

New Soybean Oil–Styrene–Divinylbenzene Thermosetting Copolymers. I. Synthesis and Characterization

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ABSTRACT: The cationic copolymerization of regular soybean oil, low-saturation soybean oil (LoSatSoy oil), or conjugated LoSatSoy oil with styrene and divinylbenzene initiated by boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$) or related modified initiators provides viable polymers ranging from soft rubbers to hard, tough, or brittle plastics. The gelation time of the reaction varies from 1×10^2 to 2×10^5 s at room temperature. The yields of bulk polymers are essentially quantitative. The amount of crosslinked polymer remaining after Soxhlet extraction ranges from 80 to 92%, depending on the stoichiometry and the type of oil used. Proton nuclear magnetic resonance spectroscopy and Soxhlet extraction data indicate that the structure of the resulting bulk polymer is a crosslinked polymer network interpenetrated with some linear or less-crosslinked triglyceride oil–styrene–divinylbenzene copolymers, a small amount of low molecular weight free oil, and minor amounts of initiator fragments. The bulk polymers possess glass-transition temperatures ranging from approximately 0 to 105°C, which are comparable to those of commercially available rubbery materials and conventional plastics. Thermogravimetric analysis (TGA) indicates that these copolymers are thermally stable under 200°C, with temperatures at 10% weight loss in air (T_{10}) ranging from 312 to 434°C, and temperatures at 50% weight loss in air (T_{50}) ranging from 445 to 480°C. Of the various polymeric materials, the conjugated LoSatSoy oil polymers have the highest glass-transition temperatures (T_g) and thermal stabilities (T_{10}). The preceding properties that suggest that these soybean oil polymers may prove useful where petroleum-based polymeric materials have found widespread utility. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 658–670, 2001

Key words: soybean oil; cationic copolymerization; gelation; thermosets

INTRODUCTION

Nonbiodegradable, petroleum-based polymeric materials have brought about many environmental concerns.^{1,2} The growing demands for such nonrenewable, indestructible materials have increased our dependence on crude oil. Biodegradable polymeric materials, especially those prepared from

readily available, renewable, and inexpensive natural resources, such as carbohydrates, starch, and proteins, have thus become increasingly important. However, relatively little work has been done on the conversion of fats and oils to high molecular weight polymers.^{3,4}

Soybean oil is a biodegradable vegetable oil, which is readily available in bulk from a renewable natural resource. About 80% of the soybean oil produced each year is used for human food. A further 6% is used for animal feed, whereas the remainder (14%) finds nonfood uses (soap, fatty acids, lubricants, coatings, etc.).⁵ The polyunsatu-

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ration of soybean oil and low-saturation soybean oil (LoSatSoy oil), with still higher polyunsaturated fatty acid content,⁶ makes it possible to polymerize or copolymerize these natural oils into useful new materials. Boron trifluoride has been used to initiate polymerization of the methyl esters of the fatty acids of soybean oil.⁷ The polymeric oils obtained are dark in color, and have high acid numbers and a viscosity of P or above on the Gardner scale. Boron trifluoride ether complexes of dimethyl ether, diethyl ether, dioxane, and tetrahydrofuran have also been used as initiators. These initiators produce polymeric oils at 120–160°C with improved color. Polymerization of the free fatty acids of soybean oil has also been initiated by boron trifluoride, and the products are extremely viscous oils, although crosslinked gels have not been reported.⁸ Soybean oil itself has been directly used as an adhesive in the manufacture of pressboard.⁹ However, all work on the polymerization of soybean oil materials that has appeared so far in the literature has produced viscous oils, primarily by the polymerization or copolymerization of the fatty acids obtained from soybean oil.

We recently reported the direct conversion of soybean oil into useful solid polymers by cationic copolymerization with divinylbenzene initiated by boron trifluoride diethyl etherate or related modified initiators.¹⁰ The resulting polymers have room temperature moduli and glass-transition temperatures that are comparable to those of conventional plastics. However, the hard rigid polymers obtained have rather high crosslinking densities and nonuniform crosslinking structures.^{10,11} As a result, the soybean oil–divinylbenzene plastics are very brittle, which significantly limits their applications. Recently, much effort has been dedicated to improving the mechanical properties of these soybean oil polymers by deliberate structure design.¹²

In this work, styrene was used as a major comonomer. A small amount of divinylbenzene, norbornadiene, or dicyclopentadiene comonomer serves as a crosslinking agent to control the crosslinking density of the resulting polymers. It has been found that the use of monofunctional styrene successfully reduces the nonuniformity of the crosslinking structure. Thus, the mechanical properties of the resulting plastics have been significantly improved.¹² In addition to tough plastics, a wide range of viable polymeric materials, including elastomers, rubbery materials, and even functional polymeric materials (e.g., shape-memory polymers) have been obtained.

Almost all of the polymers prepared from the new styrene compositions have viable mechanical properties, making them suitable replacements for petroleum-based polymeric materials. This study reports our results on the synthesis and characterization of the soybean oil–styrene–divinylbenzene copolymers. The mechanical properties of the various polymeric materials will be discussed in a forthcoming study.¹²

EXPERIMENTAL

Materials

The natural oils used in this study are food-grade soybean oil and LoSatSoy oil commercially available in supermarkets, which have been used without further purification. Conjugated LoSatSoy oil was prepared by the rhodium-catalyzed isomerization of regular LoSatSoy oil.¹³ The percentage conjugation was calculated to be approximately 100%. Styrene, divinylbenzene, norbornadiene, and dicyclopentadiene were purchased from Aldrich Chemical (Milwaukee, WI) and used as received. The distilled-grade boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$) used to initiate cationic polymerization of the various soybean oils was also supplied by Aldrich. Norway Pronova fish oil ethyl ester (EPAX 5500 EE) and soybean oil methyl esters (Soygold-1100, Soygold-2000, and a Soygold methyl ester prepared from LoSatSoy oil; AG Environmental Products, L.L.C.) were used to modify the original initiator, boron trifluoride diethyl etherate.

