

Chapter 12

Novel Polymeric Products Derived from Biodiesel

Atanu Biswas,^{1,*} Zengshe Liu,¹ Roselayne Furtado,²
Carlucio R. Alves,³ and H. N. Cheng^{4,*}

¹National Center for Agricultural Utilization Research, USDA Agricultural Research Service, 1815 N. University St., Peoria, Illinois 61604, United States

²Embrapa Tropical Agroindustry, Fortaleza-CE 60511-110, Brazil

³Departamento de Química, Universidade Estadual do Ceará, Fortaleza-CE 60740-903, Brazil

⁴Southern Regional Research Center, USDA Agricultural Research Service, 1100 Robert E. Lee Blvd., New Orleans, Louisiana 70124, United States

*E-mail: atanu.biswas@ars.usda.gov; hn.cheng@ars.usda.gov

Biodiesel (produced by reacting a triglyceride with an alcohol) is increasingly being used as diesel fuel and heating oil, especially in Europe. Because of its availability and favorable environmental profile, it may be useful as a renewable feedstock for new polymers. In this work we introduced the epoxide functionality into biodiesel and converted it into a polymer through cationic polymerization with fluorosulfonic acid. Because of the stereochemistry involved, both linear and cyclic products were found. Copolymerization with epoxidized soybean oil produced polymers that ranged from liquids to solids. The use of a comonomer (e.g., diepoxides and propylene oxide) produced more diverse polymer structures. The NMR spectra of these materials provided helpful information on the reaction mechanism. These products may perhaps find applications as additives in lubricants, specialty elastomers, thickeners in coatings, and ingredients in oil-based commercial formulations.

Introduction

Products from agro-based raw materials are attractive because potentially they have the benefits of sustainability, environmental friendliness, and price stability relative to petroleum-based products (1–4). One of the more successful biobased products in recent years is biodiesel, which is typically produced through transesterification of triglyceride oil with methanol in the presence of a catalyst (5, 6). Common triglycerides being used include edible oils from plant and animal sources and waste cooking oils. Because it is renewable and has a favorable environmental profile, it can be used a “green” alternative in pure form or blended with petroleum diesel for diesel engines or in heating oil. One of the biodiesels derived from soybean oil is commonly known as “methyl soyate” (7). Because it is available, relatively low-priced, renewable, and biodegradable, we are examining its applications as a renewable feedstock for specialty polymers. Thus far, there seem to be very few papers on the use of methyl soyate or epoxidized methyl soyate as a renewable monomer for polymerization.

Previously a direct polymerization methodology has been developed to convert the olefins to epoxides in plant oils and to polymerize the epoxides via cationic means; a range of polymeric materials have been obtained (8–13). The catalyst for most of the work done so far has been BF_3 etherate; however, the polymers derived from such polymerization are crosslinked and insoluble (9, 10). In an earlier work (14, 15), we have shown that fluorosulfonic acid as a catalyst can polymerize epoxidized soybean oil and produce products that are soluble in organic solvents. In this article, we have carried out preliminary work to use methyl soyate as the starting material for the synthesis of polymeric products in order to increase the range of utility of this biobased raw material.

Experimental Section

Materials

Methyl soyate was obtained from Cooperative Producers, Inc. (Hastings, Nebraska) as SoyGold® 1000. It was made via alkaline methanolysis of soybean oil. Soybean oil came from a local grocery store. The following reagents were acquired from Sigma Aldrich (Milwaukee, WI): ethyl acetate, fluorosulfonic acid, 1,2,7,8-diepoxyoctane, bisphenol A diglycidyl ether, poly(ethylene glycol) diglycidyl ether (average M_n 500), and propylene oxide. Deuteriochloroform came from Cambridge Isotope Laboratories, Inc., Andover, MA.

Reactions

The epoxidation reaction was carried out using formic acid and hydrogen peroxide. The reaction was followed by NMR to ensure complete conversion of the olefins. More details on this reaction are available elsewhere (16, 17).

A typical polymerization procedure involved the addition of 1 g epoxidized methyl soyate and 2 mL ethyl acetate in a glass vial with stir bar, screw cap and

septum. About 5-20 mg of fluorosulfonic acid was added to the vial. The vial was placed in a React-Therm™ reactor set at 25-35°C for 24 hours with the reaction under nitrogen and stirring. As a precaution, an extra needle in the cap was inserted to prevent pressure buildup. After 24 hours, water was added to the vial, mixed, and decanted off. Sodium bicarbonate solution (5%) was then added, mixed, and decanted off. The product was washed twice with deionized water and then dried in vacuo at 60°C to remove ethyl acetate. In this procedure product recovery was almost quantitative except for transfer loss.

