can be synthesized by end-capping the oligomers with photo reactive groups. Photopolymerization of maleimide terminated oligomers was studied by some research groups. Maleimide group exhibited a strong UV absorbance in the 300 nm region, due to the C=C conjugation with the carbonyl group. In order to take advantage of the high photo reactivity of maleimide group and excellent thermal, mechanical and electrical properties of the polyimide, maleimide terminated imide oligomers were proposed for UV-curable coatings. It is a promising area in the development of radiation curable resins and polyimide application.

Synthesis and characterization of maleimide terminated imide oligomers with controlled molecular weight was discussed in Chapter VI. Maleimide terminated imide oligomers were synthesized and the UV-curing kinetics as well as the properties of cured films have been studied. Finally, Chapter VII summarizes the results obtained from Chapter III-VI about the e-beam radiation crosslinking SBCs and UV-curable imide oligomers.
CHAPTER II
BACKGROUND

Radiation curing technology is an energy efficient, environmental friendly and high throughput method to crosslink coating formulations and elastomers, and because of this it has draw much attention. The intent of this chapter is to give a brief introduction of styrenic block copolymers (SBCs), and radiation technology, especially electron beam (e-beam) and ultraviolet (UV) radiation technologies. It also summarizes recent studies in the area of e-beam crosslinking elastomers and the polyimide chemistry. In addition, it will cover the topics of effect of e-beam radiation on properties of polymers with emphasis on elastomers, and pro-rads widely used in rubber industries. This will be followed by an overview of polyimide synthetic methods and application as well as structure-properties relationship of polyimide. Last, UV-curing photochemistry of bismaleimide containing system will be summarized.

2.1 Styrenic block copolymers (SBCs)

Styrenic Block Copolymers (SBCs) are class of thermoplastic elastomers which contain polystyrene end-block and rubbery mid-block. Due to phase separation, SBCs form physically crosslinked networks at ambient temperature. SBCs are the most widely applied thermoplastic elastomers. Like other thermoplastic elastomers, SBCs possess the mechanical properties of vulcanized rubbers, as well as the processing characteristics of thermoplastics. Without any chemical vulcanization process, these
materials provide most of the useful mechanical properties of conventional rubbers, such as vulcanized natural rubbers or polybutadiene. Moreover, SBCs can be processed by various plastics processing techniques widely used in industry, such as injection molding, film blowing and melting extrusion.  

2.1.1 Structure and chemistry of SBCs

The basic structure of SBC is ordered A-B-A triblock copolymer, where A is the polystyrene block and B is the elastomeric block. The most common structure of the elastomeric block B, is polydiene, such as polybutadiene and polyisoprene. Two representative SBCs are poly(styrene-block-butadiene-block-styrene) (SBS) and poly(styrene-block-isoprene-block-styrene) (SIS), as shown in Scheme 2-1. The most important characteristic of these types of copolymers is that they form phase separated systems. This is due to the incompatibility of polystyrene and polydiene blocks, which have carefully designed block lengths and weight fractions. Two glass transition temperatures are usually observed in SBCs, unlike the random copolymers of polystyrene and polydiene, which only have a single intermediately $T_g$. Therefore, the copolymer has many properties of each homopolymer. At ambient temperature, the polystyrene phase is hard and rigid, while the polyisoprene or polybutadiene phase is soft and elastic. This rigid polystyrene phase acts as the crosslinker and provides the physically crosslinked network, as shown in Scheme 2-2, which is similar to the chemically vulcanized rubbery network. The yellow spheres represent the polystyrene aggregations, which are the physical crosslinkers in SBCs. However, unlike the chemically crosslinked network, this polystyrene domain can be softened at temperature above the $T_g$. These materials are capable of flowing and being processed by melting processing methods, just
like plastics. In addition, this behavior is thermally reversible. When the materials are cooled down to the temperature below the $T_g$ of polystyrene, the polystyrene become rigid and the crosslinked network and shape of the materials are regained. In addition, the SBCs are soluble in many organic solvents, such as cyclohexane, toluene and chloroform. These solvents are usually the solvents for each homopolymer. After evaporating the solvent, the initial elastomeric properties will regain.\textsuperscript{25-27}

Scheme 2-1 Structures of styrenic block copolymers (SBCs)

The properties of SBCs are strongly affected by the morphology of the copolymers. There are several types of equilibrium morphologies for SBCs, such as sphere, laminar or cylinder, depending on the composition of copolymers.\textsuperscript{61-63} As the styrene content is increased, the morphology changes from sphere to cylinder dispersed in the continuous rubbery phase. If the volume fractions of styrene and rubbery phase are equal to each other, an alternating lamellae morphology is formed.\textsuperscript{64} A representative morphology of SBS block copolymer is shown Figure 2-1. The two phases are aggregated into different
domains. The ordered cylinders are all oriented either perpendicular or parallel to the substrate due to the variation of film thickness.\textsuperscript{65}

![Scheme 2-2 Schematic representation of phase separation in SBCs](image)

Figure 2-1 AFM image of a 42 nm film of SBS, spin-coated on a silicon wafer. The color height scale is indicated. Reprinted with permission from\textsuperscript{65} (van Dijk, M. A.; van den Berg, R., Macromolecules 28 (20). Copyright (1995) American Chemical Society.

SBCs are mostly synthesized by anionic polymerization.\textsuperscript{64, 66} This polymerization method can precisely control the molecular weight and the structure of copolymers. Reaction condition must be strictly controlled. No oxygen, water and other impurities that can react with the propagating species are allowed. The reaction is usually carried out in an inert solvent, like cyclohexane or toluene. Organolithium is the catalyst typically used.
The polymerization proceeds either sequentially or by coupling. The block copolymers are usually synthesized by sequential living anionic polymerization.\textsuperscript{66} For a coupling reaction, polymerization starts at each end of the molecule and molecules are joined together by a coupling agent to form either a linear or radial structure.

2.1.2 Structure-property relationships of SBCs

The mechanical properties of SBCs at ambient temperature are similar to the vulcanized rubber due to the physically crosslinked network formed by phase separated systems.\textsuperscript{27} The most important property of SBC is that the stress-strain behavior is equivalent to or even better than the vulcanized natural rubber or vulcanized styrene-butadiene rubber (SBR). Such a phenomenon is commonly explained by two mechanisms.\textsuperscript{57} The first mechanism involves the polystyrene domain acting as reinforcement filler and crosslinker simultaneously. This significantly increases the tensile strength of materials. The second mechanism involves the slippage of the entangled polydiene chains and leads to the high tensile strength of SBCs. The high performance of SBCs may be attributed to both mechanisms.

As long as the SBCs have phase separated morphology, the tensile modulus and tensile strength of SBCs are not molecular weight and block length dependent.\textsuperscript{26,67} The tensile modulus depends on the polystyrene content and glass transition temperature of the hard phase.\textsuperscript{68} The total molecular weight has little effect on the modulus and tensile strength of the materials at the ambient temperature as long as the styrene content is held constant. According to Morton’s research,\textsuperscript{67} the stress-strain curves of SBS with same polystyrene content and different block length almost overlapped. SBS with higher
polystyrene content leads to a higher tensile modulus. In addition, the modulus of the rubbery phase is inversely proportional to the molecular weight between entanglements ($M_e$). This molecular weight is different from the molecular weight of mid-block in copolymers. It is much lower than the molecular weight of the mid-block of the copolymers. The values of $M_e$ for polyisoprene and polybutadiene are listed in Table 2-1. Based on the data, SIS copolymer is softer than SBS. The high elastic modulus is also attributed to the trapped entanglements in the elastomer mid-block which act as crosslinks. The molecular weight between entanglements is a critical parameter, which is related to the elastic modulus and the degree of swelling in solvent.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_e$ g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyisoprene</td>
<td>6,100</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>1,900</td>
</tr>
</tbody>
</table>

There are several possible mechanisms for the tensile failure of SBCs: elastic failure of the polydiene block, ductile failure in the polystyrene domain, and brittle fracture of the polystyrene domain. If the end block was changed from polystyrene to poly (α-methylstyrene), both tensile strength and modulus were increased due to the higher glass transition temperature of poly (α-methylstyrene). This observation supports the fact that the ductile failure of the styrenic domain is the most probable mechanism for the failure of the SBCs. As a matter of fact, one failure mechanism may be predominant in a particular situation, depending on the test conditions, such as temperature and
composition of the copolymers. The failure of SBCs could be attributed to the combination of all three mechanisms.

2.1.3 Applications of SBCs

A variety of applications have been found for SBCs since they have been synthesized and commercialized in the early 1960s by the Shell Chemical Company. The balance between high performance and good processability gives them unique properties. They are widely applied in adhesives, sealants, and coating industrials.\textsuperscript{10, 25, 70-72} SBCs are usually not used by themselves. They are compounded with other ingredients, such as polyolefin, polystyrene, bitumen, tackifying resins, oil, and various fillers, which allow tailoring of properties of final product.\textsuperscript{25, 27, 73} The end-usage of SBCs containing products range from hot melt adhesives to medical devices.

There are several ways for compounding the formulation from SBCs, including melting mixing, dry blending and solution mixing. The temperature has to be at least 40 °C above the glass transition temperature of polystyrene phase in melting compounding. The solution mixing method is useful in solvent-borne coatings, sealants, and adhesives.\textsuperscript{54} The common solvents must fulfill the requirements that the two phases are both soluble. Cyclohexane, toluene and diethyl ether are usually used in solution mixing. In most of the cases, the melting mixing is the preferred processing method in industrial process, such as extrusion, injection molding, rotational molding, blow molding, and compression molding, etc. The processing temperature should not exceed 400 °F and usually range from 300 °F to 390 °F. The unsaturated midblocks of SBCs tend to degrade or crosslink at high temperature and shearing rate.\textsuperscript{74}
2.2 Effect of electron beam radiation on polymers

High energy electron beam has significant effect on polymeric materials. The ionizing energy generates a series of reactive species that can initiate the chain reactions in materials. Polymers undergo either chain degradation or crosslinking reaction depending on their chemical structures. These reactions can change the structure of materials which results in the property changes. Most research activities in this field focused on the crosslinking effect by e-beam radiation. However, e-beam radiation usually initiates several chain reactions simultaneously. Knowing various reaction pathways in a particular polymer system is quite important yet complicated. A brief introduction of e-beam radiation technology and process as well as its effect on polymers, especially elastomers, is summarized in the following section.

2.2.1 Electron beam radiation

E-beam radiation is normally generated by an electron accelerator under high vacuum (~10^{-6} torr) to give beams with radiation energies in the MeV range. The corresponding penetration depth depends on the power of the electron beam generator and electron density of the materials. For an electron beam source, the electrons are generated by the electron gun and accelerated through a high electrical voltage. The electrons then pass through a window onto the materials.

The e-beam and UV are usually classified as an ionizing radiation source due to its high energy, which results in greater penetrating power, while the IR radiation is non-ionizing radiation. The major difference between the ionizing radiation and non-ionizing radiation is the initial event following absorption of the radiation energy. In the
case of ionizing radiation, it carries enough energy to remove an electron from an atom or molecule and generate secondary electrons. The initial absorption of ionizing radiation is typically a spatially random process and leads to the formation of free radicals or ionic species. For the non-ionizing process, it excites the motion of the atoms and molecules, or it excites an electron from an occupied orbital into an empty, higher-energy orbital. The absorption is molecular site specific and leads to an electronically excited state.³

The most important specification for the irradiation process is the absorbed dose. The effect of radiation highly depends on this parameter. Energy absorption is expressed as dose in Rad or Gray (Gy). Gray is defined as absorption of 1 Joule of energy per kilogram of material.⁸⁻⁵ The amount of radiation absorbed can be measured either directly or indirectly using a variety of dosimeters and calculated based on the following equation.⁸⁻⁶

\[
dose = \frac{\text{Absorbed energy (kJ)}}{\text{Mass (kg)}} = \frac{P(\text{kW}) \times t(s)}{M(\text{kg})} = \frac{E(\text{MeV}) \times I(\text{mA}) \times t(s)}{M(\text{kg})}
\]

(2-1)

where \( P \) is beam power, \( E \) is electron beam energy (MeV), \( I \) is beam current (mA), \( t \) is time (s), and \( M \) is mass (kg). The current is adjustable and it provides the flexibility of utilization of the accelerator for a variety of processing requirements according to the application of products.

Electron beam offers several advantages. For example, (1) the process is very fast, takes usually few seconds or minutes; (2) the electron beam can be controlled to meet the requirement of various geometrical shapes of products; (3) the high penetrating power of the electron beam allows the efficient curing of thick polymeric articles, highly
pigmented inks and coatings; (4) it is an environmental friendly process; (5) large throughputs; (6) more precise control over the process and the production of products with high quality.\textsuperscript{87}

2.2.2 Electron beam radiation on polymers

The interaction of high-energy electron beam with polymers is a very complex process.\textsuperscript{2, 21-23} The energies involved and exposed to the materials are much greater than the binding energy of any electron to an atomic nucleus. Therefore, high-energy electron beam irradiation is non-selective.\textsuperscript{88} The resulting changes are primarily a consequence of energy transfer and chain reactions. Most of the energy was dissipated as form of heat.

High-energy electron beam radiation causes both ionization and excitation in polymers upon exposure, as shown in Scheme 2-3(a). The ionization also generates secondary electrons. These excited and ionized reactants are the initial reactive species. The resultant excited molecules may undergo bond scission reactions through either a hemolytic or heterolytic way. In addition, the cations may undergo spontaneous decomposition or ion-molecule reactions. The radicals generated from the primary process will go through various secondary reactions, as shown in Scheme 2-3(b), including abstraction of hydrogen atoms or halogen atoms, addition to the double bonds, decompositions to generate small molecule products, such as CO\textsubscript{2} or H\textsubscript{2}, and chain scission and crosslinked molecules.\textsuperscript{21, 89-90}
Although the absorption of the radiation energy occurs spatially at random on a molecular scale, the subsequent chemical reactions in polymers are not random. Some of the chemical groups and bonds are more sensitive to the radiation than others, such as C=C, COOH, C-Halogen, -SO₂⁻, and NH₂. Some chemical groups are classified as radiation-resistant groups, such as aromatic groups, which have been known to have significant radiation resistance. The presence of aromatic rings in the polymers exhibit a strongly stabilizing influence on the yield of radiation induced crosslinking or chain scission. The intramolecular protective effect by phenyl groups in polymers, such as polystyrene or polyarylene sulfones was shown by low yield in crosslinking. Studies on...
insulating property of polystyrene have also shown that it is the most radiation-resistant plastic among all the plastics applied for insulating purposes in electronic circuitry.\(^1\) The aromatic group has a protective effect because the resonant structure of the aromatic ring is able to absorb a considerable amount of energy without rupture of the bonds. Poly (butadiene-styrene) with higher content of styrene showed lower yield of crosslinking.\(^91\) The sensitivity of polymer upon e-beam radiation can be compared from their G value, which is defined as the number of molecules or ions produced or destroyed per 100 eV energy absorbed. The G value describes the yield of the radiation induced reactions. It is written as G(X) and G(S) for crosslinking and chain scission, respectively.\(^92\)

Research on radiation of polymers was started from early 1940s.\(^93\) It was found that the effects of the radiation on polymeric materials are not always detrimental. In some case, certain properties of polymers were enhanced. Irradiation of polystyrene causing an increase in electrical conductance was observed.\(^93\) Polyethylene after radiation turning into a crosslinked, insoluble and heat resistant material was first observed by Charlesby.\(^94\) Later, researchers found that polymers may either crosslink or degrade depending on their chemical structure nature.\(^75,95-96\) In fact, polymers typically undergo a simultaneous chain scission and crosslinking reaction. Some common polymers listed in Table 2-2 are classified according to their response to e-beam radiation. In a particular polymeric material, one process may be predominant during radiation. The overall response of the polymer upon e-beam radiation is usually determined by the predominant process. The additives or plasticizer and the change in irradiation condition may switch the polymers from one group to the other.
Table 2-2 Classification of polymers based on reactions upon e-beam radiation. 19

<table>
<thead>
<tr>
<th>Mainly crosslinking</th>
<th>Mainly scission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>Polyisobutylene</td>
</tr>
<tr>
<td>Polyacrylates</td>
<td>Polymethacrylates</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>Polymethylstyrene</td>
</tr>
<tr>
<td>Polysiloxanes</td>
<td>Polymethacrylamides</td>
</tr>
<tr>
<td>Polyamides</td>
<td>Polyvinylidene chloride</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>Polyacrylamides</td>
<td>Polypropylene ether</td>
</tr>
<tr>
<td>Ethylene vinylacetate</td>
<td>Cellulose</td>
</tr>
</tbody>
</table>

For the polymers mainly undergo chain crosslinking reactions, the molecular weight increases after radiation. The higher degree of crosslinking will result in the formation of a three dimensional network in the materials. By increasing the radiation dose, the polymer will be insoluble in solvent, which is similar to the thermosetting polymers or vulcanized rubbers. If chain scission is predominant for materials under radiation, the molecular weight decreases. The properties of the polymers undergo a tremendous change during irradiation, especially the mechanical properties, such as tensile strength, modulus, viscoelastic properties and rheological properties. 3, 13, 32, 81, 89, 96-98 Polymers have the following structure, as shown in Scheme 2-4 tend to undergo chain scission reaction. R and R’ produce a steric strain that weaken the bonds of the backbone chain. 75 Small molecular by products may also generated during the irradiation process. These products result from bond scission followed by abstraction or combination reactions, which can give important information of the degradation mechanism.
The curing extent and uniformity on polymers depends on the penetration of energized electrons. Thickness and density of materials are two factors that decide the penetration depth of the radiation. If materials have higher density, it usually needs double side radiation to obtain a more uniform crosslinking. The thickness of the articles for uniform penetration can be estimated as:

\[ T = \frac{8.0 \times E}{\rho} \]  

(2-2)

where \( \rho \) is density of materials (g/cm\(^3\)), \( E \) is electron energy (MeV) and \( T \) is thickness of sample (mm). The effect of the electron beam on properties of polymers also depends on a variety of factors, such as radiation atmosphere, temperature, dose rate and total dose absorbed. \(^{99-100}\)

2.2.3 Electron beam crosslinking elastomers

Radiation-induced crosslinking of polyethylene was a typical and the earliest application of radiation modification on polymers and it has already gained commercially success. \(^{101-103}\) Crosslinked polyethylene has improved mechanical and thermal properties. \(^{104-105}\) Because e-beam radiation has high enough energy to initiate chain reaction, no initiator is needed during the crosslinking process. Currently, e-beam
radiation crosslinking method has already been an alternative way to conventional chemical vulcanization method.\textsuperscript{12,78}

Polyisoprene usually has four different isomers, as shown in Scheme 2-5, depending on the catalysts and polymerization condition. The sequential arrangement and tacticity of different isomers in polymer chain generate different types of polyisoprene. The chemical structure differences of polyisoprene not only cause variation on physical properties of materials but also affect their response to radiation exposure. During the radiation, many transient chemical species were produced. The primary radical observed in natural rubber and synthetic polyisoprene after irradiation was of allylic type radical. These allylic radicals were generated by hydrogen abstraction.\textsuperscript{106-107} The existence of other forms, such as ionic structure and excited states of the polyisoprene, are generally considered as the precursors of the allylic radicals. The coupling of the allylic radical produced during the radiolysis was the main reason for the crosslinking reaction of the polyisoprene.\textsuperscript{2,21-23} About 98 % of the gas produced during radiation of natural rubber and polyisoprene contains hydrogen. Decrease of unsaturation is the most obvious change of the chemical structure of the polyisoprene upon radiation exposure.\textsuperscript{108} Radiation crosslinking of natural rubber latex or synthetic polyisoprene have been performed instead of common vulcanization techniques due to its high efficiency.\textsuperscript{109-110}
Polybutadiene has three different isomers depending on polymerization condition, as shown in Scheme 2-5. For polybutadiene and butadiene-styrene copolymers, the radical formed during irradiation was an allylic radical.\textsuperscript{111} The radical production is linear with radiation dose.\textsuperscript{17} The yield of crosslink depends on the microstructure and the purity of the polymers as well as the irradiation atmosphere. For polybutadiene copolymers, introducing styrene block to the materials was found to retard the crosslinking reaction.\textsuperscript{91} This effect was attributed to the intramolecular energy transfer from the butadiene to styrene. The most dominating effect observed in the radiolysis of polybutadiene and its copolymers was the decay of unsaturation.\textsuperscript{14,83} The rate of decay was strongly dependent on dose, with the largest rate of consumption of unsaturation occurring during the initial stage.\textsuperscript{83} Polyisoprene and polybutadiene undergoes a radiation-induced loss of unsaturation and cis-trans isomerization.\textsuperscript{112}
The crosslinking modes in elastomers mainly have two pathways: one is the crosslinking by means of primary ionic species and the other is via the free radicals. Two polymeric free radicals are expected to terminate and contribute greatly to the crosslinking reactions, as shown in Scheme 2-6 reaction (1). Unsaturated groups also participate in crosslinking reactions, as shown in Scheme 2-6 reaction (2). The propagation step in polymerization process is expected to occur in unsaturated polymers. Radicals formed in the radiation of unsaturated elastomers are mainly the allylic type. The mutual recombination of these resonance stabilized transient species is always occurred. If the radiation is carried out in an atmosphere containing O₂, the radical also involves a reaction with O₂. So the radical addition to the unsaturation may take place at a slow rate. The reactions of ions and radical ions also have contributions to crosslinking. Several reactions involve ions and radical ions were reported.¹¹³⁻¹¹⁴

Scheme 2-6 Crosslinking reactions in elastomers.²
The most important changes of properties for elastomers after e-beam crosslinking are the tensile properties and crosslink density.\textsuperscript{84, 115-116} Tensile strength, modulus, elongation-at-break and crosslink density varied with radiation dose.\textsuperscript{84, 117} In addition, molecular weight characteristics of elastomers are also affected by irradiation.\textsuperscript{9} At higher radiation dose, gels will be formed if the crosslinking reaction predominates in the materials. Gel content of the materials will also change according to the radiation dose. There have been some studies done about the radiation vulcanization of rubbers and thermoplastic elastomers. The most widely investigated e-beam radiation crosslinked elastomers include natural rubber,\textsuperscript{81, 107, 118-121} acrylonitrile-butadiene rubber (NBR),\textsuperscript{12, 98} polybutadiene,\textsuperscript{14, 83} SBS,\textsuperscript{84, 116, 122} and ethylene-propylene rubber (EPDM).\textsuperscript{13}

The tensile strength of elastomer is affected by various factors, such as degree of crosslinking, regularity of the polymer network, distribution of crosslinks, molecular weight characteristics\textsuperscript{123} and the type of crosslink bonds introduced by vulcanizing process.\textsuperscript{124-125} Covalent bond connections depend on crosslinking methods. The connections in the system would affect the tensile strength of elastomers due to the bond strength difference.\textsuperscript{124, 126-127} Peroxide vulcanization and e-beam radiation curing without direct crosslink promoters yields carbon-carbon crosslinks, whereas a sulfur accelerator system introduces several types of chemical crosslinks, such as monosulfide, disulfide and polysulfide structure. The order of the different bond strength is as follows: C\textsuperscript{-C}>C\textsuperscript{-S-C}>C-S\textsuperscript{-C}>C-S\textsuperscript{2-C}>C-S\textsuperscript{n>2-C}.\textsuperscript{127} The bond strength difference was associated with the tensile strength difference of material. The weaker bonds, such as carbon-sulfide, yield higher tensile strength than a carbon-carbon connection due to the ability to dissipate localized stress concentration more evenly.\textsuperscript{128}
Equilibrium swelling is one of the most useful methods to calculate the concentration of elastically effective chains or crosslink density. Bishop and coworkers used a modified swelling approach to measure the swelling progress of SBS and SIS. Selective swelling of the mid-block was used in their studies. The swelling solvent fulfilled the requirement of significantly swelling the polyisoprene or polybutadiene segment, while keeping the polystyrene domain intact. Isooctane (2, 2, 4-trimethylpentane), 2, 4-dimethylpentane, and neohexane (2, 2-dimethylbutane) were found to fulfill this requirement. And these solvents were chosen to study the equilibrium swelling of the block copolymers. In this case, the end-block phase was treated as hard unswollen particles which did not contribute to the elastic network. The resulting effective molecular weight between crosslinks \( M_c \) was the normal chain entanglement length, not the segment length of the mid-block. \( M_c \) was much smaller than the molecular weight of the mid-block of copolymer, which was proven by Bishop and coworkers through equilibrium swelling experiment in isooctane. These entanglements in the elastomeric phase also have effects on the crosslink and mechanical properties. The molecular weight between entanglements can be calculated from the Flory-Rehner Equation:

\[
M_c = \frac{\rho_2 V_1 (\phi_2^{1/3} - \phi_2 / 2)}{\ln(1 - \phi_2) + \phi_2 + \chi_1 \phi_2^2}
\]

where \( M_c \) is the molecular weight between effective crosslinks, \( \rho_2 \) is the density of the elastomer in the unswollen state, \( V_1 \) is the molar volume of the swelling solvent, \( \phi_2 \) is the volume fraction of the elastomer in the swollen state, and \( \chi_1 \) is the Flory-Huggins solvent interaction parameter.
The crosslink density of rubber can also be calculated based on the storage modulus in the rubbery plateau.

\[ E' = 3\nu_v RT \]  

(2-4)

where \( E' \) is the storage modulus (MPa) in rubbery plateau, \( \nu_v \) is the crosslink density (mol/cm\(^3\)), and \( T \) is temperature (K). The crosslink densities in elastomers obtained by equilibrium swelling or dynamic storage modulus are usually larger than the actual number of chemical crosslinks induced by radiation. The reason is due to the network restraints of entanglements.

