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Novel Sustainable Polymers Derived from Renewable Rosin and Fatty Acids

Perry Wilbon
University of South Carolina - Columbia

Novel Sustainable Polymers Derived from Renewable Rosin and Fatty Acids

by

Perry Wilbon

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Accepted by:

Chuanbing Tang, Major Professor

Brian Benicewicz, Committee Member

Wayne Outten, Committee Member

Harry Ploehn, Committee Member

Lacy Ford, Vice Provost and Dean of Graduate Studies

DEDICATION

To my entire family and everyone in Flint, MI, without their support and

inspiration, none of my accomplishments would be possible.

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ABSTRACT

In the work of this dissertation, polymers derived from renewable bio-based resources prepared by various polymerization techniques were investigated. The properties of these polymeric materials were characterized and discussed. Rosin was first converted into acrylate or methacrylate monomers for atom transfer radical polymerization (ATRP). Second, rosin was combined with vegetable oil to produce completely renewable novel polyesters by acyclic diene metathesis (ADMET) polymerization. Third, degradable block copolymers were synthesized composed of polycaprolactone and rosin grafted polycaprolactone with the aid of ring-opening polymerization (ROP). Finally, degradable polyesters were produced using vegetable oil derivatives as starting materials. These new rosin and fatty acid based renewable polymer materials will have potential applications as sustainable thermoplastics, thermoplastic elastomers, etc.

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LIST OF SYMBOLS

T_g glass transition temperature

T_m melting temperature

T_{d5} temperature at 5% weight loss

T_{d10} temperature at 10% weight loss

M_n number average molecular weight

LIST OF ABBREVIATIONS

αClεCL ....α-Chloro-ε-caprolactone

ADMET .... Acyclic Diene Metathesis

AEDA ....2-acryloyloxyethyl dehydroabieticcarboxylate

AFM .... Atomic Force Microscopy

AIBN .... Azobisisobutyronitrile

ATRP .... Atom Transfer Radical Polymerization

Đ ....Dispersity

DA ....Dehydroabietic Acid

DAPE.. Dehydroabietic Propargyl Ester

DBTDL...Dibutyltin Dilaurate

DBU... 1,8-Diazabicyclo[5.4.0]undec-7-ene

DHAA..Dehydroabietic Acid

DMF .... *N,N*-Dimethylformamide

DSC .... Differential Scanning Calorimetry

FTIR .... Fourier Transform Infrared Spectrometry

GPC ....Gel Permeation Chromatography

HEBiB .... and 2-hydroxyethyl 2-bromoisobutyrate

Me6Tren .... Tris(2-(dimethylamino)ethyl)amine

PCL...Poly(ε-caprolactone)

PDI .... Polydispersity Index

ROP .... Ring-Opening Polymerization

CHAPTER 1

GENERAL INTRODUCTION[1]

1.1 Renewable bio-based polymers

One of the most pressing issues for future generations is the development of a sustainable society. Fossil fuel used for both energy production and plastic manufacturing has finite availability. Within the next century it will be nearly depleted. Approximately 7% of the global production of fossil fuel goes into the synthesis of plastic materials.[1-13] In the United States alone, approximately 13% of fossil fuel consumption goes towards nonfuel chemical production. Global energy demands are expected to increase in the coming decades, further increasing the price of petroleum and other non-renewable resources as the supply struggles to meet the demand. While there is an increased investment in finding non-renewable energy sources for global transportation and heating, the chemical industry should not be neglected. In addition to the economic influence, the undesirable environmental impact by non-renewable resources has contributed to the rebirth of renewable resource alternatives. Burning fossil fuel has led to increased greenhouse gas emissions, reduced air quality, and global warming.[14] Most plastics derived from non-renewable resources have led to water and land pollution due to their inability to undergo biodegradation.

The environmental concerns, along with depleting oil reserves, have led to an increased interest in the development of green plastics derived from renewable natural resources.[3, 6, 7, 10-12, 15-29] The large scale production of green plastics primarily depends on the integration of biorefineries.[8, 9, 30] A biorefinery, as defined by the National Renewable Energy Laboratory, is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass and is analogous to today's petrochemical refineries.[31] The importance of these refineries to develop green

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plastics, without impacting the food and feed production in a negative manner, is essential for future growth.

Green plastics can be classified into three primary categories. The first class of natural resources is natural polymers including lignin, cellulose, hemicellulose, polysaccharide, and chitin.[22, 32-43] Many of these biopolymers display excellent biocompatibility and biodegradability. These natural polymers have long been exploited without any modifications. Currently, common approaches involve physical blending and limited chemical modifications. However the ill-defined already-built-in macromolecular structures could be further manipulated by implementing advanced polymerization techniques and potentially serve as a building block toward diverse polymeric architectures and therefore rich properties.[44] The second class of renewable polymers can be obtained in nature by microorganism fermentation of sugar or lipids. These polymers include polyhydroxyalkanoates (PHAs) such as poly(hydroxybutyric acid).[27, 45] The third category of green plastics pertains to the use of small molecular biomass that can be derivatized and further polymerized.[7, 15, 18, 19, 46-51] Vegetable oils, fatty acids, and lactic acids are a class of small molecular biomass, which are usually obtained directly from forestry and agriculture products or by microorganism fermentation. These materials could be precisely engineered at a molecular level into renewable polymers in a way similar to some plastics derived from petroleum chemicals.

1.2 Renewable Rosin acids

As one of the major classes of petroleum chemicals, cycloaliphatic and aromatic compounds such as benzene, cyclohexane and cyclohexene offer rigidity and hydrophobicity to polymers derived from them. There are great opportunities to develop

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renewable polymers from natural resources containing rich cycloaliphatic and aromatic structures.[17, 51, 52] Terpenes, terpenoids and rosin are a class of important natural molecular biomass containing cycloaliphatic and/or aromatic structures.[28, 29, 53-55] Particularly, they are also major components of resin, which is an exudate obtained from trees, especially pine trees and conifers.

Rosin is the non-volatile solid form of resin and produced by heating fresh liquid resin to vaporize the volatile liquid terpene components. Rosin consists primarily of abietic- and pimaric-type resin acids (or rosin acids) with characteristic hydrophenanthrene structures and about 10% neutral materials (Figure 1.1). The hydrophenanthrene rings are considered to have cycloaliphatic and aromatic structures. The production of rosin is more than 1 million metric tons per year.[28, 51, 53, 55, 56] The predominant rosin acid is abietic acid (AA) with the empirical formula $C_{20}H_{30}O_2$. Other acidic constituents of rosin differ mainly from abietic acid in that they are isomers of abietic acid having double bonds at different positions in the hydrophenanthrene moieties, which are often further hydrogenated or dehydrogenated with the aid of transition metal catalysts. The intrinsic acidity and rigidity, coupled with other chemical properties, enable rosin acids to be converted to a large number of downstream derivatives such as salts, esters and maleic anhydride adducts, and hydrogenated, disproportionated rosins which are used in a wide range of applications such as in the manufacture of adhesives, paper sizing agents, printing inks, solders and fluxes, surface coatings, insulating materials, and chewing gums.[52, 57-65]

Rosin-based thermoplastic polymers can be divided into two categories: main-chain polymers and side-chain polymers, according to the position of the

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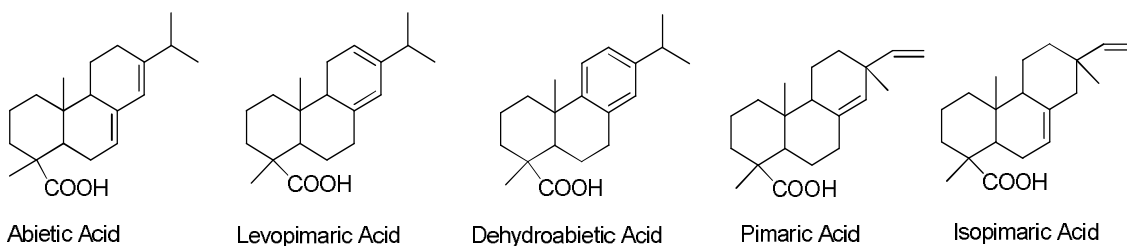
Figure 1.1 A few representative components of rosin

hydrophenanthrene structure of rosin in the polymer structures. Although main-chain rosin-based polymers can be prepared by various condensation methods, only low molecular weight polymers could be obtained. Steric hindrance, monomer impurities, and stoichiometric control are the primary reasons on why only low molecular weight is obtained.[28, 52, 53, 62, 66] The synthesis of side-chain rosin-based polymers by radical polymerization tends to avoid these problems associated with their main-chain counterparts. Radical polymerization of rosin-derived vinyl, acrylic, or allyl ester group monomers is utilized to produce side-chain rosin-based polymers.[52] Rosin is an abundant renewable resource that has shown promise in the field of polymer science. In order for its full potential to be realized, an improvement in the polymerization of rosin based monomers must be achieved.

1.3 Vegetable Oil

Vegetable oils are an exceptional natural renewable resource for polymer synthesis, with an annual global production that is projected to exceed 150 million metric tons in 2012.[67] This natural abundance, along with their inexpensive cost, and an ever increasing desire to find alternatives to non-renewable starting materials make vegetable oils an ideal polymeric starting material. The chemical structure of vegetable oils can be viewed as a triglyceride with three fatty acid chains as seen in Figure 1.2. Figure 1.3

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displays some of the more common fatty acids obtained from vegetable oils. The length of the fatty acid chains varies from 12 to 22 carbons and the amount of unsaturated C=C bonds vary from zero to 6 per fatty acid chain. Other functional moieties such as hydroxyl or epoxy groups may also be present in certain types of vegetable oil.
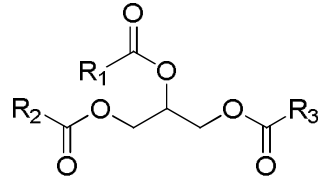
Figure1.2 Triglyceride structure where R1, R2, and R3 represent fatty acid chains

The final composition of the vegetable oil is a mixture of more than one triglyceride, with one or two structures representing the majority of this mixture. The reactivity of the unsaturated bonds of both the triglyceride and the isolated fatty acid is what allows vegetable oil to be used in a variety of polymerizations.[68-74]

1.3 Polymerization Techniques and "Click" Chemistry

Atom Transfer Radical Polymerization (ATRP) [75-83] Controlled radical polymerization (CRP) allows for the synthesis of well-defined polymers with controlled molar mass, narrow molecular weight distribution, and well-defined architectures and functionalities.[44, 81, 83-94] ATRP involves a fast dynamic equilibrium between dormant species and active radical species to provide control. The conditions of the
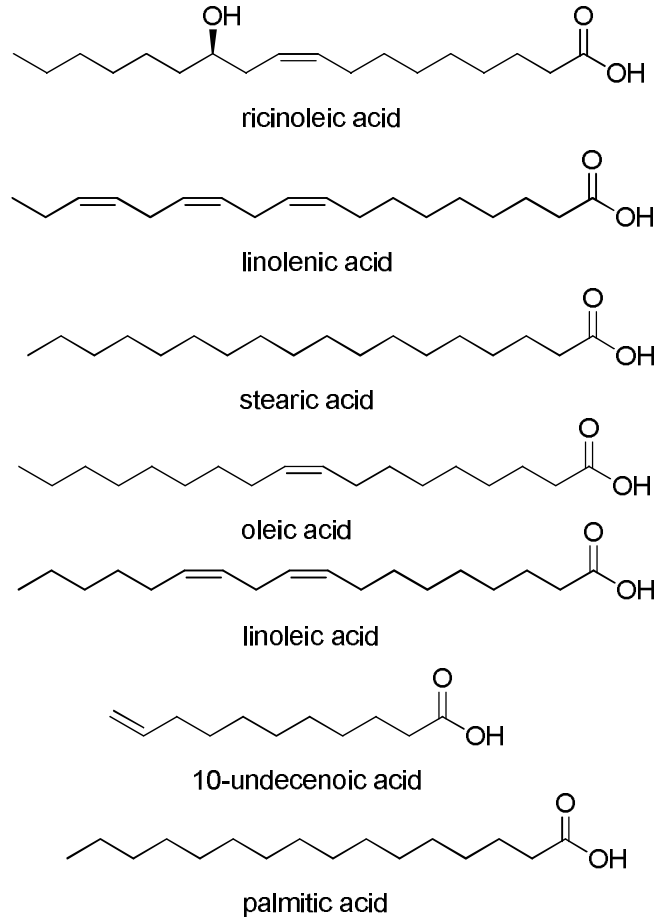
Figure 1.3 Common fatty acids obtained from vegetable oil triglycerides

polymerization, using transition-metal complexes, are selected so that the equilibrium between dormant and active species is strongly shifted toward dormant species in order to establish a low concentration of propagating radicals and to reduce proportion of unavoidable termination reactions. The general mechanism of ATRP is showed in Figure 1.4. The radicals (active species) R• are generated by a reversible redox process in the presence of a transition metal complex. The dormant species R-X is formed by an oxidation reaction between the transition metal complex CuX/L with the halogen atom X. The equilibrium between propagating radicals R• and dormant species R-X is what

controls this polymerization method. Monomers, initiators, catalysts, reaction solvents and reaction temperature are all key features that effect ATRP.

$$R\text{-}X + CuX/L \underset{k_d}{\overset{k_a}{\rightleftarrows}} CuX_2/L + R\cdot$$

with k_p (Mon) cycle and k_t leading to R-R/ R-H & R=

Figure 1.4 Overall mechanism of atom transfer radical polymerization

Ring-Opening Polymerization (ROP)[95-98] ROP is a useful technique for the production of biodegradable polyesters in a controlled manner. These polyesters have been used in many biomedical applications due to their excellent biocompatibility. Anionic, cationic, organo-catalytic and coordination-insertion are the primary methods in which ROP occurs. Metal based catalysts, such as tin(II) bis(2-ethylhexanoate) ($Sn(Oct)_2$) and aluminum(III) isopropoxide, have been used for many years, however metal free catalysts have been gaining much attention due to their reduced environmental impact. Figure 1.5 illustrates the ROP of trimethylene carbonate and several representative catalysts.

Acyclic Diene Metathesis Polymerization (ADMET)[99-101] ADMET polymerization is a step-growth polymerization. The release of ethylene gas is the driving force for this polymerization. In order for the reaction to produce high molecular weight polymers, ethylene gas must be removed to shift the equilibrium towards the product side. Monomers that contain α,ω-dienes are polymerized by way of ADMET to produce linear polyethylene backbone polymers. Figure 1.6 displays the ADMET polymerization of a

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Figure 1.5 ROP of trimethylene carbonate and representative ROP catalysts

Figure 1.6 ADMET polymerization of α,ω-diene monomer with examples of Grubbs'
catalysts

typical unsaturated monomer. With the aid of a ruthenium based Grubbs' catalyst, high
molecular weight polymers are readily produced at room temperature by way of ADMET
polymerization.

"Click" Chemistry[102-104]   "Click Chemistry" is a term referring to chemical reactions
that meet a certain criteria according to Sharpless et al.   Simple chemical reaction

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conditions, quantitative yields, and simple purification are just a couple of the criteria that must be met in order for a reaction to be classified as a "click" reaction. Two particularly useful "click" reactions in the field of polymer science are copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) and thiol-ene reactions. CuAAC, first discovered in 2002, has become one of the most influential methods for post-polymerization modifications. CuAAC is a variation of the Huisgen 1,3-dipolar cycloaddition reaction between terminal alkynes and azides (Figure 1.7). This reaction has been used in conjunction with ATRP and ROP to produce a wide variety of functional polymers.
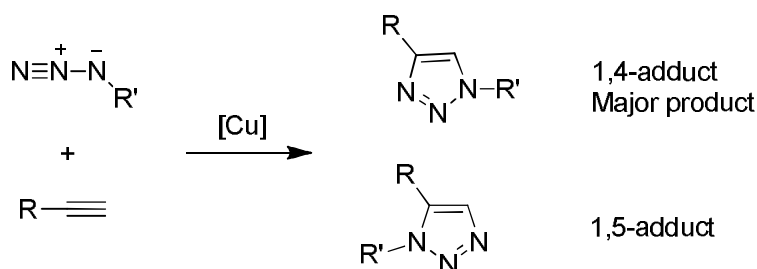
Figure 1.7 Copper catalyzed azide-alkyne cycloaddition (CuAAC)

Another useful reaction in the area of polymer engineering is thiol-ene "click". Thiols are highly reactive and can undergo several chemical reactions. As seen in Figure 1.8, the thiol-ene "click" reaction is simply the hydrothiolation of a C=C bond. Although this reaction has been known for over 100 years, it has recently gained interest in the field of
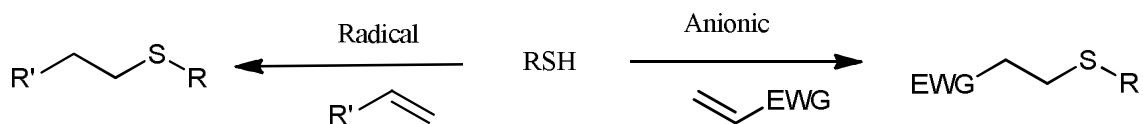
Figure 1.8 Thiol "click" chemistry reactions

polymer science. A wide range of thiols and alkenes can undergo this reaction, with near quantitative yields and simple reaction conditions, making this an ideal reaction for polymer chemistry. The hydrothiolation reaction most often takes place by way of a

radical process (Figure 1.9). This reaction occurs in a matter of minutes and is tolerant towards moisture, making it ideal for polymer modification.
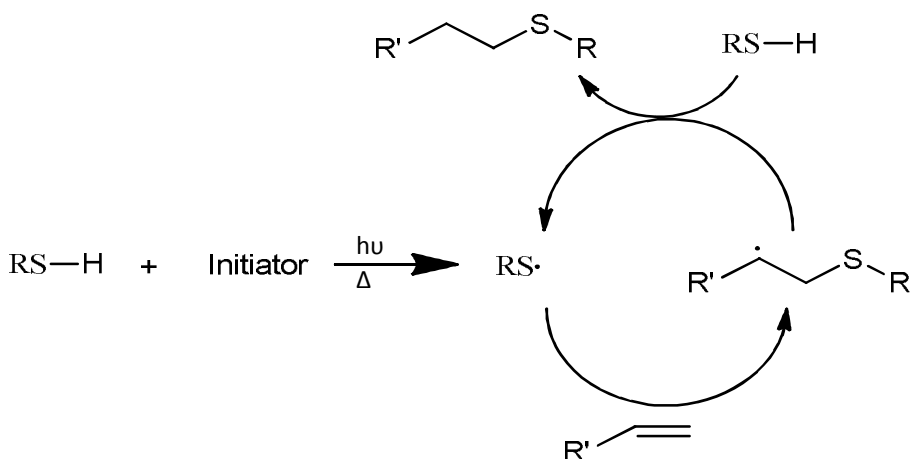
Figure 1.9 Radical initiated hydrothiolation reaction

1.4 Research Objectives

In Chapter 1, the overall background and recent development of renewable bio-based polymers is introduced. Major research objectives of my doctoral work are described.

The preparation of renewable bio-based polymers is provided from Chapter 2 to Chapter 5. In Chapter 2, the preparation of novel polymers derived from renewable gum rosin by atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP) was described. In Chapter 3, sustainable polymers derived from renewable rosin and fatty alcohol were accomplished by acyclic diene metathesis (ADMET) polymerization. These polymers displayed excellent thermal properties. Chapter 4 described the preparation of different rosin containing pentablock copolymers. Rosin containing polycaprolactone (PCL) was prepared by a combination of ROP and "click"

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chemistry. In Chapter 5, renewable polyesters derived from castor oil were prepared by ADMET and thiol-ene "click" polymerization. These polymers were degradable and displayed superb thermal properties.

Finally, a summary is given in Chapter 6. In addition, some suggestions about future research directions on the renewable polymer materials are provided.

CHAPTER 2

RENEWABLE DEGRADABLE ROSIN ACID-CAPROLACTONE BLOCK
COPOLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION AND RING-
OPENING POLYMERIZATION[2]

2.1 Abstract

The first renewable degradable rosin acid-caprolactone block copolymers were prepared by atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP). Two-step chain-extension reactions using either poly(2-acryloyloxyethyl dehydroabieticcarboxylate)-OH (PAEDA-OH) or poly(ε-caprolactone)-Br (PCL-Br) as macroinitiators resulted in well-defined block copolymers with low polydispersity. One-pot polymerization was carried out with three different sequential feeds of AEDA and ε-CL monomers. The control of one-pot polymerization depended on the interactions of ATRP catalysts and co-existing ROP catalysts. While the minimal interactions between copper (I) and tin (II) catalysts produced well-defined block copolymers, excess copper II) or tin (II) led the formation of block copolymers with polydispersity > 1.5. It was suggested that the tin (II) catalysts reduced the persistent radicals copper (II) of ATRP, leading to a poorly controlled polymerization. These block copolymers exhibited excellent degradability under acidic conditions. Thermal behaviors of these block copolymers showed a strong dependence of polymer compositions due to the potential crystallization of the PCL block.

2.2 Introduction

Synthetic plastics account for consumption of ~7% of fossil fuels worldwide.[105-107] Energy shortage and environmental concerns prompt opportunities to seek developing renewable resources for manufacturing of "green" plastics.[2, 107-110] There are two major classes of natural resources. The first class of natural resources is natural polymers including cellulose, hemicellulose and lignin.[109-113] These natural polymers have long

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been exploited without any modifications. Currently, common approaches involve physical blending and limited chemical modifications. Due to their complexity and already-existing macromolecular skeletons, it is challenging to carry out precise macromolecular engineering toward diverse properties. In contrast, the second class of natural resources is small molecular biomass such as lactic acids and vegetable oils, which can be derivertized into monomers for polymerization.[105-107] Particularly, lactic acid-derived polymers have achieved enormous success due to their ability to be molecularly engineered to allow precise and controlled polymerization. As one of the major classes of petroleum chemicals, cycloaliphatic and aromatic compounds offer rigidity and chemical stability to polymers derived from them. However, such important polymeric materials are largely missing or ignored in the communities of renewable polymers.

