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Sustainable Polymeric Materials Derived from Novel Soybean Based Monomers and Polymers: From Synthesis to Applications

Nathan Trenor
University of South Carolina - Columbia

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SUSTAINABLE POLYMERIC MATERIALS DERIVED FROM NOVEL SOYBEAN
BASED MONOMERS AND POLYMERS: FROM SYNTHESIS TO APPLICATIONS

by

Nathan Trenor

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Accepted by:

Chuanbing Tang, Director of Thesis

Brian Benicewicz, Reader

Lacy Ford, Senior Vice Provost and Dean of Graduate Studies

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DEDICATION

To my entire family, my high school and undergraduate teachers, my lab mates, and all of my friends. Their support and inspiration helped me attain all of my current achievements.

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ABSTRACT

In this thesis, monomers and polymers derived from high oleic soybean oil are investigated. The properties of these monomers and polymeric materials are characterized and discussed.

Chapter 1 describes an overall background of bio-based resources, monomers, polymers, and their potential impact on society. Polymerization techniques are introduced, and the overall objective of my research is described.

Chapter 2 outlines the large scale preparation of a soybean based monomer and the use of this monomer in thermoset elastomers. The synthetic procedures and characterizations of the monomers and polymers are discussed. A model study using oleic acid is described and proved to be successful. The methods from the model study were applied to a soybean based monomer to obtain novel thermoset elastomers which incorporated high weight percentages of the soy based monomer and showed promising mechanical properties. Different curing experiments were completed and two different curing processes were developed.

In Chapter 3 a hydrogen bonding donor/acceptor strategy was used to create thermoplastic elastomers by free radical polymerization. The use of high T_g monomers with hydrogen bonding properties allowed for good mechanical properties to be achieved,

ranging from thermoplastic elastomers to thermoplastics. The synthetic procedures and characterizations of the polymers are discussed. Promising results were obtained using even higher weight percentages of the soybean based monomer than in the thermoset elastomers. This led to creating a one pot method to form a triblock TPE using the same monomers as before. To achieve this, a difunctional RAFT agent was synthesized and a one pot RAFT polymerization method was developed. The synthetic strategies for both the difunctional RAFT agent and the one pot polymerization method are discussed.

An overall summary of my research as well as suggestions on future research directions in my projects and renewable polymer materials are given in Chapter 4.

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x

LIST OF SYMBOLS

M_n number average molecular weight

Đ   dispersity

T_g glass transition temperature

LIST OF ABBREVIATIONS

4VP… ....4-vinyl pyridine

AA...Acrylic acid

AFM... Atomic Force Microscopy

AIBN..Azobisisobutyronitrile

CTA…... Chain transfer agent

DCM… ....Dichloromethane

DCP…..Dicumyl peroxide

DiRAFT .... Difunctional RAFT agent

DMA…………………………………………………….Dynamic Mechanical Analysis

DMAP ....4-dimethylamino pyridine

DMF…..Dimethylformamide

DMSO…..Dimethyl sulfoxide

DSC...Differential Scanning Calorimetry

FTIR... Fourier Transform Infrared Spectrometry

GPC... Gel Permeation Chromatography

HEMA…... 2-hydroxyethyl methacrylate

HOSO…... High oleic soybean oil

MAA… ....Methacrylic acid

CHAPTER 1

GENERAL INTRODUCTION

1.1 Renewable bio-based polymers and their potential impact on society

Our current polymer industry relies heavily on fossil fuels. Presently, 90% of the chemicals used worldwide are fossil fuel based, and the production of synthetic plastics accounts for the consumption of about 7% of fossil fuels[1-6]. In the United States, about 13% of fossil fuels are used towards non-fuel chemical production[3, 7]. Environmental concerns and the desire to change our dependence on fossil fuels have led to an upsurge in the research of sustainable polymers[4, 5, 7-18]. Goals have been set by the United States Department of Agriculture and the Department of Energy to reach 25% of chemical use from biomass by 2030[6]. Biomass can be divided two classes; small molecules and natural polymers. Natural polymers such as natural rubber, cellulose, polysaccharides, lignin, chitin, and chitosan are extensively studied, but lack processability, defined structures, and uncontrolled mechanical properties[3, 5, 14, 17, 19-25]. Common small molecule biomasses include plant oils, fatty acids, rosin acids, lactic acid/lactide, and many others[3, 5, 9, 14, 15, 17, 18, 21, 24-34]. Recently, these small molecule biomasses have opened new windows to synthesize renewable monomers and polymers, with the potential of being made on an industrial scale to replace synthetic plastics through a concept of biorefinery[6, 17]. The biggest challenge to overcome is to produce materials with similar properties as their synthetic counterparts at a reasonable cost. Higher expenses and inferior performance have resulted in a small market share (<5%)[5, 35]. The future of this field relies on practical synthetic strategies involving simple and industrially useful monomer and polymer synthesis from a copious biomass.

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1.2 Vegetable Oil

Vegetable oils are an extraordinary natural and renewable feedstock for polymer synthesis, with annual global production increasing from 84.6 million tons in 2000 to 137.3 million tons in 2010[26]. Their natural abundance, inexpensive cost, and ease of functionalization make them an ideal polymer feedstock in a world with an increasing desire to find renewable alternatives to fossil fuels. The chemical structure of vegetable oils consists of a triglyceride with three fatty acid chains. There are many common fatty acids obtained from vegetable oils, which are displayed in **Figure 1.1**. The length of the fatty acid chains and amount of unsaturation varies from 12 to 22 carbons and 0 to 6 per fatty acid chain respectively.
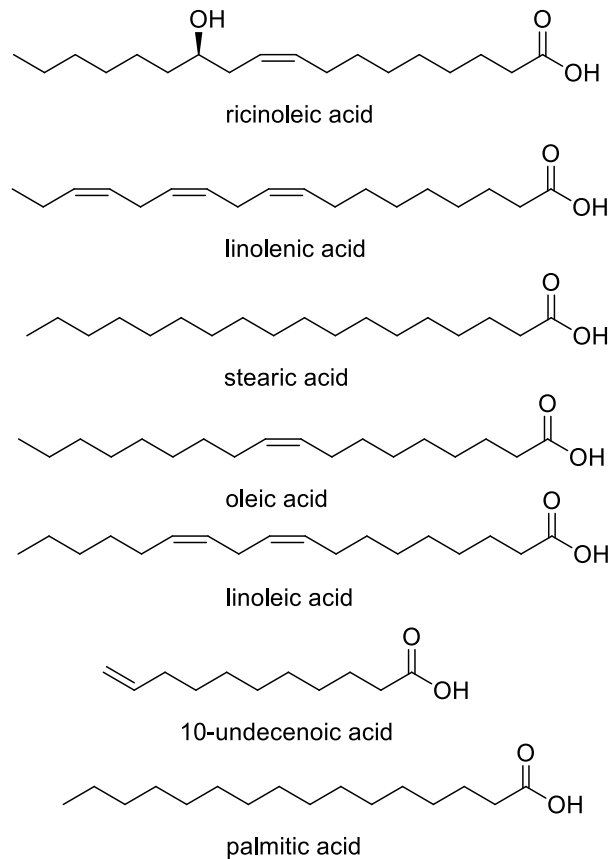
Figure 1.1. Common fatty acids found in vegetable oil.

1.3 Polymerization Techniques

Reversible Addition-Fragmentation Chain-Transfer (RAFT) Polymerization

RAFT polymerization is an extremely advantageous controlled radical polymerization technique which has been employed for nearly 20 years. RAFT polymerization has been used to prepare a myriad of polymers with complex architectures, including block copolymers, brush polymers and dendrimers[36-39]. Reversible addition-fragmentation transfer (RAFT) was first reported in literature by Rizzardo et al. in 1998[40]. RAFT entails a chain transfer between an active and a dormant species, which is achieved by utilizing a chain transfer agent which has the appropriate Z and R groups for an efficient transfer process (**Figure 1.2**). Common CTAs include dithioesters and trithioesters. Generally, the Z group of the RAFT agent favors the formation of the radical intermediate. Phenyl rings and functionalized phenyl rings are frequently used as Z groups. The R group typically includes steric hindrance and contains an electron stabilizing group for the active radical species. The fragmentation capability of the radical intermediate is largely dependent on the R group. Commonly R groups are cumyl and cyanoisopropyl groups[40, 41].

Figure 1.2. Overall mechanism of RAFT polymerization.

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1.4 Research Objectives

The objectives of this work consist of developing useful polymeric materials from a sustainable resource. This included synthesizing novel soybean oil based monomers and polymers. A highly efficient and scalable process was used to produce a soybean oil based methacrylate m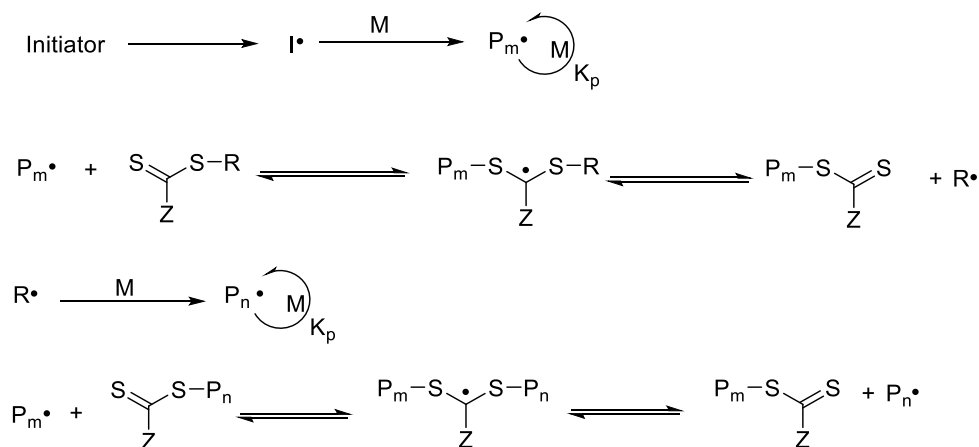onomer. Free radical polymerization was used to prepare polymers, which were crosslinked to give the thermoset elastomers. Two curing processes, one solvent assisted and one solvent free, were developed to obtain thermoset elastomers and improve the mechanical properties. Good properties were achieved using high weight percentages of the soybean based methacrylate monomer. Because this methodology is scalable and efficient, the thermoset elastomers have potential to be used for packaging products, fabric materials, in the clothing industry, etc.

The second objective is to make thermoplastic elastomers from the same soybean based monomer used in the thermoset elastomers. This was done using two different methods. One utilized free radical polymerization of the soybean based monomer with two other co-monomers that contain hydrogen bonding donor/acceptor groups. The hydrogen bonding interactions helped to improve the mechanical properties. Good properties were achieved using even higher weight percentages of the soybean based methacrylate monomer. The process is also scalable and efficient, so the resulting polymers could see similar applications in packaging, fabric materials, the clothing industry, rubber materials, etc. The second method involves a one pot RAFT polymerization method to prepare triblock TPEs from the soybean based monomer and the same hydrogen bonding monomers. This entails the synthesis of a difunctional RAFT agent, polymerizing the

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soybean based monomer, then subsequent polymerization the other monomers. The showed promise, but future research is needed for this project.

CHAPTER 2

THERMOSET ELASTOMERS PRODUCED FROM A NOVEL HIGH OLEIC SOYBEAN

OIL BASED MONOMER

2.1 Abstract

Thermoplastics, thermoplastic elastomers, and thermoset elastomers are extremely vital in our current society. These materials are based heavily on the petroleum market. There is a yearning to change our dependence on fossil fuels as a materials feedstock and maintaining similar physical properties of our current polymeric materials is of paramount importance. This has led to a massive research area in producing useful materials from a bio-renewable and sustainable feedstock. It has been shown that plant oil based triblock TPEs prepared using controlled techniques tend to have low tensile strengths due to the low chain entanglement caused by their inherent long fatty acid side chains. We hypothesized useful materials could be prepared by using free radical polymerization. Encouraging initial studies using an oleic acid based monomer (OMA) led to the preparation soybean based thermoset elastomers. High oleic soybean based copolymers were prepared using a soybean based monomer (SBMA) and styrene as a high glass transition temperature (T_g) co-monomer. A curing process was applied and promising mechanical properties were achieved using high weight percentages of SBMA, ranging from elastomeric to thermoplastic type behavior. The properties were tuned by the polymer composition, the curing agent concentration, and the curing time. A solvent free curing process was also developed, resulting in similar properties to that from solvent assisted curing.

2.2 Introduction

From all the existing biomass, high oleic soybean oil has proven to be a very popular choice, seeing applications in surfactants, paints, resins, coatings, biofuels, and polymers[13, 17, 18, 42, 43]. Soybean oil itself saw a 56% increase in production from the year

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2000 to 2010[26]. The fatty acid composition of high oleic soybean oil consists of about 75% oleic acid, around 7% linoleic acid, and less than 3% lenolenic acid, meaning it is mostly monounsaturated. The main structural component of high oleic soybean oil is a triglyceride. These triglycerides are useful in many chemical reactions such as hydrolysis,[44] transesterification,[45] amidation,[18, 46] hydrogenation,[47] polymerization,[17, 18, 48, 49] epoxidation,[50] oxidation,[51, 52] and addition[53, 54]. The chemical structure of high oleic soybean oil can also be modified using the unsaturated carbon-carbon double bonds. These *cis* alkenes can be transformed into epoxide groups and then polymerizable monomers with further reactions, mostly resulting in thermoset polymers[55-57]. The alkenes can also be used for post polymerization modification to create thermoset polymers using free radical initiators and high temperatures.

Thermoplastic elastomers (TPEs) combine properties from both thermoplastics as well as thermoset materials/vulcanized rubbers. They possess the processability thermoplastics as well as the mechanical properties of both thermoplastics and rubber materials. Conventional thermoplastic elastomers (TPEs) are prepared from either triblock copolymers or multigraft polymers. These polymeric designs combine the elasticity of a low T_g polymer with the toughness of a high T_g polymer to create a material with both high tensile strengths and strain at break[17, 20, 58-62]. TPEs prepared from triblock or multigraft polymers undergo microphase separation, giving arise to an ordered morphology. These morphologies allow the formation of reversible physical crosslinks between the soft and hard domains, which play a large role in the mechanical properties of the material. Preparing polymers of this type from vegetable oil and fatty acid based monomers is extremely challenging and requires the use of controlled radical polymerization techniques,

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which can be highly air and moisture sensitive. The subsequent thermoplastic elastomers prepared from these types of polymers tend to have inferior performance to fossil fuel based TPEs. It is well known that chain entanglement also plays a large role in the mechanical properties of a material. The lesser mechanical properties of these bio-based materials is a result of the high molecular weight between chain entanglement (M_e) values due to the long alkyl sidechains that exist in these polymers. This means vegetable and fatty acid based polymers have little to no chain entanglement, making it very difficult to prepare materials with high tensile strengths[17, 63-65].

Since controlled radical techniques are quite sensitive and can involve the use of expensive reagents, we wanted to try to avoid using controlled radical techniques, hypothesizing that useful materials could be prepared by simply using free radical polymerization. This was done by preparing copolymers using plant oils and fatty acids as the rubbery low T_g component and styrene as the rigid and high glass transition temperature (T_g) component. To address the chain entanglement issue, a solvent assisted curing process was used to create crosslinks between the unsaturated side chains of the soybean based monomer to improve the mechanical properties. Promising mechanical properties ranging from elastomeric to thermoplastic type behaviors were obtained by tuning the polymer composition, the curing agent concentration, and the curing time. A solvent free curing process was also developed, resulting in similar properties to that from solvent assisted curing method.