2.2.4 Pro-rads

In order to achieve the equivalent crosslink density to those obtained from conventional vulcanization, high e-beam radiation dose is usually required during the vulcanization.\(^{130-131}\) Therefore, considerable investigation has been done to find out additives to promote the crosslinking reaction of elastomers at a lower radiation dose.\(^{11}\).\(^{132-133}\) Materials that are capable of promoting crosslinking reactions of elastomers under e-beam radiation are called pro-rads.\(^{134-136}\) Pro-rads are a class of materials that are capable of generating more reactive species, such as free radicals and ions, than the polymer itself and accelerating the crosslinking reactions of the materials. Therefore, with the presence of 1 wt%-5 wt% of pro-rads, lower radiation dose might be required to obtain a high crosslink density.

According to their functions during radiation crosslinking process, pro-rads are generally classified into two groups, indirect pro-rads and direct pro-rads. The indirect
pro-rads just enhance the formation of reactive species and are not part of the crosslinked network. Direct pro-rads not only promote the formation of reactive species, but also act as crosslinkers in the vulcanized elastomers. Halides, nitrous oxide, sulfur monochloride and bases are commonly used indirect pro-rads. Direct pro-rads are usually multifunctional monomers or oligomers, such as polythiols, bismaleimides, and polyacrylate or methacrylate compounds. Decker et al. used trimethylolpropane mercaptopropionate to promote the UV-induced thiol-ene crosslinking reaction in styrene-butadiene rubber with a high vinyl content. The crosslinking efficiency increased significantly by adding small amount of pro-rads. The mechanism for crosslinking elastomers with thiols is based on a thiol-ene reaction, which is the addition of thiols to double bonds. This reaction mechanism was extensively investigated in the past. Addition reaction proceeds by a radical mechanism. Acrylate and methacrylate compounds accelerate crosslinking in elastomers. A number of polyfunctional acrylate compounds, such as diacrylates, triacrylate, dimethacrylate and trimethacrylates tested in elastomers and plastics were reported to show an increase in modulus and tensile strength. In addition, the rate of formation of insoluble network in polymers was also significantly increased.

2.3 UV-curing technology

UV-curing technology uses the energy of photons from a radiation source to form reactive species, such as free radicals or cationic ions, which can initiate a fast chain growth polymerization of monomers and oligomers. If the monomer contains more than one reactive group, the liquid formulation will be converted to a solid film within seconds. Free radical photopolymerization has been extensively studied and applied in
In UV-curing formulations, photo initiator is used because the direct cleavage process of monomer or oligomer is not efficient enough in most cases. The photo initiator is designed to have high efficiency in absorbing photon and forming reactive species. Advantages of UV-curing technology include low to zero volatile organic compound (VOC), 100% solid content, low energy consumption, high product throughput rate, reduced space requirement, and processability for heat-sensitive substrates. There is also some drawbacks for UV-curing technology such as difficult curing of pigmented coatings, and no curing in the shadow areas. The radiant power of the UV lamp decreases with the square of the distance, which also limits the UV-curing technology to three dimensional products. However, UV technology is still the one of the most widely used technology in coating and printing industrials.

A typical UV-induced free radical photopolymerization process includes light absorption, radical generation, initiation, propagation and termination, as depicted in Scheme 2-7. Firstly, energy of light (hv) is absorbed by the photoinitiator (PI) to produce excited species (PI*) which will decompose to radicals. The radicals then initiate polymerization. This step is followed by successive addition of monomer units to the growing polymer chains in the propagation step. Since photo induced polymerization takes place in short time, usually several seconds for acrylated resins, it is possible that the growing polymer chain may not be terminated and is trapped in the crosslinked network after radiation. Free radical photoinitiators are mainly classified into type I and type II systems. Type I initiators are those compounds that undergo a cleavage reaction and generate two free radicals. In general, excited ketones can cleave into two radicals. Only one radical is reactive and initiates the chain reactions. Type II initiators are a class...
of compounds that can get excited after absorbing the photon and abstract the hydrogen or electron from a suitable donor molecule. Both free radicals generated in this process can initiate the polymerization. This means type II photoinitiator usually generated more radicals.¹⁴⁶

<table>
<thead>
<tr>
<th>Light absorption</th>
<th>$\text{PI} \xrightarrow{k_v} \text{PI}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radical generation</td>
<td>$\text{PI}^* \rightarrow \text{R}^*$</td>
</tr>
<tr>
<td>Initiation</td>
<td>$\text{R}^* + \text{M} \xrightarrow{k_i} \text{RM}^*$</td>
</tr>
<tr>
<td>Propagation</td>
<td>$\text{RM}^<em>_n + \text{M} \xrightarrow{k_p} \text{RM}^</em>_n+1$</td>
</tr>
<tr>
<td>Termination</td>
<td>$\text{RM}^<em>_n + \text{RM}^</em>_m \xrightarrow{k_f} \text{polymer}$</td>
</tr>
</tbody>
</table>

RM$^*$ $\xrightarrow{k_f}$ polymer trapped

Scheme 2-7 Free radical photopolymerization process initiated by UV radiation.⁷

For a special curing system consisting of a donor and acceptor combination, where N-substituted maleimide is the acceptor monomer and vinyl ether is the donor monomer, the reactivity of such a system without any photoinitiator was found to be in the order of the acrylate resins containing a photoinitiator.⁴⁶, ⁵⁰-⁵¹, ⁵³ Two types of initiation mechanisms were proposed.⁷ The first is the intermolecular excimer formation to generate bi-radical species and the second is hydrogen abstraction from the triplet state of maleimide, as shown in Scheme 2-8.
Maleimide homopolymerization without additional photoinitiator in solvent (tetrahydrofuran, THF) was first reported by Yamada.\textsuperscript{147} Then Decker, Jonsson and Hoyle also reported that the multifunctional maleimide/vinyl ether system also generated crosslinked network upon exposure to UV radiation.\textsuperscript{46,49,52} Maleimide itself can also be used as photoinitiator to initiate the photopolymerization of the acrylate system, which was investigated by Hoyle and Clark using photo-DSC, as shown in Figure 2-2.\textsuperscript{148} The initiation process is via the hydrogen abstraction by excited N-substituted maleimide.

\begin{equation}
\text{Initiating radical}
\end{equation}

Figure 2-2 Exotherms of 1, 6-hexanediol diacrylate (HDDA) with 10 wt\% various N-substituted maleimide upon exposure to UV radiation (19 mw/cm²). Reprinted from Polymer, 38(22), C.E. Hoyle, S.C. Clark, S. Jonsson, M. Shimose, Photopolymerization using maleimides as photoinitiators, 5695, Copyright (1997), with permission from Elsevier.\textsuperscript{148}
An industry based UV-curing process on two-dimensional substrates is shown in Scheme 2-9. First, the substrate is coated using a film casting line and then passes through a UV lamp to expose to radiation. During the radiation, the liquid formulation transferred to a solid crosslinked network by photopolymerization. A typical UV-curing composition contains 25 wt%-90 wt% oligomeric resins, which is the most important component in formulation that determines the final properties of films or coatings. Reactive diluents are usually low molecular compounds, which are responsible for adjusting the viscosity of the formulation to the requirement of processing. The reactive diluents share 15 wt%-60 wt% compositions and will also be incorporated into the crosslinked network. 1 wt%-8 wt% photoinitiator as well as other additives, such as surfactants, pigments, and stabilizers are added to the UV-curing formulations.

![Diagram of UV-induced crosslinking process]

Scheme 2-9 A schematic description of UV-induced crosslinking process

The mechanisms of UV and e-Beam processes are different. Take acrylate system as an example, the UV-curing process was initiated by free radical generated by photoinitiator. The crosslinked coating or film reflects the functionality of the acrylate. The new bonds formed after UV radiation in the system were produced by the acrylate functionality together with a few crosslinks generated towards the end of the
polymerization process via chain termination reaction. However, in the e-beam curing of acrylate, the radiation generates radicals at random sites in the oligomers or monomers not only form crosslinks via the acrylate functionality, but also from the radicals in the backbone. Crosslinking can take place via radical-radical combination or radical attack the acrylate group.  

2.4 Polyimides

Polyimides are a class of high performance polymers synthesized through condensation reaction of diamine and dianhydride monomers. According to their main chain compositions, polyimides can be classified as aliphatic, semi-aromatic and aromatic polyimides. According to the main chain connection, polyimides can be divided into two groups, thermosetting polyimides and thermal plastic (pseudo-thermoplastic) polyimides. Polyimide chemistry involves a variety of monomers selection and several synthetic routes. The final properties of polyimides highly depend on the selection of monomers and the main chain structures. Even a slight difference on the diamine and dianhydride structures may cause tremendous variation on the properties of polyimides. This section covers not only the synthetic methods of several typical thermoplastic, thermosetting polyimides and bismaleimides, but also the structure-property relationships of polyimides.

2.4.1 Thermoplastic (pseudo-thermoplastic) polyimides

Thermoplastic polyimides are also called pseudo-thermoplastic polyimide. Actually, the melting temperature of most aromatic thermoplastic polyimide is higher than their thermal decomposition temperatures. Therefore, it is impossible to process them under
melting condition. This type of polyimides can only be processed in poly(amic acid) state, such as Kapton, developed by DuPont.\textsuperscript{152} By selecting particular diamine and dianhydride monomers, melting processable polyimides can be synthesized, like Ultem polyetherimide (PEI) resins developed by Sabic. For these two types of polyimides, the synthetic methods are also different.

The classic method of synthesis of aromatic polyimides includes two steps: the first step is preparing a poly (amic acid) solution by reacting diamine with dianhydride at ambient temperature in a polar aprotic solvent, such as dimethylacetamide (DMAc) or N-methyl-2-pyrrolidone (NMP). Intermediate poly (amic acid) was formed due to the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group. The resulting poly (amic acid) is fully soluble in solvent. Thus the polymer solution can be processed by solution casting on the substrate to form a film or coating. The second step is the imidization through cyclodehydration reaction, which is accomplished by heating the poly (amic acid) solution at elevated temperature (200 °C-300 °C). The overall reaction scheme is shown in Scheme 2-10. Fully imidized aromatic polyimide is infusible and insoluble in any solvent. The reason is attributed to high intermolecular association force (high density of cohesive energy), molecular stiffness, and high polarity.\textsuperscript{153} Kapton, developed by DuPont, was produced from the condensation reaction of pyromellitic dianhydride (PMDA) and 4, 4’-oxydiphenylamine (ODA), as shown in Scheme 2-11. It can remain thermally stable in a wide range of temperature, from -273 °C to 400 °C. Kapton is used in flexible printed circuits and other high temperature application areas.
High temperature solution imidization is the most widely applied method for the synthesis of soluble polyimide. This process involves heating a stoichiometric mixture of diamine and dianhydride monomers in a high boiling point aprotic solvent or a mixture of solvents at around 160 °C-180 °C.\textsuperscript{154-156} Compared to the classic two-step polyimide synthesis, the difference is that the imidization process takes place in the solution; water generated during the condensation reaction is distilled off continuously using an azeotropic agent. The reaction scheme for LaRC-SI (Langley Research Center - Soluble Imide) is shown in Scheme 2-12. It is an amorphous thermoplastic developed by
The structure of another processable polyimide, such as Ultem, is shown in Scheme 2-13.

![Scheme 2-12 Synthetic scheme for LaRC\textsuperscript{TM}-SI. Reproduced from High Performance Polymers, Copyright (1996), with permission from SAGE Publications.]

Scheme 2-13 Repeating unit of Ultem.

2.4.2 Thermosetting polyimides and bismaleimides

Thermosetting polyimides, also called addition polyimides, are extensively studied and applied in aerospace engineering for high performance composite matrix.\textsuperscript{160} This type of polyimide is defined as low molecular weight, at least difunctional monomers or oligomers carry reactive functional end groups and imide structure on their backbone.
These reactive end groups can undergo homo-and/or copolymerization upon heating or catalytical methods.\textsuperscript{161} The thermosetting polyimide can be synthesized via diester-diacid route or via reacting the tetracarboxylic dianhydride and diamine in the presence of a mono-functional end-capper. The molecular weight of oligomers could be tailored by controlling the monomer ratio and synthetic condition. Two factors needs to be taken into account in designing the chemical structure of imide oligomers. One is the backbone structure, which is responsible for the performance of the crosslinked polymer, the others are the glass transition ($T_g$) and melting temperature ($T_m$), which determine the temperature of processing and application.\textsuperscript{162}

The first addition polyimide was norbornene (nadic) terminated polyimide developed by the NASA Lewis Research Center and named PMR resin. The first paper published about PMR-15 was in 1972.\textsuperscript{48} PMR stands for polymerization of monomeric reactants and 15 stands for and average molecular weight of 1500 g/mol. This resin is a mixture of monomers in which the benzophenone tetracarboxylic acid and the nadic acid are employed in their half ester form with 4,4’-diaminodiphenylmethane (MDA) dissolved in a low boiling point solvent, methanol. The reaction scheme is shown in Scheme 2-14. The PMR resins achieved the easy processing with fibers in the advanced composites developments. During 1964-1974, the research in the area of thermosetting polyimides was focused on the polyimides produced through the reactions of maleimide-, nadimide- and ethynyl terminated groups, as shown in Scheme 2-15.

The synthetic method for PMR-15 resin is called diester-diacid route, and was initially developed by NASA in 1970s.\textsuperscript{48} The difference compared to the tradition polyimide synthesis is that the dianhydride reacted with aliphatic alcohol first to form a
tetracarboxylic acid diester. The hydrolytic stability of the system is highly improved because the reaction between tetracarboxylic acid diesters and diamine is quite slow at ambient temperature. The stable monomer solution can be stored and processed much more easily. The imidization reaction takes place at elevated temperature. Scheme 2-14 shows the overall reaction scheme of PMR-15 synthesis. Polymerization proceeds through two steps, the first step involves heating at 120 °C-230 °C, which will cause the imidization to occur. The second step takes place at 275 °C-325 °C, which allows the norbornene end group to crosslink. Some thermosetting polyimides were synthesized by this way. 163-167

Scheme 2-14 Reaction scheme of PMR-15 polyimide
Scheme 2-15 Reactive functional end-groups in thermal setting polyimide

Melting processable bismaleimide system is one of the most extensively studied systems in thermosetting resins. Maleimide group can undergo a series of chemical reactions. The reactivity of the double bond is a consequence of the electron withdrawing nature of the two carbonyl groups which makes it an electron-deficient double bond. Therefore, it is susceptible to homo and/or copolymerization. Several representative bismaleimides and their processing temperatures are listed in Table 2-3. The melting temperature and polymerization temperature were characterized by differential scanning calorimetry (DSC). The crosslinked poly (bismaleimide) has high thermal stability, chemical resistance and high strength. The major concern of poly (bismaleimide) is the inherent brittleness due to their high crosslink density. Maleimide-terminated imide oligomer were also developed as thermosetting polyimides, as shown in Scheme 2-16, and studied for thermal curing high performance composites. However, high temperature and pressure are still required, thus leading to high energy costs and equipment requirement.
Table 2-3 Chemical structure of melting processable bismaleimides.

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Name</th>
<th>$T_m$, $T_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>1, 1’-(4-methylene 1-phenylene) bismaleimide</td>
<td>$T_m=158 , ^\circ\text{C}$, $T_p=204 , ^\circ\text{C}$</td>
</tr>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>N,N’(1,3-phenylene) bismaleimide</td>
<td>$T_m=203 , ^\circ\text{C}$, $T_p=218 , ^\circ\text{C}$</td>
</tr>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Fluorinated bismaleimide</td>
<td>$T_m=136 , ^\circ\text{C}$</td>
</tr>
</tbody>
</table>

$T_m$, melting point, $T_p$, polymerization temperature

Scheme 2-16 Chemical structure of maleimide-terminated imide oligomer

2.4.3 Structure-property relationships of polyimides

Despite their excellent thermal, mechanical and electrical properties, the applications of aromatic polyimides are limited, because they are normally insoluble and infusible. This is due to the formation of charge transfer complex between dianhydride and diamine, as well as the inter-chain interaction. Aromatic polyimide chains consist of both electron-rich and relatively electron-poor segments. In this case, intermolecular charge polarization might occur. This is the reason for the formation of charge transfer complex. The stiffness of rigid-rod polyimide causes the chains to align along their axes, which contributes to the formation of the short-range order and the crystallinity.
Reducing the stiffness of the polymer backbone or lowering the inter-chain interactions are two approaches that can improve the solubility and melt flow ability of polyimide. Several methods were proposed to synthesize soluble polyimide. The first is to introduce aliphatic or other flexible segment to reduce the chain stiffness. The second is to introduce side bulky substituent along the backbones, which can hinder molecular packing and crystallization. The third is to use a kinked linkage, such as 1, 3-substituted instead of 1, 4-substituted monomers, or asymmetric monomers which lower regularity and molecular ordering. The forth method is to incorporate enlarged monomers containing angular bonds, which suppress coplanar structures. The last method is disrupting the symmetry of the polymer chain via copolymerization.

Fluorinated polyimides are one of the most important polyimide applied in the electronics. Introducing fluorine atoms into the polyimide structure, either as a substituent of the carbon atom on the polyimide backbone or as a side substituent is one of the most successful way to synthesize processable polyimide. Compared to the conventional aromatic polyimide, the presence of trifluoromethyl groups significantly changes the properties of polyimide. This is due to the combination of electronic and steric effects of trifluoromethyl groups, which reduces the inter-chain interactions and particularly hinders the formation of charge transfer complexes. This is one of the major factors which cause molecular packing and intractability in aromatic polyimides. In addition, the C-F bond has higher bonding energy than C-C bond. Therefore, the polyimides containing fluorine have high $T_g$ and excellent thermal properties. Furthermore, fluorinated polyimides also show some improvements in many properties, such as low dielectric constant, high optical transparency, increased solubility, excellent
mechanical properties, and low refractive index. These advantages make fluorinated polyimides very attractive in many areas, like high temperature coatings and films, high performance structural resins, and other electronic applications.
CHAPTER III
EFFECT OF ELECTRON-BEAM RADIATION ON TENSILE AND VISCOELASTIC PROPERTIES OF STYRENIC BLOCK COPOLYMERS

3.1 Abstract

The effect of electron beam (e-beam) radiation on styrenic block copolymers (SBCs) was investigated. These SBCs included poly (styrene-\textit{block}-butadiene-\textit{block}-styrene) (SBS), poly (styrene-\textit{block}-isoprene-\textit{block}-styrene) (SIS) and a newly developed poly (styrene-\textit{block}-isoprene/butadiene-\textit{block}-styrene) (SIBS). Tensile and viscoelastic properties, molecular weight and crosslink density were studied. The crosslink density and tensile moduli of SBCs increased with increasing e-beam radiation dose. The tensile strength of SIBS and SIS decreased at lower e-beam radiation doses (< 120 kGy) and increased at higher radiation doses (> 190 kGy). The tensile strength of SBS decreased by 30% at a high e-beam radiation dose (240 kGy). This was attributed to the differences between entanglement before e-beam radiation and the homogeneity of the crosslink network after exposure. E-beam also showed significant effect on stress relaxation of SBCs. Relaxation speed was inversely proportional to the radiation dose.

3.2 Introduction

E-beam radiation as an efficient way to crosslink polymers has advantages of short residence time and initiation without use of initiator.\textsuperscript{3, 190-191} The commercial interest
leads to the extensive research on studying the effect of e-beam radiation on polymeric materials.\textsuperscript{70-71, 192} The important commercial applications involve improving the properties of plastics and rubbers. E-beam radiation technology has been widely applied in various industries particularly in wire, cable, coatings, microelectronic and tire industries.\textsuperscript{92, 97, 193-195} The properties of materials are subjected to change by chain scission or crosslink reaction due to a series of chemical reactions subsequent to the ionization and excitation by high energy electron beam radiation.\textsuperscript{2, 21, 23}

The industrial applications of e-beam focused on crosslinking elastomers.\textsuperscript{10, 14, 16} Generally, rubbers are vulcanized by heating at high temperature with sulfur or peroxide.\textsuperscript{196-200} The disadvantage is that the long time heating may cause side reactions which may affect the final properties of the materials, plus it is not energy efficient. While radiation curing, on the other hand, is a process which is performed at room temperature and under controlled conditions, such as radiation dose, atmosphere and penetration depth.\textsuperscript{3} In addition, the radiation crosslinking process can lead to an improvement of desired physical properties of rubbers, such as tensile strength, modulus and abrasion resistance at a competitive cost.\textsuperscript{92, 117}

Styrenic block copolymers (SBCs) as a class of thermoplastic elastomers (TPEs) contain phase separated polystyrene block and rubbery blocks. Poly (styrene-\textit{block}-butadiene-\textit{block}-styrene) (SBS) and poly (styrene-\textit{block}-isoprene-\textit{block}-styrene) (SIS) are two types of widely used SBCs in the market.\textsuperscript{26-27, 56, 67} The poly (styrene-\textit{block}-isoprene/butadiene-\textit{block}-styrene) (SIBS) with hybrid mid-block was newly developed by Kraton Polymers. There haven’t been any reports about the effects of e-beam radiation on properties of the SIBS. The SBCs form physically crosslinked network due to the
thermodynamic incompatibility of the styrene end-block and the rubber mid-block.\textsuperscript{28-29} Like other thermoplastic elastomers, SBCs possess the mechanical properties of vulcanized rubbers and the processing characteristics of thermoplastics.\textsuperscript{27} However, SBCs suffer from poor chemical resistance, lower strength and modulus. Many efforts have been put to improve the properties and performance of SBCs by either modifying the end-block or mid-block. Morton et al. replaced polystyrene with poly-\textalpha-methylstylene to improve the tensile strength of SIS.\textsuperscript{68} Jerome et al. used poly(methyl methacrylate) as end-block to modify the properties of SBS.\textsuperscript{201} These approaches required sophisticated synthetic process. Because of the presence of polydiene mid-blocks, SBS, SIS and SIBS are capable of crosslinking upon heating or radiation. The crosslinking process provides an efficient way to improve the chemical resistance, high temperature stability, tensile properties and barrier properties of the materials.\textsuperscript{19, 78, 92, 202-203}

Although there have been some papers published on thermal initiated crosslinking of SBCs,\textsuperscript{63, 84, 116-117, 135, 195, 197-198, 204-205} little research has been done to study the effect of e-beam radiation initiated crosslinking reaction of SBCs. The objective of this paper is to investigate the effect of e-beam radiation on mechanical and viscoelastic properties of SBCs. Three types of SBCs with different mid-blocks were investigated. Tensile properties of SBCs under uniaxial stretching were evaluated. Crosslink density of each copolymer before and after e-beam radiation was calculated based on dynamic mechanical analysis (DMA). Stress relaxation behaviors of the SBCs were also studied as functions of e-beam radiation dose and temperature. Molecular weight characterizations of block copolymers and homopolymers of polyisoprene and polybutadiene were
conducted using size exclusion chromatography (SEC) to elucidate what type of reaction was predominant in SBCs.

3.3 Experimental

3.3.1 Materials

SBCs were provided by Kraton Polymers, Houston, TX. The material information is listed in Table 3-1. Polybutadiene (PB) and polyisoprene (PI) were purchased from Sigma-Aldrich. Polystyrene was obtained from Americas Styrenics, Marietta, OH with product No. of D4030.01. The information of homopolymers is listed in Table 3-2. Solvents were purchased from Sigma-Aldrich and used as received. Cyclohexane (ACS reagent, ≥ 99 %), tetrahydrofuran (THF) (HPLC grade, ≥ 99.9 %).

<table>
<thead>
<tr>
<th>Table 3-1 Composition information of styrenic block copolymers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>Type</td>
</tr>
<tr>
<td>Styrene content</td>
</tr>
<tr>
<td>Structure</td>
</tr>
<tr>
<td>Mid-block</td>
</tr>
<tr>
<td>(a) Butadiene, (b) Isoprene</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3-2 Composition information of homopolymers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>Polybutadiene</td>
</tr>
<tr>
<td>Polybutadiene</td>
</tr>
<tr>
<td>Polysoprene</td>
</tr>
</tbody>
</table>
3.3.2 Film fabrication

Films for e-beam crosslinking studies were prepared by solution casting. All the SBCs are soluble in cyclohexane. The low solid content (15 wt %) and slow evaporation process were used for casting, so that the residual stress did not develop in the films. The procedure is as follows: SIBS (50 g) was dissolved in cyclohexane (283 g) and stirred for 5 h until a homogeneous solution with 15 wt% solid content was obtained. The solution was poured onto a PTFE plate and kept in a solvent evaporation chamber at room temperature. The film was first kept in a closed chamber for 3 days, and then put in the hood for two days. Finally, the film was dried in vacuum oven for additional two days at room temperature to remove any residual solvent. All the films were prepared following the same procedure.

3.3.3 Electron beam radiation conditions

E-beam exposure was performed at the NEO beam crosslinking facility in Middlefield, OH. The e-beam radiation was conducted under following the conditions: voltage: 4.48 MV, current: 30.0 mA, atmosphere: air, line speed: 15 feet/min, radiation time: ~ 30 s. The e-beam radiation dose is listed in Table 3-3. The dose was measured by a dosimeter consists of alanine films manufactured by Kodak BioMax with lot number of B0308A. The dosimeters are measured in a Bruker e-scan ESR spectrometer. Alanine film dosimeters are commonly used in the radiation dose measurement. Alanine, a crystalline amino acid, can form a very stable free radical when subjected to ionizing radiation. The alanine free radical can yield an electron spin resonance (ESR) signal that is dose dependent.
Table 3-3 E-beam radiation doses.

