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SUSTAINABLE POLYMERIC MATERIALS DERIVED FROM PLANT OILS: FROM SYNTHESIS TO APPLICATIONS

by

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I would also like to thank Dr. John Lavigne, Dr. Harry Ploehn, Dr. John Ferry and Dr. Melissa Moss for being members of my committee and give me helpful ideas and encouragement for my research projects. I also want to give my sincere appreciation to all my colleagues, Dr. Zhongkai Wang, Dr. Liang Yuan, Dr. Shichao Xu, Dr. Mitra Ganewatta, Anisur Rahman, Tianyu Zhu and my best partner Meghan Lamm. Working with you all has been a lot of fun and I want to thank you all for your advices and supports.

Finally, I would like to thank the University of South Carolina, the United Soybean Board, and DuPont for funding supports and supply.

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. The overall objective of my research is described. Chapter 2 outlines a new large-scale preparation of a soybean based monomer and the use of this monomer in thermoplastic elastomers. The synthetic procedures and characterizations of the monomers and polymers are discussed. In Chapter 3, potential applications of soybean oil monomers in both supramolecular polymers and poly(phosphoester)s are introduced. Thiol-ene reaction was used to introduce metal-ligand interaction into the sidechain of soybean homopolymers. The synthetic procedures and characterizations of the polymers are discussed. An overall summary of my research and outlook are given in Chapter 4.

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LIST OF SYMBOLS

M_n	number average molecular weight
$Đ$	polydispersity
$\mathrm{T_g}$	glass transition temperature

CHAPTER 1

GENERAL INTRODUCTION

The production of commodity chemicals has considerable history in human society. At the beginning of the 20th century, many industrial materials such as dyes, solvents, and synthetic fibers were made from trees and agricultural crops. However, due to increased market demand and lower price of petrochemical feedstocks, most chemicals used in last half century were made from these petroleum sources. This can be very environmentally harmful because of the harvesting and processing.[1-3] About 8% of fossil fuels are consumed for the synthesis of plastics worldwide each year.[4] If we can replace these with green plastics from renewable natural resources, we can increase sustainability of the world. The ultimate goals for us are to develop eco-friendly chemical processes and products that would prevent pollution in the first place. Through the practice of "green" chemistry, we can create alternatives to petroleum, using smaller amounts of energy while keeping the competitiveness.[5-12]

Green plastics can be defined into two major categories: natural polymers, including lignin and cellulose; or small molecular biomass, such as vegetable oils and rosin, which are usually obtained directly from forestry and agriculture products.[13-16] These natural polymers are extensively studied, but they lack processability, defined structures and have uncontrolled mechanical properties.[17-23] My research focused on plant oil, specifically soybean oil. Plant oil is an important class of abundant natural resources. Among various vegetable oils, the highest production and most commonly used oils would be soybean oil. The global soybean production in 2016 was 312.97 million metric tons, with 117.29 million in the United States.[24] These oils are relatively cheap and plentiful. The main component of soybean oils is triglyceride. Triglyceride has three ester bonds, which can be hydrolyzed to form glycerol and three fatty acids. These fatty chains contain double bonds and can be further functionalized. These triglycerides are useful in many chemical reactions such as hydrolysis, transesterification, amidation, hydrogenation, polymerization, epoxidation, oxidation, and addition.[25-32] The high oleic soybean oil we used is provided by DuPont, having a triglyceride structure composed of ~75% oleic acid (one double bond), ~12% linoleic acid (two double bonds), and ~12% stearic acid (no double bond), averagely one double bond per fatty chain. Our group has already prepared soybean oil based mono-functional monomers using various amino alcohols followed by (meth)acrylation.[33-34] Homopolymers with a wide range of T_gs and properties were obtained. Based on these developments, we have also been able to make a variety of materials such as thermoplastic elastomers, shape memory materials and high-performance bioplastics.[35-38]

My research objective is to explore further this research, trying to make better materials using existing or new soybean-based monomers with similar synthetic counterparts.

CHAPTER 2

THERMOPLASTIC ELASTOMERS FROM A NEW SOYBEAN OIL BASED MONOMER

2.1 Introduction

As previously discussed, the Tang group prepared soybean oil based monomers using a variety of amino alcohols followed by (meth)acrylation.[33-34] Although quantitative yield is achieved, the whole process has some restrictions. Firstly, it needs multiple work-up steps using an excess of organic solvent like dichloromethane, which is infeasible in industry. Another issue is the cost of reagents; some amino alcohols, methacrylic anhydride and (meth) arcylation catalyst are relatively expensive. Considering both cost and industrial relevance, a major aim of my work is to make monomers suitable for commercial scale. Ideally this will occur with a one-pot procedure, using cheaper reagents, and simple work-up steps.

Thermoplastic elastomer (TPE) is a broad class of materials that can be reprocessed at elevated temperature, for example, by molding or extrusion, meanwhile is elastomeric at ambient temperature. Typically, such behavior arises through a phase-separated microstructure in which “hard” domains are embedded in “soft” rubbery matrix. When a stress is applied to the material, the hard domains serve to “pin” the polymer chains and prevent macroscopic deformation, while the rubbery chains provide elasticity through the connectivity of the network.

The most studied TPEs are styrene-based linear ABA triblock copolymers, such as poly(styrene-b-butadiene-b-styrene) (SBS) or poly(styrene-b-isoprene-b-styrene) (SIS), in which polystyrene serves as the “hard” domains and polybutadiene or polyisoprene as the “soft” matrix.[39] Polymers with low T_g and similar soft, elastic properties such as poly soybean acrylate (PSBA) have been utilized to replace the petroleum based polybutadiene or polyisoprene. Our group has successfully made such a crosslinked PS-b-PSBA-b-PS triblock thermoplastic elastomer.[35] One of the goals here is to make better TPEs combining the sustainable elastic biomass with typical hard domains like polystyrene (PS) or poly lactic acid (PLA).[40-42]