Cationic Copolymerization

The following reaction procedure was usually employed, unless otherwise stated in the text. The desired amounts of styrene and divinylbenzene were added to the soybean oil. The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of a modified initiator. The modified initiator was prepared by mixing an additive, such as Norway fish oil ethyl ester or Soygold methyl ester, with the original initiator, boron trifluoride diethyl etherate. The modified initiator was usually required to produce homogeneous reactions, as well as homogeneous polymers. The total amount of reactants was around 65 g. The reaction mixture was then injected into a Teflon mold, which was sealed by silicon adhesive and heated for a given time at the appropriate temperatures, usually 12 h at room

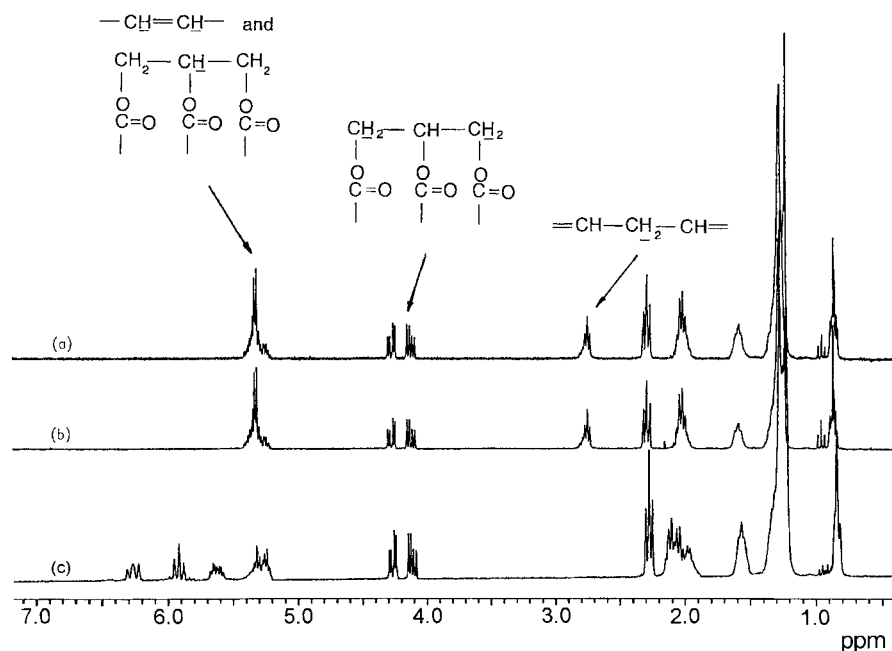


Figure 1 ^1H -NMR spectra of (a) regular soybean oil, (b) LoSatSoy oil, and (c) conjugated LoSatSoy oil.

temperature, followed by 12 h at 60°C and then 24 h at 110°C. The yields of resulting polymer are essentially quantitative. The nomenclature adopted in this work for the polymer samples is as follows: SOY, LSS, and CLS represent regular soybean oil, LoSatSoy oil, and conjugated LoSatSoy oil, respectively; ST is the styrene comonomer; DVB, NBD, and DCP represent divinylbenzene, norbornadiene, and dicyclopentadiene comonomers, which serve as crosslinking agents. BFE is the initiator boron trifluoride diethyl etherate. NFO, SGI, SGII, and SGIII are Norway fish oil ethyl ester, Soygold-2000, Soygold-1100, and LoSatSoy oil methyl ester Soygold, respectively. For example, LSS45-ST32-DVB15-(NFO5-BFE3) corresponds to a polymer sample prepared from 45 wt % LoSatSoy oil, 32 wt % styrene, 15 wt % divinylbenzene, and 8 wt % NFO-modified BFE initiator (5 wt % NFO plus 3 wt % boron trifluoride diethyl etherate).

Soxhlet Extraction by Methylene Chloride

A 2-g sample of the bulk polymer was extracted for 24 h with 100 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated by rotary evaporation and subsequent vacuum drying. The soluble substances were isolated for further characterization. The insoluble solid was dried under vacuum for several hours before weighing.

Characterizations

The glass-transition temperatures of the bulk polymers were obtained using a Perkin-Elmer dynamic mechanical analyzer DMA Pyris-7e (Perkin-Elmer, Foster City, CA) in a three-point bending mode. The rectangular specimens, which were made by copolymerizing the reactants in an appropriate mold, have a dimension of 20 × 5 × 2 mm. The measurements were performed at a heating rate of 3°C/min and a frequency of 1 Hz.

A Perkin-Elmer Pyris-7 thermogravimeter was used to measure the weight loss of the polymeric materials in air. The samples were heated from 30 to 650°C at a heating rate of 20°C/min. Generally, 6 mg of bulk polymer was used in the thermogravimetric analysis. All ^1H -NMR spectra were recorded in CDCl_3 using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 300 MHz.

RESULTS AND DISCUSSION

Molecular Structures and the Homopolymerization of Soybean Oil, LoSatSoy Oil, and Conjugated LoSatSoy Oil

Figure 1(a) shows the ^1H -NMR spectrum of regular soybean oil. The peaks at 4.1–4.4 ppm originate from the protons in the methylene groups of

the triglyceride moiety. The vinylic hydrogens are detected at 5.2–5.5 ppm. The protons in the CH₂ groups between two carbon–carbon double bonds appear at 2.7–2.8 ppm. The regular soybean oil is calculated from the ¹H–NMR spectrum to have approximately 4.5 carbon–carbon double bonds per triglyceride. The three side chains of the soybean oil triglyceride are typically composed of esters comprising 20–30% oleic acid (one C=C), 50–58% linoleic acid (two C=C), and 5–10% linolenic acid (three C=C). Figure 1(b) shows that the low-saturation soybean oil (LoSatSoy oil) used in this study has a structure similar to that of the regular soybean oil, but with relatively more carbon–carbon double bonds in the triglyceride side chains. Specifically, the LoSatSoy oil has approximately 5.1 carbon–carbon double bonds per triglyceride based on the ¹H–NMR calculation. Figure 1(c) is the ¹H–NMR spectrum of the conjugated LoSatSoy oil. It clearly shows that conjugation does not change the triglyceride structure or the degree of unsaturation of the LoSatSoy oil. The peaks at 2.7–2.8 ppm, which correspond to the protons in the CH₂ groups between two carbon–carbon double bonds, completely disappear. The percentage conjugation, which is calculated by integrating the vinylic hydrogens (5.36/5.61–6.33 ppm) in the conjugated LoSatSoy oil and taking into account the known fatty acid composition of this oil, is approximately 100%.

The high degree of unsaturation of the regular soybean oil and LoSatSoy oil makes it possible to polymerize these triglyceride oil molecules into high-molecular polymers using boron trifluoride diethyl etherate as an initiator.^{14–16} The reactivity of the carbon–carbon double bonds in the triglyceride oil is expected to increase upon conjugation. However, because of chain branching and the resulting low mobility of the oil, plus the limited miscibility between the triglyceride oil and the initiator boron trifluoride diethyl etherate,¹⁰ the homopolymerization of regular soybean oil, LoSatSoy oil, and even conjugated LoSatSoy oil results in only viscous fluids or soft weak polymers with limited utility.

Cationic Copolymerization of Soybean Oil, LoSatSoy Oil, or Conjugated LoSatSoy Oil with Styrene and Divinylbenzene, Norbornadiene, or Dicyclopentadiene

Hard, rigid polymers have been produced by cationic copolymerization of the various soybean oils

with a more reactive comonomer, that is, divinylbenzene.¹⁰ However, because of the high crosslinking density and nonuniform crosslinking structure,^{10,11} the resulting hard plastics are very brittle, which significantly limits their applications. It has been found that the use of monofunctional styrene successfully reduces the nonuniformity of the crosslinking structure. Thus, the mechanical properties of the resulting polymers are significantly improved.¹² In this study, styrene was used as the major comonomer. A small amount of divinylbenzene, norbornadiene, or dicyclopentadiene was used to control the crosslinking density of the resulting polymers.