<table>
<thead>
<tr>
<th>Nominal Dose (kGy)</th>
<th>Measured Dose (kGy)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>59.7</td>
<td>4</td>
</tr>
<tr>
<td>100</td>
<td>118.4</td>
<td>3.5</td>
</tr>
<tr>
<td>150</td>
<td>186.1</td>
<td>14.6</td>
</tr>
<tr>
<td>200</td>
<td>240</td>
<td>Estimated from the previous runs</td>
</tr>
</tbody>
</table>

3.3.4 Characterizations

3.3.4.1 Tensile test

Tensile test was performed on Instron universal electromechanical tester 5567 at extension speed of 500 mm/min (20 in/min). According to ASTM D-412, five dumbbell shape specimens were used to perform the tensile test. Averages are reported.

3.3.4.2 Molecular weight

Size Exclusion Chromatography (SEC) was used to determine the polymer molecular weight and polydispersity index (PDI). The SEC used tetrahydrofuran (THF) as the mobile phase, and was equipped with a Waters 1515 isocratic pump, three Waters Styragel columns (HR 3, HR 4, HR 4E) and a Waters 2414 refractive index (RI) detector. The columns were calibrated with narrow distribution polystyrene (PS) standards.

3.3.4.3 Viscoelastic properties

Dependence of dynamical modulus on temperature was obtained on dynamic mechanical analysis (DMA) Q-80 (TA Instruments, Inc) in a multi-frequency strain mode. Films were tested under the following conditions: tension mode, heating rate is 3 °C/min,
and frequency is 1 Hz. The maximum of tan delta was used to determine the glass transition temperature, while the crosslink density was calculated by utilizing the storage modulus ($E'$) in the rubbery plateau.

$$v_e = \frac{E'}{3RT} \quad T \gg T_g$$  \quad (3-1)

where $E'$ is the storage modulus in rubbery plateau (Pa), $v_e$ is the crosslink density (mol/m$^3$), $R$ is gas constant (8.31 J·mol$^{-1}$·K$^{-1}$), $T$ is temperature (K).

Stress relaxation tests were also performed on dynamic mechanical analysis (DMA) Q-80 (TA Instruments, Inc). Test was performed at various temperatures (30, 40, 50, 60 °C) with 1% strain for 30 min.

3.4 Results

The SBCs with different mid-blocks were investigated and compared. The mid-blocks were polyisoprene, polybutadiene and copolymer of isoprene and butadiene, respectively. It was anticipated that the different mid-blocks would result in differences in crosslink density and thus tensile properties upon e-beam radiation. Four e-beam radiation doses (60, 120, 190 and 240 kGy) were investigated. The e-beam radiation doses were selected based on the industrial cost and safety consideration.

3.4.1 Effect of e-beam radiation on tensile properties of SBCs

Uniaxial tensile test of SIBS was performed and the stress-strain behaviors are shown in Figure 3-1. The modulus of e-beam irradiated SIBS increased gradually as the e-beam radiation dose increases. The tensile strength appeared to decrease by 9% at
lower e-beam doses (e.g. 60 kGy and 120 kGy). While at higher e-beam doses (e.g. >190 kGy), the tensile strength increased by 16 % compared to the tensile strength of SIBS before e-beam radiation. This means the tensile strength of SIBS decreased first and then started to increase as the e-beam radiation dose increases. 300 % modulus of the SIBS increased continuously with increasing e-beam radiation dose, as shown in Table 3-4. At 240 kGy, the 300 % modulus of SIBS increased by 64 %, and the elongation-at-break decreased by 26% compared to the SIBS without modification.

![Stress-Strain Curve](image1)

Figure 3-1 Effect of e-beam radiation on stress-strain behaviors of SIBS.

![Tensile Test Results](image2)

Figure 3-2 Comparison of (a) tensile strength and (b) elongation-at-break of SIBS.
The change of tensile property of SBS as a function of e-beam radiation dose was also studied. The stress-strain behaviors of SBS irradiated with different e-beam doses are shown in Figure 3-3. The tensile strength slightly increased at lower e-beam doses (< 120 kGy). However, it decreased at high e-beam radiation doses (e.g. 190 and 240 kGy). SBS with the highest e-beam radiation dose (240 kGy) had the lowest tensile strength, as shown in Figure 3-4 (a). Elongation-at-break also decreased with increasing the e-beam radiation dose. Previous researchers also found the similar results for radiation crosslinked SBS. This observed property change indicated that even though the modulus was enhanced after e-beam radiation, e-beam crosslinking process did not significantly increase the tensile strength of the SBS. The elongation-at-break of the SBS without e-beam exposure was 1518 %; while the elongation-at-break of the SBS films with e-beam a radiation dose of 240 kGy was 988 %. This was just 65 % of the initial value. High e-beam radiation dose significantly decreased the elongation-at-break of the SBS. This was because the high crosslink density of the SBS after e-beam radiation reduced the extensibility.

The 300 % modulus of SBS increased continuously with increasing e-beam radiation dose, as shown in Table 3-4. This was due to the increase of the crosslinking density of the materials through introducing a secondary crosslinking network by e-beam radiation. After e-beam exposure with radiation dose of 60 kGy, the 300 % modulus increased 14 %, compared to the initial value. It was found that each 60-70 kGy e-beam dose increased 14 % of 300 % modulus, which was the case for SBS with e-beam dose of 60, 120 and 190 kGy. For SBS with 240 kGy, the 300 % modulus just increased 5 % compared to
SBS with e-beam radiation dose of 190 kGy. This was attributed to the more extensive chain scissions caused by high dose of e-beam radiation.

Figure 3-3 Effects of e-beam radiation on stress-strain behaviors of SBS.

Figure 3-4 Comparison of (a) tensile strength and (b) elongation-at-break of SBS.

Stress-strain behaviors of the SIS with four e-beam radiation doses are shown in Figure 3-5. The modulus of the SIS appeared to increase as the e-beam radiation dose increases. The comparison of tensile strength and 300% modulus are shown in Figure 3-6. The change of tensile strength of SIS after e-beam radiation appeared to be different
from SBS. The tensile strength of SIS after e-beam radiation was lower compared to SIS before e-beam radiation. This means that e-beam radiation did not increase the tensile strength of SIS. The trend was similar to the SIBS. For the peroxide crosslinked SIS copolymers, even though the increase of crosslink density was obtained, decrease of the tensile strength after crosslinking was observed. However, the modulus at 300% strain increased, as shown in Figure 3-6 (b). This indicated that the stiffness and crosslink density of SIS did increase.

Figure 3-5 Effect of e-beam radiation on stress-strain behaviors of SIS.

Figure 3-6 Comparison of (a) tensile strength and (b) 300 % modulus of SIS.
### Table 3-4 Tensile properties of SBCs with four e-beam radiation doses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength/MPa</th>
<th>Elongation-at-break/%</th>
<th>300 % Modulus/MPa</th>
<th>Tensile modulus/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIBS-0 kGy</td>
<td>12.50 ± 0.18</td>
<td>1700 ± 30</td>
<td>1.70 ± 0.05</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td>SIBS-60 kGy</td>
<td>11.41 ± 0.10</td>
<td>1500 ± 20</td>
<td>1.92 ± 0.03</td>
<td>0.31 ± 0.01</td>
</tr>
<tr>
<td>SIBS-120 kGy</td>
<td>11.53 ± 0.67</td>
<td>1380 ± 45</td>
<td>2.27 ± 0.06</td>
<td>0.38 ± 0.02</td>
</tr>
<tr>
<td>SIBS-190 kGy</td>
<td>14.54 ± 0.75</td>
<td>1460 ± 60</td>
<td>2.44 ± 0.07</td>
<td>0.47 ± 0.03</td>
</tr>
<tr>
<td>SIBS-240 kGy</td>
<td>14.41 ± 1.12</td>
<td>1250 ± 81</td>
<td>2.79 ± 0.08</td>
<td>0.51 ± 0.04</td>
</tr>
<tr>
<td>SBS-0 kGy</td>
<td>34.46 ± 1.60</td>
<td>1518 ± 60</td>
<td>3.72 ± 0.05</td>
<td>0.57 ± 0.04</td>
</tr>
<tr>
<td>SBS-60 kGy</td>
<td>35.64 ± 2.58</td>
<td>1453 ± 64</td>
<td>4.25 ± 0.06</td>
<td>0.69 ± 0.07</td>
</tr>
<tr>
<td>SBS-120 kGy</td>
<td>34.83 ± 4.09</td>
<td>1330 ± 54</td>
<td>4.90 ± 0.09</td>
<td>0.87 ± 0.13</td>
</tr>
<tr>
<td>SBS-190 kGy</td>
<td>27.45 ± 6.78</td>
<td>1127 ± 90</td>
<td>5.66 ± 0.11</td>
<td>1.26 ± 0.45</td>
</tr>
<tr>
<td>SBS-240 kGy</td>
<td>21.77 ± 2.66</td>
<td>988 ± 91</td>
<td>5.96 ± 0.03</td>
<td>1.40 ± 0.43</td>
</tr>
<tr>
<td>SIS-0 kGy</td>
<td>24.28 ± 0.76</td>
<td>2019 ± 74</td>
<td>1.28 ± 0.04</td>
<td>0.23 ± 0.01</td>
</tr>
<tr>
<td>SIS-60 kGy</td>
<td>22.93 ± 0.69</td>
<td>1995 ± 67</td>
<td>1.46 ± 0.05</td>
<td>0.30 ± 0.15</td>
</tr>
<tr>
<td>SIS-120 kGy</td>
<td>15.26 ± 0.86</td>
<td>1564 ± 87</td>
<td>1.63 ± 0.05</td>
<td>0.39 ± 0.07</td>
</tr>
<tr>
<td>SIS-190 kGy</td>
<td>19.07 ± 0.57</td>
<td>1766 ± 58</td>
<td>1.72 ± 0.04</td>
<td>0.81 ± 0.06</td>
</tr>
<tr>
<td>SIS-240 kGy</td>
<td>21.09 ± 0.79</td>
<td>1850 ± 80</td>
<td>1.79 ± 0.04</td>
<td>1.08 ± 0.09</td>
</tr>
</tbody>
</table>

### 3.4.2 Effect of e-beam radiation on dynamic mechanical properties of SBCs

The dynamic mechanical analysis was performed to study the crosslink density of the SBCs before irradiated under e-beam. This is helpful in elucidating the reason for the different responses of SBCs to the e-beam radiation. Storage modulus of SBCs before e-beam radiation is compared in Figure 3-7. The crosslink densities calculated based on the
storage modulus in the rubbery plateau are listed in Table 3-5. The crosslink density of SBS was ten times larger than the crosslink density of SIS and SIBS. This data indicated that the difference in crosslink density of materials might be the reason for the differences in tensile strength upon e-beam exposure.

![Graph](image)

Figure 3-7 Variation of storage modulus ($E'$) of SBCs as a function of temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>T$_g$ (°C)</th>
<th>T$_g$+50 (°C)</th>
<th>T (K)</th>
<th>$E'_{\text{min}}$ (Pa)</th>
<th>$\nu_e$ (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS</td>
<td>-82</td>
<td>-32</td>
<td>241</td>
<td>9.68E+06</td>
<td>1610.38</td>
</tr>
<tr>
<td>SIBS</td>
<td>-56</td>
<td>-6</td>
<td>267</td>
<td>7.40E+05</td>
<td>111.12</td>
</tr>
<tr>
<td>SIS</td>
<td>-43</td>
<td>7</td>
<td>280</td>
<td>5.60E+05</td>
<td>80.19</td>
</tr>
</tbody>
</table>

SBCs with four e-beam radiation doses were analyzed by DMA. Variations of storage modulus and tan delta as a function of temperature are shown in Figure 3-8-Figure 3-10. It was found that the storage modulus in rubbery plateau increased with increasing radiation dose. The storage modulus in rubbery plateau indicated the change of
crosslink density of elastomers. The higher value of storage modulus in rubbery plateau indicated the higher crosslink density of the materials. Therefore, the crosslinking reaction should be the predominant reaction during the e-beam radiation.

Figure 3-8 (a) Storage modulus and (b) Tan delta vs. temperature for SIS.
Table 3-6 Glass transition temperature and crosslink density of SIS determined by DMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g(°C)$</th>
<th>$T_g+50(°C)$</th>
<th>T(K)</th>
<th>$E'_\text{min}$ (Pa)</th>
<th>$v_e$(mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS-0 kGy</td>
<td>-43.34</td>
<td>6.66</td>
<td>279.66</td>
<td>5.60E+05</td>
<td>80.28</td>
</tr>
<tr>
<td>SIS-60 kGy</td>
<td>-42.03</td>
<td>7.97</td>
<td>280.97</td>
<td>1.16E+06</td>
<td>165.53</td>
</tr>
<tr>
<td>SIS-120 kGy</td>
<td>-40.21</td>
<td>9.79</td>
<td>282.79</td>
<td>1.45E+06</td>
<td>205.58</td>
</tr>
<tr>
<td>SIS-190 kGy</td>
<td>-38.58</td>
<td>11.42</td>
<td>284.42</td>
<td>1.54E+06</td>
<td>217.08</td>
</tr>
<tr>
<td>SIS-240 kGy</td>
<td>-38.79</td>
<td>11.21</td>
<td>284.21</td>
<td>1.68E+06</td>
<td>236.99</td>
</tr>
</tbody>
</table>

Figure 3-9 (a) Storage modulus and (b) Tan delta vs. temperature for SBS.
Table 3-7 Glass transition temperature and crosslink density of SBS determined by DMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g(\degree C)$</th>
<th>$T_g+50(\degree C)$</th>
<th>T(K)</th>
<th>$E'_\text{min}$ (Pa)</th>
<th>$v_e$(mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS-0 kGy</td>
<td>-82.33</td>
<td>-32.00</td>
<td>241.00</td>
<td>9.68E+06</td>
<td>1610.38</td>
</tr>
<tr>
<td>SBS-60 kGy</td>
<td>-76.23</td>
<td>-26.23</td>
<td>246.77</td>
<td>1.73E+07</td>
<td>2810.75</td>
</tr>
<tr>
<td>SBS-120 kGy</td>
<td>-75.14</td>
<td>-25.14</td>
<td>247.86</td>
<td>1.76E+07</td>
<td>2846.92</td>
</tr>
<tr>
<td>SBS-190 kGy</td>
<td>-74.79</td>
<td>-24.79</td>
<td>248.21</td>
<td>1.80E+07</td>
<td>2907.51</td>
</tr>
<tr>
<td>SBS-240 kGy</td>
<td>-73.36</td>
<td>-23.36</td>
<td>249.64</td>
<td>2.21E+07</td>
<td>3549.33</td>
</tr>
</tbody>
</table>

Figure 3-10 (a) Storage modulus and (b) Tan delta vs. temperature for SIBS.
Table 3-8 Glass transition temperature and crosslink density of SIBS determined by DMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) ((^\circ)C)</th>
<th>( T_g +50 ) ((^\circ)C)</th>
<th>T (K)</th>
<th>( E'_\text{min} ) (Pa)</th>
<th>( \nu_c ) (mol/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIBS-0 kGy</td>
<td>-56.05</td>
<td>-6.05</td>
<td>266.95</td>
<td>7.40E+05</td>
<td>111.12</td>
</tr>
<tr>
<td>SIBS-60 kGy</td>
<td>-50.37</td>
<td>-0.37</td>
<td>272.63</td>
<td>8.02E+05</td>
<td>117.94</td>
</tr>
<tr>
<td>SIBS-120 kGy</td>
<td>-47.45</td>
<td>2.55</td>
<td>275.55</td>
<td>9.89E+05</td>
<td>143.90</td>
</tr>
<tr>
<td>SIBS-190 kGy</td>
<td>-48.51</td>
<td>1.49</td>
<td>274.49</td>
<td>1.21E+06</td>
<td>176.59</td>
</tr>
<tr>
<td>SIBS-240 kGy</td>
<td>-48.06</td>
<td>1.94</td>
<td>274.94</td>
<td>2.21E+06</td>
<td>322.42</td>
</tr>
</tbody>
</table>

Glass transition temperature is one of the most important characteristics of polymer. It is related to the structure and molecular weight of the material. As a polymer film is cooled through \( T_g \), the motion of individual segment undergo a dramatic change. Therefore, any experiment can measure the local relaxation behavior verse temperature can be used to locate the \( T_g \). Based on the DMA results, the glass transition temperature is the temperature when the tan delta reaches the maximum value. According to the DMA results, glass transition temperature of polydiene phase slightly increased after e-beam radiation, which was consistent with Kanbara’s results. The glass transition temperatures of SBCs increased as e-beam radiation dose increases, as shown in Table 3-6 to Table 3-8.

3.4.3 Effect of e-beam radiation on stress relaxation behaviors of SBCs

The stress relaxation behaviors of SBS are shown in Figure 3-11. Controlled temperature (30 \(^\circ\)C) and strain (1 %) were chosen to compare the stress relaxation process of SBCs at four e-beam radiation doses. Before e-beam radiation, SBS relaxed to 50 % of its initial stress within 30 min; while after e-beam irradiated at 240 kGy, SBS relaxed to 75 % of its initial stress after 30 min. The stress relaxation behaviors of SIS are shown in Figure 3-12. Before e-beam radiation, SIS relaxed to almost zero within 30...
min. After e-beam crosslinking at 60 kGy, SIS relaxed to 67% of its initial stress after 30 min. This was attributed to the increased crosslink density of materials, which slowed down the relaxation of the polymer chain and maintain a higher stress after holding for 30 min.

Figure 3-11 Stress relaxation of SBS (@ 30 °C).

Figure 3-12 Stress relaxation of SIS (@ 30 °C).
Influences of both e-beam radiation dose and temperature on stress relaxation of the SIBS were investigated. Effect of radiation dose on stress relaxation behaviors of the SIBS are shown in Figure 3-13. The relaxation rate of SIBS slowed down as the radiation dose increases. The effect of temperature on stress relaxation behavior was studied at controlled e-beam dose. Heating accelerated the stress relaxation process due to the high mobility of the polymer chain at high temperature. By increasing the temperature, SIBS relaxed faster to a lower stress level.

Figure 3-13  Stress relaxation of SIBS (@ 30 °C).
3.4.4 Effect of e-beam radiation on molecular weight

Studying the molecular weight characteristic of polymer is a direct way to know whether chain scission or crosslinking reaction occurred during e-beam radiation. Copolymers with an e-beam radiation dose of 60 kGy were soluble in THF. The molecular weight could be measured by SEC. This provided the information about the initial change of the polymer chain during the e-beam radiation process.

Copolymers with radiation dose higher than 60 kGy, formed gel after irradiated under e-beam. It was difficult to measure the molecular weight by SEC. The SEC
chromatograms in Figure 3-15-Figure 3-17 shows that both molecular weight and polydispersity index increased for SBCs irradiated with a dose of 60 kGy. This indicated that crosslinking reaction was the predominant reaction rather than the main chain scission. Molecular weight characteristics before and after e-beam radiation are listed in Table 3-9.

Figure 3-15 SEC chromatograms of SIBS.

Figure 3-16 SEC chromatograms of SBS.
Molecular weight characteristics of polybutadiene, polyisoprene and polystyrene were also compared. This information will help elucidate the reaction of each block of SBCs during the e-beam radiation. There is a shoulder on SEC chromatogram of polyisoprene at the shorter elution time, as shown in Figure 3-18. This indicated the formation of high molecular weight polyisoprene after e-beam radiation. No significant amount of lower molecular weight polyisoprene was observed after radiation. Therefore, the crosslinking reaction was predominant in polyisoprene block. EffectS of e-beam radiation on molecular weight of polybutadiene with both high and low vinyl content
were also studied. SEC chromatograms of polybutadiene with ~80 % cis-and trans-1, 4 structures are shown in Figure 3-19 (a). Peak position moved to the shorter elution time side, which indicated the formation of a higher molecular weight polybutadiene. Figure 3-19 shows that the peak position in SEC chromatograms of polybutadiene with 90 % vinyl content did not move. Formation of higher molecular weight polybutadiene was observed. For the PS homopolymer, no higher molecular weight polystyrene was observed from SEC chromatogram after e-beam radiation, as shown in Figure 3-20. This means polystyrene block are relatively stable under e-beam radiation. Slight chain scission may occur. The molecular weight characteristics are shown from Table 3-10 to Table 3-12.

![SEC chromatograms for polyisoprene.](image-url)
Table 3-10 Molecular weight characteristics of polyisoprene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-0 kGy</td>
<td>17249</td>
<td>74313</td>
<td>4.31</td>
</tr>
<tr>
<td>PI-60 kGy</td>
<td>17907</td>
<td>79649</td>
<td>4.45</td>
</tr>
<tr>
<td>PI-120 kGy</td>
<td>19228</td>
<td>95205</td>
<td>4.95</td>
</tr>
<tr>
<td>PI-190 kGy</td>
<td>16986</td>
<td>90493</td>
<td>5.33</td>
</tr>
</tbody>
</table>

Figure 3-19 SEC chromatograms for (a) polybutadiene and (b) high vinyl polybutadiene.

Table 3-11 Molecular weight characteristics of polybutadiene.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>High vinyl PB-0 kGy</td>
<td>4173</td>
<td>6010</td>
<td>1.44</td>
</tr>
<tr>
<td>High vinyl PB-60 kGy</td>
<td>4341</td>
<td>6997</td>
<td>1.61</td>
</tr>
<tr>
<td>High vinyl PB-120 kGy</td>
<td>4962</td>
<td>8783</td>
<td>1.77</td>
</tr>
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Table 3-12 Molecular weight characteristics of polystyrene.

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</table>

3.5 Discussion

E-beam radiation can initiate both chain scission and crosslinking reaction on polymeric materials,\textsuperscript{122, 209} knowing what reaction is predominant at a given radiation dose is quite important. In addition, for block copolymers, different blocks may have different reaction upon e-beam radiation, which makes it a more complicated system than homopolymers. The properties of the SBCs would change consequently if the crosslinking reaction or chain scission reaction occurred during the e-beam radiation. There are several possible scenarios. E-beam radiation might only initiate one type of
reaction in materials. Or two types of reactions took place simultaneously, and one reaction was the predominant reaction. Since macro-properties of the materials strongly depend on the chemical structure of polymer chains, the ratio of chain scission to bond formation, albeit crosslinking, will control the material properties. A series studies was also conducted to compare the molecular weight characteristics of each block in the copolymers and the copolymers after e-beam exposure.

The comparison of the molecular weight as functions of mid-block and e-beam exposure dose shed some light on which chemical process predominate. At lower e-beam radiation doses (< 60 kGy), the SBCs were still soluble in the solvent. In this case, the molecular weight characteristics reflected the initial response of the materials to e-beam radiation. For the copolymer systems, the effect of e-beam radiation is the overall consequence of all the blocks. Based on the molecular weight characterization of three types of SBCs, it was found that these copolymers all undergo crosslinking reaction after e-beam radiation with an e-beam dose of 60 kGy. In order to find out the reaction of each block under e-beam radiation, molecular weight characteristics of each block were also studied. Since lower molecular weight polyisoprene (17 k) and polybutadiene (< 6 k) were selected, the materials were still soluble at higher e-beam dose (> 120 kGy). The molecular weight characterization showed that the e-beam radiation (< 240 kGy) mainly initiated crosslinking reactions of polyisoprene and polybutadiene blocks. The e-beam radiation did not initiate crosslink reactions on polystyrene phase, as the SEC chromatograms of polystyrene did not show any shoulder at the shorter elution time. Polystyrene is known as radiation resistant material and relatively stable under e-beam radiation. The properties of SBCs after e-beam radiation mainly depended on the
polydiene phase. In addition, the crosslink densities of SIBS, SIS and SBS calculated based on the DMA results showed the increase of the modulus in rubbery plateau. This indicated the increase of overall crosslink density after e-beam radiation.

![Diagram showing microstructure of e-beam crosslinked SBCs.](attachment:diagram.png)

**Scheme 3-1 Microstructure of e-beam crosslinked SBCs.**

In order to elucidate the reason for the different effect of e-beam radiation on tensile properties of SBCs, it is essential to discuss the microstructures and the failure mechanisms of SBCs under the uniaxial stretch. The typical morphologies of styrenic tri-block copolymers, such as SBS and SIS are illustrated graphically in Scheme 3-1. Due to the incompatibility of the polystyrene and polydiene chains, a two-phase morphology is formed. Polystyrene domain acts as physical crosslinker, which makes the styrenic block copolymers have high tensile strength and similar properties to vulcanized rubbers. The molecular weight between crosslinks is much lower than the molecular weight of mid-block. This means there are plenty of chain entanglements in the rubbery phase. Therefore, there are two physical crosslinking networks in the materials. One is the polystyrene domain which aggregates and acts as crosslinker and reinforcing fillers, the other is the chain entanglement in the rubbery phase. These two factors are
both important for the high tensile strength of SBCs. Before e-beam crosslinking, the slippage of entanglements in the polydiene chain helps to distribute the stress more evenly and delay the failure of the bulk material.\textsuperscript{210-211} After e-beam crosslinking, another network was introduced to the system, as shown in Scheme 3-1, which was the chemically crosslinked polydiene. This led to the change of the microstructure structure and the tensile properties of the copolymers.

The crosslinked network regularity changed as a function of e-beam radiation dose. Before e-beam exposure, the physically crosslinked network formed by phase separation of two blocks were uniformly distributed in the materials. This is very important for distribution of the stress evenly during the uniaxial stretching. After e-beam exposure, new crosslinking junctions were introduced into the system. At lower e-beam radiation doses, the regularity of the network decreased compared to the initial state due to the formation of a few crosslinks. The network became heterogeneous, as shown in Scheme 3-2 (b). In this case, the highly crosslinked cluster would have stress concentration under the uniaxial stretching. This clusters might break first during the tensile test, as shown in Scheme 3-2 (c). This might be the reason for the decrease of tensile strength for SIBS and SIS at low radiation doses (60 and 120 kGy). However, by increasing the e-beam dose, a new network was formed with higher crosslink density and network regularity, as shown in Figure 3-21 (a). The network regularity plays a very important role in the uniaxial tensile stretch. In Figure 3-21 (b), the first drop of the tensile strength was due to the decrease of the network regularity, and the second drop was attributed to the high crosslink density which reduced the extensibility of the materials.
Scheme 3-2 Schematic models for styrenic block copolymer networks: (a) A homogeneous network formed by phase separation, (b) A heterogeneous network at lower radiation doses, (c) A heterogeneous network deformed under uniaxial stretching.