2.2. Results and Discussion

2.2.1 Epoxidized methyl oleate acrylate (EMOA) monomer derived from soybean oil

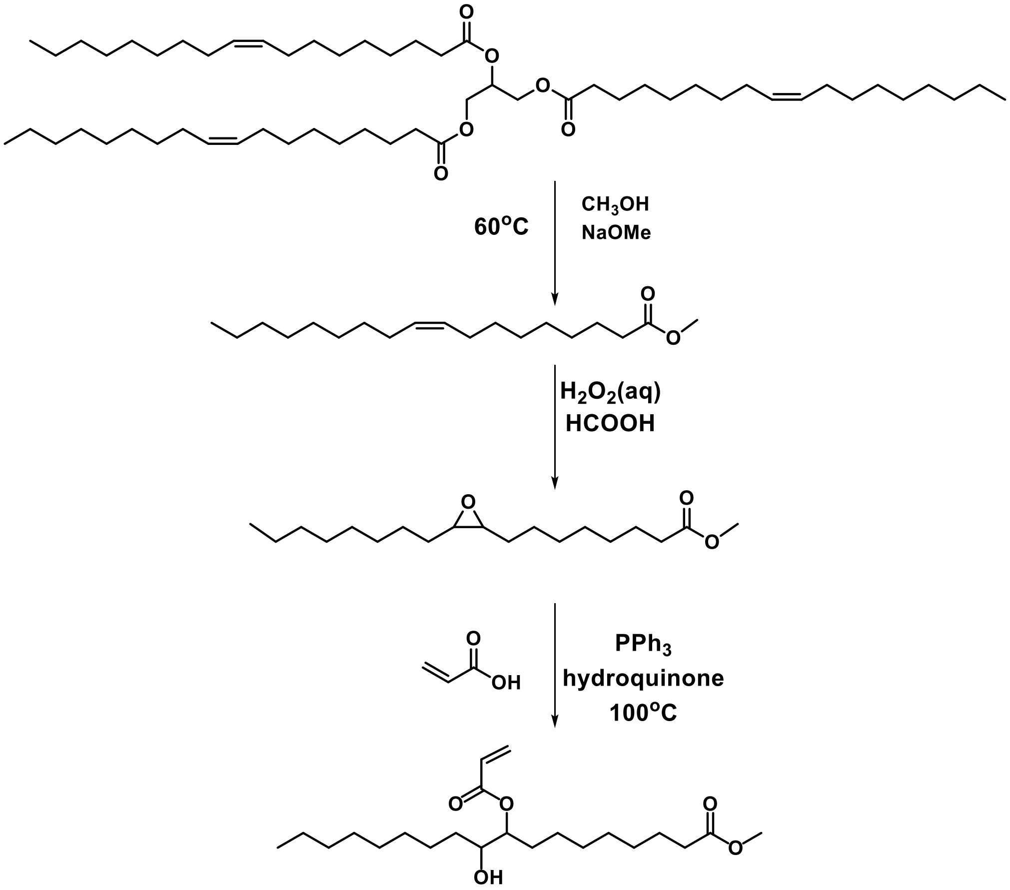

Figure 2.1 Derivatization of high oleic soybean oil into epoxidized methyl oleate acrylate (EMOA) monomer.

The first step is the transesterification of triglyceride to methyl esters. This step is well studied and produces glycerol as a side-product that can be easily separated due to its immiscibility with the fatty methyl esters (FMEs). These FMEs can then be epoxidized using hydrogen peroxide and formic acid.[43] The epoxy group can be further functionalized using acrylic acid.[44] Similarly, the aqueous layer can be drained out from the mixture. The whole process utilizes cheap and industrially-compatible chemicals in a one-pot synthesis, without the toxic organic solvent previously needed.

^{1}H NMR spectra (**Figure 2.2**) shows that the epoxidation step reaches full conversion at room temperature. The acrylation was attempted at a lower reaction temperature to avoid polymerization of acrylic acid, however, residual epoxides remained. In this case, 5mol% of hydroquinone as inhibitor was added to prevent polymerization.

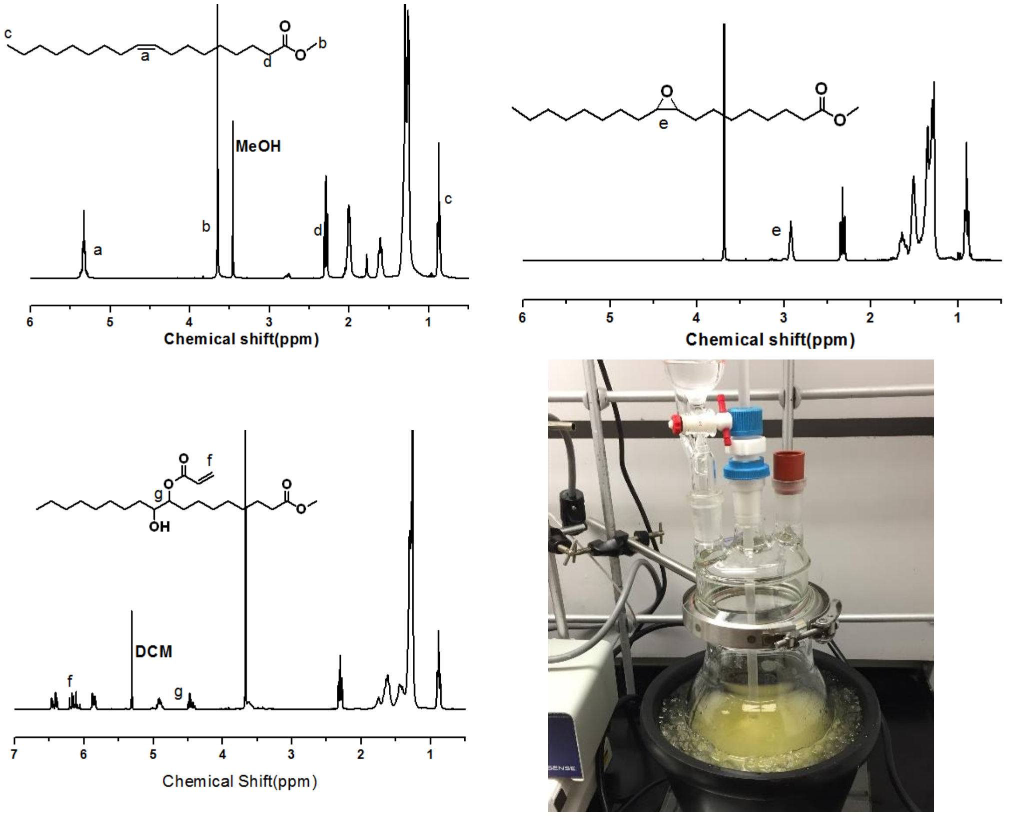

Figure 2.2 ^{1}H NMR spectra of methyl ester (top left), epoxidized methyl ester (top right) and epoxidized methyl oleate acrylate monomer (EMOA) (bottom left) and 3L scale of epoxidation (bottom right).

A 3L scale of transesterification and epoxidation has already been completed with a quantitative yield. The acrylation had issues as it can easily crosslink, even with higher levels of inhibitors. Future work could attempt using lower temperature or switching to more active anhydride. Another alternative could be a methacrylate monomer, synthesized using methyl methacrylate and a cheap base catalyst. Overall, further work is needed to produce EMOA with minimal impurity at a large scale.