Styrene and divinylbenzene are monomers suitable for cationic polymerization.^{14–16} They have lower molecular weights and much higher densities of carbon–carbon double bonds per molecule than do the various soybean oils used in this study. Conjugation of the carbon–carbon double bonds with the aryl group in these molecules makes these monomers quite reactive toward cationic polymerization. In fact, addition of 0.1 wt % of the BF₃·OEt₂ initiator to pure styrene or divinylbenzene produces a very rapid reaction. Thus, the copolymerization of mixtures of the less-reactive soybean oil with the more-reactive styrene and divinylbenzene results in moderate reactions. A wide range of viable polymeric materials can be obtained when appropriate compositions are employed.¹²

Like the soybean oil–divinylbenzene systems we studied earlier,¹⁰ the copolymerization of the triglyceride oil, styrene, and divinylbenzene is also heterogeneous when using the initiator boron trifluoride diethyl etherate. The reason for the heterogeneous reactions appears to be the immiscibility of the triglyceride oil and the initiator.¹⁰ In the triglyceride oil–styrene–divinylbenzene systems, solid particles are formed at the beginning of the reaction, which are apparently copolymers of styrene and divinylbenzene, rather than polymers of the triglyceride oils. Some styrene–divinylbenzene copolymers formed at the early stage of the reactions are linear or less crosslinked, and thus are still soluble in the liquid starting materials. However, in the triglyceride oil–divinylbenzene systems, highly crosslinked divinylbenzene homopolymers first appear, which are insoluble in any solvents.¹⁰ Thus, fewer white solid particles are observed in the triglyceride oil–styrene–divinylbenzene systems examined in this study than those of the triglyceride oil–divinylbenzene systems reported earlier.¹⁰

Table I Various Initiator Additives and Average Number of C=C Bonds per Additive Chain

Entry	Designation	Additive	No. of C=C per Chain
1	SGI	Soygold-2000: soybean oil methyl ester	1.5
2	SGII	Soygold-1100: soybean oil methyl ester	1.7
3	SGIII	LoSatSoy Soygold: LoSatSoy oil methyl ester	2.2
4	NFO	Pronova 5500 EE: Norway fish oil ethyl ester	3.6

To obtain homogeneous copolymerization, the initiator boron trifluoride diethyl etherate has to be modified by various additives listed in Table I. These additives are soybean oil methyl esters (SGI, SGII, and SGIII) or a fish oil ethyl ester (NFO) with different degrees of unsaturation. It has been found that these additive-modified initiators give rise to completely homogeneous reactions with as little as 5 wt % of the additive in the original composition. This is less than the 10 wt % generally used in the triglyceride oil–divinylbenzene copolymerizations.¹⁰ Table II (entries 1–4) shows that the copolymerization of LoSatSoy oil, styrene, and divinylbenzene has essentially the same gelation time using the different additive-modified initiators. The reactions yield approximately 82–84% of crosslinked polymers after extraction, irrespective of variations in the initiating systems.

Figure 2 shows the effect of the triglyceride oil concentration on the gelation time of the reactions, and Figure 3 indicates the yield of crosslinked polymers using the NFO-modified initiator (5 wt % NFO + 3 wt % BFE). The yield of crosslinked polymers was measured by Soxhlet extraction in methylene

chloride. For both LoSatSoy oil and conjugated LoSatSoy oil systems, the gelation time increases, and the yield of crosslinked polymers gradually decreases when increasing the triglyceride oil concentration in the original composition. Compared with the comonomers used in this study, both LoSatSoy oil and conjugated LoSatSoy oil have much lower mobility and reactivity. Thus, increasing the triglyceride oil concentration decreases the mobility and reactivity of the starting materials. As a result, the gelation time of the copolymerization increases. The gradual decrease in yield of crosslinked polymers as shown in Figure 3 may be ascribed to two phenomena: (1) The triglyceride oil molecules do not copolymerize completely because of their relatively low reactivity. This means that increasing the triglyceride oil concentration in the original composition is equivalent to increasing the amount of the unreacted triglyceride oil in the resulting products. Thus, the percentage of the starting materials converted to crosslinked polymers decreases. (2) Increasing the triglyceride oil concentration decreases the comonomer concentration, especially the divinylbenzene concentration in the original composition. Since divinylbenzene is an effective crosslink-

Table II Copolymerization of Various Oils with Styrene and Divinylbenzene, Norbornadiene, or Dicyclopentadiene Initiated by Different Modified Initiators

Entry	Original Composition (wt %)				Gelation Time (s)	Yield (%) of Crosslinked Polymer after Extraction
	Triglyceride Oil	Comonomers	Initiators			
1	45% LSS	32% ST + 15% DVB	5% SGI + 3% BFE		3.0×10^2	83
2	45% LSS	32% ST + 15% DVB	5% SGII + 3% BFE		3.0×10^2	82
3	45% LSS	32% ST + 15% DVB	5% SGIII + 3% BFE		3.0×10^2	83
4	45% LSS	32% ST + 15% DVB	5% NFO + 3% BFE		3.0×10^2	84
5	45% SOY	32% ST + 15% DVB	5% NFO + 3% BFE		2.4×10^2	80
6	45% LSS	32% ST + 15% DVB	5% NFO + 3% BFE		3.0×10^2	84
7	45% CLS	32% ST + 15% DVB	5% NFO + 3% BFE		6.6×10^2	92
8	45% CLS	32% ST + 15% DVB	5% NFO + 3% BFE		6.6×10^2	92
9	45% CLS	32% ST + 15% NBD	5% NFO + 3% BFE		3.5×10^3	89
10	45% CLS	32% ST + 15% DCP	5% NFO + 3% BFE		2.1×10^5	80

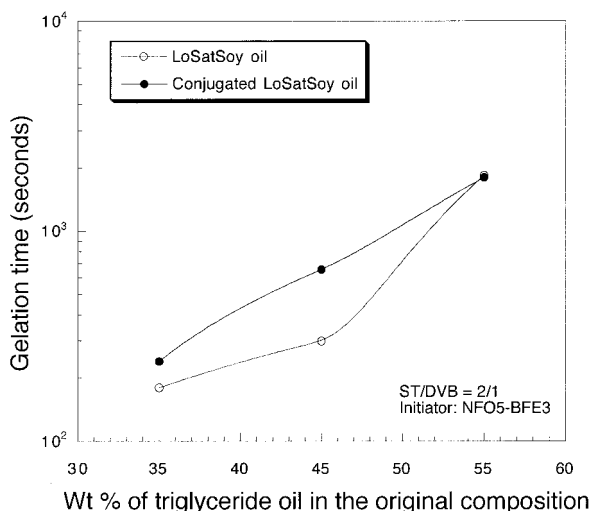


Figure 2 Effect of triglyceride oil concentration on the gelation of the copolymerization for both the LoSatSoy oil and the conjugated LoSatSoy oil systems.

ing agent, a reduction in the concentration of divinylbenzene reduces the overall yield of crosslinked polymer.