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2.3 Experimental Section

2.3.1 Materials

Oleic acid (tech. 90% Alfa Aesar), oxalyl chloride (98% TCI), dicumyl peroxide (99% Acros Organics), high oleic soy oil (Plenish® Dupont), 2-(methylamino) ethanol (99% Sigma-Aldrich), methacrylic anhydride (94% Sigma-Aldrich), sodium methoxide (5.4 M 30 wt.% solution in methanol Sigma-Aldrich), and 4-(Dimethylamino) pyridine (99% Sigma-Aldrich), were used as received. 2-Hydroxyethyl methacrylate (97%, stab. with ca 500ppm 4-methoxyphenol Acros Organics) was passed through alumina to remove the 4-methoxyphenol inhibiter. Triethylamine (99% Acros Organics) was distilled over calcium hydride (95% Sigma-Aldrich) and stored over molecular sieves. Styrene (99% stabilized 4-tertbutylcatechol Sigma-Aldrich) was passed through basic alumina to remove the 4-tertbutylcatechol inhibiter. Azobisisobutyronitrile (98% Sigma-Aldrich) was recrystallized from methanol before use. Tetrahydrofuran (THF) and toluene were obtained from dry stills and stored over molecular sieves before use. Teflon molds used for film casting were machined to have the following dimensions: length 2.76 in, width 1.95 in, and depth 0.274 in.

2.3.2 Characterization

^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. Molecular weights and distribution of polymers were determined using gel permeation chromatography (GPC) using a Waters system equipped with a 1525 Binary HPLC pump, a 2414 refractive index detector, and three Styragel columns (HR1, HR3, HR5E in the effective molecular weight range of 100–

5 K, 500–30 K, and 2 K–4 M, respectively) with HPLC grade THF as the eluent at 35°C and a flow rate of 1.0 mL per minute. GPC samples were prepared by dissolving the sample in THF with a concentration of 5.0 mg/mL. The dissolved samples were filtered through microfilters with a pore size of 0.2 μm (Teflon, 17mm Syringes Filters, National Scientific, USA). The columns were calibrated against polystyrene standards. Fourier transform infrared spectrometry (FTIR) spectra were taken on a PerkinElmer spectrum 100 FTIR spectrometer. The glass transition temperature (T_g) of polymers was observed through differential scanning calorimetry (DSC) conducted on a DSC Q2000 (TA instruments). The samples were heated from 25 °C to 200 °C at a rate of 10 °C per minute, cooled to -50 °C at a rate of 10 °C per minute, and then heated to 200 °C at a rate of 10 °C per minute. Data was obtained from the 3rd cycle. The average sample mass was 10 mg and the nitrogen flow rate was 50 mL per minute. Thermogravimetric analysis (TGA) was conducted on a Q5000 TGA system (TA instruments), ramping from 25 °C to 1000 °C with a rate of 10 °C /min. The average sample mass was 10 mg. Tensile testing (stress-strain) was performed on an Instron 5543A. Dumbbell samples with a length of 22 mm and a width of 5 mm were cut from the casted films. The films were tested at room temperature with an extension rate of 20 mm per minute. A Carver Laboratory Press Model C was used to prepare films of the SBMA-co-St polymers at 150 °C to be used for the solvent free curing process.

2.3.3 Synthetic methods

Synthesis of Oleic Methacrylate (OMA). Oxalyl chloride (3.8 mL, 0.0424 mol) was added to a round bottom flask containing 50 mL of THF and cooled to 0 °C. Oleic acid (11 mL, 0.0346 mol) was then added dropwise via syringe, and allowed to react at 0 °C for 1 hour and at room temperature for 18 hours. A 2 M potassium hydroxide bath was used to

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neutralize the hydrochloric acid gas formed by the reaction. The crude product was concentrated on a rotary evaporator. The resulting acid chloride was diluted with 10 mL of dry THF and cooled to 0 °C. Triethyl amine (6 mL, 0.043 mol) and 2 hydroxyethylmethcrylate (5.1 mL, 0.042 mol) were diluted with 40 mL of THF in a separate flask, added dropwise to the acid chloride under a nitrogen atmosphere, and allowed to react at 0 °C for 1 hour and at room temperature for 18 hours. The salt byproduct, triethyl ammonium chloride, was removed using suction filtration. The crude OMA product was concentrated on a rotary evaporator, purified by silica gel chromatography, and dried under vacuum to afford a yellow oil. Yield 90%. ^{1}H NMR (CDCl$_2$): 6.1 ppm (s, 1H, CH_2=C); 5.57 ppm (s, 1H, CH_2=C); 5.31 ppm (m, 2H, -CH=CH-); 4.31 ppm (m, 4H, -OCH_2CH_2O-).

Copolymerization of OMA with Styrene. The following procedure prepared a 15:85 OMA:St copolymer. To prepare different polymer ratios, the same procedure was followed, changing the feed ratios accordingly. Oleic methacrylate (0.302 g, 0.761 mmol), styrene (0.448 g, 4.31 mmol), azobisisobutyronitrile (8.3 mg, 0.051 mmol), and 1 mL of toluene were added to a 10 mL schlenk flask. The contents were heated to 80 °C and allowed to react for 20 hours. The crude polymer solution was then diluted with 5 mL of THF, and precipitated twice in cold methanol to remove the unreacted monomers from the polymer. The methanol was then decanted, and the polymer was concentrated on a rotary evaporator and dried under vacuum. ^{1}H NMR (CDCl$_2$): 7.25-6.25 ppm (br, ArH); 5.35 ppm (br, -CH=CH-).

Synthesis of Soybean Methacrylate Monomer (SBMA). High oleic soybean oil (844 g, 0.94 mol) was added to a 2 L reaction vessel and was heated to 100 °C. The contents were

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purged with nitrogen at 100 °C for one hour. The contents were then cooled to 60 °C. 2-(methylamino) ethanol (352.97 g, 4.7 mol) and 5.4 M sodium methoxide (13 mL, 1.5 wt% to oil) were added to the vessel. The contents were allowed to react at 60 °C, and full conversion was obtained in 1 hour. The contents were transferred to a 3 L separation vessel, washed with a brine solution using mechanical stirring, and decanted into an Erlenmeyer flask. The collected SBOH was washed with anhydrous magnesium sulfate, filtered, concentrated on a rotary evaporator, and then dried under vacuum, affording an orange/brown liquid. SBOH (500 g, 1.47 mol) was added to a round bottom flask, heated to 100 °C, and purged with nitrogen for 1 hour. The contents were then cooled to 60 °C. Methacrylic anhydride (238.53 g, 1.55 mol) and DMAP (3.6 mg, 2 mol% to SBOH) were added to the flask. The contents were allowed to react at 60 °C, and full conversion was reached in 18 hours. The contents were transferred to a 3 L separation vessel, washed with a sodium bicarbonate solution using mechanical stirring, and decanted into an Erlenmeyer flask. The collected SBMA was washed with anhydrous magnesium sulfate, filtered, concentrated on a rotary evaporator, and then dried under vacuum, affording a yellow liquid. Yield 95%. ^{1}H NMR (CDCl$_2$): 6.1 ppm (s, 1H, CH_2=C); 5.57 ppm (s, 1H, CH$_2$=C); 5.34 ppm (m, 2H, -CH=CH-); 4.29 ppm (m, 2H, -OCH_2CH$_2$N-); 3.67ppm (m, 2H, -OCH$_2$CH_2N-); 2.97 ppm (m, 3H, NCH_3).

Copolymerization of SBMA with St. The following procedure prepared PSBMA56. To prepare different polymer ratios, the same procedure was followed, changing the feed ratios accordingly. SBMA (11 g, 0.027 mol), styrene (8.43 g, 0.081 mol), azobisisobutyronitrile (0.1771 g, 0.00098 mol), and 20 mL of toluene were added to a 100 mL round bottom flask. The contents were heated to 80 °C and allowed to react for 20 hours. The crude

polymer solution was then diluted with 5 mL of THF, and precipitated twice in cold methanol to remove the unreacted monomers from the polymer. The methanol was then decanted, and the polymer was concentrated on a rotary evaporator and dried under vacuum. ^{1}H NMR (CDCl$_2$): 7.25-6.25 ppm (br, Ar*H*); 5.35 ppm (br, -C*H*=C*H*-).

Film Preparation and Curing of P(OMA-co-St) and P(SBMA-co-St) copolymers. The following procedure prepared a cured film of PSBMA54. To prepare different cured films, the same procedure was followed, changing the variables accordingly. 0.73 g of PSBMA54 and 22.49 mg of DCP were dissolved in 15 mL of THF and added to a Teflon mold. The mold was covered with a petri dish to allow the solvent to slowly evaporate. After 3 days, the mold was placed in a vacuum oven at 45 °C for 12 hours with no vacuum applied, 25 °C under vacuum for 12 hours, and 45 °C under vacuum for 4 hours. This process ensured removal of any residual solvent. The film was then cured under vacuum at 130 °C in for 3 hours, affording a free standing film with an average thickness of 0.25 mm. Dogbone cuts were made from the cured film for tensile testing.

Solvent Free curing process. The following procedure prepared a cured film of PSBMA54. To prepare different cured films, the same procedure was followed, changing the variables accordingly. PSBMA54 was milled to obtain a flat sheet. A pocket was then created in the polymer sheet, the curative was added into the pocket, and then folded into the polymer sheet. The sheet containing the curative was then milled again to ensure the curing agent was well dispersed throughout the polymer. A film of the polymer containing the curing agent was then prepared using a hot press at 150 °C and a metal mold. The metal mold was placed between two Teflon sheets, which was placed between to metal pieces. The film was then placed in a vacuum oven and a weight was placed on top of the metal

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pieces to keep the polymer film flat. The film was then cured in a vacuum oven at 130 °C for three hours, affording a free standing film with an average thickness of 0.3 mm. Dogbone cuts were then prepared for tensile testing.

2.4 Results and Discussion

2.4.1 Thermoset elastomers from oleic acid derived copolymers P(OMA-co-St) as a model study

The first step to addressing this issue was to design a model study. Oleic acid, a monounsaturated C18 acid with one double bond between C9 and C10, is a naturally occurring fatty acid found in numerous vegetable oils.[26, 66] A two-step monomer synthesis was used to convert the acid into a readily polymerizable methacrylate monomer, named oleic methacrylate (OMA). The first step involved the conversion of oleic acid into oleoyl chloride using oxalyl chloride in THF. Afterwards, oleoyl chloride was reacted with 2-hydroxy ethyl methacrylate (HEMA) with the presence of triethylamine (TEA) in THF. The structure of the OMA monomer was confirmed by ^{1}H NMR **(Figure 2.2)** using CDCl$_3$ as the solvent. The labeled spectra shows the methacrylate peaks at 6.1 ppm (s, 1H, CH_2=C) and 5.57 ppm (s, 1H, CH_2=C), the double bond peak at 5.31 ppm (m, 2H, -CH=CH-) and the methylene protons at 4.31 ppm (m, 4H, -OCH_2CH_2O-).
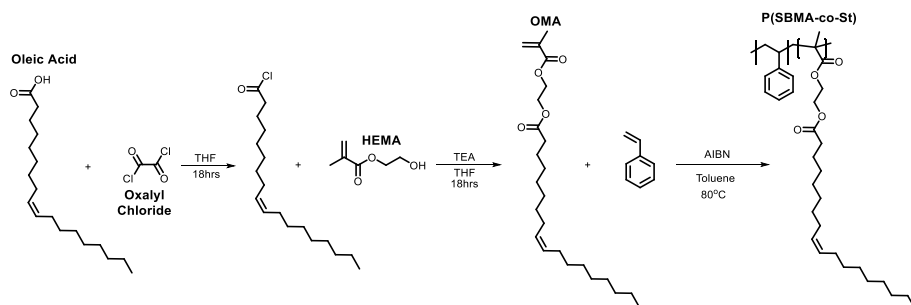

Figure 2.1. Synthetic routes for the OMA monomer and the P(OMA-co-St) copolymers.

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As shown in **Figure 2.1**, the oleic acid based monomer OMA was copolymerized with styrene by free radical polymerization, utilizing OMA as the low T_g soft component and styrene as the high T_g hard component. The polymerizations were conducted at 80 °C using azobisisobutyronitrile (AIBN) as the initiator and dry toluene as the solvent. Keeping the ratio of AIBN as 1 mol% to the monomers, copolymers P(OMA-co-St) were prepared with varied monomers feeding ratios. All the polymerizations could reach high conversion (over 85%). **Table 2.1** outlines the copolymers with varying monomer feeding ratios, actual ratios (mole percent and weight percent), and displays their resulting physical properties (T_g, M_n, and Đ). As expected, the glass transition temperature (T_g) of the copolymers exhibited an apparent dependence on the weight percentage of styrene in the final copolymers. By increasing content of styrene from 11 wt% to 71 wt%, the T_g of copolymers increased from -38 °C to 35 °C accordingly. Conferring to the results from GPC characterization, the molecular weights of the copolymers were in the range of 19-60 K with dispersity values between 1.6 and 1.9. The labeled ^{1}H NMR spectra POMA42$_2$ shows the aromatic region at 7.25-6.25 ppm (br, Ar*H*) from polymerized styrene and the double bond peak from polymerized OMA at 5.35 ppm (br, -C*H*=C*H*-) (**Figure 2.2**).
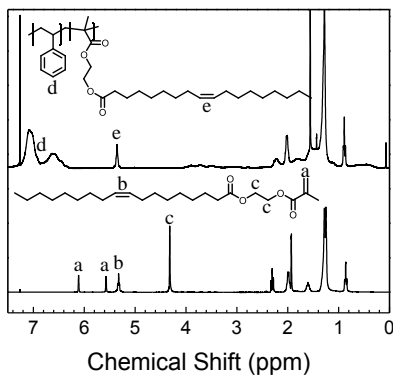

Figure 2.2. ^{1}H NMR of OMA monomer and POMA42$_2$.

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Table 2.1. P(OMA-co-St) copolymers and their physical properties.

Polymer[a]	Feed Ratio OMA:St	Mole Ratio OMA:St[b]	Weight Percent OMA:St[c]	T_g (°C)[d]	$\overline{Mn}$ (g/mol)[e]	Đ[f]	[M]:[I]
POMA89	70:30	68.5:31.5	89.2:10.8	-38.0	60K	1.8	100:1
POMA77	50:50	47.1:52.9	77.1:22.9	-24.0	42K	1.9	100:1
POMA61	30:70	29.1:70.9	60.8:39.2	-14.8	38K	1.7	100:1
POMA52	20:80	21.9:78.1	51.5:48.5	5.0	29K	1.9	100:1
POMA42	15:85	16:84	41.9:58.1	20.5	23K	1.8	100:1
POMA42$_2$	15:85	16.7:83.3	43.1:56.9	20.2	76K	2.8	500:1
POMA29	10:90	9.9:90.1	29.4:70.6	34.6	19K	1.6	100:1

[a] The numbers after "POMA" represent the wt% of POMA in the copolymer. [b,c] Determined by ^{1}H NMR. [d] Measured by DSC. [e,f] Measured by GPC.