2.2.2 TPEs using epoxidized methyl oleate acrylate (EMOA) monomers

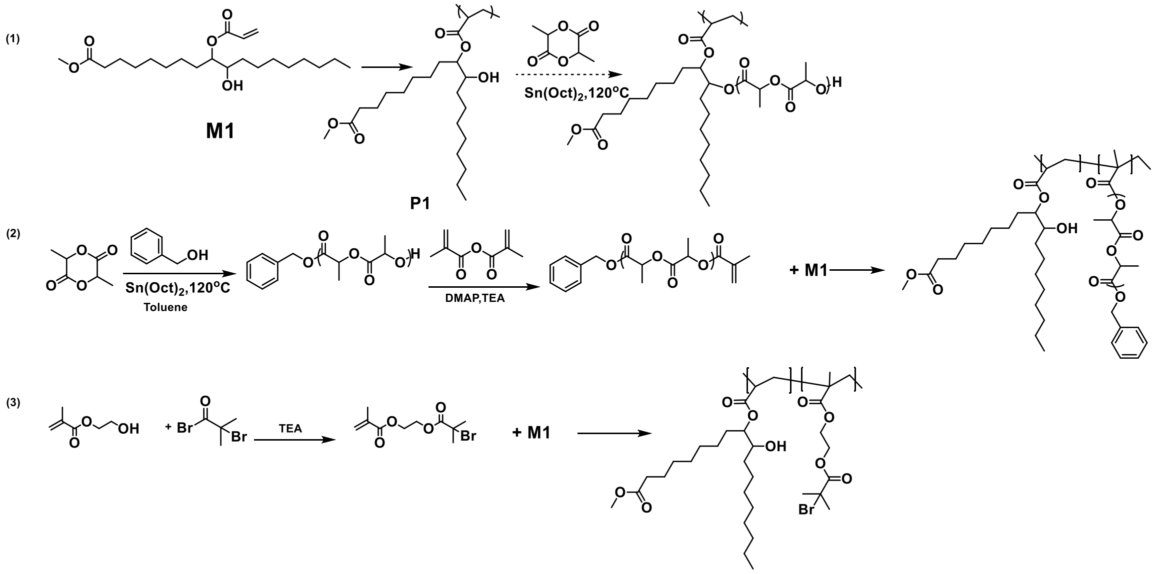

Figure 2.3 Attempts to make TPEs with (1) graft polylactic acid (PLA), (2) random copolymer with PLA, (3) Macro initiator for ATRP.

To investigate this new monomer, homopolymerization can be done using free radical polymerization with a benzoyl peroxide initiator. Characterization using DSC shows the homopolymer (PEMOA), which is tacky and viscoelastic, has a T_g near -40^{o}C. This property indicated it could be served as the soft block in TPEs.

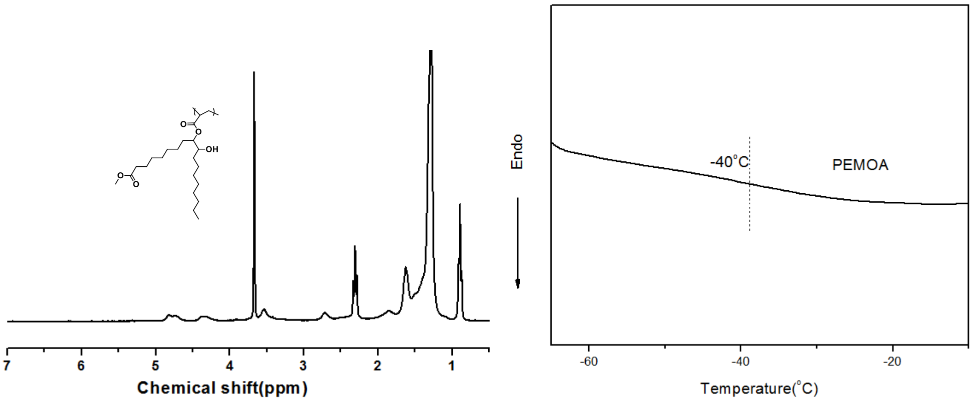

Figure 2.4 ^{1}H NMR spectra of homopolymer (PEMOA) and DSC curve.

Initially, a grafted polymer strategy was approached using lactide to directly carry out ring-opening polymerization (ROP) on the hydroxyl group along the fatty chain. This method failed to achieve good graft polymers with high molecular weight. One reason could be that either the steric hindrance of the acrylate backbone or the slight moisture affects the ROP process, possibly preventing the initial conversion on the monomer.

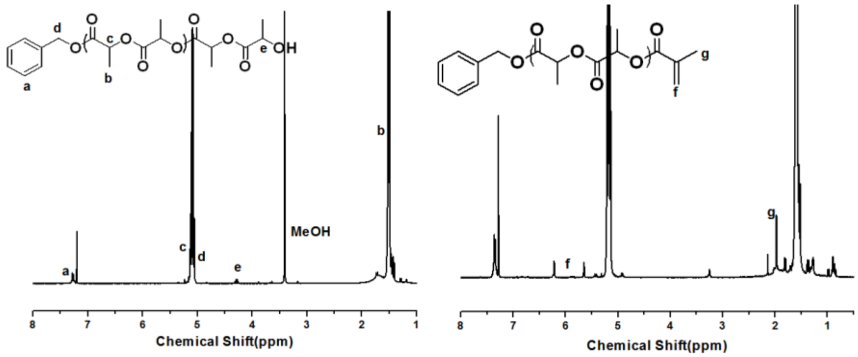

Figure 2.5 ^{1}H NMR spectra of modified polylactic acid(PLA).

As shown in **Figure 2.3** (2), new methods to synthesize a TPE were approached. A random copolymer using the acrylate and a modified PLA macromonomer (M_n=3600 g/mol, Đ =1.67, as determined by GPC). The final PEMOA-r-PLA copolymer has a M_n of 9000 g/mol and Đ of 1.64, consists of 14 repeat units of EMOA in a polymer chain. This degree of polymerization is too low to serve as a continuous soft matrix in TPEs. **Figure**

2.6 (left) shows a scheme of ideal microphase separation in TPEs, as previously discussed. The spheres represent the hard domains like polystyrene or polylactic acid in this work. These spheres are surrounded by a soft matrix like polybutadiene or PEMOA. Because these blocks are convalently bonded to each other, they form nanoscale morphologies. The film using PEMOA-r-PLA (**Figure 2.6**(right)) was very brittle and had macrophase separation.