Figure 3 also shows that the type of triglyceride oil has an effect on the yield of the crosslinked polymer. The carbon-carbon double bonds in the conjugated LoSatSoy oil are evidently more reactive than those of the LoSatSoy oil, as one would expect. As a result, the percentage of conjugated LoSatSoy oil participating in the copolymerization is relatively high. Thus, conjugated LoSatSoy

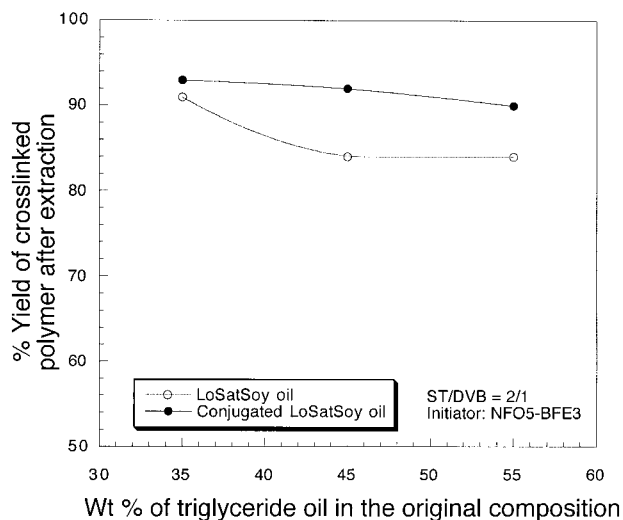


Figure 3 Effect of triglyceride oil concentration on the yield of crosslinked polymers for both the LoSatSoy oil and the conjugated LoSatSoy oil systems.

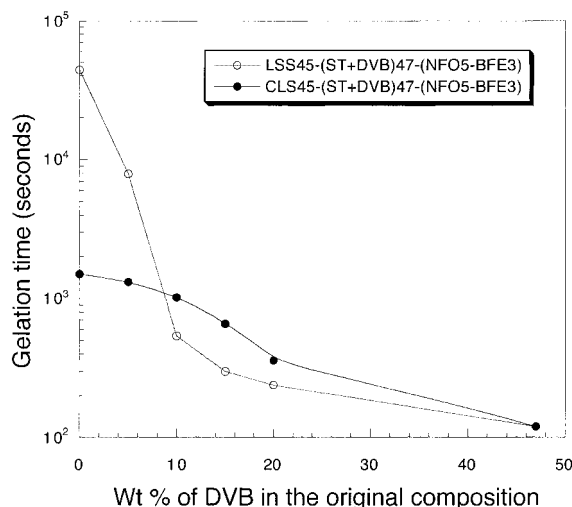


Figure 4 Effect of divinylbenzene concentration on the gelation of the copolymerization for both the LoSatSoy oil and the conjugated LoSatSoy oil systems.

oil systems yield more crosslinked polymer than do the LoSatSoy oil systems when using the same composition. However, the gelation time of the conjugated LoSatSoy oil systems is higher than that of the LoSatSoy oil systems (see Fig. 2). Table II (entries 5–7) further indicates that the least-reactive soybean oil has the lowest gelation time under the same conditions.

Figure 4 illustrates the effect of the divinylbenzene concentration on the gelation time of the triglyceride oil-styrene-divinylbenzene systems when the total styrene-divinylbenzene comonomer concentration remains constant. As the divinylbenzene concentration increases in the original composition, the gelation time of both the LoSatSoy oil and the conjugated LoSatSoy oil systems decreases. The reactions of the LoSatSoy oil systems appear to be more sensitive to the divinylbenzene concentration, especially when the concentration of divinylbenzene is less than 10 wt%. The results show that the LoSatSoy oil-styrene system has a gelation time much higher than that of the conjugated LoSatSoy oil-styrene system when no divinylbenzene is used. As a small amount of divinylbenzene is added, the gelation time of the LoSatSoy oil systems sharply decreases. When the divinylbenzene reaches 10 wt%, the gelation time of the LoSatSoy oil system drops below that of the conjugated LoSatSoy system. As expected, divinylbenzene is a good crosslinking agent. The yield of crosslinked polymer, therefore, increases when increasing the divinylbenzene concentration in the original compo-

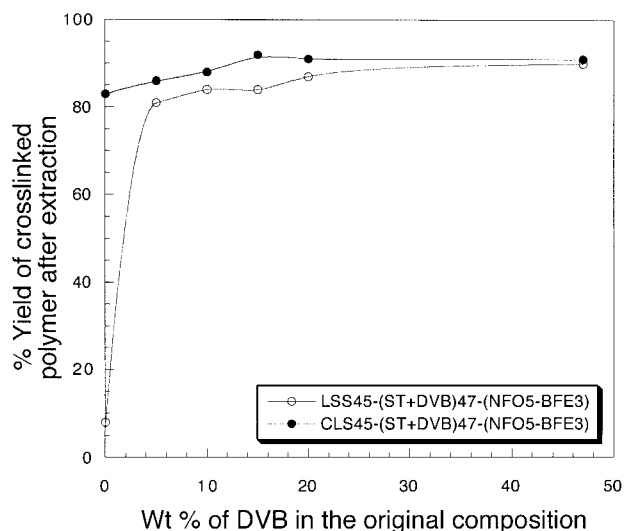


Figure 5 Effect of divinylbenzene concentration on the yield of crosslinked polymers for both the LoSatSoy oil and the conjugated LoSatSoy oil systems.

sition (see Fig. 5). The conjugated LoSatSoy oil results in higher yields of crosslinked polymers than does the LoSatSoy oil when employing the same composition.

The copolymerization of conjugated LoSatSoy oil and the comonomers used in this study was expected to result in a lower gelation time than that of copolymerization of the LoSatSoy oil system because of the relatively high reactivity of the conjugated LoSatSoy oil. However, the above-noted results do not support this hypothesis. In most cases, the conjugated LoSatSoy oil system has higher gelation times (Fig. 4).

We have reported the copolymerization of tung oil and divinylbenzene.¹⁷ The gelation times there do not change monotonously as a function of divinylbenzene concentration in the original composition. Instead, they show a maximum when the divinylbenzene reaches approximately 30 wt %. Tung oil has a rather high reactivity toward cationic polymerization, comparable in fact to that of divinylbenzene. In that work, the peak-gelation-time phenomenon can be explained by a competition between copolymerization of a tung oil molecule and a divinylbenzene comonomer.¹⁷ However, the soybean oil, even the conjugated LoSatSoy oil used in this study, is much less reactive than the tung oil previously used. We are therefore unable to ascribe the unusual gelation times observed with soybean oils to this same type of competition.

