Boron trifluoride catalyzed ring-opening polymerization of epoxidized soybean oil in liquid carbon dioxide†

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Ring-opening polymerization of epoxidized soybean oil (ESO) catalyzed by boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$), in liquid carbon dioxide, was conducted in an effort to develop useful biobased biodegradable polymers. The resulting polymers (RPESO) were characterized by FTIR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), ^{1}H NMR, ^{13}C NMR, solid state ^{13}C NMR spectroscopies and gel permeation chromatography (GPC). The results indicated that ring-opening polymerization of ESO occurred at mild conditions, such as at room temperature, and a subcritical CO_2 pressure of 65.5 bar. The formed RPESO materials were highly crosslinked polymers. The glass transition temperatures of these polymers ranged from −11.9 °C to −24.1 °C. TGA results showed that the RPESO polymers were thermally stable at temperatures lower than 200 °C and significant decomposition mainly occurred above 340 °C.

Introduction

Recently, attention has been focused on the development of environmentally friendly replacements for volatile organic solvents.[1–4] One promising candidate is supercritical carbon dioxide ($scCO_2$). The low toxicity of CO_2 and lack of toxic solvent residues in the final products make CO_2 an attractive medium for the synthesis and processing of polymers and biomaterials.[5–7] Also CO_2 is inexpensive, readily available and nonflammable.

The most studied polymerizations in supercritical CO_2 are those using a free-radical mechanism. For example, the polymerization of styrene and different methacrylates[8–11] were reported. Since fluorinated polymers exhibit superior properties such as chemical inertness, high thermal stability, excellent weatherability, low flammability, low dielectric constant, low refractive index, and so on, they are much more important polymers. Some researchers reported fluorinated polymers prepared in $scCO_2$ in order to omit fluorinated solvent, such as trifluoromethane.[12–14] In particular, conducting homogeneous phase and precipitation polymerizations in $scCO_2$ in order to avoid the use of any stabilizers appears to be very promising. However, ionic polymerizations,[15] such as ring opening polymerizations (ROPs),[16–18] are less documented in the literature.

Current interest in cheap, biodegradable polymeric materials has encouraged the development of such materials from readily available, inexpensive renewable resources.[19] Among synthesized biobased products from agricultural resources, natural oils are useful raw materials in the synthesis of polymers to replace or augment traditional petrochemically-based polymers. Increasing social emphasis on issues concerning the environment, waste disposal, the depletion of non-renewable resources and high crude oil prices are the main reasons driving development of biobased products. Natural oils are triacylglyceride esters comprised of three fatty acids joined by a glycerol center.[20] Natural oils such as linseed and tung oil have long found various uses in the coatings, printing inks and varnish industries. Soybean oil, safflower oil, sunflower oil and canola oil have also been used in industrial applications including: plastics; lubricants; adhesives; inks; paints; coatings; fuels/biodiesel; solvents; surfactants.[21–27]

In 2009 soybeans accounted for about 23.4% of planted acreage in the United States, just behind corn, which accounts for about 26.1%, and ahead of wheat, which accounts for about 18.0%. Because oil comprises ~20 wt% of a soybean, that soybean oil plays an important part in the renewable resource economy of the United States. Soybean oil possesses three unsaturated fatty acids, oleic (23%), linoleic (54%) and linolenic (8%), which contain 1, 2, and 3 double bonds, respectively, in their hydrocarbon chains.[28] These double bonds are reactive sites and allow for the chemical modifications of soybean oil for various applications. On the other hand, because the double bond location is in the middle of the fatty acid chain, their activities are relatively low compare to double bounds located at the end of a chain. However, these double bonds may be converted into more reactive oxirane (or epoxide) moieties by reaction with peracids or peroxides. Epoxidized soybean oil (ESO) used as a raw material for the synthesis of new polymers has been reported.[29–33] Recently Liu and Erhan reported the direct polymerization of ESO in dichloromethane solvent.[34] Although ESO is liquid at room temperature, it is difficult to

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† Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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get homogenous polymers without reaction media due to its relative high viscosity (4.2 St at 25 °C), and large molecular weight (1000 g mol^{-1}).

