

Synthesis and Polymerization of the Bromoacrylated Plant Oil Triglycerides to Rigid, Flame-Retardant Polymers

Tarik Eren, Selim H. Küsefoğlu

Department of Chemistry and Polymer Research Center, Boğaziçi University, Bebek, İstanbul 34342, Turkey

Received 9 April 2003; accepted 10 July 2003

ABSTRACT: Simultaneous addition of bromine and acrylate to the double bonds of fatty acids in triglycerides was achieved. In the first part of the study, methyl oleate was bromoacrylated in the presence of acrylic acid and *N*-bromosuccinimide as a model compound for the application of the reaction to the triglycerides. Next, soybean oil and high oleic sunflower oil were bromoacrylated by using the same procedure. The products were characterized by GC, IR, ¹H-NMR, ¹³C-NMR, and mass spectrometry. The bromoacrylation yields for soybean oil and sunflower oil were 75 and 55%, respectively. A rigid thermoset polymer was prepared from the radical copolymerization of bromoacrylated soybean oil with styrene. The bromoacrylated sunflower oil-styrene copolymer showed semirigid properties. The crosslinked network structure of the copolymers was examined by their swelling behavior in different solvents. Glass-

transition temperatures were also determined and soybean oil-based polymer and sunflower oil-based polymer showed a glass transition at 55–65 and 20–30°C, respectively. The storage moduli of the soybean-based and sunflower-based polymers at room temperature were approximately 1.0×10^{10} and 1.1×10^8 Pa, respectively. Photopolymerization was also carried out by using 2,2-dimethoxy-2-phenyl-acetophenone as initiator. The response of the cured polymers to the thermal energy produced by a small flame was also tested by the ignition respond index method according to ASTM D 3713-78 and was found to be 5 B at 2.00 mm. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2700–2710, 2004

Key words: renewable resources; biodegradable; flame retardance; photopolymerization; halogenated

INTRODUCTION

The predominant raw material used for the synthesis of commercially important polymers has been petroleum for the last 50 years. Synthesis of polymers from renewable resources such as plant and animal products is attractive because of the diminishing reserves and the increasing price of petroleum. Social acceptance of polymers from renewable, agricultural raw materials is also high because they represent a high-tech use for the traditional agricultural products. Usually biodegradable and cheap polymers are obtained from agricultural raw materials. Industrially, triglycerides are excellent examples of renewable resources. For example, soybean oil has double bonds (iodine number 142), but it does not give homo- or copolymer by a radical-initiated polymerization. This is also true for the new sunflower oil (83% oleic acid, iodine number 100). The internal, *cis* double bonds are too unreactive for polymerization and the allylic positions and the naturally occurring tocopherols in the oil are excellent chain-transfer agents and free-radical inhibi-

tors. Therefore, to be useful as a monomer for radical polymerization, the triglyceride molecule has to be suitably functionalized. One method we¹ and others² have used is to convert the triglyceride double bonds first to an epoxide and then open the epoxy groups with acrylic acid to yield hydroxy acrylated oils.¹ This is necessarily a two-step process and involves reactions that are not very attractive on a large scale. Radical polymerization of this monomer gives successful polymers as shown in Figure 1.

Given that the precursor triglyceride is polyunsaturated there is more than one oxirane group on the epoxidized oil (soybean 4.2, sunflower 2.9, on average). The acrylated product also contains numerous acrylate groups so that a network polymer is obtained when such monomers are free-radically polymerized.

Electrophilic addition of large, polarizable electrophiles to alkenes is known to proceed through nonclassical three-centered carbonium ions.³ The best evidence is the predominantly *trans* additions of halogens to cyclic alkenes. The initial three-centered nonclassical ion should behave like the epoxy group and allow the addition of acrylic acid. This would result in the one-step addition of bromide and acrylate groups to the triglyceride molecule as shown in Figure 2 and is the subject of our present article.

The product should not only be able to polymerize through the reactive acrylate, but the presence of bro-

Correspondence to: S. Küsefoğlu (kusef@boun.edu.tr).

Contract grant sponsor: Boğaziçi University Research Fund; contract grant number: 02S101.

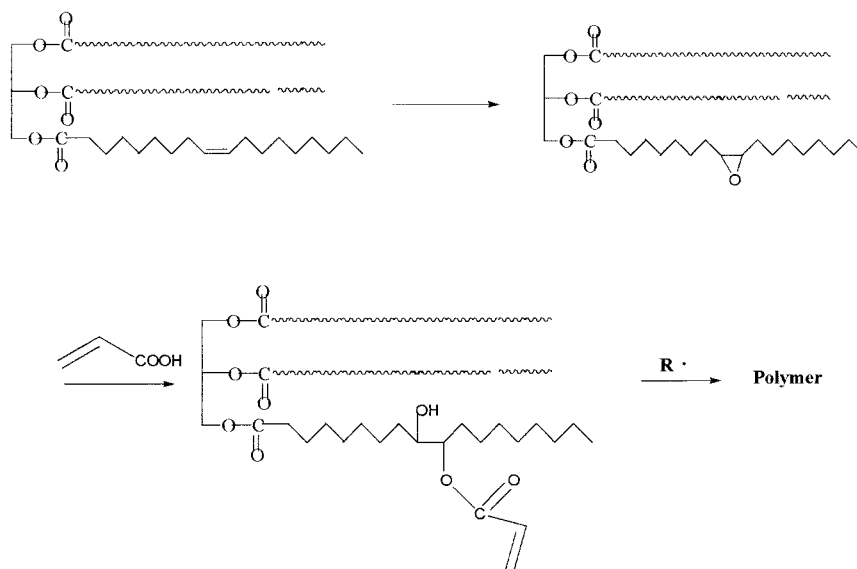


Figure 1 Synthesis and polymerization of hydroxyacrylated triglycerides.

mine should impart considerable flame resistance to the product polymer. Examples of direct addition of a halogen and a carboxylate to an olefin can be found in the literature. One such example is the reaction of propene with a mixture of iodine and peracetic acid in a mixed solvent acetic acid and ethyl ether to give

1-iodo-2-acetoxypropane in 54–80% yield.⁴ Jovtscheff⁵ studied the bromoacetoxylation of unsaturated fatty compounds such as methyl ricinoleate, oleic acid, methyl oleate, linoleic acid, methyl linoleate, and so forth. Bromoacetoxylation of the unsaturated fatty compounds occurred with high conversion. We now