Figure 3-21 Variation of tensile strength for SBCs as functions of (a) crosslink density and (b) radiation dose.

The variation of tensile strength for SIBS, SIS and SBS as functions of crosslink density and radiation dose are shown in Figure 3-21(b). The tensile strength of SIBS decreased at lower doses and increased at higher e-beam dose. The tensile strength of SIS also decreased first at lower e-beam dose, and then increased as the e-beam radiation dose increases. This phenomenon was different from the vulcanized rubbers. For traditional rubber, there is no crosslink before vulcanization. The tensile strength was
usually found to pass through a maximum as the degree of crosslink increased from zero. This maximum point is primarily due to changes in the viscoelastic properties after crosslinking.\textsuperscript{213} However, the SIBS copolymer already had certain amount of physical crosslinks before e-beam radiation due to the phase separation of polystyrene and polydiene segments. Polystyrene acted as the crosslinkers at the temperature below the T\textsubscript{g} of polystyrene. Therefore, the variation of tensile strength of SIBS was different from the traditional rubbers, such as polyisoprene and polybutadiene. The tensile strength of SBS increased a little bit at lower e-beam dose and then it continuously decreased with increasing e-beam dose. The trend was more like a traditional vulcanized rubber. Actually, only the influence of the radiation dose on the tensile strength were taken into account when the comparison was made. However, the crosslinking density of each material before e-beam exposure and at same radiation dose were different, as shown in Table 3-5. These three types of SBCs fell into different ranges in terms of crosslink density. For SIBS and SIS, the crosslink densities were 111.12 and 80.19 mol/m\textsuperscript{3}, respectively. These values were much lower than the crosslink density of the SBS (1610.38 mol/m\textsuperscript{3}). The differences of initial physical crosslink density and the crosslinking efficiency determine the effect of e-beam radiation on the tensile properties of the SBCs. More generally, if a process has both bond breaking and bond making capabilities (as in e-beam), the degree of physical entanglements for polymeric chains which can not be disentangled other than bond breaking is important.

Viscoelastic property is an important characteristic of block copolymers.\textsuperscript{214-215} The e-beam radiation introduced chemical crosslinking network to the system. The change of macroscopic mechanical properties is due to the consequences of molecular motion,
which are generally difficult to measure directly. However, it can be readily observed in stress relaxation experiment.\textsuperscript{216-217} There are three processes causing stress relaxations of SBCs: physical flow of the polydiene phase, disentanglement of the polydiene chains, and conformational change of the phenyl ring side group in the polystyrene phase. It has been reported that physical flow was the fastest relaxation process, while the relaxation of domains is the slowest.\textsuperscript{218-219} E-beam radiation crosslinked the polydiene phase. Consequently, the relaxation process was slowed down. The relaxation speed of SBCs decreased with increasing e-beam radiation dose. This indicated that the physical flow and disentanglement of polydiene phase was restricted after e-beam exposure. The stress relaxation of SBCs also had a temperature dependence. The higher temperature increased the mobility of polymer chains. The higher relaxation rate was be attributed to physical flow of both phases.

This is the first study to investigate the effect of e-beam radiation on properties of SBCs by comparing three types of the most widely used SBCs, including a newly developed SIBS. During the past, studies focused on either one of the block copolymer\textsuperscript{14, 112, 116} or homopolymers of elastomers.\textsuperscript{81, 217, 220} The molecular weight change of SBCs under e-beam radiation has not been investigated thus far. Since in the SBCs, styrene as a common block with different mid blocks, it was helpful to perform a systematic study of three types of SBCs and find out the key factors that controlled the properties of SBCs upon e-beam radiation. The block copolymers systems were found to be more complicated than the parent homopolymers. The e-beam crosslinking process highly depends on radiation dose as well as the initial structure of the materials. Although, the initial physical crosslink density plays an important role in determining the tensile
strength of copolymers upon e-beam radiation, the properties of SBCs can be adjusted by varying the e-beam dose.

3.6 Conclusions

The Effect of e-beam radiation on SBCs, including SBS, SIS and SIBS were investigated as a function of e-beam radiation dose. It was found that the crosslinking reaction was the predominant reaction in all copolymers investigated. The overall crosslink density increased as e-beam radiation dose increased. The tensile strength of SBCs highly depended on both crosslink density and network regularity. The decrease of network regularity could prevent the uniform stress distribution during uniaxial stretching and cause the decrease of tensile strength. However, at higher e-beam dose, the increase of the tensile strength was attributed to the increase of the both crosslink density and the network regularity. After passing a maximum point, the tensile strength started to decrease as the e-beam radiation dose increased. This was attributed to the high crosslink density induced low extensibility. Therefore, knowing the crosslink density of the materials before e-beam radiation was quite important in modifying the tensile properties of the SBCs. The relaxation rate of the crosslinked SBCs decreased with increasing e-beam radiation dose and increased with increasing temperature. This indicated that the crosslinks introduced by e-beam radiation slowed down the disentanglement of the polydiene segments. And higher temperature increased the overall physical flow of SBCs.
CHAPTER IV
INVESTIGATION OF ELECTRON BEAM INITIATED REACTIONS OF
STYRENIC BLOCK COPOLYMERs

4.1 Abstract

Electron beam (e-beam) radiation initiated reactions in styrenic block copolymers (SBCs), including poly (styrene-block-butadiene-block-styrene) (SBS), poly (styrene-block-isoprene-block-styrene) (SIS) and a newly developed poly (styrene-block-isoprene/butadiene-block-styrene) (SIBS) were investigated. The gel content of SBCs after e-beam exposure was calculated and the molecular weight characteristic of soluble portion was analyzed by size exclusion chromatography (SEC). The results showed that gel content increased with the e-beam radiation dose, and the low molecular weight material was generated after e-beam exposure. This indicated that both crosslinking and chain scission reaction took place during the e-beam exposure. The crosslink reaction was the predominant reaction. The structures of gel portion of SBCs were analyzed by solid state nuclear magnetic resonance (NMR). Equilibrium swelling showed that a tighter network was formed at higher radiation dose. Cylindrical morphologies were observed by both small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM). The effect of e-beam on morphologies of ozone etched SBCs was also investigated. It was found that the films of SBCs after e-beam crosslinking were able to maintain a relatively intact morphology after ozonolysis, while SBCs without e-beam
crosslinking lost the cylindrical morphology after ozonolysis.

4.2 Introduction

Radiation technology has been utilized to modify and crosslink oligomers and polymers.\textsuperscript{3} Electron beam (e-beam) radiation as one of the high energy output methods has been widely applied in crosslinking polymeric materials.\textsuperscript{2, 22, 89} It has been successfully used in crosslinking polyethylene and polyvinyl chloride.\textsuperscript{102, 221} The e-beam crosslink offers many advantages, including improving durability, abrasion resistance, solvent and chemical resistance, tensile and impact strength, creep resistance, environmental stress crack resistance and barrier properties.\textsuperscript{3} Since the energy of the electron beam is much higher than the bond energy of polymers, the electron beam is capable of initiating both chain crosslinking and chain scission reactions. Depending on the chemical structures of materials, one reaction might predominate.\textsuperscript{75} Polymers can be classified into two groups based on their responses to the e-beam radiation. One group of polymers is more likely to undergo chain scission reactions, while the other groups are more likely to have chain crosslinking reactions.\textsuperscript{23}

There has been considerable interest in radiation vulcanization of elastomers. Bik reported e-beam crosslinking hydrogenated acrylonitrile-butadiene rubber (NBR).\textsuperscript{12} Durkee used e-beam to selectively crosslink polyisoprene block of poly (α-methylstyrene-\textit{block}-isoprene) copolymer and degraded the poly (α-methylstyrene) micro-phase to produce microporous, crosslinked films.\textsuperscript{109} E-beam crosslinked ethylene propylene diene monomer (EPDM) reported by Eldred showed similar properties as sulfur crosslinked EPDM and exhibited greatly improved compression set and oil
Raven investigated the radiation-induced crosslinking and cyclization in 1,2-polybutadiene and found that the pendent vinyl group in 1,2-polybutadiene were more reactive than the vinyl groups in the backbone of 1,4-polybutadiene. Reaction of the carbonium ions with a vinyl group resulted in either crosslinking or cyclization. If carbonium ion reacted with vinyl group in a same polymer chain, cyclization was generated, whereas reaction with vinyl groups in a neighboring chain, crosslinking would be formed. Pearson studied the radiation crosslinking of polybutadiene and found that crosslinking reaction rate increased with increasing amount of vinyl unsaturations. Different isomers of polybutadiene had different contributions to the total crosslinking rates, vinyl \( > \) cis-1,4 \( > \) trans1,4. Little attention has been given to study the e-beam initiated reaction in styrenic block copolymers (SBCs), such as poly (styrene-block-butadiene-block-styrene) (SBS), poly (styrene-block-isoprene-block-styrene) (SIS) and a newly developed poly (styrene-block-isoprene/butadiene-block-styrene) (SIBS).

SBCs are a class of thermoplastic elastomers which contain polystyrene and rubbery segments. Due to phase separation, SBC forms a physically crosslinked network. The copolymer system made it difficult to investigate what type of chain reactions could take place in the system under e-beam radiation. Polydiene and polystyrene block were connected by covalent bonds. High energy e-beam radiation may cause reaction on either block as well as the coupling agent used during the ionic polymerization. Studying the e-beam initiated chain reaction in SBCs is quite important in terms of applying e-beam radiation technology in modifying SBCs to meet their end usages.

The purpose of this work is to investigate the reactions of SBCs under e-beam radiation. Gel contents of the material at four radiation doses were calculated. The gel
portions of SBS, SIS and SIBS were separated from soluble portion and the structures were analyzed by solid state nuclear magnetic resonance (NMR) spectroscopy. Molecular weight characteristics of the soluble portion were investigated by size exclusion chromatography (SEC). Equilibrium swelling was also performed to compare the network crosslink density. Morphology of film was studied by both atomic force microscopy (AFM) and small-angle X-ray scattering (SAXS). Effect of e-beam radiation on morphology of ozone etched SBCs was compared as well.

4.3 Experimental

4.3.1 Materials

SBS, SIS and SIBS were provided by Kraton Polymers, Houston, TX. The detailed information of SBCs is listed Table 3-1.

4.3.2 Film Fabrication

Films for e-beam crosslinking studies were prepared by solution casting method as described in the Chapter III. Films for morphology studies were prepared by the spin-coating method on the silicon wafers. Silicon wafer used as the substrate for thin films were purchased from Silicon Quest Intel. Before depositing the block copolymer solutions on 1 cm x 1 cm wafers, they were cleaned under a UVO cleaner (JELIGHT company, Inc. Model 42) to remove any remaining organics on the surface. Cyclohexane was used as solvent. The concentration was typically ranging from 10-20 mg/mL. All samples were spin coated at ambient temperature for 20 s at 3000 rpm. Thermal annealing was used to increase the long-range order. After spin coating, films were annealed at 130 °C for 48 h and slowly cooled to room temperature.
4.3.3 Electron beam radiation conditions

E-beam exposure was performed at the NEO beam crosslinking facility in Middlefield, OH. The e-beam radiation was conducted under following conditions: voltage: 4.48 MV, current: 30.0 mA, atmosphere: air, line speed: 15 feet/min, radiation time: ~30 s. The e-beam radiation dose is listed in Table 3-3. The dose was measured by a dosimeter consisted of alanine films manufactured by Kodak BioMax with lot number B0308A. The dosimeters were measured in a Bruker e-scan electron spin resonance (ESR) spectrometer. Alanine film dosimeters are commonly used in the radiation dose measurement.\textsuperscript{3, 206-207} Alanine, a crystalline amino acid, can form very stable free radicals when subjected to ionizing radiation. The alanine free radicals can yield an ESR signal that is dose dependent.

4.4 Characterizations

4.4.1 Molecular weight

Two Size Exclusion Chromatography (SEC) instruments with different detectors were used to determine polymer molecular weight and polydispersity index (PDI) of SBCs. One of the SEC used tetrahydrofuran (THF) as the mobile phase, which was equipped with a Waters 1515 isocratic pump, Waters Styragel columns and a Waters 2414 refractive index (RI) detector. The columns were calibrated with narrow distribution polystyrene (PS) standards. The other one was HLC-8320SEC, EcoSEC (TOSOH Corporation), which was equipped with a dual-flow RI detector and a UV detector. Chloroform was used as mobile phase. The second one was used to analyze the lower molecular part of the copolymer after e-beam radiation.
4.4.2 Gel content

Gel content was measured after being extracted in cyclohexane for three days. The gel content was calculated based on the equation (2).

\[ Gel\% = \frac{100 \times W}{W_0} \] (4-1)

where \( W \) is the weight of solid film after extraction and drying, \( W_0 \) is the initial weight of film before extraction.

4.4.3 Equilibrium swelling

2, 2, 4-trimethylpentane was chosen to selectively swell the mid-block of SBCs copolymers, while keeping the polystyrene phase intact. The weight of swollen film was measured after two days. The volume fraction of the mid-block in the swollen gel was calculated based on equation (3).

\[ \phi_{IB} = \frac{0.8W_{IB}/\rho_{IB}}{W_{SIBS}/\rho_{SIBS} + W_{Solvent}/\rho_{Solvent}} \] (4-2)

where \( W_{SIBS} \) is the weight of dry SIBS film, \( W_{Solvent} \) is the uptake weight of trimethylpentane at equilibrium swelling, \( \rho_{SIBS}, \rho_{IB} \) and \( \rho_{solvent} \) are the densities of SIBS, SIBS mid-block and solvent, respectively.

4.4.4 Bulk and thin film morphology

The bulk morphology of the materials was analyzed by SAXS. SAXS is capable of studying the block copolymers on phase separation and resulting morphology of the bulk film. SAXS data were collected with a Rigaku MicroMax-002+ sealed tube X-ray
generator coupled with multi wire position sensitive X-ray detector at room temperature. The exposure time for each SAXS test was 2 min.

The morphologies of SBC films were also investigated AFM. AFM imaging was performed using a Digital Instruments Nanoscope IIIa in tapping mode. Spun coated block copolymer thin films were analyzed with AFM to provide information on the phase and height contrast of the thin film. Data analysis was performed with Nanoscope III software.

4.4.5 Ozonolysis

Effect of e-beam on the morphology of block copolymer upon ozonolysis was investigated. In order to compare the effect of e-beam crosslinking on the morphology of the copolymer, both uncrosslinked and crosslinked samples were prepared. Thin films on silicon wafers were crosslinked at e-beam radiation dose of 80 kGy. Ozonolysis was performed on UVO-Cleaner, Model 42 (JELIGHT company, Inc). For SBS, the following ozonolysis conditions were chosen: 5 min, 10 min and 15 min. For SIS and SIBS, shorter ozonolysis time was chosen, 1 min, 3 min and 5 min. The reason for choosing the shorter ozonolysis time was because isoprene was more susceptible to ozone, after 5 min ozonolysis, most of the materials were etched away. After ozonolysis, sample was washed by deionized water and dried under N₂ flow before test. The morphology of each sample before and after e-beam crosslink and ozonolysis were studied.

4.5 Results and Discussion

E-beam initiated reactions in three types of widely applied SBCs were investigated. These SBCs include SBS, SIS and SIBS. The mid blocks of these materials contain the
most commonly used elastomers, which are polyisoprene and polybutadiene. By investigation of the influences of e-beam radiation on these three representative SBCs, it is anticipated to elucidate the reaction type and crosslinked structure of SBCs. Four e-beam radiation doses (60, 120, 190, and 240 kGy) were chosen to investigate based on the industrial cost and safety considerations. At high e-beam doses (> 60 kGy), sol and gel portions of copolymers were analyzed separately. The molecular characteristics of sol portion of SBCs with four e-beam radiation doses were analyzed by SEC. The structures of gels were characterized by solid state NMR. The ozonolysis was performed to observe the morphology change of SBCs with e-beam exposure.

4.5.1 Effect of e-beam radiation on gel content of SBCs

Gel content analysis was used to determine the weight fraction of insoluble portion of polymer in overall materials after e-beam radiation. The effect of e-beam radiation on gel content of the SBS copolymer is shown in Figure 4-1. Before e-beam radiation, SBS was completely soluble in cyclohexane. At low radiation dose (60 kGy), almost no gel was formed. An infinite network had not formed yet. Therefore, SBS was still soluble in solvent. At e-beam radiation dose of 120 kGy, part of the SBS was insoluble in solvent. Gel content of SBS increased to ~52 %. The gel content of SBS increased with increasing e-beam radiation dose. The gel content of SBS reached almost 90 % at radiation dose of 240 kGy. Figure 4-2 and Figure 4-3 show the gel content of SIS and SIBS as a function of e-beam radiation dose. Similar trend was observed for both SIS and SIBS. At low e-beam dose (60 kGy), there was no gel found, and gel content increased with increasing e-beam radiation dose. The gel content of SIS was over 85 % at e-beam dose of 240 kGy. And the gel content was approximately 82 % for SIBS at radiation dose of 240 kGy.
Figure 4-1 Effect of e-beam radiation dose on gel content of SBS.

Figure 4-2 Effect of e-beam radiation dose on gel content of SIS.

Figure 4-3 Effect of e-beam radiation dose on gel content of SIBS.
During the radiation crosslinking process, the molecular weight generally increased with radiation dose until partial gelation occurred. The gel fraction increased as the crosslink reaction continued.\textsuperscript{209} The gel content of polymers that are prone to chain scission reaction upon e-beam radiation will remain zero for non-crosslinked system or continue to decrease for crosslinked systems. In addition, molecular weight continues to decrease as the radiation dose increase. For instance, the molecular weight of poly(tetrafluoroethylene) (PTFE) significantly decreased as the irradiation dose increased.\textsuperscript{223-224} E-beam irradiation of PTFE results in the formation of powders with low molecular weight.\textsuperscript{225} Therefore, the gel content of the copolymers was one of the most important criteria to evaluate what type of chain reaction is occurred upon e-beam radiation. In this case, the gel content increased as the radiation dose was increased, as shown in Figure 4-1 and Figure 4-3. The increase of gel content of SBCs indicated that the crosslinking reaction took place during this process. At higher e-beam radiation dose, the high gel content was attributed to the high degree of crosslinking reaction induced by e-beam radiation.

The critical extent of reaction for the gel point of random crosslinks can be expressed as following equation.\textsuperscript{66}

\[ P_c = \frac{1}{N} \quad (4 - 3) \]

where \( P_c \) is the critical extent of reaction for the gel point, \( N \) is the degree of polymerization. According to this equation, a higher the degree of polymerization leads to a lower critical gel point. The degree of polymerization for polybutadiene block in SBS was \( \sim 1333 \). For polyisoprene block in SIS, the degree of polymerization was \( \sim 2000 \).
Theoretically, if these two polymers have similar response to the e-beam radiation, the SIS should have a lower critical gel point, which means the SIS should have a higher gel content than SBS at a given e-beam radiation dose. However, the result got from the gel content measurements was that SBS had higher gel content than SIS at a given e-beam radiation dose. This indicated the butadiene block was more easily to be crosslinked by e-beam radiation than isoprene.

4.5.2 Molecular weight characteristics

The gel content of copolymer was more than 40% for e-beam radiation dose greater than 120 kGy. It was only possible to get molecular weight characteristics of the soluble portion of the materials. SEC chromatograms of SBS with four e-beam radiation doses are shown in Figure 4-4. By increasing the e-beam dose, a small peak appeared at the elution time of ~17 min, which indicated the formation of low molecular weight materials and chain scission occurring at high e-beam dose. In addition, the area of peak located at the elution time of 17 min increased with increasing e-beam dose, which indicated higher e-beam dose caused a higher degree of chain scission. The shoulder in the SEC chromatogram located at the elution time between 14 min and 15 min, as shown in Figure 4-4, increased with increasing e-beam dose. Based on the SEC chromatogram, it was found that more di-blocks were generated at higher e-beam radiation dose during the radiation. Molecular weight characteristics of SBS are listed in Table 4-1. Molecular weight of the sol portion of SBS decreased, and the PDI increased from 1.15 to 2.33.

Since the SEC column used to obtain the data was equipped with a refractive index detector, it was not clear whether this low molecular weight chain was a polystyrene or polybutadiene block. In order to know which block formed low molecular weight chains,
the sol portion of SBS with e-beam dose of 240 kGy was analyzed by a SEC equipped with both RI and UV-Vis detectors. Figure 4-5 shows the SEC chromatograms of SBS irradiated with an e-beam dose of 240 kGy. SEC data obtained from UV and RI detectors had small peaks, which means both polystyrene and polybutadiene had chain scissions during e-beam radiation. However, the chromatograms at elution time of 18 min had a different peak area, which means different amount of low molecular weight materials were detected. The area on SEC chromatogram from UV detector at elution time of 18 min was larger than the area on SEC trances from the R.I. detector, as shown in Table 4-2. This indicated that more polystyrene blocks were detached from the SBS copolymer chains.

Figure 4-4 SEC chromatograms of soluble portion of e-beam irradiated SBS.
Table 4-1 Molecular weight characteristics of SBS-sol

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Figure 4-5 SEC chromatograms of soluble portion of SBS with e-beam radiation dose of 240 kGy

Table 4-2 Molecular weight characteristics of SBS-sol with e-beam radiation dose 240 kGy

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<thead>
<tr>
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<td>3302</td>
<td>604</td>
<td>54:39:7</td>
</tr>
</tbody>
</table>

The molecular weight characteristic of soluble part of e-beam irradiated SIBS was also investigated. SEC chromatograms of SIBS are shown in Figure 4-6. By increasing
the e-beam dose, a small peak appeared at the elution time of 17min, which indicated the existence of shorter polymer chains generated during e-beam radiation. In addition, the area of this small peak increased with increasing e-beam dose, which indicated higher e-beam dose caused higher degree of chain scissions. Since SIBS contains 25% of diblock, the shoulder located at the higher elution time of SEC chromatogram was attributed to the existence of diblock. By increasing the e-beam dose, the diblock content increased and the SEC elution peak broadened, which indicated the polydispersity increase of SIBS. The shoulder located at shorter elution time indicated the formation of high molecular weight SIBS, while at the longer elution time, the increase of diblock content means SIBS broken into diblocks. In order to figure out which block of SIBS was detached from the copolymer chain, the SEC equipped with both UV and RI detectors was chosen to rerun the molecular weight characterization. Based on the SEC chromatogram in Figure 4-7, both low molecular weight polydiene and polystyrene blocks were observed. However, based on calculated ratio, more polystyrene blocks formed low molecular weight chains, as shown in Table 4-4.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\bar{M}_n$ (g/mol)</th>
<th>$\bar{M}_w$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIBS</td>
<td>156041</td>
<td>187560</td>
<td>1.20</td>
</tr>
<tr>
<td>SIBS -60 kGy-Sol</td>
<td>170514</td>
<td>237181</td>
<td>1.39</td>
</tr>
<tr>
<td>SIBS -120 kGy-Sol</td>
<td>169118</td>
<td>235702</td>
<td>1.39</td>
</tr>
<tr>
<td>SIBS -190 kGy-Sol</td>
<td>101805</td>
<td>168896</td>
<td>1.66</td>
</tr>
<tr>
<td>SIBS -240 kGy-Sol</td>
<td>63094</td>
<td>127298</td>
<td>2.02</td>
</tr>
</tbody>
</table>
Figure 4-6 SEC chromatograms of soluble portion of e-beam irradiated SIBS.

Figure 4-7 SEC chromatograms of soluble part of SIBS with e-beam radiation dose of 240 kGy

Table 4-4 Molecular weight characteristics of SIBS-sol after radiation (240 kGy)

<table>
<thead>
<tr>
<th>SEC detector</th>
<th>Peak area/mV·s</th>
<th>Peak area/mV·s</th>
<th>Peak area/mV·s</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>407</td>
<td>1415</td>
<td>289</td>
<td>19:67:14</td>
</tr>
<tr>
<td>RI</td>
<td>1328</td>
<td>3623</td>
<td>353</td>
<td>25:68:7</td>
</tr>
</tbody>
</table>
Molecular weight characteristic of SIS is shown in Figure 4-8. At low e-beam dose (e.g., 60 kGy), there was no significant chain scission reaction occurred, since no peak was observed at elution time above 14 min on SEC chromatogram. By increasing the radiation dose, a small peak appeared at an elution time of 17 min, which indicated the chain scission reaction took place at radiation dose of 120 kGy. In addition, the SEC chromatogram become broader compared to the initial state, which means SIS had chain scission reaction during e-beam radiation and molecular weight distribution increased. Unlike the SBS, there was no evidence for diblock formation after e-beam radiation. The number average molecular weight of SIS changed from 169 k to 71 k, and the PDI changed from 1.1 to 2.3, as shown in Table 4-5. Figure 4-9 shows the SEC chromatograms obtained from both RI and UV-vis detectors. There is no significant difference observed.