As discussed above, $scCO_2$ is an environmentally benign medium for the polymerizations. The critical parameters of CO_2 are P_c (critical pressure) of 73.8 bar and T_c (critical temperature) of 31.1 °C. Although the critical temperature is low, obtaining the high critical pressure may not be easy. However, carbon dioxide in the liquid state provides many of the advantages of the supercritical system, but at a lower pressure and temperature. In this study, we report the boron trifluoride catalyzed ring-opening polymerization of ESO in liquid carbon dioxide medium as depicted in Fig. 1. The formed polymers are referred to as RPESO polymers. Effects of polymerization temperature, initiator concentration and monomer concentration on the thermal properties of RPESO polymers were investigated. The structure of the RPESO polymers was characterized and confirmed using FTIR, ^{1}H NMR, ^{13}C NMR, and solid state ^{13}C NMR spectroscopy. The thermal properties of these polymers were studied by DSC and TGA.

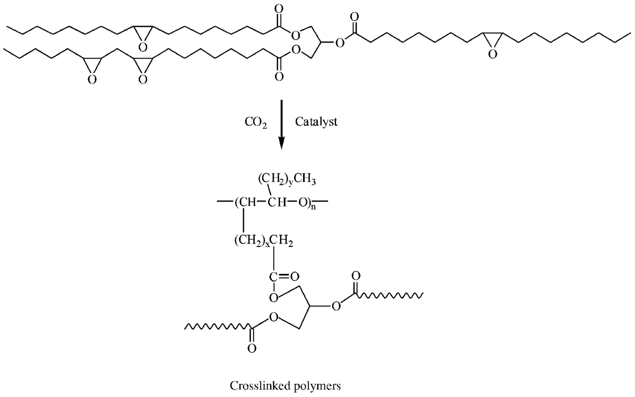

Fig. 1 Scheme for the synthesis of RPESO.

Experimental

Materials

ESO was obtained from Elf Atochem Inc. (Philadelphia, PA, USA) and used as received. Purified and redistilled boron trifluoride diethyl etherate, ($BF_3{\cdot}O(C_2H_5)_2$), was obtained from Aldrich Chemical Inc. (Milwaukee, WI, USA). Carbon dioxide (>99.8%) was obtained from Linde Gas LLC. (Independence, OH, USA). Sodium bicarbonate was purchased from Aldrich Chemical Inc. (Milwaukee, WI, USA). Tetrahydrofuran (THF), A.C.S. grade, and hexane (≥98.5%) were obtained from Aldrich Chemical Inc. (Milwaukee, WI, USA).

Analysis

Infrared. FTIR-ATR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI, USA) coupled with Smart ARK accessory for liquid samples in a scanning range of 650–4000 cm^{-1} for 32 scans at a spectral resolution of 4 cm^{-1}. Solid samples were recorded on this FTIR system coupled with Smart Orbit accessory.

NMR. ^{1}H NMR and ^{13}C NMR spectra for extracted soluble substances from RPESO samples were recorded using a Bruker ARX 500 NMR spectrometer (Bruker, Rheinstetten, Germany) operating at a frequency of 500.13 and 125.77 MHz, respectively, using a 5 mm inverse *Z*-gradient probe in $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA, USA). Solid state ^{13}C NMR spectra for extracted insoluble substances were recorded using a Bruker ARX-300.

