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From Oligomers to Molecular Giants of Soybean Oil in Supercritical Carbon Dioxide Medium: 1. Preparation of Polymers with Lower Molecular Weight from Soybean Oil

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Polymers with a low molecular weight derived from soybean oil have been prepared in a supercritical carbon dioxide medium by cationic polymerization. Boron trifluoride diethyl etherate was used as an initiator. Influences of polymerization temperature, amount of initiator, and carbon dioxide pressure on the molecular weight were investigated. It is shown that the higher polymerization temperature favors polymers with relatively higher molecular weights. Larger amounts of initiator also provide polymers with higher molecular weights. Higher pressure favors polymers with relatively higher molecular weights. The applications of these soy-based materials will be in the lubrication and hydraulic fluid areas.

Introduction

During the past few years, there has been a growing interest in the use of polymers obtained from renewable resources because of their low production cost and being biodegradable in some cases.[1] The importance of natural products for industrial applications also becomes very clear with the increasing social emphasis on issues concerning the environment, waste disposal, and the depletion of non-renewable resources. Among products from agricultural resources, natural oils may constitute raw materials useful in polymer synthesis. In the United States, the major source of vegetable oil for industrial applications is soybean oil. For example, the United States annually produces one billion pounds of soybean oil in excess of current commercial demand. This excess capacity has resulted in lower prices for soybean oil as well as other agricultural commodities. Development of economically feasible new industrial products from soybean oil or commercial processes is highly desirable.

Currently, soybean oil is mainly used for food applications. Refined soybean oil is composed of 99% triglycerides. These triglycerides are composed of three fatty acids connected by a glycerol center as shown in Figure 1. These fatty acids vary from 14 to 22 carbons in length with 0 to 3 double bonds per fatty acid. The average number of carbon−carbon double bonds per molecule of soybean oil of North American origin is approximately 4.6. Because of the many different fatty acids present, it is apparent that on a molecular level the oils are composed of many different types of triglycerides with varying levels of unsaturation. Therefore, it is possible to attach some functional groups to vegetable oils with unsaturated fatty acid components through chemical modifications to produce hydroxylated, epoxydized, or maleinized triglycerides, which are all capable of polymerization. Triglyceride-based polymers have been used as toughening agents in poly(vinyl chloride) and epoxy resins[2] and as the major component of a number of natural resins,[3,4] composites,[5] and pressure-sensitive adhesives.[6]

Li et al.[7] reported the direct conversion of soybean oil to useful solid polymers by cationic copolymerization of soybean oil with styrene and divinyl benzene initiated by boron trifluoride diethyl etherate ($BF_3{\cdot}O(C_2H_5)_2$). The resulting polymers formed range from soft rubbers to hard plastics, depending on the reagents, stoichiometry, and initiator used. Wool and co-workers developed a soybean-oil-based resin acrylated epoxidized soybean oil (AESO) to make composites with natural fiber mats of flax, cellulose, pulp, and hemp.[8] The composites with natural fiber reinforcement of approximately 10−50 wt % increased the flexural modulus to a range between 1.5 and 6 GPa depending on the nature of the fiber mat. Guo et al.[9] reported the preparation of polyols and polyurethanes from hydroformylation of soybean oil and studied the physical properties and mechanical properties of these polyurethanes. In our previous articles,[10−12] we reported the preparation of epoxidized soybean oil/epoxy-based composites, reinforced with carbon, glass, and mineral fibers or with combinations of fiber and clay, by extrusion solid free-form fabrication methods. These polymeric composites demonstrate a variety of properties, ranging from elastomers to rigid plastics. Most of the aforementioned works converted soybean oils to useful solid polymers with other major components in the polymer matrix. In other words, the research focuses on improving the physical properties of solid thermoplastics and thermoset materials, because the triglyceride-based materials demonstrated low molecular weights and light cross-linking, incapable of displaying the necessary rigidity and strength required for structural applications by themselves.