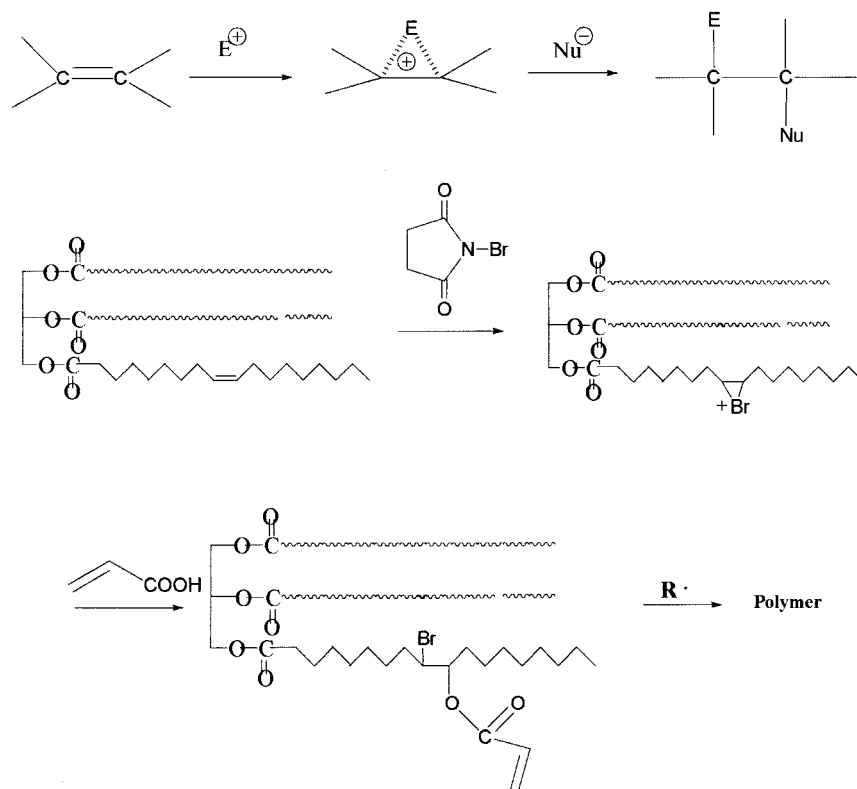


Figure 2 Synthesis and polymerization of bromoacrylated triglycerides.

report bromoacrylation of plant oil triglycerides and homo- and copolymerization of the bromoacrylated products.

EXPERIMENTAL

Reagents and instruments

The soybean oil (Marsa) used was food grade and used without further purification. New sunflower oil and methyl oleate was obtained from Henkel KgaA. *N*-Bromosuccinimide (NBS) was obtained from Fluka (Buchs, Switzerland) and used without purification. Acrylic acid was obtained from Aldrich (Milwaukee, WI). CDCl_3 (Aldrich) was used for ^1H - and ^{13}C -NMR analyses. Styrene was purchased from Fluka. The radical initiator methyl ethyl ketone peroxide (MEKP, Lucidol) was also used without further purification. 2,2'-Azobis(isobutyronitrile) (AIBN) was obtained from Fluka and was purified by recrystallization from methanol. The photoinitiator used was 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, MW 256.29, Aldrich).

The ^1H - and ^{13}C -NMR spectra were recorded on a Varian 400-MHz NMR instrument (Varian Associates, Palo Alto, CA) operating at a frequency of 399.986 MHz for proton and 100.587 MHz for carbon. The spectra were reported as ppm (δ) with TMS as internal standard. Mass spectra were obtained using a MAT 212-mass spectrometer and Zabspec for FAB technique. The IR analysis was performed on a Genesis FTIR spectrometer using NaCl windows. Analytical GC was performed on a Carlo Erba Fractovap 2150 with a FID (DB5-column, 28 m). The swelling behaviors of the polymers were tested in CCl_4 by using a Geartner 7109-46 traveling microscope. The dynamic mechanical thermal analyses of the samples were performed using a dynamic mechanical thermal analyzer (DMTA; Polymer Laboratories, Poole, UK).

Bromoacrylation of methyl oleate

In a N_2 -purged flask 2.57 g (8.6 mmol) methyl oleate (MO) and 150 mL (2.18 mol) acrylic acid were mixed. Then 2.82 g (15.8 mmol) NBS was added to the reaction mixture. The flask was covered with aluminum foil to prevent entry of light and stoppered. After all of the NBS dissolved (it took about 2–3 min), the mixture was kept at room temperature without mixing for 1 day. The reaction was quenched by an excess amount of H_2O and ether. The ether layer was extracted with aqueous KI (10 g/200 mL H_2O) and $\text{Na}_2\text{S}_2\text{O}_8$ (5 g/200 mL H_2O) to remove excess NBS. The unreacted acrylic acid was removed by aqueous NaOH (10%) extraction. The ether layer was dried with Na_2SO_4 and then evaporated, and 3.20 g of an orange-yellow oily product was obtained. Yield was 90%.

^1H -NMR. (CDCl_3) δ : 0.88 (t, 3H, H-18), 1.10–1.30 [m, 18H, $(\text{CH}_2)_9$], 1.51 (tt, 2H, H-3), 1.61 [dt, 2H, H-11 (8)], 2.20 (t, 2H, H-2), 3.60 (s, 3H, OCH_3), 4.00 (dt, 1H, $-\text{HCBr}-$), 5.00 [dt, 1H, $-\text{HCO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$ rsqb], 5.71 [d, 1H, $-\text{O}(\text{C}=\text{O})\text{CH}=\text{CHaHb}$], 6.15 [dd, 1H, $-\text{O}(\text{C}=\text{O})\text{CH}=\text{CHaHb}$], 6.34 [d, 1H, $\text{O}(\text{C}=\text{O})\text{CH}=\text{CHaHb}$].

^{13}C -NMR. (CDCl_3) δ : 14.93, 22.34, 24.57, 24.97, 25.05, 27.32, 27.39, 28.42, 28.70, 28.81, 28.89, 29.06, 29.40, 31.54, 31.64, 31.87, 31.89, 33.66, 34.33, 34.41, 35.34, 35.37, 51.63 ($-\text{OCH}_3$), [57.71, (57.75), $-\text{CHBr}-$], [75.33, (75.37), $-\text{CHO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], [128.37, 131.32, $-\text{CHO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], 165.44 [$-\text{CHO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], 174.12 [$-\text{C}(\text{O})\text{OCH}_3$].

MS. (PCI, *i*-Butane): 449.1 (M+H)⁺, 369.3 [(M+H)⁺—Br], 297 [(M+H)⁺—Br]— $\text{CH}_2=\text{CH}-\text{COOH}$].

IR (film). ν (cm^{-1}): 2952 (s, CH), 2855 (s, CH), 1741 (s, C=O), 1729 (s, C=O), 1636 (m, $-\text{HC}=\text{CH}-$), 1462 (m, CH_2 , Def.), 1436 (m, CH_3O , Def.), 1404 (m, $=\text{CH}_2$, Def.), 1294–1264 (m, C—O—C, Def.), 1186 (m, CO, Def.; C—O—C, Def.), 984 (m, $=\text{CH}$, Def.), 808 (m, $=\text{CH}_2$, Def.), 724 (m, C—Br).

Bromoacrylation of soybean oil

The procedure for bromoacrylation of methyl oleate was repeated using 1.37 g (1.58 mmol) soybean oil, 60 mL (875 mmol) acrylic acid, and 1.19 (6.7 mmol) NBS. The reaction was run and quenched as discussed above, and 1.85 g of an orange viscous oily residue was obtained. Yield was 75%.

^1H -NMR. (CDCl_3) δ : 0.95 (CH_3-); 1.2 ($-\text{CH}_2-$); 1.5 [$-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-$]; 1.6 [$-\text{CH}_2-\text{CH}(\text{Br})\text{CH}[\text{OC}(\text{O})\text{C}=\text{CH}_2]-\text{CH}_2-$]; 4.0 ($-\text{CHBr}$); 4.05 [$-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}-$]; 4.11 [$-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}-$]; 5.0 [$-\text{CHOC}(\text{O})\text{CH}=\text{CH}_2$]; 5.1 [$-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}-$]; 5.8 [$\text{O}(\text{C}=\text{O})\text{CH}=\text{CHaHb}$]; 6.1 [$-\text{O}(\text{C}=\text{O})\text{CH}=\text{CHaHb}$]; 6.4 [$-\text{O}(\text{C}=\text{O})\text{CH}=\text{CHaHb}$].