GPC. GPC profiles were obtained on a Waters HPLC system including a 1515 isocratic HPLC pump, 717 plus automated injector, and column heater, controlled with Breeze software, obtained from Waters Corporation (Milford, MA, USA). Columns used for separation were a pair of PLgel 3 μm MIXED-E, 300 × 7.5 mm and a PLgel 5 μm Guard, 50 × 7.5 mm (part number PL1110-6300, PL1110-1520, respectively) from Polymer Laboratories (Varian Inc., Amherst, MA, USA). Signals generated from a miniDAWN TREOS triple-angle light scattering detector and Optilab rEX refractive index detector, obtained from Wyatt Technology Corporation (Santa Barbara, CA, USA) were processed using ASTRA V macromolecular characterization software, also from Wyatt Technology Corporation. THF was used as the mobile phase at a flow rate of 1 mL min^{-1}, and columns were maintained at 40 °C. The liquid phase samples were brought into solution with tetrahydrofuran stabilized with butylated hydroxytoluene from Fisher Scientific (Suwanee, GA, USA) at a known concentration near 4.00×10^{-3} g mL^{-1}. The Waters Autosampler was used to make 100 μL injections from a 1 mL sample vial. 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 RPESO. Astra V software was used to calculate molecular weight.

DSC. DSC thermograms of the test samples were recorded using a TA Instruments (New Castle, DE, USA) Q2000 model with an autosampler. Typically about 10 mg of the RPESO sample was accurately weighed in an aluminium pan and sealed with pin-perforated lids. The DSC oven was ramped at 10 °C per minute to 110 °C to eliminate thermal history and possible moisture. A refrigerated cooling system was used to equilibrate the sample at –90 °C, from 110 °C at a rate of 5 °C per minute. Data was recorded while the oven temperature was raised from –90 °C to 320 °C at a rate of 5 °C per minute. The DSC method applied an inert atmosphere by purging the oven with nitrogen at 50 mL per minute. Thermal Advantage and Universal Analysis software provided by TA instruments were used for data analysis.

TGA. A TA Q500 thermogravimeter with an autosampler from TA Instruments (New Castle, DE, USA) was used to measure the weight loss of the RPESO samples under a flowing nitrogen atmosphere. Generally, 20 mg of RPESO sample was used in the thermogravimetric analysis. The samples were heated from 30 to 600 °C at a heating rate of 10 °C min^{-1} and the weight loss was recorded as a function of temperature.

Ring-opening polymerization procedure in CO_2

Ring-opening polymerization reactions were carried out in a 300 mL high pressure reactor. The reactor was a Parr (Moline, IL, USA) 4560 mini benchtop unit equipped with a Parr 4843 controller and thermocouple. The reactor body was equipped with quartz viewing windows. The schematic diagram of the experimental set-up used for ring-opening polymerization of ESO is depicted in Fig. 2. 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, 30 g of ESO (the liquid sample shown in Fig. 3) 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 reactor pressure, 62.1 bar, was reached. A controller (Parr 4843) was used to control temperature. Once the reactor was brought to the appropriate temperature, $BF_3{\cdot}OEt_2$ was charged into the reactor by using a Rheodyne injector. Then CO_2 was pumped in to clear the injection loop at a pump pressure of 65.5 bar. After reaction for 2 h, 2 mL of ethanol–H_2O (1 : 1) was added to the reactor to deactivate the catalyst. The white polymers (RPESO) shown in Fig. 3 were washed sequentially with H_2O, 5% aqueous sodium bicarbonate, and H_2O. The RPESO polymer (shown in Fig. 3, in the dish) was dried in the vacuum at 60 °C. About 28–30 g RPESO sample was obtained. Soxhlet extraction with hexane as the refluxing solvent was used to extract the soluble substance from the RPESO samples for FTIR, ^{1}H NMR, ^{13}C NMR spectroscopy and molecular weight characterization. The insoluble substances remaining after Soxhlet extraction were used for DSC, TGA and solid ^{13}C NMR spectroscopic analyses.