Gum Rosin, whose major components are resin acids (or rosin acids as we refer below), has characteristic hydrocarbon-based hydrophenanthrene rings, similar in rigidity and chemical stability to petroleum chemicals-based cycloaliphatic and aromatic compounds.[54, 55, 63, 114, 115] Therefore, it is reasonably expected that polymers with hydrophenanthrene building blocks have the potential to resemble many plastics derived from petroleum chemicals.[55, 116-123] We have recently synthesized a series of rosin acid-derived model monomers and shown that they can be polymerized to form well-defined vinyl polymers by atom transfer radical polymerization (ATRP).[124]

Polycaprolactone (PCL) is a hydrophobic, semi-crystalline (bio)degradable polymer, which is generally prepared by ring-opening polymerization (ROP).[125, 126] The use of PCL as degradable polymers has numerous advantages including nontoxicity,

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permeability, suitable degradation time, exceptional blend-compatibility, tailorable degradation kinetics and mechanical properties, ease of shaping and manufacturing. To be successful in new applications, it is desired that degradable polymers exhibit a broad spectrum of physical properties while retaining the degradability of the parent polymers. Common approaches used to tune the physical properties of degradable polymers include copolymerization, the preparation of block copolymers, and synthesis of substituted degradable monomers.[127-136] However, caprolactone is not a renewable biomass, but a classical petroleum chemical.
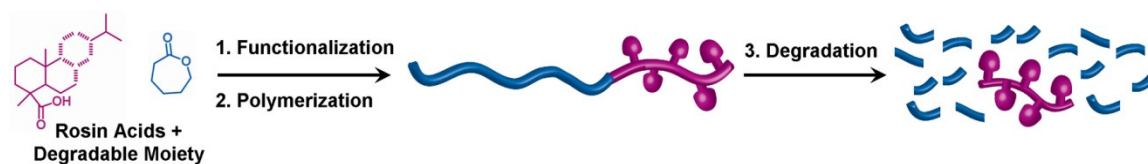
Figure 2.1 A general strategy toward renewable degradable rosin acid-caprolactone block copolymers

Due to the microbial degradation of rosin acids,[137, 138] gum rosin is more compatible with the environment than petroleum-based chemicals. Therefore, integration of the rosin moiety holds new opportunities for the design of degradable polymers. To the best of our knowledge, this is an area that has never been explored in the literature. We believe that it is possible to integrate renewable rosin acid-moiety and degradable caprolactone into a block copolymer through suitable functionalization and appropriate polymerization techniques (Figure 2.1). Development of rosin acid-containing degradable polymers will have two major benefits: (1) increasing the use of renewable components in the degradable materials that are not renewable (e.g. caprolactone); (2) providing novel properties originating from the rosin moiety. Herein, we report the first preparation of

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block copolymers containing a rosin acid-derived model monomer and caprolactone by a combination of ATRP and ROP.

2.3 Experimental Section

2.3.1 Materials

Dehydroabietic acid (DA, ~90%) was obtained from Wuzhou Chemicals, China. Tetrahydrofuran (THF, Aldrich) and toluene (Aldrich) was refluxed with sodium and distilled out just before use under nitrogen atmosphere. Tris(2-(dimethylamino)ethyl)amine (Me$_6$Tren) and 2-hydroxyethyl 2-bromoisobutyrate (HEBiB) were prepared according to reported literatures.[139] Oxalyl chloride, triethylamine, Sn(II) 2-ethylhexanoate (Sn(EH)$_2$) and copper(I) bromide (99.999%) were used as received (Aldrich). Monomer 2-acryloyloxyethyl dehydroabieticcarboxylate (AEDA) was prepared according to our recent report.[124] ε-Caprolactone (CL, Aldrich) was dried with CaH$_2$ and distilled out before use.

2.3.2 Characterization

^{1}H NMR spectra were recorded on Brucker ARX300 and ARX400 spectrometers. The chemical shifts were recorded in ppm (δ) relative to tetramethylsilane. Gel permeation chromatography (GPC) was performed at room temperature on a Varian system equipped with a Varian 356-LC refractive index detector and a Prostar 210 pump. The columns were STYRAGEL HR1, HR2 (300×7.5 mm) from Varian. HPLC grade THF was used as eluent at a flow rate of 1 mL/min. Samples were filtered over a microfilter with pore size of 0.2μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). GPC was calibrated using polystyrene as standards. Fourier Transform

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Infrared Spectrometry (FTIR) was conducted on a Shimadzu 8400 FTIR spectrometer. Thermal transitions were recorded using differential scanning calorimetry (DSC) on a TA Q200 calorimeter in a temperature range from 0 to 200 °C at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. All the data were collected during the second heating process after cooling at 10 °C min^{-1} from 200 °C. The average sample mass was about 5 mg, and the nitrogen flow rate was 50 mL min^{-1}. Tapping mode atomic force microscopy (TMAFM) studies were carried out with the aid of a multimode NanoScope V system (Veeco Instruments, Santa Barbara, CA), equipped with a J-type vertical engage scanner. TMAFM observations were performed at room temperature in air using silicon cantilevers with spring constant of 20-80 N/m and resonance frequency of 292-333 kHz (standard silicon NCHV probes).

2.3.3 Synthesis

Preparation of PCL-Br Macroinitiator by ROP (Table 1.1, Run #1): A mixture of CL (2.00 g, 1.75×10^{-2} mol), HEBiB (74.2 μL, 3.5×10^{-4} mol), Sn(EH)$_2$ (14 mg, 3.5×10^{-5} mol), and toluene (2 mL) was introduced into a Schlenk flask. After three freeze-pump-thaw cycles, the flask was placed into a preheated oil bath set at 120 °C. After the overnight reaction, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M$_n$ (NMR) = 4,700 g/mol, PDI (GPC) = 1.25. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 4.0-4.2 (t, -O*CH2*-); 2.2-2.4 (t, -*CH2*CO-); 1,9-1.95 (s, -C*(CH3)$_2$*Br), 1.3-1.8 (broad, -*CH2CH2CH2*-). IR (neat): 3020-2820 cm^{-1} (CH stretching); 1723 cm^{-1} (C=O stretching).

Chain-Extension to Prepare PCL-*b*-PAEDA-Br by ATRP (Table 2.1, Run #2): A mixture of AEDA (1.00 g, 2.5×10^{-3} mol), Me$_6$Tren (2.9 mg, 1.2×10^{-5} mol), PCL–Br macroinitiator (0.1 g, 2.5×10^{-5} mol; M_n (NMR) = 4,700 g/mol, M_w/M_n (GPC) = 1.25) and THF (1 mL) was introduced into a polymerization tube. After three freeze-pump-thaw cycles, CuBr (1.8 mg, 1.2×10^{-5} mol) was added to the tube while the contents were at a solid state and deoxygenated by vacuum followed by back-filling with nitrogen three times. The tube was placed into a preheated oil bath set at 90 ^{o}C. After 16 hours, the tube was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 20,100 g/mol, PDI (GPC) = 1.36. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.8-7.2 (broad, aromatic, PAEDA); 4.1-4.3 (s, O*CH2CH2*O, PAEDA); 4.0-4.1 (t, -O*CH2*-, PCL); 2.8-3.0 (s, protons next to aromatic ring, PAEDA); 2.2-2.4 (t, -*CH2*CO-, PCL). IR (neat): 3070-2800 cm^{-1} (CH stretching); 1723 cm^{-1} (C=O stretching).

Preparation of PAEDA-OH Macroinitiator by ATRP (Table 2.1, Run #3): A mixture of AEDA (1.00 g, 2.5×10^{-3} mol), Me$_6$Tren (2.9 mg, 1.2×10^{-5} mol), HEBiB (5.3 μL, 2.5×10^{-5} mol) and THF (1 mL) was introduced into a polymerization tube. After three freeze-pump-thaw cycles, CuBr (1.8 mg, 1.2×10^{-5} mol) was added to the tube while the contents were at a solid state and deoxygenated by vacuum followed by back-filling with nitrogen three times. The tube was placed into a preheated oil bath set at 90 ^{o}C. After 16 hours, the tube was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 20,000 g/mol, PDI (GPC) = 1.30. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.7-7.2 (broad, aromatic); 4.0-4.4 (t, O*CH2CH2*O);

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2.8-3.0 (protons next to aromatic ring). IR (neat): 3060-2790 cm^{-1} (CH stretching); 1732 cm^{-1} (C=O stretching).

Chain-Extension to Prepare PAEDA-*b*-PCL-OH by ROP (Table 2.1, Run #4):
PAEDA-OH macroinitiator (0.24 g, 1.2×10^{-5} mol; M_n (NMR) = 20,000 g/mol, M_w/M_n (GPC) = 1.30), CL (0.76 g, 6.7×10^{-3} mol), Sn(EH)$_2$ (0.5 mg, 1.2×10^{-6} mol), and toluene (1.2 mL) were mixed in a Schlenk flask. The mixture was degassed by conducting three FPT cycles. The flask was placed into a preheated oil bath set at 120 ^{o}C. After the overnight reaction, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 77,000 g/mol, PDI (GPC) = 1.18. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.9-7.2 (broad, aromatic, PAEDA); 4.1-4.4 (s, O*CH2CH2*O, PAEDA); 4.0-4.1 (t, -O*CH2*-, PCL); 2.8-3.0 (s, protons next to aromatic ring, PAEDA); 2.2-2.4 (t, -*CH2*CO-, PCL).

One-Pot Polymerization to Prepare PCL-*b*-PAEDA by ATRP and ROP

(1) Simultaneous Feeds of AEDA and CL (Table 2.1 Run #5): A mixture of AEDA (0.50 g, 1.25×10^{-3} mol), CL (0.14 g, 1.22×10^{-3} mol), Sn(EH)$_2$ (0.5 mg 1.2×10^{-6} mol, Me$_6$Tren (1.4 mg, 6×10^{-6} mmol), HEBiB (2.5 μL, 1.2×10^{-5} mol) and toluene (1 mL) was introduced into a Schlenk flask. After three freeze-pump-thaw cycles, CuBr (0.9 mg, 6×10^{-6} mol) was added to the flask while the contents were at a solid state and deoxygenated by vacuum followed by back-filling with nitrogen three times. The flask was placed into a preheated oil bath set at 120 ^{o}C. After 24 hours, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M_n (NMR) = 24,400 g/mol, PDI (GPC) = 1.24. ^{1}H NMR (300 MHz,

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CDCl$_3$, δ): 6.9-7.2 (broad, aromatic, PAEDA); 4.2-4.4 (t, O*CH2CH2*O, PAEDA); 4.0-4.2 (t, -OCH2-, PCL); 2.8-3.0 (protons next to aromatic ring, PAEDA); 2.2-2.4 (t, -*CH2*CO-, PCL).

(2) Sequential Feeds from AEDA to CL (Table 2.1 Run #7): A mixture of AEDA (1.00 g, 2.5×10^{-3} mol), Me$_6$Tren (2.9 mg, 1.2×10^{-5} mol), HEBiB (5.3 μL, 2.5×10^{-5} mol) and toluene (1 mL) was introduced into a polymerization tube. After three freeze-pump-thaw cycles, CuBr (1.8 mg, 1.2×10^{-5} mol) was added to the tube while the contents were at a solid state and deoxygenated by vacuum followed by back-filling with nitrogen three times. The tube was placed into a preheated oil bath set at 120 °C. After the overnight reaction, a deoxygenated mixture of of CL (1.00 g, 8.8×10^{-3} mol), Sn(EH)$_2$ (4.0 mg, 9.9×10^{-6} mol), and toluene (1 mL) was added to the flask under nitrogen. After 16 hours, the flask was opened and the reaction mixture was diluted with toluene. The polymer was precipitated and washed by methanol. M$_n$ (NMR) = 7,960 g/mol, PDI (GPC) = 1.51. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.9-7.2 (broad, aromatic, PAEDA); 4.0-4.4 (s, O*CH2CH2*O, PAEDA); 2.8-3.0 (s, protons next to aromatic ring, PAEDA).

(3) Sequential Feeds from CL to AEDA (Table 2.1 Run #8): A mixture of CL (1.00 g, 8.8×10^{-3} mol), Sn(EH)$_2$ (9.0 mg 2.22×10^{-5} mol), HEBiB (9.0 μL, 4.27×10^{-5} mol) and toluene (1 mL) was introduced into a Schlenk flask. After three freeze-pump-thaw cycles, the flask was placed into a preheated oil bath set at 120 °C. After the overnight reaction, a deoxygenated mixture of AEDA (1.00 g, 2.51×10^{-3} mol), CuBr (1.8 mg, 1.2×10^{-5} mmol), Me$_6$Tren (2.9 mg, 1.2×10^{-5}) and toluene (1 mL) was added to the flask under nitrogen. After 16 hours, the flask was opened and the reaction mixture was diluted with THF. The polymer was precipitated and washed by methanol. M$_n$ (NMR) = 30,800 g/mol, PDI

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(GPC) = 1.38. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.9-7.2 (broad, aromatic, PAEDA); 4.1-4.4 (t, OCH_2CH_2O, PAEDA); 4.0-4.1 (s, -OCH_2-, PCL); 2.8-3.0 (s, protons next to aromatic ring, PAEDA); 2.2-2.4 (t, -CH_2CO-, PCL).

2.3.4 Degradation of Block Copolymers

A mixture of block copolymers (~ 23 mg), 3.0 M HCl (aq) (0.2 mL), and THF (2 mL) was introduced into a small vial. The solution was then refluxed overnight at 65 ^{o}C. The solution was then evaporated to dryness.

2.4 Results And Discussions

Atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP) were combined to prepare 2-acryloyloxyethyl dehydroabieticcarboxylate (AEDA) and caprolactone (CL) diblock copolymers. Two strategies and five different synthetic routes were carried out to optimize the control of polymerization: two-step sequential polymerization including PCL-first or PAEDA-first, and one-pot polymerization. All polymerizations were involved the use of a difunctional initiator, 2-hydroxyethyl bromoisobutyrate (HEBiB), which allowed for both ROP and ATRP. The two-step synthesis of diblock copolymers employed the use of either PCL-Br or PAEDA-OH as a macroinitiator for chain-extension with PAEDA or PCL with the aid of CuBr/Me$_6$Tren or tin(II) 2-ethylhexanoate (Sn(EH)$_2$) as the catalyst system respectively. The one-pot polymerization involved the use of monomers at different feeding sequences including simultaneous feeds of a mixture of CL and AEDA, sequential feeds from CL to AEDA and from AEDA to CL.

1. Two-Step Sequential Polymerization

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(1) Chain-Extension from PCL-Br to PAEDA: Diblock Copolymers PCL-*b*-PAEDA-Br: The synthetic procedures of two-step sequential polymerizations are presented in Figure 2.2. The -OH and -Br functional groups of the HEBiB initiators were used as initiating sites for ROP of CL and ATRP of AEDA respectively.
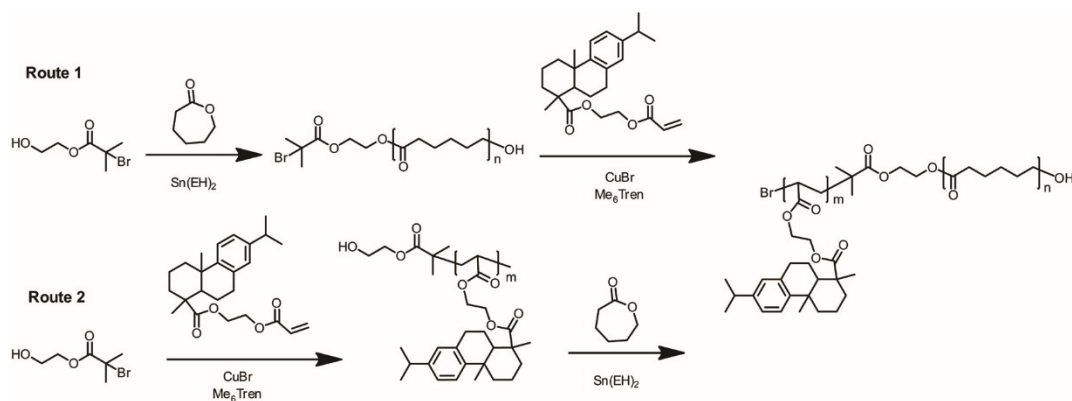
Figure 2.2 Preparation of CL and AEDA diblock copolymers by two-step sequential polymerization

Similar to earlier published work from other research groups,[140, 141] the ROP of CL was carried out straightforward using HEBiB and $Sn(EH)_2$ as the initiator and the catalyst respectively in the presence of dry toluene, yielding a bromine-terminated PCL-Br. As shown in Figure 2.3, ^{1}H NMR spectrum of PCL-Br polymers shows characteristic signals

Table 2.1 Preparation of Block Copolymers Containing CL and AEDA by ROP and ATRP

Run	[Monomer]/[Inititaor]	Polymer	Monomer Conv. (%)	M_n (g/mol) (NMR)	PDI (GPC)
1	[CL]/[HEBiB]=50	PCL-Br	82% (CL)	4.7K	1.25
2[a]	[AEDA]/[HEBiB]=100	PCL$_{41}$-PAEDA$_{41}$-Br	41% (AEDA)	4.7K-16.4K	1.36
3	[AEDA]/[HEBiB]=100	PAEDA$_{50}$-OH	50% (AEDA)	20K	1.30
4[b]	[CL]/[HEBiB]=556	PAEDA$_{50}$-PCL$_{500}$-OH	90% (CL)	20K-57K	1.18
5[c]	[CL]/[HEBiB]=100 [AEDA]/[HEBiB]=100	PAEDA$_{52}$-PCL$_{32}$	52% (AEDA) 32% (CL)	20.8K-3.6K	1.24
6[c]	[CL]/[HEBiB]=360 [AEDA]/[HEBiB]=100	PAEDA$_{16}$-PCL$_{320}$	16% (AEDA) 89% (CL)	6.4K-36.5K	1.66
7[d]	[CL]/[HEBiB]=349 [AEDA]/[HEBiB]=100	PAEDA$_{20}$-PCL$_{\sim0}$	20% (AEDA) 0% (CL)	7.96K-0K	1.51
8[e]	[CL]/[HEBiB]=200 [AEDA]/[HEBiB]=60	PCL$_{200}$-PAEDA$_{20}$	100% (CL) 22% (AEDA)	22.8K-8.0K	1.38

*a.Chain-extension from PCL-Br (run #1) to PAEDA; b. Chain-extension from PAEDA-OH (run #3) to PCL; c. One-pot simultaneous polymerization; d. one-pot polymerization with sequential feeds from AEDA to CL; e. one-pot polymerization with sequential feeds from CL to AEDA.

at 3.9-4.1 ppm and 2.2-2.4 ppm corresponding to the methylene protons of $-CH_2O-$ and $-COCH_2-$ of the caprolactone unit respectively. The peak at 1.9 ppm corresponds to the methyl protons of $-C(CH_3)_2-$ from the initiator moiety at the end of polymer chain. The molecular weight based on NMR end-group analysis was in good agreement with the one calculated from NMR reaction conversion, indicating all polymer chains retained the end group $-Br$. The molecular weight can be facilely tuned through adjustment of the ratio of monomers to initiators. GPC traces show unimodal peaks with PDI at 1.1-1.25 for all PCL-Br polymers synthesized although the GPC-based molecular weight was a little higher than those obtained from NMR analysis. These well-defined PCL-Br polymers were then used as macroinitiators for chain-extension with PAEDA.
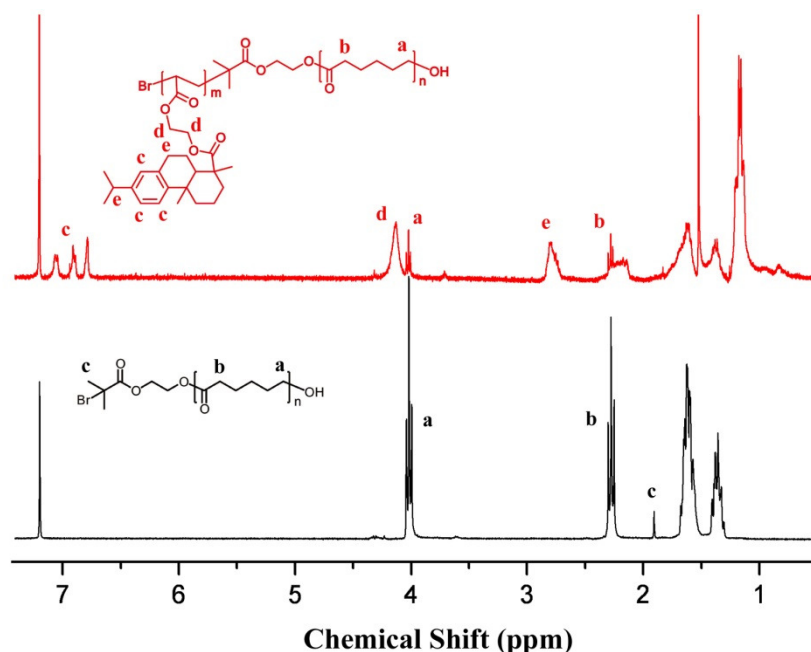
Figure 2.3 ^{1}H NMR spectra of PCL-Br, and PCL-*b*-PAEDA-Br diblock copolymers prepared by sequential ROP and ATRP (Runs #1 and #2 from Table 2.1)
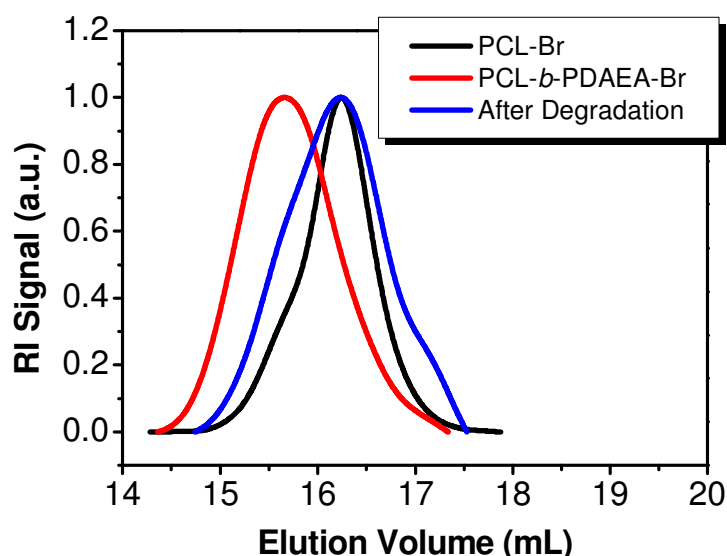
Figure 2.4 GPC traces of PCL-Br, and PCL-*b*-PAEDA-Br prepared by sequential ROP and ATRP (Runs # 1 and # 2 from Table 2.1)

ATRP of AEDA from PCL-Br was carried out at a temperature of 90 $^{\circ}$C in THF (50% v/v of the monomer) using CuBr/Me$_6$Tren as the catalyst system, as shown in Scheme 2.2. We have previously demonstrated the living homopolymerization of AEDA by ATRP using ethyl 2-bromoisobutyrate as initiators in a similar reaction condition.[124] Figure 2.3 shows a typical ^{1}H NMR spectrum of the resulting PCL-*b*-PAEDA-Br diblock copolymer. Peaks at 2.6-2.9 ppm, 4.1-4.3 ppm, 6.7-7.1 ppm are assigned to the protons next to the phenyl ring, the methylene protons of –OCH$_2$CH$_2$O– and aromatic protons of the PAEDA block respectively, while peaks at 4.0-4.1 ppm and 2.2-2.4 ppm from the PCL block. All other peaks of dehydroabietic side groups were nearly same as PAEDA homopolymers reported in our earlier work.[124] All these indicated that the PCL-Br has initiated the polymerization of AEDA. The compositions of block copolymers could be calculated by the integration areas of the characteristic protons from respective AEDA

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and CL blocks and are presented in Table 2.1. The GPC traces shifted clearly to a higher molecular weight with PDI ~ 1.3 (Figure 2.4), indicating the successful chain-extension of PAEDA from the PCL-Br macroinitiator.

