

Photolytic and Free-Radical Polymerization of Cinnamate Esters of Epoxidized Plant Oil Triglycerides

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ABSTRACT: Epoxidized soybean oil was reacted with cinnamic acid with triphenyl phosphine as a catalyst. Cinnamic acid reacted with 79% of the available epoxy groups, and this yielded cinnamate esters of epoxidized soybean oil (ESOCA). $^1\text{H-NMR}$, IR, and mass spectra of the new cinnamate derivatives confirmed the proposed structure. The mass spectra revealed that the average number of cinnamate groups per triglyceride molecule was 3.33. ESOCA could be photopolymerized with UV light. ESOCA could also be homopolymerized into a soft and insoluble polymer by free-radical initiation and copolymerized with styrene, vinyl acetate, and methyl methacrylate. A mixture of ESOCA with 25 wt % styrene had a viscosity of 410 cP and could be

free-radically polymerized with benzoyl *tert*-butyl peroxide at elevated temperatures. Differential scanning calorimetry confirmed the formation of copolymers. The ESOCA homopolymer and its copolymers all showed a first-order transition by differential scanning calorimetry around -1.5°C that was attributable to side-chain relaxations of the triglyceride fatty acids. The styrene copolymer of ESOCA showed a $\tan \delta$ peak at 66.6°C . © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3882–3888, 2003

Key words: photopolymerization; radical polymerization; renewable resources

INTRODUCTION

In our continuing efforts to synthesize new rigid and load-bearing thermosetting polymers from renewable resources that are suitable for structural composites, we have worked with cinnamate esters of epoxidized soybean oil (ESOCA).

Epoxidized triglycerides can be found in naturally occurring oils, such as vernonia oil, and are easily synthesized from the more common unsaturated oils, such as linseed, sunflower, and soybean oils, by standard epoxidation reactions.¹ Recently, soybean oil has been epoxidized by enzymatic pathways with greater than 90% conversion,² and numerous commercial efforts to produce genetically modified soybean plants containing higher amounts of oil and higher amounts of oleic acid in their triglycerides have been disclosed. These make epoxidized soybean oil (ESO) an attractive raw material for the synthesis of successful thermoset resins. ESO has been used as a safe plasticizer for poly(vinyl chloride)³ and has successfully been polymerized by photocationic ring-opening polymerization with onium salts.⁴ We earlier converted ESO into its acrylate ester by a reaction with acrylic acid, which can be free-radically polymerized or copoly-

merized with reactive diluents such as styrene (STYR) to give thermoset resins with mechanical properties that are similar to those of commercially successful polyester and vinyl ester resins.^{5,6} We have examined soybean oil and ESO chemistry in some depth and reported our results in earlier publications.^{6–8} Cinnamic acid and its esters are known to undergo photolytic 2+2 cycloaddition.^{9,10} For example, the oldest synthetic photocrosslinkable polymer, poly(vinyl cinnamate), is believed to undergo a cycloaddition reaction during crosslinking. With the potential availability of cheap ESO and the possibility of photoinduced crosslinking reactions, we decided to synthesize cinnamate esters of epoxidized soybean oil [or ESO/cinnamic acid adduct (ESOCA)] and study their homopolymers and copolymers. The chemistry is shown in Figure 1.

EXPERIMENTAL

Cinnamic acid, calcium chloride, sodium bicarbonate, carbon tetrachloride, and diethyl ether were purchased from Merck (Darmstadt, Germany). ESO was obtained from Cargill (Minneapolis, MN). An average molecular weight of 950 was assumed for ESO, and it had 4.2 epoxy groups per triglyceride molecule. STYR, methyl methacrylate (MMA), and vinyl acetate (VA) were purchased from Fluka (Buchs, Switzerland). Triphenyl phosphine and benzoyl peroxide were purchased from Fischer Scientific Co. (Pittsburgh, PA), and benzoyl peroxide was recrystallized from metha-

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ple was performed with a Polymer Laboratories dynamic mechanical thermal analyzer (Amherst, MA). Samples with dimensions of 20 mm × 10 mm × 2 mm were scanned at a frequency of 1 Hz and at a heating rate of 5°C/min under a nitrogen gas atmosphere. The dynamic tan δ values were determined in a temperature range of -30 to 80°C.