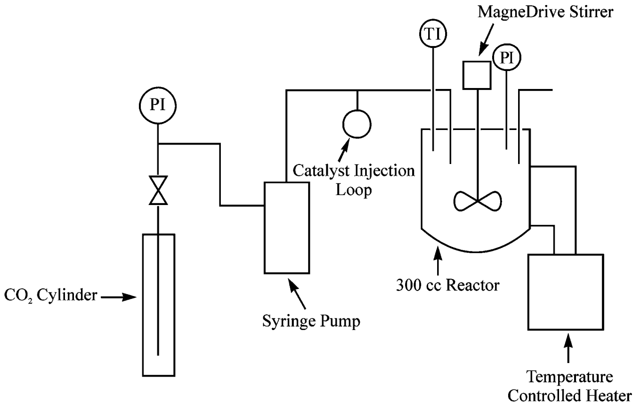

Fig. 2 Schematic diagram of the experimental set-up.

Fig. 3 Photo of RPESO polymers (dish) and starting material, ESO (bottle).

Results and discussion

1. Effect of temperature

The ring-opening polymerization of ESO was conducted at different temperatures ranging from 20 °C to 35 °C. A control experiment was also conducted at 20 °C without initiator ($BF_3{\cdot}OEt_2$). Fig. 4 shows the FTIR spectra of ESO and the control experiment. It can be seen that the characteristic oxirane absorption at 838 cm^{-1} in ESO is also present in the ESO control experiment. This means no ring-opening polymerization or other side reactions occur under these conditions.

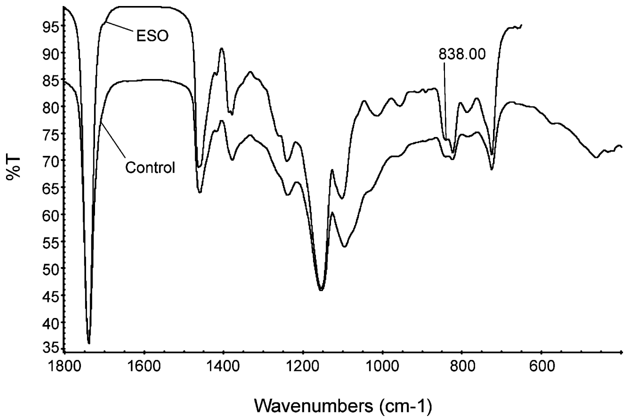

Fig. 4 FTIR spectra of ESO and ESO control experiment.

The glass transition temperature (T_g) of the RPESO polymers synthesized with $BF_3{\cdot}OEt_2$ catalyst (non-soluble fraction after extraction) was measured by DSC. It is well known that the crosslinking density influences T_g. As the crosslinking density decreases, the free volume of a material increases, and T_g decreases correspondingly. Fig. 5 shows a typical DSC curve of RPESO-I prepared with 2.79 mmol of $BF_3{\cdot}OEt_2$ at 20 °C. The T_g was determined to be the temperature at the inflection point. The results of measured T_g of the RPESO polymers prepared at various temperatures are summarized in Table 1. As can be seen from Table 1 there is a slight decrease of the T_g of the RPESO

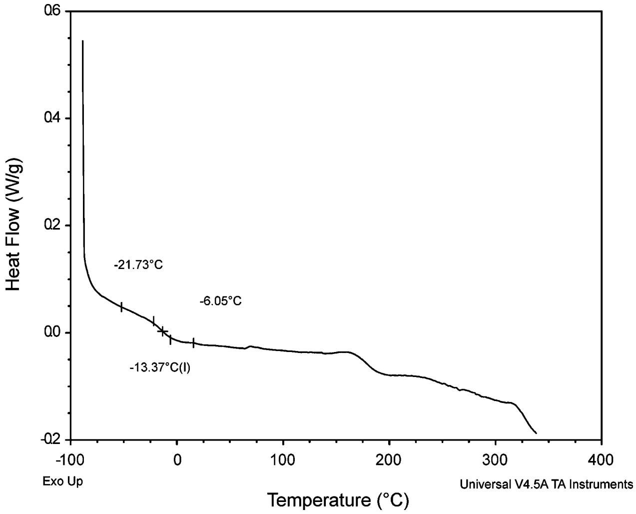

Fig. 5 DSC measurement of RPESO-I.