(2) Chain-Extension from PAEDA-OH to PCL: Diblock Copolymers PAEDA-*b*-PCL-OH: In parallel, PAEDA-OH prepared by ATRP was used as the macroinitiator for chain-extension with PCL. PAEDA-OH was prepared using HEBiB as the initiator, CuBr/Me6Tren as the catalyst system in the presence of THF, similar to the procedure reported in our earlier work.[124] ^{1}H NMR spectrum (Figure 2.5) of PAEDA-OH shows characteristic signals of aromatic protons, methylene protons of $-OCH_2CH_2O-$, protons from $-CH_2-CH-$ backbone and all other protons of dehydroabietic side groups. Hydroxy-terminated PAEDA polymers were further used for ROP of CL using $Sn(EH)_2$ as the catalyst in the presence of toluene, yielding PAEDA-*b*-PCL-OH diblock copolymers. ^{1}H NMR spectrum clearly indicated the formation of PAEDA-*b*-PCL-OH block copolymers with characteristic protons from both blocks, similar to those from PCL-*b*-PAEDA-Br diblock copolymers. GPC traces (Figure 2.6) of the diblock copolymers shifted further into the higher molecular weight with PDI ~ 1.3, indicating efficient chain-extension. The chain length of the PCL block can be controlled by changing the molar ratio of monomers to macroinitiators. As high as DP = 500 was obtained for the PCL block, while keeping the PDI of PAEDA-*b*-PCL-OH block copolymers as low as 1.18.

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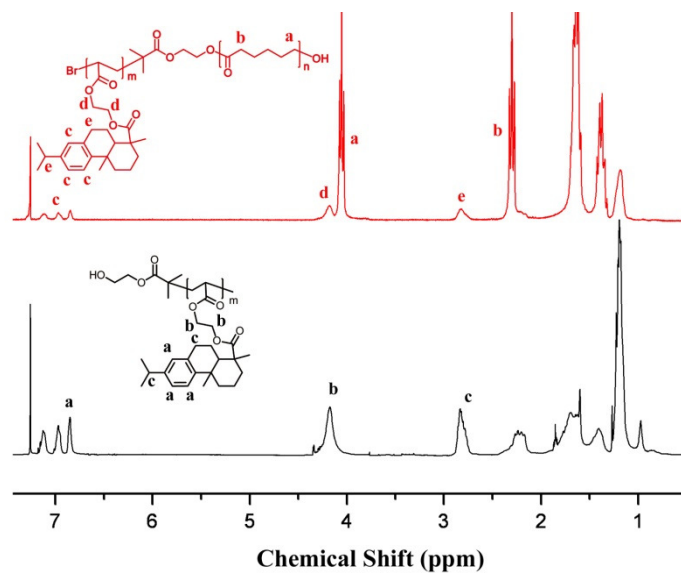
Figure 2.5 ^{1}H NMR spectra of PAEDA-OH, and PAEDA-*b*-PCL-OH prepared by two-step sequential ATRP and ROP (Runs #3 and #4 from Table 2.1)
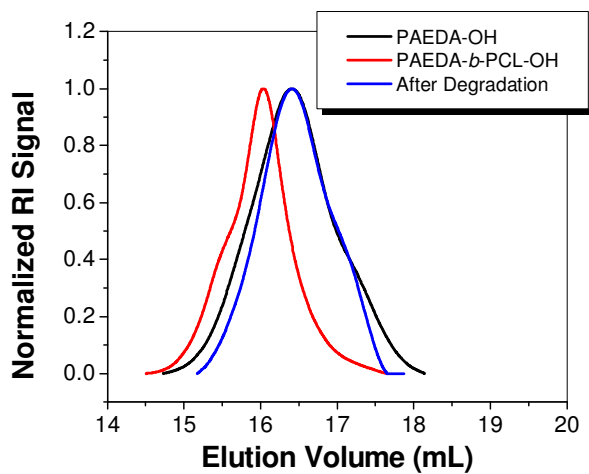
Figure 2.6 GPC traces of PAEDA-OH, and PAEDA-*b*-PCL-OH prepared by two-step sequential ATRP and ROP (Runs #3 and #4 from Table 2.1)

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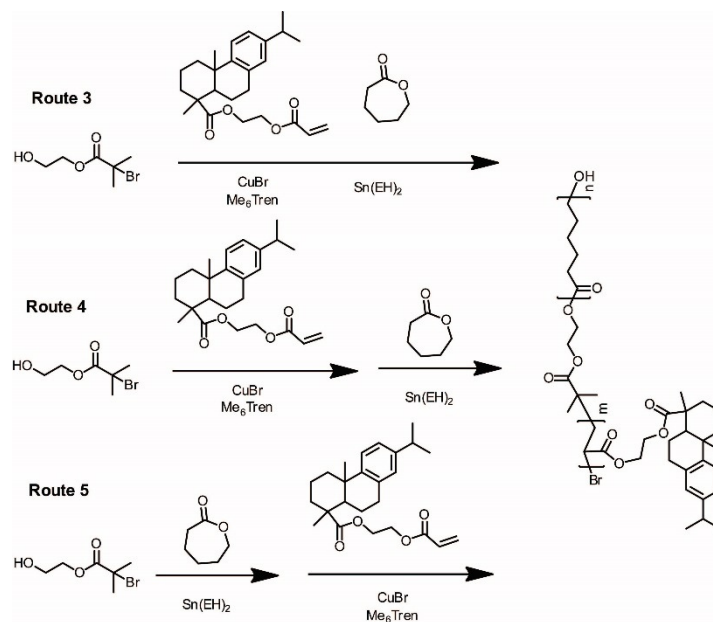
Figure 2.7 One-pot polymerization of CL and AEDA to prepare diblock copolymers by ROP and ATRP

One-Pot Polymerization: Although there are many precedent reports on the combination of ROP and ATRP in one pot,[140-145] the preparation of caprolactone-based renewable degradable block copolymers is rare. The two-initiating sites of the HEBiB initiator have the potential to allow the synthesis of block copolymers in one pot without an intermediate workup step.[140, 141] We carried out the one-pot polymerization using three different routes, as shown in Figure 2.7. Route 3 was used to polymerize CL and AEDA simultaneously in one pot. Route 4 and Route 5 adopted a one-pot sequential feeding polymerization, in which one monomer was polymerized first followed by adding the second monomer into the first monomer reaction system without an intermediate workup step.

(1) One-Pot Simultaneous Polymerization (Route 3): The mixture of CL, AEDA and HEBiB with same molar ratios of monomers to initiators

([CL]/[HEBiB]=[AEDA]/[HEBiB]=100) in dry toluene was employed for simultaneous co-polymerization with $Sn(EH)_2$ and $CuBr/Me_6Tren$ as the catalysts for ROP and ATRP respectively. After 24 h polymerization, ^{1}H NMR spectrum (Figure 2.8) shows a typical block copolymer composition distribution although the PCL block (DP=32) was shorter
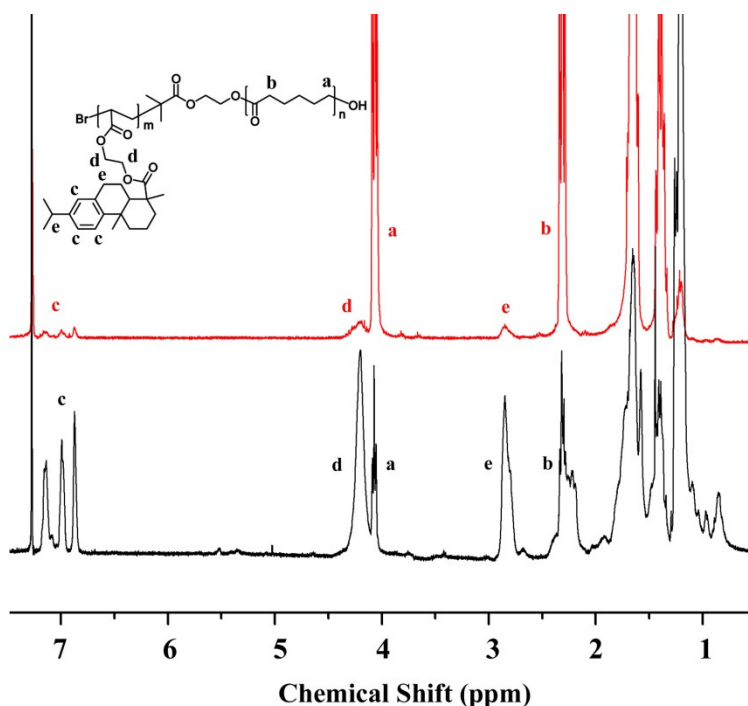
Figure 2.8 ^{1}H NMR spectra of AEDA and CL diblock copolymers prepared by one-pot simultaneous ROP and ATRP (Runs #5 (bottom NMR) and #6 (top NMR) from Table 2.1)

than the PAEDA block (DP = 70). The GPC trace of the obtained block copolymers (Figure 2.9) shows narrow molecular weight distribution with the PDI = 1.24, indicating a good control on both blocks. When the molar ratio of CL to HEBiB increased ($[Sn(II)(EH)_2]$ proportionally increased, but [AEDA]/[HEBiB] maintained at 100), the molecular fraction of CL in the block copolymers significantly increased. However, the

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PDI of block copolymers also increased. When the DP of PCL was 320 ([CL]/[HEBiB]=360), the PDI was 1.66, while the DP of PAEDA was only 16. The increase of PDI indicated the increasing poor control of polymerization, probably due to the undesirable interactions between the Sn(II) catalysts of the ROP system and the copper (II) catalysts of the ATRP system, which will be discussed in the later section of this paper.
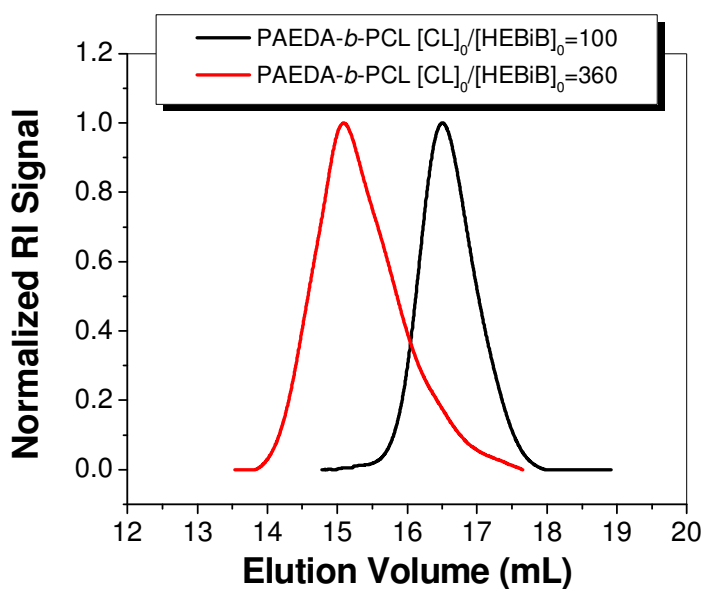
Figure 2.9 GPC traces of AEDA and CL diblock copolymers prepared by one-pot simultaneous ROP and ATRP (Runs #5 (right trace) and #6 (left trace) from Table 2.1)

(2) One-Pot Polymerization with Sequential Feeds. Route 4: from AEDA to CL:

To further explore the ATRP system effect on the ROP of CL, one-pot polymerization with sequential feeds from AEDA to CL was carried out. ATRP of AEDA was employed first with use of CuBr/Me$_6$Tren, HEBiB and toluene. After a 24h reaction, a deoxygenated mixture of CL, Sn(EH)$_2$ and toluene was added into the above reaction

flask. As shown in Figure 2.10, the GPC trace shows an asymmetric broad distribution with a high PDI=1.51 (Table 2.1, Run #7), indicating the poor control of ROP. Surprisingly, ^{1}H NMR of the final polymers did not exhibit any characteristic signals from the PCL block, but all from the PAEDA block, as shown in Figure 2.11. These results indicated that the ROP of CL was completely suppressed, most likely due to the poison of Sn(II) catalysts by accumulated Cu(II) catalysts after prolonged ATRP of AEDA.
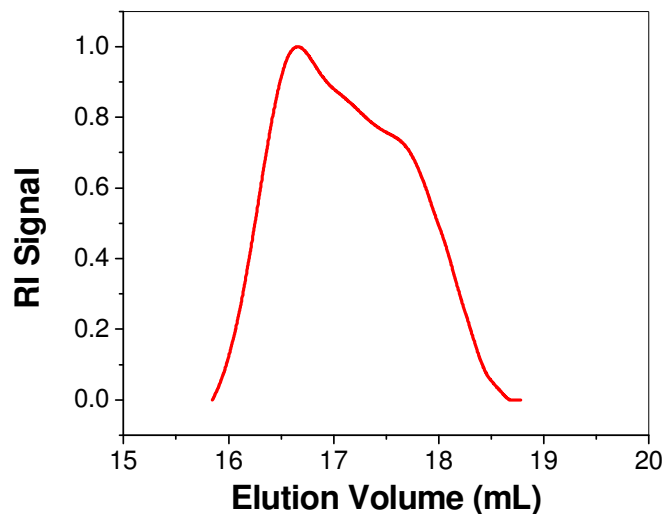
Figure 2.10 GPC trace of diblock copolymers prepared by one-pot polymerization with sequential feeds from AEDA to CL (Run #7 from Table 2.1)

(3) One-Pot Polymerization with Sequential Feeds. Route 5: from CL to AEDA:

To circumvent the influence of the ATRP copper catalyst on the ROP, CL was first added to carry out ROP in the presence of Sn(EH)$_2$ using HEBiB as the initiator and toluene as the solvent. After 16h, a deoxygenated mixture of AEDA, CuBr/Me$_6$Tren and toluene was added into the above polymerization system to start the ATRP of AEDA. ^{1}H NMR spectrum (Figure 2.12) shows that this strategy did allow the preparation of block

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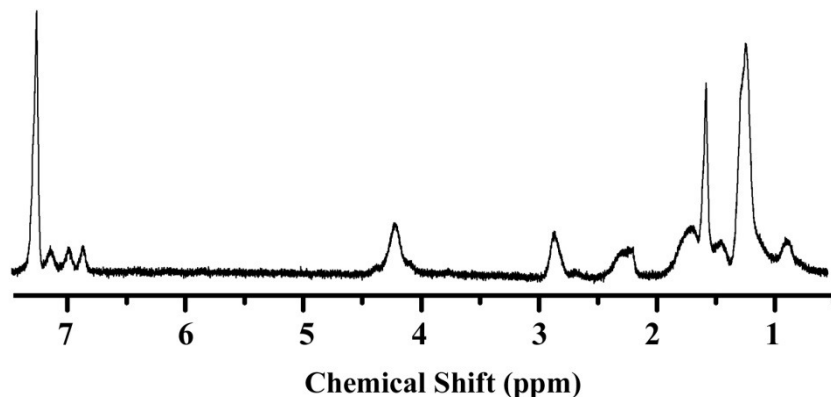
Figure 2.11 ^{1}H NMR spectrum of diblock copolymers prepared by one-pot polymerization with sequential feeds from AEDA to CL (Run #7 from Table 2.1)
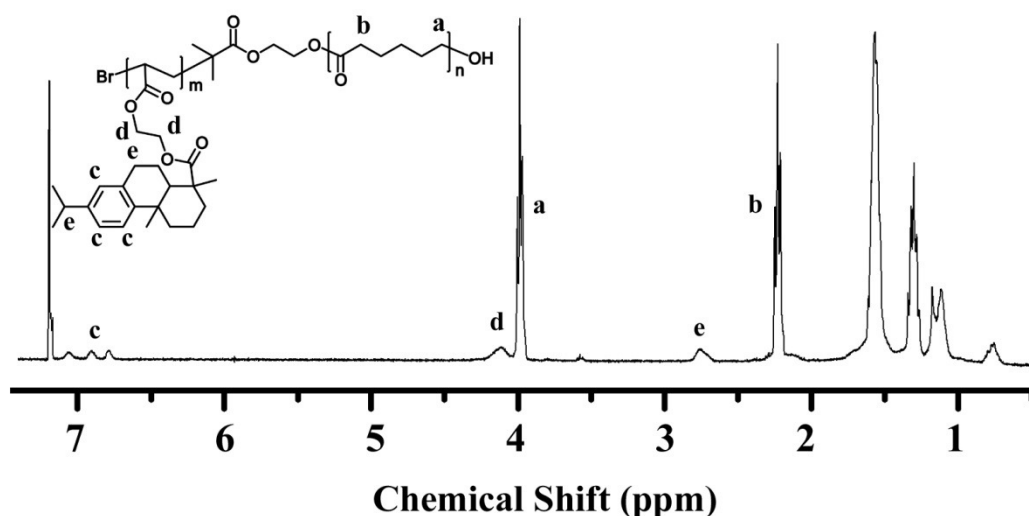
Figure 2.12 ^{1}H NMR spectrum of diblock copolymers PCL-*b*-PAEDA prepared by one-pot polymerization with sequential feeds from CL to AEDA (Run #8 from Table 2.1)

copolymers with desirable lengths of PCL and PAEDA blocks. Even the PCL block has a

DP as high as 200, a DP of 20 for the PAEDA block was achieved when the feed ratio of

[AEDA]/[HEBiB] was 60, indicating that the end group –Br from the PCL chain was

efficient to initiate the polymerization of AEDA. The GPC trace (Figure 2.13) shows a
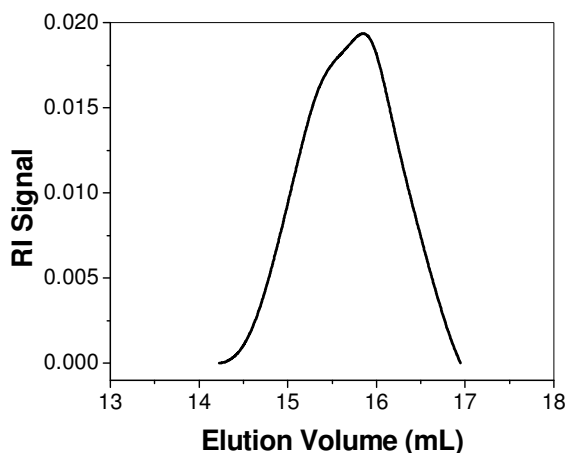
Figure 2.13 GPC trace of diblock copolymers prepared by one-pot polymerization with sequential feeds from CL to AEDA (Run #8 from Table 2.1)

slightly asymmetric distribution, with a reasonable low PDI = 1.38. It also indicated that the tin-based catalyst had minimal impact on the ATRP of AEDA. The higher DP of AEDA can be achieved by changing the feed ratio of [AEDA]/[HEBiB].