^{13}C -NMR. (CDCl_3) δ : 13.77, 13.90, 22.24, 22.33, 22.46, 24.59, 25.09, 27.27, 27.46, 28.53, 28.90, 29.15, 29.27, 29.48, 31.28, 31.62, 31.72, 32.03, 33.78, 33.93, 34.84, [56.19, 56.99, 57.34 ($-\text{CHBr}-$)], 61.90 [$-\text{C}(\text{O})\text{OCH}_2-$], 68.77 [$-\text{C}(\text{O})-\text{OCH}-$], [74.38, 74.55, 74.95, 75.56 [$-\text{CHO}(\text{C}=\text{O})-\text{CH}=\text{CH}_2$]], [122.69, 122.82, 124.92, 125.06, 128.06, 128.75, 130.52, 130.88, 131.12, 131.90, 132.90, 133.09, 133.76, 133.95 [$-\text{CHO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$] and $-\text{CH}=\text{CH}-$]], [165.18, 165.28 [$-\text{CHO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$]], [172.51, 172.92 ($-\text{C}(\text{O})\text{OCH}_2-$].

IR (film). ν (cm^{-1}): 2957 (s, CH), 2860 (s, CH), 1743 (s, C=O), 1739 (s, C=O), 1636 (m, $-\text{HC}=\text{CH}-$), 1457 (m, CH_2 , Def.), 1404 (m, $=\text{CH}_2$, Def.), 1264 (m, C—O—C, Def.), 1185 (m, CO, Def.; C—O—C, Def.), 983 (m, $=\text{CH}$, Def.), 808 (m, $=\text{CH}_2$, Def.), 726 (m, C—Br coincides with $=\text{C}_{\text{cis}}$).

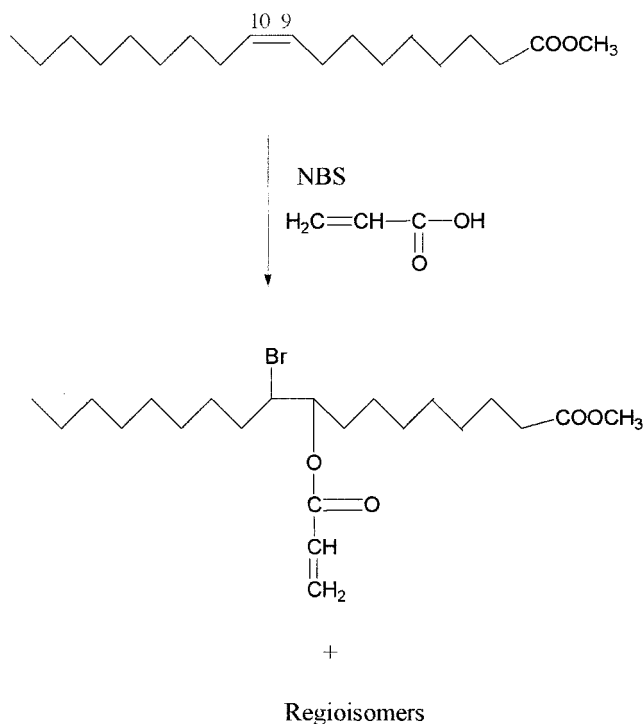


Figure 3 Bromoacrylated adduct of methyl oleate.

Bromoacrylation of new sunflower oil

The procedure for bromoacrylation of methyl oleate was repeated using 2.35 g (2.6 mmol) new sunflower oil, 35 mL (500 mmol) acrylic acid, and 0.91 g (5.1 mmol) NBS. The reaction was followed and quenched

as discussed above, and 2.85 g of a yellow oily residue was obtained. Yield was 55%.

$^1\text{H-NMR}$. (CDCl_3) δ : 0.95 (CH_3 -); 1.2 ($-\text{CH}_2-$); 1.4 [$-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-$]; 1.6 [$-\text{CH}_2-\text{CH}(\text{Br})\text{CH}[\text{OC}(=\text{O})-\text{C}=\text{CH}_2]-\text{CH}_2-$]; 3.9 ($-\text{CHBr}$); 4.05 [$-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}-$]; 4.11 [$-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}-$]; 4.9 [$-\text{CHOC}(=\text{O})\text{CH}=\text{CH}_2$]; 5.1 [$-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2-\text{O}-$]; 5.8 [$-\text{O}(\text{C}=\text{O})\text{CH}=\text{CHaHb}$]; 6.1 [$-\text{O}(\text{C}=\text{O})-\text{CH}=\text{CHaHb}$]; 6.4 [$-\text{O}(\text{C}=\text{O})\text{CH}=\text{CHaHb}$].

$^{13}\text{C-NMR}$. (CDCl_3) δ : 13.87, 22.42, 24.55, 24.63, 25.10, 26.96, 26.99, 27.46, 28.71, 28.88, 28.95, 29.10, 29.31, 29.48, 31.60, 31.69, 31.99, 33.73, 33.77, 34.81, 57.23 ($-\text{CHBr}-$), 61.85 [$-\text{C}(=\text{O})\text{OCH}_2-$], 68.74 [$-\text{C}(=\text{O})-\text{OCH}-$], 74.88 [$-\text{CHO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], [128.06, 130.97, $-\text{CHO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], (129.44, 129.74, $-\text{CH}=\text{CH}-$), 165.17 [$-\text{CHO}(\text{C}=\text{O})\text{CH}=\text{CH}_2$], {172.38, 172.77, 172.81 [$-\text{C}(=\text{O})\text{OCH}_2-$]}.

IR (film). ν (cm^{-1}): 2957 (s, CH), 2860 (s, CH), 1743 (s, C=O), 1730 (s, C=O), 1636 (m, $-\text{HC}=\text{CH}-$), 1465 (m, CH_2 , Def.), 1404 (m, $=\text{CH}_2$, Def.), 1264 (m, C—O—C, Def.), 1186 (m, CO, Def.; C—O—C, Def.), 984 (m, $=\text{CH}$, Def.), 807 (m, $=\text{CH}_2$, Def.), 723 (m, C—Br coincides with $=\text{C}_{cis}$).

