Simultaneous Interpenetrating Polymer Networks Based on Bromoacrylated Castor Oil Polyurethane

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ABSTRACT: In the first part of this study, simultaneous addition of bromine and acrylate to the double bonds of castor oil was achieved. In the second part of the study, bromoacrylated castor oil (BACO) was reacted with toluene-diisocyanate (TDI), to form a prepolyurethane (BACOP). The prepolyurethanes were reacted with styrene (STY), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and 3-(acryloxy)-2-hydroxy propyl methacrylate (AHPMA) free radically, using the acrylate functional group to prepare the simultaneous interpenetrating polymer networks (SINs). 2,2'-Azobis (isobutyronitrile) (AIBN) was used as the initiator and diethylene glycol dimethacrylate (DEGDMA) was used as the crosslinker. BACO and BACOP were characterized by IR, ^{1}H-NMR, and ^{13}C-NMR techniques. Synthesized polymers were characterized by their resistance to chemical reagents, thermogravimetric analysis, and dynamic mechanical thermal analyzer (DMTA). All the polymers decomposed with 6–10% weight loss in a temperature range of 25–240°C. MMA-type SIN showed the highest T_g (126°C), while STY-type SINs showed the highest storage modulus (8.6×10^9 Pa) at room temperature, with respect to other synthesized SINs. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2947–2955, 2006

Key words: renewable resources; interpenetrating networks; flame retardance; halogenated; *N*-bromosuccinimide

INTRODUCTION

Petroleum has been the predominant raw material used for the synthesis of commercially important polymers, for the last 50 years. Synthesis of polymers from renewable resources, such as plant and animal products, is attractive because of diminishing reserves and increasing price of petroleum. Social acceptance of polymers from renewable, agricultural raw materials is also high, since they represent a hightech use for traditional agricultural products. Usually, biodegradable and cheap polymers are obtained from agricultural raw materials. Industrially, fats and oils containing mainly triglyceride esters of fatty acids are excellent examples of renewable resources.

Castor oil, obtained from castor beans grown mainly in India is unique in containing hydroxyl groups on its triglycerides. Ricinoleic acid, which makes up 85–90% of all the fatty acids in castor oil, contains a secondary hydroxyl group beta to the vinylidene group, as shown in Figure 1. Castor oil contains 2.7 hydroxyl groups per molecule, on an average. The hydroxyl groups on castor oil have been used to form polyesters and polyurethanes by interpenetrat-

ing network (IPN) formation, and these polymers have been used as surface coatings.[1–4]

IPNs contain two or more polymers, each in network form. The two networks may be chemically linked to each other or may simply interpenetrate without chemical bonds. IPNs can be prepared either sequentially or simultaneously. Simultaneous interpenetrating networks (SINs) involve the mixing of all polymer components at an early stage. Then, the formation of both networks by independent reactions occurs simultaneously. One reaction, for example, can be a polyesterification or a polyurethane stepwise reaction, whereas the other is an addition reaction via free radical chemistry.[5,6] Sequential IPNs are usually made by swelling one network in the monomer of the other network, followed by polymerization and crosslinking of the monomer.

Acrylated castor oil has been used as comonomer for emulsion polymerization, to produce latex polymers.[7] We have earlier[8] demonstrated that acrylation of epoxidized soybean oil by ring opening of epoxy groups with acrylic acid, followed by the reaction of the newly formed hydroxyl groups with isocyanates is feasible. The acrylates were separately copolymerized with styrene (STY) by free radical pathway. In this study, castor oil was bromoacylated in one step, by adding bromine and acrylate groups to the double bonds, and then, the hydroxyl groups were used for polyurethane synthesis. Figure 2 shows the chemistry. The resulting triglyceride derivative is now capable of
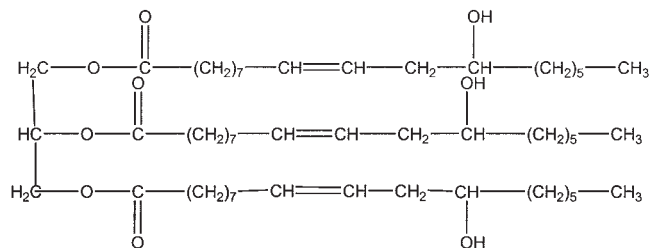
Figure 1 Structure of castor oil.

free radically polymerizing through the acrylate, and is capable of forming a urethane through the hydroxyl group. In principle, these reactions can be done in any desired order or simultaneously.

In addition to the interesting mechanical properties expected from the SINs, the presence of bromine should impart considerable flame resistance.