(4) The Role of Tin Catalysts *vs.* Copper Catalysts in One-Pot Polymerization:

From the one-pot polymerization, it appeared that both the monomer feed sequence (therefore the catalyst feed sequence) and the catalyst amount played important roles in the polymerization control. From the work of activator regenerated by electron transfer (ARGET) ATRP,[146, 147] it is well known that Sn(II) can reduce Cu(II) catalysts of ATRP to form Sn(IV) and Cu(I). From this perspective, it is understandable that one-pot polymerization with sequential feeds from AEDA to CL was not well controlled. Prolonged ATRP of AEDA would produce significant persistent radicals Cu(II) species, which can oxide the newly added Sn(II) catalysts when CL was feed. The resulting Sn(IV) is not an active catalysts for ROP of CL. Therefore, poorly controlled block

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copolymers were obtained. On the other hand, it is expected that $Sn(II)(EH)_2$ and $Cu(I)Br$ can co-exist and respectively catalyze the ROP and ATRP of CL and AEDA simultaneously. This is exactly what has been observed from the simultaneous polymerization ($AEDA_{52}$-CL_{32}, Table 2.1, Run #5). However, when CL and $Sn(II)(EH)_2$ were proportionally increased (therefore the increase of molar ratio of $[Sn(II)(EH)_2]/[Cu(I)Br]$), a decrease of the AEDA block length and an increase of the CL block length were observed ($AEDA_{16}$-CL_{320}, Table 2.1, Run #6), probably due to the undesirable reduction of persistent radical ($Cu(II)Br_2$) by the excess of Sn(II) species in the reaction system. The proposed mechanism of one-pot polymerization by ROP and ATRP is summarized in Figure 2.14.

Figure 2.14 A proposed mechanism for one-pot polymerization of CL and AEDA by ROP and ATRP

Degradability of Diblock Copolymers of AEDA and CL: Diverse diblock copolymers of AEDA and CL prepared from the above five routes were employed the degradability test. The block copolymers were dissolved in THF with a concentration of 30% HCl. After the hydrolysis in acidic solution, the GPC traces (Figure 2.4) show clear shift to lower molecular weight with symmetric distribution, presumably from the un-degraded PAEDA-Br block. Additional evidence of PCL degradation is from the two-step chain-

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extension from PAEDA-OH to PCL. GPC traces (Figure 2.6) indicated that the macroinitiators PAEDA-OH had an identical trace with the un-degraded polymers after the hydrolysis. ^{1}H NMR analysis indicated that the purified un-degraded polymers did not show structures from the PCL block, but all characteristic signals originating from the PAEDA block, further confirming the successful degradation of the PCL block.
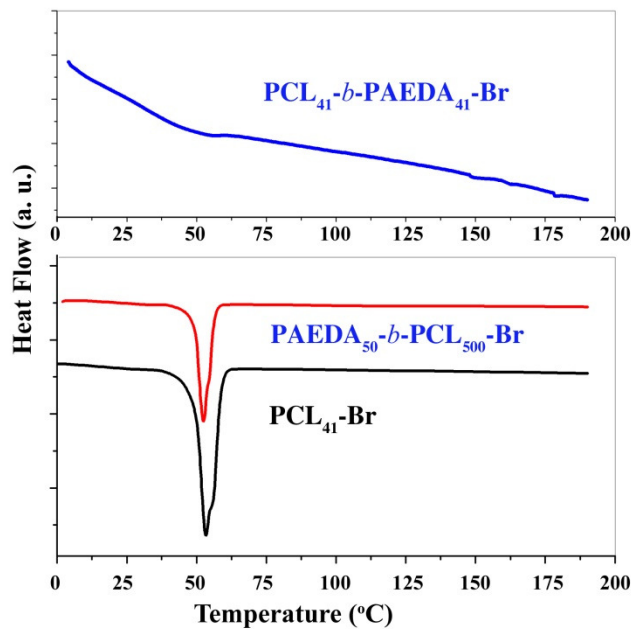
Figure 2.15 DSC traces of polymers PCL-Br, PAEDA-*b*-PCL-OH and PCL-*b*-PAEDA-Br

Thermal Properties of Diblock Copolymers of AEDA and CL: The thermal properties of diblock copolymers of AEDA and CL were characterized with the aid of differential scanning calorimetry (DSC). As expected, homopolymers PCL-Br show a characteristic strong endothermic melting peak at ~ 55 $^{\circ}$C. Thermal behaviors of CL and AEDA diblock copolymers have a strong correlation with the length and fraction of the PCL

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block in the block copolymers (Figure 2.15). Block copolymers with high fractions of PAEDA (PCL_{41}-b-$PAEDA_{41}$-Br) exhibited suppression of PCL crystallization. The DSC curve shows only the T_g of the PAEDA block at ~ 50 ^{o}C, an amorphous block consistent with our earlier report.[124] No melting peak was observed, indicating the suppression of crystallization of the PCL block. However, a strong endothermic peak at ~ 55 ^{o}C was observed for block copolymers with high fraction of the PCL block ($PAEDA_{50}$-b-PCL_{500}-OH), corresponding to the melting of the PCL block. Although the T_g of the PAEDA block is also close to the melting temperature of the PCL block, it is not surprising that the glass transition was shadowed within the strong endothermic peak.

Such thermal behaviors were further confirmed by AFM experiments on thin films of diblock copolymers of CL and AEDA. Tapping-mode AFM imaging (Figure 2.16) was carried out at ambient conditions. AFM height images of block copolymers with high fractions of the PCL block ($PAEDA_{50}$-b-PCL_{500}-OH) reveal the formation of small crystals with an average size of a half micron and a roughness of ~ 20 nm. In contrast, thin films of block copolymers with a short length of the PCL block (PCL_{41}-b-$PAEDA_{41}$-Br) appeared to be very smooth with an average of roughness below 5 nm. No island-like morphology was observed.
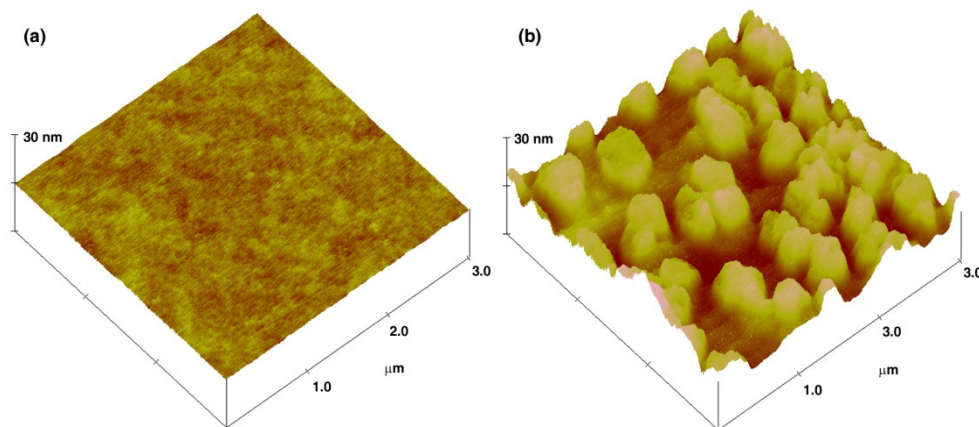
Figure 2.16 Tapping-mode AFM height images of diblock copolymers of (a) PCL_{41}-b-$PAEDA_{41}$-Br and (b) $PAEDA_{50}$-b-PCL_{500}-OH

2.5 Conclusions

In conclusion, we have developed a versatile strategy to prepare novel well-defined renewable degradable rosin acid-caprolactone block copolymers. Two-step sequential polymerization and one-pot polymerization were used to prepare dehydroabietic acid-derived acrylate and CL diblock copolymers with the aid of atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP). The two-step polymerization with either PCL or PAEDA as a macroinitiator yielded block copolymers with controlled molecular weight and compositions and narrow molecular weight distribution. The one-pot polymerization demonstrated that ROP of CL was greatly affected by the co-existing copper catalysts of ATRP, while ATRP of AEDA was also perturbed with the presence of excess the Sn(II) catalyst. A redox process between Sn(II) and Cu(II) catalysts was suggested explaining the control of one-pot polymerization. These block copolymers exhibited excellent degradability under acidic conditions. Thermal behaviors of these block copolymers showed a strong dependence of

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polymer compositions. The successful synthesis of rosin acid-caprolactone block copolymers has the potential to be extended to other degradable polymers such as lactide polymers, opening a new avenue toward development of a variety of rosin-derived renewable degradable polymeric materials for advanced applications.

CHAPTER 3

RENEWABLE ROSIN-FATTY ACID POLYESTERS: THE EFFECT OF BACKBONE STRUCTURE ON THERMAL PROPERTIES[3]

3.1 Abstract

Two novel polyesters were prepared from renewable natural molecular biomass castor oil-derived fatty acid and rosin. Highly efficient monomer syntheses including thiol-ene click chemistry and condensation polymerization techniques including transesterification and ADMET were carried out. Their thermal properties were compared based on flexible and rigid structural motifs on the polymer backbone. While linear polymer backbone led to the formation semicrystalline polymers, polymers with fused-ring structure in the backbone were amorphous. The presence of the rosin moiety in the backbone also resulted in higher glass transition temperature compared to the flexible linear counterpart.

3.2 Introduction

Fossil resources that are currently used for both energy and chemical production are of finite availability. The synthesis of plastics accounts for nearly 7% of the global fossil fuel production.[1-3, 5-12] Depleting oil reserves coupled with a rise in global energy demands has led to an increased interest in the development of energy and materials derived from renewable resources. A variety of green plastics have been derived from either abundant and low cost natural polymers such as cellulose, lignin, and chitosan,[32, 38, 39, 42, 43, 46, 112] or natural molecular biomass such as vegetable oil, lactic acid, fatty acid, terpenes, and rosin.[7, 10, 19, 46, 51] Usually obtained directly from forestry and agriculture products or by microorganism fermentation, these natural resources are important because their derived polymers could mimic plastics manufactured from petroleum chemicals.

Among natural molecular biomass, fatty acids have shown to be a prime resource

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for polymer chemistry.[47, 148-151] Derived from castor oil, 10-undecenoic acid is one of the most important fatty acids with a flexible, linear structure and can undergo a number of synthetic reactions to produce renewable monomers for polymer synthesis.[150, 152, 153] In contrast, rosin, which is obtained from pine resin, is available with a more rigid fused-ring structure, and can also undergo a pyramid of reactions.[51, 52, 62, 63, 154-159] Olefin metathesis and thiol-ene reactions are just a few examples of highly efficient reactions that take advantage of the unsaturated terminal olefins to produce valuable monomers.[50, 160-162] With a range of renewable monomers, it is important to understand how monomers with different structural characteristics affect the properties of their corresponding renewable polymers. Herein we report the combination of castor oil-derived fatty acids and rosin to prepare novel polyesters. Our preliminary aim of this study is to compare rigid renewable polyesters derived from fatty acids and rosin with those linear flexible polyesters solely derived from fatty acids. Polyesters were analyzed by GPC, NMR, DSC and TGA.

3.3 Experimental Section

3.3.1 Materials

10-Undecenoic acid, 1,2-ethanedithiol, triethylamine and Hoveyda-Grubbs second generation catalysts (Sigma-Aldrich), abietic acid and acrylic acid (Acros), 10-undecen-1-ol (Alfa-Aesar), titanium (IV) n-butoxide (Ti(OBu)$_4$), oxalyl chloride (Fisher Scientific), and ethylene glycol (VWR) were purchased from commercial sources and used as received. 2,2'-Azobisisobutryonitrile (AIBN, Aldrich) was recrystallized from methanol prior to use. Tetrahydrofuran (THF, Aldrich), dichloromethane (DCM, Aldrich)

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and methanol (MeOH, Aldrich) were refluxed with sodium and distilled under nitrogen atmosphere prior to use.

3.3.2 Characterization

^{1}H NMR spectra were recorded on Brucker ARX300 and ARX400 spectrometers. The chemical shifts were recorded in ppm (δ) relative to tetramethylsilane. Gel permeation chromatography (GPC) was performed at room temperature on a Varian system equipped with a Varian 390-LC multi detector and a Varian 290 pump injection module. The columns were PLgel MIXED-BLS (300×7.5 mm, with capability to characterize molecular weight in the range of 500 to 10,000,000 g/mol) from Polymer Laboratories. HPLC grade THF was used as eluent at a flow rate of 1 mL/min. Samples were filtered over a microfilter with pore size of 0.2μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). GPC was calibrated using polystyrene as standards. Fourier Transform Infrared Spectrometry (FTIR) was conducted on a Shimadzu 8400 FTIR spectrometer. Thermal transitions were recorded using differential scanning calorimetry (DSC) on a TA Q200 calorimeter in a temperature range from -70 to 100 °C at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. All the data were collected during the second heating process after cooling at 10 °C min^{-1} from 100 °C. The average sample mass was about 5 mg, and the nitrogen flow rate was 50 mL min^{-1}. Thermal gravimetric analysis (TGA) was operated on a TGA Q500 apparatus (TA instruments), ramping from 30 to 600 °C at a rate of 10 °C/min, and maintained at 600 °C for 5 min under nitrogen gas at a flow rate of 100 mL min^{-1}.

3.3.3 Synthesis

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Synthesis of 6,6'-(ethane-1,2-diylbis(sulfanediyl))dihexanoic acid: To a 50 mL round bottom flask, 10-undecenoic acid (20.00 g, 1.09×10^{-1} mol), 1,2-ethanedithiol (3.0 mL, 3.62×10^{-2} mol) and AIBN (40 mg, 2.47×10^{-4} mol) were added. While under a continuous flow of nitrogen, the flask was placed into a preheated oil bath set at 80 °C. After 12 h the reaction was stopped and a white solid was observed. The final product was then recrystallized from THF and a white crystalline material (86% yield) was obtained. Mp 115 °C; ^{1}H NMR (300 MHz, DMF-d_7, δ): 2.9-3.0 (s, -*SCH2*-); 2.7-2.8 (t, -*CH2S*-); 2,4-2.5 (t, -*CH2*CO), 1.3-1.8 (broad, -*CH2CH2CH2*-). IR (neat): 3400-300 cm^{-1} (OH stretching); 3020-2820 cm^{-1} (CH stretching); 1720-1690 cm^{-1} (C=O stretching).

Synthesis of diester monomer dimethyl 6,6'-(ethane-1,2-diylbis(sulfanediyl))dihexanoate: A solution of 6,6'-(ethane-1,2-diylbis(sulfanediyl))dihexanoic acid (33.90 g, 7.32×10^{-2} mol) in THF (200 mL) was introduced into a round bottom flask under nitrogen. Oxalyl chloride (20 mL, 2.30×10^{-1} mol) was slowly added to the above mixture at 0 °C for one hour. The mixture was allowed to react for 24 h at room temperature. After 24 h the solvent and any unreacted oxalyl chloride were removed by vacuum distillation. The product was dissolved in THF (50 mL) and placed in a round bottom flask under nitrogen. A second mixture composed of triethylamine (25 mL, 1.79×10^{-1} mol), methanol (15 mL, 3.71×10^{-1} mol) and THF (300 mL) was placed in a separate round bottom flask under nitrogen. The diacid solution was slowly added to this mixture at 0 °C for one hour. The reaction was run at room temperature for 24 h. The flask was opened and the final product was precipitated in MeOH as an off white crystalline material (92% yield). Mp 59 °C; ^{1}H NMR (300 MHz, CDCl$_3$, δ): 3.6-3.7 (s, CH3O-); 2.9-3.0 (s, -*SCH2*-); 2.7-2.8 (t, -*CH2S*-); 2,4-2.5 (t, -

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*CH2*CO), 1.3-1.8(broad, *-CH2CH2CH2-*). IR (neat): 3020-2820 cm^{-1} (CH stretching); 1720-1690 cm^{-1} (C=O stretching).

Synthesis of fatty acid and rosin based monomer: Acrylopimaric acid (APA) was synthesized according to the literature.[62] APA (2.5g, 6.67×10^{-3} mol) was mixed with THF (50 mL) and introduced into a round bottom flask under nitrogen. Oxalyl chloride (2.3 mL, 2.70×10^{-2} mol) was slowly added to the above mixture at 0 ^{o}C for one hour. The mixture was allowed to react for 24 h at room temperature. After 24 h the solvent and any unreacted oxalyl chloride were removed by vacuum distillation. The product was dissolved in THF (50 mL) and placed in a round bottom flask under nitrogen. A second mixture composed of triethylamine (2.2 mL, 1.58×10^{-2} mol), 10-undecen-1-ol (5.5 mL, 2.75×10^{-2} mol) and THF (50 mL) was placed in a separate round bottom flask under nitrogen. The APA solution was slowly added to this mixture at 0 ^{o}C for one hour. The reaction was run at room temperature for 24 h. The monomer was purified by silica gel column chromatography (7:1 hexane: diethyl ether) to yield a colorless liquid (44% yield). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 5.7-5.8 (s, *-CHCH2-*); 5.2-5.3 (s, *-CCH-*); 4.8-5.0 (d, *CH2CH-*); 3.8-4.0 (d, *-CH2O*), 2.4-2.5(s, *-CHCOO-*); 2.4-2.2 (s, *-CHC-*); 1.9-2.0(s, *-CH2CH-*). 0.6-1.8(broad, *-CH2CH2CH2-*). IR (neat): 3080-3040 cm^{-1} (CH alkene stretching); 3020-2820 cm^{-1} (CH stretching); 1720-1690 cm^{-1} (C=O stretching) 1640-1660 cm^{-1} (C=C stretching); 1130-1190 cm^{-1} (C-O stretching).

Melt polymerization of diester monomer: Prior to polymerization, the diester monomer was dried at 80 ^{o}C for 2 h. The diester (8.08 g, 1.65×10^{-2} mol), ethylene glycol (1.09 g, 1.76×10^{-2} mol), and Ti(OBu)$_4$ (12.0 mg, 3.53×10^{-5} mol) were placed in a 3-neck round bottom flask. The flask was then equipped with a distillation arm, a nitrogen outlet and a

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stir rod. The stir rod was attached to an overhead mechanical stirrer and the stir rate was maintained at 60 RPM for the duration of the polymerization. A vacuum pump was connected to the distillation and several nitrogen purges were conducted using a Firestone valve. Once the reaction vessel had been purged, temperature was slowly increased until the monomers melted. A vacuum was applied and gradually increased throughout the polymerization until a final vacuum of 25 mm Hg was reached. Temperature was gradually increased throughout the reaction until a final temperature of 200 $^{\circ}$C was obtained. At this point, the reaction was stopped and the polymer solution was allowed to slowly cool to room temperature. The polymer was then dissolved in DCM and precipitated into MeOH. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 4.2-4.4 (s, -CH2O-); 2.7-2.8 (s, -*SCH2*-); 2.4-2.6 (t, -*CH2S*-); 2,3-2.4 (t, -*CH2*CO), 1.3-1.8 (broad, -*CH2CH2CH2*-).

ADMET polymerization of rosin-fatty acid monomer: Rosin-fatty acid monomer (0.2 g, 2.95×10^{-4} mol) was placed in a round bottom flask and purged with nitrogen for 10 min. Hoveyda-Grubbs catalyst (2.3mg, 3.67×10^{-6} mol) was added to the flask and the temperature was raised to 80 °C while under a constant flow of nitrogen. After one hour, a 5 ml solution of ethyl vinyl ether in THF was added to the flask. The final polymer was obtained by precipitating in cold methanol. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 5.2-5.5 (d, -*CHCH2*-); 3.9-4.1 (s, -*CH2O*-); 2.4-2.5(s, -*CHCOO*-); 2.4-2.2 (s, -*CHC*-); 0.6-2.1 (broad, -*CH2CH2CH2*-).

3.4 Results and Discussion

Synthesis and Polymerization of Diester Monomer: Figure 3.1 shows the synthesis of castor oil-derived fatty acid based monomer. The radical addition of thiols to terminal

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alkenes is a well-established and efficient click reaction.[104] Using a slight excess of fatty

acid to thiol, the intermediate diacid was obtained in high yield (86%) after
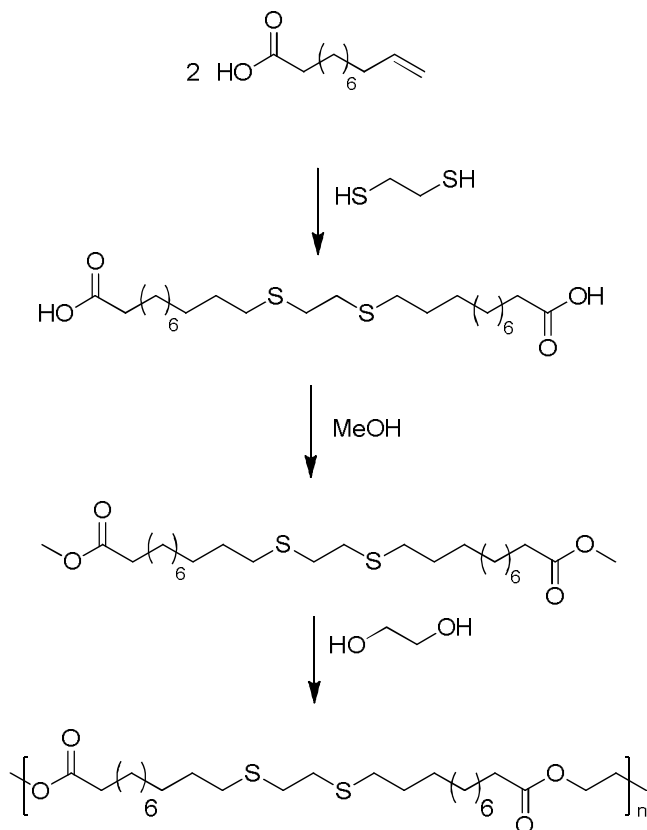
Figure 3.1 Synthesis and polymerization of castor oil-derived based monomer

recrystallization. The diacid was further converted to a diester by esterification with

methanol.