Table 1 The glass transition temperatures of RPESO prepared at various temperatures

Samples	Polym. temp./°C	Initiator/mmol	T_g/°C
RPESO-I	20	2.79	−13.4
RPESO-II	25	2.79	−15.9
RPESO-III	30	2.79	−16.8
RPESO-IV	35	2.79	−17.7

polymers as the polymerization temperature is increased from 20 °C to 35 °C.

It is well known that the most important factor that determines whether a cyclic monomer can be converted to a polymer is thermodynamic. It is the relative stabilities of the cyclic monomer and formed polymer structure that control the reaction favorability.[35,36] Ring-opening polymerization of a 3-membered ring is favored thermodynamically (ΔG, free-energy change, is negative).[37] Considering the thermodynamic relation $\Delta G = \Delta H - T\Delta S$, where ΔH is enthalpy change, ΔS is entropy change, T is temperature (K). At the temperatures used in this system, ΔH is the major factor for determining ΔG for the 3-membered ring, while ΔS would be more important for the 5- and 6-membered ring-opening reactions. The reported value of ΔH is strongly negative (−13.0 kJ mol^{-1}) for the 3-membered ring.[35,36] Therefore, temperature, T, is not a significant factor in this reaction. Therefore, since multiple epoxy groups are present in the ESO molecules, the crosslinked polymers are easily formed by ring-opening polymerization.

2. Soxhlet extraction and identification of structure of RPESO soluble

All the RPESO samples were extracted with hexane refluxing in a Soxhlet extractor for 16 h. The extracted soluble substances from the RPESO samples ranged from 3 to 24 wt%, as shown in Table 2. The extracted soluble substances and insoluble substances were characterized by analysis methods mentioned above. The results are described below.

Fig. 6 shows FTIR spectra of ESO, the hexane-extracted soluble substances, and the insoluble portion of an RPESO sample. It can be clearly seen that absorption at 838 cm^{-1} for the oxirane group has disappeared in the IR spectra of insoluble RPESO indicating that ring-opening polymerization of ESO has taken place. The data also show the oxirane absorption band from ESO is not present in the hexane-extracted soluble substances. The results suggest the hexane-extracted soluble substances are the ring-opening products with low molecular weights.

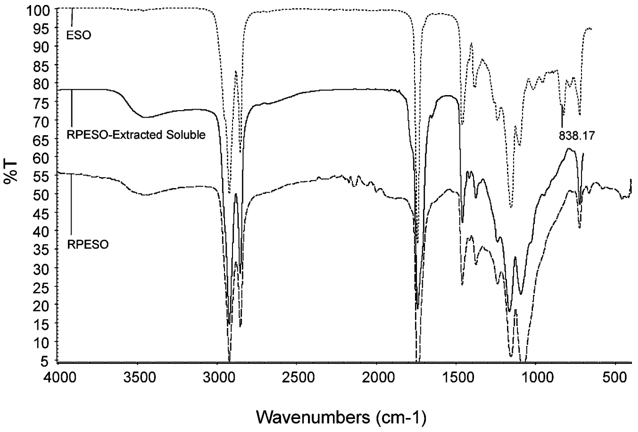

Fig. 6 FTIR spectra of RPESO polymer (soluble and insoluble fractions) and starting material, ESO.