EXPERIMENTAL

Reagents and instruments

Pharmaceutical-grade castor oil was obtained from Çağdas Laboratory (Istanbul, Turkey) and was found to have a hydroxyl number of 145, according to ASTM D 1957–63. This corresponds to 2.6 —OH groups per mole of castor oil. N-Bromosuccinimide (NBS) was obtained from Fluka (AG, Switzerland) and used without purification. STY was purchased from Fluka. 2,2′-Azobis(isobutyronitrile) (AIBN) was obtained from Fluka and was purified by recrystallization from methanol. CDCl$_3$ (Aldrich, Milwaukee, WI) was used for ^{1}H- and ^{13}C-NMR analysis. Acrylic acid was obtained from Aldrich. 2,2-Dimethoxy-2-phenyl-aceto-phenone (DMPA, M_w 256.29; Aldrich) was used as the photoinitiator. 2-Hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and 3-(acryloxy)-2-hydroxy propyl methacrylate (AHPMA) were obtained from Aldrich. Diethylene glycol dimethacrylate (DEG-DMA) and toluenediisocyanate (TDI) were obtained from Fluka. ^{1}H and ^{13}C-NMR spectra were recorded on a Varian 400 MHz NMR (Varian Associates, Palo Alto, CA), operating at a frequency of 399.986 MHz for proton and 100.587 MHz for carbon. Spectra were reported as ppm (δ), with TMS as the internal standard. The IR analysis was performed on Genesis FT-IR spectrometer (New Castle, DE), using NaCl windows. The dynamic mechanical thermal analysis of the samples was performed using Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA, Polymer Laboratories, Poole, UK). Thermal Gravimetric Analysis (TGA) was performed in nitrogen with NETZSCH STA 449C (National Physical Laboratory, Teddington, UK) at a heating rate of 10°C/min and scanned from 25°C to 550°C.

Determination of hydroxyl number

Hydroxyl number was determined according to ASTM D 1957–63, by reacting the oil with excess acetic anhydride, hydrolyzing the unreacted anhydride with aqueous KOH, and back titrating the formed acetic acid to phenolphthalein end point. Hydroxyl number of the castor oil used was found to be 145 and this corresponds to 2.6 OH groups per mole of castor oil and molecular weight of castor oil was taken as 920 ± 46.[9]
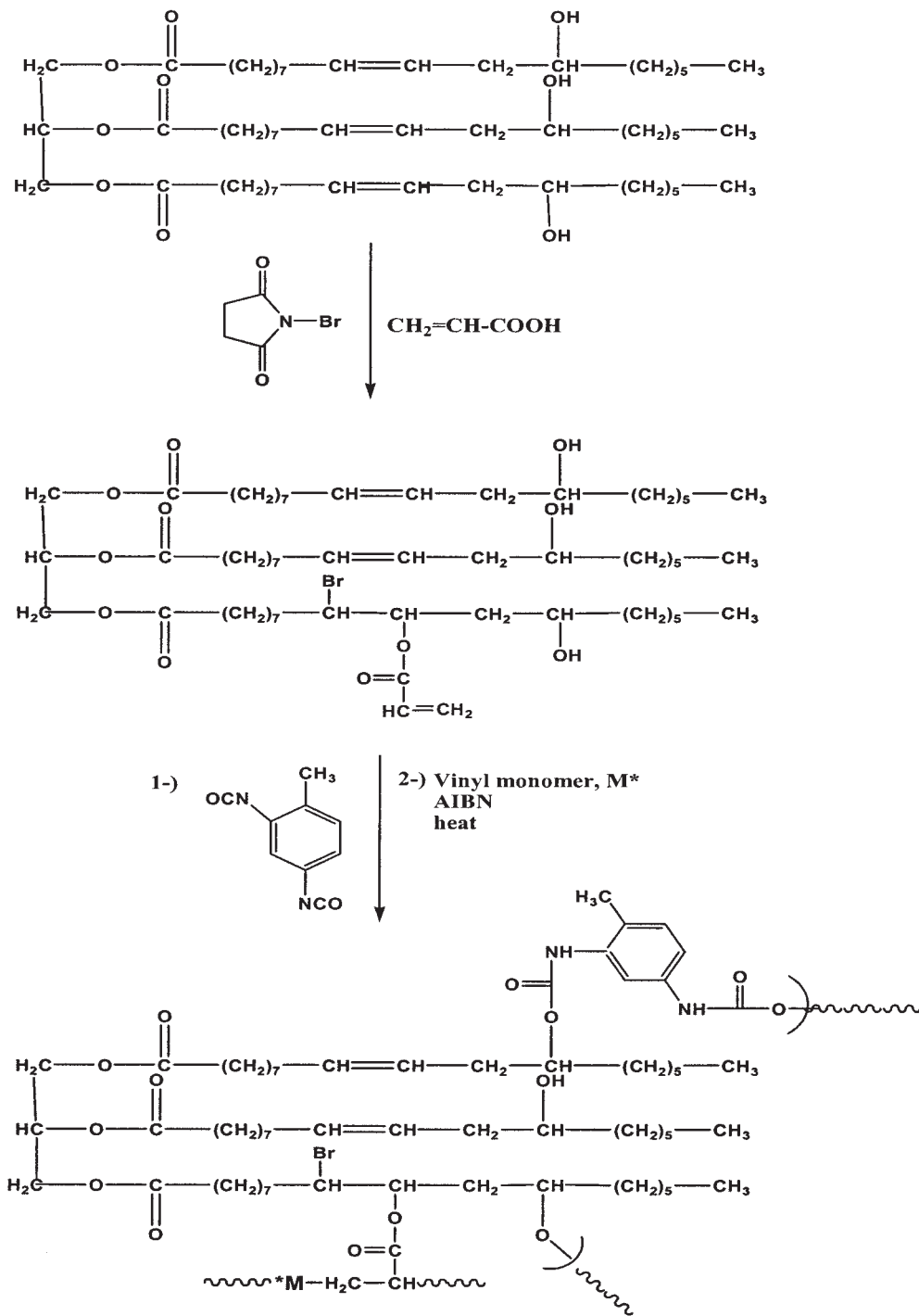
Castor oil bromoacrylate