Lubricants account for 1.2% of the total petroleum use. Those lubricants from petroleum stock are toxic to the environment and difficult to dispose. There is also increasing concern for environmental pollution from excessive mineral oil use and disposal, especially in loss lubrication, military applications, and outdoor activities such as forestry, mining, railroads, dredging, fishing, and agricultural hydraulic systems. Vegetable oils are considered to be potential substitutes for conventional mineral-

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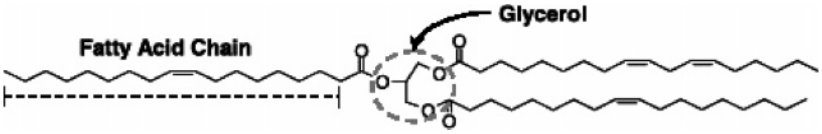

Figure 1. Molecular structure of a typical triglyceride molecule.

oil-based lubricating oils and synthetic esters. Vegetable oils are preferred over synthetic fluids because they are biodegradable and inexpensive in some cases. However, vegetable oils have poor oxidation stability primarily due to the presence of bisallylic protons. Also, low-temperature studies have shown that most vegetable oils undergo cloudiness, precipitation, poor flow, and even solidification at −10 °C upon long-term exposure to cold temperature, which is in sharp contrast to mineral-oil-based fluids. Before widespread use of vegetable oils as the base fluid for environmentally friendly lubricants and hydraulic fluids is possible, their oxidation and cold flow properties need to be improved. Polymerization of vegetable oils, such as soybean oil, is a useful approach. It is generally considered difficult to polymerize vegetable oils themselves, except castor oil, due to their lack of active functional groups. As Li et al. point out[7] in the cationic homopolymerization of soybean oil using boron trifluoride diethyl etherate as the initiator, due to the relatively high molecular weight and multiple chain structures of soybean oils, their reactivity is rather low. Furthermore, soybean oil has been found to be immiscible with the initiator employed. Thus, the $BF_3{\cdot}O(C_2H_5)_2$-initiated homopolymerization of pure soybean oil is relatively difficult. Erhan and Bagby[13] reported the thermal polymerization of vegetable oils at a high temperature, i.e., 330 °C, under nitrogen atmosphere. The polymers obtained under these conditions show a weight average molecular weight (M_w) ranging from 2600 to 8900. The significant drawbacks of thermal polymerization are long reaction times and high temperatures. Another disadvantage is that the molecular weight of the polymer is very difficult to control.

Supercritical carbon dioxide ($scCO_2$) has been shown to be a promising alternative solvent medium for organic transformations and polymerization reactions. This stems from a list of advantages ranging from solvent properties to practical environmental and economic considerations. Moreover, no residual solvent remains in the polymer product. Additionally it is inexpensive, readily available, and nonflammable.

The present work reports the direct conversion of soybean oils themselves in supercritical carbon dioxide to polymers with low molecular weights. We focus on the effects of pressure (P), temperature (T), and the amount of catalyst on the molecular weight of the soybean-oil-based polymers. The resulting polymers with relatively low molecular weights are liquid, which could be used as lubricants and hydraulic fluids. The advantages of these polymers are their low cost, availability from a renewable resource, their biodegradability, and "green" processing methods. The characterization and applications of the resulting liquid polymers as lubricants and hydraulic fluids will be reported in a future publication.

Experimental Section

Materials. Soybean oil (SO-5) was purchased from Purdue Farms Inc., Refined Oil Division (Salisbury, MD). Boron trifluoride diethyl etherate ($BF_3{\cdot}O(C_2H_5)_2$), purified and redistilled, from Aldrich Chemical Inc. (Milwaukee, WI) was used as received. Carbon dioxide (>99.8%) was obtained from Linde Gas LLC (Independence, OH). Sodium bicarbonate and magnesium sulfate were purchased from Aldrich Chemical Inc. Tetrahydrofuran (THF, ACS grade) was obtained from Aldrich Chemical Inc.

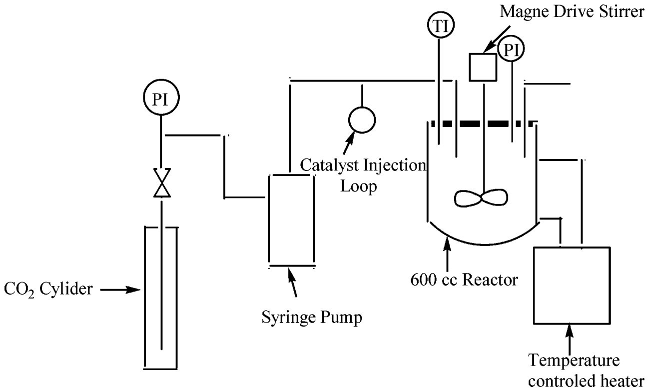

Figure 2. Schematic diagram of the experimental setup.