NMR Analysis

NMR spectra were acquired on a Bruker DRX 400 spectrometer (Karlsruhe, Germany). The NMR solvent used was d-chloroform; tetramethyl-silane served as the ¹³C chemical shift reference at 0 ppm. Standard operating conditions were used with 30° pulse angle and 3 s between pulses. Spectral assignments were made using empirical chemical shifts rules and automated shift prediction software (18, 19).

High Frequency Reciprocating Rig (HFRR) Test

The HFRR test is often used to evaluate the lubricity of diesel fuel. We followed the procedure as given in ASTM D6079-99 (20). Basically a 2-mL test specimen was placed in the test reservoir of an HFRR unit and heated to 60°C. A test steel ball was immersed in the specimen and then vibrated against a test disk at a frequency of 50 Hz for 75 min. The wear scar on the ball was then measured under a microscope. A smaller number is considered more desirable.

Results and Discussion

Epoxidized soybean oil is available commercially, but epoxidized methyl soyate is apparently not. In this work we chose to epoxidize soybean oil and methyl soyate ourselves. They were then used for polymerization.

Polymerization of Epoxidized Methyl Soyate

We first carried out homopolymerization of epoxidized methyl soyate (EMS) with a cationic initiator. Whereas several methods could be used (9–13), we chose, in light of our previous studies (14, 15), to use fluorosulfonic acid (FSA) in nitrogen with ethyl acetate as solvent. The FSA level varied from 5 mg to 20 mg. The reaction temperature varied from 25° to 35°C. In all cases, liquid products were obtained, indicating the formation of oligomers. A list of selected runs is given in Table 1.

Table 1. Polymerization^a of epoxidized methyl soyate and amounts^b of minor reaction products

<i>sample</i>	<i>Wt of FSA (mg)</i>	<i>product form</i>	<i>ketone %</i>	<i>furan %</i>	<i>dioxolane %</i>	<i>dioxane %</i>
A1	5	liquid	5	3	0	0
A2	10	liquid	4	5	0	0
A3	15	liquid	3	4	1	1
A4	20	liquid	3	5	2	1
A5	5	liquid	4	3	0	0
A6	10	liquid	2	4	2	1
A7	20	liquid	2	4	2	1

^a All reactions were conducted with 1 g of EMS in 2 g ethyl acetate solvent at 35°C for 24 hours under nitrogen. ^b Determined via NMR.

The ¹³C NMR spectrum of sample A4 is shown in Figure 1. Since methyl soyate consists primarily of methyl oleate and methyl linoleate, the spectrum is similar to what we found with the cationic polymerization of epoxidized methyl oleate and epoxidized methyl linoleate (14, 15). The large number of peaks at 14–40 ppm correspond to the fatty acid moiety in methyl soyate. The peaks at 51 ppm and 174 ppm come from methoxy and ester carbons, respectively. The cluster of peaks at 70–85 ppm (partly overlapping the CDCl₃ lines) belong to the oligomers. In addition, there are many smaller peaks in the spectrum due to several minor reactions. These reactions are summarized in Scheme 1.

For monoepoxides (like epoxidized oleate), the reactions with FSA lead to propagation to form a linear polymer and also rearrangements to form ketone, dioxolane, and dioxane (top part of Scheme 1). In Figure 1, the peaks at 81 ppm (ring CH) and 111 ppm (quaternary carbon on the ring) correspond to the dioxolane structure, and the peaks at 212 ppm (C=O) and 42.7 ppm (carbon α to ketone) are characteristic of the ketone. Dioxane is not observed in Figure 1 above the signal-to-noise of the spectrum.

Because of the different stereochemistry involved, the reactions of a diepoxide (like epoxidized linoleate) with FSA give different products (lower part of Scheme 1). As the epoxide functionality is protonated by FSA, one reaction pathway polymerizes diepoxides to form a cyclic polymer containing a tetrahydrofuran ring. Another pathway involving elimination and isomerization gives the polymeric furan structure. In Figure 1, the furan ring structure can be clearly seen at 105 ppm (C3 and C4) and 154 ppm (C1 and C4). Note that the 70–85 ppm region gives many peaks, showing a mixture of oligomeric structures (both linear and tetrahydrofuran-type), with different tacticity and chain ends. Because of structural complexity, it is not possible at present to assign the peaks in the 70–85 ppm region.