 The monomer was characterized by ^{1}H-NMR spectroscopy, as shown in Figure

3.2. The disappearance of the terminal alkene peaks confirmed a high conversion of

alkene to thioether. Also, the emergence of the thioether peaks at 2.5 and 2.7 ppm further

indicated that the click reaction was highly efficient. The esterification of the diacid with
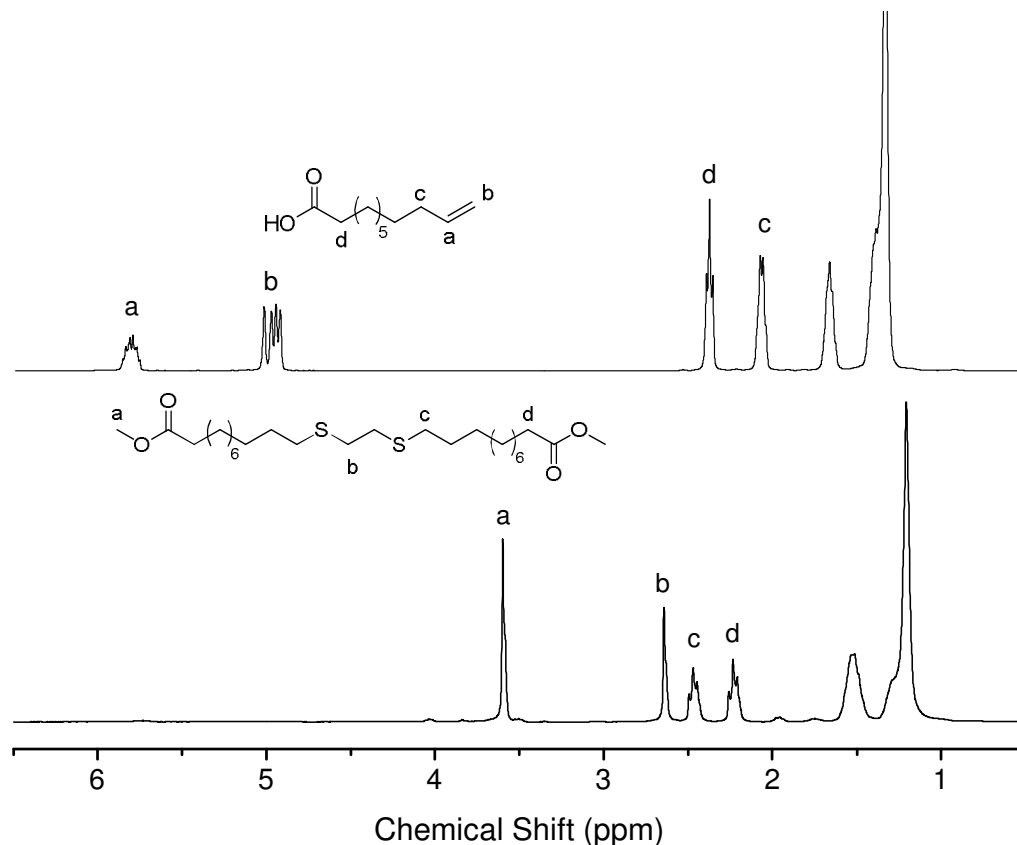
Figure 3.2 ^{1}H-NMR spectra of 10-undecenoic acid and dimethyl 6,6'-(ethane-1,2-diylbis(sulfanediyl))dihexanoate monomer

excess MeOH produced the final diester monomer in high yield (92%) after recrystallization. The emergence of the methyl ester peak at 3.7 ppm was an indication of successful esterification.

The next step was to polymerize the diester monomer as shown in Figure 3.1. Meier et al. polymerized vegetable oil based monomers by condensation polymerization.[162-164] In the current work, ethylene glycol was chosen as a comonomer in order to produce polyesters by condensation polymerization. The catalyst utilized for the polymerization was Ti(OBu)$_4$ due to its commercial availability and high efficiency in

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polymerizing aliphatic polyesters.[165] The amount of catalyst was varied from 2 mol% to 4
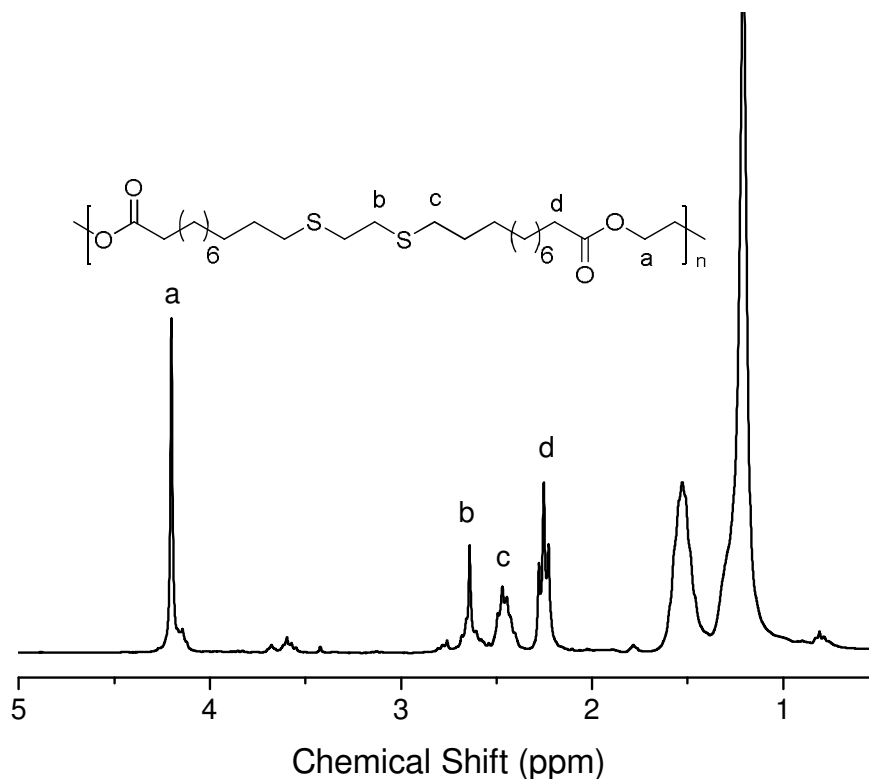
Figure 3.3 ^{1}H-NMR spectrum of fatty acid based polymer

mol%, while the 2 mol% produced the best results. ^{1}H-NMR analysis of the final

polymers, shown in Figure 3.3, confirmed the successful polymerization, as indicated by

the disappearance of the methoxy peak at 3.7 ppm and the appearance of the ethyl ester

peak at 4.2 ppm. The number average molecular weights (M_n) of the polyesters were

between 7,000–26,000 g/mol, depending on the molar ratio of starting monomers (Figure

3.4). These polyesters were solid materials and had color ranging from light brown for

the low molecular weight to black for the high molecular weight. The color of the

polymers is most likely due to the presence of the titanium based catalyst.

Synthesis and Polymerization of Rosin-Fatty Acid Based Monomer: Figure 3.5 shows synthesis of a diene monomer derived from fatty acid and rosin. APA was synthesized and purified according to the literature.[62] The esterification reaction between the diacid and the unsaturated fatty alcohol was confirmed by ^{1}H-NMR (Figure 3.6). The disappearance of the –OH peak at 3.6 ppm and the emergence of a new ester peak around 4.0 ppm as well as the vinyl protons at 4.9 and 5.8 ppm indicated the successful esterification. ADMET polymerization was used to prepare polymers.[148-151] Both Grubbs second generation and Hoveyda-Grubbs second generation catalysts were utilized; however the Hoveyda-Grubbs catalyst provided better results, including fast reactions and higher molecular weight. As shown in Figure 3.6, ^{1}H-NMR spectrum of the final polymer displayed a loss of the terminal alkene peak at 4.9 ppm, which was expected for an ADMET polymerization. The final polymer was a dark brown, sticky material with a molecular weight that varied from 4,000- 9,200 g/mol, depending on the monomer to catalyst ratio (Figure 3.4).

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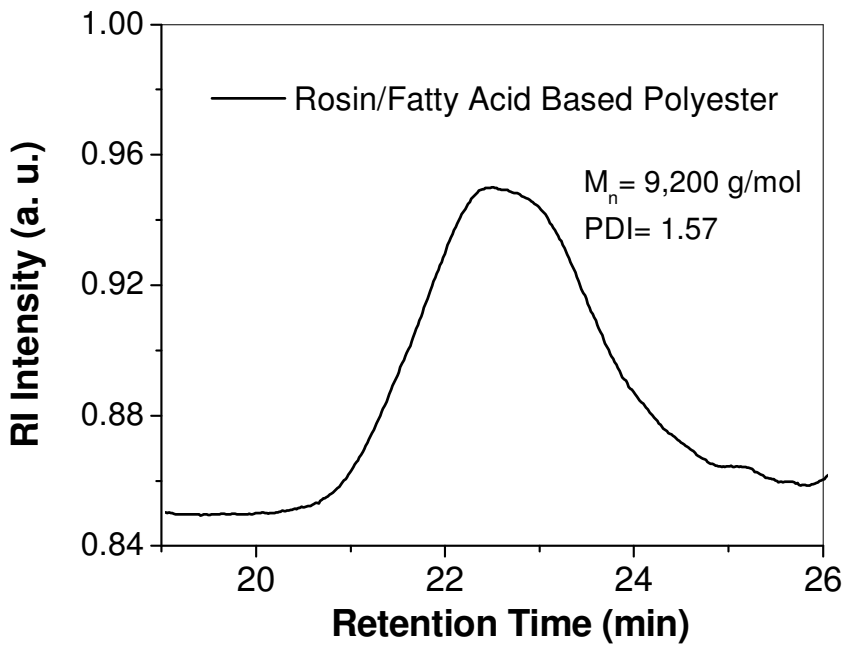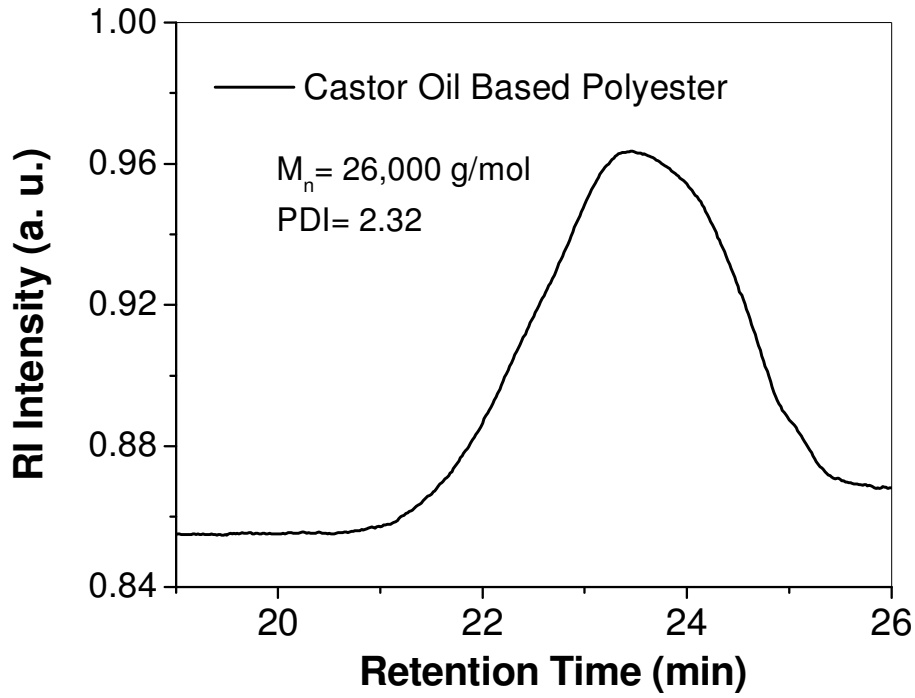
Figure 3.4 GPC traces of caster oil-derived polyesters and rosin-fatty acid based polyesters

Thermal Properties of Polyesters: Differential scanning calorimetry (DSC) was utilized to examine the thermal properties of polymers with linear flexible backbone and polymers with bulky fused-ring backbone. As shown in Figure 3.7, three endothermic melting point (T_m) in the range of 30 °C to 70 °C was observed for linear flexible polyesters. The presence of the T_m observed indicated the polyesters derived from castor oil are semicrystalline. This is consistent with previous reports.[163, 164] However, for the rosin-fatty acid based polyesters, DSC analysis revealed no melting transitions. The lack of melting transitions for these polyesters indicated that they are amorphous polymers. Our work suggested that the bulky fused-ring rosin moiety disrupts the packing of the
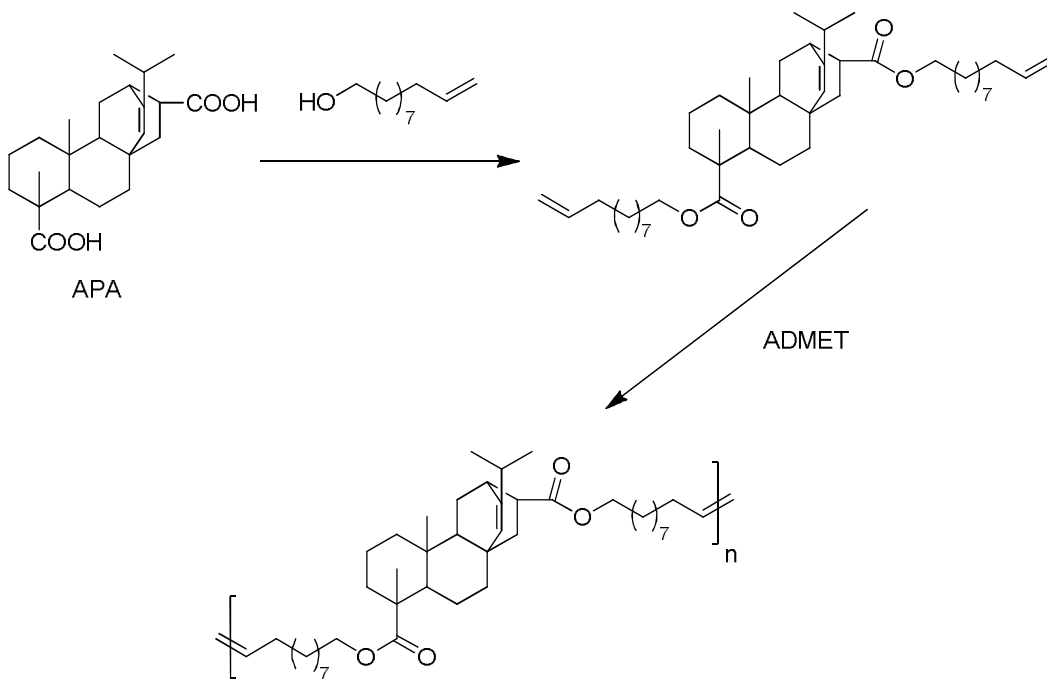
Figure 3.5 Synthesis and polymerization of rosin-fatty acid based monomer

linear alkyl group in the backbone, resulting in amorphous polymers. The glass transition temperatures (T_g) at -5 °C were observed for the rosin-fatty acid polyesters. Although no clear T_g was observed for linear castor oil-derived polyesters, Meier et al. reported a T_g as low as -68 °C for a branched polyester with the arm chains similar to our polymers. The sharp difference between these two polyesters indicated that the rotation barrier of bulky rosin moiety significantly increases the T_g.
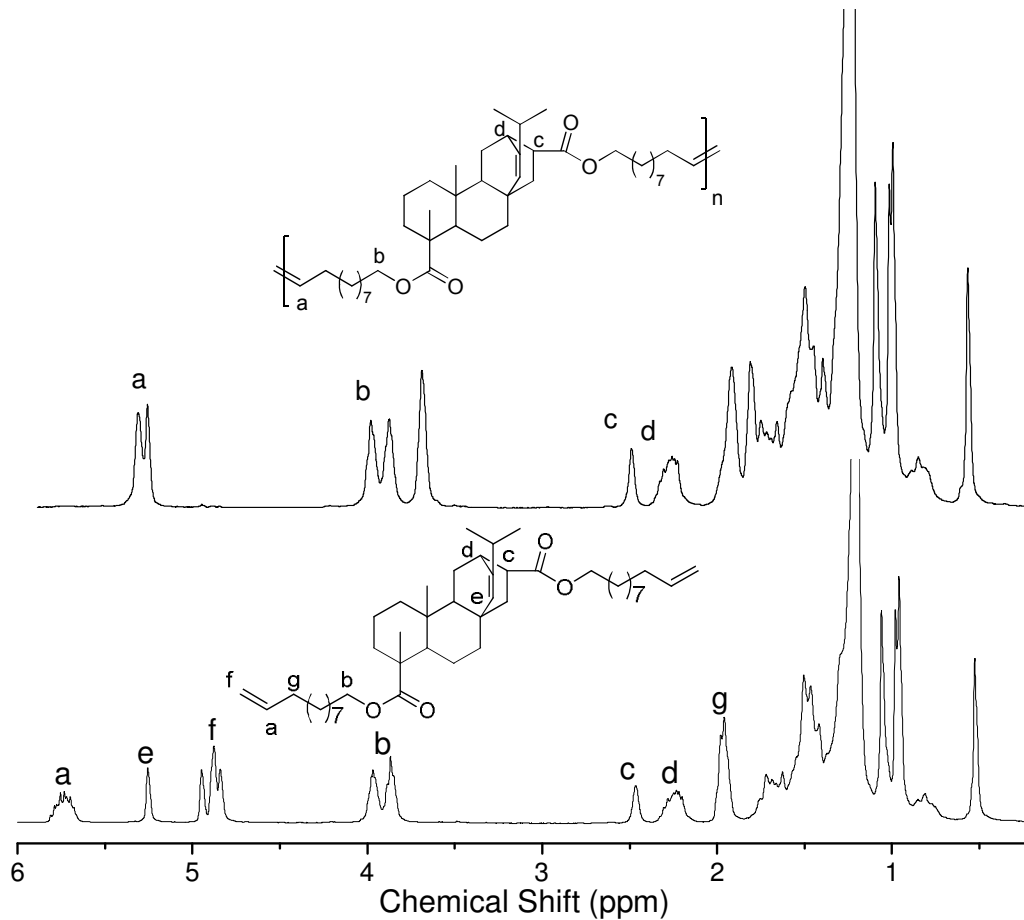
Figure 3.6 ^{1}H-NMR spectra of rosin-fatty acid monomer and polyester
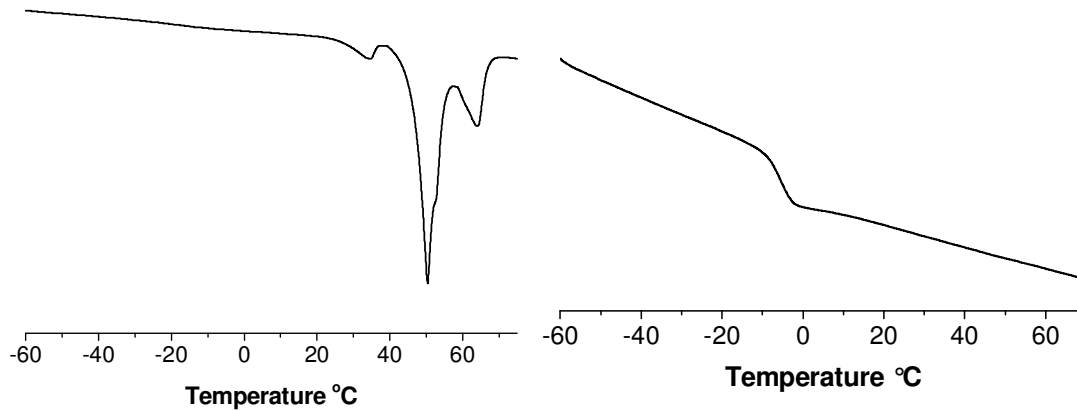
Figure 3.7 DSC thermograms (2nd heating cycle) of polyesters: (left) castor oil based polymer (M_n = 26,000 g/mol); (right) rosin-fatty acid based polymer (M_n = 9,200 g/mol)

Thermal gravimetric analysis (TGA) for the castor oil based polyesters displayed thermal stability up to ~250 °C, above which rapid thermal degradation was observed, as shown in Figure 3.8. TGA of the more rigid rosin-fatty acid based polyesters showed thermal stability up to ~300 °C. This may indicate that thermal stability of polyesters can
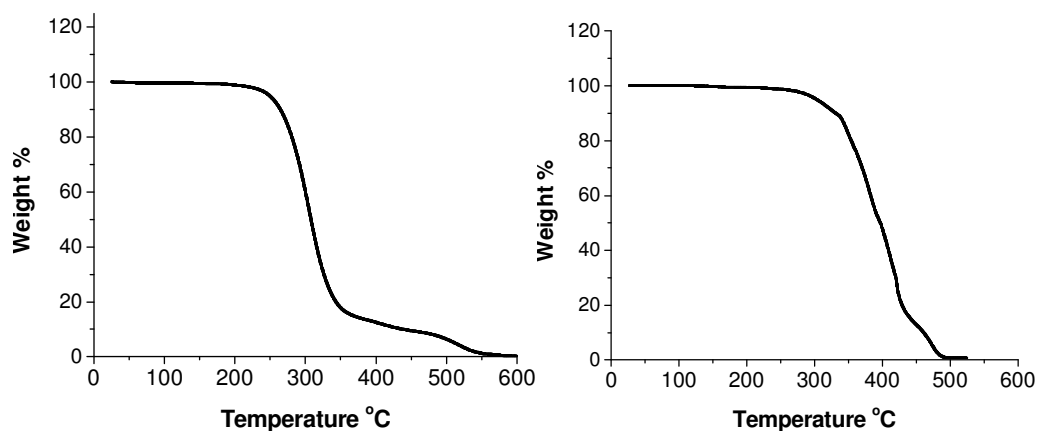
Figure 3.8 TGA thermograms of polyesters (left) castor oil based polymer (M_n = 26,000 g/mol) and (right) rosin-fatty acid based polymer (M_n = 9,200 g/mol)

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be increased by including more rigid naturally occurring structures. The thermal properties obtained for both castor oil and rosin-fatty acid based polyesters are summarized in Table 3.1.