The triglyceride oil systems polymerize by a carbocationic mechanism.^{14–16} The gelation of the

copolymerization is primarily determined by two major factors. One is the copolymerization speed, which is related to the reactivity of the various active species existing in the reaction. During the copolymerization, there are typically two active species, that is, $\sim\text{M}_2^+$ and $\sim\text{M}_1^+$ (M_1 is presumably styrene or divinylbenzene and M_2 is presumably the larger triglyceride oil). Apparently, the active species $\sim\text{M}_2^+$ propagates less readily than does the active species $\sim\text{M}_1^+$, primarily as a result of steric hindrance.¹⁶ Thus, the reaction speed is expected to slow down when more of the species $\sim\text{M}_2^+$ exists in the copolymerization. In addition, the tendency of the starting materials to form insoluble crosslinked polymers also greatly affects the gelation process. Increasing the concentration of crosslinking agent favors formation of crosslinked polymers.

The results in Figure 4 can be explained by the cooperative effect of the two factors just noted. At high divinylbenzene concentrations, both the LoSatSoy oil system and the conjugated LoSatSoy oil system easily form crosslinked polymers because divinylbenzene is a very effective crosslinking agent. That is to say, the difference in the tendency of the two triglyceride oil systems to form crosslinked polymers is negligible. On the other hand, the conjugated LoSatSoy oil is expected to be more reactive than the LoSatSoy oil. Thus, the conjugated LoSatSoy oil system should contain higher concentrations of the less-reactive species $\sim\text{M}_2^+$. As a result, the copolymerization of the conjugated LoSatSoy oil system is slowed down and, thus, the gelation time increases relative to that of the LoSatSoy oil system.

When the concentration of divinylbenzene is less than 10%, the conjugated LoSatSoy oil system still contains a higher concentration of the less-reactive species $\sim\text{M}_2^+$ than the does the LoSatSoy oil system. This inevitably reduces the rate of copolymerization of the conjugated LoSatSoy oil system. However, when less divinylbenzene is used, less crosslinked polymer is likely to be formed. Like divinylbenzene, the triglyceride oil can also serve as a crosslinking agent because of its multiple side chains and functionalities. The crosslinking nature of the triglyceride oil should become more obvious when the divinylbenzene concentration is low. In this sense, the reactive conjugated LoSatSoy oil is a better crosslinking agent than is the regular LoSatSoy oil. When employing the same composition and conditions, therefore, the conjugated LoSatSoy oil system has more opportunities to form crosslinked polymers

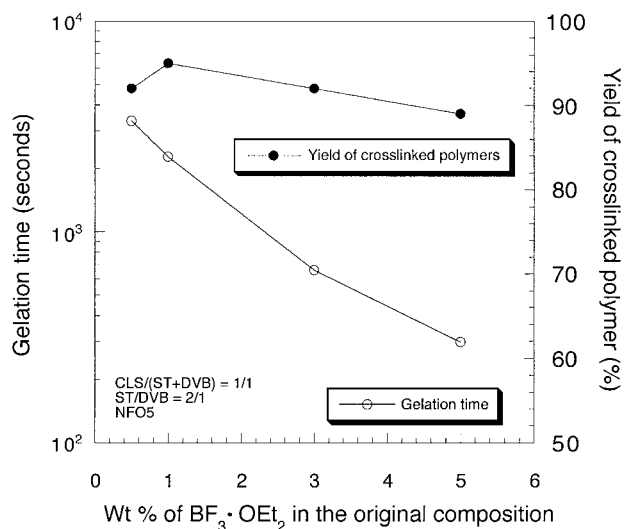


Figure 6 Effect of $\text{BF}_3 \cdot \text{OEt}_2$ concentration on the gelation of the copolymerization, and the yield of crosslinked polymers for the conjugated LoSatSoy oil system.

than does the LoSatSoy oil system. Thus, even though the species $\sim\text{M}_2^+$ may lower the rate of copolymerization, the conjugated LoSatSoy oil system can still gel faster than can the LoSatSoy oil system.

Figure 6 shows the effect of the $\text{BF}_3 \cdot \text{OEt}_2$ initiator concentration on the gelation time and the yield of crosslinked polymer after extraction in the conjugated LoSatSoy oil system. The initiator $\text{BF}_3 \cdot \text{OEt}_2$ is modified by 5 wt % NFO for all reactions. As expected, the gelation time of the reactions decreases when increasing the $\text{BF}_3 \cdot \text{OEt}_2$ concentration. However, the yield of crosslinked polymers does not monotonously change with increasing the $\text{BF}_3 \cdot \text{OEt}_2$ concentration in the original composition. The crosslinked polymer yield initially increases when increasing the $\text{BF}_3 \cdot \text{OEt}_2$ concentration. However, when the percentage of $\text{BF}_3 \cdot \text{OEt}_2$ exceeds 1%, the crosslinked polymer yield slightly decreases. This slight decrease in the yield of crosslinked polymer probably results from the presence of more residual initiator fragments in the bulk polymers, as a result in turn of increasing the $\text{BF}_3 \cdot \text{OEt}_2$ concentration in the original composition.

Table II (entries 8–10) summarizes the effect of various crosslinking agents on the reaction gelation time and the resulting yield of crosslinked polymer after extraction in the conjugated LoSatSoy oil system. Three crosslinking agents were employed in this study, that is, divinylbenzene

(DVB), norbornadiene (NBD), and dicyclopentadiene (DCP). All of them have two reactive $\text{C}=\text{C}$ bonds per molecule for cationic polymerization.¹⁶ The results clearly show that the nature of the crosslinking agent has a significant effect on copolymerization of the conjugated LoSatSoy oil system. Divinylbenzene seems to be the most effective crosslinking agent. It gives the fastest reaction and the highest yield of crosslinked polymer. Dicyclopentadiene results in the slowest reaction (i.e., several days for gelation) and the lowest yield of crosslinked polymer.

Characterization of the Resulting Bulk Polymers

A wide variety of viable polymeric materials have been obtained, ranging from soft rubbers to hard, tough, or brittle plastics with dark brown colors (Tables III–V). Typically, the products are thermosetting polymers, as evidenced by the high yield of crosslinked polymer (80–92%) measured after Soxhlet extraction by methylene chloride. Generally, 8–20% of soluble substances were extracted by methylene chloride from the bulk polymers. These extracted soluble substances are, in most cases, extremely viscous oily materials with very low fluidity.