Radical homopolymerization of the bromoacrylated triglycerides

The radical initiated homopolymerization of bromoacrylated triglyceride products was carried out in the presence of AIBN [neat or in solvent, (CDCl_2) $_2$] or MEKP as radical initiators. In a sample procedure,

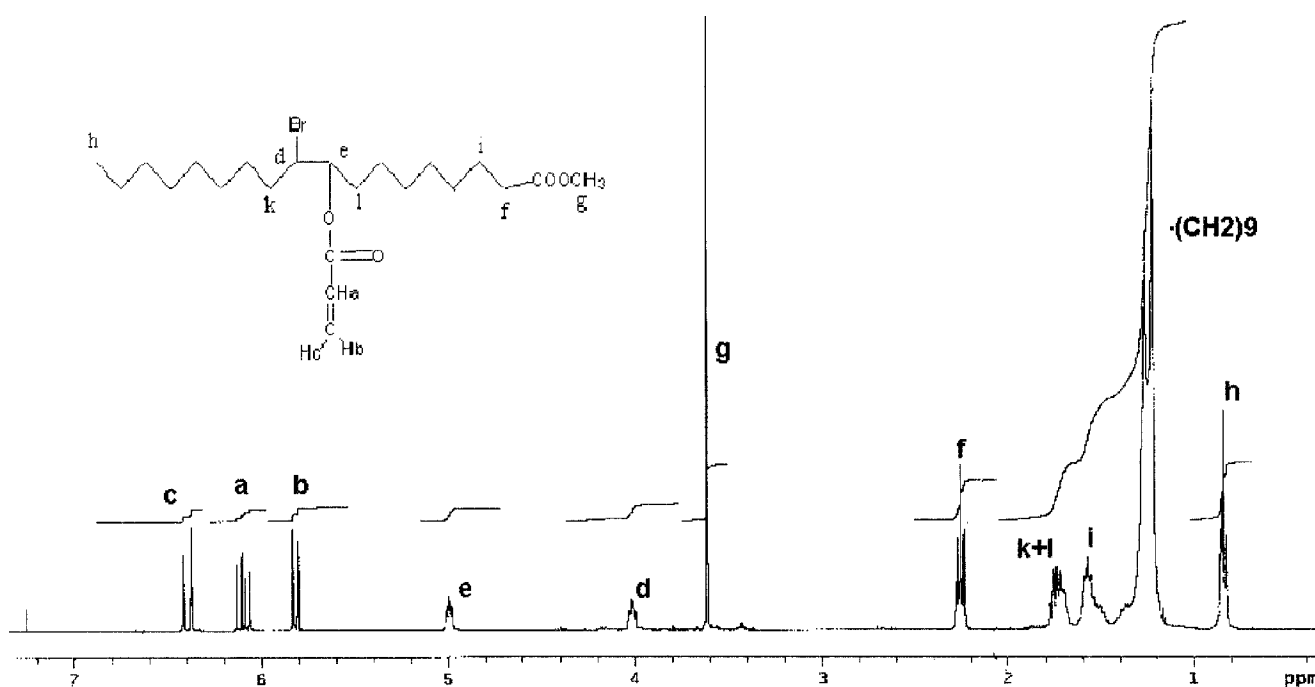


Figure 4 $^1\text{H-NMR}$ spectrum of bromoacrylated methyl oleate.

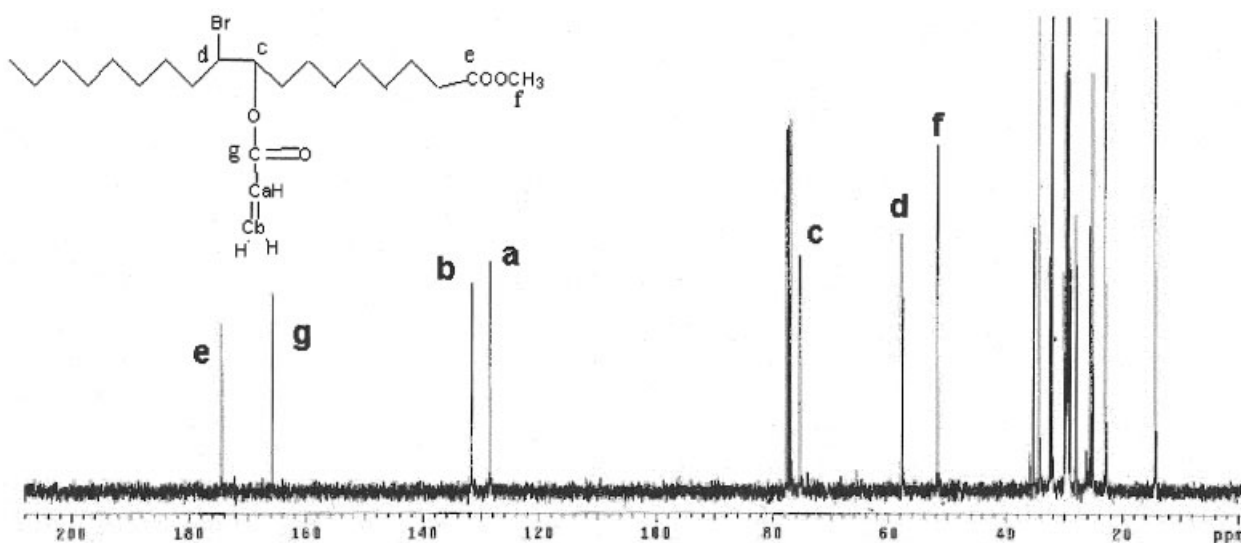


Figure 5 ^{13}C -NMR spectrum of bromoacrylated methyl oleate.

1.01 g of bromoacrylated soybean oil was mixed with 0.012 g AIBN, purged with N_2 , and heated to 85°C for 5 h. The polymerization was observed with viscosity increase in 1 h, and at the end of 3 h a soft solid was obtained. When the polymerized sample was triturated with CHCl_3 , 0.55 g of monomer was recovered. IR and ^1H -NMR (swollen in CDCl_3) showed a decrease in acrylate peak intensities; however, the homopolymerization of the acrylated triglycerides occurred to only a limited extent.

Photopolymerization of bromoacrylated triglycerides

Photopolymerization was done by using 1 wt % photoinitiator DMPA. The mixture was applied as a uniform thin film onto a NaCl crystal. Photopolymerization was done under a UV SL-25 ultraviolet lamp operating at 366 nm for 10 min. The product was found to be insoluble in CH_2Cl_2 , whereas the monomer was soluble in the same solvent.

