Castor Oil Derived Degradable Polyoxalates

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A thesis

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Indian Institute of Science Education and Research Pune
Dr. Homi Bhabha Road,
Pashan, Pune 411008, INDIA.

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Supervisor: Professor Samir Chikkali, NCL Pune
Expert: Professor Manickam Jayakannan, IISER Pune
Submitted by: Abhijith Hari Menon

Certificate

This is to certify that this dissertation entitled Castor Oil derived Polyoxalates towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Abhijith Hari Menon at National Chemical Laboratory, Pune under the supervision of Dr Samir Chikkali, Professor, Polymer Science and Engineering Division, during the year 2023-2024.

Professor Samir Chikkali

Committee:

Professor Samir Chikkali

Professor Manickam Jayakannan

Declaration

I hereby declare that the matter embodied in the report entitled "Castor-Oil based degradable polyoxalates" are the results of the work carried out by me (Abhijith Hari Menon) at the Department of Chemistry, IISER Pune, under the supervision of Professor Samir Chikkali, NCL Pune and the same has not been submitted elsewhere for any other degree. Wherever others contribute, every effort is made to indicate this clearly, with due reference to the literature and acknowledgement of collaborative research and discussions.

Date: 10th May 2024

Place: IISER, Pune

Signature of the Student

Date: 10th May 2024

Place: NCL, Pune

Signature of the Supervisor

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Contents

Abstract

The majority of polymeric materials manufactured today come from non-renewable and pollution causing petroleum based raw materials. Additionally, most of these are non-degradable, and the plastic waste generated globally causes a lot of environmental and, thus, economic problems. Castor oil is a bio-renewable resource used to make various commodities such as lubricants, surfactants, coatings and polymers. In this work, two novel castor oil-based oxalate dimethyl esters have been synthesized, one of which (monomer (5)) was used to synthesize novel, degradable polyoxalates with bio-renewable diol comonomers. The obtained polymers were amorphous and viscous liquids at room temperature, which showed good degradation in acidic media, as is expected for polyoxalate materials. Under optimized conditions, M_w of up to 20,000 g/mol with dispersities between 2.5 and 2.9 were obtained. The obtained polymers were further cross-linked using thiol-ene click chemistry to yield potentially degradable cross-linked polymers.

Introduction

1.1 Importance of Bio-renewable Materials

There is an urgent need to find alternatives to petroleum-based feedstocks due to their non-renewability and pollution. The extraction, processing and consumption of our limited global petroleum stock severely damage the environment and human health during each step.[1][2] The extraction and refining of petroleum releases many gaseous pollutants into the environment, mainly SO_2 and volatile hydrocarbons[3], which negatively affect the biosphere. Even after treatment, wastewater from the petroleum industry would contain traces of toxic organics and heavy metals, which are toxic and increase the biological and chemical oxygen demands[4].

Polymers and Plastics majorly consume the petroleum industry's end-products as monomers. Since plastics have become indispensable for everyday life, more sustainable sources must be investigated to satisfy the global demand. The degradation and disposal of post-consumer plastic waste is another challenge that needs to be overcome.[5] Microbial degradation, which has given rise to many headlines worldwide, has a long way to go before it can be commercially employed, with current reports being too inefficient for it to be practical because these materials are relatively new to the environment. Plastic waste ends up in landfills and water bodies, where it can undergo further weathering into microplastics and oxidized byproducts. The impact of microplastics on the biosphere, especially those whose particle size is less than 100 micrometres in diameter, is yet to be fully understood[6]. Due to their slow assimilation, most post-consumer waste persists in the environment and can enter the food web through any creature.

Ever since the agricultural revolution, and even before, humans have been successfully exploiting plants for food, clothing, fuel, and construction material for gross and refined products, including but not limited to shelter, furniture, transportation, storage and art. Either directly or indirectly, plants produce complex chemicals from simple and readily available compounds. Thus, plant-based raw materials can be explored for commodity polymers.

1.2 Significance of Degradability

As mentioned above, most commercial plastics are not fully degradable, and the ones that do undergo partial degradation release toxic chemicals into the environment, mostly substances used as additives in the synthesis of these materials. Plant-based natural polymers are more readily degradable by biological or chemical action or both[7].

Biodegradability is possible when the polymer has functional groups incorporated into the backbone, which can be acted upon by enzymes present in living organisms. Many microorganisms can catabolize such polymers, eventually releasing only CO_2 and H_2O into the environment. Most biodegradable polymers are used in drug-delivery applications, where they degrade to the constituent monomers or harmless byproducts and release the therapeutic[8].

Polyesters are one such class of biodegradable polymers. They are also subject to hydrolytic ageing [9], which can damage goods made from polyesters over long periods. Nevertheless, most polyesters are stable enough for commercial applications. Esterase enzymes are ubiquitous in the biosphere and have also been shown to degrade aliphatic and aromatic polyesters[10, 11].

Polyesters have desirable properties for commercial applications besides their degradability, such as their ability to form fibres and competitive mechanical strengths. Hybrid polyesters which are partially renewable are already being commercialized[12] for consumer applications, such as PET Plantbottles. Polylactic Acid is a famous example of a renewable, degradable polyester, which is largely used for medical applications.

There is still scope for improvement in plant-based degradable polymers, and plant-oil-based polyesters have the potential to fill the demand for consumer thermoplastics.

One potential raw material for polyester feedstocks is Castor Oil, produced by the Castor Bean (*Ricinus communis*). Castor oil is majorly composed of Ricinoleic Acid triglyceride, which has a hydroxyl group at the 12th Carbon (on each fatty acid moiety). Various polyesters, polyamides, and polyurethanes, among other polymers and commodity materials, have been made from Ricinoleic Acid.[13, 14, 15]

1.3 Castor-based materials

Castor oil is commonly used by automobile industries as a lubricant. Many derivatives of castor oil have also been synthesized in order to improve viscous properties[17, 18]. Due to its commercial importance, many countries around the world produce Castor Oil on an industrial scale, with India, Brazil and China being the top producers. Castor oil is a non-edible oil that has historically been used as a laxative and in medicinal formulations[19]. Nowadays, well-known chemistry is being applied to make more commercially relevant chemicals and materials from Castor Oil, with some interesting results.

Different types of polyesters are made from ricinoleic acid. Poly Ricinoleic Acid (PRA) has been synthesized by various groups using different conditions. Most notably, are the syntheses catalyzed by Lipases[20, 22], $Sn(Oct)_2$[23] and pTSOH[24]. PRA is a viscous liquid even at high weight averaged molecular weights of the order of 10^6 g/mol.

Various co-polyesters of Ricinoleic Acid have also been synthesized with Stearic acid[25], aromatic plant-based compounds such as Vanillic acid[26] and Lactic acid[27], among others. These polymers show better mechanical properties than Polyricinoleic acid and have different applications. The PolyRicinoleic Acid-co-Stearic Acid material synthesized by Abraham J Domb and Coworkers[28] was shown to be applicable as an in-situ gelling polymer that can be used for drug-delivery. The injection in vivo could be performed at room temperature, and an increase in the viscosity and melting temperature of the polymers was seen in an aqueous medium, which is useful for pharmaceutical applications. Co-polyesters with Vanillic acid generated a material with sub-zero glass-transition temperatures and with increasing Ricinoleic acid content of greater than 50%, undetectable T_m. *Domb and coworkers* had also reported Poly-L-Lactic Acid – co – Ricinoleic Acid with different compositions of each co-monomer.

Even 20% ricinoleic acid content caused the copolyesters to become viscous liquids at room temperature. Such liquid materials can find applications as sealants, which are currently sourced from petroleum, and as drug-delivery agents.

Cross-linking polymers are an efficient way to generate tough and durable materials. Their main drawback is that once formed, they are difficult to break down or recycle, which is an environmental issue. Using renewable feedstocks could thus at least reduce the load on petroleum products for the same. Castor oil has been repeatedly used as a component of many polyurethanes with different applications, such as flame-retardant coatings, leather substitutes and adhesives. Having built-in trifunctionality (double bond, alcohol, and carboxylic acid), ricinoleic acid is a good starting point and a co-monomer for synthesizing cross-linked materials. Castor oil, which has majorly Ricinoleic acid triglycerate, has been used as a polyol[29] to synthesize polyurethanes with isocyanates. Flame-retardant[30] Various non-isocyanate-based polyurethanes have been synthesized too[31].

Co-polyanhydrides made from Ricinoleic acid-based Succinate monomers and Sebacic acid yielded film-forming, degradable polymers that had mechanical properties suitable for drug-delivery applications[32]. The melt polycondensation was carried out at 150°C for 4 hours under vacuum (pressure of 0.3mm Hg), using magnetic stirring.

1.4 Polyoxalates

Oxalate polymers have been shown to be hydrolytically degradable in even mildly acidic conditions. *Garcia et al. synthesized linear aliphatic as well as aromatic poly oxalates* by reacting diols of different kinds with dimethyl oxalate under pTSOH catalysis and reduced pressure[33]. The aliphatic polyoxalates displayed some interesting properties, with an average T_{50} of around 350°C and relatively low melting and very low, often sub-zero glass-transition temperatures. For some samples, such as polydecylene oxalate, which can be potentially biorenewable, a T_g was not detected. Over the course of 13 months, there was a significant reduction in molecular weight (>70%) for the two copolymers studied. This rapid degradation enables the environmental safety of the synthesized polymers, although it only allows for shortterm uses of the polymers. Relatively harsh conditions were required for their synthesis: a temperature of 200°C at the final stages of the reaction to build up molecular weight.

Bhausaheb et al. have used plant sugar-based poly oxalates using Isohexides as the base chemical to synthesize isohexane oxalates, followed by co-polymerization with fatty-acid-derived diols. The resulting polymers were semi-solids at moderate molecular weights, and one sample (M_w = 68,000g/mol) had strong enough intermolecular forces to make films out of. Mechanical characterization revealed a rubbery-like material. An interesting point about the mechanism of the reaction was that the oxalate esters had been cleaved by the diols, followed by the reaction of the freed isohexides to form a blocky copolymer[34].

1.5 Challenges with using Castor Oil

An important consideration is that the hydroxy group of Ricinoleic acid is relatively less reactive, being a secondary hydroxy group with a long carbon chain on both sides, hence demanding relatively higher temperatures and reaction times to perform transformations with many electrophiles. Esterification reactions outside of the synthesis of Polyricinoleic Acid are rare; different groups have also shown how reacting mixtures of ricinoleic acid, dicarboxylic acids, and diols lead to blocky polymers, with PRA forming a block in such cases[35, 36]. Reactions with anhydrides and acid chlorides are more common and are mainly used in the synthesis of surfactants, lubricants, monomers, polymers (via insertion) and matrix materials[37, 38, 39, 40]. Quite often, in order to obtain materials with good mechanical properties, curing of the double bond was also performed[41]. In other cases, cross-linked polymers were directly synthesized[42]. Trans-esterification reactions have also been employed to make copolymers with Lactic Acid[43] and Steglich-type coupling reactions to make copolymers with 4-Hydroxycinnamic acid derivatives.[44]

It has been classically established that branching and unsaturation in the polymer backbone reduce the glass-transition temperature of the polymers and inhibit crystallization. A well-known example is Polyethylene, where increasing the number of hydrocarbon dangling chains reduces the density, mechanical strength, and glass transition temperatures of the polymers. Thus, Low-density polyethylene, with many side chains, is an elastic material with low tensile strength and is used for applications such as packaging foams, plastic bags and flexible parts. High-density polyethylene, with minimized branching and thus much greater strength, is used for making chairs, ropes, pipes and bottle crates. It is, therefore, reasonable to assume that the double bond and dangling chain are major contributors to the liquid nature of Polyricinoleic acid, even at high molecular weights. Using the double bond to make cross-links is one way to increase the mechanical properties of ricinoleic acid-derived materials.

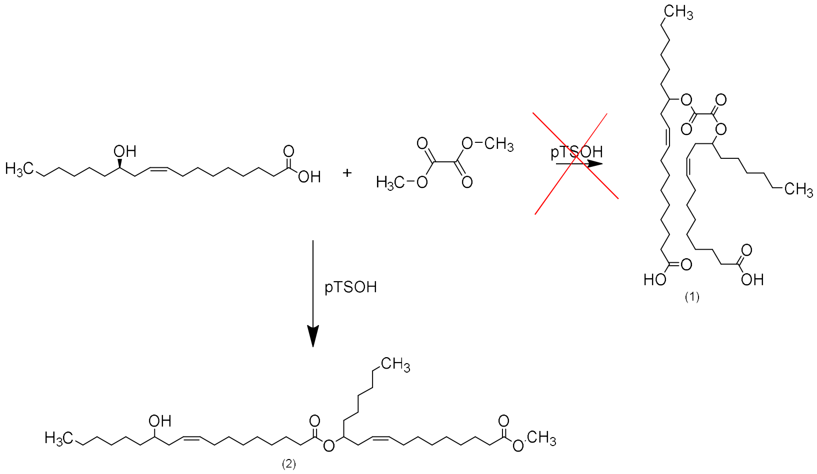
1.6 Aim

The aim of this project is to synthesize Ricinoleic Acid-based oxalate polymers to obtain renewable and readily degradable polymers with good mechanical properties. The latter is attempted by introducing long-chain hydrocarbons into the polymer to increase spacing between the double bonds and the dangling chains. The double-bond can be further cured; using the thiol-ene click reactions could enable the synthesis of degradable cross-linked materials.

Results and Discussion

Attempted Synthesis of (12R,12'R)-12,12'-(oxalylbis(oxy))dioleic acid

In order to realize the goal of a di-acid monomer with an incorporated Oxalate group, a simple trans-esterification was attempted using dimethyl oxalate. As the methanol group should be easier to knock off by vacuum compared to water (due to the formation of polyricinoleic acid), significant yields of (12R,12'R)-12,12'-(oxalylbis(oxy))dioleic acid and (R,Z)-12-(2-methoxy-2-oxoacetoxy)octadec-9-enoic acid were expected. Thus, 530 mg of Ricinoleic Acid, and 80 mg of Dimethyl Oxalate were heated at 120°C and stirred under N_2 atmosphere for 4 hours, followed by intermittent vacuum (2.5 mbar) for the next 2 hours at 150°C to knock-off the byproducts, Methanol and Water. TLC run at 25% Ethyl Acetate: Pet-Ether as well as ^{1}H NMR (Nuclear Magnetic Resonance) of the crude mixture indicated that no reaction with dimethyl oxalate happened, and self-condensation had occurred instead, resulting in di-ricinoleate as the major product.