Analysis. *Gel Permeation Chromatograpy.* The original soybean oil (SBO), the processed soybean oil under similar conditions without catalyst (SBO control), and polymers of soybean oil (PSBO) were dissolved in THF. Molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) with a differential refractive index (RI) detector using THF as the eluent. The flow rate was 1.00 mL/min at 40 °C. The injection volume was 100 μL. Linear polystyrene standards (Polymer Laboratories, $M_n = 580-100\,000$, $M_w/M_n = 1$) were used for calibration of molecular weights of all polymers of soybean oil. Two Polymer Laboratories gel 3 μm mixed E columns (300 mm × 7.5 mm) in series were used to resolve the samples.

NMR. ^1H and ^{13}C NMR spectra for SBO and PSBO samples were recorded quantitatively using a Bruker AV-500 spectrometer (Bruker, Rheinstetten, Germany) at observing frequencies of 500.13 and 125.77 MHz, respectively, on a 5 mm dual probe. For ^1H and ^{13}C experiments sample solutions were prepared in deuterated chloroform ($CDCl_3$, 99.8% D, Aldrich Chemical Inc.) in 15% and 30% v/v concentrations, respectively. ^1H NMR spectra were obtained with 16 scans at a delay time of 1 s. The integration values in ^1H NMR spectra were referenced to 4.00 in the range of 4.1−4.44 ppm.

Viscosity. A Brookfield Engineering rheometer, model DV-III, fitted with a cone/plate spindle CP-40 was used to measure the viscosity of the polymer samples. The CP-40 was chosen for its relatively small sample volume requirements (0.5 mL). The sample was measured and delivered with a syringe and allowed to equilibrate at temperature for 15 min, and then rotational force was applied. Data were collected using the Brookfield Engineering software *Rheocalic*, version 2.4. The Bingham mathematical model was used to determine viscosity. The Bingham equation is

$$\tau = \tau_0 + \mu\gamma$$

where τ is the shear stress applied to the material, γ is the shear strain rate (also called the strain gradient), τ_0 is the yield stress, and μ is the plastic viscosity.

Table 1. Fatty Acid Composition (wt %) of Soybean Oil (SO-5) by HPLC Analysis

	fatty acid				
	16:0	18:0	18:1	18:2	18:3
composition	13.1	3.53	23.87	52.93	6.47

Table 2. Effect of Catalyst Amount on the Molecular Weight of PSBO

entry	SBO (g)	P (bar)	T (°C)	reaction time (h)	catalyst amount (g)	viscosity (mPa s)	M_w (g/mol)
1 (control)	100	110	120	2	0	46.7	1103
2	100	110	120	2	1.0	108	1447
3	100	110	120	2	1.5	222	5648
4	100	110	120	2	2.0	722	10 480
5	100	110	120	2	2.5	1909	24 908

Polymerization Procedure in $scCO_2$. Polymerization reactions were carried out in a 600 cm^3 autoclave reactor from Parr Instrument Co. (Moline, IL). The reactor was attached to an Isco model 260D high-pressure syringe pump used to charge the reactor with CO_2. In a typical experiment, 100 g of SO-5 was added to the reactor, which was then sealed. N_2 was purged into the reactor for 5 min. CO_2 was pumped in until the desired pressure was reached. A controller (Parr 4843 controllers) was used to control the temperature. Once the reactor was brought to the appropriate temperature and pressure, $BF_3{\cdot}O(C_2H_5)_2$ was charged into the reactor by manual injection. Then CO_2 was pumped in to clean the initiator supply line. A schematic diagram of the experimental setup used for polymerization of soybean oil is depicted in Figure 2. After reaction for 2 h, 2 mL of ethanol/H_2O (1:1) was added into the reactor to deactivate the catalyst. The polymer product was dissolved in 100 mL of hexane and washed sequentially with H_2O, 5% aqueous sodium bicarbonate, and H_2O. The hexane solution was dried over sodium sulfate, filtered, and evaporated under reduced pressure. Approximately 100 g of polymer was obtained.

Results and Discussion

Soybean oil is light amber in color with a free fatty acid content of 0.5%. It is reported that the fatty acid composition of soybean oil shows a wide variation linked to its region of origin.[14] Saturated fatty acids range from 11% to 26%. Table 1 summarizes fatty acid composition of soybean oil (SO-5) by HPLC analysis.

It can be seen that the SBO (SO-5) is composed of 16.63% saturated fatty acids and 83.27% unsaturated fatty acids. The molecular weight (M_w) of SBO (SO-5) by GPC analysis is 1100 g/mol.