![SEC chromatograms](image)

Figure 4-8 SEC chromatograms of soluble portion of e-beam irradiated SIS
Table 4-5 Molecular weight of soluble portion of SIS before and after e-beam radiation

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\overline{M}_n$ (g/mol)</th>
<th>$\overline{M}_w$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS</td>
<td>169818</td>
<td>188665</td>
<td>1.11</td>
</tr>
<tr>
<td>SIS-60 kGy-Sol</td>
<td>169249</td>
<td>250579</td>
<td>1.48</td>
</tr>
<tr>
<td>SIS-120 kGy-Sol</td>
<td>100259</td>
<td>233952</td>
<td>2.33</td>
</tr>
<tr>
<td>SIS-240 kGy-Sol</td>
<td>71882</td>
<td>165521</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Figure 4-9 SEC chromatograms of soluble part of SIBS with e-beam dose of 240 kGy

Investigation of the molecular weight of the soluble portion of copolymers after e-beam radiation was helpful in determining what type of reaction occurred during the e-beam exposure. SBCs undergo a series of reactions upon exposure to e-beam radiation and generate free radicals, unsaturations, crosslinks, and end-links. Change in the molecular weight and distribution is a consequence of main chain scission, crosslinking, and end linking reactions. The formation of high molecular weight material was the consequence of the crosslinking reaction, while the appearance of the low molecular weight was due to the main chain scission reaction. The gel content measurements have already confirmed that the crosslink reaction took place during the e-beam radiation.
Based on the results obtained from SEC, no significant chain scission reaction was observed at low radiation dose (60 kGy), while at high radiation dose (>120 kGy), both chain crosslink and chain scission took place in SBCs. The crosslink reaction was still the predominate reaction for SBCs.

4.5.3 Equilibrium swelling

The volume fraction of mid-block in the swollen gel was obtained after equilibrium swelling in solvent. A comparison of volume fraction of mid-block in the swollen gel is shown in Figure 4-10. Before e-beam exposure, the volume fraction of mid-block of SIBS in the swollen gel was approximately 5.8%. The volume fraction of the mid-block of SIBS increased 27% after e-beam radiation at dose of 60 kGy. For SIBS with an e-beam dose of 240 kGy, the volume fraction of the mid-block increased 253%. The volume fraction of the SBS mid-block in the swollen gel increased by 6% after irradiated with an e-beam dose of 240 kGy in comparison to the SBS without any radiation. And the volume fraction of SIS mid-block in the swollen gel increased by 51% after irradiated with dose of 60 kGy, and 203% after irradiated with dose of 240 kGy.

The higher mid-block content in the swollen gel indicated the tighter network after crosslinking. The volume fraction of mid-block in the swollen gel increased with the increasing e-beam radiation dose. This indicated a tighter network was formed at a higher e-beam dose. In addition, the crosslinking reaction initiated by e-beam radiation took place in the mid-block of SBCs. The change of the volume fraction of the mid-block in swollen gel of SIBS, SBS and SIS were similar, as shown in Figure 4-10. Tighter network was formed in SBCs after e-beam radiation, and the crosslink density increased with increasing e-beam radiation dose.
For crosslinked polymers, a state of equilibrium swelling could be attained if the network structure was not dissolved by the solvent. During the swelling process, the network was significantly expanded as more solvent was absorbed by the polymer. If the effect of the heat of mixing of polymer and solvent is neglected, equilibrium will be attained when the opposing entropies, the entropy of chain configuration and the osmotic or mixing entropy become equal. Swelling techniques are proven to be useful in the investigation of crosslink networks of rubber. SBCs can also achieve equilibrium swelling in some solvents. In this case, the swelling solvents used were those can
adequately swell the polybutadiene and polyisoprene block while leaving the polystyrene domains intact. Therefore, equilibrium swelling was an effective way to investigate the change of crosslink density of mid-block in SBCs after e-beam radiation. The higher volume fraction of mid-block in the swollen gel indicated less solvent was absorbed by SBCs. Meanwhile, the network was less expanded during equilibrium swelling. The higher radiation dose led to the formation of tighter networks in copolymers. This indicated that the crosslink reaction was the predominant reaction in SBCs during e-beam radiation.

4.5.4 Gel structure analysis by solid state NMR

The structures of the insoluble portion of the materials were separated by extraction and analyzed by solid state NMR. Figure 4-11 shows the solid state $^{13}$C NMR spectra of the gel portion of SBS after e-beam exposure at several radiation doses. Resonances located at $\delta$ 110 ppm and 140 ppm were attributed to the vinyl end group due to the chain scission (vinyl C=C). The resonance located at $\delta$ 125 ppm was attributed to the 1,4 cis-C=C, and the shoulder next to it was due to the formation of trans-C=C during the radiation. The resonances located at $\delta$ 28 ppm was assigned to the cis, -CH$_2$- group and the broad shoulder resonances next to it was attributed to the trans, -CH$_2$- group. Quaternary carbon crosslinks were also observed at around $\delta$ 45 ppm. This was also observed by other researchers in studying the gamma radiation of polybutadiene.

Figure 4-12 shows the solid state $^{13}$C NMR of the SIS gel. Three aliphatic ($\delta$ 23.7, $\delta$ 26.7, and $\delta$ 32.3 ppm) and two olefinic peaks ($\delta$ 125.3 and $\delta$ 134.8 ppm) from carbons in cis-1, 4-polyisoprene can be identified in the spectra. In addition to these mobile carbon peaks, broad rigid carbon resonances were also observed. A broad resonance at $\delta$ 47.6
ppm in spectra was due to quaternary carbons crosslinked in the elastomers,\textsuperscript{118,227} which increased with the increasing of radiation dose. According to VanDerHoff\textsuperscript{\textdegree}s research,\textsuperscript{228} the polyisoprene can exhibit six mesomeric forms, as shown in Scheme 4-1. The path A yields the most abundant free radical species formed in polyisoprene. Because of resonance stabilization in path A, a quaternary carbon crosslink was formed upon coupling of the free radicals. Methyl and methylene groups of the \textit{trans} isomers were also observed at resonances of $\delta$ 16.5 ppm and $\delta$ 41.0 ppm. Resonances at $\delta$ 105.2 ppm and $\delta$ 140.5 ppm were observed in the spectrum, which were due to the vinyl end groups produced by the main chain scission from disproportionation of the allylic radical.\textsuperscript{118}

Scheme 4-1 Six types of radicals form in polyisoprene according to VanDerHoff\textsuperscript{\textdegree}s research.\textsuperscript{228}
Figure 4-11 Solid state $^{13}$C NMR spectra of SBS gel.

Figure 4-12 Solid state $^{13}$C NMR spectra of SIS gel
4.5.5 Morphologies of SBCs

Morphologies of SBCs were studied by AFM and SAXS. Cylindrical morphologies were observed for SIBS, SBS, and SIS, as shown from Figure 4-13 to Figure 4-15. Cylinders parallel to the substrate were observed for SIBS and SIS. According to Mansky’s research,\textsuperscript{229} it was the butadiene cylinders oriented parallel to the spin coated copolymer film surface, presumably sandwiched between upper and lower half bi-layers. For SBS, both parallel and perpendicular cylinders were observed in AFM phase images. This was due to the variation of SBS film thickness.\textsuperscript{65,230} 1D SAXS profiles, as shown in Figure 4-16, also confirmed the morphologies of the copolymers.

Figure 4-13 AFM phase images of SIBS.

Figure 4-14 AFM phase images of SIS.
Figure 4-15 AFM phase images of SBS.

Figure 4-16 1D SAXS profiles of (a) SIBS, (b) SBS, and (c) SIS.
Figure 4-17 AFM phase images of SIS before (a, c, e, g, i, k) and after e-beam exposure (b, d, f, h, j, l), with different ozone etching time, 1 min (a, b, c, d), 3 min (e, f, g, h), 5 min (i, j, k, l).
Figure 4.18 AFM phase images of SBS before (a, c, e, g, i, k), and after e-beam exposure (b, d, f, h, j, l) with different ozone etching time, 5 min (a, b, c, d), 10 min (e, f, g, h), 15 min (i, j, k, l).
Figure 4-19 AFM phase images of SIBS before (a, c, e, g, i, k) and after e-beam exposure (b, d, f, h, j, l) with different ozone etching time, 1 min (a, b, c, d), 3 min (e, f, g, h), 5 min (i, j, k, l).
The morphologies of SBCs thin films coated on silicon wafers were cylinders paralleled or perpendicular to the substrate. Copolymers before and after e-beam crosslinking were subjected to ozonolysis. Alkenes could be oxidized by ozone to form alcohols, aldehydes or ketones, or carboxylic acids.\textsuperscript{231} Ozone etching block copolymers containing polyisoprene or polybutadiene had previously been applied by Harrison and coworkers to fabricate masks for pattern transferring onto semiconductors.\textsuperscript{232-233} Ozone predominantly attacked the carbon-carbon double bonds in the polydiene backbone, broke the bonds and produced fragments that were washed away by water.\textsuperscript{234-235} According to the results in previous section, e-beam radiation of SBCs mainly initiated the crosslinking reaction of the polydiene phase. Reducing the unsaturation was one of the consequences of e-beam crosslinking process. Therefore, the films of SBCs after e-beam crosslinking were able to maintain a relatively intact morphology, while SBCs without e-beam crosslinking lost the initial morphology after ozonolysis, as shown in Figure 4-17, Figure 4-18, and Figure 4-19.

After ozone treatment for 1 min, no disordering of the initial pattern was observed for SIS and SIBS with e-beam crosslinking. After 3 min of ozone treatment, the morphology of SIBS with e-beam radiation was still similar to the initial pattern although with some defects. However, the morphology of SIBS without e-beam radiation had a large number of defects, as shown in Figure 4-19 (e, f, g, h). After ozone treatment for 5 min, the influence of etching was significant as the stripe order was reduced to give spots for SIBS without e-beam radiation, as shown in Figure 4-19 (i, k). However, the morphology of SIBS after e-beam radiation still maintained a cylindrical shape, as shown in Figure 4-19 (j, l). Ozone etched away SIS more quickly. After ozone treatment for 3
min, the SIS films without e-beam exposure lost the cylindrical morphology, while the SIS after e-beam exposure still had the cylindrical morphology, as shown in Figure 4-17 (e, f, g, h). For SBS with e-beam radiation, the morphology still maintained cylindrical after 5 min ozone treatment. However, the SBS without e-beam radiation after 5 min ozone treatment lost its initial morphology.

Although there have been previous reports of e-beam induced crosslinking using polyisoprene, polybutadiene and ethylene-propylene-diene monomer (EPDM) rubber, this is the first study to our knowledge using SBCs. The SBCs studied in this work also showed the increase of gel content and molecular weight under e-beam radiation, which indicated the occurrence of crosslinking reactions. Through studying the sol and gel separately, it was found that the e-beam induced reactions in SBCs, which were chain scission and crosslinking, were dependent on the radiation dose. Although the crosslinking reaction was the predominant reaction for the SBCs studied in this paper, a significant amount of chain scission reaction also occurred, especially at higher radiation dose. As a general rule, SBCs containing either polyisoprene or polybutadiene segments generate low molecular weight chains at e-beam radiation dose higher than 120 kGy, thus this could be considered the upper limit for doses. This could be important for end usages of irradiated SBCs that are sensate to soluble low molecular weight fragments. By comparing these three types of SBCs (SBS, SIS, SIBS), it was found that SBS was more easily crosslinked (lower dosage) than the SIS, and the SIBS had the intermediate reactivity.
4.6 Conclusions

E-beam radiation induced reactions of SIS, SBS and SIBS were investigated. The reaction type, crosslinking or chain scission was dose dependent. At lower e-beam radiation doses (eg. < 120 kGy), crosslinking reactions were observed. As the radiation dose increased to a higher value (> 190 kGy), both crosslinking and chain scission reactions took place and a significant amount of chain scissions were observed. The crosslinking reaction was always predominant in three types of SBCs investigated. Chain scission reaction increased with increasing e-beam radiation dose. Cis-trans isomerization was also observed in SBCs upon e-beam radiation. The cylindrical morphology was observed in SBCs. Copolymers after e-beam crosslinking were more stable during ozonolysis.
CHAPTER V

EFFECTS OF PRO-RADS ON ELECTRON BEAM RADIATION CROSSLINKING POLY (STYRENE-\textit{BLOCK}-ISOPRENE/BUTADIENE-\textit{BLOCK}-STYRENE) (SIBS)

5.1 Abstract

The effects of pro-rads on promoting e-beam radiation induced crosslinking reaction of poly (styrene-\textit{block}-isoprene/butadiene-\textit{block}-styrene) (SIBS) were studied. Ten types of pro-rads were investigated, including trimethylolpropane trimethacrylate (TMPTMA), trimethylolpropane triacrylate (TMPTA), triallyl cyanurate (TAC), polybutadiene diacrylate (PB-diacylate), ethylene glycol dimethylacrylate (EGDMA), butylene glycol dimethacrylate (BGDMA), 1, 2-polybutadiene, trimethylolpropane tris(3-mercaptopropionate) (Tri-SH), 517HP (trifunctional methacrylate containing inhibitor) and 519HP (trifunctional acrylate containing inhibitor). The effects of pro-rads type and concentration on properties of the e-beam irradiated SIBS were studied, including tensile strength, elongation-at-break, modulus, gel content, equilibrium swelling and crosslink density. The solubility of pro-rads in the SIBS was also investigated by selectively swelling. The pro-rads were found to be soluble in both phases of the SIBS. TMPTA and Tri-SH significantly improved the tensile modulus and crosslink density of the SIBS. TMPTMA and 517HP showed 50% increase of the tensile strength of the SIBS without substantially sacrificing the elongation-at-break. Melting process stability of the pro-rads was also evaluated. It was found that the viscosity of SIBS with methacrylate type
pro-rads were more stable than the others.

5.2 Introduction

Radiation curing technology, especially the electron beam (e-beam) radiation is an efficient way to crosslink elastomers. It has advantages of high energy efficiency, controlled reaction condition and initiation without use of the initiator. It has been widely applied in various industries. Extensive studies have been done to investigate the effect of e-beam radiation on polymeric materials. In order to obtain the equivalent crosslink density as vulcanized rubber, a high radiation dose is usually required. The high radiation dose will cause an increase in capital investment as well as health and safety concerns. Finding suitable additives, which could decrease the e-beam dose needed, is quite important in applying e-beam radiation technology into industrial scale.

Adding coagent is a common method to improve the crosslinking efficiency in rubber vulcanization and other polymer crosslinking process. Coagents are typically multifunctional monomers or oligomers which are capable of participating in a number of reactions, including grafting and radical addition. By increasing the crosslink density of the polymer, the overall performance of the final products can be improved. Some coagents are highly reactive and increase both the rate and final degree of curing, such as coagents containing acrylate, methacrylate, or maleimide functionality. Allylic coagents, such as allyl-containing cyanurates and isocyanurates only increase the overall degree of cure. In radiation crosslinking process, adding coagent, which is also called pro-rad, is an effective way to improve the properties of plastics and elastomers.
Two types of pro-rads, indirect pro-rads and direct pro-rads are currently used in the e-beam radiation crosslinking process. The indirect pro-rads help the formation of the reactive species, and do not enter the crosslinked network. Halogenated hydrocarbons, such as carbon tetrachloride and chloroform, have been used to reduce the dose for vulcanization of the nature rubber. However, the majority of the carbon tetrachloride stays in the material and is slowly released after exposure. Chloro-hydro carbons pose health and safety concerns. Therefore, finding nontoxic pro-rads for the e-beam radiation crosslinking process is necessary. Acrylate monomers and oligomers have been used as pro-rads before. These are direct pro-rads, that not only enhance the formation of the reactive species, but also act as crosslinkers in the cured products.

Poly (styrene-block-isoprene/butadiene-block-styrene (SIBS) as a newly developed material, is a class of styrenic block copolymer (SBC), which contains polystyrene end-block and polybutadiene/polyisoprene hybrid mid-block. Similar to other styrenic block copolymers(SBCs), SIBS forms a physically entangled network similar to crosslink due to phase separation. SIBS copolymer possesses the mechanical properties of vulcanized rubbers, as well as the processing characteristics of thermoplastics. The e-beam crosslinking SIBS has been reported in the previously chapters. A high radiation dose (>190 kGy) was required to improve the tensile strength of the SIBS.

The objective of the research is to study the effects of pro-rads on e-beam crosslinking process of SIBS and screen e-beam pro-rads which can improve the tensile strength and crosslinking efficiency of the SIBS at lower e-beam radiation doses. A series of di-functional and tri-functional monomeric and oligomeric pro-rads were compared. The SIBS by itself was also exposed to the e-beam radiation and investigated
as a control. Tensile test, gel content, equilibrium swelling, dynamic mechanical analysis (DMA), and nuclear magnetic resonance (NMR) spectroscopy were performed for the films after e-beam exposure.

5.3 Experimental

5.3.1 Materials

SIBS (D1171) was provided by Kraton Polymers, Houston, TX. SIBS is a linear structure, contains 20 % polystyrene and 80 % polydiene. The mid-block is the random copolymer of isoprene and butadiene. It also contains 0.5 % primary and secondary antioxidants. Pro-rads were obtained from Sartomer LLC, except for the last two pro-rads purchased from Sigma-Aldrich. Cyclohexane (ACS reagent, ≥99 %), 2, 2, 4-trimethylpentane (ACS, 99 %), tetrahydrofurfuryl alcohol (THFA) (99 %) were purchased from Sigma-Aldrich and used as received. Solvent for NMR spectroscopy was deuterated chloroform (CDCl₃, 99.8 %) and purchased from Cambridge Isotope laboratories. Structures of pro-rads studied are listed in Table 5-1.
Table 5-1 Pro-rads information

<table>
<thead>
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<th>No.</th>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
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<tr>
<td></td>
<td>(TMPTMA)</td>
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</tr>
<tr>
<td>SR350</td>
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<td>(TMPTA)</td>
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</tr>
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<td>1,2-Polybutadiene (approx. 90 % 1,2-vinyl)</td>
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<td>Aldrich</td>
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<td></td>
<td>Trimethylolpropane tris(3-mercaptopropionate)</td>
<td><img src="image9.png" alt="Structure" /></td>
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</table>

5.3.2 Film Fabrication

SIBS films were prepared by solution casting. A low solid content (15 wt %) and slow evaporation process was used for casting, so that the residual stress did not develop
in the films. The procedure was as following: SIBS (50 g) was stirred in cyclohexane (283 g) for 5 h until a homogeneous solution was obtained. Then, pro-rad (5 phr, 2.5 g) (phr, parts per hundred rubber) was added to the solution. Then the solution was stirred for an additional 1 h. The solution was poured onto a PTFE plate and kept in a solvent evaporation chamber at room temperature. The film was kept in the chamber for 3 days, and then in the hood for two more days. Finally, the film was dried in a vacuum oven for two days at room temperature to remove any residual solvent.

5.3.3 Electron beam radiation conditions

E-beam exposure was performed at the NEO beam crosslinking facility in Middlefield, OH. The e-beam radiation was conducted under the following conditions: voltage: 4.48 MV, current: 30.0 mA, atmosphere: air, line speed: 15 feet/min, radiation time: ~30 s. The e-beam radiation doses are listed in Table 3-3.

5.4 Characterizations

5.4.1 Tensile test

Tensile test was performed on Instron universal electromechanical tester 5567 at extension speed of 500 mm/min (20 in/min). According to ASTM D-412, five dumbbell shape specimens were used to perform the tensile test.

5.4.2 Dynamic mechanical properties

Dependence of dynamic modulus on temperature was measured on a dynamic mechanical analysis (DMA) Q-80 (TA Instruments, Inc) in a multi-frequency strain mode. Films were tested under the following conditions: rectangular film, tension mode, heating rate is 3 °C/min and frequency is 1 Hz. Each film was tested three times and error was
less than 5 %. The crosslink density was calculated from the storage modulus \( E' \) in the rubbery plateau based on the following equation.

\[
v_e = \frac{E'}{3RT}
\]  

(5-1)

where \( E' \) is the storage modulus in rubbery plateau (Pa), \( v_e \) is the crosslink density (mol/m\(^3\)), \( R \) is gas constant (8.31 J·mol\(^{-1}\)·K\(^{-1}\)) and \( T \) is temperature (K).

5.4.3 Gel content and equilibrium swelling

Gel content of SIBS was measured after being extracted in cyclohexane for three days. The gel content was calculated based on the following equation.

\[
Gel \ % = \frac{100 \times W}{W_0}
\]  

(5-2)

where \( W \) is the weight of solid film after extraction and drying, \( W_0 \) is the initial weight of the film before extraction.

5.4.4 Equilibrium swelling

2, 2, 4-trimethylpentane was chosen to selectively swell the mid-block of SIBS copolymers. The weight of swollen film was measured after two days. The volume fraction of the mid-block in the swollen gels was calculated based on equation (5-3).

\[
\phi_m = \frac{0.8W_{in} / \rho_{in}}{W_{SIBS} / \rho_{SIBS} + W_{Solvent} / \rho_{Solvent}}
\]  

(5-3)
where $W_{SIBS}$ is the weight of dry SIBS film, $W_{Solvent}$ is the uptake weight of trimethylpentane at equilibrium swelling, $\rho_{SIBS}, \rho_{IB}$ and $\rho_{solvent}$ are the densities of SIBS, SIBS mid-block and the solvent, respectively.

5.4.5 Viscosity stability of SIBS with pro-rads

Viscosity stability of the SIBS with pro-rads (5 phr) was investigated by ARES rheometer with 25 mm parallel plate. The complex viscosity was obtained at 200 °C for 30 min. The frequency is 1 Hz and shear strain is 4 %.

5.4.6 Solubility of pro-rads in SIBS

Solubility of pro-rad in two phases of the SIBS block copolymers was investigated by selectively swelling the SIBS films containing pro-rads in trimethylpentane and THFA, respectively. $^1$H NMR was used to analyze the solution after swelling for 48 h. The protons attached to the double bond were chosen to track the pro-rad in each phase. $^1$H NMR spectra were obtained on a Varian Mercury-300MHz spectrometer. Samples were dissolved in deuterated chloroform (CDCl$_3$).

5.5 Results

Pro-rads chosen for screening were due to their high reactivity under e-beam radiation and lower toxicity. Four e-beam radiation doses (60, 120, 190 and 240 kGy) were studied based on the industrial cost and safety requirements. Influence of e-beam radiation on property of the SIBS itself without any pro-rad was also investigated as a control. In the initial screening process, tensile properties and crosslink density of SIBS with the same pro-rads concentration (5 phr) and e-beam (120 kGy) were compared. Four pro-rads with significant improvement in tensile strength and crosslinking efficiency

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were down selected to further study the effects of both the pro-rads concentration and radiation dose on tensile property, crosslink density, gel content and equilibrium swelling of SIBS.

5.5.1 Effect of pro-rads on tensile properties of SIBS

Tensile properties of the SIBS with various pro-rads were compared a controlled pro-rad concentration (5 phr) and e-beam radiation dose (120 kGy). Stress-strain curves of the SIBS films with pro-rads are shown in Figure 5-1. And the comparison of tensile strength, elongation-at-break and 300 % modulus are shown in Figure 5-2-Figure 5-4. E-beam radiation in the presence of pro-rads had significant influences on stress-strain behaviors of the SIBS. Without adding pro-rads, the tensile strength of SIBS decreased at an e-beam radiation dose of 120 kGy. TMPTMA, 517HP and BGDMA (5 phr) improved tensile strength of SIBS without significantly reducing the elongation-at-break after irradiation, as shown in Figure 5-2 and Figure 5-3. Particularly, the tensile strength of SIBS with TMPTMA and 517HP (5phr) increased by 44 % compared to the SIBS without e-beam radiation. The elongation-at-break of SIBS with TMPTMA and 517HP (5phr) only decreased by 17 %. 519HP, EGDMA, TMPTA, high vinyl PB and PB-diacrylate did not show any significant improvement in tensile strength of the SIBS. The tensile strength of SIBS irradiated at 120 kGy decreased by 39 % through adding TAC (5 phr). The elongation-at-break of SIBS with 519HP and TMPTA decreased by 62 % and 78 %, respectively.

The comparison of 300 % moduli of SIBS with pro-rads is shown in Figure 5-4. The modulus of SIBS increased after being irradiated under e-beam in the presence of pro-rads. The pro-rads type also had influences on the tensile modulus of SIBS. Figure 5-4
shows the 300 % modulus in a sequence. SIBS with TMPTA showed the highest modulus, while SIBS itself without e-beam radiation had the lowest modulus. The TMPTA and 519HP increased the moduli of SIBS by 400 % and 206 %, respectively. The TMPTMA and 517HP increased the moduli of SIBS by 124 %.

Figure 5-1 Stress-strain curves of SIBS with pro-rads (5 phr, 120 kGy).
Figure 5-2 Comparison of tensile strength of SIBS with pro-rads (5 phr, 120 kGy).

Figure 5-3 Comparison of elongation-at-break of SIBS with pro-rads (5 phr, 120 kGy).
Figure 5-4 Comparison of 300 % modulus of SIBS with pro-rads (5 phr, 120 kGy).