Scheme 1:- Attempted Trans-esterification of Ricinoleic acid with Dimethyl Oxalate

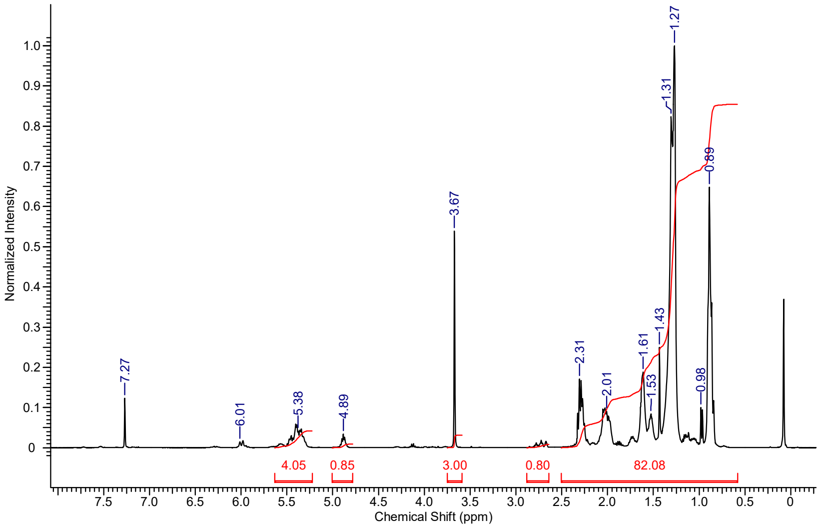
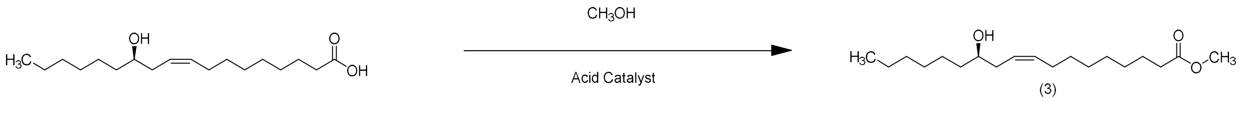


Figure 1:- ^{1}H NMR spectrum of the major product (2).

Due to the lack of selectivity in removing methanol, an alternate route for the synthesis of the desired oxalate-containing diester/diacid monomer was explored, involving the synthesis of Methyl Ricinoleate, followed by reacting with oxalic acid or its derivatives.

Synthesis of Methyl Ricinoleate

The synthesis of Methyl Ricinoleate (3) was an esterification reaction performed using different literature methods. The best method was a Fischer esterification using $BF_3.OEt_2$. The significant byproducts are dimers and trimers of Methyl Ricinoleate, a minute amount of which always elutes out with the Methyl Ricinoleate from the column at smaller scales. However, upon scale-up, pure methyl ricinoleate could be obtained in high yields (70%). The ^{1}H NMR singlet peak at 3.66 ppm and the ^{13}C NMR peak at 51.04 ppm confirm the formation of the Methyl ester. The spectra agree with previous reports.[19]

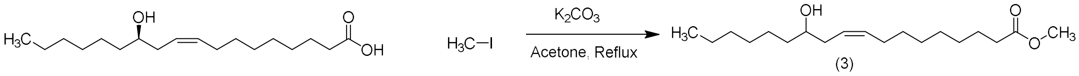


Scheme 2 – Fischer Esterification of Ricinoleic Acid to give Methyl Ricinoleate.

Table 1 – Esterification of Ricinoleic Acid with Methanol

Serial Number	Catalyst	Temperature	Time	Yield
1	$BF_3.OEt_2$	Reflux	16 hours	70%
2	pTSOH	Room Temperature	48 hours	35%
3	pTSOH	Reflux + Room Temperature	8 hours + 16 hours	63%

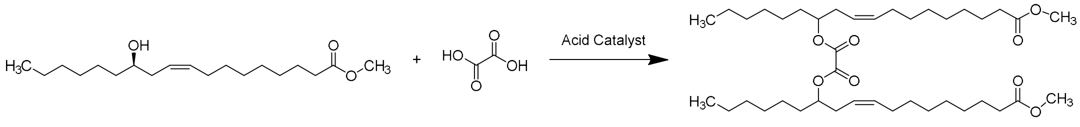
An S_N2 reaction with Methyl Iodide was also screened using K_2CO_3 as the catalyst. Similar side-products were isolated, and methyl ricinoleate was obtained with a 55% yield.



(3)

Scheme 3 – Nucleophilic attack on Methyl Iodide.

Fischer esterification of Methyl Ricinoleate with Oxalic Acid



(4)

Scheme 4 – Fischer Esterification of Methyl Ricinoleate with Oxalic Acid

In an attempt to yield a di-methyl ester monomer, Methyl Ricinoleate was Fischer esterified with oxalic acid as given in Scheme 4. Oxalic acid was dispersed in Toluene via a solution in acetone. This mixture was refluxed at 110°C with a dehydrating agent to help selectively remove water. After completion of the reaction, the excess solvent was evaporated under reduced pressure using a rota-evaporator, and purification of the product was done by column chromatography (4% Ethyl Acetate/Pet Ether). The first two products eluting from the column were dimers and trimers of Ricinoleic acid. The 3rd fraction indicated the formation of the desired dimer by NMR spectroscopy. The disappearance of the signal at 3.65 and the appearance of a new peak, a quartet, at 5.00, indicate the esterification of the C12-OH. In the ^{13}C NMR spectrum, there is only one peak corresponding to the carbon(s) of the oxalate, indicating that they are chemically identical, which is only possible if the dimer has formed, as opposed to a mono-oxalate ester. HRMS (High-resolution Mass Spectrometry) (peak at 678.5) confirmed the formation of the product. NMR characterization of the other fractions is given in the Appendix.

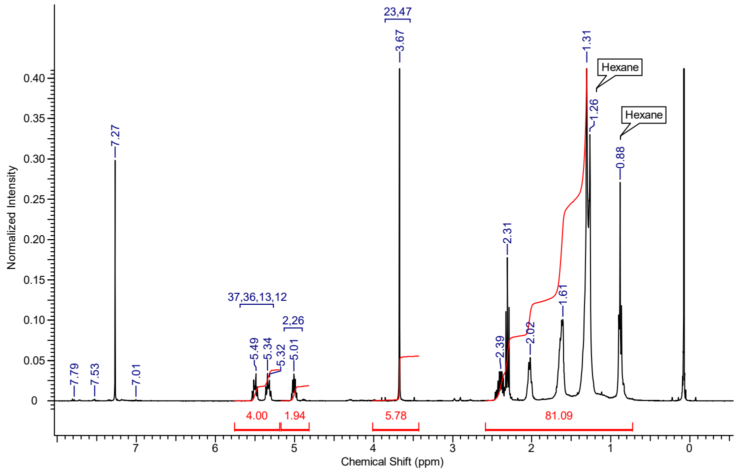
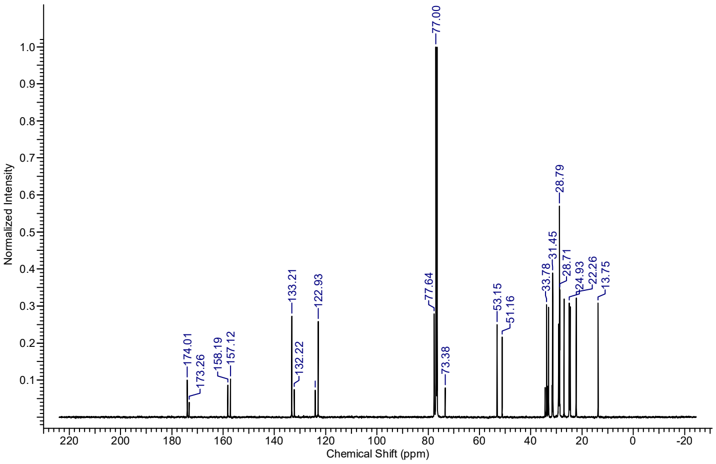
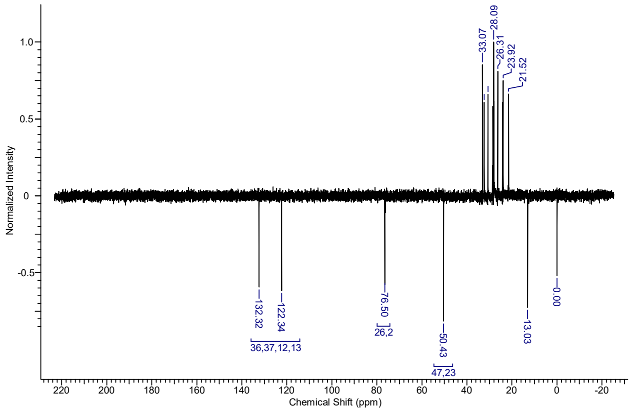


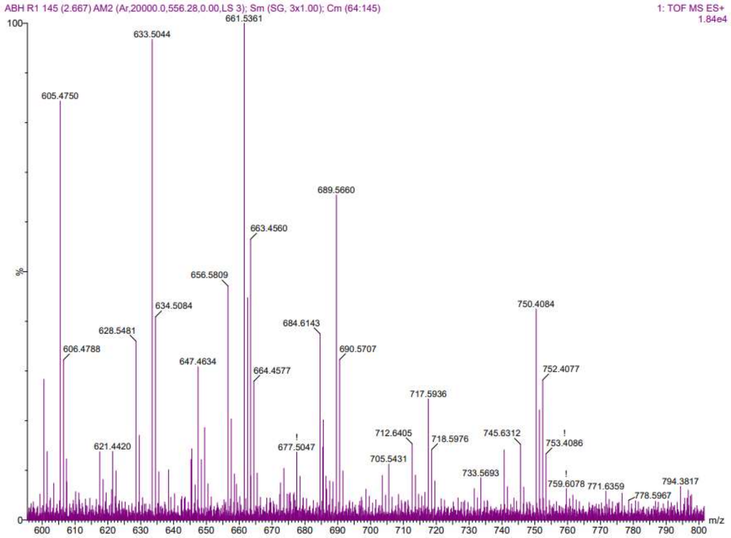
Figure 2:- ^{1}H NMR spectrum of (4)



<u>Figure 3</u> – ^{13}C NMR of (4)



<u>Figure 4</u> – DEPT (Distortionless Enhancement by Polarization Transfer) -135 NMR of (4)



<u>Figure 5</u> – HRMS data of (4)

However, the yield of the product was very low (~1%). Different conditions, solvents, catalysts, and dehydrating agents were screened with no greater success.

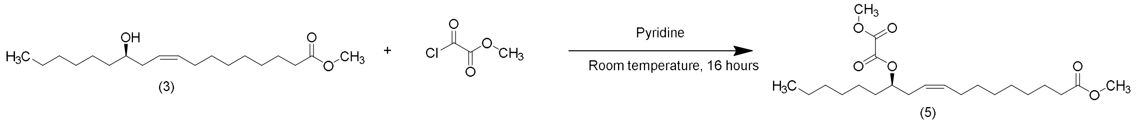
Table 2 – Synthesis of (4)

Serial Number	**Oxalic Acid Equivalents**	**Solvent**	**Dehydrating Agent**	**Time**	**Catalyst**	**Yield**
1	0.4	Toluene	None	9 hours	pTSOH	0.9%
2	0.4	Toluene	Molecular Sieves	30 hours	pTSOH	1.2%
3	0.75	Toluene	Na_2SO_4	24 hours	HCl	0.8%
4	0.55	Toluene + Dioxane	None	48 hours	pTSOH	1.8%
5	0.6	Toluene + Dioxane	Molecular Sieves	48 hours	pTSOH	5%
6	1.5	Acetonitrile	None	18 hours	Boric Acid	No Reaction

Synthesis of 18-methoxy-18-oxooctadec-9-en-7-yl methyl oxalate (5)

Methyl Chlorooxoacetate was used to attach the oxalate group to the free hydroxyl groups of the methyl ricinoleate. The final product would be a dimethyl ester, which can be reacted with diols to generate polyoxalates. The byproduct, HCl, was quenched by Pyridine to form a solid precipitate of Pyridinium Chloride, most of which can be removed by work-up with water and saturated $NaHCO_3$. The remaining traces can be removed by filtration through a short silica column. The disappearance of the proton NMR signal corresponding to the proton attached to C12 (3.64 ppm) and the corresponding ^{13}C peak at 71.09 ppm, along with the appearance of new ^{1}H peaks at

3.86 ppm (Methyl ester of the oxalate group) and 5.00 ppm (proton attached to C12, which has been esterified with the oxalate group) indicate the formation of the monomer (5). ^{13}C NMR shows a new peak at 77.92 ppm, which has been assigned to the C12 of (5). The assignments are supported by HSQC (Heteronuclear Single Quantum Correlation Spectroscopy) and HMBC NMR (given in Appendix). The yield of (4) obtained amounted to 75%.



Scheme 5 – Synthesis of the monomer (5) from Methyl Ricinoleate (3).

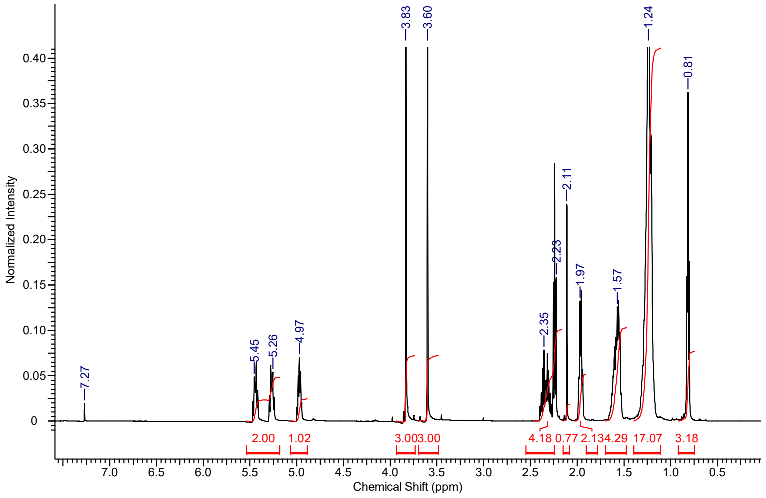


Figure 6 - ^{1}H NMR spectrum of (5)

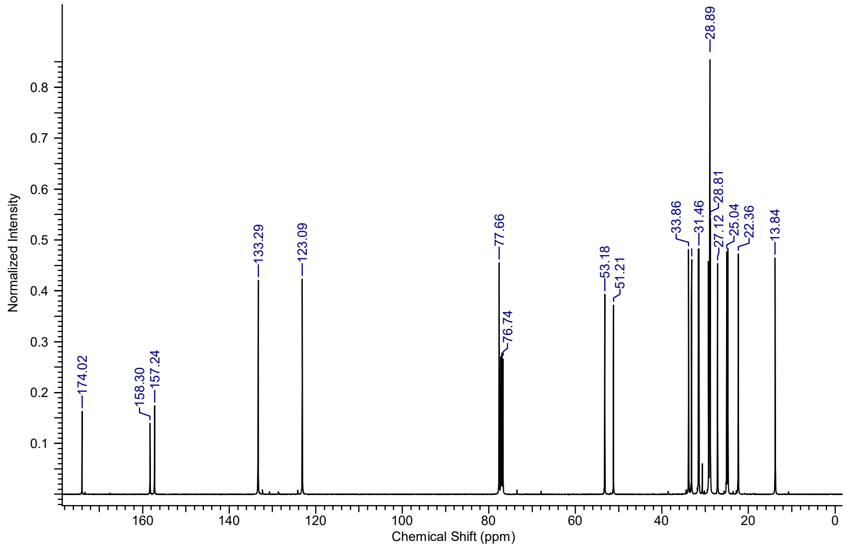


Figure 7 - ^{13}C NMR of (5)