Fig. 7 shows ^{1}H NMR spectrum of the extracted soluble substances. The disappearance of the peaks at δ 3.0–3.2 ppm region related to epoxy protons is apparent. The methine proton

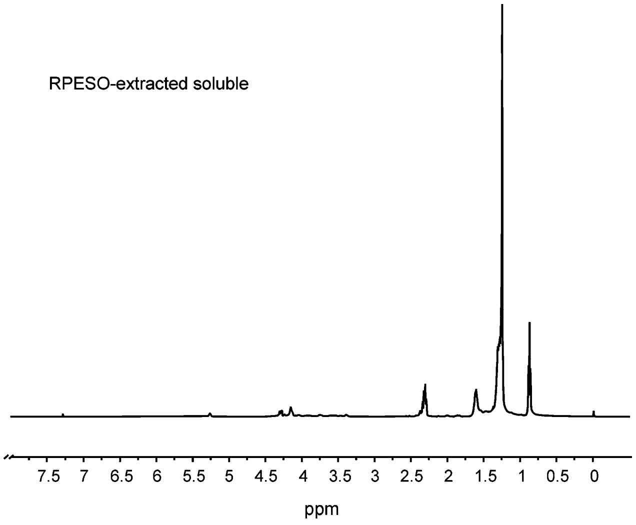

Fig. 7 ^{1}H-NMR spectra of extracted hexane-soluble fraction of RPESO.

Table 2 Data related to the extracted soluble substances from RPESO polymers

					Soxhlet extraction (wt%)	
Samples	Polym. temp./°C	Initiator/mmol	Monomer/mol	M_w(soluble)/g mol^{-1}	Soluble	Insoluble
RPESO-I	20	2.79	0.03	1040	21	79
RPESO-II	25	2.79	0.03	1937	5	95
RPESO-III	30	2.79	0.03	1429	16	84
RPESO-IV	35	2.79	0.03	1237	17	83
RPESO-V	25	1.87	0.03	2364	11	89
RPESO-VI	25	4.75	0.03	3606	3	97
RPESO-VII	25	7.72	0.03	3318	7	93
RPESO-VIII	25	2.79	0.04	4578	24	91
RPESO-IX	25	2.79	0.05	3066	20	94
RPESO-X	25	2.79	0.06	3349	17	83

–CH_2–**CH**–CH_2– of the glycerol backbone at *δ* 5.1–5.3 ppm, and methylene protons –$\mathbf{CH_2}$–CH–$\mathbf{CH_2}$– of the glycerol backbone at *δ* 4.0–4.4 ppm are observed. The ^{13}C NMR spectrum of a hexane-extracted soluble fraction is shown in Fig. 8. The peaks at *δ* 54–57 ppm corresponding to epoxy carbons have disappeared. Peaks at *δ* 69 ppm and *δ* 63 ppm assigned to **CH** and $\mathbf{CH_2}$ carbons of –$\mathbf{CH_2}$–**CH**–$\mathbf{CH_2}$– glycerol backbone are observed. The information from ^{1}H NMR and ^{13}C NMR spectroscopy confirms that the extracted soluble substances are the ring-opening products of ESO. Their molecular weights were then determined by GPC analysis.

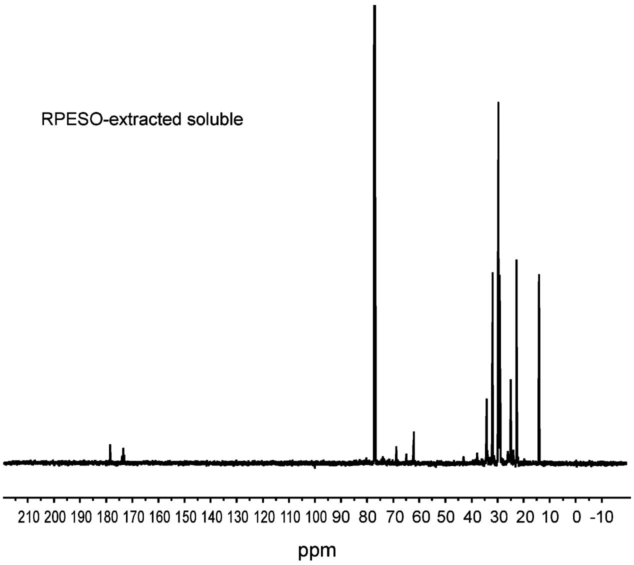

Fig. 8 ^{13}C-NMR spectra of extracted hexane-soluble fraction of RPESO.