<table>
<thead>
<tr>
<th>Pro-rads</th>
<th>Normalized* Tensile strength/(MPa)</th>
<th>Normalized* Elongation at Break/ %</th>
<th>Normalized* 300% Modulus /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>517HP</td>
<td>3.73</td>
<td>281.41</td>
<td>0.75</td>
</tr>
<tr>
<td>519HP</td>
<td>2.09</td>
<td>128.85</td>
<td>1.01</td>
</tr>
<tr>
<td>TAC</td>
<td>1.30</td>
<td>197.44</td>
<td>0.43</td>
</tr>
<tr>
<td>BGDMA</td>
<td>2.82</td>
<td>215.38</td>
<td>0.61</td>
</tr>
<tr>
<td>EGDMA</td>
<td>2.45</td>
<td>247.44</td>
<td>0.62</td>
</tr>
<tr>
<td>TMPTA</td>
<td>2.10</td>
<td>76.28</td>
<td>1.68</td>
</tr>
<tr>
<td>TMPTMA</td>
<td>3.90</td>
<td>269.87</td>
<td>0.76</td>
</tr>
<tr>
<td>High vinyl PB</td>
<td>2.26</td>
<td>282.05</td>
<td>0.40</td>
</tr>
<tr>
<td>PB Diacrylate</td>
<td>2.23</td>
<td>287.82</td>
<td>0.39</td>
</tr>
</tbody>
</table>

*Normalized: divided by weight of pro-rads (MPa/g, %/g)

Normalized values determined by tensile test are listed in Table 5-2. After initial screening, it was found that SIBS with TMPTMA, 517HP and BGDMA had the higher tensile strength than others. In addition, the elongation-at-break of SIBS with these three pro-rads did not decrease substantially. SIBS with TMPTA and 519 HP showed increase in moduli. However, both the elongation-at-break and tensile strength of SIBS with
TMPTA and 519 HP were lower than those with TMPTMA 517HP and BGDMA. SIBS with TAC, high vinyl PB and PB diacrylate did not show any increase in tensile strength and modulus.

In the following screening process, both the pro-rads concentration and e-beam radiation dose were varied to investigate the effects of TMPTMA, 517HP, BGDMA and Tri-SH on tensile properties of the SIBS. Stress-strain curves of the SIBS with 517HP (2 phr, 5 phr) are shown in Figure 5-5. Tensile strength of the SIBS with 2 phr of 517HP increased from 12.5 MPa to 17.5 MPa after irradiated at 120 kGy. In addition, elongation-at-break did not decrease significantly. Even though the tensile strength of SIBS with 5 phr of 517HP increased at radiation doses of 120 kGy and 190 kGy, the elongation-at-break decreased substantially. For SIBS with TMPTMA, similar trend was observed. SIBS with TMPTMA (2 phr) had the highest tensile strength without sacrificing too much of elongation-at-break. Tensile strength of SIBS with 2 phr of BGDMA increased with increasing radiation dose, SIBS with the highest e-beam dose (240 kGy) had the highest tensile strength. For SIBS with 5 phr of BGDMA, the tensile strength increased by 15 %-30 % at radiation doses of 120 kGy and 190 kGy. The tensile strength of SIBS with Tri-SH was even lower than the SIBS without any pro-rads.

Comparison of stress-strain curves of the SIBS with pro-rads are shown in Figure 5-9. The SIBS with higher pro-rads concentration showed higher modulus. This indicated that pro-rads effectively increased the crosslink density of the materials. The tensile strength of SIBS with TMTPMA (2 phr) and an e-beam radiation dose of 120 kGy increased by 44 % compared to the control. Meanwhile, the elongation-at-break did not decrease substantially. The tensile strength of SIBS with BGDMA (2 phr) increased by 30 % and
45% at radiation doses of 190 kGy and 240 kGy, while the elongation-at-break maintained the same value. The tensile strength of SIBS with 2 phr of 517HP and a radiation dose of 120 kGy increased by 45% compared to the tensile strength of SIBS without pro-rads. In addition, the elongation-at-break also increased by 13%. Tri-SH significantly increased the modulus of the SIBS. But it also decreased both tensile strength and elongation-at-break of SIBS.

Comparison of tensile strength and elongation-at-break of the SIBS with pro-rads irradiated under e-beam are shown in Figure 5-10 and Figure 5-11. Pro-rads were able to increase the tensile strength of SIBS at lower radiation doses (60 and 120 kGy). However, at higher e-beam doses, such as 190 kGy and 240 kGy, adding pro-rads could not improve the tensile strength of SIBS. For SIBS with pro-rads, tensile strength decreased at 240 kGy. Elongation-at-break did not change substantially at low radiation doses (<120 kGy) after adding pro-rads. However, at e-beam radiation doses of 190 kGy and 240 kGy, elongation-at-break of SIBS with 517HP and TMPTMA significantly decreased. BGDMA was more efficient at higher dose in terms of increasing tensile strength and maintaining the elongation-at-break.

![Stress-strain curves of SIBS with 2 phr of 517HP.](image)

![Stress-strain curves of SIBS with 5 phr of 517HP.](image)

**Figure 5-5** Stress-strain curves of SIBS with (a) 2 phr and (b) 5 phr of 517HP.
Figure 5-6 Stress-strain curves of SIBS with (a) 2 phr and (b) 5 phr of TMPTMA.

Figure 5-7 Stress-strain curves of SIBS with (a) 2 phr and (b) 5 phr of BGDMA.
Figure 5-8 Stress-strain curves of SIBS with (a) 2 phr and (b) 5 phr of Tri-SH.

Figure 5-9 Comparison of stress-strain curves of SIBS with (a) TMPTMA, (b) BGDMA, (c) 517HP, and (d) Tri-SH.
5.5.2 Effect of pro-rads on dynamic mechanical properties of SIBS

The dynamic mechanical analysis was performed for SIBS with pro-rads (5 phr) irradiated at 120 kGy. The storage modulus ($E'$) of SIBS with pro-rads (5 phr) varied as a function of temperature, as shown in Figure 5-12. In the rubbery plateau, the storage modulus was associated with the crosslink density of the materials. Comparison of
storage modulus in rubbery plateau for the SIBS with 5 phr pro-rads (120 kGy) is shown in Figure 5-12. SIBS with TMPMA showed the highest storage modulus ($E'$) in the rubbery plateau, which was consistent with the results obtained from tensile test. SIBS without e-beam radiation showed the lowest storage modulus ($E'$) in the rubbery plateau. SIBS itself irradiated at 120 kGy was used as a control. It was found that adding pro-rads significantly increased the storage modulus ($E'$) of SIBS in the rubbery plateau.

![Graph of Storage modulus vs. temperature for SIBS with pro-rads (5 phr, 120 kGy).](image)

Figure 5-12 Storage modulus vs. temperature for SIBS with pro-rads (5 phr, 120 kGy).
Figure 5-13 Comparison of storage modulus ($E'$) in rubbery plateau for SIBS with pro-rads (5 phr, 120 kGy).

Figure 5-14 Comparison of crosslink density of SIBS with pro-rads (5 phr, 120 kGy).

The crosslink densities calculated from the $E'$ in rubbery plateau are compared in Figure 5-14. Pro-rads significantly increased the crosslink density of SIBS irradiated
under e-beam. Depending on the pro-rads type, the crosslink density of SIBS ranged from 100 mol/m$^3$ to 600 mol/m$^3$. SIBS with TMPTA (5phr) showed the highest crosslink density, which was approximately six times of the crosslink density of SIBS. High vinyl PB and PB-diacrylate were not as efficient as others.

5.5.3 Effect of pro-rads on gel content of SIBS

Comparison of gel content of SIBS with pro-rads irradiated at an e-beam radiation dose of 120 kGy is shown in Figure 5-15. It was found that the gel content increased with increasing pro-rads concentration. The SIBS with TMTPA had higher gel content than the SIBS with TMPTMA. The gel content of SIBS with 519HP was also higher than SIBS with 519HP. In the presence of pro-rads, the highest gel content obtained was greater than 90% at 120 kGy.

The effects of both pro-rads concentration and radiation dose on gel content of SIBS were also evaluated. The comparison of gel content of SIBS with four types of pro-rads is shown in Figure 5-16. Gel content increased with increasing e-beam radiation dose and concentration of pro-rads. For SIBS with same pro-rad, higher radiation dose produced higher gel content. SIBS with 5phr pro-rads had higher gel content than SIBS with 2phr pro-rads at four e-beam radiation doses. The SIBS film with BGDMA irradiated low radiation dose (60 kGy) dissolved in cyclohexane. At 60 kGy, 517HP, TMPTMA and Tri-SH significantly increased the gel content of SIBS to 40%-80%.
Figure 5-15 Effect of pro-rads on gel content of SIBS (120 kGy).

Figure 5-16 Effect of e-beam radiation dose and pro-rads on gel content of SIBS.

5.5.4 Effect of pro-rads on equilibrium swelling of SIBS

Since the solvent used in equilibrium swelling just selectively swelled mid-block of the SIBS, the volume fraction of mid-block in the swollen gel can be used as a criteria to
compare the crosslink density of the mid-block. The higher volume fraction of polydiene phase in the swollen gel, the tighter network was after e-beam crosslinking. The comparison of effect of pro-rads concentration on equilibrium swelling of SIBS was performed at same radiation dose and four pro-rads content. The results are shown in Figure 5-17. TMPTA and 519HP were the most efficient pro-rads in terms of crosslinking efficiency. TMPTMA and 517HP were less efficient. SIBS with higher concentration of pro-rads had higher volume fraction in the swollen gel after equilibrium swelling.

The effects of both pro-rads concentration and radiation dose on equilibrium swelling of SIBS are shown in Figure 5-18. SIBS with 5 phr pro-rads showed higher volume fraction of polydiene phase in the swollen gel than SIBS with 2 phr pro-rads. Higher e-beam radiation dose significantly increased the volume fraction of polydiene phase in the swollen gel. TMPTA and Tri-SH were the most efficient pro-rads in promoting crosslinking reaction of SIBS. 517HP and TMPTMA also significantly increased the volume fraction polydiene phase in the swollen gel.
Figure 5-17 Effect of pro-rads on equilibrium swelling of SIBS (120 kGy).

Figure 5-18 Effect of radiation dose on equilibrium swelling of SIBS with pro-rads.
5.5.5 Viscosity stability of SIBS with pro-rads

Since melting extrusion was the preferred processing method for SIBS, viscosity stability of SIBS was an important factor to be considered during the screening. SIBS with pro-rads (5 phr) were used to investigate the viscosity stability of the material at 200 °C. The complex viscosity vs. time is shown in Figure 5-19. The viscosity of SIBS with the acrylate type pro-rads, such as 519HP and TMPTA, increased substantially within 30 min at 200 °C, which indicated the possibility that the materials was gelled in the extruder if processed at or above 200 °C. The viscosity of SIBS with the methacrylate type pro-rads such as TMPTMA, 517, and BGDMA, was relatively stable at 200 °C within 30 min.

![Figure 5-19: Viscosity vs. time for SIBS with pro-rads (5 phr) kept at 200 °C for 30 min.](image)

5.5.6 Investigation of solubility of pro-rads in two phases of SIBS

Solubility of pro-rads in two phases of the SIBS block copolymer was investigated by selectively swelling films with pro-rads (5 phr) in trimethylpentane and THFA.
Trimethylpentane was able to selectively swell the mid-block of the SIBS, while THFA was able to swell the polystyrene phase without significantly swell the mid-block.\textsuperscript{115,247} Pro-rads with good solubility in the mid-block would be dissolved in the trimethylpentane solution after films were swollen for 48 h. Pro-rads that soluble in polystyrene phase was in THFA solution after swelling for 48h. \textsuperscript{1}H NMR was used to analyze the solution in which the SIBS swelled for 48 h. Since the pro-rads which could increase the tensile strength of SIBS contained either methacrylate or acrylate group, the protons attached to the double bond were chosen to track the pro-rads. The \textsuperscript{1}H NMR spectrum of each pro-rad was obtained first as a reference. Then the solution after swelling was analyzed. \textsuperscript{1}H NMR of spectrum of 517HP is shown in Figure 5-20. The resonances located at δ 6.10 and δ 5.58 were attributed to the protons on the C=\text{C}. These two resonances were also shown in the \textsuperscript{1}H NMR spectra of trimethylpentane and THFA solution after swelling, as shown in Figure 5-21 and Figure 5-22. This indicated that 517HP was soluble in both polydiene and polystyrene phases. Other pro-rads, such as BGDMA and TMPTMA were also studied following the same procedure. It was found that they were soluble in both phases of SIBS.
Figure 5-20 $^1$H NMR spectrum of 517HP

Figure 5-21 $^1$H NMR spectrum of 2,2,4-trimethylpentane solution after swelling SIBS with 517HP (5 phr)
5.6 Discussion

The purpose of adding pro-rads was to improve the crosslink efficiency and increase the tensile strength of the SIBS. The pro-rads, are a class of materials that are capable of generating more reactive species, such as free radicals or reactive ions, than polymer itself.\(^{3}\) Using suitable pro-rads can improve the properties of materials at a reduced e-beam radiation dose.\(^{2}\) The change of tensile property of material is an important criterion in evaluating the effect of pro-rads on e-beam irradiated SIBS. The effects of pro-rads on tensile properties of e-beam irradiated SIBS have not been studied thusfar.

According to the tensile test, it was found that the modulus of the SIBS increased with increasing pro-rads concentration and e-beam radiation dose. This indicated that e-beam radiation initiated crosslinking reaction of SIBS was promoted by adding pro-rads. The 300 % modulus increased as the crosslink density of the material increased.\(^{248}\) The high moduli of SIBS films with TMPTA and 519HP were due to the high reactivity of

Figure 5-22 \(^1\text{H}\) NMR spectrum of THFA solution after swelling SIBS with 517HP (5 phr)
acrylate group, which significantly increased the crosslink density of the materials after e-beam exposure. This phenomenon was further observed by comparing the crosslink density of materials. Even though the TMPTA and 519HP were very efficient crosslinkers, a high crosslinking efficiency did not always translate to an increase in tensile strength.\textsuperscript{126} The tensile strength of SIBS with TMPTA and 519HP were not the highest. This was due to the reduced extensibility of the materials after being highly crosslinked.

SIBS with TMPTMA and 517HP had the highest tensile strength. These two pro-rads were both tri-functional methacrylates. The reason was attributed to the medium reactivity of the methacrylate group and a higher glass transition temperature of methacrylate compared to the acrylate group. In other words, SIBS with TMPTMA and 517HP had an optimum crosslink density at a radiation dose of 120 kGy. BGDMA was not as efficient as 517HP and TMPTMA in terms of increasing the tensile strength of the SIBS at a low radiation dose. This was because BGDMA was di-functional pro-rads. Tri-SH enhanced the modulus of SIBS, but it sacrificed both the tensile strength and the elongation-at-break substantially. This was due to the high reactivity of thiol-ene reaction,\textsuperscript{137, 236, 249} which over increased the crosslink density of the SIBS at low pro-rad concentration and e-beam radiation dose.

At lower e-beam doses (60 and 120 kGy), adding pro-rads was a very effective way to improve the tensile strength of SIBS without significantly decreasing the elongation-at-break. This is because at low e-beam dose, the concentration of reactive species formed by SIBS was relatively low. Pro-rads effectively generated more reactive species and promoted the crosslinking reaction. However, at higher radiation dose, adding pro-
rads, especially the tri-functional pro-rads, such as TMPTMA and 517 HP, not only decreased the tensile strength of SIBS, but also significantly decreased the elongation-at-break. Because at higher e-beam radiation doses, the SIBS polymer itself already generated enough reactive species to obtain a high crosslink density, adding pro-rads, continued to promote the crosslinking reaction and increase the crosslink density to some extent that the extensibility of materials was significantly decreased. The materials became much stiffer. Therefore, the tensile strength and elongation-at-break decreased.

Tensile strength and elongation-at-break were not simply proportional or inversely proportional to e-beam radiation dose and pro-rads concentrations. It was found that the relationship between the tensile strength of SIBS and the e-beam radiation dose was complicated. Adding pro-rads and increasing e-beam exposure dose were two effective ways to increase crosslink efficiency and the overall crosslink density of the SIBS. However, the high crosslink density did not necessarily result in a high tensile strength.\textsuperscript{3} The optimum crosslink density and network homogeneity were two key factors to achieve a high tensile strength of SIBS without significantly sacrificing the elongation-at-break.\textsuperscript{125,127} Adjusting the pro-rads concentration and e-beam radiation dose according to a specific material are two approaches to successfully improve the tensile strength of SIBS.

Investigation of crosslink density of SIBS with different pro-rads was an effective way to screen pro-rads. At a given radiation dose, it was found that tri-functional acrylate type pro-rads, such as TMPTA and 519HP were more efficient in promoting the e-beam radiation induced crosslinking reaction than others. SIBS with TMPTMA showed lower $E'$, which means lower crosslink density. It was attributed to the lower reactivity of the
methacrylate group compared to acrylate group. A schematic model of idealized network structure of e-beam crosslinked SIBS with pro-rads is shown in Scheme 5-1. There were two types of crosslinks in the system. One was the crosslinks formed by reactive species generated directly from polymer chains; the other was the crosslinks formed by pro-rads. The pro-rads might also undergo homopolymerization and form some small clusters in the system. These clusters acted as multifunctional crosslinkers and connected the polymer chains. Since the crosslink density was calculated based on the storage modulus in rubbery plateau, it was the overall crosslink density of the copolymer with pro-rads. So the homopolymerization of low molecular weight pro-rads cluster was also a reason for the high crosslink density of the SIBS with acrylate type pro-rads.

Scheme 5-1 Schematic representation of idealized network structure of e-beam crosslinked SIBS with pro-rads.

SIBS with pro-rad showed a higher gel content than SIBS itself at a given radiation dose, which indicated that pro-rads promoted the crosslinking reaction during e-beam exposure. SIBS with methacrylate functionalized pro-rads showed lower gel content than those with acrylate type pro-rads. Di-functional pro-rads such as BGDMA and EGDMA were less efficient than tri-functional pro-rads in facilitating the formation of...
insoluble network. The gel content increased as the radiation dose increased. It was also found that pro-rads played a more important role at lower radiation dose than at higher dose in terms of increasing the gel content of SIBS. The concentration of reactive species at high e-beam dose was already high enough to initiate the crosslinking reaction of SIBS. In this case, adding pro-rads was not helpful to obtain a high gel content.

According to the equilibrium swelling results, the SIBS with TMPTA, 519HP and Tri-SH were found to be able to hold a much tighter network than others after swelling. This indicated the higher crosslink density of SIBS was obtained in the presence of these pro-rads. The reason was attributed to the high reactivity of acrylate and thiol groups.

5.7 Conclusions

The effect of pro-rads on e-beam radiation crosslinking SIBS was investigated as functions of pro-rads type, concentration, and radiation dose. It was found that adding pro-rads was an efficient way to increase the tensile strength and crosslink density of SIBS. This was because pro-rads promoted the crosslinking reaction of SIBS under e-beam radiation. It was observed that pro-rads had a larger effect at low e-beam dose (< 190 kGy) than high dose (>190 kGy). TMPTA, 519 HP and Tri-SH were the most efficient pro-rads in terms of promoting crosslink reactions of SIBS. However, the melting viscosity of SIBS with acrylate type of pro-rad was not stable. Methacrylate type pro-rads, such as TMPTMA and 517HP were the most efficient pro-rads in increasing tensile strength of SIBS. In addition, the viscosity of SIBS with methacrylate type pro-rads was relatively stable at 200 °C, which made them suitable for melting extrusion process. Pro-rads such as TMPTMA, BGDMA and 517HP were found to be soluble in both polydiene and polystyrene phases.
CHAPTER VI
SYNTHESIS AND CHARACTERIZATION OF UV-CURABLE
MALEIMIDE-TERMINATED IMIDE OLIGOMERS

6.1 Abstract

Maleimide terminated imide oligomers, also called bismaleimide (BMI) with three different molecular weights were synthesized and characterized by nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and size exclusion chromatography (SEC). The maleimide polyimide oligomers were formulated with two reactive diluents, N, N-dimethylacrylamide (DMAA) or N-vinylpyrrolidone (NVP), and were photopolymerized with and without a photoinitiator (PI). The reaction rate and conversion were improved by adding a photoinitiator. The kinetics of film formation was investigated using real-time FTIR and photo-differential scanning calorimetry (DSC). Thermal and viscoelastic properties of UV-cured films were studied by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and DSC. Maleimide terminated imide oligomer with low molecular weight (~ 2k g/mol) had the highest reaction rate and final conversion. More than 90 % of conversion was achieved after being exposed to UV light for 60 s. A wide glass transition for all the UV-cured films was observed indicating a heterogeneous system. When no photoinitiator was used, the imide/NVP formulations polymerized and the DMAA/imide formulations did not. It was surmised that the NVP reacted via a donor/acceptor complex, and the DMAA
could not due to electron-poor double bonds.

6.2 Introduction

Polyimides were first developed in 1955 as thermoplastics. The rigid aromatic ring provides a high glass transition temperature and good mechanical strength. Polyimides have been widely used in electric and space engineering due to their excellent thermal oxidative stability, chemical resistance, and low dielectric constant.

Most aromatic polyimides in fully imidized state are insoluble and infusible. Thus, polyimides are typically processed in the form of poly (amic acid) (PAA) precursors. After casting, the films or coatings will be subsequently heated up to fully imidized state at evaluated temperature (~300 °C). High processing temperature limits its application in heat sensitive substrates. Another problem with this process is that the PAA solution is sensitive to humidity, which may result in the chain scission during the storage period. In addition, the water released from the imidization process may cause voids in the products, especially using relatively high molecular weight polymer to produce thick films or composites. Even though the thermoplastic polyimide with good solubility in common solvents had been developed to solve these problems, the drawback of the soluble polyimide is the poor chemical resistance.

To ameliorate some of the processing issues with thermoplastic polyimide, thermosetting polyimide was developed by NASA in early 1960s. Thermosetting polyimides are usually low molecular imide oligomers with reactive functional groups on the backbone or side chains that crosslink upon heating. The reactive functional groups, such as nadimide, maleimide and acetylene, can undergo homo or copolymerization upon
heating.\textsuperscript{161} However, the high crosslinking temperature is still a major concern for their applications in heat sensitive substrates. Lower the curing temperature of thermosetting polyimide is one of the requirements for expanding the applications of polyimides.

Photopolymerization of maleimide-terminated oligomers was studied by several research groups.\textsuperscript{46,49-53} The maleimide group exhibits a strong UV absorbance in the 300 nm region due to the C=C double bond conjugated with the carbonyl group.\textsuperscript{48} It is capable of undergoing homopolymerization or copolymerization without any additional photoinitiator.\textsuperscript{34,171} However, most of the research focused on the mechanism studies of photopolymerization with model compounds.

The overall goal of this research is to develop a UV-curable imide oligomer to improve the processability of polyimide and expand the application of polyimides to UV-curable coating area. Maleimide terminated imide oligomers, also called bismaleimide (BMI) were synthesized and characterized by SEC, NMR, and FTIR. Imide oligomers were formulated with reactive diluents, \textit{N}, \textit{N}-dimethylacrylamide (DMAA) and \textit{N}-vinylpyrrolidone (NVP). The glass transition temperature ($T_g$) and thermal stability of UV-cured films were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Structure of imide oligomers were characterized by wide angle X-ray diffraction (XRD). Real-time FTIR and photo-DSC were used to study the UV-curing kinetics. Viscoelastic properties were investigated by dynamic mechanical analysis (DMA). Solution and films after solvent extraction in chloroform were studied by \textsuperscript{1}H NMR and solid state \textsuperscript{13}C NMR to elucidate the crosslinking mechanism and structure.
6.3 Experimental

6.3.1 Materials

*N*-Methyl-2-pyrrolidinone (NMP) (anhydrous, 99.5 %, dried over molecular sieve) dimethylacrylamide (DMAA) (99 %), *N*-vinylpyrrolidone (NVP) (> 99 %), *m*-xylene (anhydrous, >99 %) and methanol (ACS reagent, 99.8 %) were purchased from Sigma-Aldrich. 4, 4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) (purity > 99 %) was purchased from Akron Polymer Systems, Inc, and recrystallized from acetic anhydride and dried under vacuum at 160 °C for 24 h before use. Maleic anhydride (>95 %) was purchased from Sigma-Aldrich and recrystallized from toluene before use. 4, 4′-(1,3-phenylenediisopropylidene) bisaniline-m was obtained from Mitsui Chemicals Inc. and vacuum dried before use. Irgacure 184 was obtained from Ciba. All of the other reagents and solvents are commercially available ACS reagents and were used without further purification.

6.3.2 Instrumentation and characterization

Size exclusion chromatography (SEC) with tetrahydrofuran as the mobile phase was used to determine polymer molecular weight and polydispersity index (PDI), using a Waters 1515 isocratic pump, three Waters styragel columns and a Waters 2414 refractive index detector. The columns were calibrated with narrow-distribution polystyrene standards. FTIR spectra were recorded on a Thermo Scientific Nicolet 380 Fourier transform infrared spectrometer by casting thin films on KBr crystals from chloroform solution. Data spacing is 4 cm⁻¹, and the resolution is 32. UV-vis spectra were recorded on a Perkin-Elmer Model LS-5 spectrometer. A dilute solution of sample in acetonitrile
was put in a quartz cell for test. $^1$H NMR and $^{13}$C NMR were recorded on Mercury-300 spectrometer (Varian) in chloroform-$d$.

UV radiation was performed on a bench top conveyor LC-6 with an ultraviolet lamp system (Fusion UV systems, Inc). The Fusion lamp system uses microwave radiation to energize the lamp. Intensity was measured by a UV POWER PUCK® high energy UV integrating radiometer. Thermal stability was studied on a TGA 2950, (TA Instruments, Inc). Samples were put on a platinum pan and heated up with a heating rating of 20 °C/min. Nitrogen was used as the furnace purging gas. The decomposition temperature was recorded and the first derivative was made. The glass transition temperature ($T_g$) was measured by a DSC Q-200 (TA Instruments, Inc). For the glass transition temperature test, 3-5 mg samples that were sealed in aluminum hermetic DSC pans and heated from room temperature at a heating rate of 10 °C/min. The data were chosen by a second scan. The first scan was run to remove the thermal history. The glass transition temperature ($T_g$) was taken as the midpoint of the transition region using TA Universal Analysis. DMA test was performed on DMA Q-80 (TA Instruments, Inc). Films were tested under the following conditions: tension mode, a heating rate of 3 °C/min, and a frequency of 1 Hz. The maximum of the tan delta was used to determine the $T_g$, while the crosslink density was determined by utilizing the storage modulus ($E'$) in the rubbery plateau. The crosslink density of the film has been defined as the moles of elastically effective network chains per cubic meter of film. The storage modulus ($E'$) value in the rubbery plateau is an indication of crosslink density. The crosslink density was calculated by using the following equation derived from the theory of rubber elasticity.
\[ v_e = \frac{E'}{3RT} \]  \hspace{1cm} (6-1)

where \( v_e \) is the crosslink density, \( R \) is the gas constant, \( T \) is the absolute temperature and \( E' \) is the value of storage modulus in the rubbery plateau.