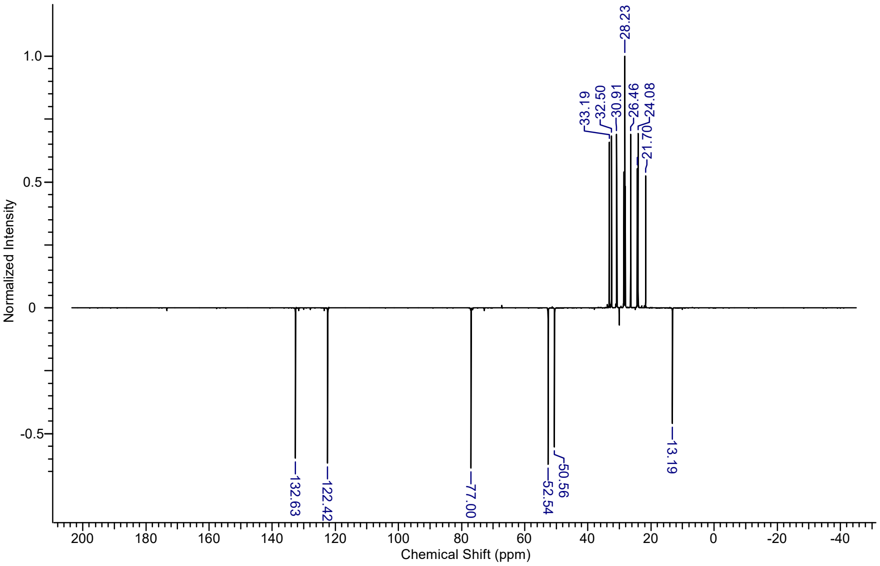
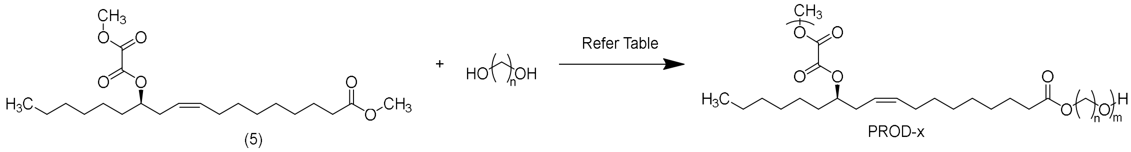


Figure 8 - DEPT-135 spectrum of (5)

Preliminary Polymerizations



Scheme 6 – Polymerisation with various diols.

The dried monomer 3 and two different diols were reacted in a 100 mL Schlenk Round-Bottom Flask, as shown in **Table 2**. The ratio of monomers was taken such that there is a 1:1 correspondence between the hydroxyl groups of the diol and the methyl ester groups of the oxalate monomer, accounting for the trimers present in the monomer sample. The solid material obtained upon polymerization with 1,10-Decanediol was washed with acetone and methanol. It is insoluble in most organic solvents at room temperature and moderately soluble in Toluene and DMSO upon heating at 100^{o}C for 8 hours with stirring. It was characterized by ^{1}H NMR in DMSO-d_6 and solid state ^{13}C NMR, both at 400MHz. The NMR data indicated the formation of the ester with the diol (^{1}H NMR: 4.36 and ^{13}C NMR: 63.67) and the preservation of the double bonds.

Table 3 – Polymerisation of (5) with Diols

No.	Sample Name	Oxalate Monomer amount (mg)	Diol (mg)	$Ti(OiPr)_4$ equivalents with respect to Oxalate monomer	Conditions			Mass of Residue obtained
					Temperature (^{o}C)	Argon/Vacuum	Time	
1	64A	350	1,10-Decanediol (113)	0.01	120	Argon	1 hr	45 mg
					150	Vacuum	2 hrs	
2	72A	90	1,10-Decanediol (40, 0.230)	0.01	100	Vacuum	15 mins	Crude analyzed
3	79A	256	Ethylene Glycol (	0.01	80^{o}C	Vacuum	4 hrs	Crude analyzed
4	74A	140	1,6-Hexanediol (32, 0.271)	0.01	120	Argon	2 hrs	75 mg
					120	Vacuum	3 hrs	

Another reaction was carried out for 15 minutes with 1,10-Decanediol, as shown in entry 2 of Table 1. The $CDCl_3$ soluble portion of this crude was submitted for ^1H NMR to elucidate the chemical reaction(s) happening. A reduction in intensity was seen in both the methyl ester signals (3.88 and 3.65), with a greater reduction in the oxalate ester with respect to the double bond (5.20-5.60), which is not expected to react under the given conditions.

To observe the effect of diol chain length on solubility, 1,6-Hexanediol was used as the diol comonomer. A solid material was obtained, which was insoluble in many organic solvents, just as before. $CDCl_3$ soluble fraction from the crude mixture was submitted for 1H NMR; the reduction in the intensity of the oxalate methyl ester is more than that of the fatty acid methyl ester, indicating that the oxalate methyl ester reacted more rapidly and to a larger extent than the fatty acid methyl ester group. The insoluble fraction has yet to be fully characterized.

Bulk Polymerization Reactions

Upon receiving interesting results in the preliminary reactions, scaled-up reactions were performed. Different catalysts were screened, and initial studies were done using $Ti(OiPr)_4$ (Titanium Isopropoxide) and then in $pTSOH.H_2O$ (para-Toluene Sulfonic Acid). The reactions with $Ti(OiPr)_4$ resulted in the reaction mixture becoming solid after ~6-7 hours under vacuum. The soluble fraction in Chloroform was submitted for ^1H NMR, and the mixture contains mostly oligomers. The insoluble fraction (named PROD-1; PROD standing for Poly-Ricinoleate-Oxalate-co-Diol) was characterized by TGA (Thermogravimetric Analysis) and DSC (Differential Scanning Calorimetry) with a degradation temperature at around and no transitions seen in the DSC, from 25^oC to 200^oC. The reaction was repeated with Benzoquinone[42] in order to prevent possible cross-linking; but with no major changes in the final result.

As Ti(IV) complexes have been previously reported to be used with diols and other methyl esters, a simple experiment was conducted to understand if the monomer (5) is reacting with the Titanium Isopropoxide used. Two reactions were carried out, one with Benzoquinone and the other without. In both cases, an insoluble fraction was obtained, and the $CDCl_3$ soluble fraction revealed the formation of dimers and trimers of ricinoleic acid, with significant loss of the oxalate moiety.

Thus, the catalyst was changed to $pTSOH.H_2O$, which has been proven to perform polycondensations, albeit with lower efficiency.

Both the obtained crude reaction mixture and their precipitates n-Hexane were soluble in chloroform and could be characterized by ^1H NMR. n-Hexane was chosen as the solvent for precipitation in order to maximize the yield of the precipitate. GPC of the THF soluble fractions indicated the formation of low-molecular-weight polymers. The precipitates obtained were highly viscous waxy materials. The n-Hexane soluble fraction shows the presence of unreacted dimers and trimers. As mentioned before, PROD stands for Polyricinoleate-oxalate-co-diol.

Table 4 – Bulk polymerizations under pTSOH catalysis.

Sample Code	**Monomer loading (mg)**	**Diol used, mass (mg)**	**pTSOH equivalents**	**Summary of Conditions**	**Yield of precipitate (mg)**	**M_w (g/mol) (GPC)**	**PDI**
PROD-2	500	1,10-DDO, 220	0.01	7 hours, 100 °C,	290	-	-
PROD-3	500	1,10-DDO, 220	0.01	5 hours at 100 °C, 20 hours at 120°C	270	-	-
PROD-4	500	1,10-DDO, 220	0.01	5 hours at 100 °C, 20 hours at 150°C	500	4000	2.747
PROD-5	500	1,10-DDO, 220	0.01	5 hours at 100 °C, 40 hours at 150 °C	450	7,300	1.498
PROD-6	520	1,10-DDO, 220	0.1	6 hours at 100 °C, 20 hours at 150°	120	7,200	2.682
PROD-7	700	1,12-DDO, 355	0.1	100 °C for 3 hours, 150 °C for 23 hours.	230	-	-

All of the reactions mentioned in table 4 were conducted under a vacuum of 2.5mbar, after stirring under N_2 atmosphere at 100°C for 30 minutes.

In order to help improve yields and molecular weights, Sn $(Oct)_2$ was screened as the catalyst. Sn $(Oct)_2$ was has been previously used for transesterification reactions, and for the synthesis of Polyricinoleic Acid[23], and thus is expected to be a compatible metal catalyst for (5).

A preliminary reaction was carried out with 0.01 equivalents of $Sn(Oct)_2$ (Tin (II) 2-ethylhexanoate). The mixture was stirred under N_2 atmosphere for 2 hours at 100 °C, 1 hour of vacuum at 100 °C, followed by 3 hours at 150 °C under vacuum. The precipitate in n-hexane yielded 110mg of a white semi-solid.

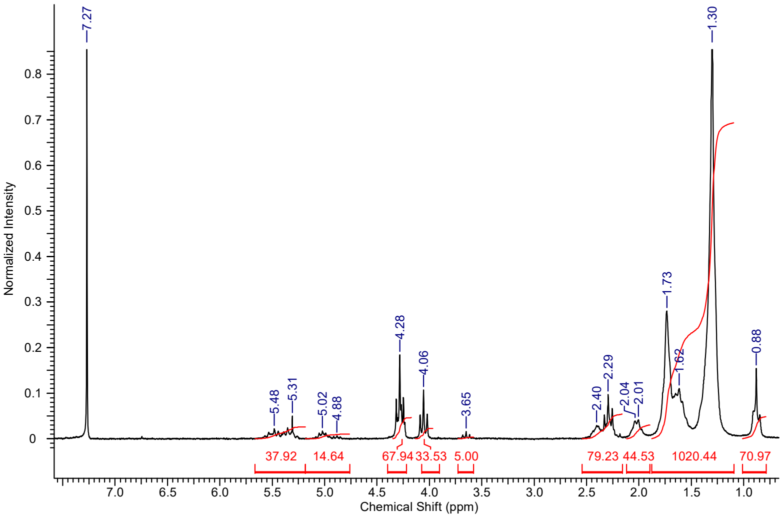


Figure 9 - ^1H NMR spectrum for precipitated PROD-3

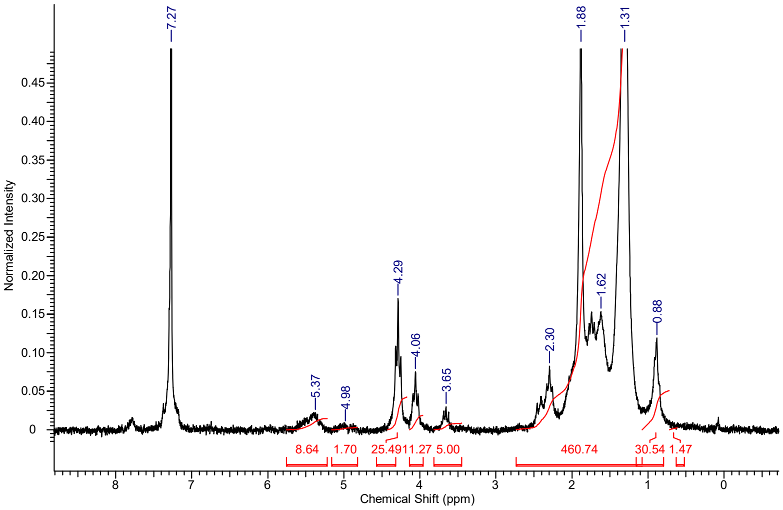


Figure 10 - ^{1}H NMR spectrum for precipitated PROD-6

^{1}H NMR spectra of some of the crude reaction mixtures and the other precipitates are given in the appendix.

Over-night Polymerizations under reduced pressure

In order to better maintain the vacuum overnight, Overnight vacuum experiments were performed in a Round-bottom Schlenk flask. Again, the co-monomers were taken in a 1:1 ratio, and a melt polycondensation was performed. The yields improved with the overnight reduced pressure reactions (2.5mbar) and $Sn(Oct)_2$ catalyst. The polymers obtained were now precipitated in Methanol, with very low amounts of the crude mixture being soluble in Methanol, indicating higher molecular weight formation. The obtained polymers with 1,10-decanediol and with 1,8-octanediol were highly viscous liquids. The molecular weights were determined by both ^{1}H NMR and Chloroform GPC. GPC data is given in the appendix. An important observation is that the reactions with $Sn(Oct)_2$ largely preserved the oxalate ester in the monomer, whereas those with pTSOH caused transesterification of the internal ester.

Table 5 – Polymerization with $Sn(Oct)_2$ catalysis.

Sample Code	Monomer Loading (mg)	Diol Used, mass (mg)	$Sn(Oct)_2$ loading (equivalents)	Yield of the Precipitate (mg)	M_n from ^{1}H NMR (g/mol)
PROD-8	700	1,10-DDO, 310	0.05	Crude analyzed	-
PROD-9	500	1,10-DDO, 220	0.02	110	500
PROD-10	700	1,10- DDO, 314	0.05	400	3200
PROD-11	700	1,10 – DDO, 314	0.05	590	5000
PROD-12	700	1,8-ODO, 257	0.05	675	6700
PROD-13	700	1,10-DDO, 314	0.05	750	7400

PROD-9 is mostly composed of a mixture of diol-oxalates, monomer (5), Methyl ricinoleate, and Fatty acid ester of monomer (5) with the diol, among others, with little polymerization occurring. This is hinted at by the M_n being lower than the expected repeating unit mass.

Summary of Conditions after catalyst addition

1. PROD-8: 100°C for 1 hour under vacuum.
2. PROD-9: 120°C for 2 hours under Argon, then 1 hour under vacuum, followed by 150°C under vacuum.
3. PROD-10: 90°C for 5 hours, followed by 16 hours at 150°C, under vacuum.

4. PROD-11: 90°C for 5 hours, followed by 40 hours at 150°C, under vacuum.
5. PROD-12: 100°C for 5 hours, followed by 40 hours at 150°C, under vacuum.
6. PROD-13: 100°C for 5 hours, followed by 80 hours at 150°C, under vacuum.

^{1}H NMR Data for the precipitates obtained, as well as additional NMR characterization for PROD-13, are given in the appendix.

Table 6- Molecular weights obtained with $Sn(Oct)_2$ catalysis.

PROD	M_n (NMR) (g/mol)	M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	PDI (GPC)
PROD-11	5000	4,600	13,500	3.0
PROD-12	6700	6,600	19,200	2.9
PROD-13	7400	7,800	21,300	2.7

Reactivity of the ester of the monomer

Air stability of the monomer was established by ^{1}H NMR.