The insoluble substances remaining after Soxhlet extraction are the highly crosslinked polymers. These materials are not soluble in solvents such as THF, $CHCl_3$ and CH_2Cl_2. Solid state ^{13}C NMR spectroscopy provided valuable information on these insoluble materials. Fig. 9 shows the solid state ^{13}C NMR spectrum of the insoluble substances obtained after the extraction of the RPESO sample. The spectrum clearly shows the presence of ester carbonyls (*δ* 167 ppm) from oil triglyceride structure. There is no signal at *δ* 52 ppm which shows that the carbon–carbon epoxy bond has disappeared. This indicates that ESO was polymerized through the ring-opening polymerization and the highly crosslinked polymers were formed.

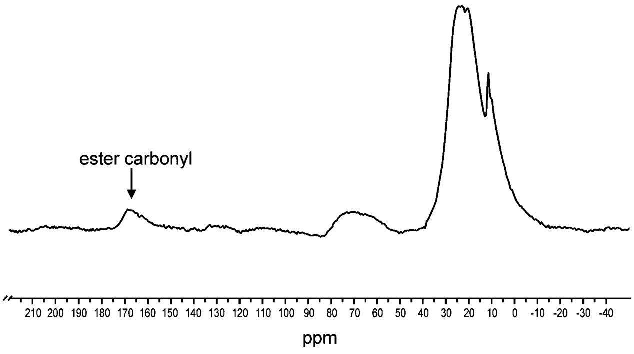

Fig. 9 Solid ^{13}C-NMR spectrum of RPESO.

Table 3 The glass transition temperatures of RPESO polymers prepared at various initiator loadings

Samples	Polym. temp./°C	Initiator/mmol	T_g/°C
RPESO-V	25	1.87	−13.8
RPESO-II	25	2.79	−15.9
RPESO-VI	25	4.75	−15.7
RPESO-VII	25	7.72	−24.1

The GPC profile results of the extracted soluble substances from RPESO polymers are summarized in Table 2. The average molecular weights range from about 1040 to 4578 g mol^{-1}. Along with the FTIR and NMR analysis, the GPC results are further evidence that the extracted soluble substances are the ring opening products of ESO with low molecular weights.

3. Effect of initiator concentration

The initiator loading, ranging from 1.87 mmol to 7.72 mmol, was determined to have an effect on the thermal properties of the resultant RPESO polymers. Table 3 shows that T_g decreases with increasing initiator loading. This result was expected, since the molecular weight of a linear polymer usually decreases with increasing initiator concentration. As discussed above, since the crosslink density of the polymer decreases as its molecular weight decreases its T_g decreases correspondingly. A comparison of the RPESO-VI and RPESO-I indicates that changing initiator loadings from 1.87 mmol to 7.72 mmol causes a T_g change from −13.8 to −24.1 °C in the resultant material. At this point, it is clear that initiator concentration critically affects the molecular weight of formed polymers thereby influencing the thermal properties.

4. Effect of monomer concentration

The effect of monomer loading, from 0.03 mol to 0.06 mol, on the thermal properties of the resultant RPESO polymers was studied. The results are summarized in Table 4. The glass transition temperature, T_g, decreased slightly with increasing monomer concentration. As expected, increasing monomer concentration created RPESO polymers with lower molecular weight. The lower molecular weights of polymers exhibit a lower T_g due to the lower crosslink density.

5. Thermal stability of RPESO

To better understand the thermal properties of RPESO polymers, TGA was used to investigate their thermal decomposition behavior under a nitrogen atmosphere. Fig. 10 shows the TGA curve of the RPESO-IX (non-soluble fraction after extraction).