Table 3.1 Properties measured for Vegetable oil and Castor oil based polymers

	M_n (g/mol)	T_m	T_g	T_{d5}	T_{d10}
castor oil based polyesters	26,000	50°C	N/A*	249 °C	264 °C
Rosin fatty acid based polyesters	9,200	N/A	-5 °C	303 °C	331 °C

T_{d5}: Temperature at 5% weight loss

T_{d10}: Temperature at 10% weight loss

3.5 Conclusion

In conclusion, we developed a method for the conversion of naturally occurring castor oil-derived fatty acids and rosin into useful monomers for the preparation of polyesters. Thiol-ene chemistry was utilized for the castor oil based monomer synthesis with high yield. The resultant flexible castor oil based polyesters prepared by condensation polymerization are semicrystalline polymers with moderate molecular weights. A more rigid rosin-fatty acid based monomer was synthesized in high yield and subsequently polymerized by ADMET technique. In contrast, these polyesters are

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completely amorphous with higher glass transition temperature and increased thermal stability. The incorporation of rigid natural biomass with linear flexible molecules could lead to polymers with different thermal properties, expanding potential applications for fatty acid derived polymers.

CHAPTER 4

NOVEL ROSIN CONTAINING PENTABLOCK COPOLYMERS

4.1 Abstract

We have carried out the synthesis of novel rosin containing pentablock copolymers. The first copolymer consists of rosin modified poly(ε-caprolactone) (PCL) as the major weight fraction and PCL as the minor weight fraction. The second copolymer is the exact opposite, in which PCL is the major weight fraction and rosin modified PCL is the minor fraction. Both methods were successful in producing the desired pentablock copolymers, although the second method created the most promising results. Even though the molecular weights were too low to conduct any useful mechanical tests, this study illustrates a general strategy to prepare a novel class of degradable polymers.

4.2 Introduction

Approximately 7% of the global production of fossil fuel goes into the synthesis of plastic materials.[105-107] Energy shortage and environmental concerns prompt opportunities to seek developing renewable resources for manufacturing of "green" plastics.[2, 107-110, 166] There are two major classes of natural resources. The first class of natural resources is natural polymers including cellulose, hemicellulose, lignin and chitosan, which are considered as abundant and low-cost feedstock.[109-113] Natural polymers have long been exploited without any modifications. Currently, common approaches involve physical blending and limited chemical modifications. However the ill-defined already-built-in macromolecular structures could be further manipulated by implementing advanced polymerization techniques and potentially serve as a building block toward diverse polymeric architectures and rich properties. In contrast, natural resources like vegetable oils, fatty acids, hydroxyalkanoates and lactic acids (LA) are a class of small molecular biomass, which could be precisely engineered at a molecular

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level into renewable polymers in a way similar to some plastics derived from petroleum chemicals.[105-107] As one of the major classes of petroleum chemicals, cycloaliphatic and aromatic compounds such as benzene and cyclohexane offer rigidity and hydrophobicity to polymers derived from them. However, such important polymeric materials are largely missing or neglected in the current set of renewable polymers. Rosin is the major product from pine resin obtained by tapping living pine trees.[16, 54, 114] Its global production exceeds 1 million metric tons annually.[55, 63] Gum rosin consists primarily of resin acids that have built in hydrophenanthrene rings that are considered to have cycloaliphatic and aromatic structures, thus providing rosin with renowned hydrophobicity. [16, 54, 55, 114] Functionalization of the carboxyl group or conjugated dienes of rosin acids allows the integration of rosin moiety into polymers as backbone or side chain.

Molecular architectures largely dictate physical properties of polymers, especially mechanical properties.[167-170] The bulky hydrophenanthrene moiety of rosin would certainly have a large impact on the mechanical properties of their polymers. One of the direct consequences on the incorporation of this bulky moiety onto the side group of polymers is the significant change of their chain entanglement density ν_e and therefore entanglement molecular weight M_e, which is defined as the molecular weight between adjacent temporary entanglement points. M_e plays a key role in mechanical properties of polymers, e.g. plateau modulus.[171] A low ν_e leads to a susceptibility to crazing and brittle fracture.[172, 173] High M_e facilitates polymers to form weak crazes that break down readily to generate cracks. With the increase of the size of the side group, M_e generally increases. Therefore, it is expected that the bulky hydrophenanthrene moiety would significantly

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increases the M_e of rosin polymers when the moiety is placed at the side group, thus making them brittle.

It has been showed by Kramer et al. that pentablock copolymers can increase the network density that disfavors both craze formation and premature craze breakdown by bridging chains between highly entangled segments.[174] It is well known that polymers with a low M_e (high entangled strand density) tend to form shear deformation zones rather than crazes. In this regard entangled network strands behave identically so that "cross-linking" can convert a polymer that crazes in tension, and whose crazes break down to form cracks, into a polymer that deforms only by forming deformation zones that are less subject to breakdown. Therefore in ABABA pentablock copolymers, in which B block has low M_e with A block containing rosin, microphase separated minority domains B can be bridged through the matrix A, thus favoring the formation of shear deformation zones rather than crazes and increasing ductility. In the case of side-chain rosin-containing polymers, the B block can be those polymers with low M_e such as caprolactone polymers. Although the pentablock copolymer approach sounds not economically plausible for renewable polymers, it certainly helps to understand the key fundamental structure-property relationship.

4.3 Experimental Section

4.3.1 Materials

Dehydroabietic acid (DHAA, ~90%) was obtained from Wuzhou Chemicals, China and used as received. Toluene and tetrahydrofuran (THF) were refluxed with sodium and distilled out just before use under nitrogen atmosphere. ε-Caprolactone was dried over

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calcium hydride and purified by vacuum distillation before polymerization. 2-Chlorocyclohexanone, 1,2-ethanedithiol, 10-undecen-1-ol, m-chloroperoxybenzoic acid (mCPBA), oxalyl chloride, triethylamine, propargyl alcohol, Sn(II) 2-ethylhexanoate (Sn(Oct)$_2$), dibutyltin dilaurate (DBTDL)**,** 4,4′-methylenebis(phenyl isocyanate) (MDI), dichloromethane (CH$_2$Cl$_2$), *N, N*-dimethylformamide (DMF), methanol, sodium azide, copper iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from various sources and used as received. 2,2'-Azobisisobutryonitrile (AIBN, Aldrich) was recrystallized from methanol prior to use. α-Chloro-ε-caprolactone (αClεCL) and dehydroabietic propargyl ester (DAPE) were prepared according to the literature.[133, 175]

4.3.2 Characterization

^{1}H NMR spectra were recorded on Brucker ARX300 and ARX400 spectrometers. The chemical shifts were recorded in ppm (*δ*) relative to tetramethylsilane. Gel permeation chromatography (GPC) was performed at room temperature on a Varian system equipped with a Varian 390-LC multi detector and a Varian 290 pump injection module. The columns were PLgel MIXED-BLS (300×7.5 mm, with capability to characterize molecular weight in the range of 500 to 10,000,000 g/mol) from Polymer Laboratories. HPLC grade THF was used as eluent at a flow rate of 1 mL/min. Samples were filtered over a microfilter with pore size of 0.2μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). GPC was calibrated using polystyrene as standards. Fourier Transform Infrared Spectrometry (FTIR) was conducted on a Shimadzu 8400 FTIR spectrometer. Thermal transitions were recorded using differential scanning calorimetry (DSC) on a TA Q200 calorimeter in a temperature range from -40 to 100 °C at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. All the data were

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collected during the second heating process after cooling at 10 °C min^{-1} from 100 °C. The average sample mass was about 5 mg, and the nitrogen flow rate was 50 mL min^{-1}. Thermal gravimetric analysis (TGA) was operated on a TGA Q500 apparatus (TA instruments), ramping from 30 to 600 °C at a rate of 10 °C/min, and maintained at 600 °C for 5 min under nitrogen gas at a flow rate of 100 mL min^{-1}.

4.3.3 Synthesis

5,5'-(ethane-1,2-diylbis(sulfanediyl))bis(pentan-1-ol): To a 50 mL round bottom flask, 10-undecen-1-ol (20.00 g, 1.17×10^{-1} mol), 1,2-ethanedithiol (3.0 mL, 3.62×10^{-2} mol) and AIBN (40 mg, 2.47×10^{-4} mol) were added. While under a continuous flow of nitrogen, the flask was placed into a preheated oil bath set at 85 °C. After 12 h the reaction was stopped and a white solid was observed. The final product was then recrystallized from toluene and a white crystalline material (83% yield) was obtained. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 3.6-3.7 (t, -*CH2*O); 2.7-2.8 (s, -*SCH2*-); 2.5-2.6 (t, -*CH2S*-); 1.3-1.6 (broad, -*CH2CH2CH2*-). IR (neat): 3400-300 cm^{-1} (OH stretching); 3020-2820 cm^{-1} (CH stretching).

One-Pot pentablock copolymer: To a 10 mL Schlenk flask, 0.15 g of αClεCL, 12 mg of diol initiator, 3 μL of Sn(Oct)$_2$, and 1 mL of toluene were added under continuous nitrogen flow. The polymerization was run for 12 h at 120 °C, after which 0.15g of caprolactone and 2 μL of Sn(Oct)$_2$ in 2mL of toluene was added and allowed to react for 3.5 h at 120 °C. Finally 0.15g of αClεCL in 1 mL of toluene was added and allowed to react for 4 h at 120 °C. The final polymer was dissolved in THF, precipitated in cold methanol and allowed to dry under vacuum overnight. The conversion of the poly(α-chloro-ε-caprolactone) blocks to the rosin ester-containing polycaprolactone blocks were

prepared according to literature.[175] ^{1}H NMR (CDCl$_3$, δ, ppm): 7.80 (s, CH=C, triazole); 6.78–7.20 (m, aromatic, DAPE); 5.02–5.43 (s, triazole–CH–CO, O–CH$_2$–triazole); 3.88–4.28 (s, –OCH$_2$–); 2.60–2.93 (m, protons next to aromatic ring); 2.3-2.4(s, *-CHCOO-*); 1.5-1.7 and 1.2-1.5 (broad, *-CH2CH2CH2-*).

Multi-step pentablock copolymer (majority rosin): To a 10 mL Schlenk flask, 0.5 g of αClεCL, 15 mg of diol initiator, 22 μL of Sn(Oct)$_2$, and 2 mL of toluene were added under continuous nitrogen flow. The polymerization was run for 20 h at 120 ^{o}C, after which the polymer was dissolved in THF and precipitated in cold methanol. Next, 0.2 g of poly(α-chloro-ε-caprolactone), 0.2 g of caprolactone, 2 μL of Sn(Oct)$_2$, and 2 mL of toluene were added to a 10 mL Schlenk flask under continuous nitrogen flow. The polymerization was run for 9 h at 120 ^{o}C, after which the polymer was dissolved in THF and precipitated in cold methanol. Finally, 0.2 g of the triblock copolymer, 0.1 g of of αClεCL, 2 μL of Sn(Oct)$_2$, and 2 mL of toluene were added to a 10 mL Schlenk flask under continuous nitrogen flow. The polymerization was run for 10 h at 120 ^{o}C, after which the polymer was dissolved in THF and precipitated in cold methanol. The conversion of the poly(α-chloro-ε-caprolactone) blocks to the rosin ester-containing polycaprolactone blocks were prepared according to literature.[175] ^{1}H NMR (CDCl$_3$, δ, ppm): 7.80 (s, CH=C, triazole); 6.78–7.20 (m, aromatic, DAPE); 5.02–5.43 (s, triazole–CH–CO, O–CH$_2$–triazole); 3.88–4.28 (s, –OCH$_2$–); 2.60–2.93 (m, protons next to aromatic ring); 2.3-2.4(s, *-CHCOO-*); 1.5-1.7 and 1.2-1.5 (broad, *-CH2CH2CH2-*).

Multi-step pentablock copolymer (minority rosin): To a 10 mL Schlenk flask, 0.3 g of caprolactone, 12 mg of diol initiator, 12 μL of Sn(Oct)$_2$, and 2 mL of toluene were added

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under continuous nitrogen flow. The polymerization was run for 4 h at 120 $^{\circ}$C, after which the polymer was dissolved in THF and precipitated in cold methanol. Next, 0.2 g PCL, 0.2 g αClεCL, 2 μL of Sn(Oct)$_2$, and 2 mL of toluene were added to a 10 mL Schlenk flask under continuous nitrogen flow. The polymerization was run for 20 h at 120 $^{\circ}$C, after which the polymer was dissolved in THF and precipitated in cold methanol. Finally, 0.2 g of the triblock copolymer, 0.1 g caprolactone, 2 μL of Sn(Oct)$_2$, and 2 mL of toluene were added to a 10 mL Schlenk flask under continuous nitrogen flow. The polymerization was run for 8 h at 120 $^{\circ}$C, after which the polymer was dissolved in THF and precipitated in cold methanol. The conversion of the poly(α-chloro-ε-caprolactone) blocks to the rosin ester-containing polycaprolactone blocks were prepared according to literature.[175] ^{1}H NMR (CDCl$_3$, δ, ppm): 7.80 (s, CH=C, triazole); 6.78–7.20 (m, aromatic, DAPE); 5.02–5.43 (s, triazole–CH–CO, O–CH$_2$–triazole); 3.88–4.28 (s, –OCH$_2$–); 2.60–2.93 (m, protons next to aromatic ring); 2.3-2.4(s, *-CHCOO-*); 1.5-1.7 and 1.2-1.5 (broad, *-CH2CH2CH2-*).

Polyurethane chain-extension (PCL example): To a 100 mL Schlenk tube, 5 g PCL (^{1}H NMR Mn=10,000 g/mol), 158 mg MDI, and 150 μL of DBTDL were added under continuous nitrogen flow. The Schlenk tube was placed in an oil bath set at 80 °C and 3 mL of dry toluene was added. After 2 minutes 2 mL of toluene was added and the temperature was increased to 100 °C. After 1 h the reaction was stopped, the polymer was dissolved in THF and precipitated in cold hexanes. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 3.9-4.1 (s, *-CH2O-*); 2.3-2.4(s, *-CHCOO-*); 1.5-1.7 and 1.2-1.5 (broad, *-CH2CH2CH2-*).

4.4 Results and Discussions

Pentablock synthesis (one-pot): The preparation of such the pentablock copolymers were carried out by sequential ring-opening polymerization (Figure 4.1). The synthesis of the rosin containing pentablock copolymer was achieved by a one pot, sequential addition, method. The benefit of using this method is that there is only one purification step, making this method economically feasible. The polymerization was monitored by both ¹H NMR and GPC. The molecular weight of the ABA triblock varied from 20,000 to 26,000 g/mol according to GPC. When these higher molecular weight triblocks were used to produce the final pentablock, no shift in the GPC curves was observed, however there was a change in the ¹H NMR spectra. This problem is associated with the final ROP of the αClεCL monomer. This monomer tends to produce lower molecular weight homopolymers and can easily polymerize without the addition of any initiator. The end groups of the ABA copolymer may not have been accessible to properly initiate all of the monomer, leading no change in molecular weight of the final copolymer due to the presence of the poly(α-chloro-ε-caprolactone) homopolymer.

Pentablock synthesis (multistep polymerization): To avoid the problems associated with using the one-pot method, a multistep procedure was utilized to produce the desired pentablock copolymer. Although this method is more time consuming, it is very useful

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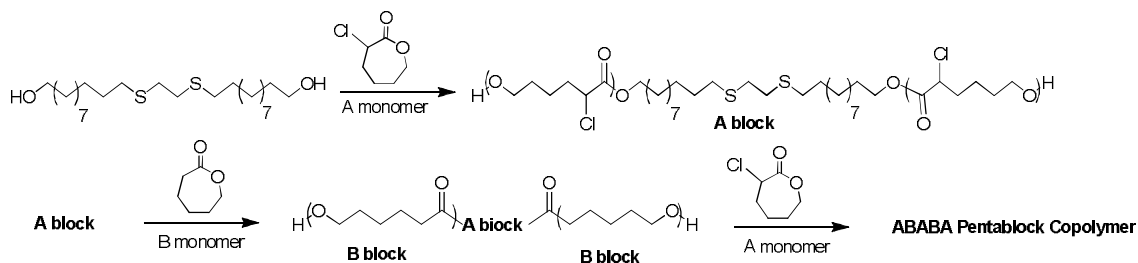
Figure 4.1 Pentablock synthetic strategy and attachment of rosin moiety

for tailoring the molecular weight of the final copolymer. An initial attempt at creating a pentablock copolymer in which the triblock had a molecular weight of 20,000 g/mol was unsuccessful. The same problem associated with the one-pot method was observed, indicating that the size of the triblock is the key factor in the synthesis of the final pentablock copolymer. In order to address this problem, the molecular weight of the triblock copolymer was lowered to make the end groups more accessible. Lowering the

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molecular weight of the triblock to 8,000 g/mol allowed for the formation of the final pentablock. This was confirmed by both ^{1}H NMR and GPC. The final ^{1}H NMR spectra displays characteristic peaks for both blocks with a final rosin composition of 60% (Figure 4.2). The final molecular weight was only 13,000 g/mol according to GPC (Figure 4.3). Even though the desired copolymer was achieved; this molecular weight is too low to conduct any useful mechanical test.
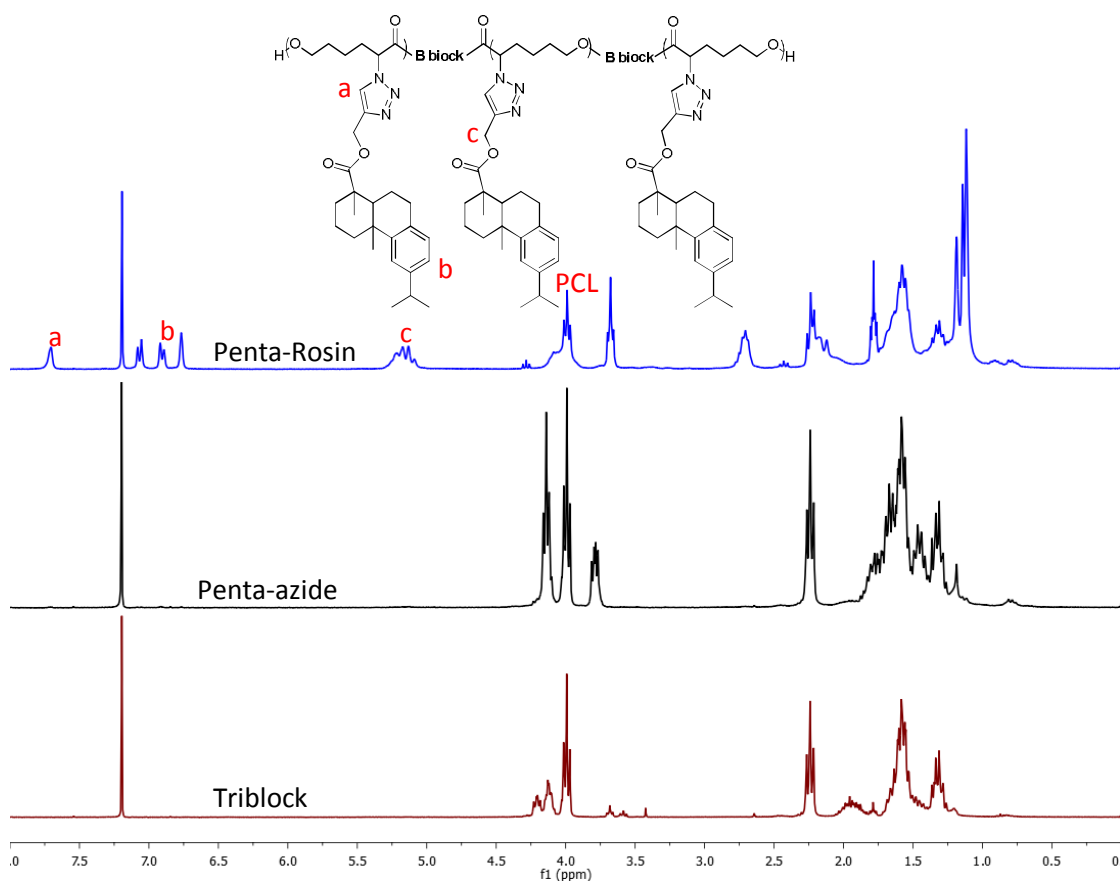
Figure 4.2 ^{1}H NMR of rosin containing pentablock copolymer (60% rosin)

Multistep synthesis (minority rosin): To overcome this problem a new synthetic route was utilized to produce a similar pentablock copolymer. The new route used caprolactone

as the A block and αClεCL as the B block. To confirm that this strategy worked, a multistep method was utilized to monitor the reaction by both GCP and ^{1}H NMR. Based upon the results from the previous method, a triblock of 10,000 g/mol and 20,000 g/mol was employed to produce the final pentablock copolymer. For this strategy, both triblocks were successful in making the final copolymer. The GPC traces for the 20,000 g/mol triblock display a clear shift in molecular weight from the polycaprolactone homopolymer to the rosin containing pentablock copolymer (Figure 4.4). This was also
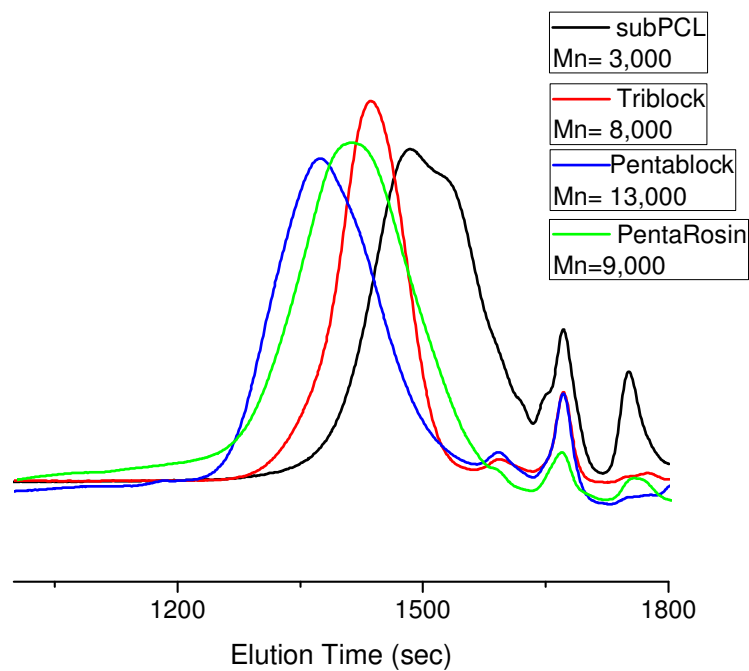
Figure 4.3 GPC curve of rosin containing pentablock copolymer (60% Rosin)

confirmed by ^{1}H NMR (Figure 4.5). This new route worked however, there was a maximum molecular weight of approximately 50,000 g /mol with a rosin content of 25% that could be achieved (Table 4.1). This final molecular weight was not large enough to create any useful materials to test the mechanical properties of the final pentablock

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copolymer. Increasing the molecular weight of the ABA triblock copolymer once again led to no change in the GPC trace of the final copolymer. Thermal properties were also obtained for these copolymers (Figure 4.6). The DSC trace shows a melting point of 50°C from the polycaprolactone blocks, however there is no glass transition temperature observed for the rosin containing blocks. This may be evidence that there is no microphase separation of the two blocks. The rosin containing blocks were not large enough to form aggregates, thus preventing any microphase separation from occurring. Increasing the size of these rosin containing blocks could potentially lead to microphase separation.