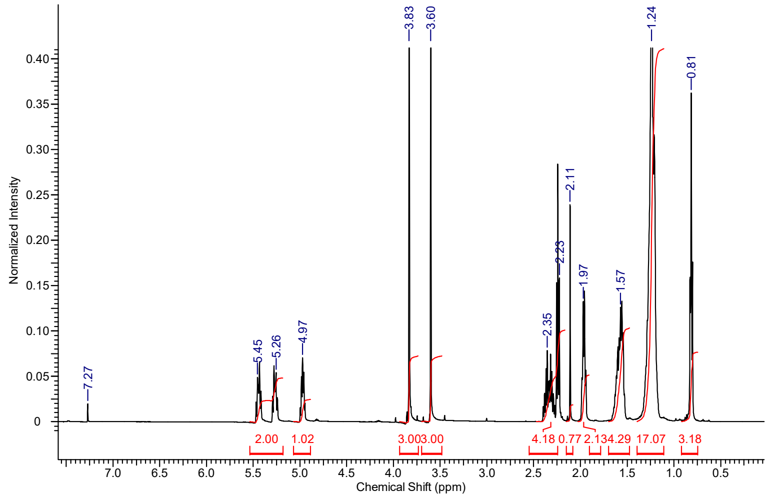


Figure 11 - ^{1}H NMR of (5) after purification.

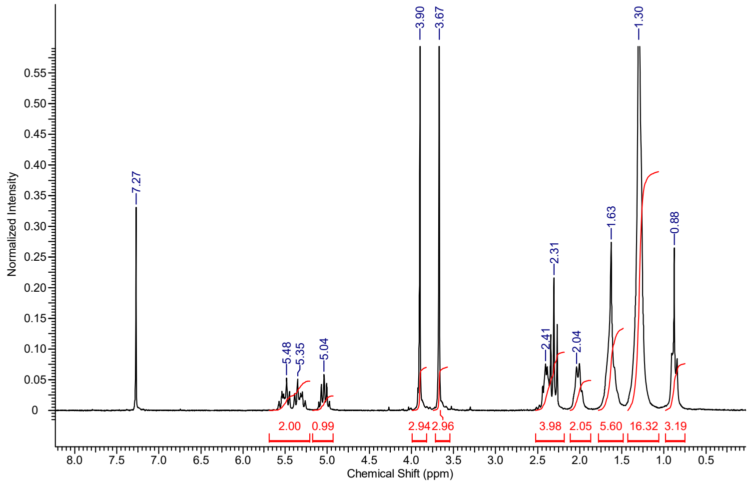


Figure 12 - ^{1}H NMR of (5) after 14 days exposed to air.

The preservation of the relative intensity of the oxalate ester at 5 ppm, as well as the absence of the multiplet at 3.6 ppm, indicate that no hydrolysis has occurred. This air stability could be due to the hydrophobicity of the oil, preventing moisture absorbance.

The reactivity of the internal ester of the monomer during the polymerization reactions is minimal, as indicated by the 1H NMR of the various precipitates obtained after the polymerization at various times (given in the appendix). This is unlike what was observed by *Bhausaheb et al* in their Isohexide oxalates, where the oxalate ester groups attached to the isohexide backbone had initially reacted with the diol, resulting in a copolymer with some blockiness. The same is not true here. The near-equal intensities for the oxalate-diol ester and fatty acid-diol ester groups' protons in the NMR spectra add further evidence for the same. A possible reason for this could be the steric hindrance at the C12-Oxalate site. The observation that the internal ester cleavage is reduced further when using a bulkier Sn(Oct)2 Catalyst adds evidence to this hypothesis.

Thermal Properties of the Polymers

The thermal stability of the polymer was ascertained by Thermo-gravimetric analysis. All samples studied showed a degradation temperature of around 300 °C; which can be assigned to the cleavage of the Oxalate ester of Ricinoleic acid. The isohexide oxalates synthesized by *Bhausaheb et al* start degradation at around 350 °C. The degradation after that point is gradual, until around 475 °C, when mass reaches zero.

TGA Plots for select samples

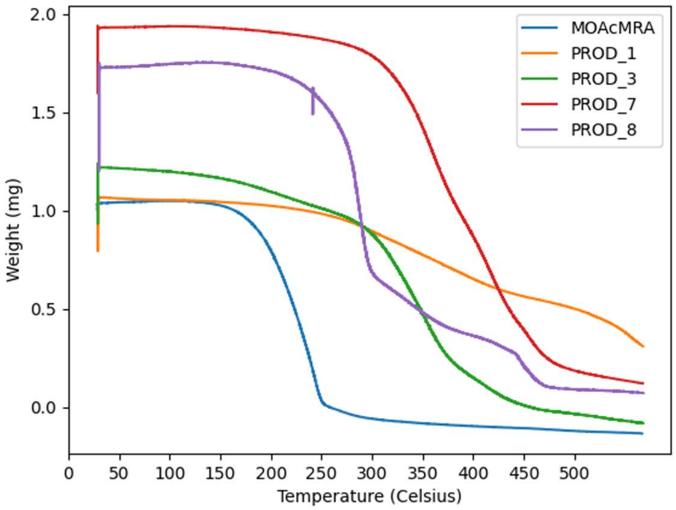
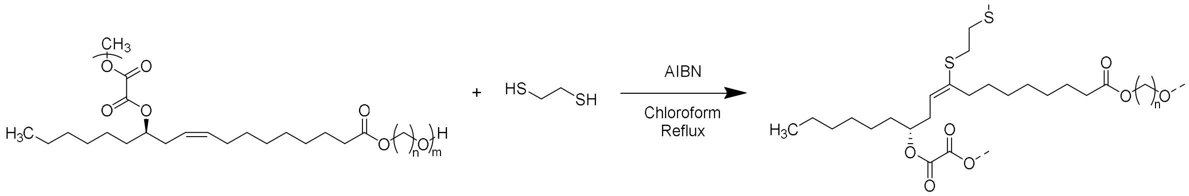


Figure 13 - Cumulated TGA plots. Plotted using Python (matplotlib. pyplot library).

PROD-8, which is a reaction mixture, shows initiation of degradation at around 250 °C, in contrast to what is seen in the TGA of monomer (5), where degradation starts at around 200 °C. This could be because of the methyl oxalate ester of the monomer (5) having undergone complete trans-esterification with the diol.

Thermal Thiol-ene Click Reaction of the prepared Polymers



Scheme 7 – Cross-linking of the polymers using thiol-ene click chemistry.

Following a previously reported procedure for a thiol-ene click reaction on Ricinoleic acid, 200mg of PROD-10 was dissolved in Chloroform along with 0.01 equivalents of AIBN, and an excess of 1,2-Ethanedithiol was then added, all under an Ar atmosphere. The reaction mixture was then heated to reflux temperature and was allowed to react for two different durations (7 hours and 18 hours). After cooling to room temperature, Methylene Chloride was added, and the mixture had almost completely dissolved in the solvent, indicating the failure of complete cross-linking. However, the recovered material after precipitation in Methanol revealed an increase in thickness, suggesting that the reaction had occurred to a minor yet significant extent. This conclusion was further supported by ^{1}H NMR spectroscopy. The appearance of a new peak at 2.81 and the reduction in relative intensity of the double bond indicates the successful thiol-ene click reaction. There is still some unreacted dithiol (2.71), the removal of which was performed via centrifugation using Methanol to dissolve the dithiol.

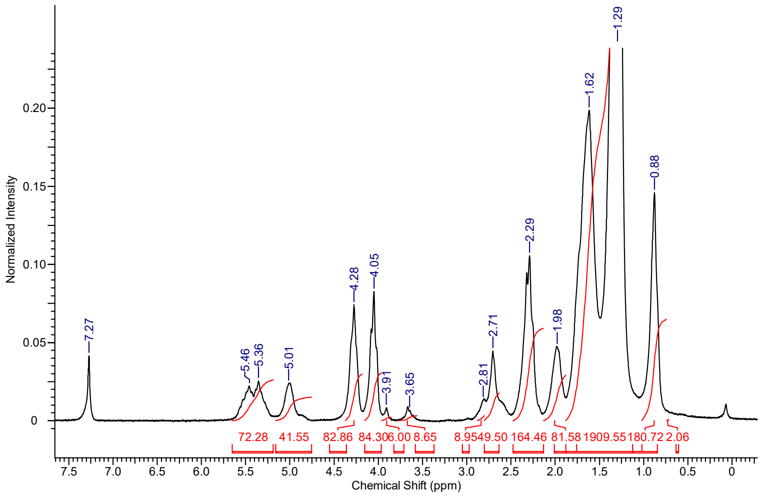


Figure 14 – ^{1}H NMR spectrum after 7 hours of reaction.

The reaction, which was kept for a longer duration, showed a reduction in the oxalate ester peak, possibly due to a nucleophilic attack by dithiol in the $CDCl_3$ soluble fraction. Of the 200 mg used, 65 mg of an insoluble fraction (PRODET-1) was recovered, which underwent swelling in Methylene Chloride.

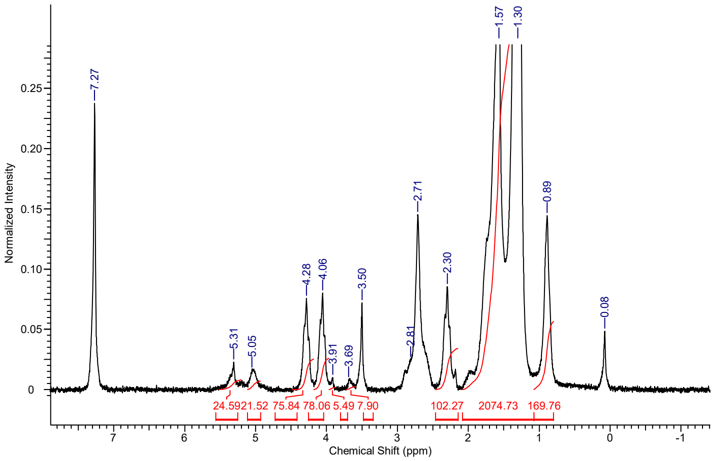


Figure 15 - ^1H NMR spectrum of the $CDCl_3$ soluble fraction after reaction for 18 hours.

Procedures followed for handling and disposal of 1,2-Ethylene dithiol are given in the Appendix.

Figure 16, 17, 18 (Left to right) – Swelling of the obtained PRODET-1 in Methylene Chloride after suspension for 5 minutes. Left – Dry sample, Middle – In 1.5 mL Methylene Chloride, Right – Swollen material.

Degradation Studies

The degradability of a polymer ensures its potential for safe disposal. The synthesized polyoxalates are expected to degrade under acidic conditions, as both the oxalate group as well as fatty acid methyl esters are degradable under acidic conditions. In order to test for degradation, 15 mg of PROD-5 was suspended in ~10% HCl using a glass rod; being a highly viscous liquid and insoluble in water, the sample remained attached to the glass rod. ^{1}H NMR of a small portion of the suspended sample was used to check for degradation after 40 hours of exposure. Due to hydrophobicity, degradation is expected to be slow in these conditions.

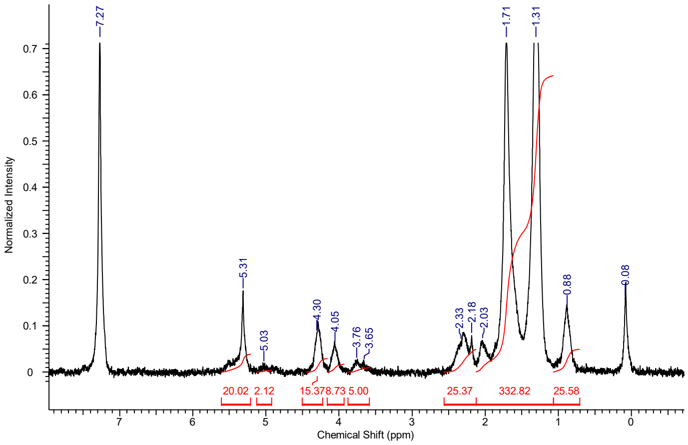


Figure 19 - ^{1}H NMR spectrum of the PROD-5 exposed to acidic conditions.

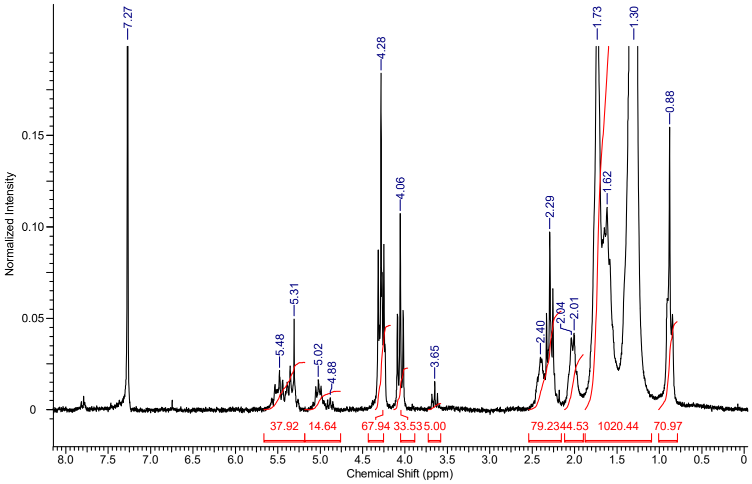


Figure 20 - ^{1}H NMR spectrum of synthesized PROD-5.

The significant reduction in the peak at 4.8-5.02, 4.28, 4.08 and the increase in the intensity of the peaks at 3.60-3.66 indicate the hydrolysis of the ester groups into the corresponding carboxylic acids/alcohols. The viscosity of the sample exposed to the acid also seemed to decrease, and the dissolution in solvents such as Dichloromethane and Chloroform was faster. All these indicate an overall reduction in molecular weight over 40 hours.

Conclusions

Synthesis of polyoxalates based on Ricinoleic acid and potentially biorenewable diols has been successfully carried out. Their structure, molecular weight, and thermal properties were studied, and their degradation in an acidic medium was demonstrated. Curing reactions have been screened, and the thiol-ene click reaction seems promising.

Future plans

Characterization of the cross-linked PRODET is under progress via IR and TGA. Synthesized polymers can be screened for application as lubricants or coatings by viscosity measurements. The synthesis of Cross-linked polyesters can be directly attempted via condensation with polyols.

DSC measurements are currently under optimization.

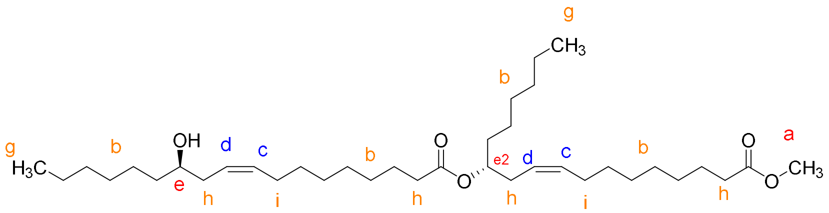
Experimental Section

Materials and Methods

Ricinoleic acid was purchased from BLD Pharma. Methyl Chloroxoacete, Methanol, Tin(II) 2-ethylhexanoate and Titanium Isopropoxide were purchased from Sigma Aldrich. 1,10-Decanediol and 1,8-Octanediol were purchased from Loba Chemie. NMR measurements were done on Bruker Ascend Series Spectrometers. Gel Permeation Chromatography was done on Viscotek Waters Gel-Permeation Chromatography systems (THF and GPC) with triple detectors (RI, DLS and UV-Vis Absorbance) with a flow rate of 1 mL/minute calibrated using Polystyrene standards.

Attempt to synthesize (1)

Ricinoleic acid, Dimethyl oxalate and para-Toluene sulfonic acid were added to a Schlenk RB under an inert atmosphere. The mixture was heated with stirring to 100 °C with intermittent vacuum, followed by refilling with N_2 for 6 hours and at 150 °C for 3 hours. The reaction mixture was subsequently cooled under inert gas flow and purified by column chromatography. (5% Ethyl Acetate in Pet Ether). The major product was a dimer of methyl ricinoleate.