ESOCA

To ESO (10.0 g, 10.5 mmol, under the assumption of an average molecular weight of 950 g/mol for ESO), cinnamic acid (4.91 g, 33 mmol) and triphenyl phosphine (0.1 g) as a catalyst were added. The mixture was heated with continuous stirring at 120°C for 10 h. The reaction product was then dissolved in diethyl ether and was extracted four times with 5% (aqueous) sodium bicarbonate for the removal of unreacted cinnamic acid. The ether layer was dried with anhydrous calcium chloride and evaporated to dryness. The product was a straw-colored, viscous liquid weighing 9.50 g.

$^1\text{H-NMR}$ (CCl_4 , δ): 0.9 ($-\text{CH}_3$ of fatty acids), 1.2–1.4 ($-\text{CH}_2-$ of fatty acids), 2.2 ($-\text{CH}_2\text{CO}-$), 4.2 ($-\text{COCH}_2-$), 6.2–6.5 ($-\text{CH}=\text{CH}-$ of cinnamic acid), 7–7.6 (aromatic protons). IR (KBr): 3476, 1739, 1712, 1638 cm^{-1}

ESOCA homopolymer

ESOCA (2.00 g, 1.43 mmol, under the assumption of an average molecular weight of 1440 g/mol for ESOCA with 3.3 cinnamate groups per triglyceride) was polymerized in bulk, after nitrogen purging, at 140°C with 1% Trigonox C (0.02 g, 0.09 mmol) for 4 h. The homopolymer of ESOCA was triturated with acetone twice, and 1.63 g of a brown, soft solid insoluble and infusible in all solvents was obtained.

ESOCA-MMA copolymer

ESOCA (2.00 g, 1.43 mmol) and MMA (0.70 g, 7 mmol) were mixed to give a feed molar ratio of 16% ESOCA and 84% MMA. Benzoyl peroxide (0.02 g, 0.15 mmol) was added, and the mixture was purged with nitrogen and heated at 100°C for 5 h. The product was triturated with acetone twice and dried to give 2.3 g of the copolymer. The copolymer molar composition was 10% ESOCA and 90% MMA according to NMR analysis. The product was an opaque, hard, and insoluble solid.

ESOCA-VA copolymer

ESOCA (2.00 g, 1.43 mmol) and VA (0.70 g, 8.1 mmol) were mixed to give a feed molar ratio of 15% ESOCA and 85% VA. Benzoyl peroxide (0.02 g, 0.15 mmol)

was dissolved in the mixture. The mixture was purged with nitrogen and heated at 100°C for 5 h. The product was triturated with acetone twice and dried to give 2.1 g of copolymer as an opaque, soft, and insoluble solid. The copolymer molar composition was 26% ESOCA and 74% VA according to NMR analysis.

ESOCA-STYR copolymer

ESOCA (2.00 g, 1.43 mmol) was dissolved in STYR (0.70 g, 6.7 mmol), and benzoyl peroxide (0.02 g, 0.15 mmol) was added. The solution was then purged with nitrogen, and the vial was sealed. After 5 h of heating at 100°C, a hard, transparent, and insoluble solid weighing 2.50 g was obtained. The copolymer composition could not be determined by NMR as the chemical shifts of the aromatic protons of the two monomers coincided.