In an N$_2$-purged flask, 2.90 g (3 mmol) castor oil and 200 mL (3 mol) acrylic acid were mixed. About 2.86 g (16 mmol) of NBS was then added to the reaction mixture. The flask was covered with aluminum foil to prevent entry of light and was stoppered. After all of the NBS dissolved (~2–3 min), the mixture was kept at room temperature without mixing for 2 h. Reaction was quenched by an excess amount of H$_2$O and ether. Ether layer was extracted with aqueous KI (10 g/200 mL H$_2$O) and Na$_2$S$_2$O$_8$ (5 g/200 mL H$_2$O) to remove excess NBS. Unreacted acrylic acid was removed by aqueous NaOH (10%) extraction. Ether layer was dried with Na$_2$SO$_4$ and then evaporated. About 3.70 g of orange oily viscous product was obtained. ^{1}H-NMR indicated 76% conversion.

^{1}H-NMR (CDCl$_3$) δ: 0.95 (CH$_3$—); 1.2 (—CH$_2$—); 1.4 (—(CH$_2$)$_4$—CH$_2$—CH(OH)—); 1.6 (—CH_2—CH$_2$—C(=O)—); 1.6–2.0 (—CH_2—CH(Br)CH(OC(=O)C=CH$_2$)—CH_2—); 2.2 (—CH$_2$—C(=O)—O—); 3.4–3.8 (—CH(OH)—); 4.05–4.10 ((—CHBr—) coincides with —O—CH_2—CH(O—)—CH$_2$—O—); 4.20 (—O—CH$_2$—CH(O—)—CH_2—O—); 5.0 (—CHOC(=O)CH=CH$_2$); 5.1 (—O—CH$_2$—CH(O—)—CH$_2$—O—); 5.8 (—O(C=O)CH=CHaHb); 6.1 (—O(C=O)CH=CH-aHb), 6.4 (—O(C=O)CH=CHaHb). ^{13}C-NMR (CDCl$_3$) δ: 14.93–32.11, 37–43 (—CH—CHOH—), 54–58 (—CHBr—), 62.4 (—COCH$_2$(CHO—)), 69.2 (—COCH$_2$(CHO—)—), 63–76 (—CH(OH)— and (—CHOC(=O)CH=CH$_2$), 128–131 ((—O(C=O)CH=CH$_2$), 165–167 ((—O(C=O)CH=CH$_2$), 174.12–176 (—(C=O)—O—CH$_2$—CH(O—)—CH$_2$—O—(C=O)—). IR (Film) ν (cm^{-1}): 3467 (s, OH), 2927 (s, CH), 2855 (s, CH), 1743 (s, C=O), 1726 (s, C=O), 1636 (m, —HC=CH—), 1457 (m, CH$_2$, Def.), 1405 (m, =CH$_2$, Def.), 1264 (m, C—O—C, Def.), 1186 (m, CO, Def.; C—O—C, Def.), 984 (m, =CH, Def.), 808 (m, =CH$_2$, Def.), 725 (m, C—Br).

Castor oil bromoacrylate polyurethane (BACOP)

Castor oil bromoacrylate (BACO) (1.17 g, 0.8 mmol) was reacted with TDI (0.32 g, 1.6 mmol) to maintain NCO/OH ratio at 1.54:1. The reaction was carried out

M* = styrene (STY), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and 3-(acryloxy)-2-hydroxy propyl methacrylate (AHPMA)

Figure 2 Formation of simultaneous interpenetrating polymer networks based on bromoacrylated castor oil polyurethane. M* = STY, HEMA, MMA, and AHPMA.

at 55°C with continuous stirring for 45 min. The prepolymer was isolated as an orange-yellow viscous liquid. By following the intensity of peaks —CH—O—C(=O)—NH— at 4.9 ppm and —CHOH signal at 3.4–3.8 ppm in the ^{1}H-NMR of the product, the conversion was found to be 40%. The unreacted

TDI was kept in the mixture to allow complete polymerization in the next step.