Unlike the soybean oil–divinylbenzene system,¹⁰ the extracted soluble substances in this study contain some linear or less-crosslinked polymers that are soluble in methylene chloride. Figures 7 and 8 show the $^1\text{H-NMR}$ spectra of the

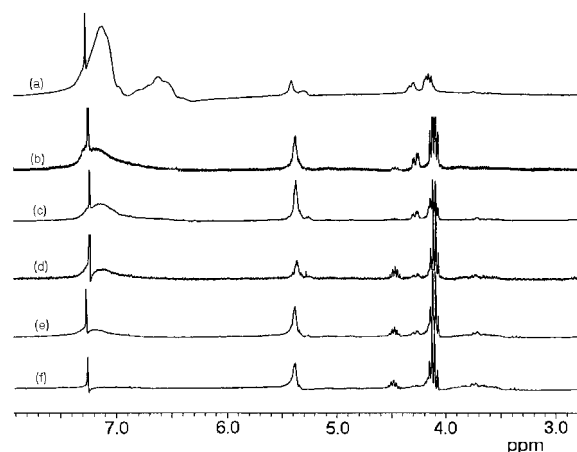


Figure 7 $^1\text{H-NMR}$ spectra of the soluble substances extracted from the various LoSatSoy oil bulk polymers LSS45-(ST+DVB)47-(NFO5-BFE3) containing (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, (d) 15 wt %, (e) 20 wt % and (f) 47 wt % divinylbenzene in the original composition.

Table III Characteristics of Various Triglyceride Oil Polymers Prepared Using Different Modified Initiators

Entry	Polymer Sample	T_g^a (°C)	TGA Results (°C)		Product Appearance	Extraction ^b (%)	
			T_{10}	T_{50}		Insoluble	Soluble
1	SOY45-ST32-DVB15-(NFO5-BFE3)	68	342	468	hard, ductile plastic	80	20
2	LSS45-ST32-DVB15-(NFO5-BFE3)	61	347	470	hard, ductile plastic	84	16
3	CLS45-ST32-DVB15-(NFO5-BFE3)	76	400	475	hard, ductile plastic	92	8
4	LSS45-ST32-DVB15-(SGI5-BFE3)	57	325	472	hard, ductile plastic	83	17
5	LSS45-ST32-DVB15-(SGII5-BFE3)	58	328	470	hard, ductile plastic	82	18
6	LSS45-ST32-DVB15-(SGIII5-BFE3)	55	324	469	hard, ductile plastic	83	17
7	LSS45-ST32-DVB15-(NFO5-BFE3)	61	347	470	hard, ductile plastic	84	16

^a Data obtained from dynamic mechanical analysis.

^b Soxhlet extraction conducted using methylene chloride for 24 h.

soluble substances obtained from the LoSatSoy oil and conjugated LoSatSoy oil polymers, respectively, after Soxhlet extraction by methylene chloride. It is found that the extracted soluble substances are composed of initiator fragments (4.0–4.2 ppm), triglyceride molecules (4.2–4.5 ppm), and polymers containing polystyrene segments with aromatic protons (6.4–7.5 ppm). These extracted substances are soluble in methylene chloride and acetone, but are poorly soluble in hexane. This means that the extracted linear or less-crosslinked polymers detected after extraction by ¹H-NMR spectroscopy are likely to be triglyceride oil–styrene–divinylbenzene copolymers, rather than pure polystyrene, in that acetone is a poor solvent for homopolystyrene.

Figures 7 and 8 also show that the aromatic segments of the triglyceride oil–styrene–divinylbenzene copolymers decrease in the extracted substances as the divinylbenzene concentration increases in the original composition. It is known that divinylbenzene is an effective crosslinking agent. When increasing the divinylbenzene concentration, the previously soluble linear or less-crosslinked triglyceride oil–styrene–divinylbenzene copolymers may become insoluble in the extraction solvent (i.e., methylene chloride in this study) as a result of the increased crosslinking density. As divinylbenzene completely replaces styrene in the original composition, no evidence of aromatic protons can be observed [Figs. 7(f) and 8(f)], which indicates that all of the comonomer has been incorporated into the crosslinked polymer network. The extracted substances are composed almost exclusively of free oils and initiator

fragments. This is consistent with our previous results.¹⁰ Thus, the structure of the bulk polymer is that of a crosslinked polymer network interpenetrated by some linear or less-crosslinked triglyceride oil–styrene–divinylbenzene copolymers, a small amount of low molecular weight free oils, and initiator fragments.

Table III (entries 1–3) lists the thermophysical properties of the regular soybean oil, LoSatSoy oil, and conjugated LoSatSoy oil polymers. The poly-

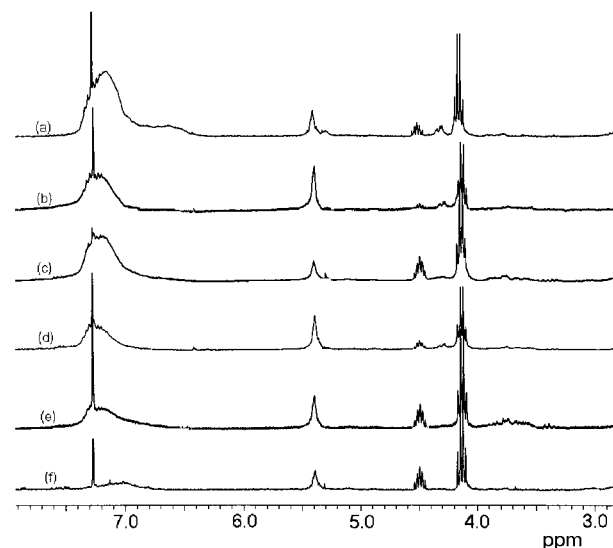


Figure 8 ¹H-NMR spectra of the soluble substances extracted from the various conjugated LoSatSoy oil bulk polymers CLS45-(ST+DVB)47-(NFO5-BFE3) containing (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, (d) 15 wt %, (e) 20 wt % and (f) 47 wt % divinylbenzene in the original composition

Table IV Characteristics of LoSatSoy Oil Polymers Prepared Using NFO-Modified Initiators

Entry	Polymer Sample	T_g^a (°C)	TGA Results (°C)		Product Appearance	Extraction ^b (%)	
			T_{10}	T_{50}		Insoluble	Soluble
1	LSS55-ST25-DVB12-(NFO5-BFE3)	32	314	468	soft rubber	84	16
2	LSS45-ST32-DVB15-(NFO5-BFE3)	61	347	470	hard, ductile plastic	84	16
3	LSS35-ST39-DVB18-(NFO5-BFE3)	80	347	468	hard, ductile plastic	91	9
4	LSS45-ST47-DVB00-(NFO5-BFE3)	×	312	445	soft rubber	8	92
5	LSS45-ST42-DVB05-(NFO5-BFE3)	43	314	459	soft rubber	81	19
6	LSS45-ST37-DVB10-(NFO5-BFE3)	48	323	468	hard, ductile plastic	84	16
7	LSS45-ST32-DVB15-(NFO5-BFE3)	61	347	470	hard, ductile plastic	84	16
8	LSS45-ST27-DVB20-(NFO5-BFE3)	71	349	470	hard, ductile plastic	87	13
9	LSS45-ST00-DVB47-(NFO5-BFE3)	71	355	474	hard, brittle plastic	90	10

^a Data obtained from dynamic mechanical analysis.