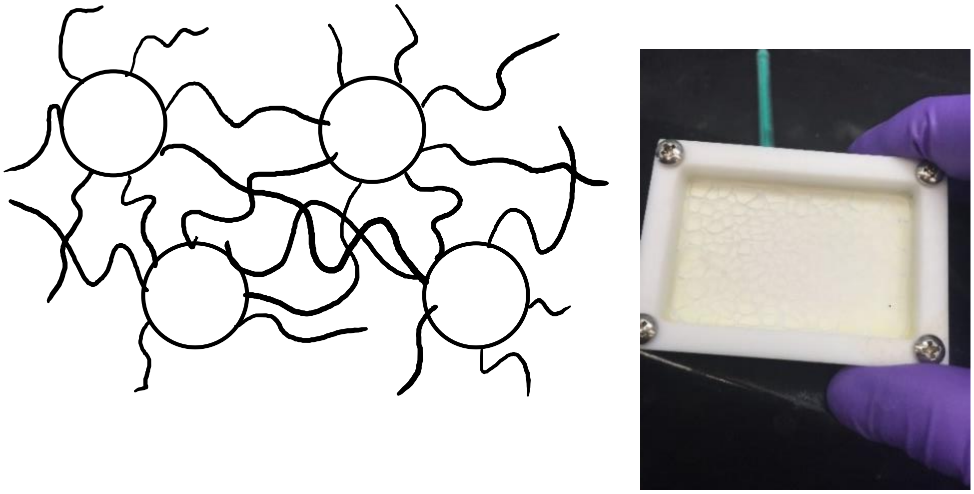

Figure 2.6 Schematics of an ideal microphase separation of TPE (left) and macroscopically phase separation in the film of PEMOA-r-PLA (right).

Table 2.1 P(EMOA-co-HEMA-Br) copolymers reaction conditions and results

[EMOA]: [Br]: [I]	**Temp(ºC)**	**Initiator**	**Solvent**	**Result**
100:5:3	100	BPO	Toluene	M_n=80000 g/mol
100:5:3	100	BPO	Toluene	M_n=131000 g/mol

For another approach (**Figure 2.3** (3)), an ATRP initiator-monomer (HEMA-Br) was synthesized using 2-bromo-2-methylpropionyl bromide (BiBB) and 2-hydroxyethyl methacrylate (HEMA). HEMA can undergo free radical polymerization with EMOA, while the initiator can undergo ATRP with a hard domain monomer, like styrene. With the feed ratio of HEMA-Br to EMOA of 1:20, higher molecular weight copolymers (M_n=80000 g/mol and 131000 g/mol) were obtained.

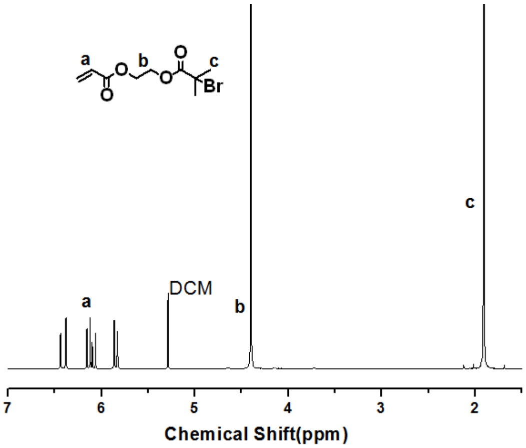

Figure 2.7 ^{1}H NMR spectra of ATRP initiator-monomer (HEMA-Br)

The challenge is to obtain a higher molecular weight of the soft blocks. Copolymerization with nBA (butyl acrylate) was attempted to achieve a larger soft block. The nBA should undergo polymerization easier due to less steric hindrance than EMOA. The ratio of [EMOA]: [nBA]: [HEMA-Br]: [initiator] used is 100:50:5:3, but it gelled at low temperature like 60^{o}C. Further polymerization using the ATRP initiator containing polymer and styrene is needed to form the final copolymer. Polymers with different ratios of two monomers can be used to tune the properties further. Characterization would be needed to obtain morphological, mechanical, and thermal data.

If higher molecular weight soft blocks are not obtained, a new method will be used. Radical addition fragmentation transfer (RAFT) polymerizations will be attempted to hopefully obtain a well-controlled acrylate polymer. The use of a new methacrylate monomer, from epoxided methyl oleate, may solve the problem, as it has higher activity during polymerization.

2.3. Conclusions

A strategy was deployed to prepare high oleic soybean oil based monomer. The homopolymer (PEMOA) was prepared using free radical polymerization. DSC shows it has a T_g near -40°C, indicating it could be served as the soft block in thermoplastic elastomers (TPEs). Attempts to make TPEs were carried out. Low molecular weight copolymers were obtained, and possible reasons were investigated.

2.4. Experimental

2.4.1 Materials and Characterization

Plenish high oleic soybean oil (HOSO) was provided by DuPont. Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from methanol twice. Dry THF and toluene were dry from LiAlH4 and vacumm distilled before use. L-Lactide (98%, Aldrich) was recrystallized from hexane three times. Other monomers were run through basic alumina to remove inhibitors. All other reagents were obtained from commercial sources and used as received unless otherwise mentioned.

^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. Molecular weights and size distributions of polymers were determined by gel permeation chromatography (GPC) equipped with a 2414 RI detector, a 1525 Binary Pump and three Styragel columns. The columns consisted of HR 1, HR 3 and HR 5E with effective molecular weight ranges of 100−5K, 500−30K, and 2K−4M respectively. THF was used as eluent at 35 °C with a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards obtained from Polymer

Laboratories. GPC samples were prepared by dissolving the sample in THF with a concentration of 3.0 mg/mL and passing through microfilters with average pore size of 0.2 μm. The glass transition temperature (Tg) of polymers was tested through differential scanning calorimetry (DSC) conducted on a DSC 2000 instrument (TA Instruments). Samples were first heated from −70 to +200 °C at a rate of 10 °C/min. After cooling down to −70 °C at the same rate, the data were collected from the second heating and cooling scan. About 10 mg of each sample was used for the DSC test with nitrogen gas at a flow rate of 50 mL/min.

2.4.2 Synthetic methods

2.4.2.1. Synthesis of methyl oleate

High Oleic Soybean oil (HOSO) (100 g, 0.344 moles) was placed in a 500-mL round bottom flask. The flask was placed in a 100 ^{o}C oil bath for 1 h. The oil bath was cooled to 60 ^{o}C before adding methanol 60ml and sodium methoxide (1.5 mL, 0.008 moles) to the flask. The flask was sealed and left to stir for 4 h. The reaction was monitored by ^{1}HNMR. Upon completion, the reaction mixture was extracted with DCM (500 mL) and washed three times with brine. The resulting organic layer was dried with magnesium sulfate and the solvent was evaporated using a rotary evaporator. Yield: 103 g (98% yield).