Photopolymerization of the ESOCA monomer

ESOCA (2.00 g, 1.43 mmol) was dissolved in 10 mL of acetone. The solution was divided into two parts, and each part was cast on the outside of a 15-cm test tube to yield a thin film. One of the test tubes was covered with aluminum foil, and both were filled with water and placed in the Rayonet photochemical reactor, which was equipped with 16 250-nm lamps and purged with nitrogen. After 30 min of irradiation, both of the glass tubes were washed with CCl_4 . The thin film on the unmasked test tube did not dissolve, whereas the film on the masked test tube dissolved. The polymerized thin film of ESOCA was gently lifted off the glass tube and analyzed by IR.

RESULTS AND DISCUSSION

Synthesis and characterization of ESOCA

The average number of epoxy groups per triglyceride in the ESO used in this work is 4.2. This number was specified by the manufacturer as the percentage of oxirane oxygen and was also determined experimentally by epoxy equivalent analysis. This then is the maximum number of cinnamate ester groups that one can attach to each triglyceride molecule. Terminal epoxides react with carboxylic acids at room temperature, but internal epoxides are considerably less reactive. Higher temperatures, tertiary amine catalysts, or sometimes both are needed to obtain high yields. A competing reaction is the ring-opening polymerization that the alkoxide intermediate may cause, as shown in Figure 2. Although this reaction increases the molecular weight of the adduct, it has the drawback of consuming epoxide groups without introducing cinnamate groups, thereby reducing the functionality of the product. The best synthetic procedure for

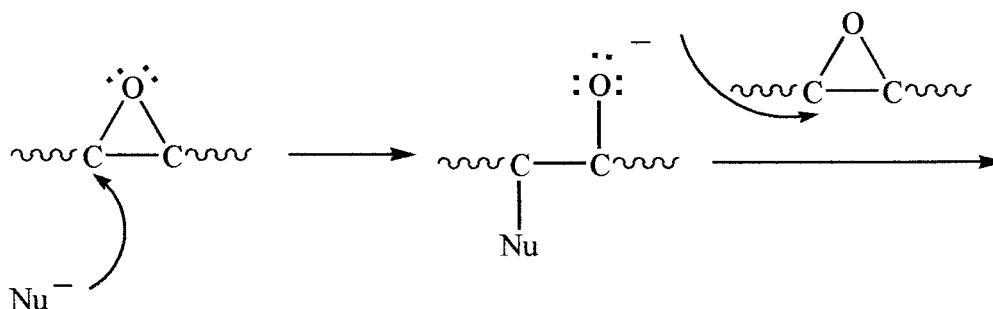


Figure 2 Ring-opening homopolymerization of epoxide groups.

the synthesis of ESOCA was found to be heating cinnamic acid and ESO in the presence of catalytic amounts of triphenyl phosphine at 120°C for 7 h. The ¹H-NMR spectrum of the cinnamate adduct shows vinyl protons at 7.6 and 6.4 ppm, benzene ring protons at 7.3 ppm, and the usual alkyl protons of the fatty acid between 0.8 and 2.3 ppm. The ¹H NMR spectrum of the cinnamate adduct is shown in Figure 3. The average number of cinnamate groups per triglyceride was followed by ¹H-NMR by a comparison of the peak integrals of cinnamate benzene protons and protons on the carbon α to the carbonyl of the triglyceride. In our work, an average number of 3.33 cinnamate groups per triglyceride has been achieved out of the possible 4.2. This represents a 79% conversion to the desired material. The rest of the epoxide groups are either unreacted, as witnessed by the presence of a small peak in the IR spectrum at 843 cm⁻¹, or consumed in the ring-opening polymerization side reaction.