POMA42 demonstrates a glass transition temperature around room temperature, which is useful for a thermoset elastomer, but its molecular weight was quite low (23 K). By reducing the content of AIBN to 0.2 mol% of the monomers, a higher molecular weight polymer POMA42$_2$ (76 K) was prepared, while the composition and T_g of the final product were similar to POMA42 (**Table 2.1**). A free standing film was prepared from POMA42$_2$ using a solvent casting method using a concentration of 5% solids, but the resulting film was soft, highly elastic, and showed low mechanical strength. A *cis* internal double bond is present in the OMA side chain of POMA42$_2$, so cross-linking based on the unsaturation was employed to improve the mechanical properties.

Dicumyl peroxide (DCP) is a well-known curing agent that has been used for rubber vulcanization based on a radical mechanism[67-71]. Initial study of P(OMA-co-St) curing process was done with DCP. DCP (8.0 mol% to double bond in the polymer) was dissolved together with POMA42$_2$ in THF and poured into a Teflon mold. After evaporation of the

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solvent, the film was placed in a vacuum oven at 130 °C and allowed to cure for 3 hours. After the curing process, it was apparent that the strength and toughness of the polymer films had increased. Dogbone specimens were cut from the cured film (**Figure 2.3**), and monotonic tensile testing was used to determine the mechanical properties of the crosslinked POMA42$_2$. The result was a thermoset elastomer with a stress at break value of around 1.7 MPa and a strain at break value of 396%.
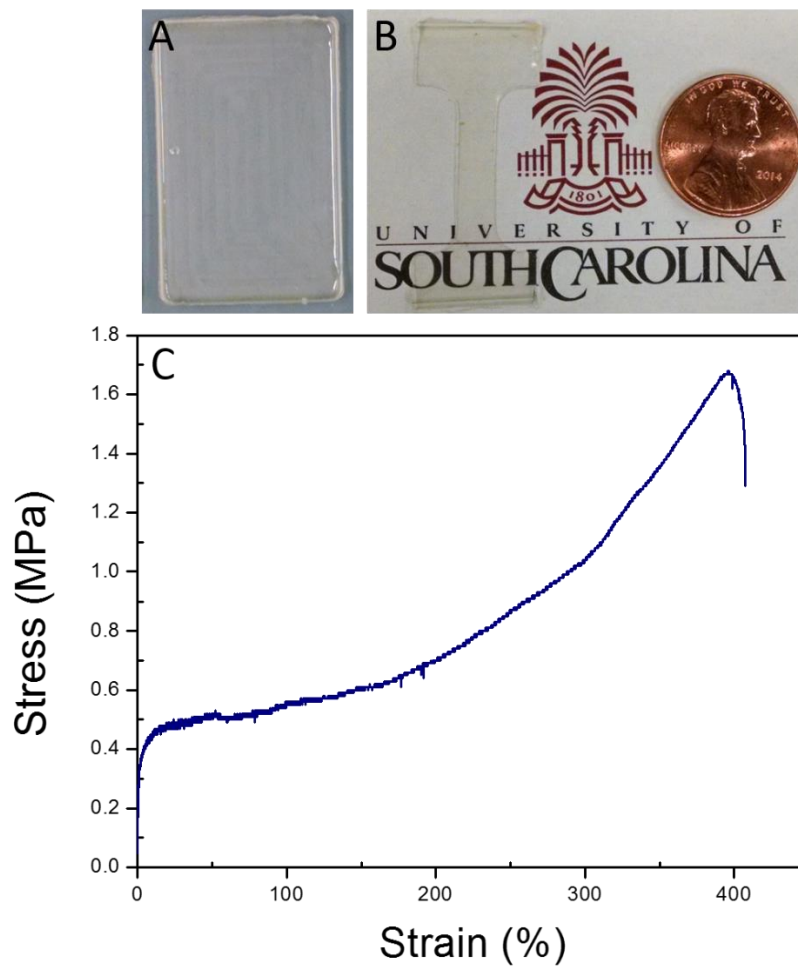

Figure 2.3. (A) Cured POMA42$_2$ film, (B) Dog-bone specimen from cured POMA42$_2$ film, (C) Stress-strain curve for cured POMA42$_2$.

2.4.2 Preparation of soybean oil derived copolymers P(SBMA-co-St)

As discussed above, random copolymers were prepared from an oleic acid derived monomer, and thermoset elastomers were obtained through a curing process based on the unsaturation from OMA using DCP as the thermal curing agent. The developed method served as an initial model study to examine the possibility of making functional materials from plant oil based fatty acids. Since oleic acid is a product that requires a stringent purification process from plant oils, it could be more practical if polymerizable monomers could be derived directly from plant oils. As unsaturation is also present in the fatty acid chains of plant oils, the developed curing process could also be applied to improve the mechanical properties of plant oil based polymers. Facile procedures to make plant oil based polymerizable monomers are critical to expand the developed method.
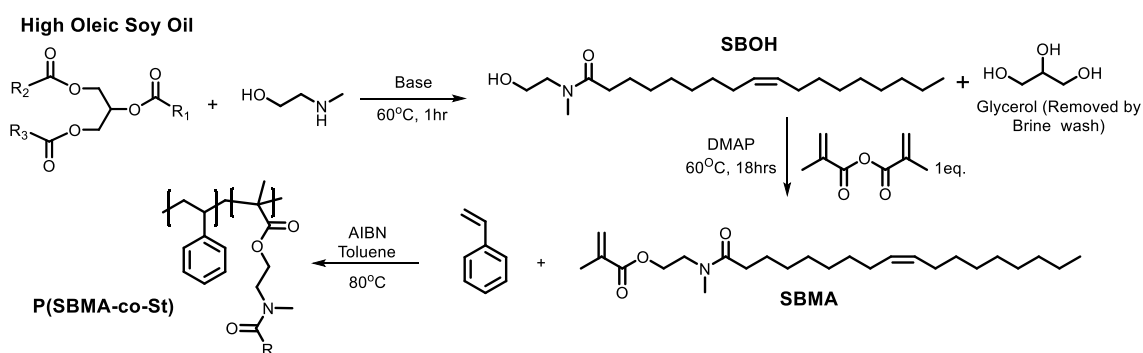
Figure 2.4. Synthetic route for the SBMA monomer and the P(SBMA-co-St) copolymers.

Recently, we reported a highly efficient two-step synthetic route to prepare (meth)acrylate monomers from HOSO. A methacrylate monomer (SBMA) was prepared from HOSO, which gave a homopolymer with a $T_g = -6\ ^{o}C$ after free radical polymerization. As shown in **Figure 2.4**, the monomer preparation involves a base catalyzed amidation of HOSO by 2-(methylamino) ethanol into a *N*-hydroxyalkyl amide (SBOH), which was then

methacrylated with methacrylic anhydride by the aid of catalytic DMAP at 60 °C[18, 46]. Full conversion, as demonstrated by fourier transform infrared spectrometry and ^{1}H NMR (**Figure 2.5B-D**), was obtained for both steps, and purification was done through simple aqueous washing. Since the monomer synthesis is so highly efficient, it shows great promise for scalability. In our current research, the SBOH has been successfully prepared on a 1.9 lb scale using a 2 L reaction vessel and a mechanical stirrer (**Figure 2.6A**). Full conversion was confirmed by IR (**Figure 2.5B**), which shows the appearance of the SBOH hydroxyl stretch, the amide carbonyl stretch, and the disappearance of the HOSO ester carbonyl stretch. After full conversion of HOSO, the product was washed with brine solution in a 3.0 L separation flask with mechanical stirring (**Figure 2.6B**). After stopping the stirrer, clear phase separation could be observed within one hour (**Figure 2.6C**) and the product could be obtained as an orange/brown liquid (**Figure 2.6D**). Subsequently, the preparation of monomer SBMA was done on a 1.0 lb scale with the same instrument. The structures of SBOH and SBMA were confirmed by ^{1}H NMR (**Figure 2.5C&D**). The labeled spectra in **Figure 2.5D** shows peaks for the methacrylate group at 6.1 ppm (s, 1H, C*H$_2$*=C) and 5.57 ppm (s, 1H, CH$_2$=C), the double bond from fatty chains at 5.34 ppm (m, 2H, -C*H*=C*H*-), the methylene next to the ester at 4.29 ppm (m, 2H, -OC*H$_2$*CH$_2$N-), the methylene next to the amide at 3.67 ppm (m, 2H, -OCH$_2$CH$_2$N-), and the methyl protons on the amide group at 2.97 ppm (m, 3H, NC*H$_3$*).

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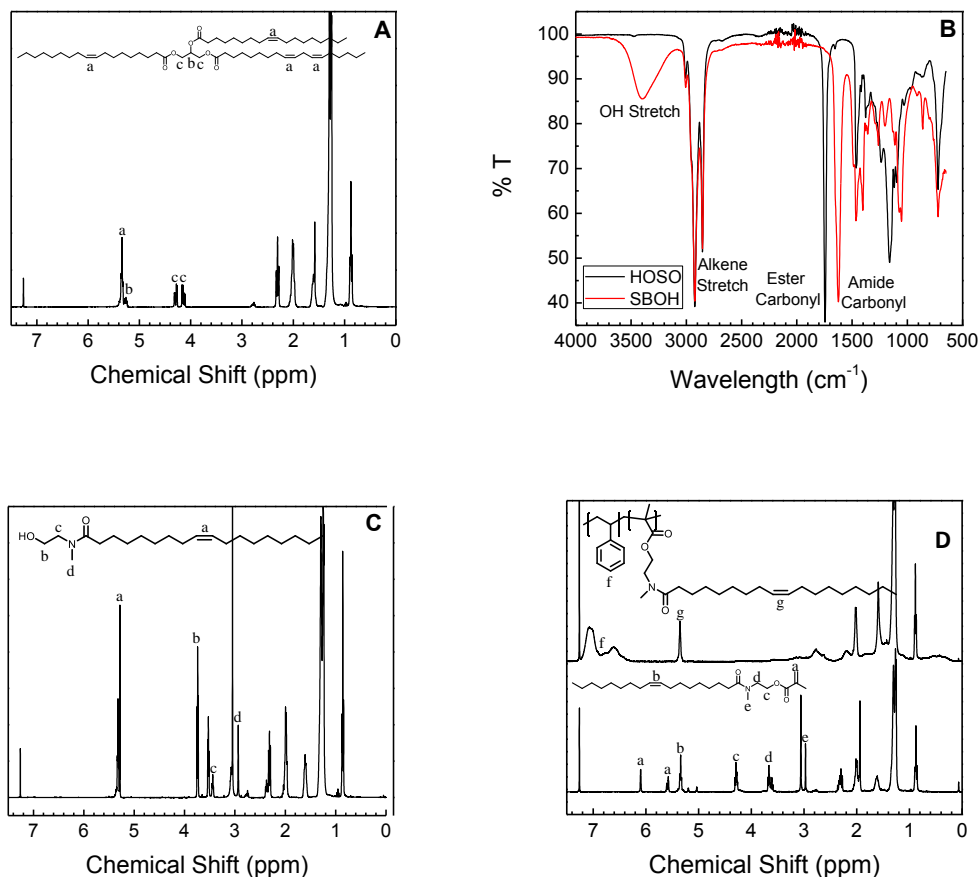**Figure 2.5.** (A) ^{1}H NMR of HOSO, (B) FTIR spectra of HOSO and SBOH, (C) ^{1}H NMR of SBOH, (D)^{1}H NMR spectra of SBMA monomer and PSBMA54.
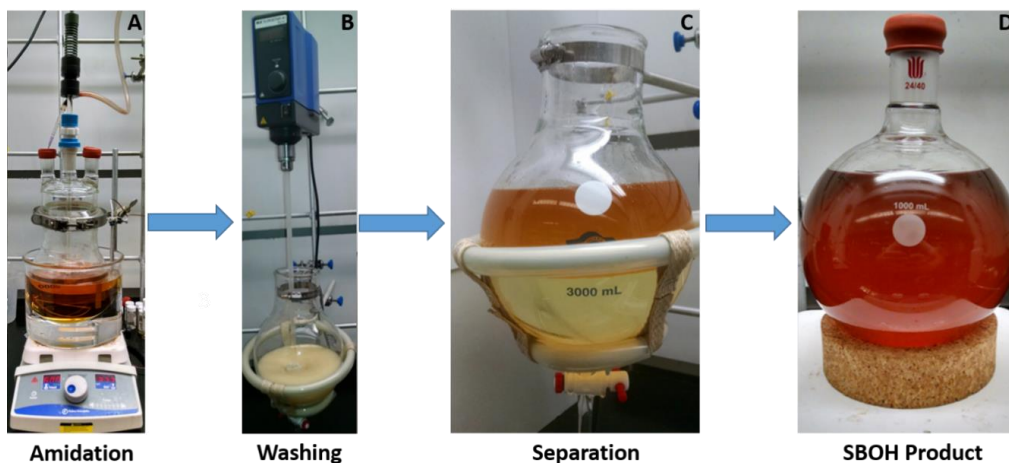

Figure 2.6. (A) Amidation of 1.9 lbs HOSO in a 2.0 L reaction vessel, (B) aqueous washing of SBOH product in a 3.0 L separation flask with mechanical stirring, (C) separation of organic phase from aqueous phase, (D) SBOH product from 1.9 lbs. scale reaction.

After demonstrating the scalable preparation of SBMA, the copolymerization behavior of SBMA with styrene was examined. As shown in **Figure 2.4,** P(SBMA-co-St) copolymers were prepared from SBMA and St using the same method as that in the model study. In P(SBMA-co-St) copolymers, SBMA served as the soft component and styrene served as the hard component. The polymerizations were conducted at 80 °C using AIBN as the initiator and dry toluene as the solvent. Different ratios of SBMA and St were used to obtain a series of copolymers with varied composition. The ^{1}H NMR spectrum of PSBMA54 shows the aromatic region at 7.25-6.25 ppm (br, Ar*H*) from polymerized styrene and the double bond peak from polymerized SBMA at 5.35 ppm (br, C*H*=C*H*-) (**Figure 2.5D**). **Table 2.2** outlines the copolymers with varying monomer feeding ratios, actual ratios (mole percent and weight percent), and displays their resulting physical properties (T_g, M_n, and Đ). GPC was used to characterize the molecular weights and dispersity of the polymer chains (**Figure 2.7A).**

Table 2.2. P(SBMA-co-St) copolymers and their physical properties.