2.4.2.2 Synthesis of epoxdied methyl oleate

200.0 g (0.67 mol) of methyl oleate is placed in a 500-mL round-bottom flask equipped with an overhead stirrer. Next, 102 g (2.2 mol) of formic acid was slowly added, forming a layered mixture. The reaction flask is cooled in an ice bath, and 163 g of 30% hydrogen peroxide (1.44 mol) is added over ~5 min. The reaction is allowed to proceed at room temperature overnight. The product dissolved in ~200 mL of hexanes and the aqueous/formic acid layer was discarded. The organic layer was washed with saturated sodium bicarbonate solution until the pH of the solution is >7 (three times). The organic layer was then washed with saturated brine three times. The hexane layer was dried over anhydrous magnesium sulfate and filtered through a fritted funnel, and the hexane was removed with rotary evaporation. Yield was 221.1 g (97%).

2.4.2.3 Synthesis of epoxidized methyl oleate acrylate

To EMO (20.0 g), acrylic acid (6.8g) and triphenyl phosphine (0.4 g) as a catalyst hydroquinone (60mg) as inhibitor were added. The mixture was heated with continuous stirring at 100°C for 10 h. The reaction product was then dissolved in diethyl ether and was extracted four times with 5% (aqueous) sodium bicarbonate for the removal of unreacted acrylic acid. The ether layer was dried with anhydrous magnesium sulfate and evaporated to dryness. The product was a straw-colored, viscous liquid weighing 21g.

2.4.2.4 Synthesis of modified polylactic acid

To an oven dried 25ml flask, benzyl alcohol(25mmol,25ul), L-actide(1.225g,85mmol), $Sn(Oct)_2$(34mg,1mol%),6ml dry toluene were added. The mixture was heated to 120^{o}C over 5h. The polymer was precipitated in methanol and dried under vacuum. 330mg methacrylate anhydride, 6mg DMAP and 5ml THF were added to it and left overnight at 60^{o}C. The modified polymer was precipitated in methanol and dried under vacuum again.

2.4.2.5 Synthesis of HEMA-Br

To 2.6g HEMA was added 4.6g BBiB ,3ml TEA and 40ml DCM under ice bath. The mixture was left at room temperature overnight. The reaction mixture was washed three times with brine. The resulting organic layer was dried with magnesium sulfate and the solvent was evaporated using a rotary evaporator.

2.4.2.6 Free radical polymerization of polymers

A typical procedure was as followed. Monomers and AIBN were placed in a 25 mL round bottom flask and dissolved in toluene (4 mL). The flask was sealed and purged with nitrogen for 15 min. The flask was placed in an 80 ^{o}C oil bath and the reaction was allowed to proceed overnight. The resulting polymer was precipitated three times into methanol and dried for 24 h in a 50 ^{o}C vacuum oven. Other soy-based polymers were synthesized by the same FRP method by varying the monomer, radical initiator, and reaction temperature and time.

CHAPTER 3

SUPRAMOLECULAR POLYMERS WITH SOYBEAN OIL DERIVATIVES

3.1 Introduction

While traditional chemistry focuses on covalent and ionic bonding, supramolecular chemistry examines the weaker and reversible noncovalent interactions between molecules. These forces include hydrogen bonding, metal-ligand interaction, hydrophobic effects and π–π stacking.[45-46] A major motivation to utilize reversible supramolecular interactions in the context of polymer technology is the promise of simpler processing and recyclability. These interactions can also be used to introduce stimuli-responsive properties, such as mechanochromism, self-healing, shape memory behavior and others.[47-56]

The typical strategy for these interactions in polymers involves reversible junctions in a transient network, or put simply, introduces active sites onto the polymers.[57-60] However, side chain modification may be a better idea compared to these backbone strategies because it is easily tunable. A good example of this is the soybean oil derived monomers previously discussed. Differences in backbone between the norbornene polymers and its methacrylate analogues, introduce greater space between side chains, resulting in weaker or even no hydrogen bonding and a major reduction in T_g. However, using the same methacrylate backbone, the secondary amide-containing polymers have higher T_g than their counterpart tertiary ones due to the hydrogen bonding of the amide proton with the carbonyl group.[33-34]

One of the state-of-the-art applications is self-healing polymers based on zinc-ligand interactions. Applied forces lead to the temporary disconnection of reversible zinc-ligand interactions in polymers. Energized by either light or heat, those stray soft domains move around, allowing the dispersed zinc fragment to recontact with ligand again, effectively reversing the damage and repairing the material. Burnworth[48] et al made optically healable microphase-separated polymers using poly(ethylene-co-butylene) core and terpyridine terminals. Mozhdehi[61] et al (**Figure 3.1)** improved the healability by using a polystyrene backbone and an imidazole modified soft brush. With a broad tunability, their polymer showed self-healing ability under ambient conditions without any intervention.

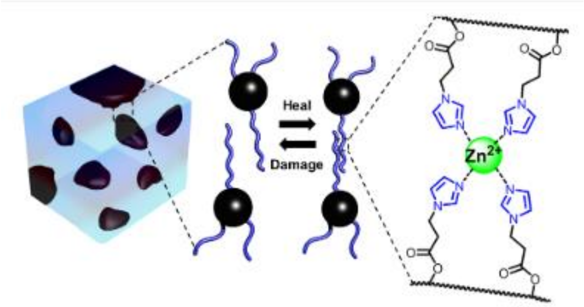

Figure 3.1 Design concept of self-healing polymers using metal-ligand interaction.[49]

It is worth noting that few of these supramolecular applications are based on renewable biomass materials. However, our group developed a hydrogen-bonding shape memory nanocomposite.[36] Prepared with cellulose and soybean oil derivatives, we demonstrated that biomass shows promise for use in this field.

3.2 Results and Discussion

3.2.1 Supramolecular polymers with soybean oil derivatives

This project used zinc-ligand interactions to synthesize a self-healing polymer using soybean oil monomers. 1-vinyl imidazole (VIm, T_g=175 ^oC) is the simplest commercial imidazole-containing monomer, which can be easily copolymerized with soybean (meth)acrylate monomers (SB(M)A).