Table 4.1 Summary of Pentablock Copolymers

Homopolymer	Homopolymer Mn (g/mol)	Triblock Mn (g/mol)	Pentablock Mn (g/mol)
poly(α-Cl-ε-CL)	3,000	8,000	13,000
poly(α-Cl-ε-CL)	9,100	25,000	No Rxn
poly(α-Cl-ε-CL)	20,000	No Rxn	No Rxn
PCL	10,000	22,000	32,000
PCL	16,000	26,000	33,000
PCL	26,000	37,000	48,000
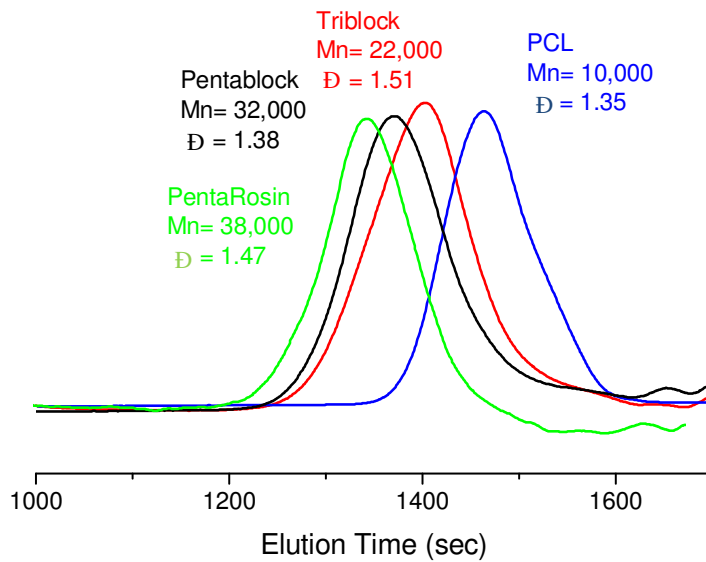
Figure 4.4 GPC curve of rosin containing pentablock copolymer (25% Rosin)
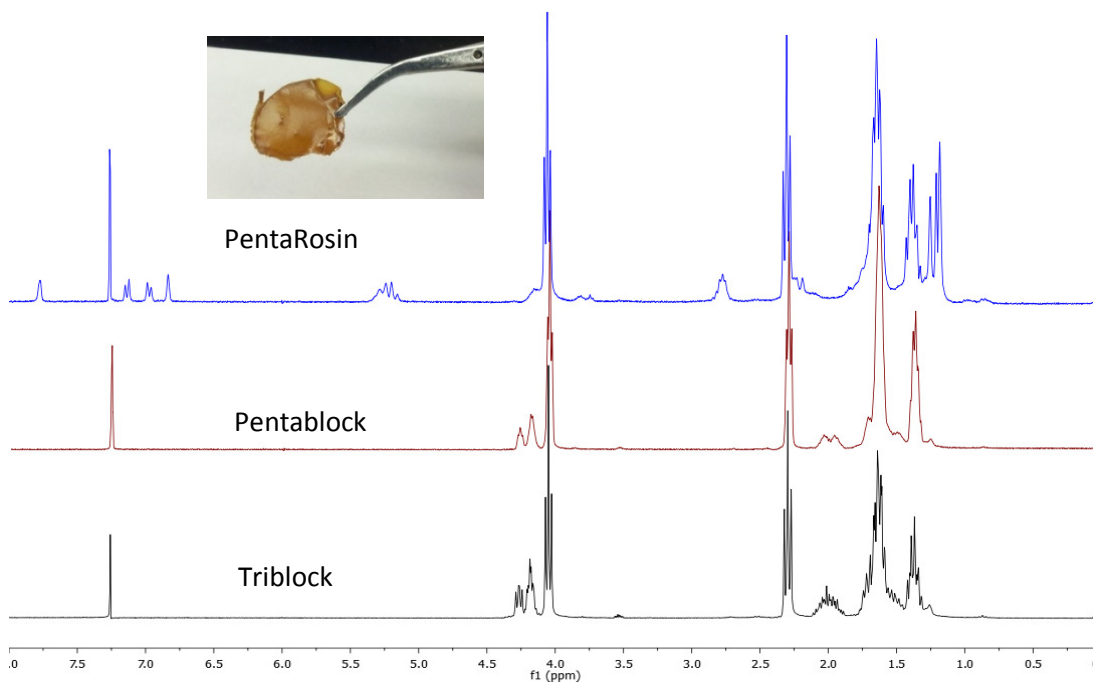
Figure 4.5 ^{1}H NMR of rosin containing pentablock copolymer (25% rosin)

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Polyurethane chain-extension: To increase the molecular weight of the pentablock copolymers, MDI was used to link together two or more polymer chains. PCL was used as an example to test if this would produce the desired results. Using PCL with a Mn=25,000 g/mol according to GPC analysis, the molecular weight of the modified polymer increased to 100,000 g/mol in a matter of minutes (Figure 4.7). Not only did the
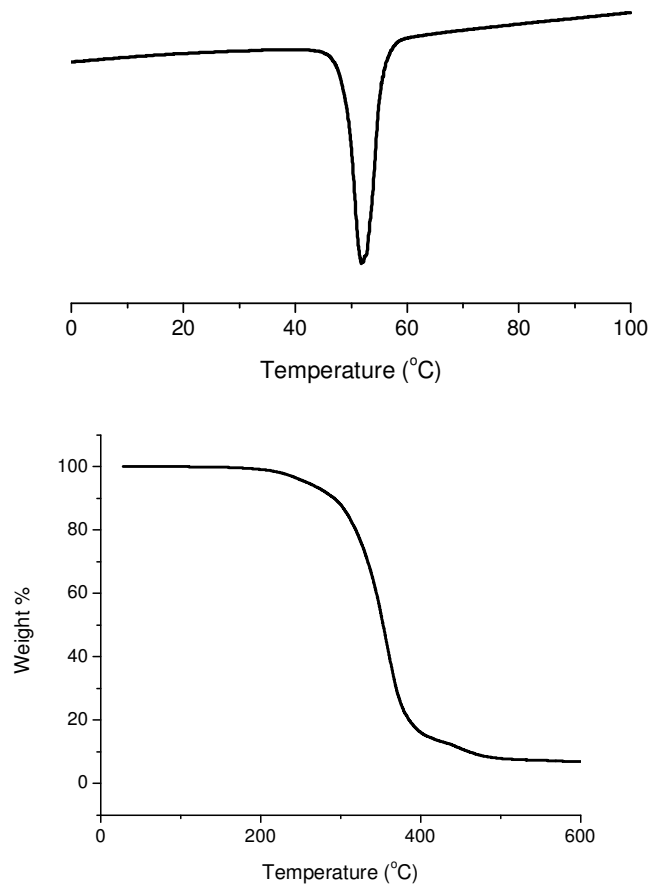
Figure 4.6 DSC (top) and TGA (bottom) curves for rosin containing pentablock copolymer

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molecular weight increase the appearance of the polymer changed. The PCL homopolymer was a fine powder; however the modified polyurethane had an appearance similar to that of a fiber (Figure 4.8). With these promising results, the same reaction was run on both pentablock copolymers, however there was on change in molecular weight or physical appearance for either copolymer. This may have due to the presences of the bulky rosin moiety attached to the polymer chain. Next, the pentablocks without the rosin side-groups were modified; however this also produced no change in the final molecular weight of the copolymers. Attempts were also run with the ABA triblock copolymers and the poly(α-chloro-ε-caprolactone) homopolymer again, no change in the final molecular weight was observed. It is not understood what is causing this reaction to not work. Perhaps the presence of so many chloro groups are decreasing the overall reactivity of the poly(α-chloro-ε-caprolactone) homopolymer.
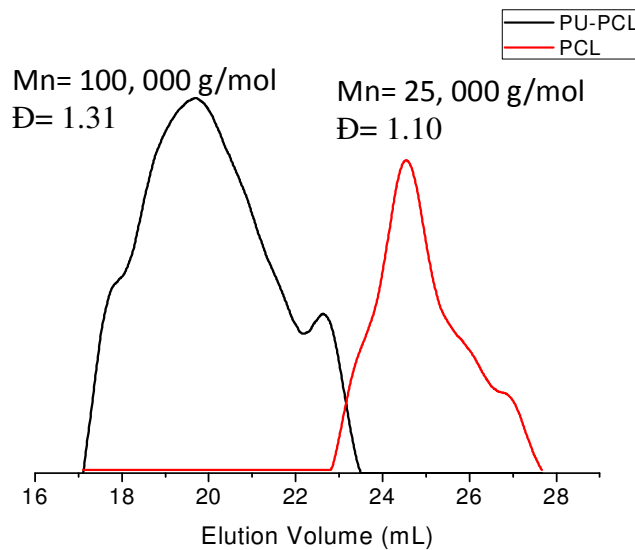
Figure 4.7 GPC traces of PCL and modified PCL

Figure 4.8 PCL (left) and polyurethane (right)

4.5 Conclusions

In conclusion, rosin containing pentablock copolymers have been successfully produced by two different methods. Low molecular weight hindered the study of the mechanical properties to test if the rosin containing blocks increase the ductility of the final copolymers and attempts to increase the molecular weight by way of urethane linkage were futile. Addressing the molecular weight issue, as well as replacing the polycaprolactone blocks with a soft polymer needs to be accomplished before a true understanding of how the rosin moiety effects the overall mechanical properties of the final copolymer is achieved.

CHAPTER 5

DEGRADABLE-VEGETABLE OIL BASED POLYESTERS

5.1 Abstract

We have carried out the synthesis of novel vegetable oil based polyesters. A series of castor oil based monomers were synthesized using either 10-undecen-1-ol, 10-undecenoic acid, or a combination of both. These monomers were polymerized by either ADMET or thiol-ene polycondensation reactions. Both methods produced similar results in terms of thermal properties and the final molecular weight. These polymers were found to degrade under acidic conditions. This study illustrates a general strategy to prepare a novel class of renewable polyesters.

5.2 Introduction

One of the key issues facing the chemical industry is the depletion of fossil oil reservoirs. Although, only 7% of the global production of fossil fuel goes into the synthesis of plastic materials, this number will decrease over time as the demand for petroleum based fuels continues to grow .[105-107] Depleting oil reserves coupled with a rise in global energy demands has led to an increased interest in the development of energy and materials derived from renewable resources. A variety of green plastics have been derived from either abundant and low cost natural polymers such as cellulose, lignin, and chitosan, or natural molecular biomass such as vegetable oil, lactic acid, fatty acid, terpenes, and rosin. [109-113] Usually obtained directly from forestry and agriculture products or by microorganism fermentation, these natural resources are important because their derived polymers could mimic plastics manufactured from petroleum chemicals.

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Vegetable oils are an exceptional natural renewable resource for polymer synthesis, with an annual global production that is projected to exceed 150 million metric tons in 2012.[67] This natural abundance, along with their inexpensive cost, and an ever increasing desire to find alternatives to non-renewable starting materials make vegetable oils an ideal polymeric starting material. The chemical structure of vegetable oils can be viewed as a triglyceride with three fatty acid chains as seen in Figure 5.1. Figure 5.2
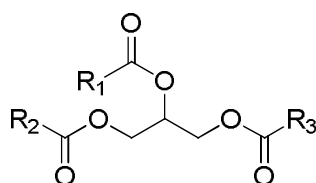
Figure5.1 Triglyceride structure where R1, R2, and R3 represent fatty acid chains

displays some of the more common fatty acids obtained from vegetable oils. The length of the fatty acid chains varies from 12 to 22 carbons and the amount of unsaturated C=C bonds vary from zero to 6 per fatty acid chain. Other functional moieties such as hydroxyl or epoxy groups may also be present in certain types of vegetable oil. The final composition of the vegetable oil is a mixture of more than one triglyceride, with one or two structures representing the majority of this mixture. The reactivity of the unsaturated bonds of both the triglyceride and the isolated fatty acid is what allows vegetable oil to be used in a variety of polymerizations.[68-74]

Among natural molecular biomass, fatty acids derived from vegetable oils have shown to be a prime resource for polymer chemistry.[47, 148-151] Derived from castor oil, 10-

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undecenoic acid is one of the most important fatty acids with a flexible, linear structure and can undergo a number of synthetic reactions to produce renewable monomers for
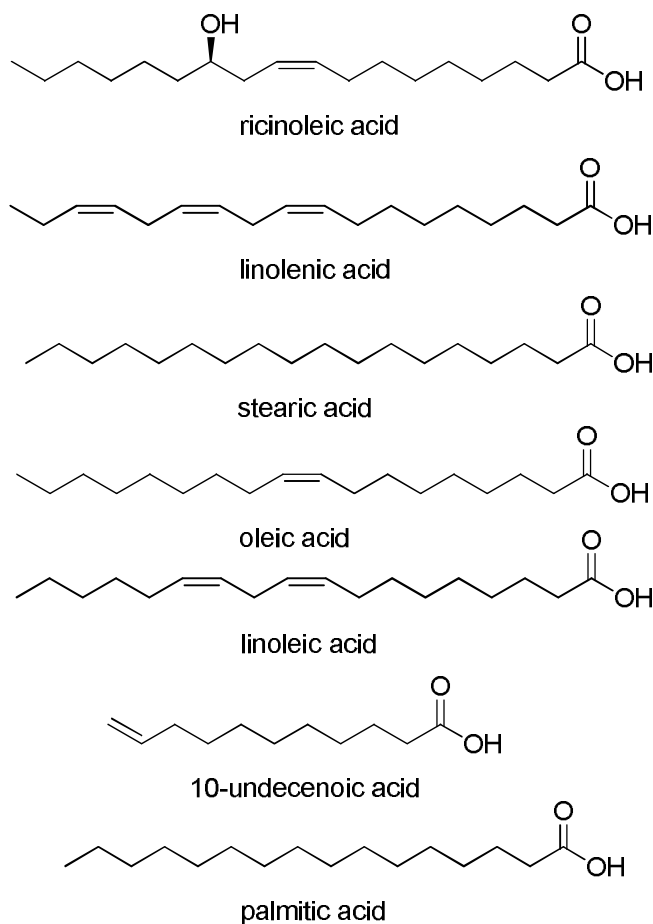
Figure 5.2 Common fatty acids obtained from vegetable oil triglycerides

polymer synthesis.[150, 152, 153] Olefin metathesis and thiol-ene reactions are just a few examples of highly efficient reactions that take advantage of the unsaturated terminal olefins to produce valuable monomers.[50, 160-162] With a range of renewable monomers, it is important to understand how monomers with different structural characteristics affect the properties of their corresponding renewable polymers. Herein we report the use of castor oil-derived fatty acids and alcohols to produce novel, degradable polyesters.

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5.3 Experimental Section

5.3.1 Materials

10-Undecenoic acid, 1,2-ethanedithiol, triethylamine and Hoveyda-Grubbs second generation catalysts (Sigma-Aldrich), 10-undecen-1-ol (Alfa-Aesar), oxalyl chloride (Fisher Scientific), and hydroquinone (VWR) were purchased from commercial sources and used as received. 2,2'-Azobisisobutryonitrile (AIBN, Aldrich) was recrystallized from methanol prior to use. Tetrahydrofuran (THF, Aldrich), dichloromethane (DCM, Aldrich) and methanol (MeOH, Aldrich) were refluxed with sodium and distilled under nitrogen atmosphere prior to use.

5.3.2 Characterization

^{1}H NMR spectra were recorded on Brucker ARX300 and ARX400 spectrometers. The chemical shifts were recorded in ppm (δ) relative to tetramethylsilane. Gel permeation chromatography (GPC) was performed at room temperature on a Varian system equipped with a Varian 390-LC multi detector and a Varian 290 pump injection module. The columns were PLgel MIXED-BLS (300×7.5 mm, with capability to characterize molecular weight in the range of 500 to 10,000,000 g/mol) from Polymer Laboratories. HPLC grade THF was used as eluent at a flow rate of 1 mL/min. Samples were filtered over a microfilter with pore size of 0.2μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). GPC was calibrated using polystyrene as standards. Thermal transitions were recorded using differential scanning calorimetry (DSC) on a TA Q200 calorimeter in a temperature range from -60 to 100 °C at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. All the data were collected during the second

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heating process after cooling at 10 °C min^{-1} from 100 °C. The average sample mass was about 5 mg, and the nitrogen flow rate was 50 mL min^{-1}.

5.3.3 Synthesis

Synthesis of ester monomer: To a 50 mL round bottom flask, 10-undecenoic acid (1.5 g, 8.83×10^{-3} mol) and 20 mL DCM were added. While under a continuous flow of nitrogen, 1.2 mL (1.38×10^{-2} mol) of oxalyl chloride was added at 0 °C and reacted for 3 hr at room temperature. The solvent and any unreacted oxalyl chloride were then removed and 10 mL of fresh DCM was added. A solution of 1.2 mL (8.83×10^{-3} mol) triethylamine and 2.0 mL (1.00×10^{-2} mol) 10-undecen-1-ol in 15 mL DCM was added to the acid solution under continuous nitrogen flow at 0 °C and reacted overnight at room temperature. The solution was extracted (3x) with a saturated sodium carbonate solution and once with D.I. water. Water was removed by the addition of magnesium sulfate. The monomer was purified by silica gel column chromatography (9:1 hexane: ethyl acetate) to yield a slightly yellow liquid. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 5.7-5.9 (m, -C=*CH*-); 4.9-5.1 (t, -C=*CH2*); 3,9-4.1 (t, -*CH2*O-), 2.2-2.4 (t, -*CH2*CO-).

Synthesis of oxalate monomer: To a 50 mL round bottom flask, 6.0 mL 10-undecen-1-ol (2.94×10^{-2} mol) and 20 mL DCM were added. While under a continuous flow of nitrogen, 1.3 mL (1.47×10^{-2} mol) of oxalyl chloride and 4.1 mL (2.94×10^{-2} mol) triethylamine were added at 0 °C and reacted for 24 hr at room temperature. The solution was then filtered and any unreacted oxalyl chloride was then removed. The monomer was purified by silica gel column chromatography (7:1 hexane: diethyl ether) to yield a slightly yellow liquid. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 5.7-5.9 (m, -C=*CH*-); 4.9-5.1 (t, -

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C=*CH2*); 3,9-4.1 (t, -*CH2*O-).

Synthesis of hydroquinone monomer: To a 100 mL round bottom flask, 10-undecenoic acid (11.0 g, 5.90×10^{-2} mol) and 40 mL DCM were added. While under a continuous flow of nitrogen, 8.0 mL (9.19×10^{-2} mol) of oxalyl chloride was added at 0 °C and reacted for 3 hr at room temperature. The solvent and any unreacted oxalyl chloride were then removed and 15 mL of fresh THF was added. A solution of 12 mL (8.83×10^{-2} mol) triethylamine and 3.8 g (3.17×10^{-2} mol) hydroquinone in 40 mL THF was added to the acid solution under continuous nitrogen flow at 0 °C and reacted overnight at room temperature. The solution was extracted (3x) with a saturated sodium carbonate solution and once with D.I. water. Water was removed by the addition of magnesium sulfate. The monomer was purified by silica gel column chromatography (1:1 hexane: DCM) to yield a white solid. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.2-7.3 (s, aromatic); 5.7-5.9 (m, -C=*CH*-); 4.9-5.1 (t, -C=*CH2*); 2.2-2.4 (t, -*CH2*CO-).