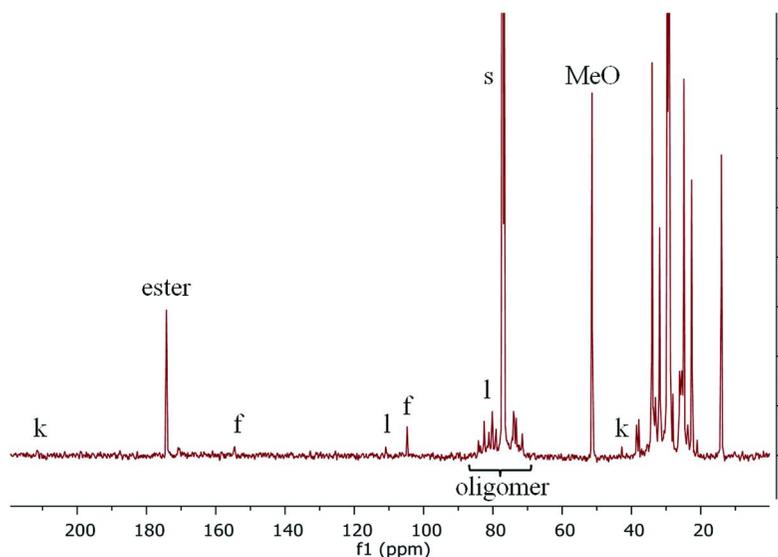


Figure 1. ^{13}C NMR spectrum of FSO_4 -initiated oligomer from methyl soyate 19560-49-3; f = furan, l = dioxolane, k = ketone, s = CDCl_3 .

Quantitative data on the minor reaction products are given in columns 4-7 of Table 1. These have been calculated from the integrated areas of appropriate ^{13}C NMR peaks by setting ω_1 carbon (methyl, at 14 ppm) or ω_2 carbon (methylene, at 22 ppm) on the fatty acid chain as 100%. In the NMR spectra, ketone and furan peaks are more easily noticeable, whereas the concentration levels for dioxolane and dioxane tend to be low and their peaks are sometimes lost in the noise. Note that the total amount of all minor reaction products is less than 10% in all the samples studied.

Copolymers of EMS and Epoxidized Soybean Oil

We next made copolymers of EMS with epoxidized soybean oil (ESO) using FSA as the catalyst. Different ratios of EMS and ESO were attempted. Polymerization was achieved in all cases, with the products that ranged from solid to liquid (Table 2). The reason for the solid formation at higher ESO levels is due to the multiple epoxy groups present in ESO, which tend to crosslink the resulting polymer.

The ^{13}C NMR spectrum of sample B5 is given in Figure 2. Since EMS and ESO are structurally similar, the copolymerization likely proceeded with the same reaction mechanism as Scheme 1. Indeed both furan and ketone can be found in Figure 2. In addition, methoxy and glycerol moiety are observed because of the presence of methyl ester and glycerate esters in EMS and ESO, respectively. As before, the peaks that correspond to the polymer can be found in the 70-85 ppm region.

Table 2. Copolymerization of EMS and ESO in the presence of fluorosulfonic acid in nitrogen^a

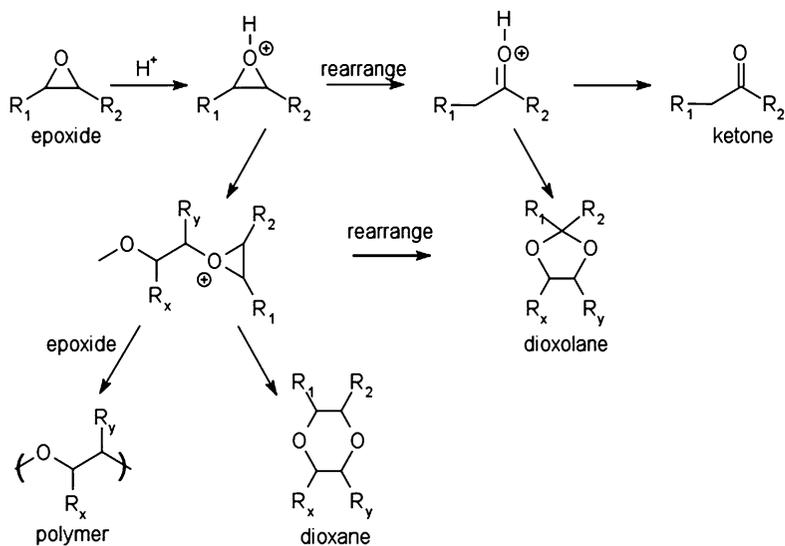
<i>sample</i>	<i>feed ratio EMS:ESO</i>	<i>obsd EMS^b %</i>	<i>obsd EMS^c %</i>	<i>product form</i>	<i>ketone (%)</i>	<i>furan (%)</i>
B1	0:100	0	0	solid	12	8
B2	10:90	9	13	solid	15	7
B3	25:75	22	22	soft solid	13	8
B4	40:60	40	35	liquid	9	7
B5	50:50	50	49	liquid	11	6
B6	75:25	77	72	liquid	3	6
B7	100:0	100	100	liquid	3	3

^a All reactions were conducted with 1 g of total starting material(s), 20 mg FSA catalyst and 2 g ethyl acetate solvent at 35°C for 24 hours. ^b Calculated from the areas of methoxy and glycerate peaks in the NMR spectra. ^c Calculated from the ester peaks in the NMR spectra.