Polymer [a]	Feed Ratio SBMA:St	Mole Ratio SBMA:St[b]	Weight Percent SBMA:St[c]	T_g (°C) [d]	$\overline{M_n}$ (g/mol) [e]	Đ[f]	[M]: [I]
PSBMA100	100:0	100:0	100:0	-6.0	47K	1.83	100:1
PSBMA62	30:70	29.1:70.9	61.6:38.4	3.2	30K	1.76	100:1
PSBMA56	25:75	24.2:75.8	55.5:44.5	6.8	38K	1.72	100:1
PSBMA54	23:77	23.1:76.9	54:46	14.2	79K	1.90	500:1
PSBMA49	20:80	20:80	49.4:50.6	19.9	69K	2.19	500:1
PSBMA45	17:83	17.4:82.6	45.2:54.8	26.4	81K	3.48	500:1

[a] The numbers after "PSBMA" represent the wt% of PSBMA in the copolymer. [b,c] Determined by ^{1}H NMR. [d] Measured by DSC. [e,f] Measured by GPC.
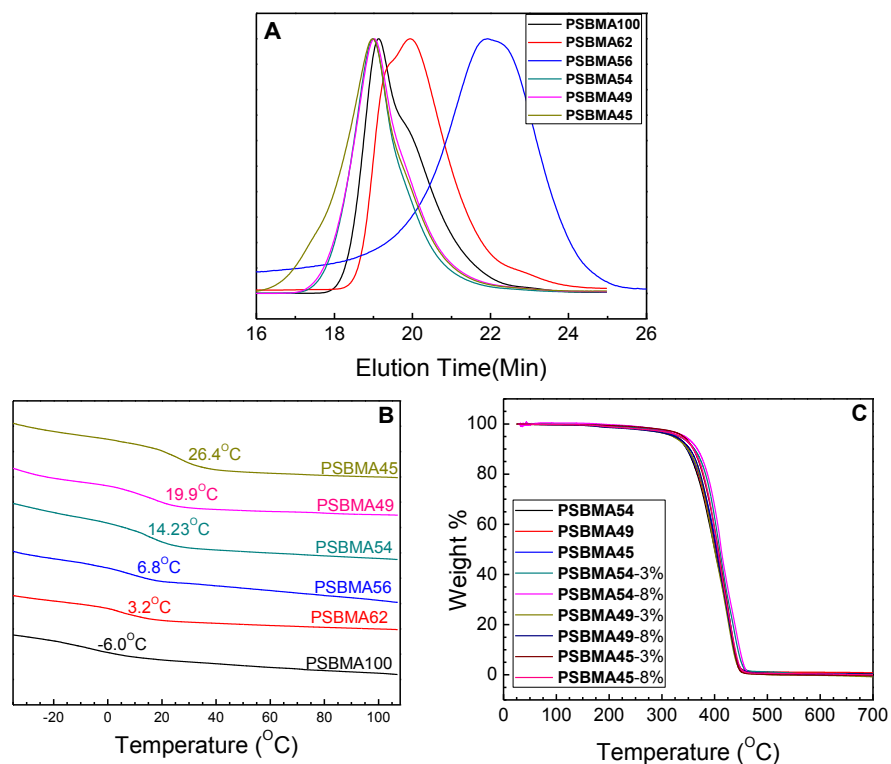
Figure 2.7. (A) GPC traces for P(SBMA-co-St) copolymers, (B) DSC curves for P(SBMA-co-St) copolymers, (C) TGA curves for (un)cured P(SBMA-co-St) copolymers.

Similar to the results in the model study, the T_g of copolymers increased with increasing contents of styrene, as shown by the DSC curves in **Figure2.7B**. All the polymerizations could reach high conversion (over 85%). PSBMA54, PSBMA49, and PSBMA45 were of interest since their glass transition temperatures were close to room temperature. Films of these copolymers were prepared by a solvent casting method in THF using a concentration of 5% solids. The film from PSBMA54 was very soft, showed high elasticity, and low tensile strength. On the other hand, films of PSBMA49 and PSBMA45 showed decent mechanical properties on their own. PSBMA49 showed properties similar to that of thermoplastic elastomers, and PSBMA45 behaved more like a thermoplastic. Decomposition temperatures of the (un)cured polymers were determined using

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thermogravametric analysis (TGA). All of the polymers began to degrade at around 340 °C (**Figure 2.7C**).

2.4.3 Curing experiments of P(SBMA-co-St) copolymers by a solvent assisted method

As in the P(OMA-co-St) copolymers, the P(SBMA-co-St) copolymers have *cis* internal double bonds in the sidechains of the SBMA portion of the copolymers that were used for post polymerization modification. In the case of the P(OMA-co-St) copolymers, the fatty acid side chains were monounsaturated because they were derived from oleic acid. Due to the fatty acid composition in high oleic soybean oil (75% oleic, 7% linoleic, and <3% lenolenic) the P(SBMA-co-St) copolymers included mostly monounsaturated and some diunsatrated/triunsaturated fatty acid sidechains, making these polymers very interesting for curing studies. DCP was used as the curing agent for the crosslinking process, aiming to improve the mechanical properties of the copolymers. Films were prepared by a solvent casting method with the assistance of THF using a concentration of 5% solids, and the films were placed in a vacuum oven for curing after removing all the solvent. Three curing experiments were designed to examine the effect of certain variables on the final mechanical properties of the copolymers. The first experiment was used to demonstrate the effect of the curing agent concentration, the second was to exhibit the effect of the polymer composition, and the last was to show the effect of the curing time. **Table 2.3** shows the parameters and the results of these experiments.

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Table 2.3. Results for the curing experiments of the P (SBMA-co-St) copolymers

Polymer	mol % DCP	Weight % of DCP	Curing Time	Stress at Yield Point	Stress at Break	Strain at Break
PSBMA54	3%	1.2%	3hrs	N/A	1.4 ± 0.1 MPa	$431 \pm 27\%$
PSBMA54	8%	3.0%	3hrs	N/A	2.1 ± 0.1 MPa	$382 \pm 4\%$
PSBMA54	8%	3.0%	4hrs	N/A	2.2 ± 0.1 MPa	$323 \pm 10\%$
PSBMA54	8%	3.0%	5hrs	N/A	2.3 ± 0.04 MPa	$292 \pm 5\%$
PSBMA54	8%	3.0%	6hrs	N/A	3.4 ± 0.04 MPa	$196 \pm 4\%$
PSBMA54	8%	3.0%	9hrs	2.0 MPa	3.6 MPa	176%
PSBMA49	3%	1.2%	3hrs	N/A	2.7 ± 0.1 MPa	$300 \pm 4\%$
PSBMA49	8%	3.0%	3hrs	N/A	3.1 ± 0.1 MPa	$222 \pm 3\%$
PSBMA45	3%	1.2%	3hrs	7.84 ± 0.43 MPa	7.4 ± 0.1 MPa	$220 \pm 5\%$
PSBMA45	8%	3.0%	3hrs	9.6 MPa	7.9 MPa	217%

Effect of curing agent concentration. All variables were held constant except the curing agent concentration. This was done using the PSBMA54 to demonstrate the effect of the curing agent concentration on the final properties. Films containing 3-8 mole% of DCP to the double bond in the SBMA side chain were prepared from the same copolymer. Both samples were cured at 130 °C for 3 hours. The result is shown in **Figure 2.9**. Increasing the curing agent concentration from 3.0% to 8.0% increased the stress at break from $1.4 \pm$ 0.1 MPa to 2.1 ± 0.1 MPa and decreased the strain at break from $431 \pm 27\%$ to $382 \pm 4\%$. This result could be explained by the higher extent of cross-linking in films with more DCP, which would increase the mechanical strength but decrease the flexibility of the polymer chains.

Effect of copolymer compositions. All variables were held constant except the polymer composition. This was done using PSBMA54, PSBMA49, and PSBMA45, which have varying glass transition temperatures. Cured films were prepared using both 3% and 8% DCP for each polymer to validate the effect of the polymer composition on the final properties. All of the samples were cured at 130 °C for three hours. The result is shown in **Figure 2.9**. Increasing the styrene content increased the toughness of the material. Cured PSBMA49 and PSBMA45 gave a higher stress at break and a lower strain at break values than films from cured PSBMA54. As stated previously, the stress and strain at break values for cured PSBMA54 samples with 3-8 mol% curing agent were 1.4 ± 0.1 MPa/$431 \pm 27\%$ and 2.1 ± 0.1 MPa/$382 \pm 4\%$ respectively. The stress and strain at break values for cured PSBMA49 with 3-8 mol% curing agent were 2.7 ± 0.1 MPa /$300 \pm 4\%$ and 3.1 ± 0.1 MPa /$222 \pm 3\%$ respectively. The stress and strain at break values for the cured PSBMA45 with 3-8 mol% of curing agent were 7.4 ± 0.1 MPa /$220 \pm 5\%$ and 7.9 MPa/217% respectively. From the results of the cured PSBMA45, it seems there is a critical point in the styrene content where the properties of cured films transition from a thermoset elastomer behavior to more thermoplastic behavior, resulting in a much higher tensile strength and an observable yield point 7.84 ± 0.43/9.6 MPa).

Dynamic mechanical analysis testing (DMA) was completed for cured PSBMA54 films containing 3-8 mol% of DCP to demonstrate the effect of the curing agent concentration on the storage modulus and glass transition temperature. Cured PSBMA49 and PSBMA45 films containing 8 mol% of DCP were also studied using DMA, validating the effect of the polymer composition on the storage modulus and glass transition temperature. Temperature sweep plots for storage modulus and tanδ are shown in **Figure**

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2.8. From the storage modulus graphs, it can be seen that cured PSBMA54 containing 3 mol% DCP fails above 80 °C, indicated a crosslinking network was not well formed in this sample. However, the other polymer compositions containing 8 mol% DCP held their storage modulus values fairly well up to 200 °C, indicated a well formed crosslinking network. This result can be explained by a higher crosslinking density existing in the samples with a larger amount of DCP. Cured PSBMA54 and PSBMA49 with 8 mol% DCP show higher storage modulus values than that of cured PSBMA45. This is due to the higher PSBMA content in PSBMA54 and PSBMA49. A higher PSBMA content means more reactive double bonds, leading to a higher crosslinking density. From the tanδ graphs it can be seen the curing process lead to an increase in the T_g of the P(SBMA-co-St) copolymers and that both an increase in the curing agent concentration as well as styrene content results in a higher T_g. T_g values for cured PSBMA54 containing 3-8 mol% DCP were 33.6 °C and 35.2 °C respectively. Cured PSBMA49 and PSBMA45 containing 8 mol% DCP showed T_g values of 39.2 °C and 44.5 °C respectively.
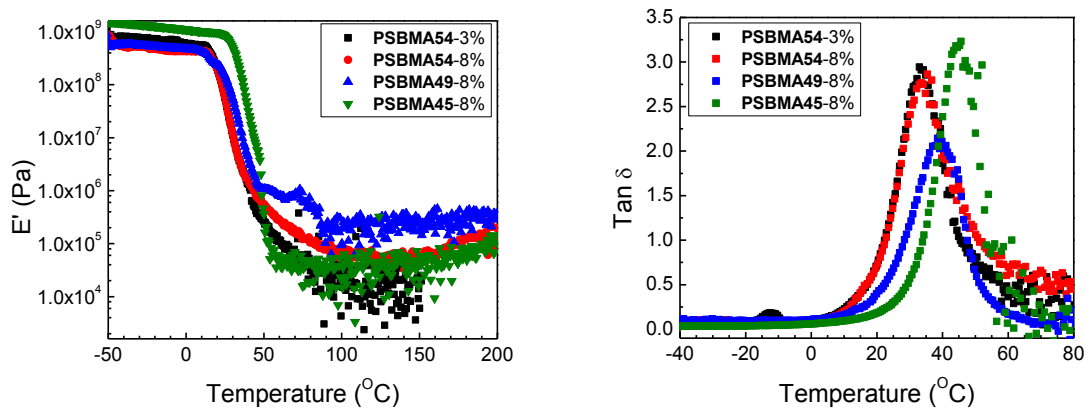

Figure 2.8. (Left) DMA E' curves for cured P(SBMA-co-St) copolymers; (Right) DMA tanδ curves for cured P(SBMA-co-St) copolymers.

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Effect of curing time. All variables were held constant except the curing time. This was done using PSBMA54, demonstrating the effect of the curing time on the final properties. Films containing 8 mol% of DCP to the double bond were prepared and cured for 3, 4 , 5 , 6 , and 9 hours. The result is shown in **Figure 2.9**. Increasing the curing time led to an increase in the stress at break from 2.1 ± 0.1 to 3.6 MPa, and a decrease in the strain at break from $382 \pm 4\%$ to 183%. It can also be noted that after six hours it seems almost all of the curing agent was consumed since there is a minuscule change in tensile properties from a curing time of six to nine hours.
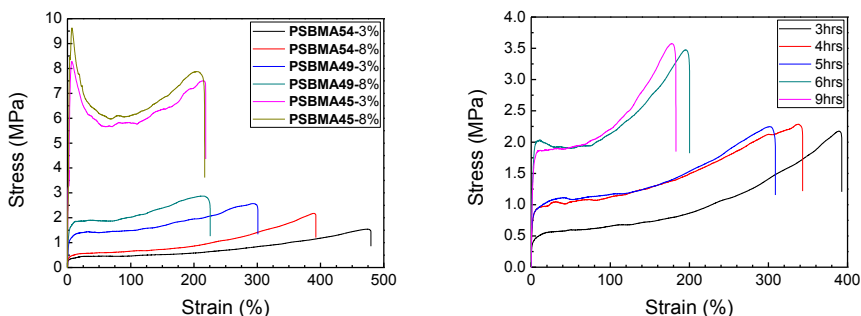
Figure 2.9. (Left) Stress-strain curves for P(SBMA-co-St) copolymers with various curing agent concentrations and different polymer compositions; (Right) different curing times.

2.4.4 Solvent Free Curing Process

From the discussion above, thermoset elastomers derived from the P(SBMA-co-St) copolymers were prepared using a DCP promoted curing process as developed in our oleic acid based model study. Controlling the curing agent ratio, copolymer composition, and curing time provided ideal adjustment over the properties of the cured films. However, THF was used to make DCP containing films before the curing process. To avoid the use of solvent and to make the process more time efficient, another curing process was developed, utilizing a miller and a hot press, shown by **Figure 2.10**. In the first step of the solvent free curing process, the polymer was milled to obtain a flat sheet (**Figure 2.10A**).

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A pocket is then created in the polymer sheet, the curative is added into the pocket, and then folded into the polymer sheet (**Figure 2.10B**). The sheet containing the curative is then milled again to ensure the curing agent is well dispersed throughout the polymer (**Figure 2.10C**). A film of the polymer containing the curing agent was then prepared using a hot press and a metal mold. The curing process was done under vacuum at 130 °C for 3 hours, resulting in the cured film with an average thickness of 0.3 mm (**Figure 2.10D**). PSBMA54 was cured using this process, and as shown from the stress vs. strain plot (**Figure 2.10E)**, the stress at break was about 2.8 ± 0.1 MPa and the strain at break was around $303 \pm 5\%$. Using the solvent free curing process actually results in a higher stress at break and lower strain at break than the solvent casting method. This could be due to the fact that the hot press method was done in an open air environment with temperatures close to 150 °C, which could oxidize the double bond in the side chain of the SBMA portion of the copolymer. The high temperatures could also cause crosslinking to occur during film preparation since the curing agent is present in the milled polymer, leading to the final film having a higher crosslinking density than with similar curing conditions using the solvent casting method, thus higher stress at break values and lower strain at break values. By using this method, cured films can be obtained in hours, compared to days from the solvent casting method and still demonstrate comparable properties.
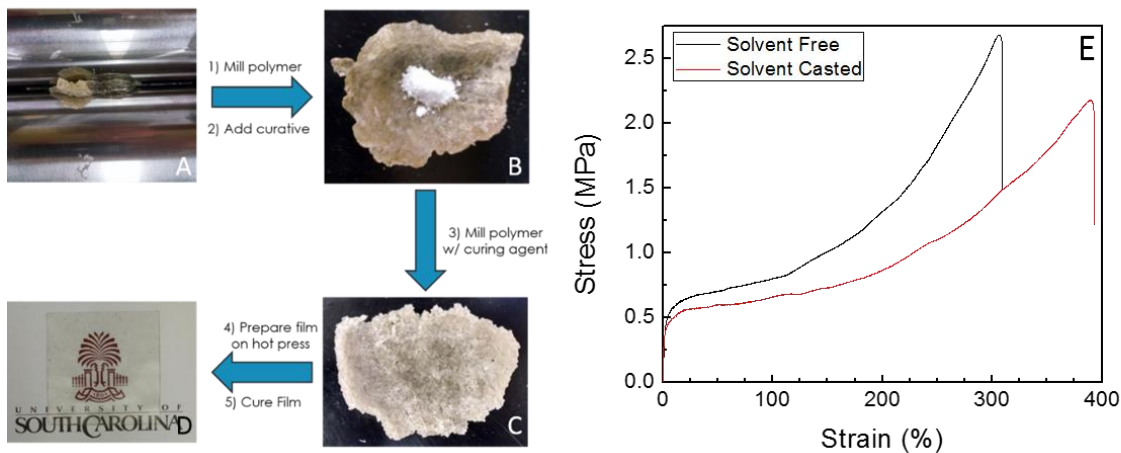
Figure 2.10. (Left) Solvent free curing process and (Right) Stress-strain curves for PSBMA54 cured using the solvent assisted and solvent free process.