^{1}H NMR ($CDCl_3$, 200MHz): δ = 0.84 (t, g), 1.26, 1.58-1.61 (br, b), 1.9-2.2 (m, i), 2.2-2.5 (m,h), 3.63 (s, b), 3.61 (m, e) 5.20-5.60 (m, f). 4.88 (t, e_2).

Synthesis of Methyl Ricinoleate (3)

Fischer Esterification

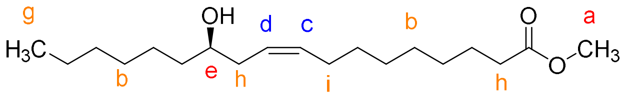
Ricinoleic Acid was dissolved in 70 equivalents of MeOH (AR grade) and refluxed in the presence of pTSOH or kept at room temperature, as shown in **Scheme 1**. The reaction was scaled up to 5 grams of Ricinoleic Acid. Characterization was done via ^1H, ^{13}C and DEPT NMR Spectroscopy. Purification was carried out by Column Chromatography (5-10% Ethyl Acetate: Pet Ether).

Lewis Acid catalysis

Ricinoleic acid dried under vacuum for 30 minutes was dissolved in x equivalents of Methanol in a Schlenk RB charged with a magnetic bead for stirring, followed by the addition of $BF_3.OEt_2$. The reaction mixture was then refluxed for 16 hours, followed by cooling to room temperature, work-up with brine solution, extraction of the aqueous phase with ethyl acetate, drying of the combined organic phase over anhydrous Na_2SO_4 and purification by column chromatography (5-15% Ethyl Acetate : PET Ether).

Via Methyl Iodide

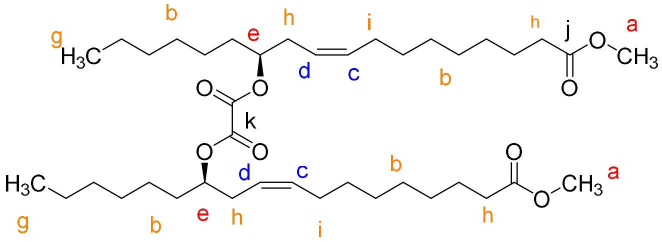
Ricinoleic acid and K_2CO_3 were dissolved in acetone in a Round-bottom flask equipped with a magnetic bead, and Methyl Iodide was added dropwise into the reaction mixture. After the addition, the mixture was refluxed for 3 hours. After completion of the reaction, excess acetone was evaporated under reduced pressure, and the mixture was washed with water, followed by extraction of the aqueous phase in Ethyl Acetate, drying the combined organic layer over anhydrous Na_2SO_4 and purification by column chromatography.



^{1}H NMR (CDCl$_3$, 200MHz): δ = 0.84 (t, g), 1.26, 1.58-1.61 (br, b), 1.9-2.2 (m, i), 2.2-2.5 (m,h), 3.63 (s, a), 3.61 (m, e) 5.20-5.60 (m, d+c).

Synthesis of (4)

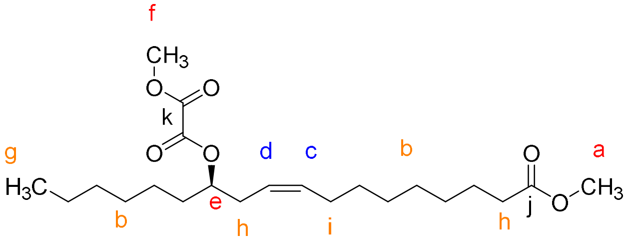
Oxalic acid was dispersed in Toluene using acetone, followed by the addition of Methyl Ricinoleate and the Dehydrating agent. The mixture was refluxed at 110°C, and after completion, excess Toluene was evaporated under reduced pressure, followed by purification by Column Chromatography (2% Ethyl Acetate in PET Ether). The obtained (3) was characterized by 1D and 2D NMR methods.



^{1}H NMR (CDCl$_3$, 400MHz): δ = 0.84 (t, g), 1.26, 1.58-1.61 (br, b), 1.9-2.2 (m, g), 2.2-2.5 (m, i), 3.63 (s, a), 5.00 (m, e), 5.20-5.60 (m, d+c).
^{13}C NMR (CDCl$_3$, 100MHz): δ = 14.0 (g), 22.5, 25.2, 27.3, 31.6, 33.3, 34.0 (b), 51.4 (a), 53.4 (f), 77.9 (e), 122.2, 132.3 (d+c) 157.0 (k), 173.3 (j).

Synthesis of 18-methoxy-18-oxooctadec-9-en-7-yl methyl oxalate (5)

Dried Methyl Ricinoleate was stirred in Pyridine (1.3 equivalents) for 10 minutes, followed by the addition of Methyl Chlorooxoacetate (1.3 equivalents) under Ar flow, as shown in **Scheme 2**. The mixture was stirred overnight under Argon. The mixture was then purified by washing with water, followed by filtration using a short silica-bed column, characterised by ^{1}H, ^{13}C, DEPT, HMBC (Heteronuclear Multiple Bond Correlation Spectroscopy) and COSY (Correlation Spectroscopy).



^{1}H NMR (CDCl$_3$, 400MHz): δ = 0.84 (t, **g**), 1.26, 1.58-1.61 (br, **b**), 1.9-2.2 (m,**h**), 2.2-2.5 (m, **i**), 3.63 (s, **a**), 3.86 (s, **f**), 5.00 (m, **e**), 5.20-5.60 (m, **d+c**).
^{13}C NMR (CDCl$_3$, 100MHz): δ = 14.0 (**g**), 22.5, 25.2, 27.3, 31.6, 33.3, 34.0 (**b**), 51.4 (**a**), 53.4 (**f**), 77.9 (**e**), 123.2, 124.3, 157.4, 132.4, 133.4 (**d+c**), 158.4, 157.4 (**k**), 173.3, 174.2 (**j**).

Polymerization Reactions

Preliminary reactions

The monomer (5) and the corresponding diol were dried under a high vacuum in a 100 mL round bottom flask, after which the round-bottom flask was filled with Ar, followed by the addition of 0.01 equivalents of Titanium (IV) Isopropoxide under positive Argon flow. The mixture was then heated and evacuated with a vacuum, according to Table 1.

The reaction mixture was transferred to a Whatman filter paper on a funnel and washed with acetone and methanol. The solid residue was further studied.

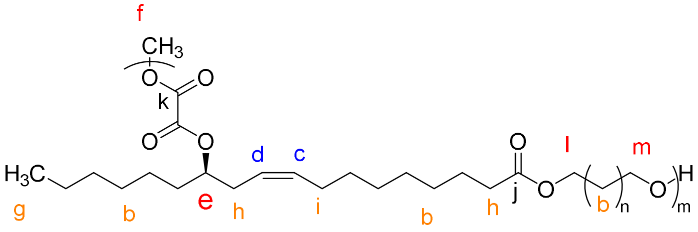
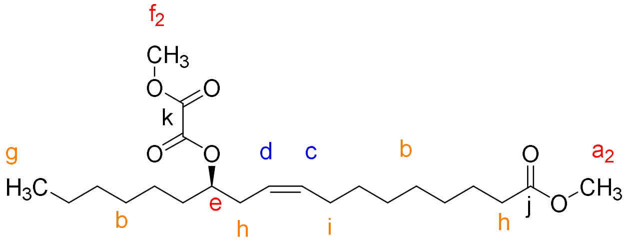


Table 1, Entry 1, Solid Residue: ^{1}H NMR, DMSO Soluble fraction (DMSO-d$_6$, 400MHz): δ = 0.85 (t, **g**), 1.2-1.6 (br, m, **b**), 1.90-2.30 (br, m, **h+i**), 3.98 (t, **f**), 4.30-4.45 (br, m, **l+m**), 5.25-5.45 (br, m, **d+c**).

Table 1, Entry 1, Solid Residue: ^{13}C NMR, CP-MAS (54.72°), 100MHz: δ = 15-16 (**g**), 20-50 (**h**), 60-70 (**h+i+h**), 127-136 (**d+c**), 165-175 (**j+k**).

Table 1, Entry 2: ^{1}H NMR, CDCl$_3$ soluble fraction of crude (CDCl$_3$), 400MHz: δ = 0.84 (t, **g**), 1.20-1.61 (br, **b**), 1.9-2.2 (m, **i**), 2.2-2.5 (m, **h**), 3.65 (s, **a$_2$**, unreacted fatty acid methyl ester), 3.88 (s, **f$_2$**, unreacted Oxalate ester), 4-4.1 (t, **d**) 4.85 (m,**e$_2$,** Ricinoleic acid homopolymer), 5.00 (m, **e**), 5.20-5.60 (m, **d+c**).



Control Reaction of Monomer with Ti(OiPr)4

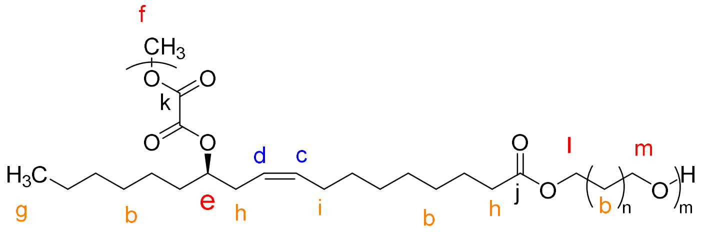
To 100mg of the dried monomer in a Schlenk RB, a drop of Ti(OiPr)4 was added, followed by heating it to 120oC and stirring it under a vacuum. After 3 hours, the heating was stopped, the RB was filled with N$_2$ and cooled to room temperature. Following this, the CDCl$_3$ soluble fraction was submitted for ^{1}H NMR. (Spectrum attached in the appendix).

Bulk Reactions with pTSOH catalysis

Diol and pTSOH (refer to table 4 for stoichiometry) were taken in a Schlenk Tube with an Over-head stirrer and air-tight septum or a Schlenk RB sealed with a glass stopper and dried under vacuum for 1 hour. Following this, the monomer (5) (1 equivalent) was added under positive N$_2$ flow. The mixture was melted in an oil bath, and the reaction was performed as mentioned in Table 4.

Reaction with $Sn(Oct)_2$ catalysis

1:1 equivalent of monomer: diol was dried via high-vacuum in a Schlenk Tube or Schlenk RB, with the same set-up as mentioned above. The mixture was subsequently heated to the starting temperature (mentioned in the table), and $Sn(Oct)_2$ was added under positive N_2 flow. Further reaction conditions are mentioned in Table 5.



^{1}H NMR ($CDCl_3$, 200MHz): δ = 0.85 (t, **g**), 1.2-1.6 (br, m, **b**), 1.90-2.30 (br, m, **h+i**), 3.98 (t, **f**), 4.30-4.45 (br, m, **l+m**), 5.25-5.45 (br, m, **d+c**).

^{13}C NMR ($CDCl_3$, 100MHz): δ = 14.04 (**g**), 22.5-33.4 (**b**), 64.4 (**l**), 67.1 (**m**), 123.3, 133.4 (**d+c**), 158 (**k**), 188.7 (**j**)

Determination of M_n by ^{1}H NMR Spectroscopy

The total number of repeating units was obtained by using the lowest intensity end group protons as a reference; in most cases, it is the oxalate methyl esters at around 3.9 ppm. Then, the number of repeating units (n) is calculated by the formula below;

$$n = \frac{(\sum x)}{(k - y)}$$

Where x is the total intensity of backbone protons of a particular signal, y is the intensity of end group protons, and k is the total number of protons in the repeating unit. M_n is calculated by;

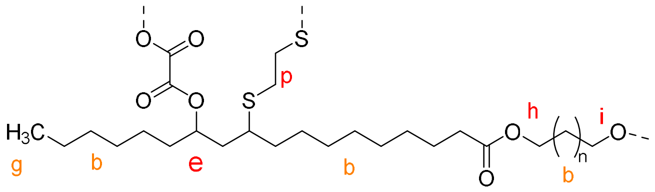
$$M_n = n * M_{rep}$$

Where M_{rep} is the mass of the repeating unit.

Thiol-ene Click Reaction

A modified literature procedure was employed for the reaction[41]. In a Schlenk RB attached to a reflux condenser, 200mg of the polymer was dried under a high vacuum for 30 minutes, followed by the addition of $CHCl_3$ and AIBN under an inert atmosphere. After stirring for another 15 minutes, 1,2-Ethanedithiol was dropped into the reaction flask under positive Ar flow, and the mixture was heated to reflux for a pre-determined time, after which the reaction mixture was dissolved in DCM and precipitated in MeOH. The MeOH fraction is then quenched in a dilute NaOCl solution to quench the dithiol.

Protocol followed for handling and disposal of 1,2-Ethylene dithiol are detailed in the Appendix.



^{1}H NMR ($CDCl_3$, 200MHz): δ = 0.85 (t, **g**), 1.2-1.6 (br, m, **b**), 1.90-2.30 (br, m, **h+i**) 2.81 (s, **p**), 3.98 (t, **f**), 4.30-4.45 (br, m, **l+m**), 5.25-5.45 (br, m, **d+c**, unreacted alkene).

Degradation Studies

Degradation under acidic conditions was performed. A weighed sample of PROD, which is a viscous liquid, was taken using a glass rod and suspended in a 10% HCl solution. Small portions of the PROD adhering to the glass rod were taken at specific time intervals, dried under a high vacuum and analyzed by ^{1}H NMR spectroscopy in $CDCl_3$.