Effects of the Amount of Catalyst. To investigate the effect of the amount of initiator on the molecular weight of PSBO, the amount of $BF_3{\cdot}OEt_2$ was varied from 0.0 to 2.5 g, while keeping the monomer, SBO, at 100 g, keeping other reaction conditions the same as mentioned in Table 2. Entry 1 in Table 2 is the soybean oil control without the initiator catalyst; it shows that weight average molecular weight did not change after 2 h under the reaction conditions. Also shown in Table 2 is the comparison to soybean oil molecular weight. Because soybean oil and SBO control have the same GPC profile, Figure 3 shows the GPC profile of soybean oil control and PSBO. The results of the catalyst concentration effect are presented in Table 2. Table 2 shows that as the $BF_3{\cdot}OEt_2$ amount increased the weight average molecular weight also increased. The weight average molecular weight changed from 1,447 to 24,908 g/mol. From the GPC profile it is noted that between the soybean oil (control) peak (1,097) and the high molecular weight peak of PSBO (19,521) there are only two peaks at (1,638) and (2,649), corresponding to dimers and trimers of the soybean oil molecule, respectively. It seems that the formation of dimers and trimers from soybean oil is the slow step for polymerization, which follows step polymerization kinetics. These formed dimers and trimers polymerize very quickly to high molecular weight and exhibit chain reaction kinetics. This phenomenon relates to the soybean oil molecule itself and larger molecules with lower activities, due to the midchain double bond location. However, the formed dimers and trimers have more functional group, i.e., unsaturated carbon−carbon double bonds, per molecule, they are easily to be polymerized to high molecular weight polymers. We propose further investigation on the possible combination of two polymerization mechanisms for the polymerization of soybean oil in $scCO_2$. Kinetics studies of soybean oil polymerization currently are being carried out in our lab.

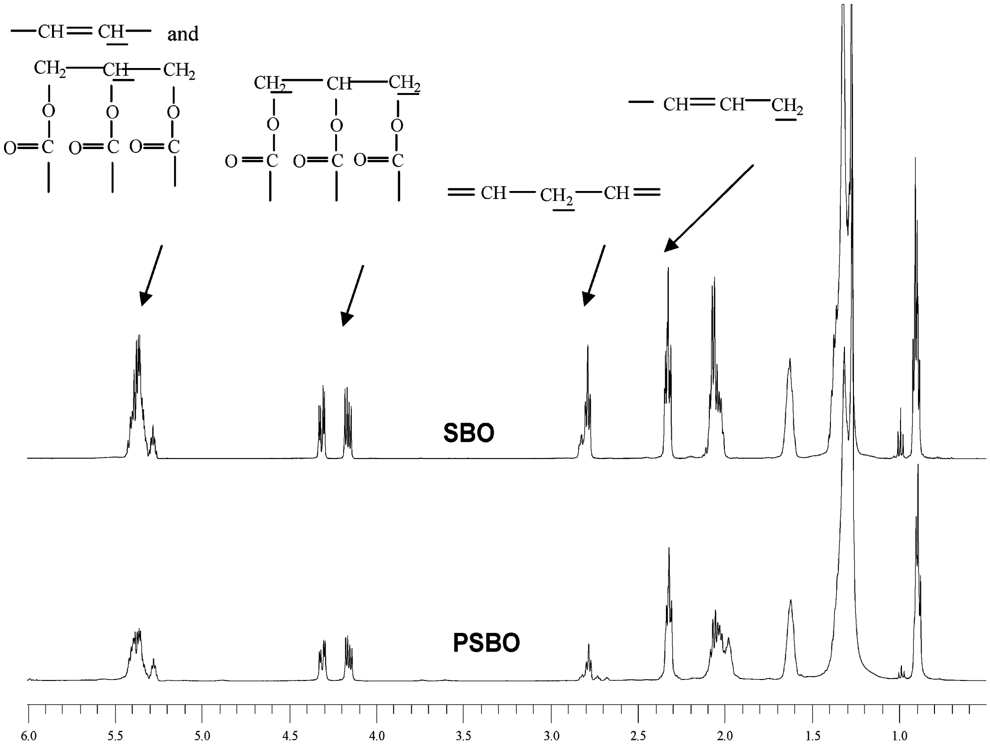

Figure 3. ^{1}H NMR spectra of SBO and PSBO.