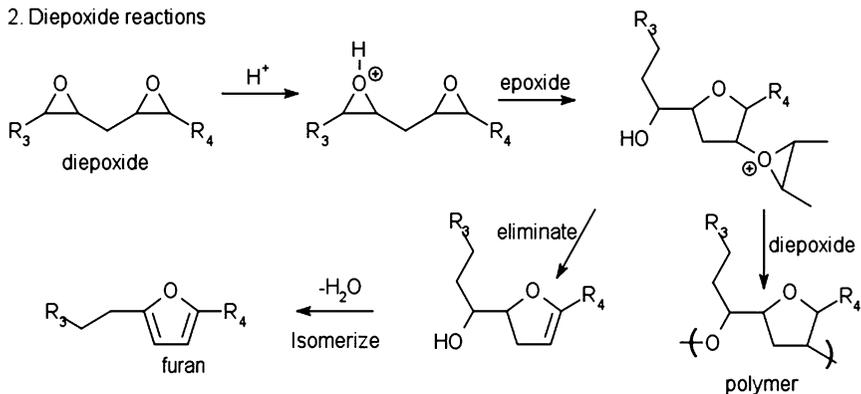
It is of interest that three distinct ester peaks are observed (Figure 2, inset). The peak at 174.2 ppm corresponds to the ester carbon of EMS, whereas the two peaks at 173.2 and 172.8 ppm come from ester carbon of ESO. These two ESO peaks are due to the two types of esters formed from glycerol: the ester for the 1,3 positions at 173.2 ppm, and the ester for the 2 position at 172.8 ppm. From the integrated intensities of these three ester peaks we can estimate the % EMS in the copolymer. Another measure of the copolymer composition is to take the ratio of the methoxy carbon peak (from EMS at 51 ppm) and glycerol peaks (from ESO at 68 and 63 ppm). The copolymer compositions derived from both calculations are shown in Table 2. These agree well with each other and with the feed ratios of EMS and ESO.

The quantitative NMR data for ketone and furan are also given in Table 2. As the amount of ESO in the copolymerization increases, there seems to be a slight increase in the levels of ketone and furan. This may be due to the increase in the viscosity of the reaction medium as the proportion of ESO increases, thereby slightly favoring the minor reactions. Note that the total amount of ketone and furan is higher (>10%) for the EMS/ESO samples relative to the EMS homopolymer.

1. Monoepoxide reactions



2. Diepoxide reactions



Scheme 1. Reactions between epoxides and fluorosulfonic acid; $x, y = 1$ or 2 .

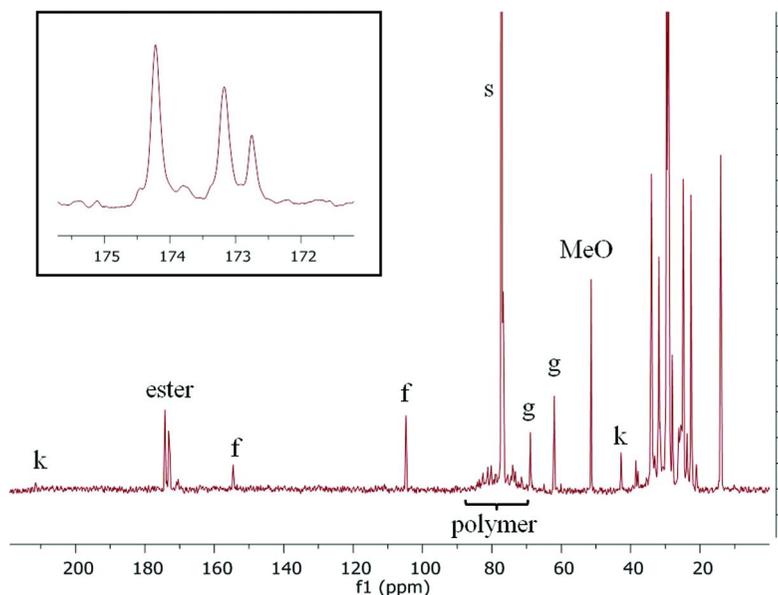


Figure 2. ^{13}C NMR spectrum of the copolymer of EMS and ESO-19560-37-2; *f* = furan, *k* = ketone, *g* = glycerol moiety, *s* = CDCl_3 . Inset: Expanded 172–195 ppm region, showing the ester peaks.