^{1}H-NMR (CDCl$_3$) δ: 6.82–7.02 (3H, ArH); 4.96 (1H, —CH—O—C(=O)—NH—); 6.8 (1 H, br, NH—C(=O)—O—). ^{13}C-NMR (CDCl$_3$) δ: 155 (—NH—C(=O)—O—); 75 (—CH—O—C(=O)—NH—); 124–123 (—N=C=O); 137 (ArC—NH—). IR (Film) ν (cm^{-1}): 3342 (N—H stretching); 2269 (N=C=O stretching); 1595 (N—H deformation); 1536 (C—N stretching, amide II band).

SIN synthesis

In a typical procedure, the urethane prepolymer prepared (BACOP) was mixed with equal weight of the reactive monomers HEMA, MMA, AHPMA, and STY in a vial. About 1.5% (w/w, based on the total mixture) of each of crosslinker DEGDMA and free radical initiator AIBN were added to each mixture. The mixtures were purged with N$_2$ for 10 min and stirred for 1 h at 50°C to form homogeneous mixture. The vial was sealed and heated in oil bath at 65°C for 24 h and 85–90°C for 14 h. The product was triturated with CHCl$_3$ to remove the unreacted monomers.

Resistance to solvents

Solvent resistance of SINs to a series of standard solvents, such as acetone, CHCl$_3$, MeOH, THF, and toluene, was studied; these SINs were observed to be stable in all standard reagents, and no soluble fraction was observed. Synthesized polymers were brittle and fragmented when swollen in CHCl$_3$ and THF.

Photopolymerization of BACO

Photopolymerization was done by using 1 wt % the photoinitiator, DMPA. The mixture of BACO and initiator in CH$_2$Cl$_2$ was applied as a uniform thin film onto an NaCl crystal. The solvent was evaporated and photopolymerization was done under a UV SL-25 ultraviolet lamp operating at 366 nm for 10 min. The distance between the lamp and the NaCl crystal was 12 cm.

RESULTS AND DISCUSSIONS

Bromination in nucleophilic solvent can lead to solvent incorporation, if the solvent is sufficiently nucleophilic.[10,11] If it is desired to favor introduction of a solvent, it is necessary to keep the concentration of the bromide ion as low as possible.[12] Heterolytic fission of N—Br bond in NBS creates bromonium ion and succinimide anion. Succinimide anion is then protonated by the acidic solvent to give a weak nucleophile, succinimide, while the carboxylate anion attacks the three centered bromonium ion. Jovtscheff[13] found that bromoacetylation of methyl ricinoleate 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 double bonds of fatty compounds. It is necessary to use an excess amount of acrylic acid to obtain a meaningful solvent participation, so that dibromide formation is minimized. Reaction flask should be covered well to prevent exposure to light, and oxygen should be avoided, since these can facilitate radical reactions. In our previous study,[14] we synthesized bromoacrylated new sunflower oil and soybean oil by one-step route, in the presence of NBS and acrylic acid in high yield. In this study, castor oil is bromoacrylated and then polymerized with reactive diluents.

Figure 3 shows the ^{1}H-NMR of the bromoacrylated castor oil (BACO). Castor oil has 5% linoleic (two double bonds) and 4% oleic (one double bond) type fatty acids in its composition and also regioisomers of the product which result in multitude of peaks in ^{1}H- and ^{13}C-NMR spectra. Although NMR spectrum of the BACO is complex, the expected signals for the bromoacrylated product of castor oil can be observed. The expected isomers of bromoacrylated structures are shown in Figure 4.

Figure 3 shows that (—CHOC(=O)CH=CH$_2$) signal is at 5.00 ppm. Hydrogen geminal to the bromine (—CHBr—) coincides with (—O—CH$_2$—CH(O—)—CH$_2$—O—) at 4.05–4.10 ppm. Hydrogen geminal to the hydroxyl group (—CH(OH)—) appears in a broad range of 3.4–3.8 ppm because of the presence of regioisomers. Acrylate vinyl protons were observed at 5.71, 6.15, and 6.34 ppm. Vinyl protons of castor oil (—CH=CH—) at 5.2 ppm and allylic hydrogens (=CH—CH$_2$—) at 2.00 ppm disappeared, as expected. By comparing the NMR peak intensities of the triglyceride α—CH$_2$ (—CH$_2$—C(=O)—O—, 2.2 ppm) and the vinyl protons in the acrylate, it was estimated that 76% yield was obtained, and this corresponds to ~2.3 bromoacrylate residues attached to one castor oil molecule.