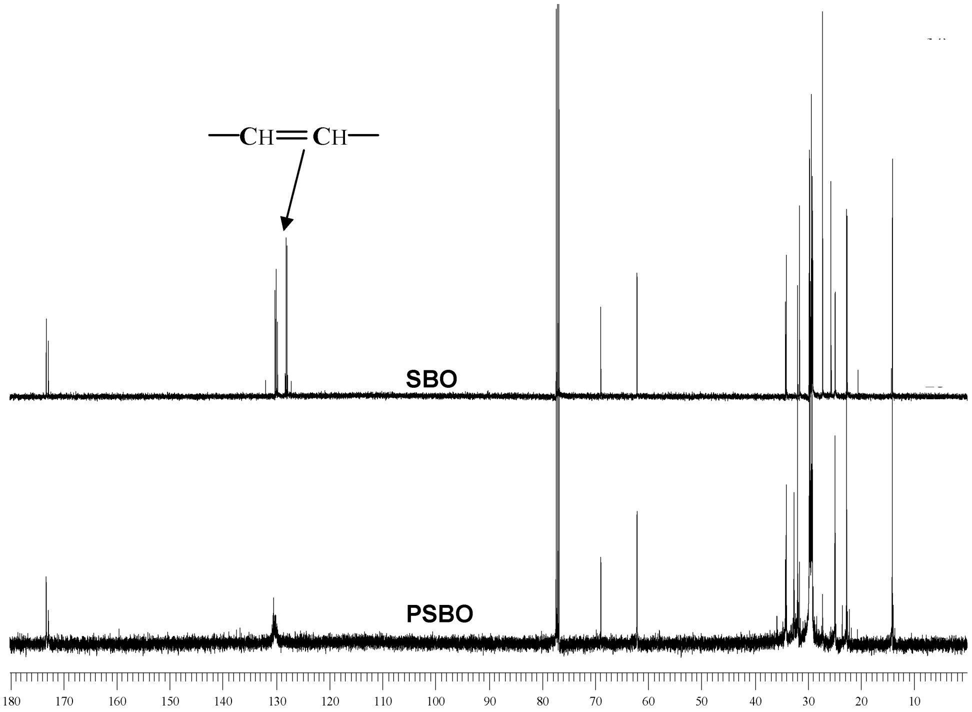

Figure 4. ^{13}C NMR spectra of SBO and PSBO.

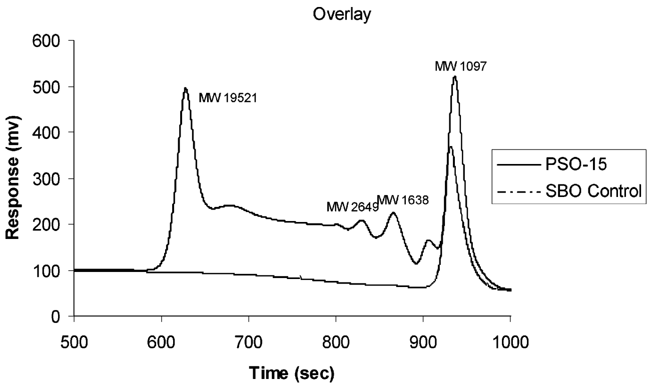

Figure 5. Overlays of SBO (control) and PSBO obtained from the RI detector of the GPC.

Figure 4 shows ^{1}H NMR spectra of SBO and PSBO. The signals at 5.40 ppm are characteristic for olefinic hydrogens, and the signal at 5.1−5.3 ppm are the methine protons of the $-CH_2-C\mathbf{H}-CH_2-$ (glycerin) backbone. The signals at 4.0−4.4 ppm are the methylene protons of the $-C\mathbf{H}_2-CH-C\mathbf{H}_2-$ (glycerin) backbone. The peak at 2.80 ppm corresponds to the protons in the $C\mathbf{H}_2$ groups between two carbon−carbon double bonds. The signals at 2.10 ppm are the α-methylene protons $C\mathbf{H}_2$ adjacent to the carbon−carbon double bonds. It can be seen from Figure 4 that the peaks at 5.1−5.4, 2.80, and 2.1 ppm of PSBO greatly decreased. This observation indicated that the polymerization of SBO occurred and the number carbon−carbon double bonds was reduced. Figure 5 shows ^{13}C NMR spectra for SBO and PSBO. The peaks at 127−132 ppm are due to olefinic carbons. It is also observed that peaks at 127−132 ppm of PSBO decreased after polymerization. Figure 6 shows ^{1}H NMR spectra of SBO and PSBO at different amounts of initiator ranging from 1.0 to 2.5 g. Figure 7 shows ^{13}C NMR spectra of PSBO at the quantities of initiator mentioned above. The intensities of olefins and associated peaks in ^{1}H NMR spectra (5.1−5.3, 2.80, and 2.1 ppm) and ^{13}C NMR spectra (127−132 ppm) are apparently reduced for PSBO compared to those of SBO as the amount of catalyst increased. The decrease in the peak intensities of olefins and associated peaks results from the polymerization of SBO. The viscosity data also shows that viscosity increased with an increasing amount of catalyst amount.