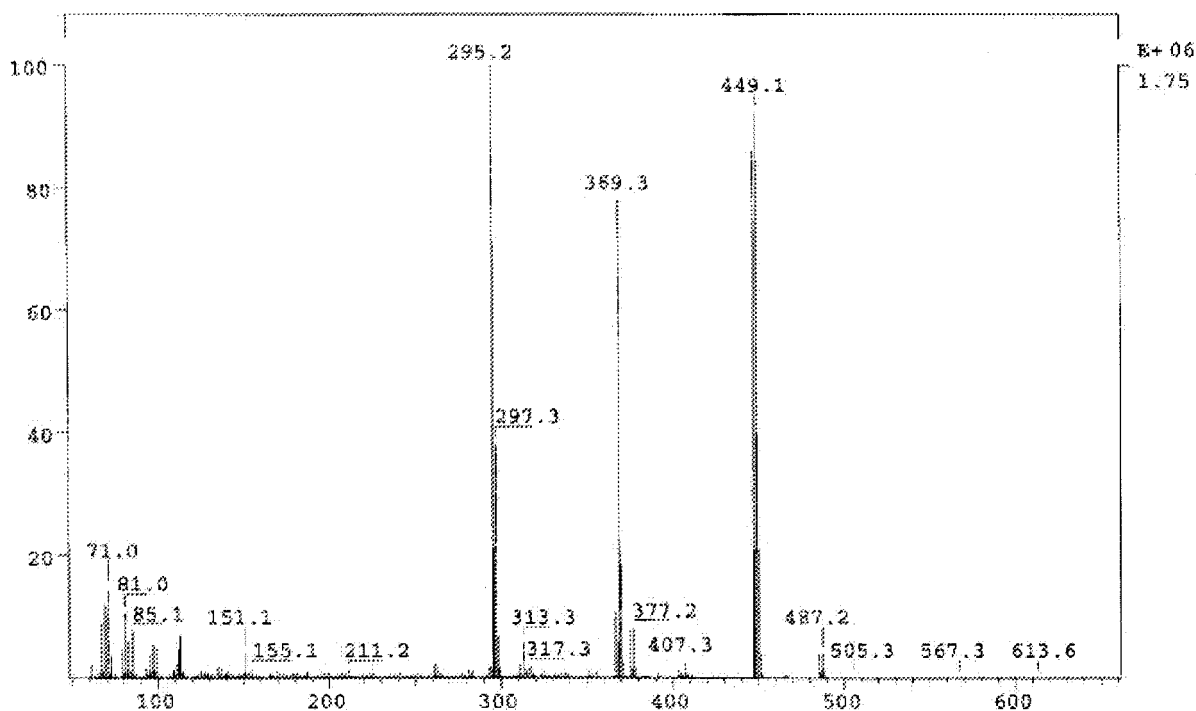


Figure 6 Mass spectrum of bromoacrylated methyl oleate.

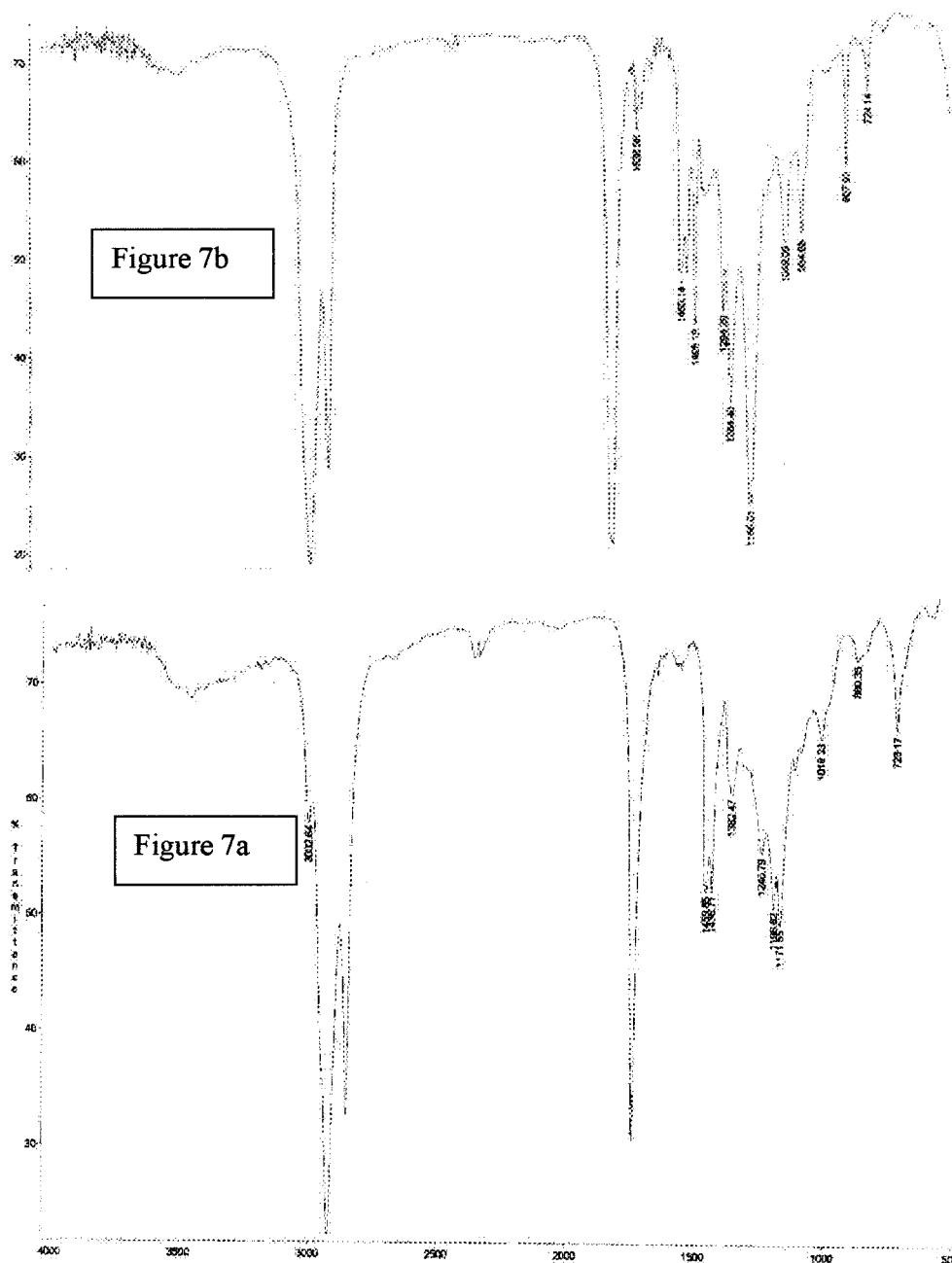


Figure 7 IR spectrum of (a) methyl oleate and (b) bromoacrylated methyl oleate.

Radical copolymerization of the bromoacrylated triglycerides with styrene

The polymerizations were run in a Teflon mold closed with a microscopic slide. Bromoacrylated triglycerides were mixed with 35% of its own weight of styrene to give a yellow colored transparent solution. Methyl ethyl ketone peroxide (MEKP; 1%) was added, the mixtures were purged with N_2 for 10 min, and cobalt naphthenate (6% solution, 0.3% based on MEKP) was added to each polymer sample. The samples were cured at room temperature for 2 days and gave quantitative yields of copolymers. Bromoacrylated soybean

oil-styrene copolymer was a rigid polymer, whereas new sunflower oil-based copolymer was a soft solid polymer. Chloroform swelled and fragmented the sample but did not extract any unreacted monomers or oligomers. This led us to conclude that the copolymer composition was the same as the feed composition.

Swelling test

Rectangular pieces (dimensions $\sim 2 \times 5 \times 10$ mm) were cut from the polymer samples. The samples were

TABLE I
Peak Clusters in the Mass Spectrum of Bromoacrylated Soybean and Sunflower Oil Adducts

Peaks (cm ⁻¹)	ΔMass	Number of residues	
		-CH(Br)-CH-O-CO- CH=CH ₂ (bromoacrylate)	-CH(Br)-CH(Br)- (dibromo)
Soybean-based			
1029	151	1	0
1038	160	0	1
1180	302	2	0
1189	311	1	1
1339	461	2	1
1331	453	3	0
1356	478	2	1
Sunflower based			
1035	151	1	0
1186	302	2	0
1337	453	3	0

placed in a closed container containing the solvent CCl₄. The lengths of the samples were measured as a function of time. The procedure was continued until the solvent uptake ceased.

Ignition response index measurement

The response of cured acrylated triglycerides to an ignition source [ignition response index (IRI)] was measured according to the ASTM D 3713-78.