^{13}C-NMR spectrum of BACO, shown in Figure 5, indicates that the product is a mixture of regioisomers, as shown in Figure 4. For example, carbon bearing acrylate ester (—CHOC(=O)CH=CH$_2$) and (—CHOH) appeared at 63.8, 66.1, 67.6, 69.5, 71.2, 72.5, 73.2, and 76.1 ppm, and this shows many isomers. Carbon bearing bromine (—CHBr—) appeared at 55.33, 54.01, and 58.74 ppm. Acrylate double bond carbons (—CHOC(= O)CH=CH$_2$) appeared between 128.06 and 130.97 ppm, respectively. New ester carbonyl (—CHOC(=O)CH=CH$_2$) was observed at 165.59, 165.04, and 166.61 ppm. IR spectrum (not shown) shows a new ester carbonyl stretching band (—OC(=O)CH=CH$_2$) at 1729 cm^{-1}, and 721 cm^{-1} peak due to the C—Br stretching. Acrylate double bonds are observed at 808, 1404, and 1636 cm^{-1}.
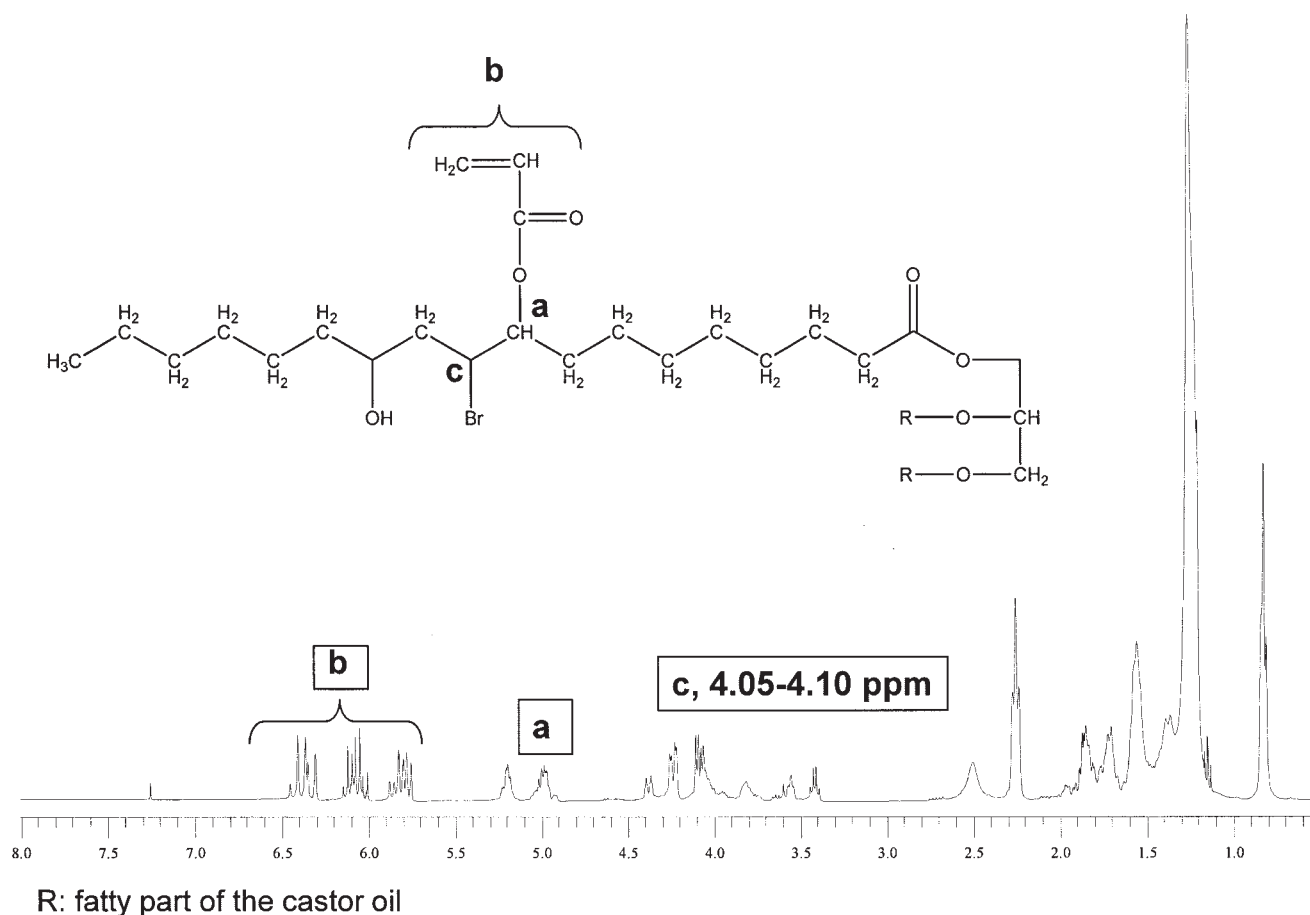
Figure 3 ^{1}H-NMR spectrum of BACO. *R*: fatty part of the castor oil.