2.5 Conclusions

An efficient and scalable strategy was deployed to prepare high oleic soybean oil based monomers and thermoset polymers. The thermoset polymers were prepared using free radical polymerization and styrene was used as a high T_g co-monomer. Solvent assisted and solvent-free curing processes were used to provide some sort of chain entanglement for the polymers to improve their mechanical properties, creating thermoset elastomers. Promising mechanical properties covering elastomers to plastics were achieved using high weight percentages of the SBMA monomer. The mechanical properties could be tuned by adjusting the polymer composition, the curing agent concentration, and the curing time. Comparable properties were observed for polymers cured by either the solvent assisted or the solvent-free methods. This process shows good potential for scalability and could be applied to different plant oils, resulting in industrially useful bio-based materials which could lower the use of petroleum based chemicals in plastics production.

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CHAPTER 3

THERMOPLASTIC ELASTOMERS PRODUCED FROM A NOVEL HIGH OLEIC

SOYBEAN OIL BASED MONOMER

3.1 Abstract

The soybean oil based thermoset elastomers demonstrated promising mechanical properties. The curing process could easily be applied to other vegetable oils, which could lead to a huge impact on lowering the use of petroleum based plastics. However, since these thermoset elastomers are crosslinked polymers, they are not reprocessable. We hypothesized that incorporating hydrogen bonding junctions into soybean oil based polymers could achieve good mechanical properties while maintaining processability, creating thermoplastic elastomers. The polymers were prepared using the soybean based monomer (SBMA) as the rubbery/low T_g monomer and MAA/4VP as both the hydrogen bonding donor/acceptor as well as high T_g co-monomers. Two methods were developed to prepare hydrogen bonding thermoplastic elastomers, one involved a free radical polymerization. The second involved a one pot RAFT polymerization process to create a triblock TPE. The first process resulted in good mechanical properties using high weight percentages of SBMA, with the properties ranging from elastomeric to thermoplastic. The properties were controlled by tuning the polymer compositions. In the second process, a difunctional RAFT agent was synthesized and used to first polymerize SBMA, then sequentially polymerize 4VP and MAA.

3.2 Introduction

Although good mechanical properties could be obtained from the thermoset elastomers by both solvent assisted and solvent free curing methods, thermoset materials suffer from the fact that they are not reprocessable, To overcome this disadvantage, a new polymeric design with the same soybean based monomer was used to create reprocessable thermoplastic elastomers with comparable properties to the thermoset elastomers.

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As previously stated, TPEs prepared from triblock or multigraft polymers undergo microphase separation, giving arise to an ordered morphology. These morphologies allow the formation of reversible physical crosslinks within the hard domains, which play an important role in the mechanical properties of the material. It has been seen that incorporating more crosslinking can increase the tensile strength of the materials, but to keep the material processable, the crosslinking needs to be reversible. One popular method used to achieve this is to incorporate supramolecular interactions, such as hydrogen bonding junctions, into the polymer design. Historically, urethane and urea groups have been commonly used to create hydrogen bonding TPEs[72-74]. More recently the 2-ureido-[1H]-pyrimidin-4-one (UPy) moiety has been extensively studied and used in hydrogen boding TPEs due to its intriguing quadruple hydrogen bonding junction and its higher dimerization free energy[62, 75, 76].

Promising results were obtained from the hydrogen bonding SBMA based thermoplastic elastomer, such as scalability, the use of higher weight percentages of SBMA, higher conversions, reprocessability, and comparable mechanical properties to that of the thermosets. The purpose of using these free radical techniques were their simplicity. As previously stated, controlled radical polymerization techniques can be quite sensitive and involve the use of expensive reagents, where free radical polymerization is the opposite. However, as these hydrogen bonding copolymers were prepared by free radical polymerization, they lack ordered morphologies. Defined morphologies resulting from microphase separation can only be obtained through controlled radical, not free radical techniques, and it has been proven that well defined morphologies play a large role in the mechanical properties of conventional TPEs[17, 20, 58-62]. To meet all of these criteria, a one

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pot process to prepare a hydrogen bonding triblock TPE utilizing RAFT polymerization was designed. It was hypothesized that better microphase separation and ordered morphologies could be obtained. We proposed that having the combination of hydrogen bonding junctions with better microphase separation would lead to better mechanical properties.

3.3 Experimental Section

3.3.1 Materials

High oleic soy oil (Plenish® Dupont), 2-(methylamino) ethanol (99% Sigma-Aldrich), methacrylic anhydride (94% Sigma-Aldrich), sodium methoxide (5.4 M 30 wt.% solution in methanol Sigma-Aldrich), 4-(Dimethylamino) pyridine (99% Sigma-Aldrich), 4-Cyano-4-(phenylcarbonothioylthio) pentanoic acid (97% Strem), 1,8-octanediol (98% Sigma-Aldrich), pivalic anhydride (98% Sigma-Aldrich and methacrylic acid (99% Sigma-Aldrich), were used as received. 4-Vinylpyridine (95% Sigma-Aldrich) was distilled before use. Azobisisobutyronitrile (98% Sigma-Aldrich) was recrystallized from methanol before use. Tetrahydrofuran (THF) and toluene were obtained from dry stills and stored over molecular sieves before use. Teflon molds used for film casting were machined to have the following dimensions: length 2.76 in, width 1.95 in, and depth 0.274 in.

3.3.2 Characterization

^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. Molecular weights and distribution of polymers were determined using gel permeation chromatography (GPC) using a Waters system equipped with a 1525 Binary HPLC pump, a 2414 refractive index detector, and

three Styragel columns (HR1, HR3, HR5E in the effective molecular weight range of 100–5 K, 500–3 0K, and 2 K–4 M, respectively) with HPLC grade THF as the eluent at 35 °C and a flow rate of 1.0 mL per minute. GPC samples were prepared by dissolving the sample in THF with a concentration of 5.0 mg/mL. The dissolved samples were filtered through microfilters with a pore size of 0.2 μm (Teflon, 17 mm Syringes Filters, National Scientific, USA). The columns were calibrated against polystyrene standards. Fourier transform infrared spectrometry (FTIR) spectra were taken on a PerkinElmer spectrum 100 FTIR spectrometer. The glass transition temperature (T_g) of polymers was observed through differential scanning calorimetry (DSC) conducted on a DSC Q2000 (TA instruments). The samples were heated from 25 °C to 200 °C at a rate of 10 °C per minute, cooled to -50 °C at a rate of 10 °C per minute, and then heated to 200 °C at a rate of 10 °C per minute. Data was obtained from the 3rd cycle. The average sample mass was 10mg and the nitrogen flow rate was 50mL per minute. Tensile testing (stress-strain) was performed on an Instron 5543A. Dumbbell samples with a length of 22 mm and a width of 5 mm were cut from the casted films. The films were tested at room temperature with an extension rate of 20 mm per minute.

3.3.3 Synthetic methods

Copolymerization of SBMA, MAA, and 4VP. 4-Vinylpyridine was distilled by vacuum distillation before use. The following procedure was used to prepare PSBMA93, to prepare different polymer ratios, the same procedure was followed, changing the feed ratios accordingly. SBMA (2 g, 0.0049 mol), MAA (0.0423 g, 4.91×10^{-4} mol), 4VP (0.0516 g, 4.91×10^{-4} mol), azobisisobutyronitrile (9.66 mg, $5.89 \times 10 \times 10^{-5}$ mol), and 2 mL of toluene were added to a 10 mL schlenk flask. The contents were purged with nitrogen for 20

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minutes, heated to 80 °C, and allowed to react for 12 hours. The crude polymer solution was then diluted with 4 mL of THF, and precipitated twice in cold methanol to remove the unreacted monomers from the polymer. The methanol was then decanted, and the polymer was concentrated on a rotary evaporator and dried under vacuum.

Preparation of difunctional RAFT agent (DiRAFT). 4-Cyano-4-(phenylcarbonothioylthio) pentanoic acid (1 g, 0.0036 mol), 1,8 octanediol (0.25 g, 0.0017 mol), pivalic anhydride (0.67 g, 0.0036 mol) were added to a 4 mL reaction vessel and dissolved in 2.4 mL of THF. The contents were placed in an oil bath at 60 °C and allowed to react until full conversion was obtained. The crude product was concentrated on a rotary evaporator, purified by silica gel chromatography, and dried under vacuum to afford a sticky pink product. ^{1}H NMR (CDCl$_2$): 7.90 ppm (d, 4H, ArH); 7.57 ppm (t, 2H, ArH); 7.39 ppm (t, 4H, ArH); 4.10 ppm (m, 4H, -OCH_2-).

One pot hydrogen bonding triblock TPE by RAFT. In a 25 mL schlenk flask SBMA (3 g, 0.0074 mol), DiRAFT (49.3 mg, 7.36×10^{-5} mol), AIBN (3.6 mg, 2.21×10^{-5} mol), and 3 mL of toluene were added. Oxygen was removed from the flask by three freeze-pump-thaw cycles and then the flask was backfilled with nitrogen. In a separate flask, MAA (0.9 g, 0.0105 mol), 4VP (1.1 g, 0.0105 mol), AIBN (2 mg, 1.22×10^{-5} mol), and 2 mL THF were added. Oxygen was removed from this flask by the same way. The flask containing the SBMA was placed in an oil bath at 80 °C and reached 90% conversion in 17 hours. The contents from the other flask were then added to the flask containing the polymerized SBMA under nitrogen, allowed to react at 80 °C, and reached 70% conversion in 9 hours. The crude polymer solution was then diluted with 6 mL of THF and precipitated twice from cold methanol to remove the unreacted monomers from the polymer. The methanol

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was then decanted, and the polymer was concentrated on a rotary evaporator and dried under vacuum.

3.4 Results and Discussion

3.4.1 Hydrogen bonding SBMA based thermoplastic elastomer

One big advantage that the thermoset polymers possessed was that they were very simple to prepare. The new polymeric design includes both advantages of simplicity and reprocessability. We hypothesized that incorporating hydrogen bonding interactions into a soybean based random copolymer could introduce physical crosslinking, leading to good mechanical properties. For the random copolymer, a soft/rubbery low T_g component and a tough/rigid high T_g component are needed. The SBMA monomer was used as the soft/rubbery component due to t low T_g when polymerized, but it does not include any hydrogen bonding donor or acceptor groups. It is well known that carboxylic acid and pyridine groups can self-assemble to form hydrogen bonding networks and this idea has been utilized in the polymer field[77-82]. Methacrylic acid (MAA) and 4-vinyl pyridine (4VP) can undergo the same self-assembly to form hydrogen bonding junctions. They also have T_g values of 228 °C and 142 °C respectively when polymerized, making them good choices for both a hydrogen bond donor/acceptor groups and as hard/rigid components. **Figure 3.1** outlines the synthetic route for the hydrogen bonding thermoplastic elastomers.
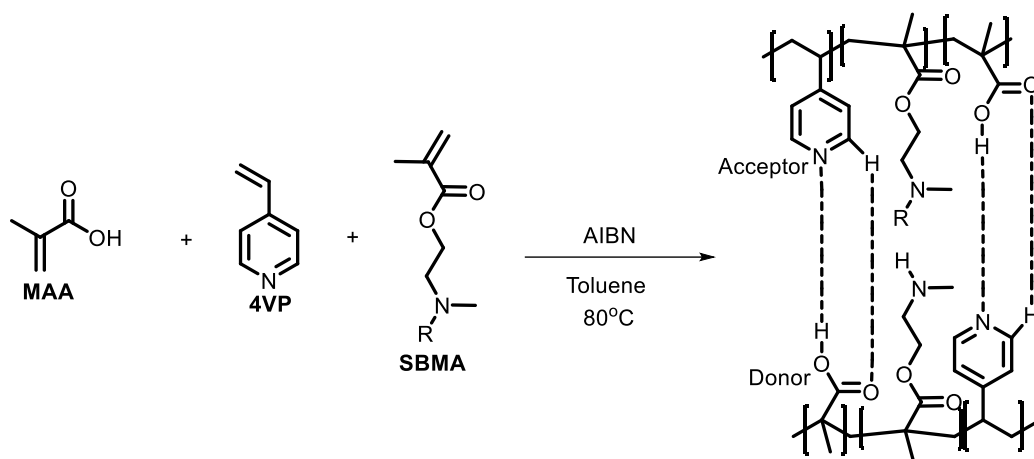
Figure 3.1. Synthetic route for hydrogen bonding thermoplastic elastomers.

The polymerizations were conducted at 80 °C using AIBN as the initiator and dry toluene as the solvent with a molar ratio of monomers to AIBN at 100:1. Different polymer compositions were prepared using different feed ratios of MAA, 4VP, and SBMA. It was observed that the polymerizations of the hydrogen bonded copolymers could reach higher conversions in a shorter time than that of the random copolymers for the thermoset elastomers (**Figure 3.2A**). The ^{1}H NMR spectra shows the monomers could nearly reach full conversion, with the vinyl peaks from 4VP and the methacrylate peaks from both methacrylic acid and SBMA almost completely disappearing after 12 hours. **Table 3.1** displays the weight percentages of the hydrogen bonded copolymers and their resulting physical properties (T_g, M_n, and Đ). DSC and GPC were used to characterize the glass transition temperatures, molecular weight, and dispersity of the polymer chains (**Figure 3.2B&C**).