Mass spectra of the cinnamate ester mixtures reveal a multitude of peaks around a specific mass number of clusters. This is a typical behavior of compounds based on plant oils because a multitude of different fatty acid esters with different molecular weights and positional isomers exist in the mixture. Under the assumption of an average molecular weight of 950 for the ESO isomer mixture, the peak clusters at $m/e = 902, 1050, \text{ and } 1198$ and the peak clusters at $m/e = 1064, 1212, \text{ and } 1360$ all indicate the presence of one, two, and three cinnamate groups ($m/e = 148$). The presence of peaks smaller than $m/e = 950$ for ESO give us a good idea about fragmented cinnamate adducts. For example, the peak at 780 corresponds to a triglyceride with one cinnamate ester that has lost one unsubstituted fatty acid. The mass numbers are 950 (ESO) + 148 (cinnamate) - 316 (one epoxidized C-18 fatty acid) = 780. In this fashion, almost all the possible fragments can be identified in the mass spectrum except a straightforward cinnamate loss. Table I gives

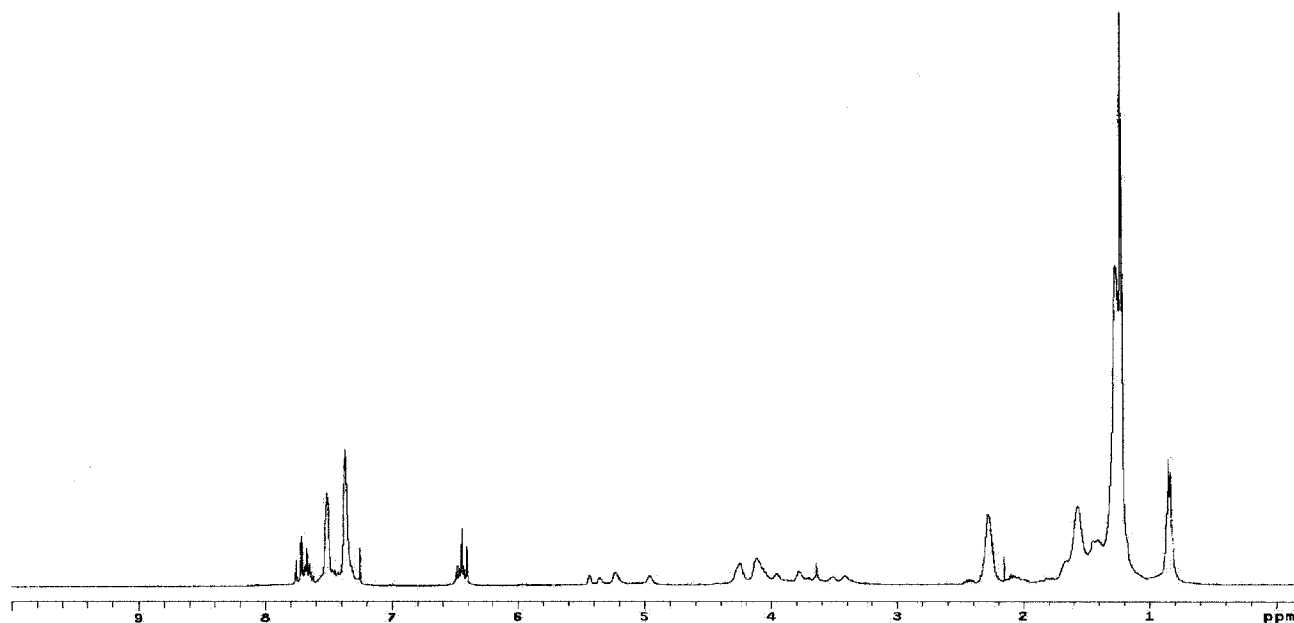


Figure 3 ¹H-NMR spectrum (400 MHz) of ESOCA.

TABLE 1
Peak Clusters in the Mass Spectrum of ESOCA Adduct

| | 1 cinnamate per triglyceride | Change in mass | 2 cinnamates per triglyceride | Change in mass | 3 cinnamates per triglyceride | Change in mass |
|-----|---------------------------------|-------------------|----------------------------------|-------------------|----------------------------------|-------------------|
| 874 | 1022 | 148 | 1171 | 149 | | |
| 888 | 1036 | 148 | 1184 | 148 | | |
| 902 | 1050 | 148 | 1198 | 148 | | |
| | 1064 | | 1212 | 148 | 1360 | 148 |
| | 1082 | | 1225 | 143 | 1373 | 148 |
| | | | 1238 | | 1388 | 150 |
| | | | 1252 | | 1400 | 148 |