For gel content measurement, the films were subjected to soxhlet extraction in chloroform for 24 h, followed by drying under vacuum at 80 °C for 5 h. Gel content of UV-cured film was determined gravimetrically by using an analytical balance. XRD was performed on Bruker AXS D8 equipped with a copper target tube and a two-dimensional detector. The X-ray generator was operated at 40 kV and 40 mA using monochromatized CuKα radiation with a wavelength of 1.5418 Å.

The UV-curing process was monitored by real-time FTIR spectrometry and photo-DSC. The instrument setup for the real-time FTIR is shown in Scheme 6-1. The formulation was sandwiched between two KBr crystals, IR illumination was at normal incidence to the sample, and UV radiation was applied at an angle of 30°-45° to the normal. During the UV radiation, the spectrum was acquired at each 1.03 s sampling interval. The transmission mode spectral series collection coupled with data processing using Thermo Scientific software named OMNIC generated the conversion vs. time profiles. The continuous change of a specific absorbance reflected the reaction extent. And the conversion of each monomer can be calculated by equation (6-2).

\[ Conversion\% = \frac{A_0 - A_t}{A_0} \times 100 \]  \hspace{1cm} (6-2)
where, $A_0$ is the IR absorbance before UV radiation, $A_t$ is the IR absorbance after UV radiation for $t$ seconds.

Scheme 6-1 Real-time FTIR spectroscopy experimental setup.

For photo-DSC measurement, samples were analyzed on a DSC Q-2000 (TA Instrument) equipped with a photo-calorimetric accessory (PCA) and Novacure N2001-A1 as a UV-light source. The wavelength ranged from 250 to 600 nm and the initiation light source was a 100 W high-pressure mercury short-arc lamp with an intensity of 50 mW · cm$^{-2}$. The samples were placed in uncovered aluminum DSC pans, and polymerization reactions were run isothermally at 40 °C. The total heat released during the polymerization was recorded. The photo DSC setup is shown in Scheme 6-2.

Scheme 6-2 Instrument set-up of Photo-DSC.

6.3.3 Synthesis of maleimide terminated imide oligomers

A typical polymerization procedure for maleimide terminated imide oligomer with an average molecular weight of 1300 g/mol is as followed: A two-necked round bottom
flask with a magnetic stirrer and nitrogen inlet was flame dried under a steady flow of nitrogen. Anhydrous NMP (20 g) and bisaniline (3.44 g, 0.01 mol) were charged to the flask. The mixture was stirred under nitrogen flow until completely dissolving the bisaniline. Then, 6FDA (2.22 g, 0.005 mol) was gradually added into the diamine solution. The mixture was stirred under nitrogen atmosphere while the anhydride was gradually dissolved. Maleic anhydride (0.98 g, 0.01 mol) was added one hour later. Once the reaction solution became homogeneous, the reaction continued at room temperature and nitrogen atmosphere for 20 h. The clear, yellow poly (amic acid) solution was obtained. Anhydrous m-xylene (15 mL) was added to the solution, and a Dean-Stark trap was filled with m-xylene. Hydroquinone (0.1 wt %) was also added to the solution as an inhibitor. The solution was heated to 165 °C, and the reaction was continued for additional 6 h. After that, the solution was cooled to room temperature, and the imide oligomers were precipitated in 800 mL of methanol under a high speed mechanical stir. After the filtration, the product was washed with methanol and dried in the vacuum oven for 48 h at 100 °C. Average yield is approximately 78 wt%. Synthetic route is shown in Scheme 6-3.

Table 6-1 Materials used in synthesis of maleimide-terminated imide oligomers.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>6FDA</th>
<th>Bisaniline</th>
<th>NMP</th>
<th>Maleic anhydride</th>
<th>Xylene</th>
<th>Hydroquinone</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6FDA-Bismaniline)-BMI (I)</td>
<td>2.22</td>
<td>5.0*10^{-3}</td>
<td>3.44</td>
<td>1.0*10^{-2}</td>
<td>20.0</td>
<td>0.98</td>
<td>1.0*10^{-2}</td>
</tr>
<tr>
<td>(6FDA-Bismaniline)-BMI (II)</td>
<td>8.88</td>
<td>2.0*10^{-2}</td>
<td>9.30</td>
<td>2.7*10^{-2}</td>
<td>54.5</td>
<td>1.37</td>
<td>1.4*10^{-2}</td>
</tr>
<tr>
<td>(6FDA-Bismaniline)-BMI (III)</td>
<td>2.22</td>
<td>5.0*10^{-3}</td>
<td>1.72</td>
<td>5.0*10^{-3}</td>
<td>25.3</td>
<td>0.04</td>
<td>4.4*10^{-4}</td>
</tr>
</tbody>
</table>
Glass panels were used as the substrate for film preparation. The substrates were cleaned with acetone and dried before casting. Due to the solubility limit of imide oligomer in reactive diluents, an imide oligomer concentration of 50 wt% was chosen. The formulations were made by thoroughly mixing 2 g of synthesized oligomer with 2 g of reactive diluents, NVP and DMAA, respectively, in glass vials at room temperature until a transparent solution was obtained. The chemical structures of the reactive diluents used in formulation are shown in Scheme 6-4. For imide oligomer and DMAA formulation, a free radical photoinitiator (3 wt %) was added. The films were cast on glass substrates using a drawdown bar with a thickness of 200 μm (8 mil). The films were UV exposed twice at belt speed of 5 feet/min, which afforded a light intensity of 1300 Mw/cm².
6.4 Results

The objective of this study was to develop imide oligomers for UV-curing applications. Oligomers with three different molecular weights were synthesized. The molecular weight was designed from 1300 g/mol to 9200 g/mol. The bisaniline and 6FDA were chosen as monomers because of the increase in solubility for prospective reactive diluents and thermal stability of synthesized oligomers. The reactive diluents, DMAc and NMP, were selected on the basis of matching solubility parameters with the polyimide oligomer. The effects of molecular weight of the imide oligomers and reactive diluents on the properties of UV-cured films were investigated. For UV-curing formulation, DMAA and NVP were chosen as reactive diluents. The reactive diluents were selected based on the reactivity with maleimide group and the solubility parameter. According to the solubility parameter calculation, the imide oligomers have good solubility in NVP and DMAA. Characterization was conducted to investigate the UV-curing kinetics of imide oligomers by real-time FTIR and photo-DSC.

6.4.1 Synthesis of imide oligomers

The maleimide-terminated imide oligomers with controlled molecular weight were synthesized from 6FDA and bisaniline-m through high temperature solution imidization.

Scheme 6-4 Chemical structures of reactive diluents.

\[
\begin{align*}
N,N\text{-dimethylacrylamide (DMAA)} & & N\text{-vinyl-2-pyrrolidone (NVP)} \\
\end{align*}
\]
route. Molecular weight was controlled by adjusting the ratio of the two monomers. Diamine was present in slight excess. The polymerization then proceeded to a point at which the dianhydride was completely used up and all the chain ends possess the amine group. Maleic anhydride was used as end-capper to form maleimide group terminated imide oligomer. In order to properly control the molecular weight, precisely adjusting the stoichiometric imbalance of the difunctional monomer was quite important. The stoichiometric ratio of monomers was varied according to the Carothers Equation in order to achieve the desired molecular weight.\(^{39}\) The number-average degree of polymerization \(\bar{X}_n\) is the total number of difunctional monomer initially present divided by the total number of polymer molecules.

\[
\bar{X}_n = \frac{N_A(1+1/r)/2}{[N_A(1-p) + N_B(1-rp)]/2} = \frac{1+r}{1+r-2rp}
\]  

(6-3)

where \(N_A\) and \(N_B\) are numbers of A and B functional groups; \(r\) is called the stoichiometric ratio, the excess reactant is conventionally the denominator so that \(r<1\). \(p\) is the extent of reaction, which is defined as the fraction of the limiting groups that have reacted at a particular time. The effect of the excess reactant is to reduce the degree of polymerization for a given value of \(p\). In the limit of complete conversion of the limiting reagent monomer, \(p \rightarrow 1\), Equation (6-3) becomes

\[
\bar{X}_n = \frac{1+r}{1-r}
\]  

(6-4)

The theoretical molecular weight was calculated using Equation (6-4). The number average molecular weight (\(\bar{M}_n\)), weight-average molecular weights (\(\bar{M}_w\)), and the
polydispersity index (PDI) of imide oligomers were characterized by SEC, as shown in Table 6-2.

Table 6-2 Molecular weight of maleimide terminated imide oligomers

<table>
<thead>
<tr>
<th></th>
<th>Theoretic MW</th>
<th>n</th>
<th>$\overline{M}_n$</th>
<th>$\overline{M}_w$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6FDA-Bisaniline)-BMI (I)</td>
<td>1300</td>
<td>1</td>
<td>2667</td>
<td>5262</td>
<td>1.97</td>
</tr>
<tr>
<td>(6FDA-Bisaniline)-BMI (II)</td>
<td>5200</td>
<td>6</td>
<td>5467</td>
<td>10944</td>
<td>2.01</td>
</tr>
<tr>
<td>(6FDA-Bisaniline)-BMI (III)</td>
<td>9200</td>
<td>11</td>
<td>10056</td>
<td>23496</td>
<td>2.34</td>
</tr>
</tbody>
</table>

Figure 6-1 Size exclusion chromatography of maleimide terminated imide oligomers.

FTIR spectra were obtained for both starting materials and synthesized imide oligomers. A comparison of these spectra is shown in Figure 6-2. Two distinct absorptions at around 3300-3500 cm$^{-1}$ were attributed to the amine group in bisaniline. For 6FDA and maleic anhydride, two absorbance bands at around 1830 cm$^{-1}$ and 1770 cm$^{-1}$ were characteristic absorptions of anhydride. The absorptions appearing at approximately 1780 cm$^{-1}$, 1720 cm$^{-1}$, 1375 cm$^{-1}$ and 720 cm$^{-1}$ confirmed the presence of imide groups. Two absorptions appearing at approximately 1780 cm$^{-1}$ and 1720 cm$^{-1}$
were attributed to C=O asymmetrical and symmetrical stretching. One distinct absorbance occurring at 1375 cm\(^{-1}\) was attributed to C-N stretching vibration. Absorption at around 720 cm\(^{-1}\) was due to C=O bending. In addition, the lack of absorbance near 3300 cm\(^{-1}\) indicated that a high degree of imidization was obtained.

Figure 6-2 IR spectra of starting materials and synthesized imide oligomer.

Figure 6-3 shows a representative \(^1\)H NMR spectrum of a maleimide terminated (6FDA-Bisaniline)-BMI imide oligomers (I) with the corresponding resonance assignments. The proton resonance located at \(\delta\) 6.78 ppm was associated with the protons on the maleimide group. Resonance located at \(\delta\) 7.1-8.2 ppm was due to aromatic protons, and the resonance located at \(\delta\) 1.7 ppm was due to the protons on methyl groups in bisaniline. \(^13\)C NMR spectrum of a maleimide terminated (6FDA-Bisaniline)-BMI imide oligmers (I) is shown in Figure 6-3 (b). The spectral region exhibited resonance at \(\delta\) 135.8 ppm, which was attributed to the vinyl carbons on maleimide groups. The carbon
resonances located at δ 30.9 ppm and δ 42.7 ppm were due to the methyl carbons and quaternary carbons in bisaniline. The carbonyl group appeared at δ 162.6 ppm and δ 167.1 ppm.

Figure 6-3 (a) $^1$H NMR and (b) $^{13}$C NMR spectra of (6FDA-Bisaniline)-BMI (I)

6.4.2 Solubility behavior

The predication of the solubility parameter using the group contribution method is based on the following equation:
\[ \delta = \left( \frac{\sum E_i}{\sum V_i} \right)^{1/2} \] (6-5)

where \( E_i \) is the additive atomic and group contribution of the repeating unit of cohesive energy and \( V_i \) is the additive atomic and group contribution of the repeating unit of molar volume. For materials of lower molecular weight, cohesive energy was considered as additive property.\textsuperscript{253-255} The values of \( E_i \) and \( V_i \) obtained from the Polymer Handbook\textsuperscript{256} are shown in Table 6-3 and the theoretical solubility parameter was calculated based on equation (6-5). The chemical structure of maleimide terminated imide oligomer is shown in Scheme 6-5. The calculated solubility parameter of the imide oligomer was 24.3 MPa\textsuperscript{1/2}, while the solubility parameters of solvent tested are listed in Table 6-4. The solubility parameter of imide oligomer was close to the solvents tested. The chemical structures of the reactive diluents used in the formulation were similar to the DMAc and NMP. Thus, the solubility parameter of reactive dilutes were close to the imide oligomer synthesized.

![Scheme 6-5 Chemical structure of maleimide terminated imide oligomers.](image)

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Table 6-3 Solubility parameter calculated by group contribution.

<table>
<thead>
<tr>
<th>Group</th>
<th>$E_i$ (J/mol)</th>
<th>$V_i$ (cm$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_3$</td>
<td>4710</td>
<td>33.5</td>
</tr>
<tr>
<td>Phenylene</td>
<td>31940</td>
<td>52.4</td>
</tr>
<tr>
<td></td>
<td>-C-</td>
<td>1470</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>4270</td>
<td>57.5</td>
</tr>
<tr>
<td>=CH-</td>
<td>4310</td>
<td>13.5</td>
</tr>
<tr>
<td>Ring closure 5 atom</td>
<td>1050</td>
<td>16</td>
</tr>
<tr>
<td>Phenyl(trisubstituted)</td>
<td>31940</td>
<td>33.4</td>
</tr>
<tr>
<td>C=O</td>
<td>17370</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>4190</td>
<td>-9.0</td>
</tr>
<tr>
<td>$\sum$</td>
<td>$\sum E_i = 477630$</td>
<td>$\sum V_i = 809.6$</td>
</tr>
</tbody>
</table>

$\delta$ (MPa$^{1/2}$) $\delta = \left( \frac{\sum E_i}{\sum V_i} \right)^{1/2} = 24.3$

Table 6-4 Solubility of (6FDA-Bisaniline)-BMI imide oligomer in common solvents.

<table>
<thead>
<tr>
<th>Solubility parameter/MPa$^{1/2}$</th>
<th>CHCl$_3$</th>
<th>CH$_2$Cl</th>
<th>DMAc</th>
<th>Acetone</th>
<th>DMF</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6FDA-Bisaniline)-BMI (I)</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>(6FDA-Bisaniline)-BMI (II)</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>(6FDA-Bisaniline)-BMI (III)</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Note: ++ means fully soluble at room temperature.

6.4.3 UV absorbance of imide oligomers

For UV-curing system, UV absorbance of photoinitiator is an important factor for the polymerization. The absorbance wavelength must also match the emitting wavelength of the source. The maleimide terminated imide oligomer exhibits a UV absorbance in the
300 nm region as shown in Figure 6-4. For imide oligomer with $M_n \sim 10k$, a weak absorbance is observed, which is due to the lower concentration of maleimide groups in the system.

![UV absorption spectra of maleimide terminated imide oligomers](image)

Figure 6-4 UV absorption spectra of maleimide terminated imide oligomers.

6.4.4 Photo-DSC

Photo-DSC was used to investigate the reactions of imide oligomers with reactive diluents. In Figure 6-5, maleimide terminated imide oligomer (I) and NVP without photoinitiator exhibited an exothermic peak upon UV exposure. After adding photoinitiator, (6FDA-Bisaniline)-BMI (I)/NVP formulation showed increased reaction rate. Homopolymerization of NVP with free radical photoinitiator was observed. Influence of the molecular weight of imide oligomers on photopolymerization (6FDA-Bisaniline)-BMI/NVP formulations are shown in Figure 6-6. Oligomers with lower molecular weight showed a higher reaction rate and larger amount of heat released during polymerization. Only the maleimide imide oligomer with DMAA did not show any
exothermic peak upon UV exposure. Exothermic peak was observed after adding photoinitiator to the (6FDA-Bisaniline)-BMI (I)/DMAA formulation. It was attributed to the free radical homopolymerization of the DMAA. This broad exothermic was attributed to the photopolymerization of the maleimide group with DMAA as well as homopolymerization of the maleimide-terminated imide oligomer. The heat of polymerization and the maximum reaction time as determined by photo-DSC are listed in Table 6-5. By adding photoinitiator, the overall conversion increased by 6-13 % for (6FDA-Bisaniline)-BMI/NVP formulations. Meanwhile, the time to reach the maximum reaction rate (t_{max}) also increased for (6FDA-Bisaniline)-BMI/NVP formulation after the photoinitiator was added.

![Photo-DSC graph](image)

Figure 6-5 Photo-DSC of maleimide terminated imide oligomer with reactive diluents.
Figure 6-6 Photo-DSC of maleimide terminated imide oligomers with NVP.

Table 6-5 Heat of polymerization and maximum reaction time determined by photo-DSC.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>ΔH/J/g</th>
<th>$t_{\text{max}}^{a}$/s</th>
<th>Conversion/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI(I)/NVP</td>
<td>338.1 ± 5.3</td>
<td>18.0 ± 2.2</td>
<td>80.5 ± 0.7</td>
</tr>
<tr>
<td>BMI(II)/NVP</td>
<td>308.6 ± 7.4</td>
<td>25.2 ± 5.6</td>
<td>78.2 ± 3.3</td>
</tr>
<tr>
<td>BMI(III)/NVP</td>
<td>258.4 ± 11.8</td>
<td>28.8 ± 6.0</td>
<td>66.9 ± 2.5</td>
</tr>
<tr>
<td>BMI(I)/NVP+PI</td>
<td>373.2 ± 13.5</td>
<td>9.5 ± 1.5</td>
<td>88.9 ± 1.6</td>
</tr>
<tr>
<td>BMI(II)/NVP+PI</td>
<td>328.3 ± 9.4</td>
<td>17.3 ± 4.4</td>
<td>83.2 ± 2.3</td>
</tr>
<tr>
<td>BMI(III)/NVP+PI</td>
<td>293.0 ± 4.5</td>
<td>19.6 ± 4.9</td>
<td>75.8 ± 2.1</td>
</tr>
<tr>
<td>BMI(I)/DMAA</td>
<td>458.6 ± 15.0</td>
<td>14.4 ± 0.5</td>
<td>98.5 ± 0.7</td>
</tr>
<tr>
<td>BMI(II)/DMAA</td>
<td>427.6 ± 9.2</td>
<td>15.2 ± 0.9</td>
<td>97.1 ± 1.2</td>
</tr>
<tr>
<td>BMI(III)/DMAA</td>
<td>403.6 ± 22.4</td>
<td>17.4 ± 1.3</td>
<td>93.4 ± 2.0</td>
</tr>
<tr>
<td>DMAA</td>
<td>458.6 ± 15.2</td>
<td>3.0 ± 0.5</td>
<td>98.8 ± 1.9</td>
</tr>
<tr>
<td>NVP</td>
<td>224.4 ± 10.5</td>
<td>17.4 ± 2.2</td>
<td>59.4 ± 0.6</td>
</tr>
</tbody>
</table>

$a$: time to maximum rate of cure
6.4.5 Real-time FTIR spectroscopy

Real-time FTIR spectroscopy is one of the most efficient ways to study the photopolymerization kinetics of monomers or oligomers through monitoring the change of their characteristic absorbance upon heating or UV radiation.\textsuperscript{39-40, 166} Compared to photo-DSC, which records the overall heat flux of the formulation,\textsuperscript{20, 257} real-time FTIR has the capability to obtain kinetics for each reactive group in the formulation. A representative real-time FTIR spectrum of photoinitiator free maleimide oligomers (II) and NVP formulation is shown in Figure 6-7. Without any additional photoinitiator a continuous decreasing of the double bond absorbance was observed.

![Real-time FTIR spectrum](image)

Figure 6-7 Representative real-time FTIR spectrum for the imide oligomer (6FDA-Bisaniline)-BMI (II)/NVP formulation without photoinitiator (absorbance @ 1629 cm\textsuperscript{-1}).
Figure 6-8 Conversion vs. time profiles for (a) Maleimide and (b) NVP in the (6FDA-Bisaniline)-BMI/NVP formulations.

Figure 6-9 Conversion vs. time profiles for (a) Maleimide and (b) DMAA in the (6FDA-Bisaniline)-BMI/DMAA formulations.

Table 6-6 Reaction kinetics data derived from the real-time FTIR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion of BMI (%)</th>
<th>Conversion of reactive diluents (%)</th>
<th>Maximum reaction rate of BMI/s^{-1}</th>
<th>Maximum reaction rate of reactive diluents/s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI(I)/NVP</td>
<td>91.1 ± 1.1</td>
<td>80.3 ± 0.7</td>
<td>4.7 ± 0.1</td>
<td>4.9 ± 0.4</td>
</tr>
<tr>
<td>BMI(II)/NVP</td>
<td>79.7 ± 2.3</td>
<td>60.8 ± 1.5</td>
<td>4.0 ± 0.2</td>
<td>3.6 ± 0.2</td>
</tr>
<tr>
<td>BMI(III)/NVP</td>
<td>58.6 ± 0.6</td>
<td>47.9 ± 0.9</td>
<td>3.1 ± 0.1</td>
<td>2.9 ± 0.1</td>
</tr>
<tr>
<td>BMI(I)/NVP+PI</td>
<td>94.1 ± 0.3</td>
<td>84.3 ± 1.3</td>
<td>4.9 ± 0.1</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>BMI(II)/NVP+PI</td>
<td>88.7 ± 0.7</td>
<td>62.6 ± 0.7</td>
<td>4.7 ± 0.3</td>
<td>3.7 ± 0.7</td>
</tr>
<tr>
<td>BMI(III)/NVP+PI</td>
<td>62.8 ± 1.4</td>
<td>54.5 ± 1.2</td>
<td>3.7 ± 0.1</td>
<td>3.1 ± 0.5</td>
</tr>
<tr>
<td>BMI(I)/DMAA</td>
<td>90.3 ± 1.2</td>
<td>99.1 ± 1.3</td>
<td>13.3 ± 0.7</td>
<td>15.5 ± 1.1</td>
</tr>
<tr>
<td>BMI(II)/DMAA</td>
<td>66.5 ± 0.8</td>
<td>88.2 ± 0.6</td>
<td>9.7 ± 0.6</td>
<td>13.4 ± 1.3</td>
</tr>
<tr>
<td>BMI(III)/DMAA</td>
<td>63.4 ± 0.7</td>
<td>83.4 ± 1.1</td>
<td>10.1 ± 0.8</td>
<td>12.4 ± 0.9</td>
</tr>
</tbody>
</table>
The curing process of maleimide-terminated imide oligomers with reactive diluents was investigated using real-time FITR. The profiles of conversion vs. time were obtained based on the decrease in a specific absorbance on the IR spectrum. Figure 6-8 displayed the photopolymerization of maleimide-terminated imide oligomers and NVP formulation with and without photoinitiator. The reaction rate and final conversion both increased by adding photoinitiator. Higher molecular weight of the imide oligomer exhibited lower conversion. This was attributed to the lower concentration of the maleimide group, which could result in the lower absorbance and initiation ability under the UV radiation. This was also consistent with the results from the UV-Vis spectroscopy. A similar trend was observed in Figure 6-9 for imide oligomer with DMAA systems. Regarding the photopolymerization rate, almost same slope of conversion vs. time curve was observed, which means the polymerization rate of maleimide terminated oligomer and NVP were same. This result was consistent with results about photopolymerization of maleimide/vinyl ether pairs studied by Jonsson and Decker.45-46, 49, 258

Figure 6-9 shows the photopolymerization of maleimide terminated imide oligomers with DMAA. For photopolymerization of DMAA, free radical photoinitiator was added into the systems, and a higher reaction rate was observed. Although the maleimide group is photosensitive and capable of initiating photopolymerization without any additional photoinitiator,53, 148, 166 a relatively low concentration of the maleimide group was present in the system. The free radical photo-initiator was added in order to get a relatively fast curing speed and a higher conversion of the system. From Figure 6-9 (b), it was observed that DMAA had a high conversion (40 %) within 5 s. After 65 s UV exposure, ~ 90 % conversion was achieved for DMAA in oligomer (I), while more than 80 % conversion
was obtained for other two formulations. The relatively low conversion was attributed to the high viscosity and low chain mobility. A lower conversion and curing speed was observed for imide oligomer, compared to DMAA. Approximately 60% of maleimide conversion was achieved after 65 s UV exposure for oligomer (II) and oligomer (III). A higher conversion was obtained for oligomer (I) as expected, which was due to the lower viscosity and higher chain mobility. The reaction kinetics data derived from the real-time FTIR are listed in Table 6-6.