RESULTS AND DISCUSSION

Synthesis and characterization of the bromoacrylated monomers

Bromination in nucleophilic solvent can lead to solvent incorporation if the solvent is sufficiently nucleophilic.^{6,7} If it is desired to introduce a solvent, it is necessary to keep the concentration of the bromide ion as low as possible.⁸ The heterolytic fission of the N—Br bond in *N*-bromosuccinimide (NBS) creates a bromonium ion and a succinimide anion. Whereas the bromonium ion is attacked by the π-system of the alkene, the succinimide anion is protonated by the acidic solvent. This gives a weak nucleophile succinimide and a carboxylate anion that attacks the three-centered carbonium ions. Jovtscheff⁵ found that the acetoxylation of fatty compound gave high yields in the presence of acetic acid and NBS. Using acrylic acid instead of acetic acid results in the addition of bromine and acrylate to the triglyceride double bonds. We applied this reaction first to methyl oleate as a model compound and found that it was necessary to use an excess amount of acrylic acid to obtain a meaningful solvent participation. At low acrylic acid concentra-

tions dibromination of the unsaturated fatty esters was observed. The reaction flask should be covered well to prevent the entry of light and oxygen, which should be avoided because these can facilitate radical reactions. Figure 3 shows the bromoacrylated product of methyl oleate.

By comparing the intensities of the NMR signal of the methoxy group (-OCH₃) in methyl oleate and the vinyl group in the acrylate, it was estimated that 90% yield was obtained and this result was correlated with GC analysis. In GC analysis, methyl palmitate was used as an internal standard for analyzing the bromoacrylate adduct peak. Methyl oleate was obtained from Henkel and it contains some methyl palmitate. Retention times for methyl palmitate and methyl oleate were observed as 17.43 and 19.41, respectively. Also, peak areas indicated the presence of 4% methyl palmitate. Under the same GC conditions, bromoacrylated methyl oleate had a retention time of 29.03.

Figure 4 shows the ¹H-NMR of bromoacrylated methyl oleate: (-CHBr-) and [-CHOC(=O)CH=CH₂] appear as a doublet of triplets at 4.00 and 5.00 ppm, respectively. The acrylate vinyl protons were seen at 5.71, 6.15, and 6.34 ppm. The vinyl protons of methyl oleate (-CH=CH-) at 5.2 ppm and the allylic hydrogens (=CH-CH₂-) at 2.00 ppm disappeared as expected. Figure 5 shows the ¹³C-NMR spectrum of bromoacrylated methyl oleate. Doubling of some peaks in the ¹³C-NMR spectrum indicates formation of regioisomers. The carbon bearing bromine (-CHBr-) appears at 57.71 ppm and its regioisomer appears at 57.75 ppm and the carbon bearing the acrylate ester [-CHOC(=O)CH=CH₂] appears at 75.33 ppm and its regioisomer appears at 75.37 ppm, respectively. The mass spectrum of the product was noteworthy. The molecular formula of the bromoacrylated methyl oleate is C₂₂H₃₉O₄Br and a base peak for the compound will be at (449) [(M+H)]⁺ by using CI with isobutane techniques. Figure 6 shows the bromine isotopes by doubling of the signals in the mass spectrum. Molecular fragmentations are seen as first a bromine elimination [(M+H)⁺-Br] at 369 and then as an acrylate fragmentation at 297 {[(M+H)⁺-Br]-CH₂=CH-COOH}. Figure 7 shows the IR spectrum of bromoacrylated methyl oleate. The IR spectrum shows a new ester carbonyl stretching band [-OC(=O)CH=CH₂] at peaks 1729 and 721 cm⁻¹ attributed to the C—Br stretching. The acrylate double bonds are observed at 808, 1404, and 1636 cm⁻¹.

Bromoacrylated methyl oleate adduct was synthesized as a model compound for the reaction of triglycerides. Although NMR spectra of bromoacrylated soybean oil and new sunflower oil spectra are more complex than the spectrum of methyl oleate, the expected signals for the bromoacrylated product can be observed. Using an excess amount of NBS and acrylic acid can

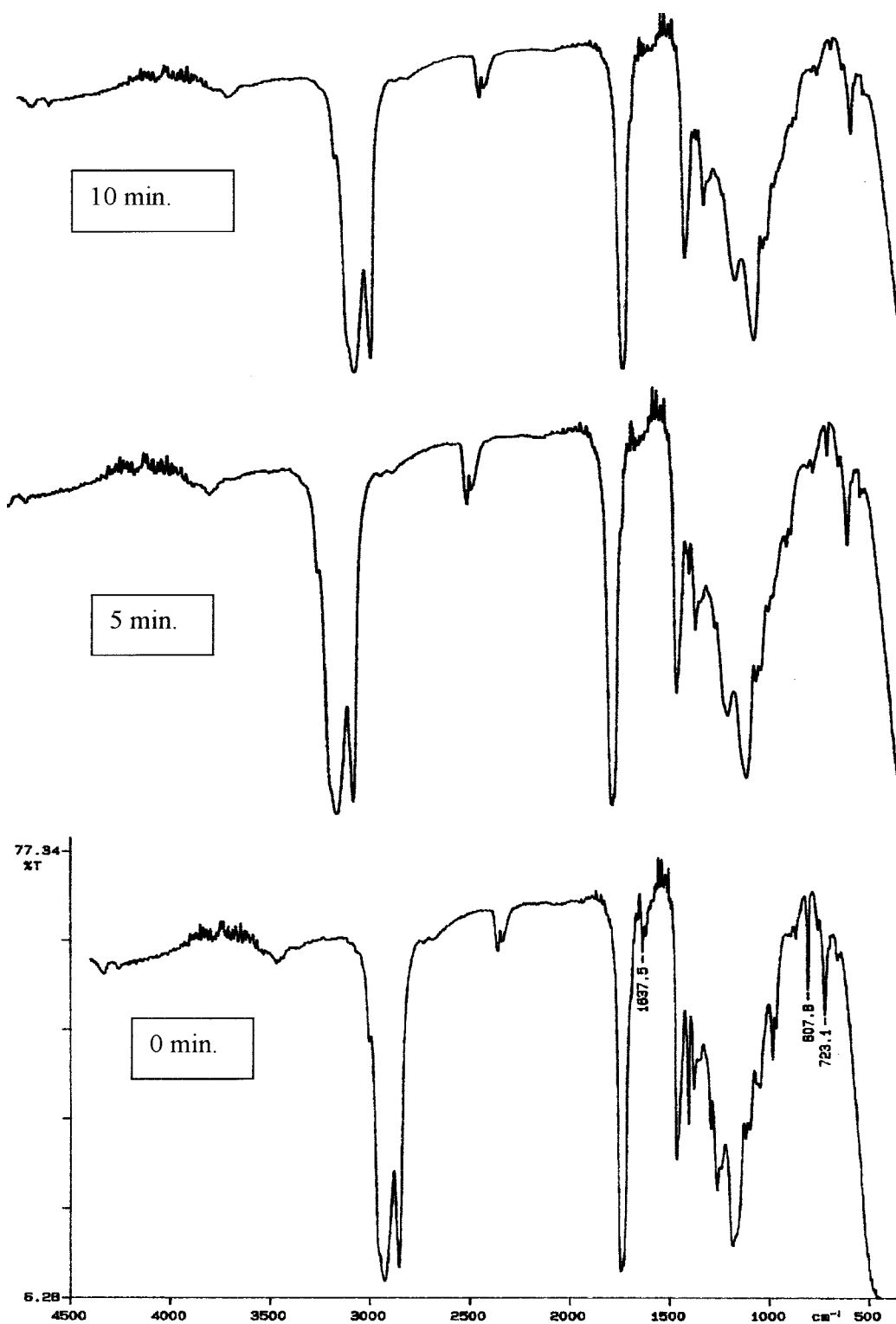


Figure 8 IR spectra of photopolymerized bromoacrylated sunflower oil at different stages of its synthesis.