^b Soxhlet extraction conducted using methylene chloride for 24 h.

mers appear to be hard and ductile plastics. The T_g of these bulk polymers are approximately 61–76°C. Of the three triglyceride oil polymers, the conjugated LoSatSoy oil polymer has the highest T_g . The thermogravimetric analysis (TGA) results of the three triglyceride oil polymers are very different from one another. The temperature at 10% weight loss (T_{10}) is generally used to evaluate the thermal stability of the bulk polymers, whereas the temperature at 50% weight loss (T_{50}) indirectly reflects the consistency of the crosslinking structure of the bulk polymers.¹⁰ The results in Table III (entries 1–3) show that the regular soybean oil and LoSatSoy oil polymers have T_{10} temperatures similar to each other, whereas the conjugated LoSatSoy oil polymer has the highest T_{10} , approximately 400°C in air.

In the previous discussion, the various modified initiators seem to have little effect on the copolymerization, that is, gelation time and yield of crosslinked polymers (Table II, entries 1–4). However, the initiators do affect the thermophysical properties of the resulting bulk polymers (Table III, entries 4–7), especially the T_{10} temperature. The bulk polymers have glass-transition temperatures of approximately 55–61°C as a result of the different initiating systems employed. The fish oil-modified initiator results in a bulk polymer having the highest T_g and thermal stability (T_{10}).

Table IV reports the thermophysical properties of the LoSatSoy oil polymers. The polymers containing different amounts of LoSatSoy oil in the original composition have glass-transition temperatures ranging from 32 to 80°C (entries 1–3).

Adding more comonomers (present in a 2 : 1 ratio) to the original composition results in harder polymers with higher glass-transition temperatures, as well as higher thermal stabilities. It has been found that the resulting bulk polymer has the highest mechanical properties when the weight ratio of LoSatSoy oil to the comonomers is approximately 1 : 1 in the original composition.¹² Based on this result, 45 wt % of LoSatSoy oil was used, and the effect of different divinylbenzene concentrations on the thermophysical properties of the resulting polymers was investigated, while the concentration of styrene + divinylbenzene comonomers remains constant in the original composition (Table IV, entries 4–9). The polymer LSS45-ST47-DVB00-(NFO5-BFE3) (entry 4) is, in fact, a thermoplastic rubbery material containing only a very small amount of crosslinked polymer (8%). It is very soft and flexible, and its glass-transition temperature ($\sim <0^\circ\text{C}$) is too low to be measured by the technique used in this study. Generally, when increasing the divinylbenzene concentration in the original composition, the resulting polymers vary from soft rubbers to hard, tough, or brittle plastics. Their glass-transition temperatures gradually increase from approximately 0°C to around 71°C, and the T_{10} temperatures gradually increase from 312 to 355°C.

When conjugated LoSatSoy oil was used, similar results were observed (Table V, entries 1–9). Polymeric materials ranging from soft rubbers to hard, tough, or brittle plastics were obtained by varying the conjugated LoSatSoy oil concentration (entries 1–3) or divinylbenzene concentration

Table V Characteristics of Conjugated LoSatSoy Oil Polymers Prepared Using NFO-Modified Initiators

Entry	Polymer Sample	T_g^a (°C)	TGA Results (°C)		Product Appearance	Extraction ^b (%)	
			T_{10}	T_{50}		Insoluble	Soluble
1	CLS55-ST25-DVB12-(NFO5-BFE3)	38	388	470	soft rubber	90	10
2	CLS45-ST32-DVB15-(NFO5-BFE3)	76	400	475	hard, ductile plastic	92	8
3	CLS35-ST39-DVB18-(NFO5-BFE3)	82	400	477	hard, ductile plastic	93	7
4	CLS45-ST47-DVB00-(NFO5-BFE3)	10	358	448	soft elastomer	83	17
5	CLS45-ST42-DVB05-(NFO5-BFE3)	45	360	460	soft plastic	86	14
6	CLS45-ST37-DVB10-(NFO5-BFE3)	60	387	468	hard, ductile plastic	88	12
7	CLS45-ST32-DVB15-(NFO5-BFE3)	76	400	475	hard, ductile plastic	92	8
8	CLS45-ST27-DVB20-(NFO5-BFE3)	75	400	470	hard, ductile plastic	91	9
9	CLS45-ST00-DVB47-(NFO5-BFE3)	105	434	480	hard, brittle plastic	91	9
10	CLS46-ST33-DVB15-(NFO5-BFE0.5)	59	401	467	hard, ductile plastic	92	8
11	CLS46-ST33-DVB15-(NFO5-BFE1)	67	400	461	hard, ductile plastic	95	5
12	CLS45-ST32-DVB15-(NFO5-BFE3)	76	400	475	hard, ductile plastic	92	8
13	CLS44-ST31-DVB15-(NFO5-BFE5)	63	364	470	hard, ductile plastic	89	11
14	CLS45-ST32-DVB15-(NFO5-BFE3)	76	400	475	hard, ductile plastic	92	8
15	CLS45-ST32-NBD15-(NFO5-BFE3)	43	331	462	soft, ductile plastic	89	11
16	CLS45-ST32-DCP15-(NFO5-BFE3)	14	327	461	soft rubber	80	20

^a Data obtained from dynamic mechanical analysis.

^b Soxhlet extraction conducted using methylene chloride for 24 h.

(entries 4–9) in the original composition. As expected, conjugated LoSatSoy oil affords higher yields of crosslinked polymers, and much higher glass-transition temperatures and T_{10} temperatures than those of the corresponding LoSatSoy oil polymers (compare entries 1–9 in both Table IV and Table V). Thus, the polymeric materials prepared from either LoSatSoy oil or conjugated LoSatSoy oil possess glass-transition temperatures, ranging from approximately 0 to 105°C, which are comparable to those of commercially available rubbers and conventional plastics.

Figure 9 summarizes the thermogravimetric analysis (TGA) results for both the LoSatSoy oil and the conjugated LoSatSoy oil polymers listed in Tables IV and V (entries 1–9). It is clear that the conjugated LoSatSoy oil polymers have T_{10} temperatures much higher than those of the corresponding LoSatSoy oil polymers. In other words, the conjugated LoSatSoy oil polymers are more thermally stable than the LoSatSoy oil polymers. It is known that the T_{10} temperature is closely related to the amount of unreacted free oil present in the triglyceride oil–divinylbenzene bulk polymers.¹⁰ In this study, different amounts of soluble substances were extracted from the bulk polymers (Tables IV and V). However, these

extracted soluble substances contain not only the unreacted free oils but also some linear or less-crosslinked soybean oil–styrene–divinylbenzene copolymers. Presently, we are not able to separate the linear or less-crosslinked copolymers from the other materials present in the extracted substances. We are, therefore, unable to calculate how much free oil is present in these extracted substances. However, it was found from Tables IV and V that greater amounts of soluble substances were extracted from the LoSatSoy oil polymers than from the conjugated LoSatSoy oil polymers. The thermal stability (T_{10}) of the triglyceride oil polymers shown in Figure 9 correlates well with the amounts of extracted substances, no matter what quantity of linear or less-crosslinked polymers are present (Tables IV and V). The above correlation is apparently the result of the much lower thermal stability of the extracted substances than that of the well-crosslinked polymer networks, even though the extracted materials consist of some weakly crosslinked polymers.