According to the study[49] of Guan's group, the following properties are needed to form a good zinc-ligand self-healing polymer: First, the T_g of polymer itself, before metal complexation, should be around -38^{o}C, so that after incorporating the metal, the T_g is still lower than room temperature and therefore the material will be flexible. Because VIm has a relatively high T_g, another low T_g component is needed to lower the T_g of the copolymer. Comparing the soybean monomers[33] synthesized by our group, the N-butylethanolamine derived ones have the lowest T_gs (SBA=-51.3 ^{o}C, SBMA=-29.3 ^{o}C). Due to the better activity of methacrylate and resulting higher homopolymer molecular weight, the butyl SBMA was chosen for further investigation. Another needed property of the zinc-ligand self-healing polymers is that imidazole content should be around 1.8mmol/g polymer to provide enough interaction sites.[49]

Table 3.1 Reaction condition and results of PSBMA-Im

[double bond]: [thiol]	Initiator	Solvent	Time(h)	Conversion%	Im(mmol/g polymer)
1:20	UV	THF	1.5	59	0.73
1:20	UV	THF	2.5	64	0.8

Figure 3.2 shows the pathway to obtain the desired polymer. First the reported method was used to obtain PSMBA.[34] Modification of double bond of fatty chain was attempted. Using a thiol-ene reaction, a hydroxyl group was introduced to the side chain. The hydroxyl group was then reacted with 1,1'-carbonyldiimidazole(CDI), introducing the imidazole moiety to the PSBMA.[62]

The thiol-ene reaction is hard to control, so excess 2-mercaptoethanol (20:1 to double bond) is needed, making similar imidazole content (1.8mmol/g polymer) difficult to obtain. For example, 65% hydroxyl converted polymer only had 0.8mmol Im/g polymer, which is far lower than the target.

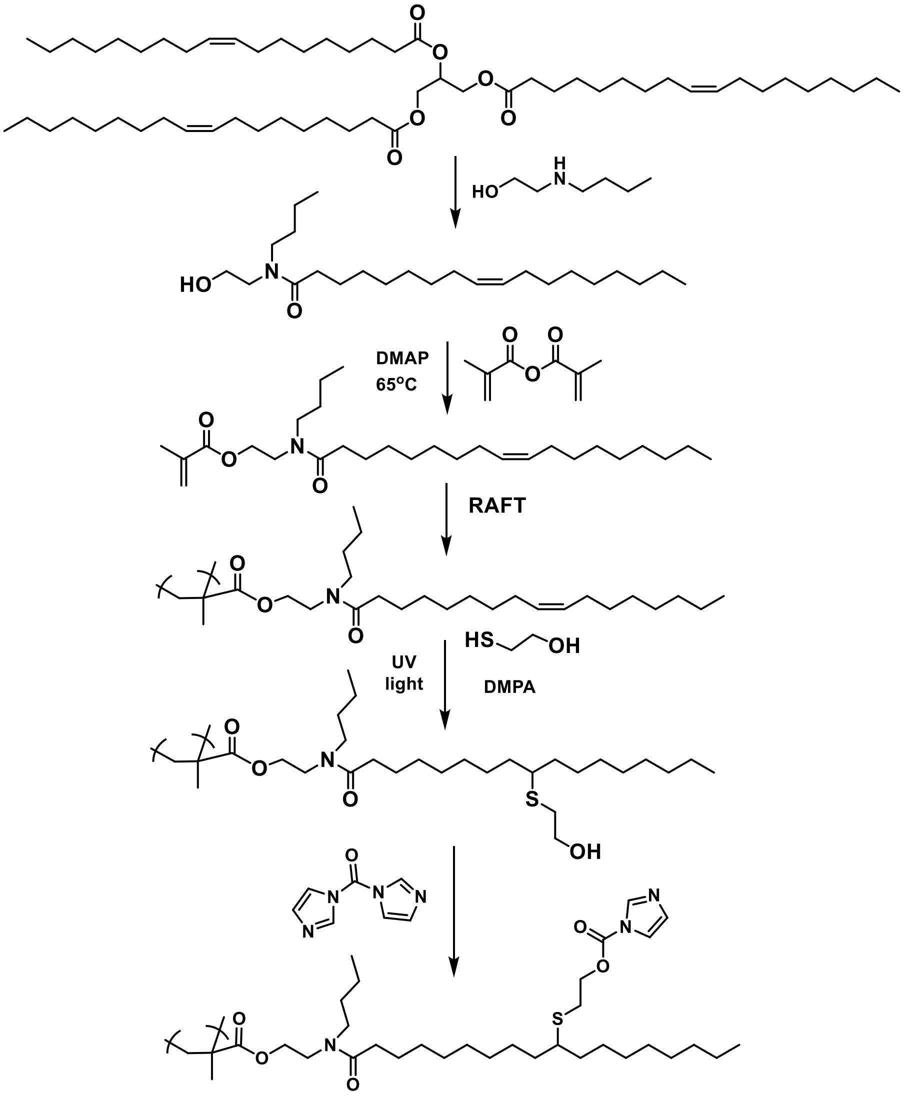

Figure 3.2. Synthetic scheme of PSBMA-Im

GPC showed the final PSBMA-Im has a molecular weight about 39k with a *Đ* of 1.82. Without the addition of metal ions, the grafted polymers were viscous oils, unable to form free-standing films. Upon addition of Zn(NTf)$_2$ and removal of solvent, they formed non-tacky elastomers. This property change showed evidence for complexation between zinc and imidazole. DSC showed the T$_g$s of PSBMA-Im, PSBMA-Im-Zinc were -29 °C, 0.53 °C respectively. Tensile test showed the sample maintained elongation at break close to 50% and final tensile strength was around 2MPa. Self-healing property was tested, although it was not detected, as expected. This is reasonable because of the low imidazole content.