Polymerization Temperature Effects. The effect of polymerization temperature on the molecular weight was investigated in a series of polymerizations conducted at temperatures ranging from 100 to 140 °C and at a constant pressure of 110 bar. In all of these experiments, the monomer, SBO, and other reaction conditions are kept constant as mentioned in Table 3. As shown in Table 3 the weight average molecular weight increased with increasing temperature. The molecular weight changed from 1,384 to 22,814. The reason is that the soybean oil itself has a relatively large molecular weight and the active site, i.e., carbon−carbon double bonds, is located in the middle of the fatty acid chain. The activity of these double bonds is relatively low compared to that of carbon−carbon double bonds located at the end of the chain. In this sense, the higher activation energy is needed. Another reason is higher temperature increases the solubility of soybean oil in $scCO_2$, therefore increasing the polymerization rate. Figure 8 shows ^{1}H NMR spectra of PSBO at different polymerization temperatures. As can be seen from Figure 8 the intensity of the peak at 5.40 ppm for olefinic hydrogens decreased with increased polymerization temperature. Figure 9 shows the ^{13}C NMR spectra of PSBO at different polymerization temperatures, and the peak at 127−132 ppm for olefinic carbon decreased. From this observation, it is evident that polymerization of soybean oil has taken place.

Pressure Effects. The pressure effect has been studied by changing the pressure of CO_2, while keeping temperature at 120 °C and using 100 g of the monomer, SBO. The results listed in Table 4 were obtained as the pressure was increased from 55 to 121 bar. It is noted that the higher pressure resulted in higher molecular weights. Additionally, it is important to note that as

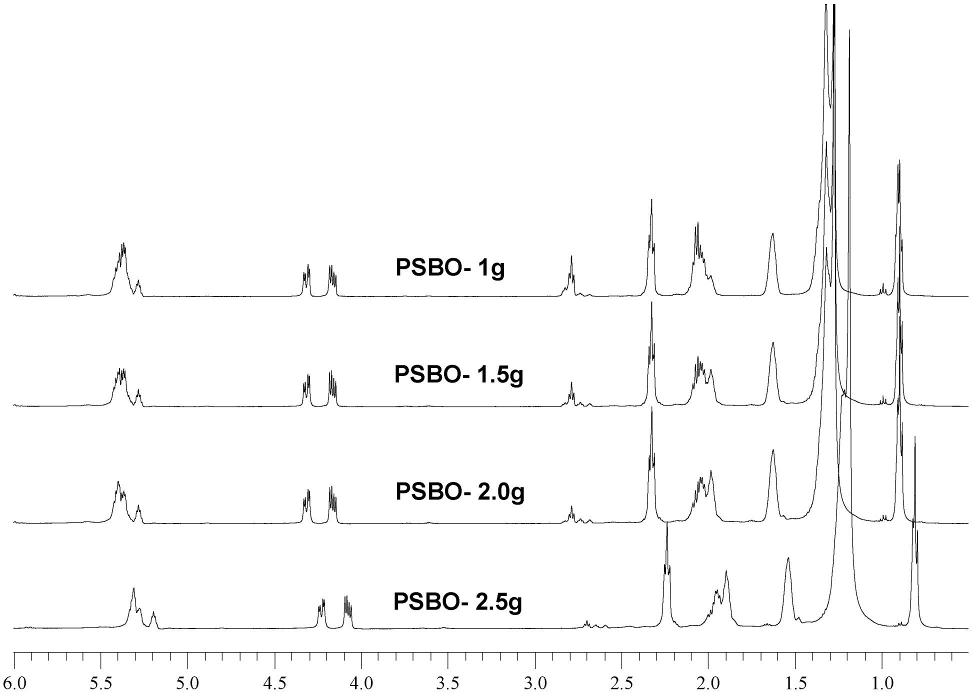

Figure 6. ^{1}H NMR spectra of PSBO obtained with different amounts of catalyst.