Other Copolymers of EMS

We also sought to make other copolymers of EMS. The first group of comonomers consisted of diolefins that could serve as crosslinkers, such as 1,2,7,8-diepoxyoctane (DEO, M_n 142), bisphenol A diglycidyl ether (BADGE, M_n 340), and poly(ethylene glycol) diglycidyl ether (PEGDE, M_n 500). The results for six copolymers are shown in Table 3. At 10 wt % diolefin level, all three EMS copolymers were liquids. At 30 wt % diolefin level, the copolymers involving DEO and BADGE were solids at room temperature, but the copolymer involving PEGDE was still a liquid.

The ^{13}C NMR spectra for the 70:30 EMS : diolefin copolymers are given in Figure 3. The NMR signals for the copolymer appear as a broad complex feature just above the baseline at 70–85 ppm. The presence of EMS can be clearly seen from the ester peak (174 ppm), methoxy peak (51 ppm), and the aliphatic peaks (14–40 ppm). For the diolefins, the epoxy functionality has almost fully reacted and the epoxy peaks (ca. 46 and 51 ppm) are not observed. The peaks for the rest of the carbons in the diolefins have been labelled in Figure 3. Thus, the ^{13}C NMR spectra confirm the successful synthesis of these three copolymers.

Table 3. Copolymerization of EMS and diepofin in the presence of fluorosulfonic acid in nitrogen^a

sample	diepofin	wt ratio EMS:diepofin	mole ratio EMS:diepofin	product form
C1	DEO	90 : 10	81:19	liquid
C2	DEO	70 : 30	53:47	solid
C3	BADGE	90 : 10	91:9	liquid
C4	BADGE	70 : 30	73:27	solid
C5	PEGDE	90 : 10	94:6	liquid
C6	PEGDE	70 : 30	80:20	liquid

^a All reactions were conducted with 1 g of total starting material(s), 20 mg FSA catalyst and 2 g ethyl acetate solvent at 35°C for 24 hours.

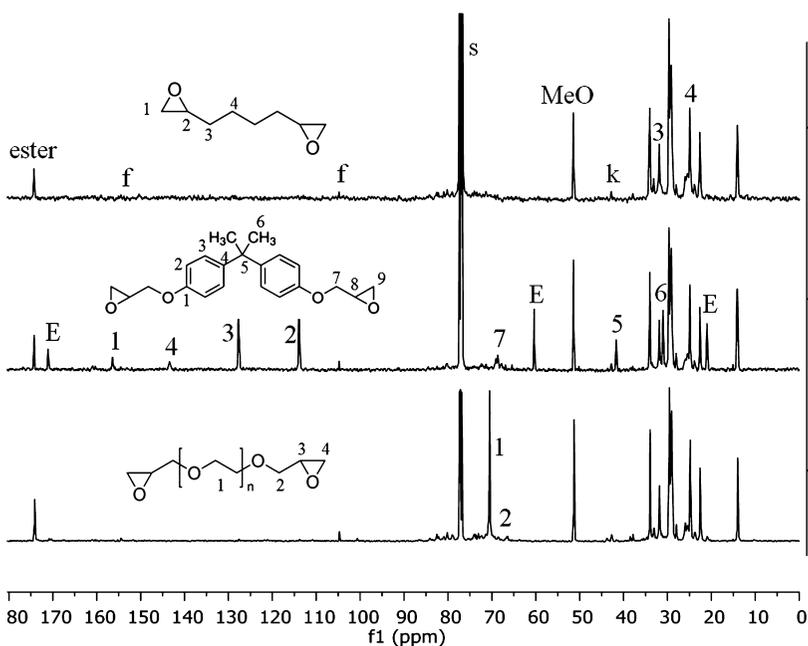


Figure 3. ¹³C NMR spectrum of the (70:30) copolymers of EMS and three diepoxides: A) diepoxyethane, B) bisphenol A diglycidyl ether, C) poly(ethylene glycol) diglycidyl ether. *f* = furan, *k* = ketone, *s* = CDCl₃, *E* = ethanol. The epoxy moiety has been fully reacted because no epoxy peaks (ca. 46 and 51 ppm) can be found.