ADMET polymerization (oxalate monomer): 1 g of monomer and 14.8 mg of Hoveyda-Grubbs catalyst (1: 0.01) were placed in a 5 mL round bottom flask. Vacuum was applied and the flask was placed in an oil bath set at 80 °C for 1 hr. The polymer was then dissolved in DCM and precipitated in cold methanol. The same monomer to catalyst ratio, temperature, and reaction time was utilized for all the other monomers.

Thiol-ene click polymerization (oxalate monomer): 1 g monomer, 0.2 mL 1,2-ethanedithiol, and 10 mg AIBN were placed in a 10 mL Schlenk tube under continues nitrogen flow. The tube was placed in an oil bath set at 80 °C for 2 hr. The polymer was then dissolved in DCM and precipitated in cold methanol.

5.3.4 Degradation of Polymers

A mixture of polymers (~ 50 mg), 0.15 M HCl (aq) (0.5 mL), and THF (5 mL) was introduced into a small vial. The solution was then refluxed for two days at 65 ^{o}C. The solution was then evaporated to dryness.

5.4 Results and Discussions

Synthesis of Monomers: Figure 5.3 displays the synthetic route used to produce the castor oil derived monomers. The final structure of each monomer was confirmed by ^{1}H NMR (Figure 5.4). The emergence of a new ester peak around 4.0 ppm as well as the vinyl protons at 4.9 and 5.8 ppm indicated the successful esterification for each monomer. For the hydroquinone monomer, the presence of an aromatic peak around 7.0 ppm is further evidence that the esterification was successful.

ADMET and Thiol-ene Polymerization: Both ADMET and thiol-ene polymerization was used to prepare the polymers. Hoveyda-Grubbs second generation catalyst was utilized for ADMET polymerization. As shown in Figure 5.5, ^{1}H-NMR spectrum of the final polymer displayed a loss of the terminal alkene peak at 4.9 ppm, which was expected for ADMET polymerization. Table 5.1 contains the final molecular weight for each polymer. The ester monomer produced the polymer with the highest molecular

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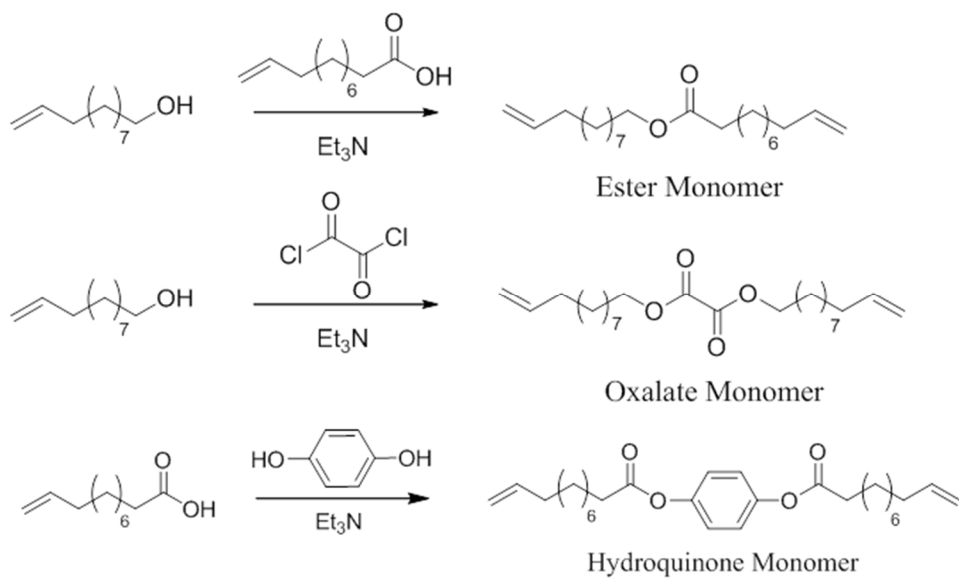
Figure 5.3 Vegetable oil based monomer synthesis
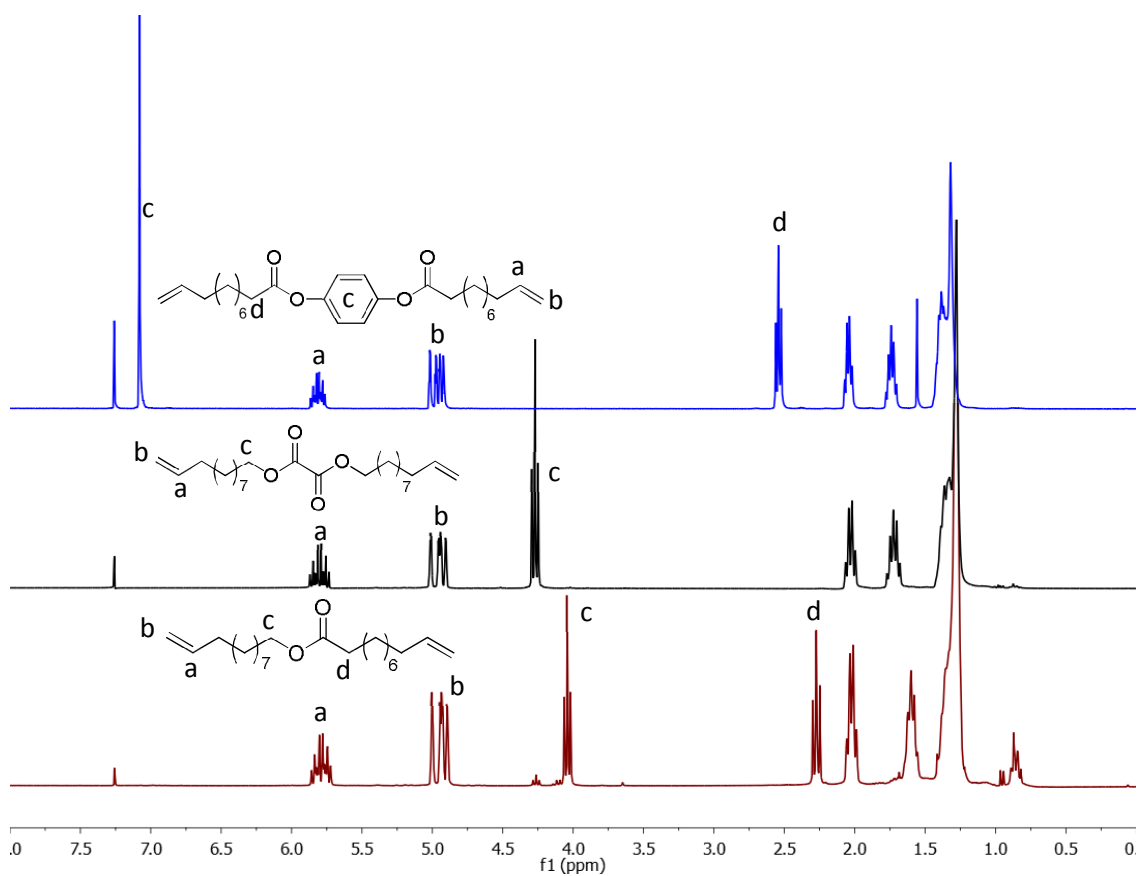
Figure 5.4 ^{1}H NMR of castor oil based monomers
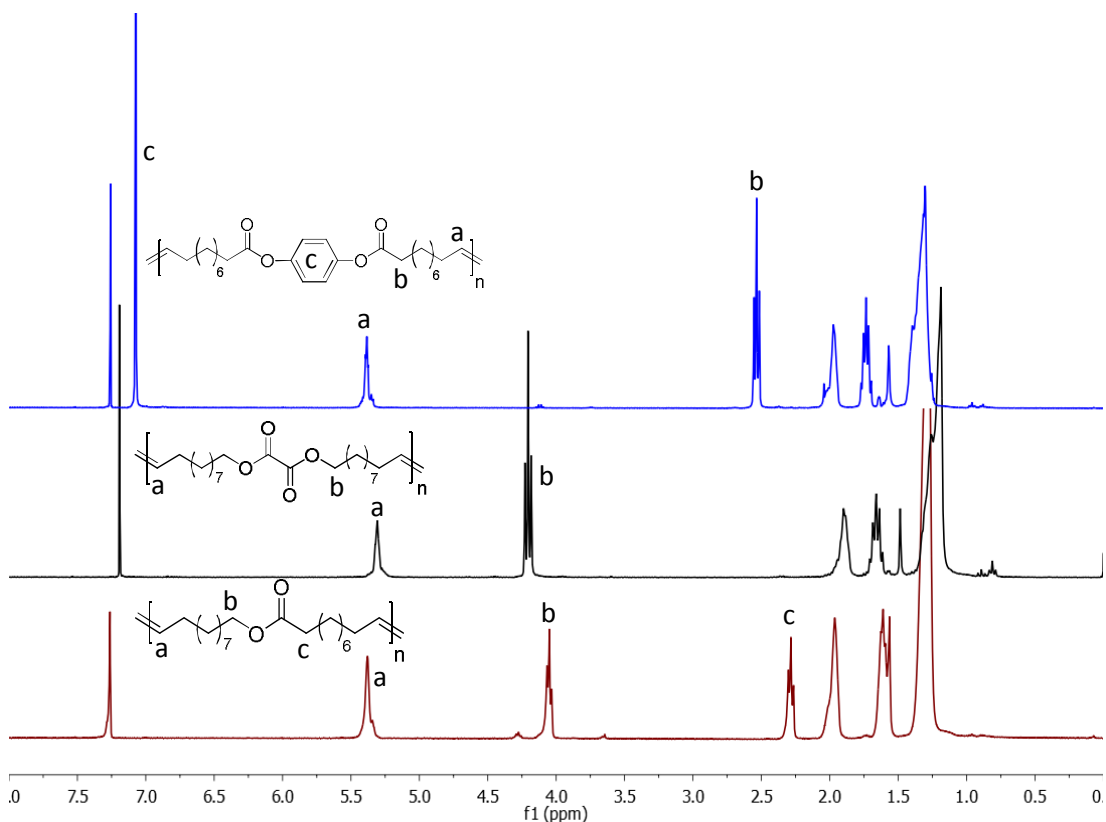
Figure 5.5 ^{1}H NMR of ADMET prepared polyesters

Table 5.1 ADMET Polymerization Results

Polymer	Mn (g/mol)	Đ
	15,000	1.50
	8,600	1.60
	30,000	1.80

weight, while the oxalate monomer produced the polymer with the lowest molecular weight. Due to the low molecular weight of the oxalate polymers when compared to the other polymers, thiol-ene polymerization was attempted in order to increase the

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molecular weight. 1,2-ethanedithiol was chosen as the thiol due to its high reactivity towards thiol-ene click reactions. AIBN is an excellent initiator for thermal thiol-ene click reactions; this is why it was chosen. The ^{1}H NMR of the final polymer shows a disappearance of the vinyl peaks around 4.9 and 5.8 ppm and the emergence of two new peaks around 2.5 and 2.8 ppm that are due to the incorporation of the thiol into the polymer backbone. A maximum M_n of 7,200 g/mol with a Đ of 2.03 was obtained. Although this molecular weight is slightly lower than that obtained by ADMET polymerization, it provides an alternative method to polymerize these castor oil based monomers without the use of expensive metal-containing catalysts.
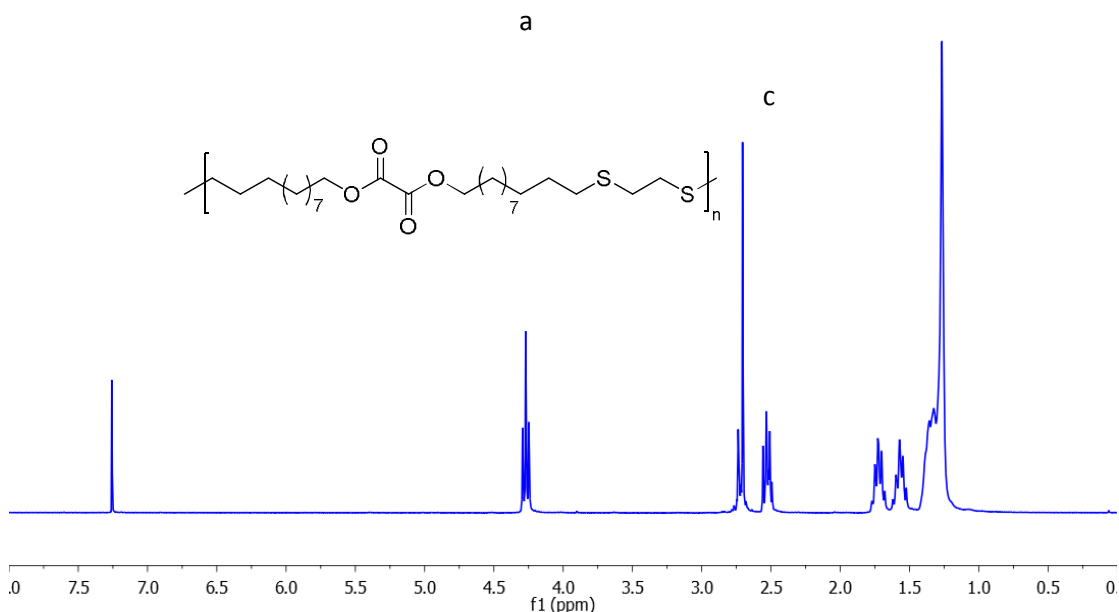
Figure 5.6 ^{1}H NMR of oxalate polymer prepared by thiol-ene polymerization

Thermal Properties of Polyesters: Differential scanning calorimetry (DSC) was utilized to examine the thermal properties of these polyesters. As shown in Figure 5.7, the melting point (T_m) varied from 40 °C to 100 °C depending on the structure of the polyester. The hydroquinone containing polyester has the highest T_m due to the increased rigidity of the

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polymer backbone. When comparing the two oxalate polymers, thiol-ene versus ADMET

polymerization, there is a noticeable difference in T_m. The ADMET prepared polymer has
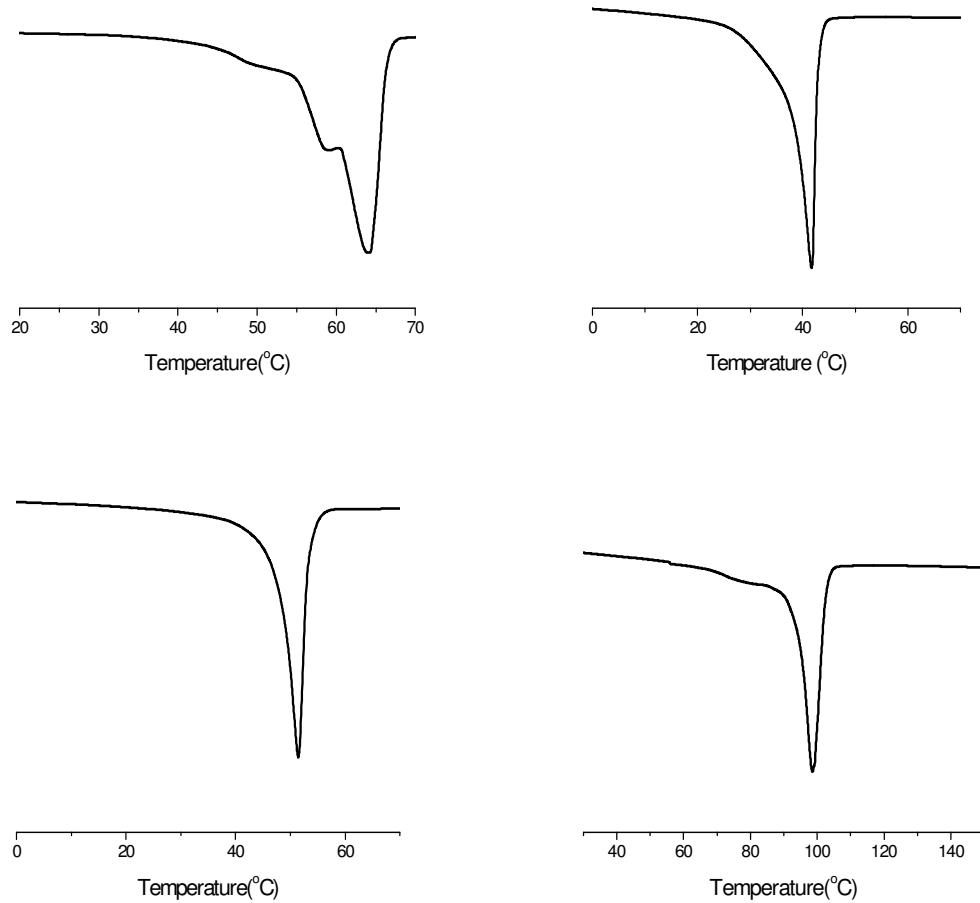
Figure 5.7 DSC thermograms (2nd heating cycle) of polyesters: (top left) thiol-ene oxalate polymer (M_n = 7,200 g/mol); (top right) ADMET prepared oxalate polymer (M_n = 8,600 g/mol); (bottom left) ester polymer (M_n = 30,000 g/mol); (bottom right) hydroquinone polymer (M_n = 15,000 g/mol)

a T_m that is nearly 25 °C lower than the thiol-ene prepared polymer, even though they have similar molecular weights. The presence of sulfur in the polymer backbone may explain this difference, as it is the only noticeable difference between the two polymers. One final thing that was observed is that all the polymers displayed a T_m and no glass transition temperature. This indicates that the polyesters derived from castor oil are semicrystalline with a glass transition temperature below -60 °C.

Degradability of Polyesters: Both oxalate polymers were subjected to acid degradation for two days. GPC was used to monitor the amount of degradation for each polymer. Figure 5.8 displays the GPC for the ADMET prepared oxalate polymer before and after degradation. Both polymers degraded to low molecular weight oligomers after only two days. This implies that in addition to being renewable, these polymers are also degradable.
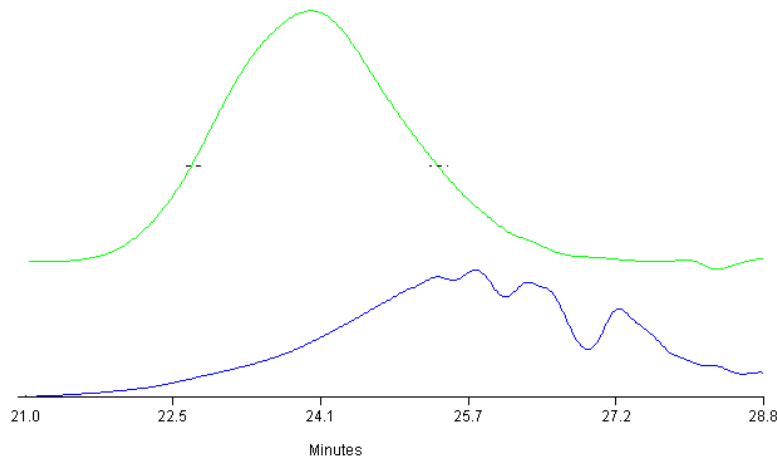
Figure 5.8 GPC traces of ADMET prepared oxalate polymer before (green, M_n= 8,600 g/mol) and after (blue, M_n= 2,400 g/mol) acid degradation

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5.4 Conclusions

Several castor oil based monomers were prepared. Using either ADMET or thiol-ene polymerization, polyesters could be produced from these renewable monomers. By varying the monomer structures, the thermal properties of the resulting polymers could be adjusted. These polymers displayed excellent degradation leading to a new class of vegetable oil based materials. Thiol-ene polymerization should be investigate further as it does not require the use of a metal catalyst and provides an economical alternative to prepare degradable, renewable polyesters.

CHAPTER 6

SUMMARY AND OUTLOOK

In this dissertation, the major research goal of developing and characterizing novel polymers based upon renewable rosin and fatty acids was achieved. Renewable rosin acids were used to develop a series of new polymers containing rosin moieties via controlled/living polymerization techniques and "click" chemistry. (1) The rosin derived acrylate monomers were polymerized by ATRP. Block copolymers were then produced by ROP of CL. The PCL blocks were shown to exhibit excellent degradation, while the rosin based blocks remained intact. The thermal properties of these novel block copolymers could be adjusted by varying the ratios of each block. (2) Rosin was combined with a vegetable oil derived alcohol to produce 100% renewable monomers and polymerized by ADMET to create a novel class of polyesters. These polymers exhibited increased thermal stability and a higher glass transition temperature due to the presence of the bulky rosin moiety. (3) Rosin containing multiblock polyesters were prepared by ROP and click reaction. Even though an upper limit molecular weight was established for these polymers, they have the potential to create a new class of highly functional degradable polyesters. (4) Several castor oil based polyesters were also prepared and characterized. These polymers displayed excellent thermal properties and were completely degradable, creating a new class of vegetable oil based materials.

Within the past decade, research on renewable bio-based polymer materials has drawn a great deal of interest from both industry and academia. When compared to other renewable resources, the use of rosin as polymeric starting materials has significant strides to make before it gains global acceptance. Low cost, abundance, and the existence of useful functional groups (conjugated diene and carboxyl acid groups) are the primary reasons why the use of rosin acids as polymeric starting materials should be endlessly

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pursued. Developing "green" monomer synthesis techniques will be essential in promoting the advancement of rosin acids research. The combination of rosin acids and other natural molecular biomass (vegetable oil, lactic acid, lignin, etc.) to prepare novel materials is an area of research that should gain interest in the years to come. Finding a way to fully exploit these natural resources will be essential for the progression of green materials research.

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