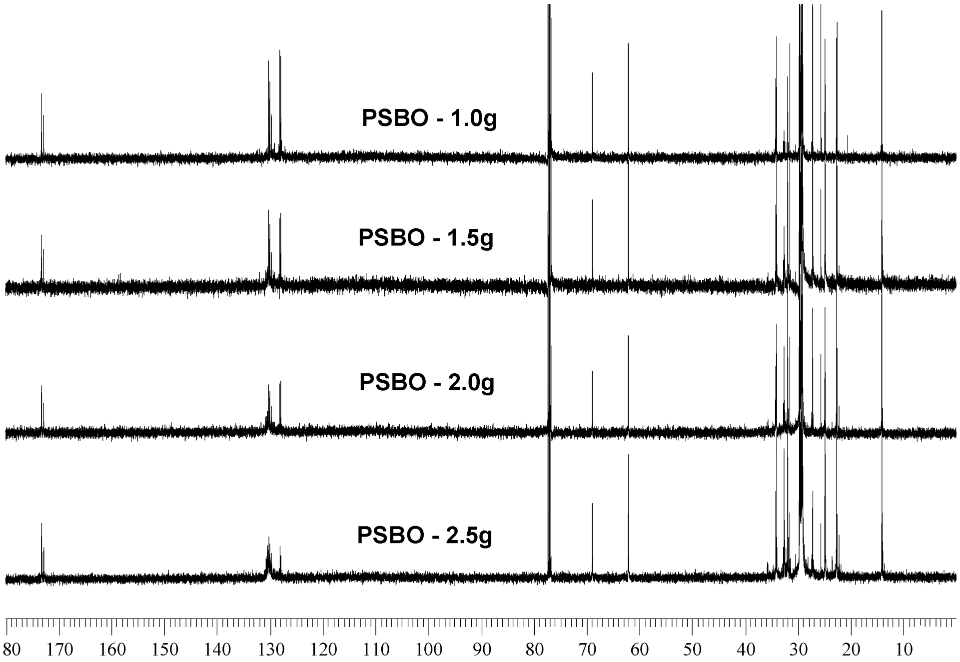

Figure 7. ^{13}C NMR spectra of PSBO obtained with different amounts of catalyst.

Table 3. Effect of Polymerization Temperature on the Molecular Weight of PSBO

entry	SBO (g)	*P* (bar)	*T* (°C)	reaction time (h)	catalyst amount (g)	viscosity (mPa s)	M_w (g/mol)
1	100	110	110	2	2.0	297	1384
2	100	110	120	2	2.0	722	10 480
3	100	110	130	2	2.0	6790	17 451
4	100	110	140	2	2.0	80 233	22 814

initial pressure was increased from 55 to 69 bar a slight increase in the molecular weight of PSBO was observed, changing from 1,536 to 2,863 g/mol. While the pressure increased to 121 bar, the molecular weight of PSBO increases to 11,349 g/mol. A possible explanation for this observed behavior at higher pressures is the increase in solubility of soybean oil in scCO$_2$. The better solubility of soybean oil in scCO$_2$ will provide a higher polymerization rate.