Next, we attempted the copolymerization of EMS with propylene oxide (PO). Under our reaction conditions with FSA, PO by itself gave a liquid product. However, when PO and EMS were copolymerized with diepoxyethane, the reaction products were solids at room temperature (Table 4). The ^{13}C NMR spectrum of sample D4 is given in Figure 4.

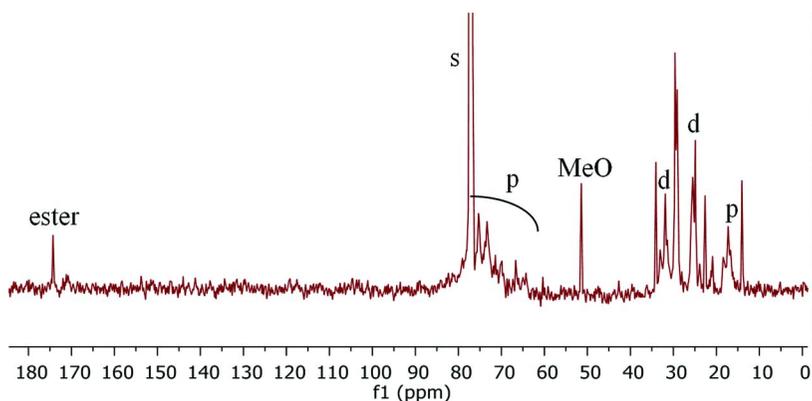


Figure 4. ^{13}C NMR spectrum of the copolymers of EMS, propylene oxide, and diepoxyoctane (20:50:30) (sample 19640-9-2); p = PO peaks, d = diepoxyoctane peaks, s = CDCl_3 . The epoxy peaks (at 47 and 51 ppm) are absent, indicating complete reaction.

Table 4. Copolymerization^a of EMS, propylene oxide, and diepoxyoctane

sample	wt ratio EMS:PO:DEO	mole ratio EMS:PO:DEO	product form
D1	70:0:30	53:0:47	solid
D2	50:20:30	24:47:29	solid
D3	43:30:30	16:60:24	solid
D4	20:50:30	6:76:18	gel
D5	0:100:0	0:100:0	liquid

^a All reactions were conducted with 1 g of total starting material(s), 20 mg FSA catalyst and 2 g ethyl acetate solvent at 35°C for 24 hours under nitrogen.

In Figure 4, the presence of EMS is evidenced by the ester peak at 174 ppm, methoxy peak at 51 ppm, and the aliphatic peaks at 14–40 ppm. The unreacted epoxy peaks for diepoxyoctane (at 47 and 52 ppm) are not observed, indicating their complete conversion to polymers. The peaks for the other two carbons in reacted diepoxyoctane are found as broad lines at 25.6 and 32.4 ppm. In agreement with the literature (21), the poly(propylene oxide) (PPO) peaks occur at about 75.5 ppm (CH), 73.5 ppm (CH₂), and 17.8 ppm (CH₃). The PPO terminal methylene

peaks occur at 72.0 and 75.6 ppm, methine at 64–68 ppm, and methyl at 17.3 and 19.3 ppm. Thus, the ^{13}C NMR data confirm the incorporation of EMS, PO, and DEO in the polymers made.

Possible Applications

In recent years, there has been a lot of interest in converting plant oil to polymers, and many different approaches have been adopted (22, 23). Examples of direct polymerization of soybean oil include thermal (24–26) and air blown polymerization (27, 28), cationic polymerization (29–31), pericyclic reactions (32, 33), and others (34). Furthermore, the plant oil can be modified in order to add more functional groups and increase the range of possible polymerizations. A number of review articles have appeared on this topic (35–37). Possible applications of these triglyceride-based polymers include lubricants, paints, coatings, adhesives, plastics, composites, and biomedical materials.

In this work, epoxidized methyl soyate has been made into homopolymers and copolymers using cationic polymerization. This family of new polymers can probably be used for many of the same aforementioned applications. For example, one obvious application is to use the new materials in lubricant formulations. A preliminary study of epoxidized methyl oleate, epoxidized methyl linoleate, and EMS was carried out using the high frequency reciprocating rig (HFRR) test (Table 5). According to the results, all six samples gave low values of wear scars. In comparison, kerosene gives a HFRR value of 675 μm , and commercial D1 and D2 fuels 578 and 376 μm , respectively (38). Thus, the polymers made in this work may perhaps be regarded as possible additives for lubricants.