Differences between the peak clusters show the loss of cinnamate fragments of mass 148.

the mass number of clusters that show a loss of cinnamate esters. Dimers and trimers that may be formed by epoxide ring-opening polymerization would lead to mass numbers that are considerably higher. For example, a dimer of triglyceride with only one cinnamate on each triglyceride would have a mass number of 2050. Peaks with such high mass numbers cannot be found in the spectra, but this should not rule out their existence, as similar epoxy ring-opening dimers and trimers were identified in our earlier work on acrylic acid derivatives of ESO. The cinnamate adduct is a high-molecular-weight monomer with an average functionality of 3.3 polymerizable double bonds per molecule and can be polymerized and copolymerized to crosslinked networks photolytically and free radically.

Photohomopolymerization of ESOCA

(2+2) cycloadditions are symmetry allowed if one of the alkenes is in an excited state. The reaction is easier if the alkene is suitably polarized. Cinnamic acid and its esters are polarized by the presence of carbonyl and phenyl groups on each side of the double bond. The resulting conjugation also increases the extinction coefficient of the chromophore at higher wavelengths. In our work, to prevent thermal polymerization, we cast the sample as a thin film on the outside of a test tube, and we filled the test tube with water. To prevent triplet oxygen inhibition, we ran the photopolymerization in a nitrogen-purged photoreactor. After 30 min of irradiation, an insoluble and infusible thin film was obtained. The $^1\text{H-NMR}$ spectrum of the product could not be obtained as it did not dissolve in common solvents. The IR spectrum of the polymeric product shows two different carbonyl peaks at 1738 and 1712 cm^{-1} corresponding to glyceride and cinnamate esters, a hydroxyl band at 3440 cm^{-1} , and the usual monosubstituted benzene ring absorptions. The loss of cinnamate double-bond absorptions is difficult to demonstrate as they overlap with benzene ring absorptions. The photopolymerized product is a trans-

parent, resilient rubber that is insoluble in all common solvents but that swells in chloroform.

Free-radical-initiated homopolymerization and copolymerization of ESOCA

Cinnamic acid does not free-radically polymerize to a high-molecular-weight polymer. This behavior is in agreement with the generally correct view that 1,2-disubstituted alkenes are poor monomers. However, ESOCA, when treated with 1% Trigonox C (benzoyl-*t*-butyl peroxide) and heated, gave a soft solid that was insoluble in all common solvents and infusible. The partial loss of the double-bond absorption in the IR spectrum indicates that the cinnamate double bonds are not completely used up, but that the connectivity is enough to render the sample insoluble and infusible. The mechanical properties of the homopolymer, as expected, are not suitable for an end use as a load-bearing part. The DSC spectrum of this homopolymer shows two transitions at -1.5 and 78.9°C that are probably due to side-chain relaxations of the long fatty acid chains and backbone relaxation, respectively.

Although cinnamate esters are poor monomers in homopolymerization, they will readily undergo copolymerization with other alkene monomers, especially with those that have electron-deficient double bonds. As the ESOCA mixture has a very high viscosity, the use of a reactive diluent to bring the viscosity to the industrially acceptable 400 cP is also required. Therefore, copolymers of ESOCA with STYR, MMA, and VA with different comonomer ratios were made. DSC spectra of ESOCA-MMA, ESOCA-STYR, and ESOCA-VA copolymers and neat ESOCA are shown in Figure 4.