6.4.6 Thermal analysis

The glass transition temperature of imide oligomer and UV-cured films of imide oligomers with reactive diluents were measured by DSC. Figure 6-10 shows the DSC thermograms of imide oligomers. A lower glass transition temperature was observed for the lower molecular weight sample, which was the imide oligomer (I) ($M_n \sim 2667$ g/mol). The glass transition temperature increased from 163 °C to 199 °C with increasing molecular weight, which was consistent with the Flory-Fox Equation about relationship of number-average molecular weight ($M_n$) and the glass transition temperature ($T_g$)$^{259}$. For UV-cured films of imide oligomers with reactive diluents, the glass transition temperature was lower compared to the neat imide oligomers. This was due to the reactive diluents with lower glass transition temperature were incorporated into the system. The glass transition temperatures of the homopolymers of DMAA and NVP were $\sim 89$ °C and $54$ °C, respectively. Glass transition temperatures of UV-cured films with DMAA and NVP as reactive diluents are shown in Figure 6-11 and Figure 6-12. Glass transition temperatures of UV-cured (6FDA-Bisaniline)-BMI/DMAA films ranged from
141 °C to 131 °C. For the UV-cured (6FDA-Bisaniline)-BMI/NVP film, the glass transition temperatures were slightly lower, changed from 143 °C to 109 °C.

The thermal stability of UV-cured imide oligomers with reactive diluents was also studied by TGA. Figure 6-13 shows the TGA thermograms of UV-cured (6FDA-Bisaniline)-BMI/DMAA films. All the films were thermally stable up to 400 °C. The maximum thermal decomposition temperature \( T_{\text{dmax}} \) was found to be around 453 °C and 550 °C for imide oligomer (II) with DMAA. The weight decrease at temperature below 400 °C was due to the low molecular weight reactive diluents in the system. Since the UV-curing process was a very fast process compared to the thermal crosslinking, small molecules might be trapped inside of the solid network when the liquid formulation turned into solid films in a very short time. Upon increasing the temperature, these low molecular reactive diluents would evaporate first. However, the weight was relatively stable between 200 °C to 400 °C, which means the covalent bonds in the oligomer chain and the bonds formed after crosslinking reaction did not break. The loss of the part of unreacted diluents did not significantly affect the stability of the crosslinked network, and the films were still thermally stable. The maximum weight loss at 427 °C was attributed to the break of the crosslinked network. For UV-cured (6FDA-Bisanline)-BMI/NVP films, TGA thermograms are shown in Figure 6-14. 5 wt% weight loss temperatures \( T_{5\%} \) for all films were at around 220 °C. Compared to (6FDA-Bisaniline)-BMI/DMAA films, maximum weight loss temperature for UV-cured oligomer with NVP was lower, at around 230 °C. This was because a small amount of monomeric NVP was still present in the system after UV radiation. By adding photoinitiator to the system, the thermal stability of the BMI/NVP films was enhanced, which was related to the increase of the
maximum weight loss temperature. TGA thermograms of neat maleimide terminated oligomer were shown in Figure 6-15. Glass transition temperatures and thermal decomposition temperature of the copolymers are shown in Table 6-7.

![Figure 6-10 DSC thermograms of imide oligomers.](image)

![Figure 6-11 DSC thermograms of UV-cured (6FDA-Bisaniline)-BMI/DMAA films.](image)
Figure 6-12 DSC thermograms of UV-cured (6FDA-Bisaniline)-BMI/NVP films

Figure 6-13 TGA thermogram of UV-cured (6FDA-Bisaniline)-BMI/DMAA films.
Figure 6-14 TGA thermograms of UV-cured (6FDA-Bisaniline)-BMI/NVP films.

Figure 6-15 TGA thermograms of (6FDA-Bisaniline)-BMI.
Table 6-7 Thermal properties of UV-cured films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$* (°C)</th>
<th>Width of $T_g$ (°C)</th>
<th>$T_{5%}$ (°C)</th>
<th>$T_{dmax1}$ (°C)</th>
<th>$T_{dmax2}$ (°C)</th>
<th>Weight @400 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI (I)</td>
<td>163.1 ± 0.8</td>
<td>4.2 ± 0.3</td>
<td>452</td>
<td>536</td>
<td>615</td>
<td>97</td>
</tr>
<tr>
<td>BMI(I)/DMAAA</td>
<td>141.3 ± 1.0</td>
<td>33.5 ± 1.1</td>
<td>242</td>
<td>427</td>
<td>531</td>
<td>87</td>
</tr>
<tr>
<td>BMI (I)/NVP</td>
<td>143.5 ± 0.4</td>
<td>16.7 ± 0.7</td>
<td>220</td>
<td>236</td>
<td>435</td>
<td>72</td>
</tr>
<tr>
<td>BMI (I)/NVP+PI</td>
<td>144.6 ± 0.3</td>
<td>18.1 ± 0.4</td>
<td>235</td>
<td>310</td>
<td>475</td>
<td>73</td>
</tr>
<tr>
<td>BMI (II)</td>
<td>180.9 ± 1.1</td>
<td>8.5 ± 0.3</td>
<td>494</td>
<td>540</td>
<td>618</td>
<td>99</td>
</tr>
<tr>
<td>BMI(II)/DMAAA</td>
<td>135.5 ± 0.9</td>
<td>36.6 ± 1.2</td>
<td>242</td>
<td>453</td>
<td>550</td>
<td>87</td>
</tr>
<tr>
<td>BMI (II)/NVP</td>
<td>109.6 ± 1.0</td>
<td>24.6 ± 0.7</td>
<td>220</td>
<td>230</td>
<td>446</td>
<td>79</td>
</tr>
<tr>
<td>BMI (II)/NVP+PI</td>
<td>123.8 ± 0.4</td>
<td>21.7 ± 0.5</td>
<td>240</td>
<td>317</td>
<td>527</td>
<td>75</td>
</tr>
<tr>
<td>BMI (III)</td>
<td>199.4 ± 1.3</td>
<td>6.0 ± 0.3</td>
<td>520</td>
<td>543</td>
<td>613</td>
<td>100</td>
</tr>
<tr>
<td>BMI(III)/DMAAA</td>
<td>131.4 ± 1.2</td>
<td>42.2 ± 1.6</td>
<td>242</td>
<td>442</td>
<td>541</td>
<td>87</td>
</tr>
<tr>
<td>BMI (III)/NVP</td>
<td>136.7 ± 0.2</td>
<td>19.5 ± 1.0</td>
<td>226</td>
<td>228</td>
<td>436</td>
<td>82</td>
</tr>
<tr>
<td>BMI (III)/NVP+PI</td>
<td>137.1 ± 0.7</td>
<td>22.1 ± 0.9</td>
<td>239</td>
<td>325</td>
<td>447</td>
<td>85</td>
</tr>
</tbody>
</table>

*T$_g$ was measured by DSC

6.4.7 Viscoelastic properties

The crosslink densities of UV-cured films were calculated based on DMA measurements. The glass transition temperature ($T_g$), storage modulus ($E'$), crosslink density and maximum tan δ for UV-cured films are listed in Table 6-8. The $T_g$ of the crosslinked films was obtained from the maximum of tan δ. Tan δ of UV-cured (6FDA-Bisaniline)-BMI/NVP films and (6FDA-Bisaniline)-BMI/DMAA films are shown in Figure 6-16 and Figure 6-17. For UV-cured MA-(6FDA-Bisaniline)-BMI/DMAA film, the glass transition temperature decreased from 163 °C to 141 °C. The crosslink density of the UV-cured film from oligomer (III)/DMAA with $M_n$~10k g/mol had the highest value of 290 mol/m³. This was due to the high mole ratio of the DMAA in the cured films,
which significantly increased the crosslink density. For the UV-cured (6FDA-Bisaniline)-BMI/NVP film, crosslink density showed a similar trend.

Figure 6-16 Tan δ vs. temperature for UV-cured (6FDA-Bisaniline)-BMI/DMAA films.

Figure 6-17 Tan δ vs. temperature for UV-cured (6FDA-Bisaniline)-BMI/NVP films.
### Table 6-8 Properties of the UV-cured films determined by DMA.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Min. Storage modulus $E'$ (MPa)</th>
<th>Crosslink density (mol/m$^3$)</th>
<th>$T_g$ by DMA (°C)</th>
<th>Max. $Tan \delta$</th>
<th>Gel content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMI(I)/DMAA</td>
<td>1.75</td>
<td>152</td>
<td>163</td>
<td>0.72</td>
<td>91.5</td>
</tr>
<tr>
<td>BMI(II)/DMAA</td>
<td>0.91</td>
<td>79</td>
<td>151</td>
<td>0.74</td>
<td>97.0</td>
</tr>
<tr>
<td>BMI(II)/DMAA</td>
<td>3.35</td>
<td>290</td>
<td>141</td>
<td>0.68</td>
<td>92.7</td>
</tr>
<tr>
<td>BMI(I)/NVP</td>
<td>3.13</td>
<td>259</td>
<td>159</td>
<td>0.64</td>
<td>81.5</td>
</tr>
<tr>
<td>BMI(II)/NVP</td>
<td>0.72</td>
<td>60</td>
<td>134</td>
<td>0.71</td>
<td>83.5</td>
</tr>
<tr>
<td>BMI(III)/NVP</td>
<td>6.14</td>
<td>508</td>
<td>145</td>
<td>0.61</td>
<td>70.3</td>
</tr>
<tr>
<td>BMI(I)/NVP+PI</td>
<td>3.39</td>
<td>273</td>
<td>162</td>
<td>0.70</td>
<td>85.5</td>
</tr>
<tr>
<td>BMI(II)/NVP+PI</td>
<td>1.65</td>
<td>145</td>
<td>137</td>
<td>0.79</td>
<td>89.5</td>
</tr>
<tr>
<td>BMI(III)/NVP+PI</td>
<td>6.65</td>
<td>528</td>
<td>149</td>
<td>0.82</td>
<td>80.3</td>
</tr>
</tbody>
</table>

6.4.8 Structure analysis

The X-ray diffraction patterns of maleimide terminated imide oligomers are shown in Figure 6-18. All samples exhibited some degree of ordered structure with three major peaks located at $2\theta \sim 4.2^\circ$, $2\theta \sim 15.8^\circ$ and $2\theta \sim 26.7^\circ$. The diffraction peak at $2\theta \sim 26.7^\circ$ was related to $d$-spacing of 3.34 Å, the diffraction peak at $2\theta \sim 15.8^\circ$ was related to the $d$-spacing of 5.61 Å, and the diffraction peak at $2\theta \sim 4.2^\circ$ was related to $d$-spacing of 21.04 Å. The first diffraction peak located at $2\theta \sim 4.2^\circ$ represented the monomer repeat unit distance of ~21.04 Å along the extended chain distance. Similar results were also observed by Yoon$^{183}$ and Takahashi.$^{184}$ A smectic-like layer of monomer repeat units might exist, but the conformation of the chain was not fully extended. After UV exposure, the cured films were also studied by XRD, as shown in Figure 6-19. The diffraction peak at $2\theta \sim 4.2^\circ$ became broad due to the existence of the reactive diluents in the cured films.
which disturb the ordering pack of the monomer units. The diffraction peak at 2θ~26.7° disappeared and only a wide amorphous peak was observed.

![Figure 6-18 XRD patterns of maleimide terminated imide oligomers.](image)

6.4.9 Structure analysis of UV-cured film and its sol portion

The UV-cured films of maleimide terminated imide oligomers with reactive diluents were studied by solid state $^{13}$C NMR. Figure 6-20 shows the $^{13}$C NMR spectra of NVP
and UV-cured film of (6FDA-Bisaniline)-BMI (II)/NVP. Disappearance of the resonance at $\delta$ 93.0 ppm confirmed the crosslink reaction between NVP and maleimide group during the UV exposure. For poly ($N,N$-dimethylacrylamide), as shown in Figure 6-21, resonance at $\delta$ 30-40 ppm was due to the methyl carbon, which was overlapped with the methyl carbon on imide oligomers. It was found that both UV-cured imide oligomer with DMAA and poly ($N,$ $N$-dimethylacrylamide) had the same resonance at $\delta$ 170-180 ppm., which means the homopolymerization of DMAA occurred during the UV radiation.

Figure 6-20 $^{13}$C NMR spectra of NVP and UV-cured (6FDA-Bisaniline)-BMI (II)/NVP film.
Figure 6-21 Solid state $^{13}$C NMR spectra of UV-cured (6FDA-Bisaniline)-BMI (II)/DMAA film and poly (N, N-dimethylacrylamide).

Figure 6-22 $^1$H NMR spectra of (a) NVP and (b) the sol portion of BMI (II)/NVP film after extraction.
Figure 6-23 $^1$H NMR spectra of (a) DMAA and (b) the sol portion of BMI (II)/DMAA film after extraction.

In order to elucidate the structure of UV-cured films, analysis of the soluble portion of the film was performed after extracting UV-cured film in chloroform for 3 days. $^1$H NMR spectra of NVP and solution after extracting film are shown in Figure 6-22. The NVP was detected in the $^1$H NMR spectrum of solution after extracting films. This means free NVP still present in the system after UV radiation. The reason was because NVP did not significantly homopolymerize without photoinitiator. Small amount of imide oligomer was also detected in the solution, as the spectral region exhibited resonance at $\delta$ 1.7 ppm, which was due to the protons on methyl group in bisaniline-m. However, no detectable resonance was found at $\delta$ 6.78 ppm associated with the protons on the maleimide group. Compared to the reactive diluents, imide oligomer chain was rigid and long which would limit the mobility during the crosslinking process. Another reason was attributed to the fast UV-curing process. During the curing process, the liquid formulation turned into solid film in a very short time ($<1$ min) compared to the thermal curing.
process. There was not enough time for all functional groups in the oligomer chains to reach other reactive groups and form crosslinked network.

$^1$H NMR spectra of DMAA and solution after extracting UV-cured BMI (II)/DMAA films are shown in Figure 6-23. Small amount of DMAA was detected in the chloroform solution after extracting films. DMAA was acrylamide which was able to undergo homopolymerization in the presence of free radical initiator. That was the reason why just small amount of DMAA was shown in the solution after extraction. Maleimide terminated imide oligomer also existed in the solution, as the spectral region exhibits resonance at $\delta$ 1.7 ppm, which was due to the protons on methyl group in bisaniline.

6.5 Discussion

There have been very few reports of UV-curable polyimide or imide oligomers in the past. In order to take advantage of high photo-reactivity of the maleimide group and the excellent thermal, mechanical and electrical properties of the polyimide, imide oligomers end-capped with UV reactive maleimide groups were developed. According to the real-time FT-IR and Photo-DSC studies, these imide oligomers were capable of polymerizing rapidly with reactive diluents under UV radiation. For imide oligomer/NVP formulations, no additional photo initiator was needed to initiate the polymerization, which might overcome many issues caused by small molecular photo initiators. The cured films were obtained and the thermal properties were studied. The high glass transition temperature and the high maximum weight loss temperature made it good materials for high performance coating application. This research might fill in the gap of UV-curable films.
in the high temperature application area. And it is a promising area in both radiation curable resins development and polyimide applications.

The properties of the oligomers are highly dependent on the monomer structure and the molecular weight. Good solubility of maleimide terminated imide oligomers in common solvents and reactive diluents was attributed to the fluorinated isopropylidene group in 6FDA. The \( sp^3 \)-hybridized carbon and attached trifluoromethyl groups disturbed the chain packing and enhanced the solubility of the polyimide.\(^{260}\) The molecular chain was expected to have a more tightly coiled preferred conformation. Thus, the chains would not be able to pack as closely as those of linear aromatic polyimide chains. This was also confirmed by the XRD studies of the imide oligomers. The predication of the solubility parameter was based on the group contribution method.\(^{256}\) For materials of lower molecular weight, cohesive energy was considered as an additive property.\(^{253-255}\) The molecular weight of oligomers was also considered as a variable during the synthesis of imide oligomers. Real-time FITR showed the oligomers with lower molecular weight had higher conversions during the photopolymerization. This was attributed to their high absorbance of in the UV region and the high chain mobility in the formulations.

Since UV radiation was used to polymerize the oligomers, the photo chemistry of oligomer is quite important. Photopolymerization of \( N \)-substituted maleimide and bismaleimide have been studied in the past by a number of researchers.\(^{45-46, 49, 261}\) Three possible reactions may account for consumption of the maleimide group: initiation of polymer chains through hydrogen atom abstraction or electron/proton transfer processes, copolymerization with the acrylic and vinyl ether monomers, and maleimide [2+2] cycloaddition reactions,\(^{45-46, 49, 53, 148, 165, 167, 178, 261-263}\), as shown in Scheme 6-6.
In general, monomers can be categorized into two major groups depending on their substituent: electron-acceptor (A) monomers and electron-donor (D) monomers. Monomers have electron withdrawing groups that are electron-acceptor monomers, such as, maleic anhydride, N-substituted maleimide and bismaleimides. Monomers have electron donating groups that are electron donor (D) monomers, such as N-vinylpyrrolidone, vinyl ethers, N-vinylamides. When Vinyl ethers were mixed with a maleate or a maleimide monomer, they readily undergo copolymerization, with formation of an alternating type copolymer. If the monomers contain at least two reactive groups, such as divinyl ethers (DVE) and bismaleimides, the polymerization develops in three dimensions to yield a highly crosslinked polymer network. A distinct feature of maleimide-based formulations was that they do not require the addition of a
photoinitiator, the UV radiation being mainly absorbed by the maleimide chromophores.\textsuperscript{46}

In the UV-curing formulations studied, NVP acted as an electron donor monomer due to its electron donating group, while maleimide-terminated imide oligomers acted as electron acceptor due its electron withdrawing group. This donor-acceptor pair can form a donor acceptor complex and then generate initiating radicals to trigger the photopolymerization, which was also proposed by Decker and his coworkers.\textsuperscript{46, 49, 261} Based on the formulations studied, the polymer network formed by maleimide-terminated oligomer and NVP is shown in Scheme 6-7. The wide glass transition according to the DMA test might also be due to these structures. Some side reactions might also occur, such as maleimide [2+2] cycloaddition reactions as shown in Scheme 6-6 path (b).\textsuperscript{53, 167}

Two mechanisms have been proposed to explain the strong alternation tendency between electron-acceptor and electron-donor monomers. The polar effect mechanism considered that interaction between an electron-acceptor radical and an electron-donor monomer or an electron-donor radical and an electron-acceptor monomer leads to a decrease in the activation energy for cross-propagation.\textsuperscript{40-41} The monomer complex participation (MCP) mechanism suggests that alternation resulted from homopolymerization of a 1:1 complex formed between donor and acceptor monomers.\textsuperscript{39} In alternating copolymerization, the monomers showed little or no tendency to homopolymerize. Maleic anhydride, dialkyl fumarates, and \(N\)-alkyl maleimides are examples of such monomers. These monomers readily form alternating copolymers with electron-donor monomers such as styrene, vinyl ethers, \(p\)-methoxystyrene and \(N\)-vinylcarbazole. \(N\)-substituted maleimides acting as electron-acceptor monomers have
been reported to copolymerize alternatingly with a variety of electron donor vinyl comonomers.\textsuperscript{34-35, 37-38}

This being the first attempt at a UV-curable polyimide, it was quite successful. In the most of UV-curable systems, reactive diluents are in high enough concentration to form a two phase system leading to a very heterogeneous polymeric material.\textsuperscript{7, 264} The amount of reactive diluent needed to solubilize the reactive oligomer is the minimum. Although the threshold of 50 wt\% for a reactive diluent, albeit a little high, is not unusual in the world of UV-curable formulations.\textsuperscript{7} It is anticipated that side groups on the BMI may decrease the amount of reactive diluent needed. Nevertheless, the thermal stability of the BMIs was better than expected, and could be useful as a higher temperature and performance resin than an epoxide.\textsuperscript{265-266}

6.6 Conclusions

UV-curable maleimide-terminated imide oligomers were synthesized and the properties were investigated. Without any additional photoinitiator, imide oligomers formulated with NVP polymerized rapidly under UV radiation. Over 90 \% of conversion was achieved for the BMI/NVP formulation with low molecular weight (2k). The polymerization rate of BMI/NVP formulation was accelerated by photoinitiator. High conversion (94 \%) for imide oligomers with DMAA was also achieved after being exposed to UV light. The UV-cured films had a wide glass transition due to the two phase system. The glass transition temperatures of the cured film are over 100 °C. This kind of material is suitable for high performance coatings and adhesive applications.
CHAPTER VII
CONCLUSIONS

In this dissertation, radiation crosslinking styrenic block copolymers and maleimide-terminated imide oligomers were investigated. E-beam radiation showed significant effects on the chemical structure and mechanical properties of three types of styrenic block copolymers, SIS, SBS and SIBS. The effect of e-beam pro-rads on SIBS was also addressed. Adding pro-rads was an effective approach to increase the tensile strength of SIBS at low radiation doses. In Chapter VI, UV-curable maleimide-terminated imide oligomers were synthesized and their structures were characterized. In addition, the UV-curing process and the properties of cured films were investigated.

The effects of e-beam radiation on tensile and viscoelastic properties of SBCs were investigated in Chapter III. The properties of the SBCs irradiated at four radiation doses (60, 120, 190 and 240 kGy) were studied. E-beam radiation had a profound effect on tensile and viscoelastic properties of SBCs. It was found that the tensile strength of SBCs was radiation dose dependent. This was because microstructures of SBCs, such as crosslink density and network regularity, were dose dependent. At low radiation doses, the decrease of the tensile strength was due to the decrease of network regularity, which prevented the uniform stress distribution during uniaxial stretching and caused the failure of the films. At high e-beam radiation doses, the increase of the tensile strength was attributed to the increase of both crosslink density and network regularity. After passing a
maximum point, the tensile strength started to decrease as the e-beam radiation dose increased. This was attributed to the high crosslink density induced low extensibility. Therefore, knowing the crosslink density of the materials before e-beam radiation was quite important in improving the tensile properties of the SBCs. The SIS showed similar behavior to the SIBS in terms of tensile strength, while the SBS differed from those two. Tensile moduli and the overall crosslink density of SBS, SIBS and SIS significantly increased with increasing e-beam radiation dose. This indicated the crosslink reaction was predominant in the SBCs during e-beam radiation. From the stress relaxation measurement, it was observed that the relaxation rate of the crosslinked SBCs decreased by increasing the e-beam radiation dose. This indicated that e-beam radiation introduced chemical crosslinks in rubbery phase which slowed down the disentanglement of the polydiene segments. It was also found that the relaxation rate increased as the temperature increased. This is because the high temperature increased the overall physical flow of the materials.

In Chapter IV, e-beam radiation initiated reactions of SBCs were studied. Molecular weight characterization of soluble portion of the copolymers at four radiation doses provided insight into the change of chemical structures of the materials. The reaction type was radiation dose dependent. Only chain crosslinking reaction was found at the low e-beam radiation dose (60 kGy) for the SBCs investigated. The lower molecular weight chains were observed for the SBCs irradiated at high e-beam radiation doses (> 120 kGy), which indicated the chain scission reactions occurred. As the radiation dose increased to a higher value (> 190 kGy), both crosslinking and chain scission reactions took place. The formation of diblocks at high radiation doses (>120 kGy) was observed in the SIBS and
SBS. In addition, the chain scission reaction increased by increasing the e-beam radiation dose. Nevertheless, the crosslinking reaction was still the predominant reaction in the copolymers investigated based on the gel content measurements. The gel content of SIBS, SIS and SBS increased with increasing e-beam radiation dose. *Cis-trans* isomerization was also observed in the SBCs upon e-beam radiation. The polydiene phase was particularly susceptible to the e-beam radiation. The equilibrium swelling measurements also proved that by increasing the radiation dose, the crosslink density of polydiene phases increased. The cylindrical morphologies of the SBCs after e-beam crosslinking were more stable during ozonolysis.

The effects of a variety of pro-rads on SIBS were investigated in Chapter V. It was found that the crosslink reaction of SIBS under e-beam radiation was promoted by pro-rads. Tensile modulus, gel content and crosslink density of the SIBS increased after irradiated under e-beam in the presence of pro-rads. The reason is that more reactive species were generated by pro-rads upon e-beam radiation which promoted the crosslinking reaction of SIBS. It was likely that pro-rads had more significant effect at low e-beam radiation doses (< 190 kGy) than high radiation doses (>190 kGy) in facilitating the crosslink reaction. Acrylate type pro-rads, such as TMPTA and 519 HP, were the most efficient in promoting the crosslinking reaction. Methacrylate type pro-rads, such as TMPTMA, 517HP and BGDMA, also promoted the crosslinking reaction of the SIBS. In addition, the viscosity of the SIBS with methacrylate type pro-rads was much more stable than with acrylate type pro-rads at elevated temperature (e.g. 200 °C). This made the methacrylate type pro-rads the most suitable additives for the melting extrusion process. It was also found that TMPTMA, BGDMA and 517 HP were soluble
in both polydiene and polystyrene phases through selective swelling of both polystyrene and polydiene phases.

In Chapter VI, UV-curable maleimide-terminated imide oligomers were synthesized and characterized. The solubility parameter was calculated as 24.3 MPa$^{1/2}$ based on the group contribution method. Good solubility in reactive diluents, DMAA and NVP, were observed. The imide oligomers formulated with NVP photopolymerized rapidly upon UV radiation without any additional photoinitiator. For the (6FDA-Bisaniline)-BMI/NVP formulations, the conversion of imide oligomers ($\overline{M}_n \sim 2k$) reached 90% after crosslinking. The crosslinking reaction proceeded by forming a donor/acceptor complex. By adding the photoinitiator, the conversion and reaction rate were further increased according to the photo-DSC and real-time FTIR study. For the (6FDA-Bisaniline)-BMI/DMAA formulations, high conversions (> 90%) were also achieved for imide oligomer ($\overline{M}_n \sim 2k$) after exposed to UV radiation for 65 s in the presence of photoinitiator. It was observed that molecular weight of maleimide-terminated imide oligomers affected the reaction rate and the final conversion of the oligomers. Lower molecular weight oligomers showed higher reaction rate and final extent of conversion due to the high absorbance of the maleimide group in the formulations. Because of the high performance of the imide structures in the system, the glass transition temperature of cured films was greater than 100 °C. The films are much more thermally stable compared to the currently UV-cured resins used in the industry. This makes it a good candidate for high temperature coatings and adhesive applications.
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