Prepolyurethane (BACOP) formation with BACO and TDI was carried out at low conversion (~40%), and Figure 6 shows the urethane product. ^{1}H-NMR showed decreasing of the —OH peak at 3.4–3.8 ppm and formation of urethane proton (—CH—O—C(=O)—) at 4.96 ppm and a broad N—H signal was observed at 6.8 ppm. The conversion to urethane was determined to be 40%, by comparing the relative intensities of the corresponding methine protons (—CHOH, a in Fig. 6) at 3.4–3.8 ppm and urethane proton (—CHO—C(=O)—, b in Fig. 6) at 4.96 ppm, according to the following equation, where *I* is the peak area of the corresponding proton peaks in the NMR spectrum and *p* is the conversion ratio of hydroxyl groups to urethane.[15]

$$p(\text{OH}) = (I_{\text{urethane}}(\text{C}_b)/(I_{\text{—CHOH}}(\text{C}_a) + I_{\text{urethane}}(\text{C}_b)) \times 10^2$$

^{13}C-NMR spectrum of prepolyurethane was complex. Urethane carbon (C_b), as shown in Figure 6, coincides with the carbon bearing acrylate ester (—CHOC(=O)CH=CH$_2$) of BACO at 71.17, 72.47, 73.14, and 76.05 ppm. Urethane carbonyl carbon (C_c–C_d) shown in Figure 6 appeared at 153.2 and 153.1

ppm. Unreacted isocyanate carbon was observed at 123–124 ppm and carbon attached to the urethane (C_b, Fig. 6) was observed at 75 ppm. IR spectrum of the prepolyurethane showed broadening of the carbonyl region at 1730 cm^{-1} because of urethane carbonyl and amide peak. N—H deformation as well as C—N stretching vibration (amide II band) at 1536 cm^{-1} and N—H bending at 1595 cm^{-1} were observed as new signals in the IR spectrum. Isocyanate stretching at 2269 cm^{-1} showed that free isocyanate group is still present, to a small degree.

In castor oil, in addition to ricinoleic acid, other fatty acid residues are randomly distributed among the glyceride backbones. Hydroxyl value of BACO was determined with the same procedure as that for castor oil, by using ASTM D 1957–63. It was observed that during bromoacrylation, hydroxyl value drops from 2.6 to 2.2. This may be either due to inhibition of acetylation during the hydroxyl number determination by the adjacent bromine or due to the displacement of some of the hydroxyl groups by bromide during the reaction.

The mixtures of the respective reactive diluents (STY-MMA-HEMA-AHPMA) with BACOP are clear

Figure 4 (a) Schematic representation of BACO. *R*: fatty part of the castor oil. (b) Expected isomers of BACO during its synthesis. +, regioisomers.

yellow solutions. This miscibility may be attributed to the strong intermolecular interaction between the molecules and increasing polarity of castor oil by the incorporation of the bromine and acryloyl groups. The prepared BACOP, which still contains unreacted TDI and hydroxyl groups, was mixed with 50% of its own weight of one of the reactive monomers, in the presence of free radical initiator, AIBN. The SINs obtained were swollen in common solvents and it was observed that they fragmented and swelled but did not dis-

solve. No unreacted monomers could be extracted into the solvents, and so we conclude that copolymer ratio is the same as the feed ratio. Table I shows the solubility behavior of the synthesized SINs. The samples were brittle and fragmented in $CHCl_3$ and THF. All polymers showed rigid or semirigid properties.

Pham and Tran[15] claim that, during urethane formation, even with hydroxyl group in excess (NCO/OH = 0.8), the conversion of isocyanate group to urethane is incomplete. IR spectrum of the synthe-