The copolymer of ESOCA with 25% (w/w) MMA is a rigid thermoset material that is infusible and insoluble. IR spectrum shows the presence of a third ester peak at 1740 cm^{-1} in addition to those of the triglyceride and cinnamate ester groups. The C—O—C band at 1168 cm^{-1} also shows broadening due to the new

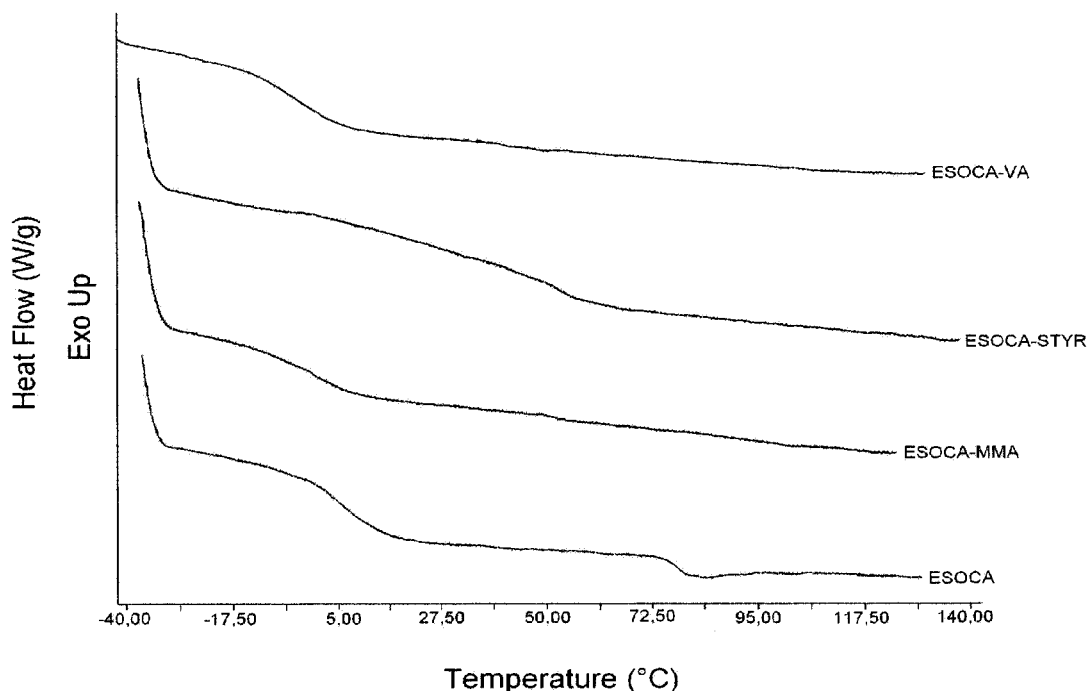


Figure 4 DSC spectra of ESOCA-MMA, ESOCA-STYR, and ESOCA-VA copolymers and neat ESOCA.

methacrylate ester. DSC spectra of this copolymer show a low-temperature phase change that was observed in the homopolymer at essentially the same temperature of -0.4°C , but as the backbone now is considerably different in structure, no glass transition due to the backbone relaxation is apparent. The backbone of the ESOCA-MMA copolymer does not show a glass-transition temperature (T_g), as the polymer is highly crosslinked. The ^1H NMR spectrum of a monomer-free ESOCA-MMA copolymer obtained as a

CDCl_3 -swollen sample indicates a copolymer molar composition of 10% ESOCA and 90% MMA. However, the feed molar ratio for this reaction was 16% ESOCA. NMR also indicates that 47% of the cinnamate double bonds are consumed.

The copolymer with 25% (w/w) VA gave a clear infusible and insoluble polymer. The IR spectrum shows the ester carbonyls at 1734 and 1710 cm^{-1} , the intensities of which are different from those of the ESOCA homopolymer. The DSC spectrum of this co-