Table 4 The glass transition temperatures of RPESO polymers prepared at various monomer amounts

Samples	Polym. temp./°C	Monomer/mol	T_g/°C
RPESO-II	25	0.03	−15.9
RPESO-VIII	25	0.04	−14.8
RPESO-IX	25	0.05	−13.8
RPESO-X	25	0.06	−11.9

Table 5 Thermal stability data of the RPESO polymers

Samples	200–220 °C	240–320 °C	340–450 °C
RPESO-I	5 wt% loss	13 wt% loss	82 wt% loss
RPESO-II	Stable	7 wt% loss	91 wt% loss
RPESO-III	5 wt% loss	14 wt% loss	81 wt% loss
RPESO-IV	3 wt% loss	12 wt% loss	82 wt% loss
RPESO-V	5 wt% loss	10 wt% loss	88 wt% loss
RPESO-VI	Stable	6 wt% loss	91 wt% loss
RPESO-VII	Stable	5 wt% loss	90 wt% loss
RPESO-VIII	5 wt% loss	15 wt% loss	82 wt% loss
RPESO-IX	2 wt% loss	12 wt% loss	83 wt% loss
RPESO-X	Stable	10 wt% loss	85 wt% loss

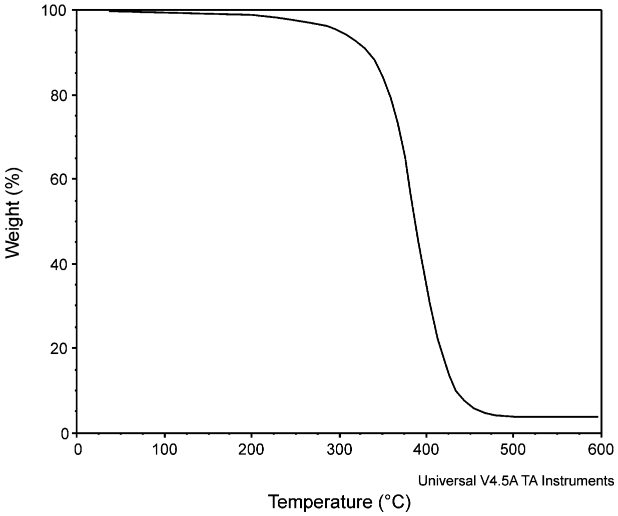

Fig. 10 TGA thermogram of RPESO-IX, weight loss *versus* temperature (under N_2 atmosphere).

It can be seen that the RPESO-IX appears to be thermally stable at temperatures below 200 °C. Two distinct temperature regions are observed where samples experienced weight loss. The material slowly loses about 2% of its weight at temperatures between 220 °C and 320 °C, followed by an abrupt weight loss of 80% between 340 and 437 °C. TGA measurement revealed a total 98% weight loss observed at temperatures between 240 and 437 °C. For the other RPESO samples obtained at various temperatures and initiator concentrations, their TGA curves have similar behavior to RPESO-IX. Some samples showed less than 5 wt% loss around 220 °C. Table 5 summarized the thermal stability results of RPESO polymers studied by TGA. It can be seen that in the first temperature region, about 15 wt% loss occurs and 79–91 wt% of the weight is lost in the second temperature region for all the RPESO polymers.

Conclusion

ESO has been polymerized by ring opening polymerization using $BF_3{\cdot}OEt_2$ initiator in liquid carbon dioxide. The ring-opening polymerization was employed at mild temperatures. The formed RPESO polymers were found to be typically highly crosslinked polymers. They have glass transition temperatures ranging from −11.9 °C to −24.1 °C. TGA analysis shows that all of the RPESO polymers appear to be thermally stable at temperatures lower than 200 °C, and decomposition temperature is found mainly after 340 °C. GPC results show the extracted soluble substances in the reaction are also ESO polymers, but with low molecular weights.

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