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Appendix

NMR Spectral data for (5)

2-D NMR

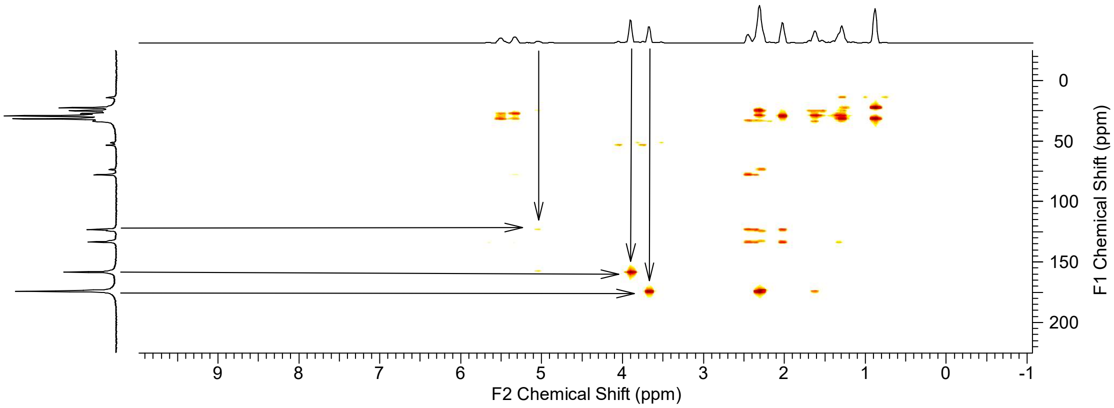


Figure A1- HMBC spectrum of (5)

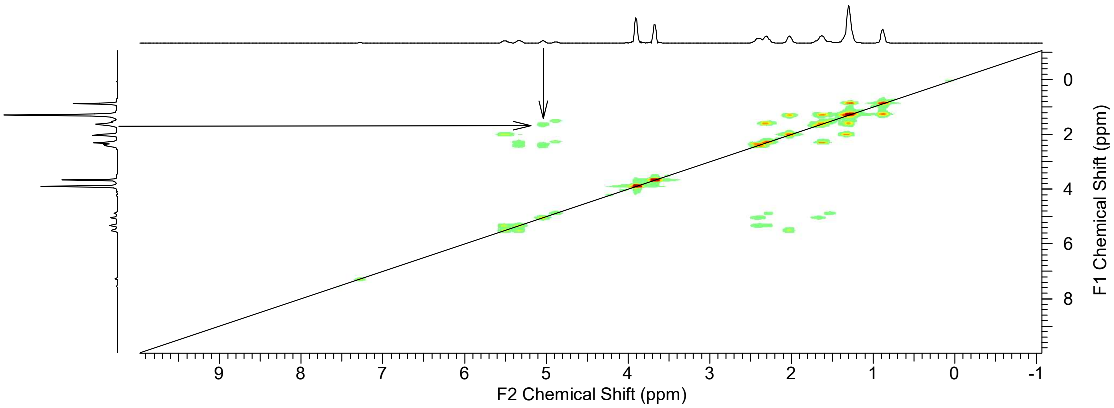


Figure A2 – COSY spectrum of (5)

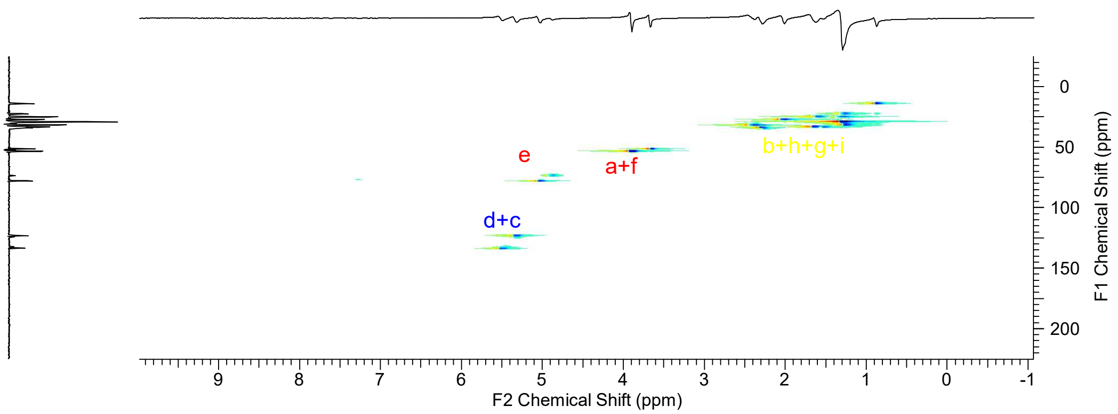


Figure A3 – HSQC spectrum of (5)

^{1}H NMR Data for polymerizations with pTSOH catalysis

Crude NMR data

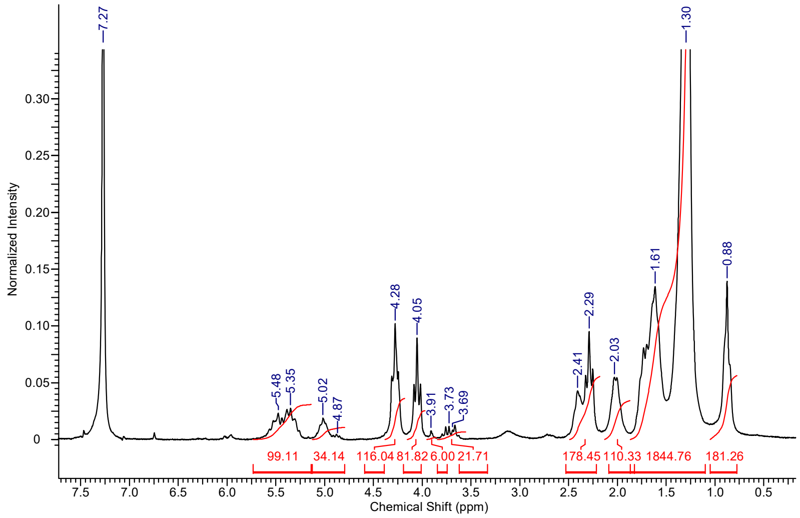
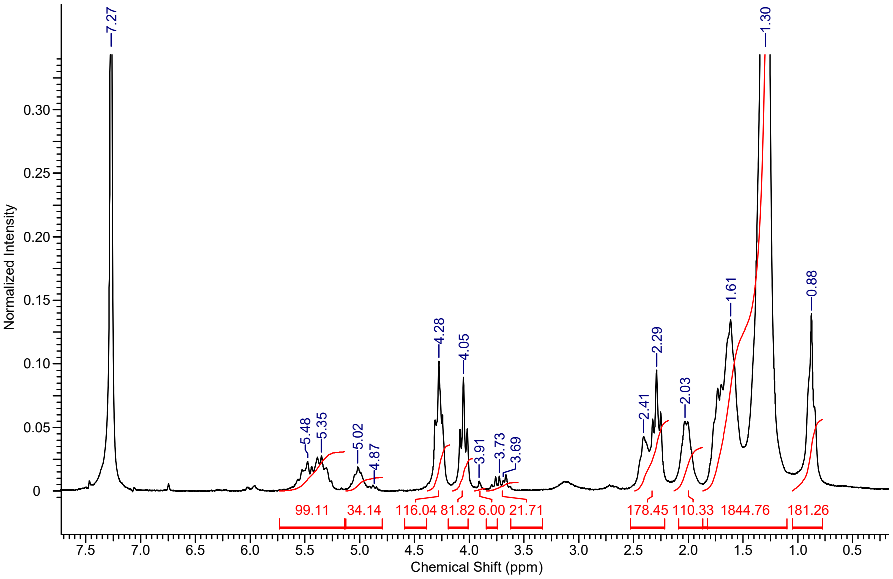
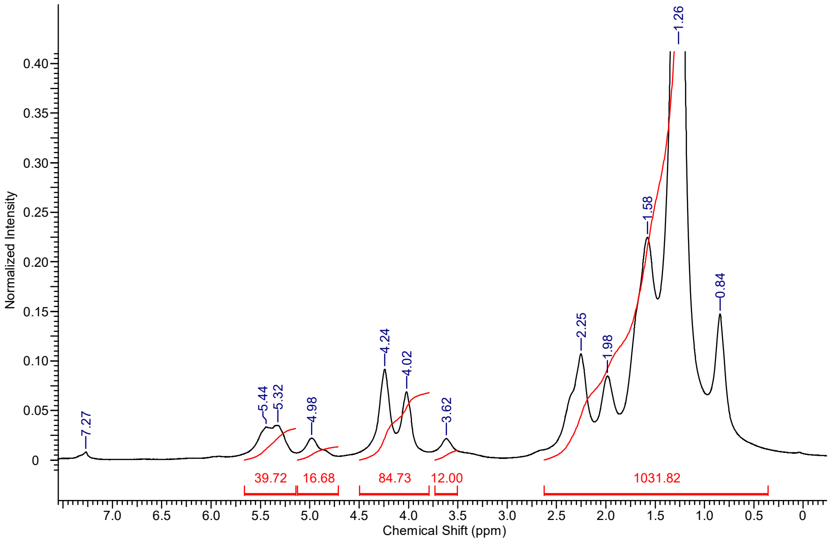


Figure A4 – ^{1}H NMR spectrum of PROD-3



<u>Figure A5</u> - ^{1}H NMR spectrum of PROD-4



<u>Figure A6</u> – ^{1}H NMR spectrum of PROD-5

NMR data of the precipitates

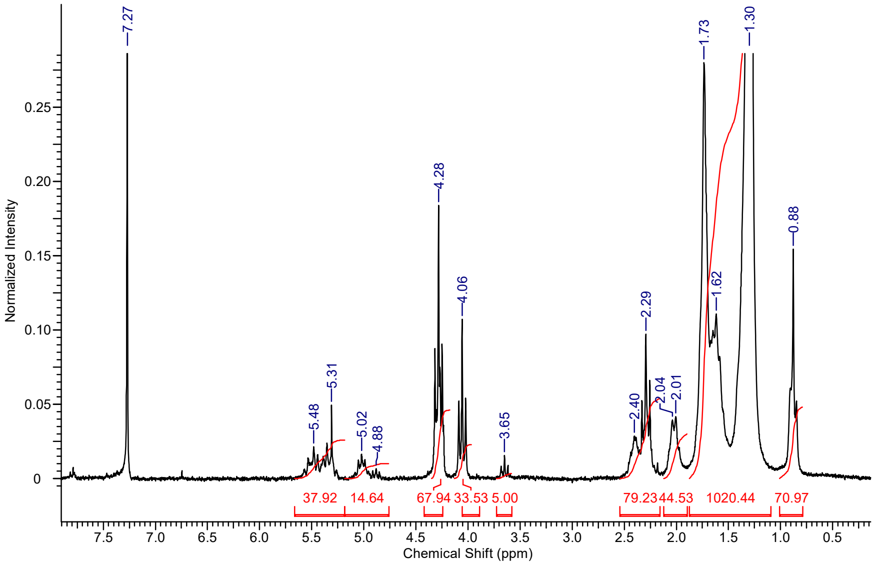


Figure A7 – ^{1}H NMR spectrum of PROD-4

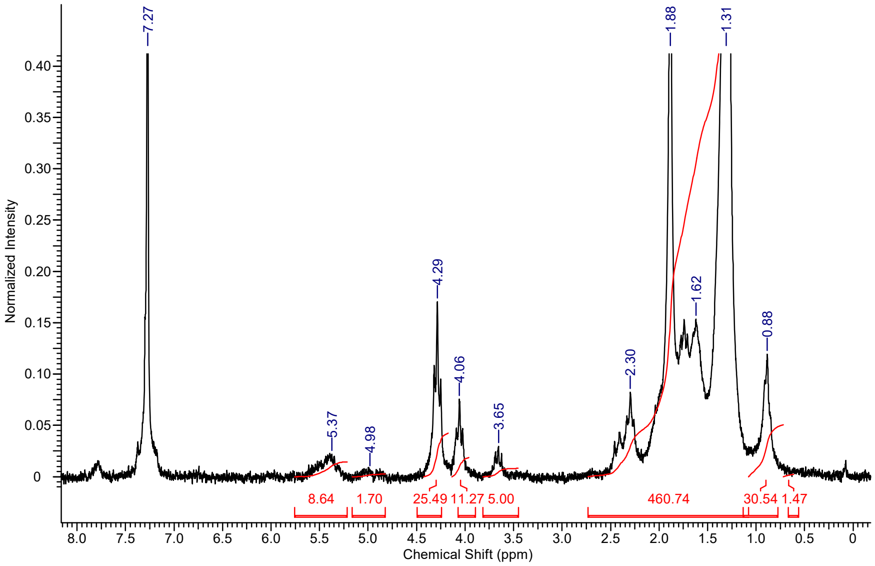
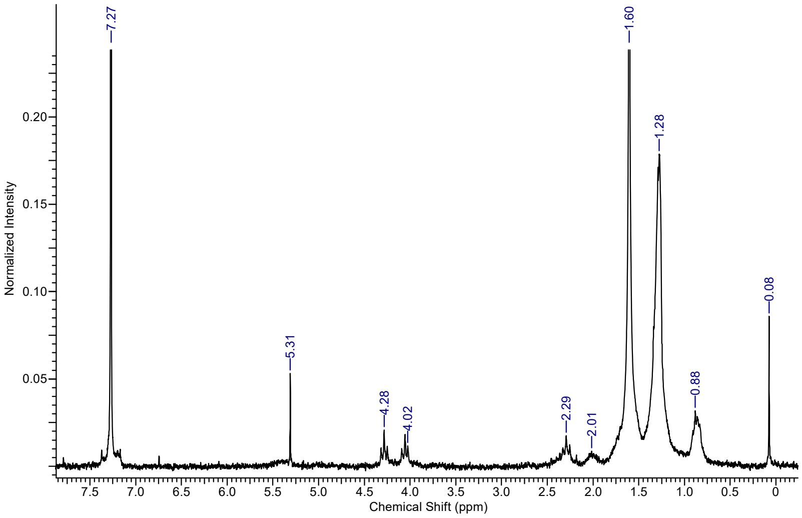
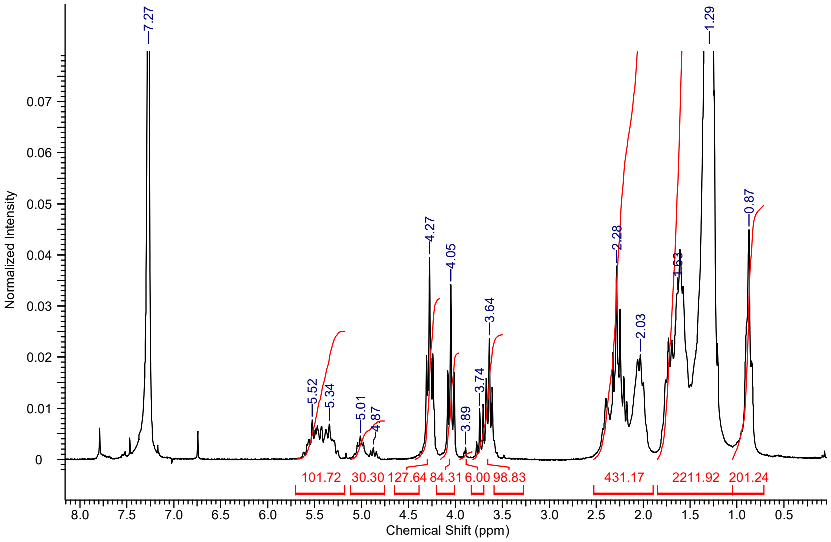