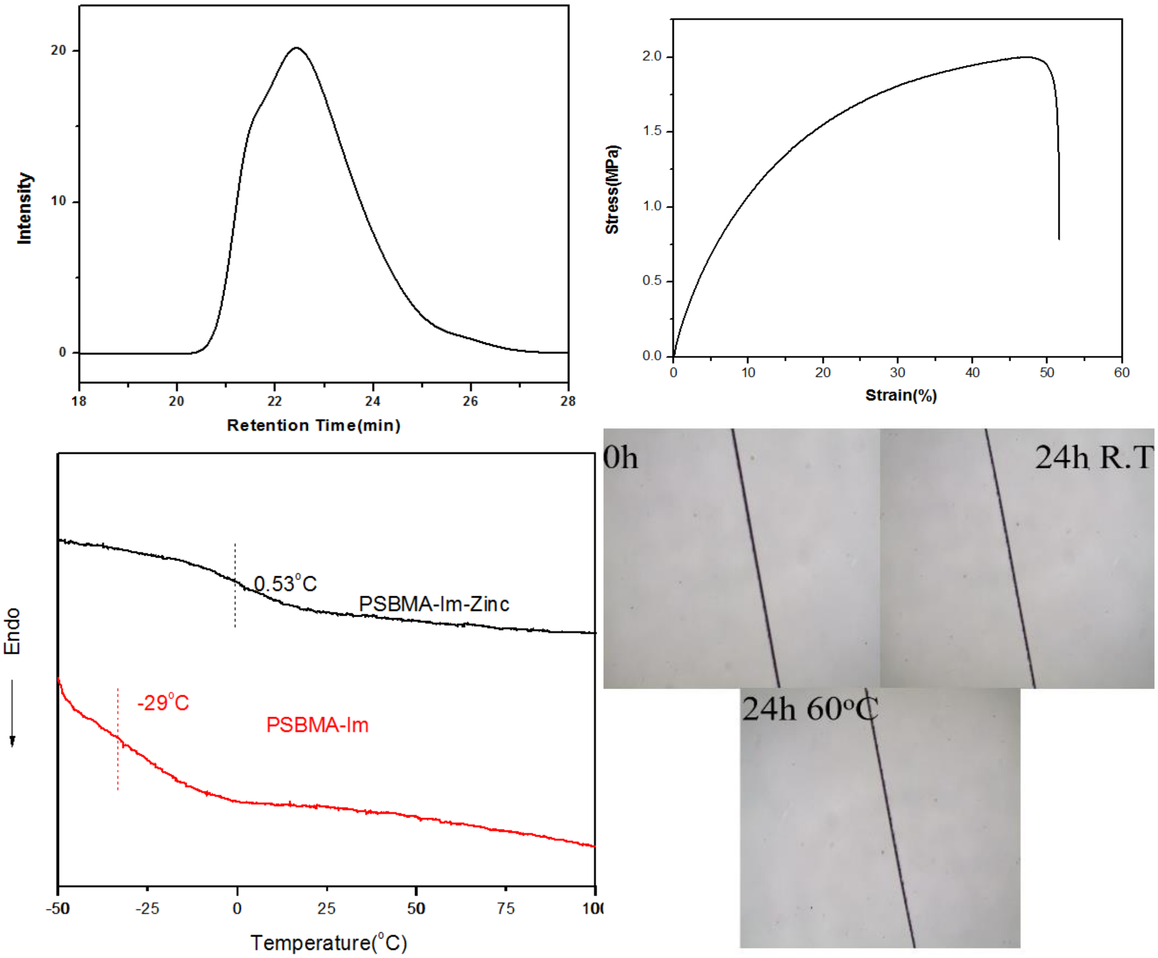

Figure 3.3 GPC (top left), tensile test (top right), before and after metal coordination (bottom left) and self-healing test using optical microscopy (bottom right) of PSBMA-Im

Further metal-binding studies were carried out to confirm the complex of zinc and imidazole. It was studied by Waite group using UV-vis that in water solution, zinc binding to imidazole showed a clear saturation at 4:1 imidazole/Zn.[63] Similar study was done first in THF solution with zinc di[bis(trifluoromethylsulfonyl)imide] ($Zn(NTf)_2$) and small molecular 1-methylimidazole (Im). The methyl group makes the other nitrogen only position to be bonded with Zinc and erases the possibility of hydrogen bonding.

Both $Zn(NTf)_2$ and 1-methylimidazole shows strongest absorptions around 231nm and 279nm. Through the addition of Zinc salt, it turned out the absorption kept increasing without saturation. The possible reason maybe the THF is too easy to evaporate through the process. Considering both solubility and stability, later tests changed to toluene solution with zinc acetylacetonate ($Zn(acac)_2$) salt instead. In toluene solution, both $Zn(acac)_2$ and 1-methylimidazole shows strongest absorptions around 281.5nm, also shows a clear saturation with the 4:1imidazole/Zn ratio.

However, the PSBMA-Im polymer solution with $Zn(acac)_2$ didn't get clear saturation at 4:1. Either the hindrance of imidazole groups on sidechain or the longer time of the polymer sample to equilibrate affects the absorption (**Figure 3.4).**