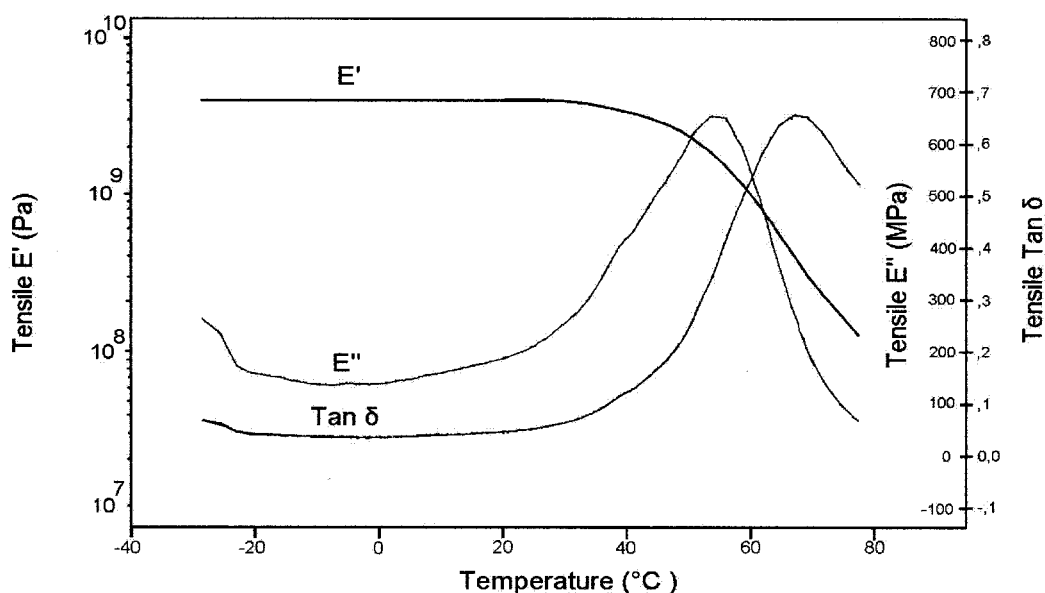


Figure 5 Storage modulus (E'), loss modulus (E''), and $\tan \delta$ versus the temperature for the ESOCA-STYR copolymer.

polymer shows the expected low-temperature transition at -1.0°C and again no glass transition because of the backbone. The ^1H NMR spectrum of the ESOCA-VA copolymer obtained as a CDCl_3 -swollen sample indicates a copolymer molar composition of 26% ESOCA and 74% VA. However, the feed molar ratio for this reaction was 15% ESOCA. NMR also indicates that 38% of the cinnamate double bonds are consumed.

Of the three copolymers produced, the one that looks promising as a structural polymer is the ESOCA-STYR copolymer. The copolymer with 25% (w/w) STYR was insoluble, infusible, hard, and transparent. The IR spectrum shows two different carbonyl peaks at 1739 and 1712 cm^{-1} belonging to the triglyceride and cinnamate ester carbonyl groups. The DSC spectrum of this copolymer shows the expected low-temperature transition at 0°C only as a shoulder, but it also shows a recognizable T_g at 53.5°C . This T_g is different from that of the homopolymer of STYR, which appears at about 100°C . The dynamic mechanical thermal analysis trace of an ESOCA-STYR sample is shown in Figure 5. Large relaxation windows can be seen with a broad $\tan \delta$ peak, and T_g was found to be 66°C , which is higher than the T_g value obtained by DSC. Having both high and broad $\tan \delta$ values and broad peaks also indicates that the material has quite an acceptable damping capacity for a relatively broad temperature range. This indicates that a copolymer, rather than a blend, is obtained. Unlike the previous copolymers, the copolymer composition of the STYR copolymer could not be determined because the aro-

matic protons of ESOCA and STYR coincided in the NMR spectrum.

CONCLUSIONS

The attachment of a cinnamate ester to epoxidized triglyceride gives entry to inherently photopolymerizable derivatives of plant oils. These can be homopolymerized or copolymerized at convenient wavelengths. Depending on the amount and nature of the comonomer, structurally rigid copolymers can be obtained by the free-radical copolymerization of the cinnamate-functionalized triglyceride and different alkene monomers.

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