result in dibromo addition to some extent and this was observed during the bromoacrylation of soybean oil. $^1\text{H-NMR}$ shows dibromo ($-\text{CHBrCHBr}-$) peaks at 4.20 ppm. Dibromo addition was not observed in the bromoacrylation of sunflower oil because the amount of NBS was not in excess. Therefore the NBS concentration

must be limited to prevent dibromination. The NMR spectrum of the soybean-based monomer shows 75% bromoacrylate, 10% unreacted *cis* double bond of triglyceride, and 15% dibromo adduct in the product, as mole ratios. Bromoacrylated new sunflower oil shows 55% of the double bonds reacted and 45% remained unreacted.

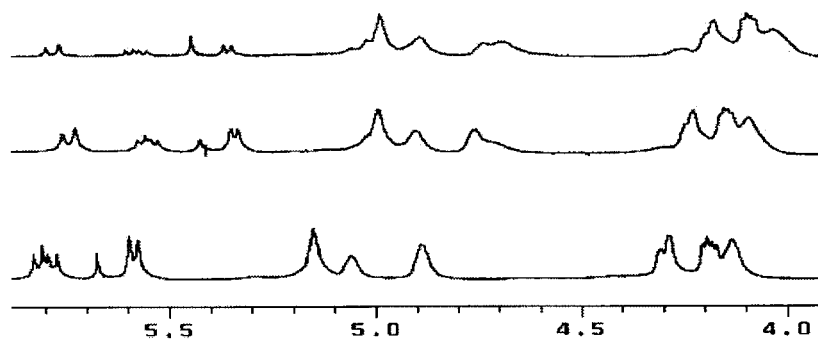


Figure 9 $^1\text{H-NMR}$ spectra of the homopolymerization of bromoacrylated sunflower oil at different stages of its polymerization.

The $^{13}\text{C-NMR}$ spectrum of bromoacrylated triglycerides shows the product and regioisomers. For instance, the carbon NMR spectrum of bromoacrylated sunflower oil showed the carbon bearing bromine ($-\text{CHBr}-$) at 57.42 ppm and its regioisomer at 57.38 and the carbon bearing acrylate ester [$-\text{CHOC}(=\text{O})\text{CH}=\text{CH}_2$] at 75.05 ppm and its regioisomer at 75.02 ppm, respectively. The acrylate double-bond carbons [$-\text{CHOC}(=\text{O})\text{CH}=\text{CH}_2$] appeared at 128.06 and 130.97 ppm, respectively. Unreacted triglyceride double bonds were still observed at 129.74 and 129.44 ppm. New ester carbonyl [$-\text{CHOC}(=\text{O})\text{CH}=\text{CH}_2$] was observed at 165.17 ppm. The $^{13}\text{C-NMR}$ spectrum of bromoacrylated soybean oil was more complex than sunflower oil because of heterogeneity of the product. For example carbon bearing acrylate ester [$-\text{CHOC}(=\text{O})\text{CH}=\text{CH}_2$] appeared at 74.38, 74.55, 74.95, and 75.56 ppm and this shows many isomers. The carbon bearing bromine ($-\text{CHBr}-$) appeared at 56.19, 56.99, and 57.34 ppm. Peaks attributed to both dibromo and bromoacrylate isomers coincide in this region.

The mass spectrum of bromoacrylated triglyceride adducts is difficult to interpret because of the heterogeneity of triglycerides attributed to the variation of the fatty acid type from molecule to molecule. Bromoacrylated soybean- and sunflower-based spectra showing the number of peaks and assignment of the peak clusters are presented in Table I. In the mass spectrum of the bromoacrylated products, the base peaks [M^+] are at 884 for sunflower oil and 878 for soybean oil. Mono addition peaks are at 1035 and 1029 for sunflower and soybean oils, respectively. The mass spectrum of the soybean oil adduct is more complex than that of sunflower oil adduct. The peak at 1038 in the mass spectrum of soybean oil adduct is attributed to the dibromo addition to the soybean oil molecule. The mass spectrum of bromoacrylated soybean oil shows the peaks at 1188 and 1339 corresponding to mono- and diadditions as well [differing by 151 (Br + Acrylate)].

Polymerization of the bromoacrylated triglycerides

Soybean oil has an average number of 4.2 per double-bonded triglyceride molecule, which is higher than that of the new sunflower oil at 2.9. Thus, after the reaction, soybean oil has more acrylate double bonds per triglyceride than the new sunflower oil. $^1\text{H-NMR}$ analysis confirms that soybean oil has higher numbers of acrylate residues per triglyceride molecule (2.3 avg) than new sunflower oil (1.5 avg).

Photopolymerization of the new monomers using DMPA initiator was attempted first. The extent of photopolymerization was followed by IR spectroscopy. Figure 8 shows the decrease of the peaks centered at 808 and 1643 cm^{-1} , corresponding to acrylate double bonds, upon irradiation. The photopolymerized samples were insoluble in CH_2Cl_2 in which the monomers were soluble.

The radical-initiated homopolymerization of the bromoacrylated triglyceride products was carried out in the presence of AIBN [neat or in solvent (CDCl_2) $_2$] or MEKP as radical initiators. Disappearance of the acrylate double bond IR absorptions at 1643 and 808 cm^{-1} was observed during polymerization. Homopolymerization of bromoacrylated soybean oil was

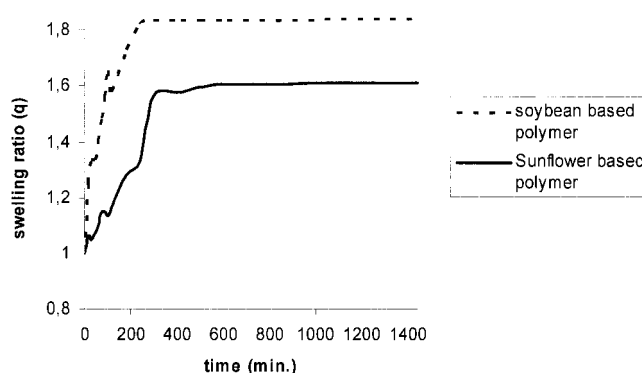


Figure 10 Swelling behaviors of the copolymers of sunflower-based and soybean-based monomers with styrene.