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Table 3.1. P(SBMA-co-MAA-co-4VP) copolymers and their physical properties

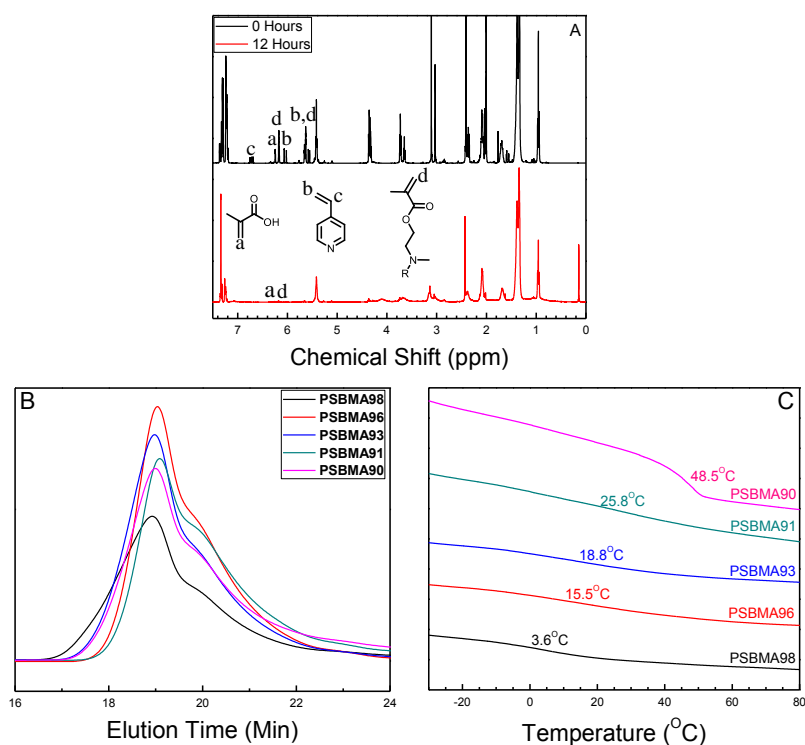| Polymer	Weight Percent of SBMA1	Weight Percent of MAA	Weight Percent of 4VP	T_g (°C)	$\overline{Mn}$ (g/mol)	$Đ^f$
PSBMA98	97.8%	1.0%	1.3%	3.6	64K	3.3
PSBMA96	95.5%	2.0%	2.5%	15.1	51K	2.1
PSBMA93	93.4%	3.0%	3.6%	18.8	58K	2.5
PSBMA91	91.4%	3.9%	4.7%	26.6	62K	2.4
PSBMA90	89.5%	4.7%	5.8%	48.5	41K	3.2

Figure 3.2. (A) ¹HNMR spectra, (B) GPC traces, (C) DSC curves for P(SBMA-co-MAA-co-4VP) copolymers.

As seen in **Figure 3.2**, the glass transitions for the PSBMA98, PSBMA96,

PSBMA93, and PSBMA91 copolymers were very broad and not easily observable, where

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the transition from the PSBMA90 copolymer was very sharp. The glass transition of the PSBMA homopolymer is fairly broad, and the change of polymer compositions by adding two co-monomers with hydrogen bonding junctions led to a broader transition. The shaper transition of the PSBMA90 copolymer could result from the higher ratio of MAA/4VP leading to some degree of phase separation. The T_g values were calculated as seen in the DSC curves in **Figure 3.2C**, and as expected, the T_g of copolymers increased with increasing contents of 4VP and MAA. PSBMA93 and PSBMA91 were of interest for use as a TPE since their glass transition temperatures were close to room temperature. PSBMA90 was of interest for use as a thermoplastic because of its higher T_g of 48.5 °C. Films of these copolymers were prepared by a solvent casting method in THF using a concentration of 5% solids. Some of the uncured P(SBMA-co-St) films discussed in section **2.4.2** were highly elastic, but soft and tacky. The P(SBMA-co-4VP-co-MAA) films also showed high flexibility and elasticity, but unlike the P(SBMA-co-St), were not as soft or tacky.   The mechanical properties of PSBMA93, PSBMA91, and PSBMA90 were determined using monotonic tensile testing. Properties ranging from elastomeric to soft thermoplastics could be obtained by tuning the copolymer compositions. **Table 3.2** shows the results of the tensile testing, and **Figure 3.3** shows the stress vs strain curves for these hydrogen-bonding copolymers. These copolymers exhibit comparable properties and many advantages over those of the thermoset elastomers. The polymerizations can reach higher conversions in a shorter time (85% in 18 hours vs ≈100% in 12 hours) and obtain comparable properties while using a higher weight percentage of the SBMA1 monomer (54-45 wt% vs 90-93 wt%).

Table 3.2. Results for the tensile testing of P(SBMA-co-MAA-co-4VP) copolymers.

Polymer	Stress at Yield Point	Stress at Break	Strain at Break
PSBMA93	N/A	1.7 ± 0.1 MPa	502 ± 11%
PSBMA91	2.1 ± 0.1 MPa	2.5 ± 0.1 MPa	277 ± 16%
PSBMA90	3.9 ± 0.2 MPa	3.2 ± 0.1 MPa	175 ± 22%

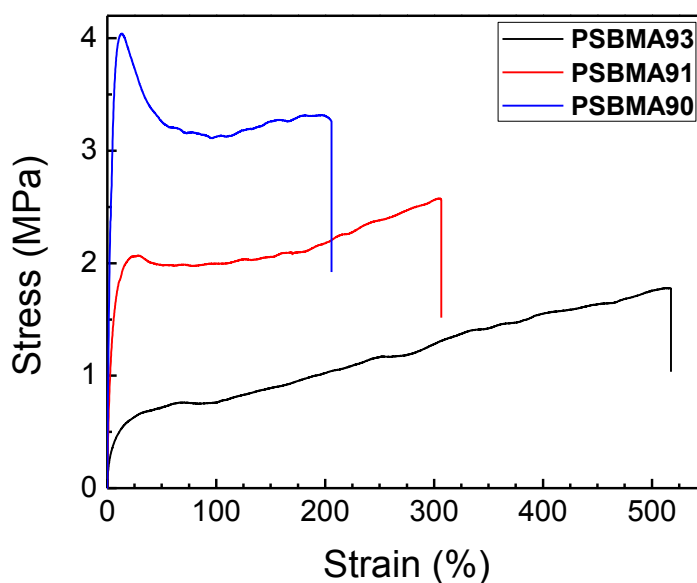**Figure 3.3.** Stress-strain curves of P(SBMA-co-MAA-co-4VP) copolymers with different polymer compositions.

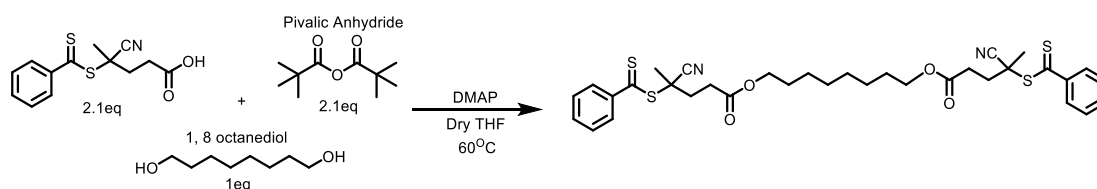### 3.4.2 One pot hydrogen bonded SBMA based triblock thermoplastic elastomer by RAFT

Figure 3.4. Synthetic route of a difuctional RAFT agent.

To synthesize a TPE by a one pot method, a difunctional RAFT agent is used to first polymerize the rubbery midblock so that the midblock can also be used as a macro

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chain transfer agent to sequentially polymerize the outside blocks. It is also necessary for the RAFT agent to be a good chain transfer agent for all of the monomers involved in preparing the triblock TPE. 4-Cyano-4-(phenylcarbonothioylthio) pentanoic acid is a common CTA used to polymerize styrenes, methacrylates, and methacrylamides, meaning it is a suitable CTA for SBMA, MAA, and 4VP. Also, it contains a carboxylic acid, which can be used to easily synthesize a difunctional RAFT agent (DiRAFT). As shown in **Figure 3.4**, the synthesis of DiRAFT involves a one-step esterification reaction using 1, 8 octanediol as the linker, pivalic anhydride as an electrophile to promote the esterification, DMAP as a catalyst, and dry THF as a solvent. As demonstrated by the ^{1}H NMR spectra in **Figure 3.5**, full conversion was obtained after reacting at 60 °C for 18 hours. **Figure 3.5** shows that after completion, the CH_2OH peaks from the 1,8-octanediol at 3.7 ppm completely disappeared and a new ester peak signifying the formation of the DiRAFT appeared at around 4.0 ppm. The product was purified by silica gel column chromatography and the structure was confirmed by ^{1}H NMR and gas probe mass spectrometry (Probe-MS). The ^{1}H NMR in **Figure 3.5** shows the ratio of the ester peaks to the aromatic peaks at 5:2 which confirms a successful reaction.
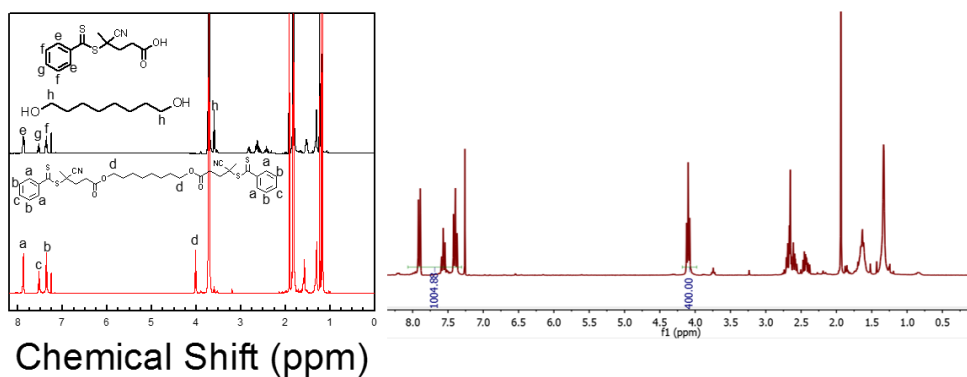

Figure 3.5. (Left) ^{1}HNMR of starting material and crude DiRAFT, (Right) ^{1}HNMR of purified DiRAFT with integrations.

After demonstrating the successful synthesis of DiRAFT, the next step was the one pot triblock copolymer synthesis. As shown in **Figure 3.6,** the triblock was prepared by first polymerizing SBMA using DiRAFT, then adding in MAA and 4VP while the reaction was still in a living condition, resulting in a hydrogen bonded pseudo triblock copolymer. The polymerizations were conducted at 80 °C using AIBN as the initiator and dry toluene as the solvent. The feed ratios were 40wt% MAA/4VP and 60 wt% SBMA. We assumed 40 wt% of the hard monomers would be too high, but wanted to use this overestimate as a starting point and to help determine what weight percentage would be best for the desired properties. The ^{1}H NMR spectra shown in **Figure 3.7** shows that ≈91% conversion of SBMA was reached in 16 hours, before feeding in MAA and 4VP, which attained ≈70% and ≈72% conversion in 9 hours respectively. The crude polymer was dissolved in THF and purified by precipitation in methanol and dried under vacuum for 24 hours.
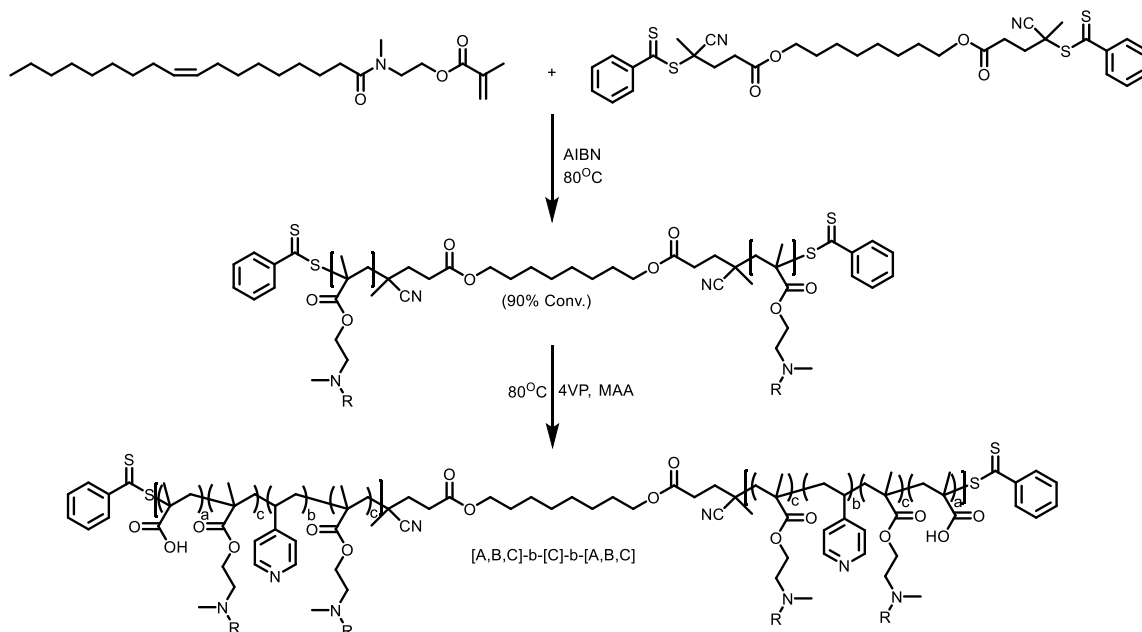

Figure 3.6. Synthetic route for one pot hydrogen bonding triblock TPE by RAFT polymerization.
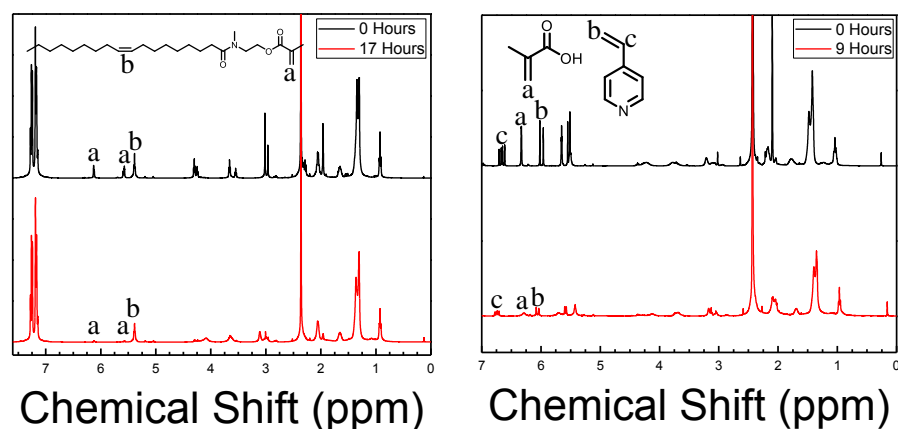
Figure 3.7. (Left) ^{1}HNMR showing conversion of SBMA, (Right) ^{1}HNMR showing conversion of MAA and 4VP.