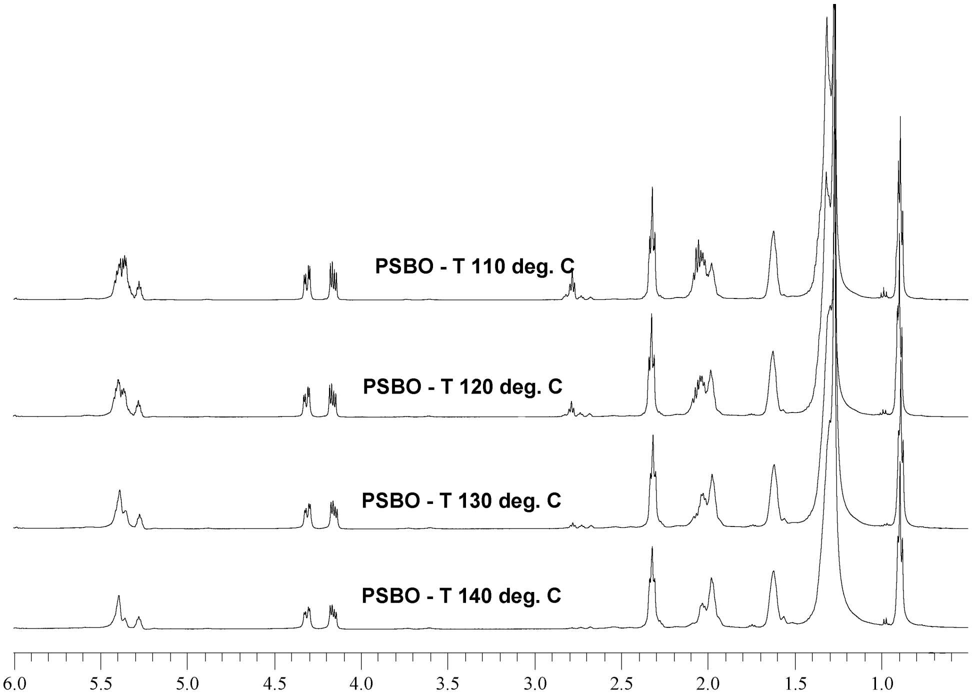

Figure 8. ^{1}H NMR spectra of PSBO obtained at different polymerization temperatures.

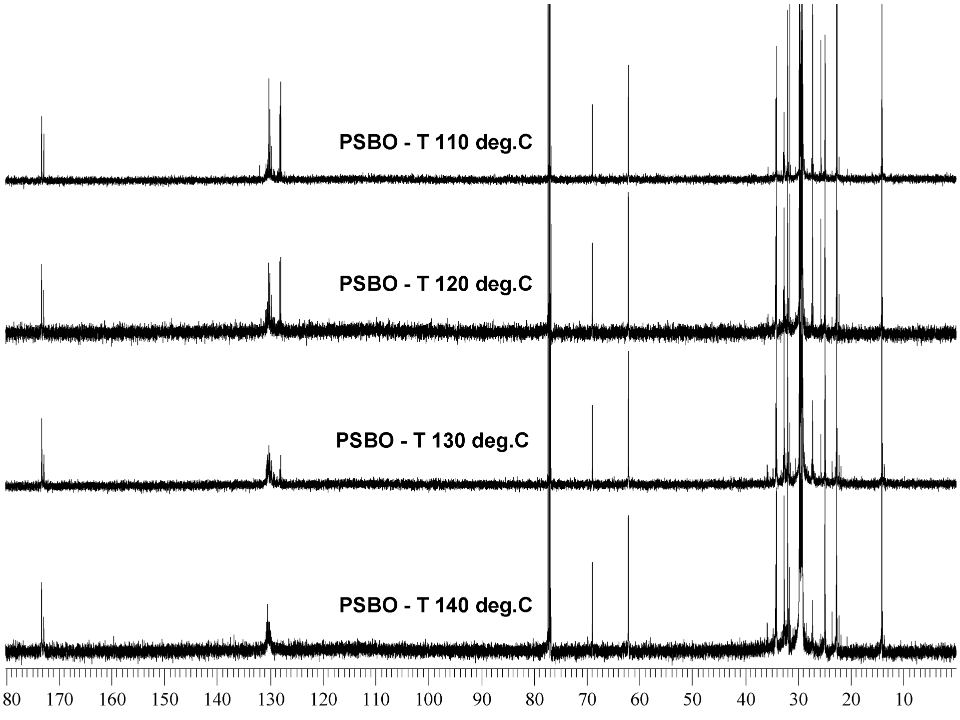

Figure 9. ^{1}H NMR spectra of PSBO obtained at different polymerization temperatures.

Table 4. Effect of Pressure on the Molecular Weight of PSBO

entry	SBO (g)	*P* (bar)	*T* (°C)	reaction time (h)	catalyst amount (g)	viscosity (mPa s)	M_w (g/mol)
1	100	55	120	2	2.0	84	1536
2	100	69	120	2	2.0		2863
3	100	76	120	2	2.0	276	4152
4	100	93	120	2	2.0	440	6228
5	100	100	120	2	2.0	458	6699
6	100	110	120	2	2.0	722	10 480
7	100	121	120	2	2.0		11 349

Conclusions

In this paper the soybean oils were polymerized in the $scCO_2$ medium initiated by $BF_3{\cdot}O(C_2H_5)_2$. Analysis of the ^1H and ^{13}C NMR spectra of the polymer gives a strong indication of soybean oil polymer formation. The resulting polymers with molecular weights ranging from 1,384 to 22,814 g/mol were observed. The effects of temperature, pressure, and catalyst concentration have been evaluated experimentally. Overall, this polymerization of soybean oil in the $scCO_2$ medium offers the potential for several key advances, including (i) the ability to produce liquid soy polymers that could be used as lubricants and hydraulic fluids and (ii) "green" processing methods.

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