Figure A8 – ^{1}H NMR spectrum of PROD-6



<u>Figure A9</u> – ^{1}H NMR spectrum of PROD-7



<u>Figure A10</u> – ^{1}H NMR spectrum of PROD-2

^{1}H NMR Data for polymerizations under $Sn(Oct)_2$ catalysis

NMR Data of PROD-13

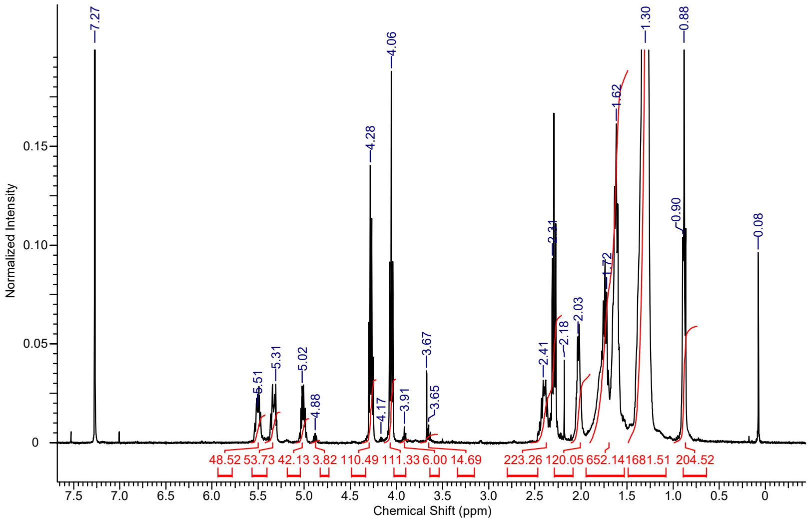


Figure A11 - ^{1}H NMR spectrum of PROD-13

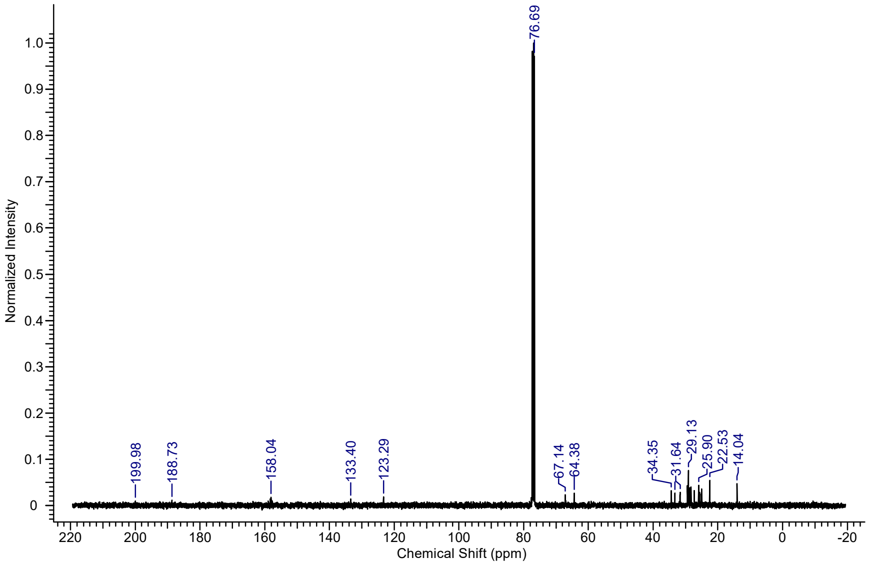


Figure A12 - ^{13}C NMR spectrum of PROD-13

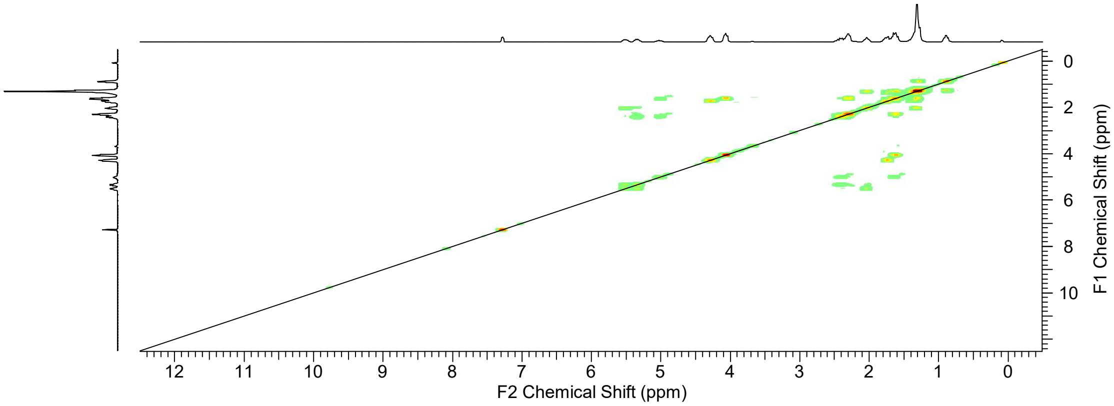


Figure A13 – COSY spectrum of PROD-13

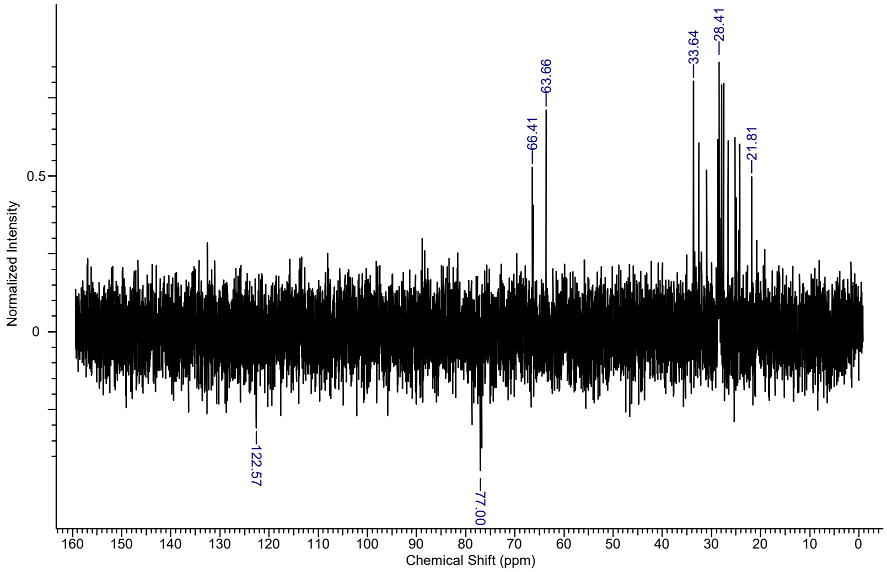


Figure A14 - DEPT-135 spectrum of PROD-13

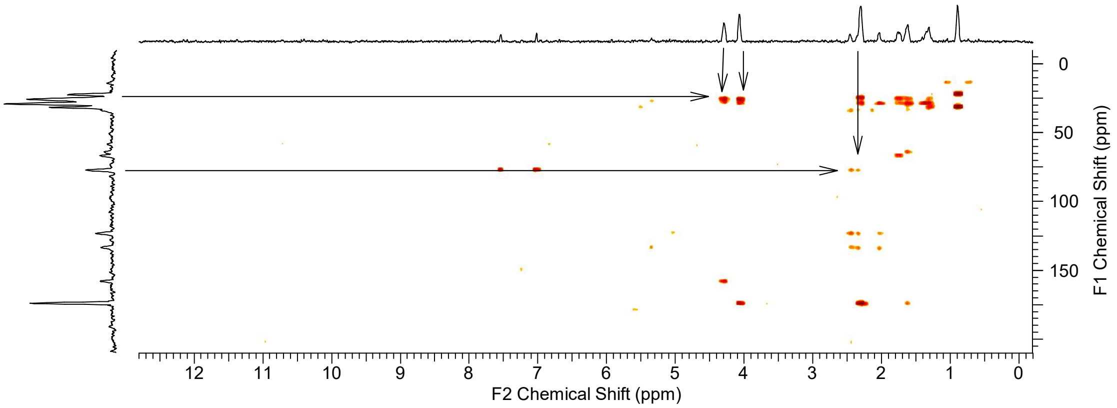


Figure A15 – HMBC spectrum of PROD-13

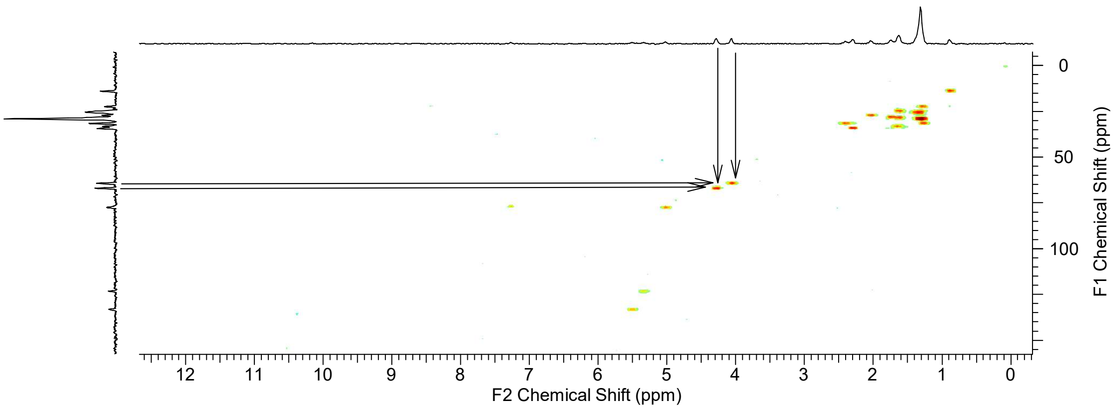


Figure A16 – HSQC Spectrum of PROD-13

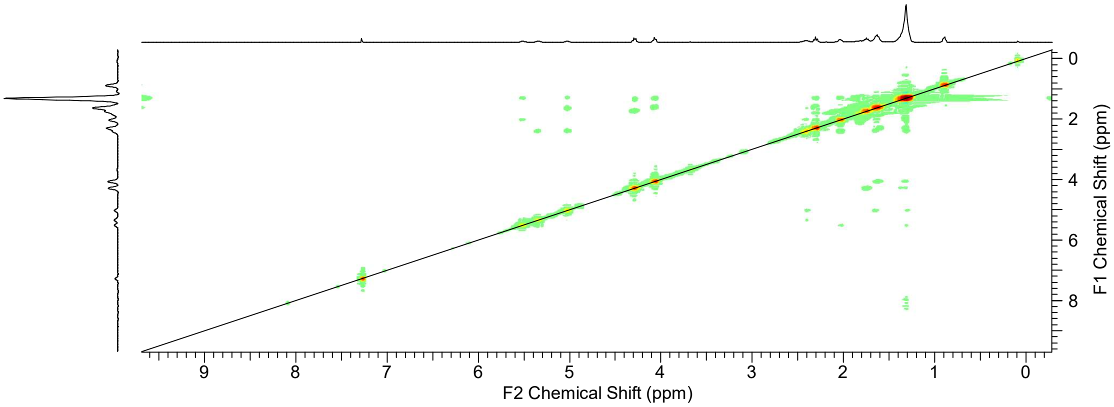


Figure A17 – NOESY (Nuclear Overhauser Effect Spectroscopy) Spectrum of PROD-13

^{1}H NMR Data of precipitated polymers

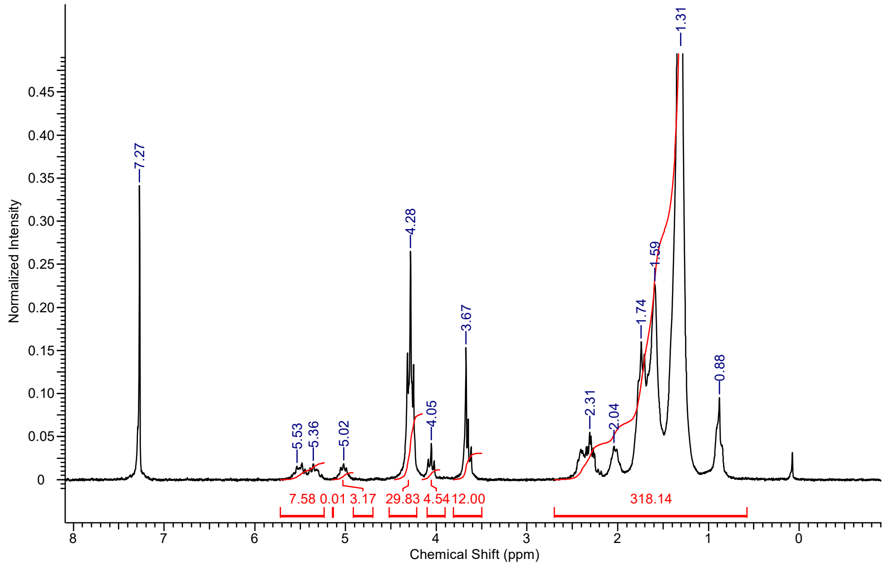


Figure A18 – ^{1}H NMR spectrum of PROD-9

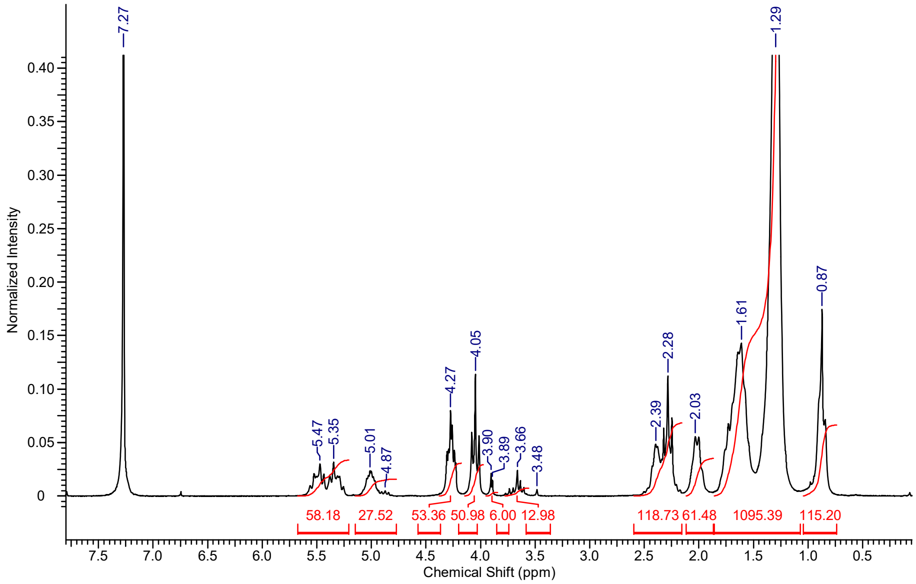
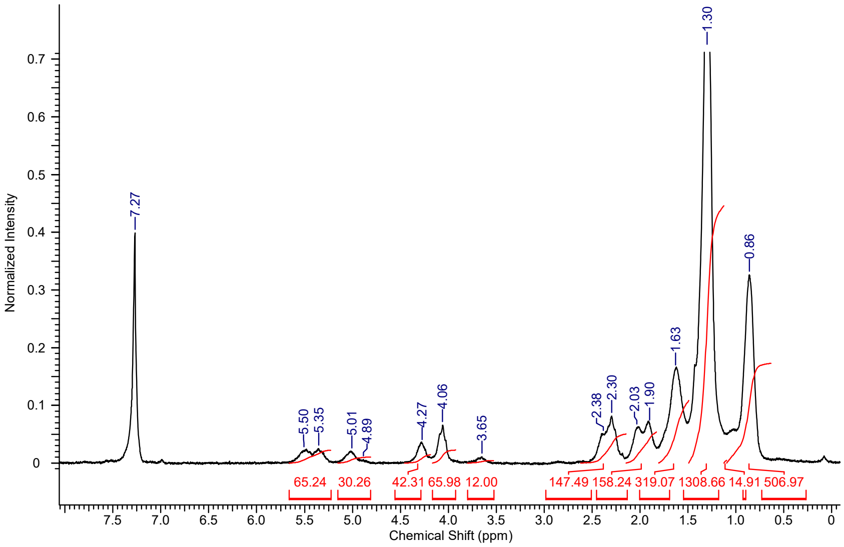
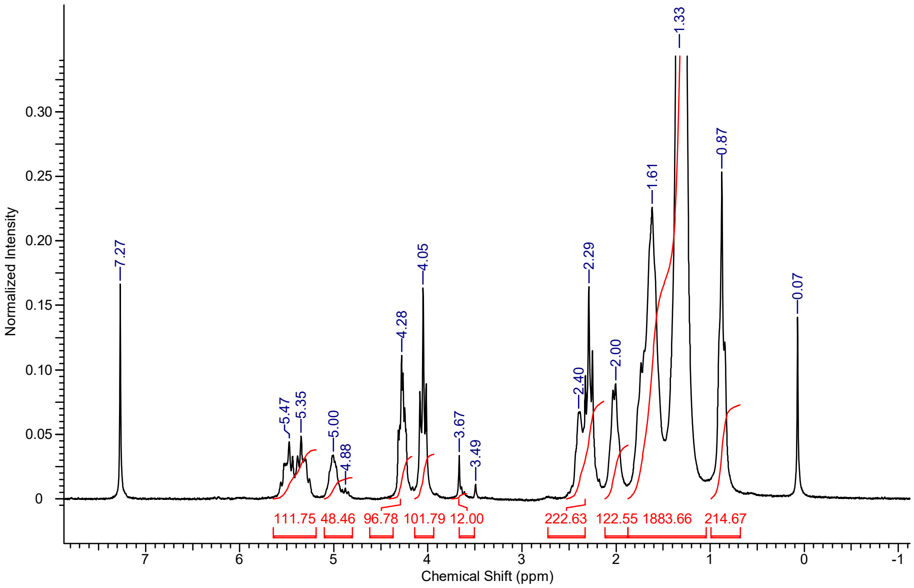


Figure A19 – ^{1}H NMR spectrum of PROD-10



<u>Figure A20</u> – ^{1}H NMR spectrum of PROD-11



<u>Figure A21</u> – ^{1}H NMR spectrum of PROD-12

^{1}H NMR data for control reaction of monomer (5) with Ti(OiPr)$_4$

Both crude NMRs show that the oxalate ester of the monomer (5) has degraded significantly, followed by self-esterification of Ricinoleic acid to yield a mixture of dimers and trimers.