54-58 ppm (-CHBr-)
63-76 ppm [(-CH(OH)- and (-CHOC(=O)CH=CH2)]
165-167 ppm(-O(C=O)CH=CH2)
128-131 ppm(-O(C=O)CH=CH2)
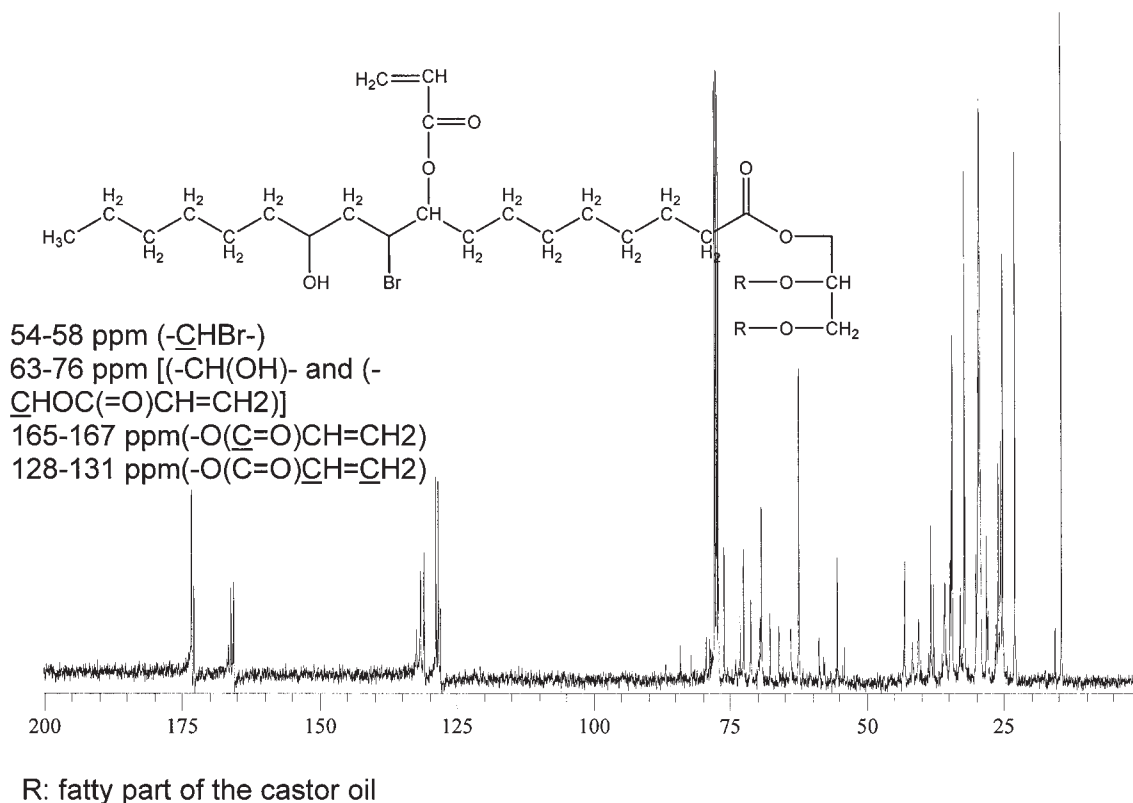
R: fatty part of the castor oil

Figure 5 ^{13}C-NMR spectrum of BACO. *R*: fatty part of the castor oil.

sized SINs samples showed very small —NCO peak at 2269 cm^{-1}. This may result from gelation during polymer synthesis, which immobilizes the isocyanate groups before they can react.

Photopolymerization of BACO using DMPA initiator was carried out, and the extent of photopolymerization was followed by IR spectroscopy.[14] The photopolymerized sample was insoluble in CH_2Cl_2 in which the monomer was soluble. A 60% decrease in the intensity of the peaks centered at 808 and 1643 cm^{-1} corresponding to acrylate double bonds was observed upon irradiation. Free radical homopolymerization of the acrylate group of BACOP was also carried out by using AIBN. Polymerization was followed by IR at different time intervals and it was observed that the rate of disappearance of the 2269

cm^{-1} due to the —NCO is faster than that of the 808 cm^{-1} peak due to the acrylate, and so, formation rate of the polyurethane network is higher than the formation rate of acrylate matrix. The literature supports[16] our determination that the isocyanate group does not inhibit free radical chemistry, and we think that the highly temperature-sensitive urethane formation was accelerated by the heat from the reaction of the free radical polymerization.

Mechanical properties

The dynamic mechanical analysis spectrum of the synthesized SINs showed a broad glass-transition temperature because of the partial compatibility between the urethane and vinyl monomer phases. Figure 7 shows
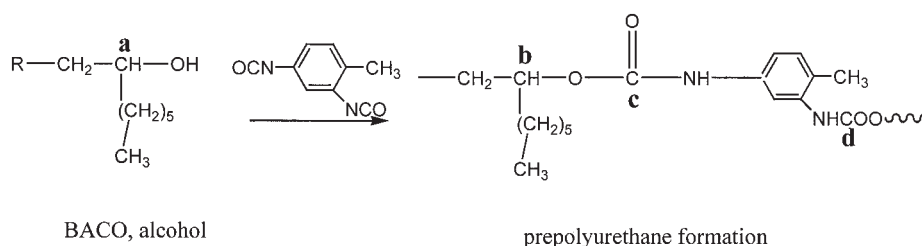

BACO, alcohol

prepolyurethane formation

Figure 6 Prepolyurethane adduct of BACO.

TABLE I
Solubility of the SINs Synthesized in Some Standard Solvents

Polymer	Solvent[a]				
	Acetone	CHCl$_3$	Toluene	THF	MeOH
BACOP (homopolymer)	s	f	i	f	i
BACOP-STY	i	f	i	f	i
BACOP-MMA	f	f	i	f	i
BACOP-HEMA	f	f	i	f	i
BACOP-AHPMA	i	f	i	f	i

[a] s, swell; i, insoluble; f, fragmented.