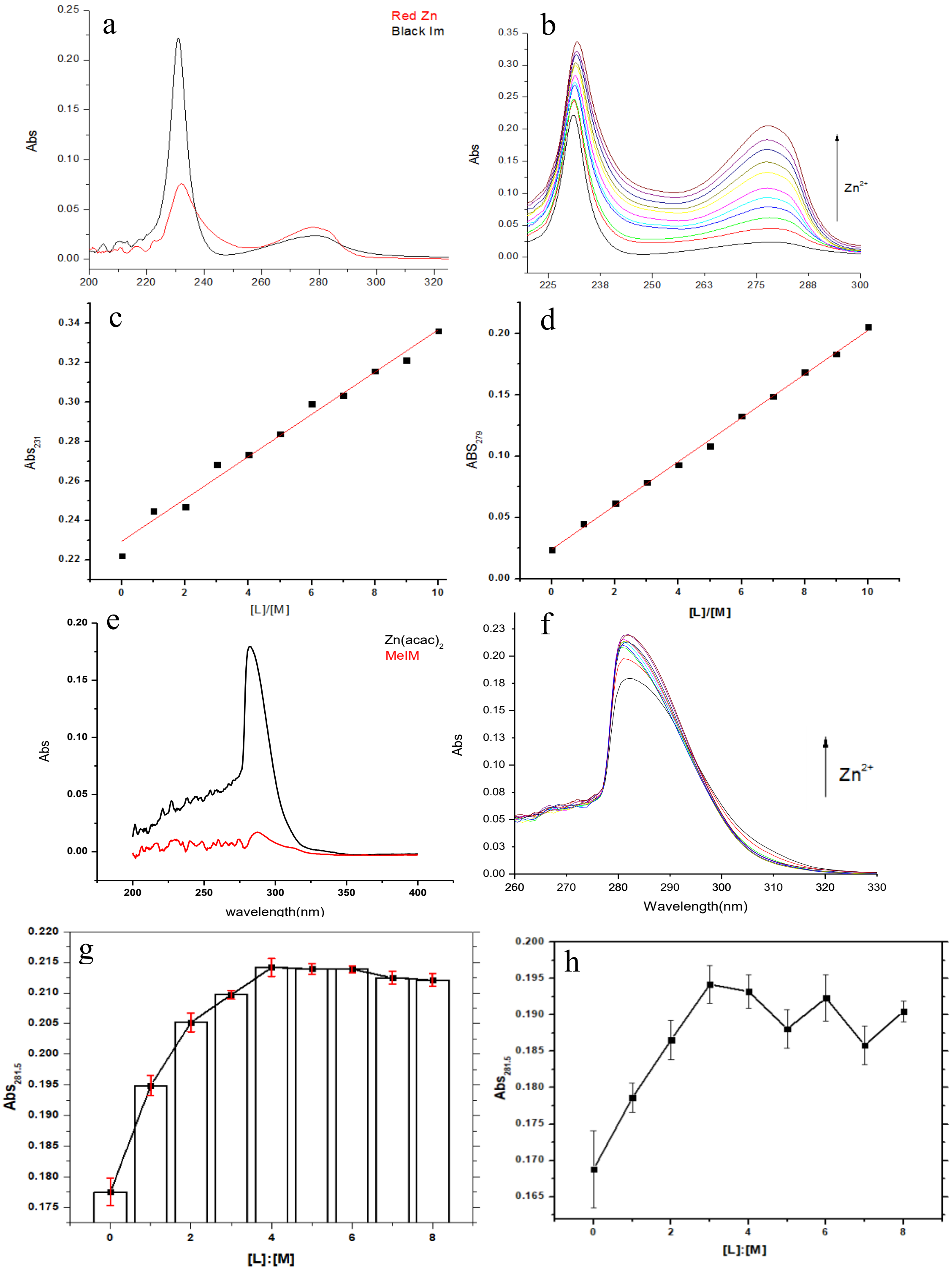

Figure 3.4 (a) UV-vis absorption of Zn(NTf)$_2$ and Im (b)absorption through the adding of Zn(NTf)$_2$ (c)&(d) curves of absorption at 231 and 279nm (e)absorption of Zn(acac)$_2$ and Im in toluene (f) absorption through the adding of Zn(acac)$_2$ (g) UV-vis absorption curve at 281.5nm of Zn(acac)$_2$ with Im and (h) UV-vis absorption curve at 281.5nm of Zn(acac)$_2$ with PSBMA-Im.

3.3 Experimental

3.3.1 Materials and Characterizations

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^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. Molecular weights and size distributions of polymers were determined by gel permeation chromatography (GPC) equipped with a 2414 RI detector, a 1525 Binary Pump and three Styragel columns. The columns consisted of HR 1, HR 3 and HR 5E with effective molecular weight ranges of 100−5K, 500−30K, and 2K−4M respectively. THF was used as eluent at 35 °C with a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards obtained from Polymer Laboratories. GPC samples were prepared by dissolving the sample in THF with a concentration of 3.0 mg/mL and passing through microfilters with average pore size of 0.2 μm.

The glass transition temperature (T_g) of polymers was tested through differential scanning calorimetry (DSC) conducted on a DSC 2000 instrument (TA Instruments). Samples were first heated from −70 to +200 °C at a rate of 10 °C/min. After cooling down to −70 °C at the same rate, the data were collected from the second heating and cooling scan. About 10 mg of each sample was used for the DSC test with nitrogen gas at a flow rate of 50 mL/min.

Tensile stress−strain testing was carried out with an Instron 5543A testing instrument. The films were prepared by dissolving 1 g of polymer in 15 mL of solvent. The solution of the polymer was poured in a PTFE mold. After the evaporation of solvent over 72 h, the film was put under vacuum for 4 h at room temperature and then 4 h at 60 °C. Dog-bone shaped specimens were cut from the cast film with a length of 20 mm and width of 5.0 mm. The thickness was measure prior to each measurement. Testing occurred at room temperature with the crosshead speed of 20 mm/min.

For self-healing tests, a well-defined cut was applied to the depth of 70-90% of sample thickness using a razor blade. The cut faces were pressed together for 1 minute and then the sample was left to heal at room temperature.

3.3.2 Synthetic methods

3.3.2.1 Thiol-ene reaction of PSMBA and 2-mercaptoethanol

To 2.75g PSBMA was added 10ml THF to dissolve first, 2-mercaptoethanol (8.82ml, 20:1 ratio to double bond) and 55mg (20mg/g polymer) 2,2-Dimethoxy-2-phenylacetophenone(DMPA) was added. The solution was purged with N_2 for 30 min and kept under UV (254 nm, 15 Watt) irradiation for 2 hours. Then the resulting polymer was precipitated three times into methanol and dried under vacuum overnight.

3.3.2.2 Synthesis of PSBMA-Im

To 2.4g SBMA-OH was added 15ml DCM and 1.32g CDI. The mixture was left at room temperature overnight. The resulting polymer was precipitated three times into methanol and dried for 24 h in a 50 ^{o}C vacuum oven.

3.3.2.3 Metal incorporation

Zinc di[bis(trifluoromethylsulfonyl)imide] was dissolved in 1.5 mL of THF and added incrementally (100 uL) to solution of polymer in THF (stock solution concentration 100-150 mg/mL). The sample was then brief sonicated until transparent, yellow solution was obtained before another aliquot of metal salt was added.

For binding studies, 3ml of imidazole solution(4μmol) were injected into the UV cuvettes. The Zinc salt solutions (0.1mol/L) were then incrementally added into the cuvettes. After well capped and sealed, the cuvettes were shaked for 30 seconds for mixing.

CHAPTER 4

SUMMARY

In this thesis, two major research goals were proposed. First, an efficient, solvent free, and scalable monomer synthesis method was developed. A new soybean oil based monomer (EMOA) can be used in simple free radical polymerization or copolymerization to achieve similar thermal and mechanical properties to monomers made before. Attempts to make thermoplastic elastomers using this new soybean oil based monomer with PLA were carried out. The EMOA can be acting as the soft and rubbery component, while the PLA acted as hard junctions. Further ATRP with styrene can be expected to have a higher molecular weight and better performance. This whole development could show promises that soybean oil based materials are competitive in the replacement with petroleum analogues.

Second, imidazole grafted supramolecular soybean based polymers have been synthesized and used as potential materials for self-healing. Grafting level can be tuned by using varied amount of thiol. Zinc metal and ligand imidazole binding in both small molecules and polymers were studied via UV-vis.

Due to the desire to change the 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 replace the petroleum counterparts, the field will continue to grow because of its great impact. Soybean is very abundant, which means it is a good candidate to be used as bio-based feedstock, not to mention that the annual production continues to grow. The chemical structure of soybean oil has a lot of potential due to it's the presence of triglyceride and unsaturated double bonds. These functional groups can be used to allow lots of chemistry to create new monomers. Our efficient and scalable method to make soybean based monomers and polymers can also been applied to other vegetable oils. In future research, the developers should focus on lowing the whole cost to maximize the use of energy and renewable resources.

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