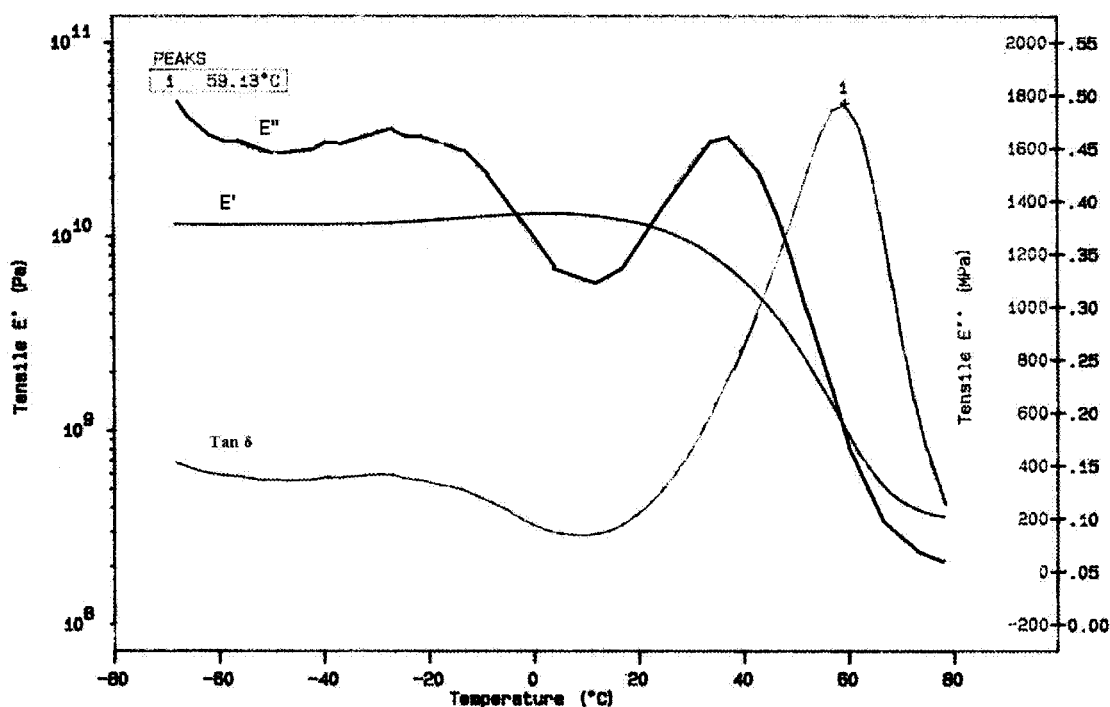


Figure 11 DMTA graph of bromoacrylated soybean oil-styrene copolymer.

also followed by NMR. Figure 9 shows the disappearance of the acrylate double bond signals at 5.8 $[-O(C=O)CH=CHaHb]$, 6.1 $[-O(C=O)CH=CHaHb]$, and 6.4 $[-O(C=O)CH=CHaHb]$ during the polymerization. NMR integral analysis also indicates that residual unreacted double bonds of the triglyceride are reduced by 8% during polymerization. Participation of the triglyceride double bonds in the styrene copolymerization reaction can result in a change in mechanical properties of the crosslinked network.

Soybean oil has a higher acrylate substitution than that of sunflower oil, and thus it can quickly reach gelation. The liquid mixture of the bromoacrylated soybean oil and styrene were transformed into a soft rubbery solid at the end of 1 h. The polymer, obtained at the end, is a transparent, light yellow colored rigid solid. Meanwhile, bromoacrylated new sunflower oil and styrene copolymers gelled within 2 h and became a semirigid solid at the end of 3 h. Unfortunately, it was impossible to analyze the bulk polymerized samples with ¹H-NMR because the polymers were insoluble in common solvents. Swelling behavior and insolubility in common solvents suggest that a crosslinked structure exists.

The swelling behaviors of the polymers in CCl₄ were examined by using a traveling microscope (Geartner 7109-46). The samples were placed in a closed container containing the solvent CCl₄, and sample lengths were measured at particular time intervals. The experiment was continued until the solvent up-

take ceased. The swelling ratio (q) was obtained by the following equation⁹:

$$q = V/V_0 = (L/L_0)^3$$

where V_0 and V are the volumes of unswollen and swollen composites, respectively; and L_0 and L are the lengths of the unswollen and swollen composites, respectively. Figure 10 shows the swelling behaviors of the copolymers. Swelling behavior is also a good indication for the crosslinking density, higher swelling being an indication of lower crosslinking density. As shown in Figure 10, the swelling ratio of the new sunflower oil-based copolymer is higher than that of soybean-based polymer.

The mechanical properties of a sample of the cured resins were also tested by DMTA. Sample dimensions of 20 × 10 × 2 mm were scanned at the frequency of 1 Hz and heating rate of 5°C/min under N₂ between a temperature range of -80 and 150°C. It is well known that crosslinking density affects the glass-transition temperature (T_g) of the networks. Sunflower-based copolymer shows a T_g at 20–30°C, whereas soybean-based copolymer shows a T_g at 55–65°C. The pendant chains act as plasticizers and affect the mechanical properties of the copolymers. Figure 11 shows the temperature dependency of the storage modulus E' of soybean-based copolymer. The storage moduli of the soybean-based and sunflower-based copolymers at room temperature are approximately 1.0×10^{10} and 1.1×10^8 Pa, respectively.

It is known that halogen-containing polymers are flame retardant because halogen radicals act as radical scavengers in the vapor phase, which inhibits the combustion. Also, the production of char protects the polymer surface from the combustion in the condensed phase and is partly responsible for the flame retardancy.¹⁰ The response to thermal energy, applied by a small flame, was measured according to ASTM D 3713-78. The ignition response index (IRI) of the cured bromoacrylated polymer was 5 B at 2.00 mm. This means that a polymer with a thickness of 2.00 mm can withstand a flame impingement time of 5 s, but will burn (flame or glow, or both) more than 30 s if ignited for 10 s or more. Bromoacrylated soybean- and sunflower-based polymers showed the same properties. It is possible to increase the flame-retardant properties of the new copolymers by mixing them with small amounts of antimony oxide or hydrated zinc borate.

CONCLUSIONS

Soybean and sunflower oil triglycerides were bromoacrylated by a one-step route. Soybean oil gave a higher acrylate substitution than sunflower oil. These new monomers were copolymerized with styrene.

Soybean oil-based copolymer, showing a T_g at 55–65°C, was a rigid, load-bearing thermoset resin with a dynamic modulus of 1.0×10^{10} Pa and ignition response index of 5 B.

Research funding was provided by the Boğaziçi University Research Fund, Grant 02S101.

References

1. Wool, R. P.; Küsefoğlu, S.; Palmese, G.; Khot, S.; Zhao, R. U.S. Pat. 6,121,398 (2000).
2. Petrovic, Z. S.; Cho, Y.; Guo, A. *J Polym Sci Part A: Polym Chem* 2000, 38, 3900.
3. March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; pp 293–500.
4. Ogata, Y.; Aoki, K. *J Org Chem* 1966, 31, 1625.
5. Jovtscheff, V. A. *J Prakt Chem* 1965, 28, 186.
6. Boerwinkle, F.; Hassner, A. *Tetrahedron Lett* 1968, 36, 3921.
7. Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part B: Reactions and Synthesis*; Plenum Press: New York/London, 1990; pp 176–185.
8. Horner, L.; Winkelmann, E. H. In: *Newer Methods of Preparative Organic Chemistry*; Foerst, W., Ed.; Academic Press: New York, 1964; p 151ff.
9. Klemptner, D.; Fristo, H. L. *J Polym Sci* 1975, 8, 921.
10. Tess, W. R.; Poehlein, W. G. *Flammability of Polymers in Applied Polymer Science*; ACS Symposium Series 000; Washington, DC, 1985; pp 305–319.