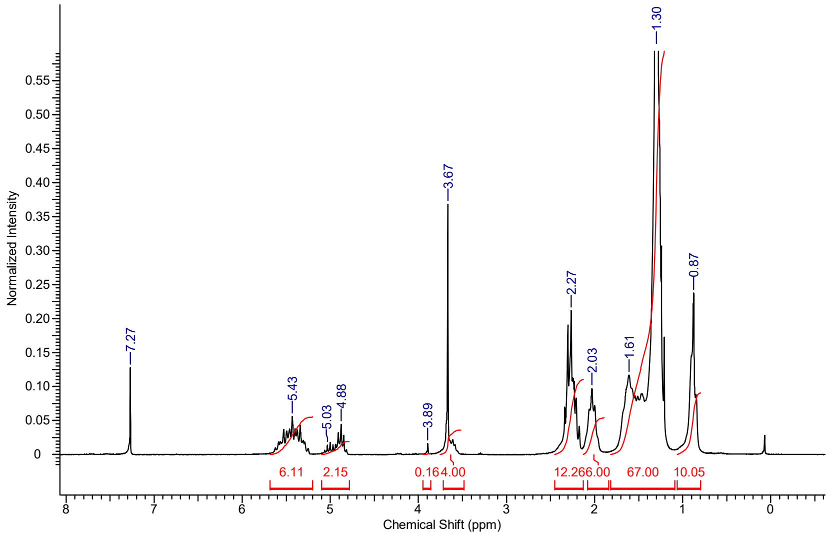


Figure A22 - ^{1}H NMR spectrum of the CDCl$_3$ soluble fraction of the crude.

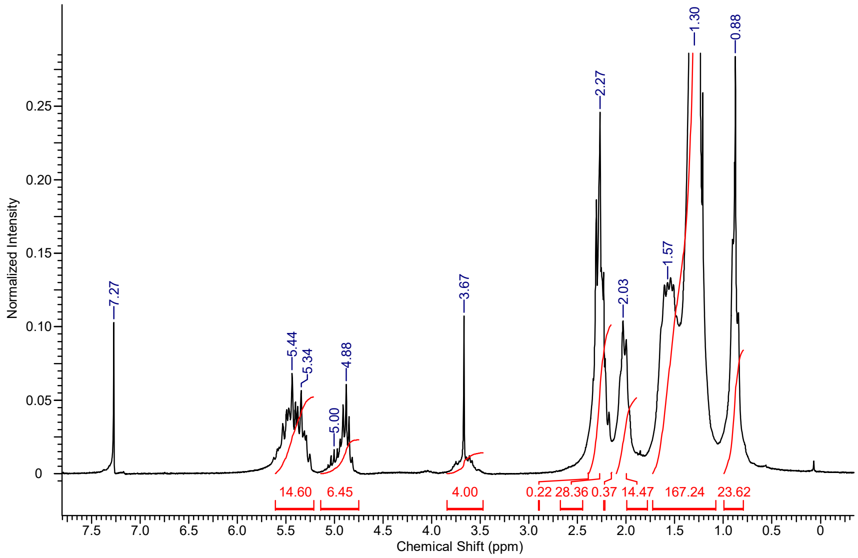
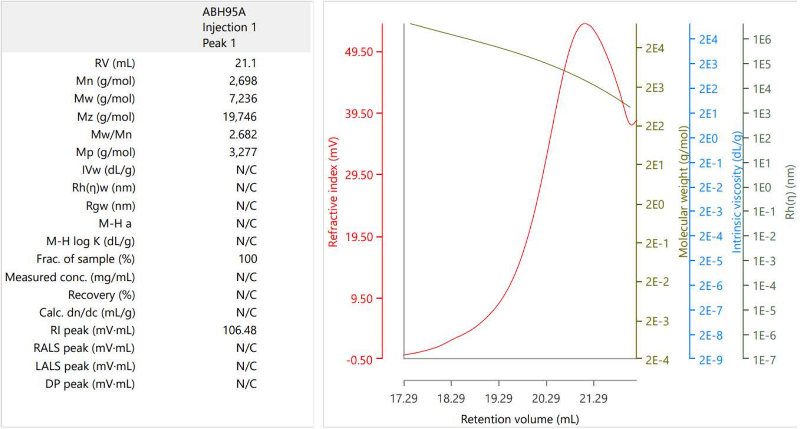


Figure A23 - ^{1}H NMR spectrum of the crude reaction mixture, after reaction in the presence of benzoquinone

Gel Permeation Chromatography Data

THF



	ABH95A Injection 1 Peak 1
RV (mL)	21.1
Mn (g/mol)	2,698
Mw (g/mol)	7,236
Mz (g/mol)	19,746
Mw/Mn	2.682
Mp (g/mol)	3,277
IVw (dL/g)	N/C
Rh(η)w (nm)	N/C
Rgw (nm)	N/C
M-H a	N/C
M-H log K (dL/g)	N/C
Frac. of sample (%)	100
Measured conc. (mg/mL)	N/C
Recovery (%)	N/C
Calc. dn/dc (mL/g)	N/C
RI peak (mV·mL)	106.48
RALS peak (mV·mL)	N/C
LALS peak (mV·mL)	N/C
DP peak (mV·mL)	N/C

Figure A24 – THF GPC plot of PROD-6

Chloroform

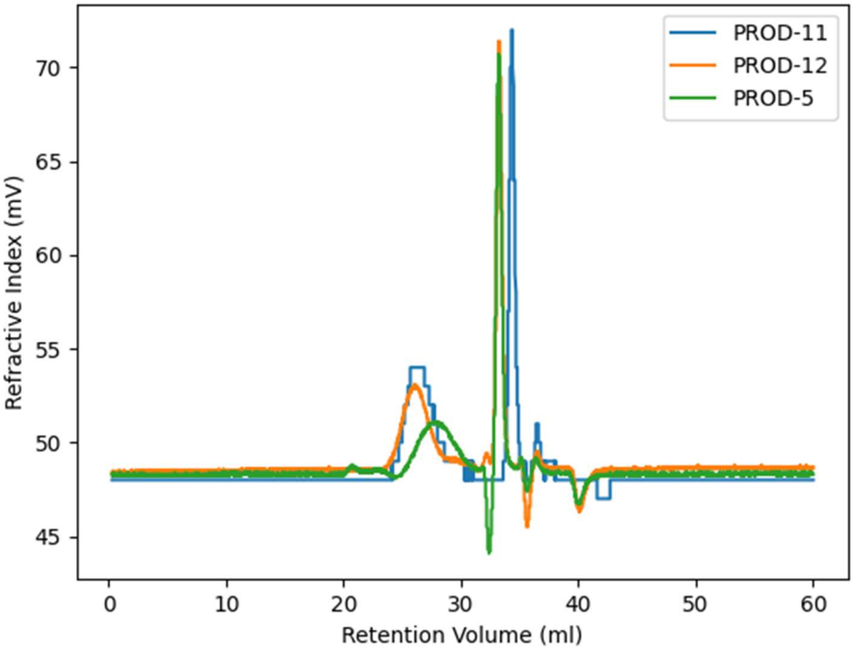


Figure A25 – Cumulated plot of GPCs in chloroform. (Plotted by Matplotlib.pyplot)

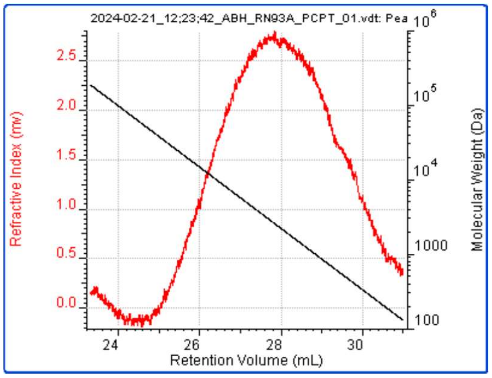


Figure A26 – GPC plot of PROD-5. M_w = 5,900g/mol, PDI = 5.3

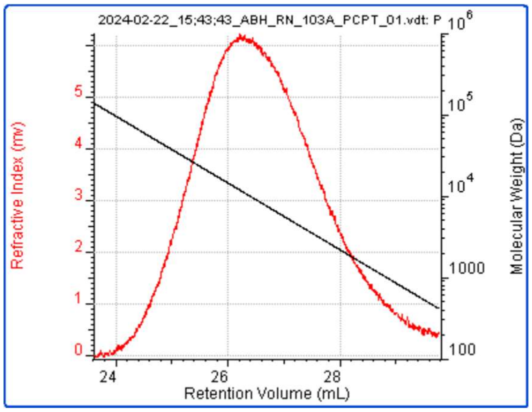


Figure A27 – GPC plot of PROD-11. M_w = 13,500 g/mol, PDI = 3.0

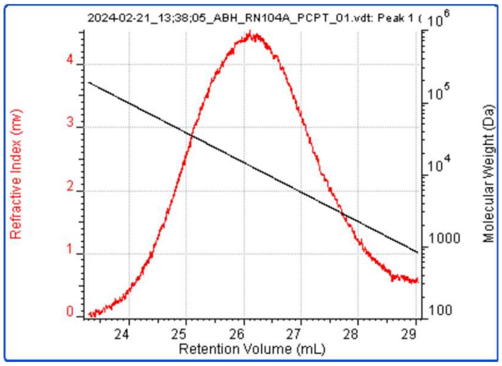


Figure A28 – GPC plot of PROD-12. M_w = 19,200 g/mol, PDI = 2.9

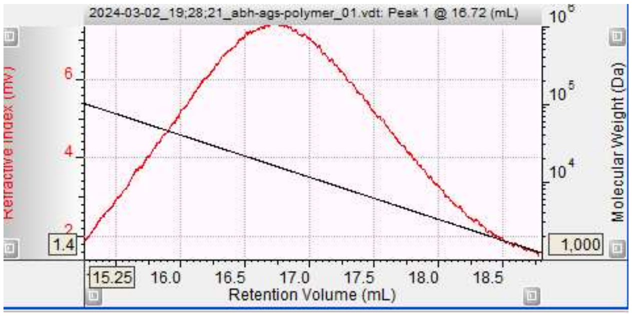


Figure A29 – GPC plot of PROD-13. M_w = 21,100 g/mol, PDI = 2.7

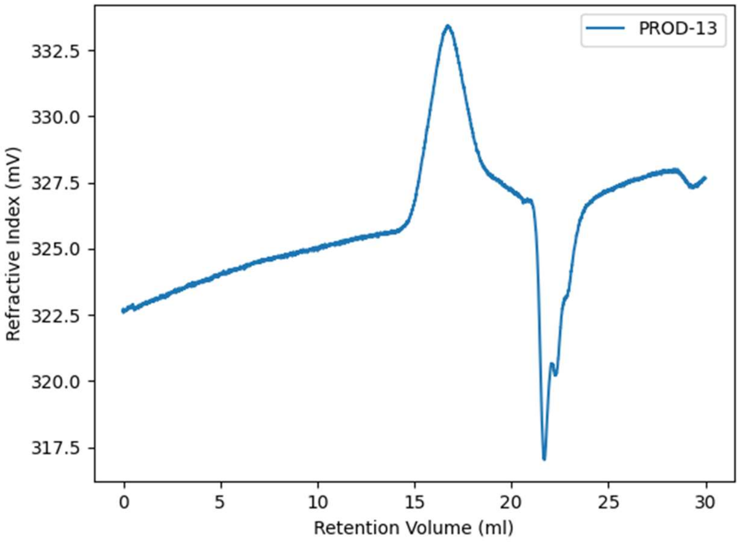


Figure A30 – GPC plot of PROD-13. Plotted using matplotlib.pyplot.

Procedure for handling dithiols

The dithiol used in this project was 1,2-Ethanedithiol. It is toxic and has a pungent smell. Thiols are quenched by Sodium Hypochlorite, which is a mild oxidizing agent that converts thiols into disulphides, which then precipitate in water. A full PPE kit should be worn while handling the dithiol or any dangerous chemical in general.

The dithiol was stored in a sealed plastic vial, wrapped with parafilm and in a cupboard with a bleach bath next to it in order to control the odorous vapours escaping into the atmosphere. During the time of addition, the vial was opened in a fume hood, with a bleach bath kept inside, with the exhaust turned on, and added into the reaction mixture with a plastic dropper. Minimize the time duration for which the vial is kept open. After adding the thiol into the reaction mixture, the dropper was immediately quenched using the bleach bath, and the set-up should ideally be sealed, or in this case, where the reaction was performed in reflux conditions, the exhaust kept on throughout the reaction. For the overnight reaction (18 hours), the reaction was performed under near-melt conditions with minimal solvent in a sealed Schlenk RB.

All disposables must first be washed in a bleach bath, followed by disposal in a separate container and be labelled as "**toxic waste**". The bleach solution used to quench the dithiol should also be disposed of in the same manner. All glassware used must be quenched in a bleach bath before regular washing and drying. All bleach baths used must be regularly disposed of and replaced.

For more information, refer to The University of Rochester's SOP. (Link:- chem.rochester.edu/notvoodoo/pages/how_to/work_with_thiols.php).