After drying the polymer, it was only partially soluble in common organic solvents such as DCM, chloroform, THF, DMF, toluene, etc. This is demonstrated by **Figure 3.8B**, where the polymer forms a very cloudy solution in THF. The solubility issue could be a result of the high weight percentages of MAA and 4VP, resulting in very strong hydrogen bonding interactions, leading to a low solubility. Because of this, GPC could not be taken, but the theoretical molecular weights, according to the ^{1}HNMR conversion values were 37 K for the middle block (SBMA) and 10.5 K for the outside blocks (4VP/MAA/SBMA). Since a one pot method was used, the middle block was not purified before feeding in the 4VP and MAA monomers. 91% conversion of SBMA was achieved for the middle block, meaning 9% of the SBMA monomers were left when the MAA and 4VP was added. This means that the outside blocks contain a small weight percentage (6%) of SBMA. The weight percentage of 4VP and MAA in the triblock copolymer was calculated to be 33.3%. DSC was used to determine the T_g of the polymer and is shown in **Figure 3.8A**. Two T_g values were observed, which is indicative of microphase separation, but other methods such as SAXS and AFM are still needed to confirm any microphase separation or ordered

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morphologies. The transition for the soft SBMA phase was broad and not immediately observable, but was calculated to be 4.43 °C. The T_g for the hard phase was a fairly sharp transition and was calculated to be 203.95 °C. Since 6 wt% of SBMA was incorporated into the outside blocks, SBMA and 4VP could lower the T_g of MAA, so the T_g value of 203.95 °C for the outside block is plausible.
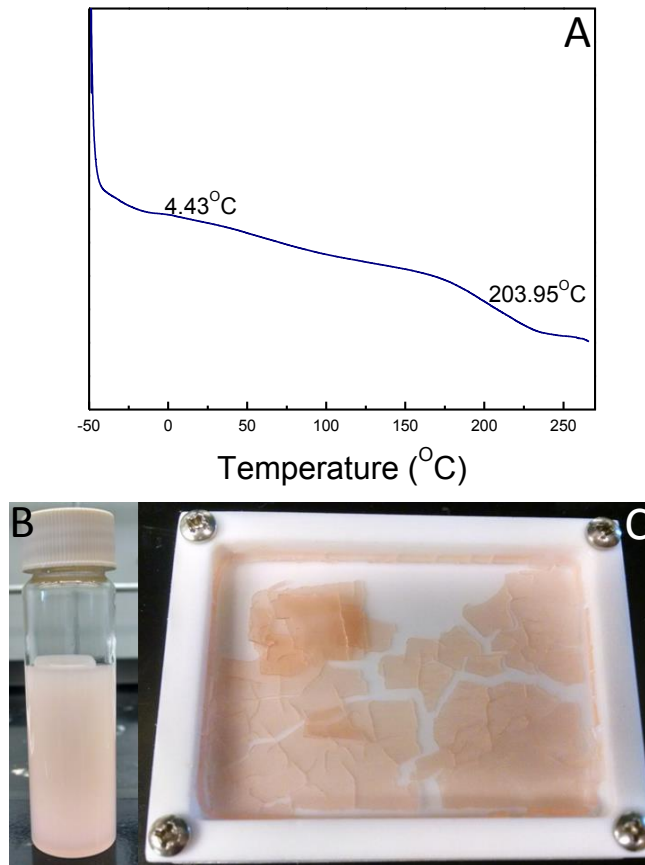
Figure 3.8 (A) DSC curve for the triblock, (B) Attempt to dissolve triblock in THF, (C) cracked film of triblock.

We attempted to make a film of the triblock hydrogen bonded TPE using a solvent casting method using a concentration of 5% solids, but the low solubility of the polymer caused difficulties. As seen in **Figure 3.8C**, instead of a uniform film, pieces of a polymer film were obtained. It is possible that a film did not form due to the solubility issue. The

midblock is soluble in THF, but since the outer blocks have a high amount of hydrogen boding, they may not be as soluble. The midblock of the polymer may have dissolved, while the outer blocks aggregated, leading to a micelle formation with a core/shell structure. When the solvent evaporated, the different phases may still have strong aggregation, causing the film to crack.

3.5 Conclusions

The thermoset elastomers showed encouraging properties, but suffered from the fact that they were not reprocessable. To overcome this, the same high oleic soybean oil based monomer was used to create reprocessable TPEs. These TPEs incorporated hydrogen bonding junctions to help improve the mechanical properties. These polymers were prepared by free radical polymerization using 4VP and MAA as the hydrogen bonding donor/acceptor groups as well as high T_g co-monomers. The synthesis of the hydrogen bonded copolymers was efficient than that of the thermoset polymers, reaching almost full conversion in just 12 hours. The hydrogen bonded copolymers incorporated much higher weight percentages of the SBMA monomer while still achieving comparable mechanical properties, ranging from elastomers to thermoplastics, without needed a curing process. The properties could be tuned by adjusting the polymer compositions. PSBMA has a T_g of -6 °C, which is fairly high for a polymer that is used as a soft/rubber phase. In the future, a lower T_g soybean based monomer could be used which may result in better mechanical properties and TPE behavior.

Both thermoset polymers and hydrogen bonded polymers prepared from SBMA were prepared by free radical polymerization. Both processes were very simple, but not well controlled and ordered morphologies cannot be achieved by using free radical

polymerization. In order to achieve better microphase separation and an ordered morphology while maintaining simplicity, a one pot RAFT process was developed to create hydrogen bonded triblock TPEs. A difunctional RAFT agent (DiRAFT) was successfully synthesized and used for the polymerization. Since the midblock was not purified before the addition of the other monomers, a small amount of SBMA monomer was also incorporated into the outside blocks. A polymer containing 33.3 wt% 4VP and MAA was prepared. Because of the strong hydrogen bonding due to the relatively high weight percentage of the donor/acceptor monomers, the polymer was not fully soluble in common organic solvents. A weight fraction of 33.3% of the hard phase meant that TPE properties could not be obtained, but this polymer could serve to help estimate what the weight fraction should be to get the desired properties. The synthesis of the DiRAFT and the preliminary data for this project shows promise. In the future, more compositions of the triblock copolymers that incorporate lower weight percentages of 4VP and MAA should be prepared. Also, a lower T_g soybean based monomer could be used as the midblock to create an array of polymer compositions and the mechanical properties of these compositions and the SBMA compositions could be compared.

CHAPTER 4

SUMMARY AND OUTLOOK

In this thesis, two major research goals were achieved. First, renewable soybean oil based thermoset elastomers with promising mechanical properties were prepared. This involved developing an efficient, solvent free, and scalable monomer synthesis, a simple polymerization process, and two effective curing processes, one being solvent assisted and one solvent free. An array of polymer compositions were prepared using free radical polymerization to co-polymerize the soft and rubbery SBMA monomer with the hard styrene monomer. The curing processes were used to increase the mechanical properties of the polymers. The properties could be tuned by the polymer composition, the curing agent concentration, and the curing time. Mechanical properties, ranging from elastomeric to thermoplastic, were achieved using high weight percentages of the SBMA monomer, The developed monomer synthesis and curing process could be applied to other vegetable oils, seeing applications in packaging, fabrics, the clothing industry, and rubber materials, resulting in lowering the use of petroleum based plastics.

Second, sustainable soybean oil based thermoplastic elastomers incorporating hydrogen bonding junctions were prepared. This entailed using free radical polymerization to prepare different compositions using the same SBMA monomer and the 4VP and MAA co-monomers. The SBMA acted as the soft and rubbery component, while the 4VP and MAA acted as the hydrogen bonding donor/acceptor junctions as well as hard components. Properties ranging from elastomeric to thermoplastic were achieved. The hydrogen bonded TPEs exhibited comparable mechanical properties to the thermoset elastomers while attaining higher monomer conversion in a shorter time, using higher weight percentages of SBMA, and remaining reprocessable. This process is also scalable, and potential applications include packaging, fabrics, the clothing industry, rubber materials, etc.

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However, microphase separation and ordered morphology cannot be obtained using free radical polymerization. To overcome this, a one pot RAFT polymerization method was developed to synthesize SBMA, 4VP, and MAA containing triblock copolymers. This involved synthesizing a difunctional RAFT agent to use in the one pot process. SBMA was polymerized by the difucntional RAFT agent, to act as a rubbery midblock as well as a macro chain transfer agent. 4VP and MAA were then sequentially polymerized as the outside blocks, acting as the hydrogen bonding donor/acceptor junctions as well as the hard components. A 33.3wt% 4VP/MAA triblock was prepared, assuming this weight percentage of the hard monomers would be too high and that this overestimate could be used as a starting point and to help determine which weight percentage would be best for the desired properties.

Due to the desire to change our dependence on fossil fuels, research in renewable bio-based polymer materials has been gaining a lot of momentum in the last decade and will keep growing in the future. Soybean based polymers are relatively new and represent a growing field. Though not many useful polymers prepared from soybean oil currently exist, the field will continue to grow because of its potential impact. Soybeans are very abundant, and the annual amount of soybeans produced continues to grow, meaning they are a good candidate to be used as a bio-based feedstock. The chemical structure of soybean oil is very intriguing due to its triglyceride and unsaturation. These functional groups can be continually used to develop new strategies to create useful monomers. Highly efficient and scalable synthetic routes that require simple purification processes are preferred. The SBMA based thermoset elastomers are an example of how a simple and scalable process can be used to take a sustainable resource and develop new polymeric materials with useful

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properties. Our highly efficient and scalable methodology to create soybean based monomers and thermoset polymers can be applied to other vegetable oils and has the potential to make a huge impact. In future research, the developed monomer synthesis and curing process could be used on other vegetable oils, allowing us to maximize the use of renewable resources for polymeric materials.

The hydrogen bonded TPEs show much promise, but more work is needed. TGA, DMA, and SAXS data should be collected for the copolymers prepared by free radical polymerization. For the one pot triblock TPE, lower weight percentages of 4VP and MAA should be tried to obtain a TPE with good mechanical properties. An array of polymer compositions should be prepared. After preparing the different polymer compositions, their properties should be compared by collecting data using GPC, DSC, TGA, tensile testing, and DMA. SAXS, SEM, TEM, and AFM should be used to confirm phase separation and to observe if any ordered morphologies were obtained. Incorporating the hydrogen bonding junctions did improve the mechanical properties, and this method could be applied to other vegetable oil based polymers. This hydrogen bonding method could effectively be used to counteract the low chain entanglement issues that are present in plant oil based polymers. In future research, a soybean based monomer with a lower T_g could be used in the same process. We have previously prepared a soybean oil based acrylate monomer (SBA) which has a lower T_g (-30°C) than the SBMA monomer (-6°C). This lower T_g could result in materials with better mechanical properties, including flexibility and elongation. The same free radical polymerization process used for SMBA, 4VP, and MAA could be carried out using SBA, 4VP and acrylic acid (AA), resulting in an SBA based hydrogen bonding TPE. This SBA monomer could also be used to replace SBMA in the one pot triblock copolymer.

2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid could be used to prepare a difunctional RAFT agent to polymerize SBA using the same synthetic process used currently. AA and 4VP could then be sequentially polymerized using the PSBA as a macro chain transfer agent, resulting in SBA based triblock copolymers with the potential to possess better mechanical properties.

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REFERENCES

1.   Okada, M. Chemical syntheses of biodegradable polymers. *Prog. in Polymer Science.* **2002,** *27*, 87-133.

2.   Ragauskas, A., ; Williams,C.; Davison, B.; Britovsek, G.; Cairney, J.; Eckert, C.; Frederick, W.; Hallet, J.; Leak, D.; Liotta, C.; Mielenz, J.; Templer, R.; Tschaplinski, T. The Path Forward for Biofuels and Biomaterials. *Science.* **2006,** *311*, 484-489.

3.   Wilbon, P. A.; Chu, F.; Tang, C. Progress in Renewable Polymers from Natural Terpenes, Terpenoids, and Rosin. *Macromol. Rapid Commun.* **2013,** *34*, 8-37.

4.   Williams, C. K.; Hillmyer, M. A. Polymers from Renewable Resources: A Perspective for a Special Issue of Polymer Reviews. *Polymer Reviews.* **2008,** *48*, 1-10.

5.   Yao, K.; Tang, C. Controlled Polymerization of Next-Generation Renewable Monomers and Beyond. *Macromolecules.* **2013,** *46*, 1689-1712.

6.   Kalita, H.; Selvakumar, S.; Jayasooriyamu, A.; Fernando, S.; Samanta, S.; Bahr, J.; Alam, S.; Sibi, M.; Vold, J.; Ulven, C.; Chisholm, B. J. Bio-based poly(vinyl ether)s and their application as alkyd-type surface coatings. *Green Chem.* **2014,** *16*, 1974-1986.

7.   Dodds, D. R.; Gross, R. A. Chemicals from Biomass. *Science.* **2007,** *318*, 1250-1251.

8.   Balandrin, M. F.; Klocke, J. A.; Wurtele, E. S.; Bollinger, W. H. Natural plant chemicals: sources of industrial and medicinal materials. *Science.* **1985,** *228*, 1154-1160.

9.   Biermann, U.; Friedt, W.; Lang, S.; Lühs, W.; Machmüller, G.; Metzger, J. O.; Rüsch gen. Klaas, M.; Schäfer, H. J.; Schneider, M. P. New Syntheses with Oils and Fats as Renewable Raw Materials for the Chemical Industry. *Angewandte Chemie International Edition.* **2000,** *39*, 2206-2224.

10.   Coates, G. W.; Hillmyer, M. A. A Virtual Issue of Macromolecules: "Polymers from Renewable Resources". *Macromolecules.* **2009,** *42*, 7987-7989.

11.   Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chemical Reviews.* **2007,** *107*, 2411-2502.

12.   Mecking, S. Nature or Petrochemistry?—Biologically Degradable

Materials. *Angew. Chem. Int. Ed.* **2004,** *43*, 1078-1085.

54

13.   Meier, M. A.; Metzger, J. O.; Schubert, U. S. Plant oil renewable resources as green alternatives in polymer science. *Chemical Society Reviews.* **2007,** *36*, 1788-1802.

14.   Ragauskas, A. J.; Beckham, G. T.; Biddy, M. J.; Chandra, R.; Chen, F.; Davis, M. F.; Davison, B. H.; Dixon, R. A.; Gilna, P.; Keller, M.; Langan, P.; Naskar, A. K.; Saddler, J. N.; Tschaplinski, T. J.; Tuskan, G. A.; Wyman, C. E. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science.* **2014,** *344*.

15.   Robertson, M., Chang, K.; Gramlich, W.; Hillmyer, M. Toughening of Polylactide with Polymerized Soybean Oil. *Macromolecules.* **2010,** *43*, 1807-1814.

16.   Sun, L.; Pitto-Barry, A.; Kirby, N.; Schiller, T. L.; Sanchez, A. M.; Dyson, M. A.; Sloan, J.; Wilson, N. R.; O'Reilly, R. K.; Dove, A. P. Structural reorganization of cylindrical nanoparticles triggered by polylactide stereocomplexation. *Nat Commun.* **2014,** *5*.

17.   Wang, Z.; Yuan, L.; Trenor, N. M.; Vlaminck, L.; Billiet, S.; Sarkar, A.; Du Prez, F. E.; Stefik, M.; Tang, C. Sustainable thermoplastic elastomers derived from plant oil and their "click-coupling" via TAD chemistry. *Green Chem.* **2015,** *17*, 3806-3818.

18.   Yuan, L.; Wang, Z.; Trenor, N. M.; Tang, C. Robust Amidation Transformation of Plant Oils into Fatty Derivatives for Sustainable Monomers and Polymers. *Macromolecules.* **2015,** *48*, 1320-1328.

19.   Edgar, K. J.; Buchanan, C. M.; Debenham, J. S.; Rundquist, P. A.; Seiler, B. D.; Shelton, M. C.; Tindall, D. Advances in cellulose ester performance and application. *Progress in Polymer Science.* **2001,** *26*, 1605-1688.

20.   Jiang, F.; Wang, Z.; Qiao, Y.; Wang, Z.; Tang, C. A novel architecture toward third-generation thermoplastic elastomers by a grafting strategy. *Macromolecules.* **2013,** *46*, 4772-4780.