Table 5. High frequency reciprocating rig (HFRR) test for polymers made from several fatty acid methyl esters^a

<i>sample</i>	<i>starting material</i>	<i>wt. FSA (mg/g)</i>	<i>wear scars (μm)</i>
E1	epoxidized methyl oleate	7.5	224
E2	epoxidized methyl oleate	15	190
E3	epoxidized methyl linoleate	10	127
E4	epoxidized methyl linoleate	15	95
E5	EMS	5	194
E6	EMS	15	129

^a Polymerization was achieved with 1 g of starting material and 2 g ethyl acetate solvent at 35°C for 24 hours under nitrogen.

Other possible applications of these polymers may include their use as bioplasticizers, specialty elastomers, and thickeners in oil-based commercial formulations. Further work is needed in order to develop the full product development potential of these materials.

Conclusion

In this work we have used biodiesel as a natural renewable raw material for the synthesis of polymers. In particular, a cationic catalyst, fluorosulfonic acid, has been shown to catalyze the polymerization of epoxidized methyl soyate. Furthermore, copolymers can be made with epoxidized methyl soyate, thereby generating a new family of polymers. The polymers may perhaps find application in a number of areas, such as lubricants, coatings, elastomers, and other oil-based commercial formulations.

It may be noted that ^{13}C NMR was found to be useful in elucidating the reaction mechanism. Because of the stereochemistry involved, monoepoxide and diepoxide engendered different reactions and produced different products when polymerized. Thus, if biodiesels from different sources (e.g., soybean oil, palm oil, cottonseed oil, animal fat, and waste cooking oil) are used for this reaction, somewhat different products may be obtained. This product diversity may be an opportunity that permits a range of different polymers to be made with different end-use performance.

Acknowledgments

Thanks are due to Janet Berfield and Gary Kuziar for expert technical assistance, Dr. Karl Vermillion for the NMR spectra, and Daniel Knetzer for helpful support. Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

References

1. *Green Polymer Chemistry: Biobased Materials and Biocatalysis*; Cheng, H. N., Gross, R. A., Smith, P. B., Eds.; ACS Symposium Series 1192; American Chemical Society: Washington, DC, 2015.
2. Mulhaupt, R. Green polymer chemistry and bio-based plastics: Dreams and reality. *Macromol. Chem. Phys.* **2013**, *214*, 159–174.
3. *Green Polymerization Methods: Renewable Starting Materials, Catalysis and Waste Reduction*; Mathers, R. T., Meier, M. A. R., Eds.; Wiley-VCH: Weinheim, Germany, 2011.
4. Gandini, A. The irruption of polymers from renewable resources on the scene of macromolecular science and technology. *Green Chem.* **2011**, *13*, 1061–1083.
5. Atabani, A. E.; Silitonga, A. S.; Badruddin, I. A.; Mahlia, T. M. I.; Masjuki, H. H.; Mekhilef, S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable Sustainable Energy Rev.* **2012**, *16*, 2070–2093.
6. Leung, D. Y. C.; Wu, X.; Lueng, M. K. H. A review on biodiesel production using catalyzed transesterification. *Appl. Energy* **2010**, *87*, 1083–1095.