In spite of the big difference in the thermal stability T_{10} , the LoSatSoy oil and conjugated LoSatSoy oil polymers have T_{50} temperatures similar to each other (Fig. 9). It is known from our previous studies that the temperature T_{50} corre-

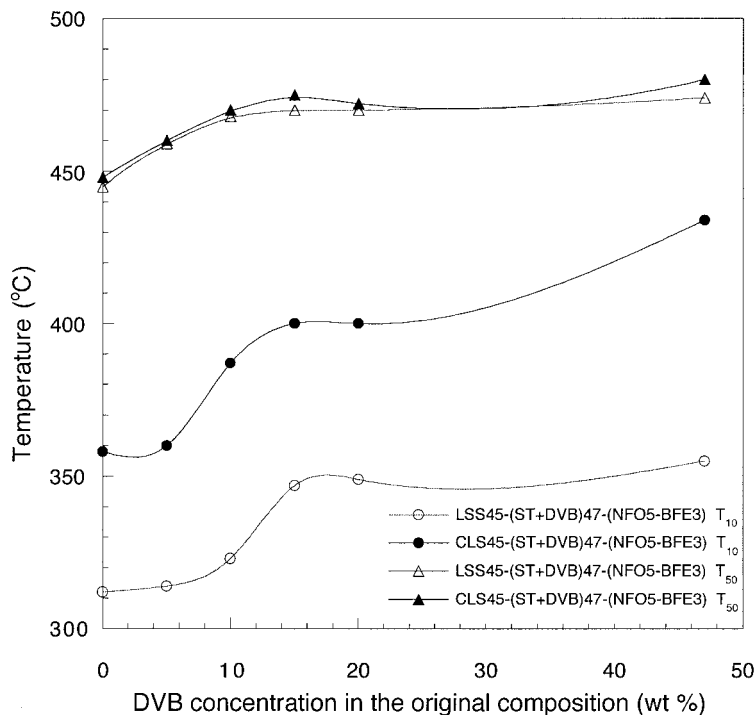


Figure 9 Thermogravimetric analysis (TGA) results for LoSatSoy oil and conjugated LoSatSoy oil polymers.

sponds to the temperature region in which the crosslinking structure of the bulk polymers undergoes the fastest degradation.¹⁰ Thus, it indirectly reflects the consistency of the crosslinking structure of the bulk polymers. For all of the polymers studied, the comonomers styrene and divinylbenzene constitute half of the starting materials by weight. In fact, these comonomers have lower molecular weights than those of the triglyceride oils used in this study. Thus, the crosslinked polymer backbones are mainly composed of styrene and divinylbenzene segments. In the conjugated LoSatSoy oil polymers, more triglyceride oil molecules were incorporated into the crosslinked polymers. However, this does not significantly influence the consistency of the crosslinked polymer structure. As a result, the LoSatSoy oil and conjugated LoSatSoy oil polymers have very similar T_{50} temperatures.

Table V also provides results from conjugated LoSatSoy oil polymers prepared using different amounts of initiators (entries 10–13) and various types of crosslinking agents (entries 14–16). When the initiator $\text{BF}_3 \cdot \text{OEt}_2$ is less than 0.5 wt %, the resulting polymers are very soft, with some amount of unreacted triglyceride oils and comonomers still present (not listed in Ta-

ble V). In this study, it seems that 0.5 wt % of the $\text{BF}_3 \cdot \text{OEt}_2$ is the lower limit for the triglyceride oil systems to polymerize into viable polymeric materials. Within the initiator concentration range studied in Table V (entries 10–13), the $\text{BF}_3 \cdot \text{OEt}_2$ concentration does not greatly affect the thermophysical properties of the resulting polymers. When the $\text{BF}_3 \cdot \text{OEt}_2$ concentration reaches 5 wt %, both the glass-transition temperature T_g and the temperature T_{10} of the resulting bulk polymer decrease. This is probably the result of the plasticizing effect of more initiator residue, which results in turn from the surplus of the initiator employed (Table V, entry 13).

Various types of crosslinking agents do significantly influence the thermophysical properties of the resulting bulk polymers (Table V, entries 14–16). When divinylbenzene or norbornadiene is used, the resulting polymers are typical plastics with glass-transition temperatures higher than room temperature. However, dicyclopentadiene results in a very soft rubbery material, whose glass-transition temperature is 14°C and T_{10} is 327°C. Divinylbenzene appears to be the most effective crosslinking agent for preparing tough plastics. The triglyceride oil polymer prepared

from divinylbenzene possesses the highest glass-transition temperature, as well as the highest thermal stability T_{10} (Table V, entry 14).

CONCLUSIONS

1. The cationic copolymerization of regular soybean oil, LoSatSoy, oil or conjugated LoSatSoy oil with styrene and/or divinylbenzene, norbornadiene, or dicyclopentadiene initiated by boron trifluoride diethyl etherate results in heterogeneous reactions. The heterogeneous nature of these reactions appears to be mainly the result of the poor miscibility between the triglyceride oils and the initiator boron trifluoride diethyl etherate.
2. Homogeneous copolymerization of the triglyceride oils with styrene and/or divinylbenzene, norbornadiene, or dicyclopentadiene has been achieved by using initiating systems modified by 5% Norway fish oil ethyl ester or various soybean oil methyl esters (Soygold). The fish oil-modified initiator results in the highest percentage of starting materials converted to crosslinked polymers.
3. The gelation time of the copolymerization is largely dependent on the stoichiometry and the types of triglyceride oils used, and ranges from 1×10^2 to 2×10^5 s at room temperature. In most cases, the LoSatSoy oil systems gel faster than do the conjugated LoSatSoy oil systems. When less divinylbenzene is used in the original composition, however, the LoSatSoy oil systems gel slower than do the conjugated LoSatSoy oil systems.
4. The yield of crosslinked polymers obtained after extraction is largely dependent on the concentration of the crosslinking agent, divinylbenzene, norbornadiene, or dicyclopentadiene. Divinylbenzene appears to be the most effective crosslinking agent. The reactivity of the triglyceride oil also affects the yield of the crosslinked polymers. Conjugated LoSatSoy oil results in the highest yield of crosslinked polymers among all of the triglyceride oils used in this study.
5. A wide variety of viable polymeric materials ranging from rubbers to hard, tough, or brittle plastics have been obtained by deliberate structure design. These polymers have glass-transition temperatures (T_g) that range from approximately 0 to 105°C, which are comparable to those of conventional rubbers and

plastics. These bulk polymers are thermally stable under 200°C in air. The temperatures at 10% weight loss (T_{10}) are around 312–434°C, and the temperatures at 50% weight loss (T_{50}) are 445–480°C.

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