21.   Liu, Y.; Yao, K.; Chen, X.; Wang, J.; Wang, Z.; Ploehn, H. J.; Wang, C.; Chu, F.; Tang, C. Sustainable thermoplastic elastomers derived from renewable cellulose, rosin and fatty acids. *Polymer Chemistry.* **2014,** *5*, 3170-3181.

22.   Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. Cellulose nanomaterials review: structure, properties and nanocomposites. *Chemical Society Reviews.* **2011,** *40*, 3941-3994.

23.   Mori, T.; Hirose, A.; Hagiwara, T.; Ohtsuka, M.; Kakuta, Y.; Kimata, K.; Okahata, Y. Single-Molecular Enzymatic Elongation of Hyaluronan Polymers Visualized by High-Speed Atomic Force Microscopy. *J Am Chem Soc.* **2012,** *134*, 20254-20257.

24.   Stanzione, J. F.; Giangiulio, P. A.; Sadler, J. M.; La Scala, J. J.; Wool, R. P. Lignin-Based Bio-Oil Mimic as Biobased Resin for Composite Applications. *ACS Sustainable Chemistry & Engineering.* **2013,** *1*, 419-426.

25.   Yu, J.; Liu, Y.; Liu, X.; Wang, C.; Wang, J.; Chu, F.; Tang, C. Integration of renewable cellulose and rosin towards sustainable copolymers by "grafting from" ATRP. *Green Chem.* **2014,** *16*, 1854-1864.

26.   Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. Oils and Fats as Renewable Raw Materials in Chemistry. *Angewandte Chemie International Edition.* **2011,** *50*, 3854-3871.

27.   Martin, O.; Averous, L. Poly (lactic acid): plasticization and properties of biodegradable multiphase systems. *Polymer.* **2001,** *42*, 6209-6219.

28.   Seniha Güner, F.; Yağcı, Y.; Tuncer Erciyes, A. Polymers from triglyceride oils. *Progress in Polymer Science.* **2006,** *31*, 633-670.

29.   Sharma, V.; Kundu, P. Addition polymers from natural oils—a review. *Progress in Polymer Science.* **2006,** *31*, 983-1008.

30.   Tsujimoto, T.; Uyama, H. Full Biobased Polymeric Material from Plant Oil and Poly(lactic acid) with a Shape Memory Property. *ACS Sustainable Chemistry & Engineering.* **2014,** *2*, 2057-2062.

31.   Türünç, O.; Meier, M. A. Thiol-ene vs. ADMET: a complementary approach to fatty acid-based biodegradable polymers. *Green Chem.* **2011,** *13*, 314-320.

32.   Wilbon, P. A.; Zheng, Y.; Yao, K.; Tang, C. Renewable rosin acid-degradable caprolactone block copolymers by atom transfer radical polymerization and ring-opening polymerization. *Macromolecules.* **2010,** *43*, 8747-8754.

33.   Yao, K.; Wang, J.; Zhang, W.; Lee, J. S.; Wang, C.; Chu, F.; He, X.; Tang, C. Degradable rosin-ester–caprolactone graft copolymers. *Biomacromolecules.* **2011,** *12*, 2171-2177.

34.   Zheng, Y.; Yao, K.; Lee, J.; Chandler, D.; Wang, J.; Wang, C.; Chu, F.; Tang, C. Well-defined renewable polymers derived from gum rosin. *Macromolecules.* **2010,** *43*, 5922-5924.

35.   Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chemical Society Reviews.* **2010,** *39*, 301-312.

36.   Li, C.; Benicewicz, B. C. Synthesis of Well-Defined Polymer Brushes Grafted onto Silica Nanoparticles via Surface Reversible Addition−Fragmentation Chain Transfer Polymerization. *Macromolecules.* **2005,** *38*, 5929-5936.

37.   Qiao, Y.; Islam, M. S.; Yin, X.; Han, K.; Yan, Y.; Zhang, J.; Wang, Q.; Ploehn, H. J.; Tang, C. Oligothiophene-containing polymer brushes by ROMP and RAFT: Synthesis, characterization and dielectric properties. *Polymer.* **2015,** *72*, 428-435.

38.   Yan, Y.; Zhang, J.; Qiao, Y.; Ganewatta, M.; Tang, C. Ruthenocene-Containing Homopolymers and Block Copolymers via ATRP and RAFT Polymerization. *Macromolecules.* **2013,** *46*, 8816-8823.

39.   Zhang, J.; Ren, L.; Hardy, C. G.; Tang, C. Cobaltocenium-Containing Methacrylate Homopolymers, Block Copolymers, and Heterobimetallic Polymers via RAFT Polymerization. *Macromolecules.* **2012,** *45*, 6857-6863.

40.   Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Living Free-Radical Polymerization by Reversible Addition−Fragmentation Chain Transfer: The RAFT Process. *Macromolecules.* **1998,** *31*, 5559-5562.

41.   Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Thang, S. H. Thiocarbonylthio Compounds (SC(Z)S−R) in Free Radical Polymerization with Reversible Addition-Fragmentation Chain Transfer (RAFT Polymerization). Effect of the Activating Group Z. *Macromolecules.* **2003,** *36*, 2273-2283.

42.   Bähr, M.; Mülhaupt, R. Linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion. *Green Chem.* **2012,** *14*, 483-489.

43.   Xia, Y.; Larock, R. C. Vegetable oil-based polymeric materials: synthesis, properties, and applications. *Green Chem.* **2010,** *12*, 1893-1909.

44.   Satyarthi, J.; Srinivas, D.; Ratnasamy, P. Hydrolysis of vegetable oils and fats to fatty acids over solid acid catalysts. *Applied Catalysis A: General.* **2011,** *391*, 427-435.

45.   Kim, H.-J.; Kang, B.-S.; Kim, M.-J.; Park, Y. M.; Kim, D.-K.; Lee, J.-S.; Lee, K.-Y. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis today.* **2004,** *93*, 315-320.

46.   Delatte, D.; Kaya, E.; Kolibal, L. G.; Mendon, S. K.; Rawlins, J. W.; Thames, S. F. Synthesis and characterization of a soybean oil-based macromonomer. *J. Appl. Polym. Sci.* **2014,** *131*.

47.   Zhao, M.-L.; Tang, L.; Zhu, X.-M.; Hu, J.-N.; Li, H.-Y.; Luo, L.-P.; Lei, L.; Deng, Z.-Y. Enzymatic Production of Zero-Trans Plastic Fat Rich in α-Linolenic Acid and Medium-Chain Fatty Acids from Highly Hydrogenated Soybean Oil, Cinnamomum camphora Seed Oil, and Perilla Oil by Lipozyme TL IM. *J. Agric. Food Chem.* **2013,** *61*, 1189-1195.

48.   Andjelkovic, D. D.; Valverde, M.; Henna, P.; Li, F.; Larock, R. C. Novel thermosets prepared by cationic copolymerization of various vegetable oils—synthesis and their structure–property relationships. *Polymer.* **2005,** *46*, 9674-9685.

49.   Li, F.; Larock, R. C. Thermosetting polymers from cationic copolymerization of tung oil: Synthesis and characterization. *J. Appl. Polym. Sci.* **2000,** *78*, 1044-1056.

50.   Tehfe, M.-A.; Lalevée, J.; Gigmes, D.; Fouassier, J. P. Green chemistry: sunlight-induced cationic polymerization of renewable epoxy monomers under air. *Macromolecules.* **2010,** *43*, 1364-1370.

51.   Louis, K.; Vivier, L.; Clacens, J.-M.; Brandhorst, M.; Dubois, J.-L.; Vigier, K. D. O.; Pouilloux, Y. Sustainable route to methyl-9-hydroxononanoate (polymer precursor) by oxidative cleavage of fatty acid methyl ester from rapeseed oil. *Green Chem.* **2014,** *16*, 96-101.

52.   Petrović, Z. S.; Milić, J.; Xu, Y.; Cvetković, I. A Chemical Route to High Molecular Weight Vegetable Oil-Based Polyhydroxyalkanoate. *Macromolecules.* **2010,** *43*, 4120-4125.

53.   Billiet, S.; De Bruycker, K.; Driessen, F.; Goossens, H.; Van Speybroeck, V.; Winne, J. M.; Du Prez, F. E. Triazolinediones enable ultrafast and reversible click chemistry for the design of dynamic polymer systems. *Nature chemistry.* **2014,** *6*, 815-821.

54.   Desroches, M.; Caillol, S.; Lapinte, V.; Auvergne, R.; Boutevin, B. Synthesis of biobased polyols by thiol− ene coupling from vegetable oils. *Macromolecules.* **2011,** *44*, 2489-2500.

55.   Lee, K.-Y.; Wong, L. L. C.; Blaker, J. J.; Hodgkinson, J. M.; Bismarck, A. Bio-based macroporous polymer nanocomposites made by mechanical frothing of acrylated epoxidised soybean oil. *Green Chem.* **2011,** *13*, 3117-3123.

56.   Esen, H.; Küsefoğlu, S.; Wool, R. Photolytic and free-radical polymerization of monomethyl maleate esters of epoxidized plant oil triglycerides. *J. Appl. Polym. Sci.* **2007,** *103*, 626-633.

57.   Fu, L.; Yang, L.; Dai, C.; Zhao, C.; Ma, L. Thermal and mechanical properties of acrylated expoxidized-soybean oil-based thermosets. *J. Appl. Polym. Sci.* **2010,** *117*, 2220-2225.

58.   Dufour, B.; Tang, C.; Koynov, K.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. Polar Three-Arm Star Block Copolymer Thermoplastic Elastomers Based on Polyacrylonitrile. *Macromolecules.* **2008,** *41*, 2451-2458.

59.   Pedemonte, E.; Turturro, A.; Bianchi, U.; Devetta, P. The cubic structure of a SIS three block copolymer. *Polymer.* **1973,** *14*, 145-150.

60.   Ruzette, A.-V.; Leibler, L. Block copolymers in tomorrow's plastics. *Nature Mater.* **2005,** *4*, 19-31.

61.   Weidisch, R.; Gido, S. P.; Uhrig, D.; Iatrou, H.; Mays, J.; Hadjichristidis, N. Tetrafunctional Multigraft Copolymers as Novel Thermoplastic Elastomers. *Macromolecules.* **2001,** *34*, 6333-6337.

62.   Söntjens, S. H. M.; Renken, R. A. E.; van Gemert, G. M. L.; Engels, T. A. P.; Bosman, A. W.; Janssen, H. M.; Govaert, L. E.; Baaijens, F. P. T. Thermoplastic Elastomers Based on Strong and Well-Defined Hydrogen-Bonding Interactions. *Macromolecules.* **2008,** *41*, 5703-5708.

63.   Wang, S.; Vajjala Kesava, S.; Gomez, E. D.; Robertson, M. L. Sustainable Thermoplastic Elastomers Derived from Fatty Acids. *Macromolecules.* **2013,** *46*, 7202-7212.

64.   Wang, Z.; Zhang, X.; Wang, R.; Kang, H.; Qiao, B.; Ma, J.; Zhang, L.; Wang, H. Synthesis and Characterization of Novel Soybean-Oil-Based Elastomers with Favorable Processability and Tunable Properties. *Macromolecules.* **2012,** *45*, 9010-9019.

65.   Fetters, L. J.; Lohse, D. J.; Milner, S. T.; Graessley, W. W. Packing Length Influence in Linear Polymer Melts on the Entanglement, Critical, and Reptation Molecular Weights. *Macromolecules.* **1999,** *32*, 6847-6851.

66.   Baumann, H.; Bühler, M.; Fochem, H.; Hirsinger, F.; Zoebelein, H.; Falbe, J. Natural Fats and Oils—Renewable Raw Materials for the Chemical Industry. *Angewandte Chemie International Edition in English.* **1988,** *27*, 41-62.

67.   Loan, L. D. Crosslinking efficiencies of dicumyl peroxide in unsaturated synthetic rubbers. *J. Appl. Polym. Sci.* **1963,** *7*, 2259-2268.

68.   Lorenz, O.; Parks, C. R. The crosslinking efficiency of some vulcanizing agents in natural rubber. *Journal of Polymer Science.* **1961,** *50*, 299-312.

69.   Fei, B.; Chen, C.; Chen, S.; Peng, S.; Zhuang, Y.; An, Y.; Dong, L. Crosslinking of poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] using dicumyl peroxide as initiator. *Polymer International.* **2004,** *53*, 937-943.

70.   Valentín, J. L.; Rodríguez, A.; Marcos-Fernández, A.; González, L. Dicumyl peroxide cross-linking of nitrile rubbers with different content in acrylonitrile. *J. Appl. Polym. Sci.* **2005,** *96*, 1-5.

71.   Valentín, J. L.; Posadas, P.; Fernández-Torres, A.; Malmierca, M. A.; González, L.; Chassé, W.; Saalwächter, K. Inhomogeneities and Chain Dynamics in Diene Rubbers Vulcanized with Different Cure Systems. *Macromolecules.* **2010,** *43*, 4210-4222.

72.   Jadzyn, J.; Stockhausen, M.; Zywucki, B. Structure of hydrogen-bonded sym-dialkylureas in nonpolar organic media. *The Journal of Physical Chemistry.* **1987,** *91*, 754-757.

73.   Koevoets, R. A.; Versteegen, R. M.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. Molecular Recognition in a Thermoplastic Elastomer. *J Am Chem Soc.* **2005,** *127*, 2999-3003.

74.   Lehn, J. Supramolecular chemistry. *Science.* **1993,** *260*, 1762-1763.

59

75.   Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding. *Science.* **1997,** *278*, 1601-1604.

76.   Söntjens, S. H. M.; Sijbesma, R. P.; van Genderen, M. H. P.; Meijer, E. W. Stability and Lifetime of Quadruply Hydrogen Bonded 2-Ureido-4[1H]-pyrimidinone Dimers. *J Am Chem Soc.* **2000,** *122*, 7487-7493.

77.   Cui, L.; Dahmane, S.; Tong, X.; Zhu, L.; Zhao, Y. Using Self-Assembly To Prepare Multifunctional Diblock Copolymers Containing Azopyridine Moiety. *Macromolecules.* **2005,** *38*, 2076-2084.

78.   Huang, W.; Han, C. D. Synthesis of Combined Main-Chain/Side-Chain Liquid-Crystalline Polymers via Self-Assembly. *Macromolecules.* **2006,** *39*, 4735-4745.

79.   Stewart, D.; Imrie, C. T. Toward Supramolecular Side-Chain Liquid Crystal Polymers. 5. The Template Receptor Approach. *Macromolecules.* **1997,** *30*, 877-884.

80.   Wang, M.; Zhang, G.; Chen, D.; Jiang, M.; Liu, S. Noncovalently Connected Polymeric Micelles Based on a Homopolymer Pair in Solutions. *Macromolecules.* **2001,** *34*, 7172-7178.

81.   Wu, S.; Shi, F.; Zhang, Q.; Bubeck, C. Stable Hydrogen-Bonding Complexes of Poly(4-Vinylpyridine) and Polydiacetylenes for Photolithography and Sensing. *Macromolecules.* **2009,** *42*, 4110-4117.

82.   Steiner, T. The Hydrogen Bond in the Solid State. *Angewandte Chemie International Edition.* **2002,** *41*, 48-76.