- United Soybean Board. <http://soynewuses.org/solvents/> (accessed May 14, 2017).
- Raghavachar, R.; Sarnecki, G.; Baghdachi, J.; Massingill, J. Cationic, thermally cured coatings using epoxidized soybean oil. *J. Coat. Technol.* **2000**, *72*, 126–133.
- Liu, Z. S.; Erhan, S. Z. Ring-opening polymerization of epoxidized soybean oil. *J. Am. Oil Chem. Soc.* **2010**, *87*, 437–444.
- Liu, Z. S.; Doll, K. M.; Holser, R. A. Boron trifluoride catalyzed ring-opening polymerization of epoxidized soybean oil in liquid carbon dioxide. *Green Chem.* **2009**, *11*, 1774–1780.
- Liu, Z. S. Preparation of biopolymers from plant oils in green media. *Bioenergy Res.* **2013**, *6*, 1230–1236.
- Liu, Z.; Knetzer, D. A. Catalyzed ring-opening polymerization of epoxidized soybean oil by hydrated and anhydrous fluoroantimonic acids. *Green Mater.* **2013**, *1*, 87–95.
- Liu, Z. S.; Biswas, A. Fluoroantimonic acid hexahydrate (HSbF₆ · 6H₂O) catalysis: The ring-opening polymerization of epoxidized soybean oil. *Appl. Catal., A* **2013**, *453*, 370–375.
- Biswas, A.; Liu, Z.; Cheng, H. N. Polymerization of epoxidized triglyceride with fluorosulfonic acid. *Int. J. Polym. Anal. Charact.* **2016**, *21*, 85–93.
- Biswas, A.; Liu, Z.; Berfield, J. L.; Cheng, H. N. Synthesis of novel plant oil derivatives: Furan and Diels-Alder reaction products. *Int. J. Agric. Sci. Technol.* **2015**, *3*, 28–35.
- Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Oxidation, friction reducing, and low temperature properties of epoxy fatty acid methyl esters. *Green Chem.* **2007**, *9*, 469–474.
- Liu, Z.; Chen, J.; Knothe, G.; Nie, X.; Jiang, J. Synthesis of epoxidized cardanol and its antioxidative properties for vegetable oils and biodiesel. *ACS Sustainable Chem. Eng.* **2016**, *4*, 901–906.
- Cheng, H. N. ¹³C NMR spectral simulation and shift prediction. *TrAC Trends Anal. Chem.* **1994**, *13*, 95–104; DOI: 10.1016/0165-9936(94)87073-X.
- NMRShiftDB. <http://nmrshiftdb.nmr.uni-koeln.de/> (accessed May 14, 2017).
- ASTM D 6079-99. Standard test method for evaluating lubricity of diesel fuels by the High Frequency Reciprocating Rig (HFRR), December 1999.
- Schilling, F. C.; Tonelli, A. E. Carbon-13 NMR Determination of Poly(propylene oxide) Microstructure. *Macromolecules* **1986**, *19*, 1337–1343.
- Xia, Y.; Larock, R. C. Vegetable oil-based polymeric materials: synthesis, properties and applications. *Green Chem.* **2010**, *12*, 1893–1909.
- Espinosa, L. M.; Meier, M. A. R. Plant oils: The perfect renewable resource for polymer science. *Eur. Polym. J.* **2011**, *47*, 837–852.
- Bernstein, I. M. Heat polymerization of nonconjugated vegetable oils. *J. Polym. Sci.* **1946**, *1*, 495–528.
- Wang, C.; Erhan, S. Z. Studies of thermal polymerization of vegetable oils with a differential scanning calorimeter. *J. Am. Oil Chem. Soc.* **1999**, *76*, 1211–1216.

26. Arca, M.; Sharma, B. K.; Price, N. P. J.; Perez, J. M.; Doll, K. M. Evidence contrary to the accepted Diels-Alder mechanism in the thermal modification of vegetable oil. *J. Am. Oil Chem. Soc.* **2012**, *89*, 987–994.
27. Christianson, R.; Noble, M.; Rourke, A.; Geiger, E.; Mahlum, L. U.S. Patent 7262311, August 28, 2007.
28. Geiger, E. J.; Becker, N. M.; Armbruster, L. A. U.S. Patent 7989647, August 2, 2011.
29. Liu, Z.; Sharma, B. K.; Erhan, S. Z. From oligomers to molecular giants of soybean oil in supercritical carbon dioxide medium. *Biomacromolecules* **2007**, *8*, 233–239.
30. Li, F.; Hanson, M. V.; Larock, R. C. Soybean oil-divinylbenzene thermosetting polymers: Synthesis, structure, properties and their relationships. *Polymer* **2001**, *42*, 1567–1579.
31. Ionescu, M.; Petrovic, Z. S. U.S. Patent 7,501,479, March 10, 2009.
32. Biswas, A.; Sharma, B. K.; Willett, J. L.; Erhan, S. Z.; Cheng, H. N. Room-Temperature Self-Curing Ene Reactions Involving Soybean Oil. *Green Chem.* **2008**, *10*, 290–295.
33. Biswas, A.; Cheng, H. N.; Kim, S.; Liu, Z. Modified Triglyceride Oil through Reactions with Phenyltriazolinedione. *J. Am. Oil Chem. Soc.* **2014**, *91*, 125–131.
34. Ronda, J. C.; Lligadas, G.; Galia, M.; Cadiz, V. Vegetable oils and platform chemicals for polymer synthesis. *Eur. J. Lipid Technol.* **2011**, *113*, 46–58.
35. Biswas, A.; Sharma, B. K.; Willett, J. L.; Erhan, S. Z.; Cheng, H. N. *Energy Environ. Sci.* **2008**, *1*, 639–644.
36. Sharma, V.; Kundu, P. P. Addition polymers from natural oils. *Prog. Polym. Sci.* **2006**, *31*, 983–1008.
37. Guner, F. S.; Yagci, Y.; Erciyes, A. T. Polymers from triglyceride oils. *Prog. Polym. Sci.* **2006**, *31*, 633–670.
38. Van Gerpen, J. H.; Soyly, S.; Chang, D. Y. Z. Evaluation of the lubricity of soybean oil-based additives in diesel fuel. http://biodiesel.org/reports/19980201_gen-070.pdf (accessed May 14, 2017).