TABLE II
Mechanical Properties of SINs

Type of SINs	tan δ (damping value)	E′ (storage moduli) (10^8) (Pa)
BACOP-STY	85°C (0.5995)	8.9
BACOP-MMA	126°C (0.5420)	8.6
BACOP-HEMA	113.1°C (0.4124)	8.4
BACOP-AHPMA	67°C (0.1271)	7.9

the dynamic storage moduli (E′), dynamic loss moduli (E″), and tan δ of the SIN polymer made with the reactive diluent STY. The modulus of the BACOP-STY SINs is evidently higher than that of the other synthesized polymers over the whole temperature range studied. Incorporation of STY unit improved the mechanical properties of the polymers. Storage moduli of BACOP-STY at room temperature is ~8.9 × 10^8 Pa and storage modulus of the other SINs are shown in Table II.

Devia et al.[17] synthesized and characterized the castor oil-TDI polyurethanes and STY-based SINs. The T_g of his castor oil-TDI polyurethane was observed at −4°C. In our work, T_g of the radical initiated homopolymerization of BACOP was found to be 55°C. BA-

COP-MMA-type SINs showed highest T_g (126°C), and this result can be attributed to the increase in crosslinking between MMA and BACOP. It is well known that crosslinking density affects glass-transition temperature of the networks. HEMA has primary —OH functionality in its structure, and so, during simultaneous SIN synthesis, it can both react with the free isocyanate groups and polymerize free radically. This would increase the crosslink density and explain the higher T_g value observed for BACOP-HEMA, compared to the BACOP-STY. All SINs showed homogeneous structures and only one T_g at high temperature range.

Although, BACOP-MMA has a higher damping temperature (126°C) than BACOP-STY, it has a lower damping value (0.5420) than STY-BACOP (0.5995). Increasing crosslinking may cause decreased damping and elevation of the damping temperature. Damping value of HEMA-BACOP and AHPMA-BACOP are shown in Table II.
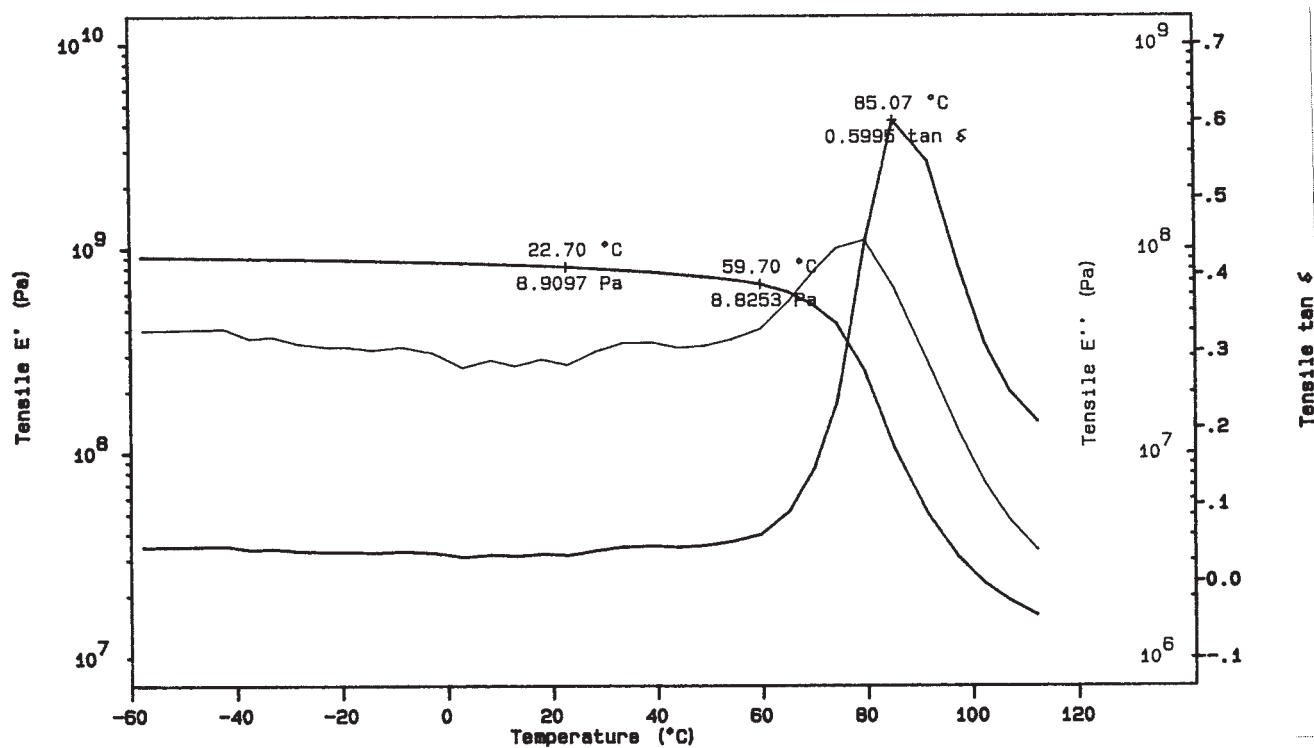

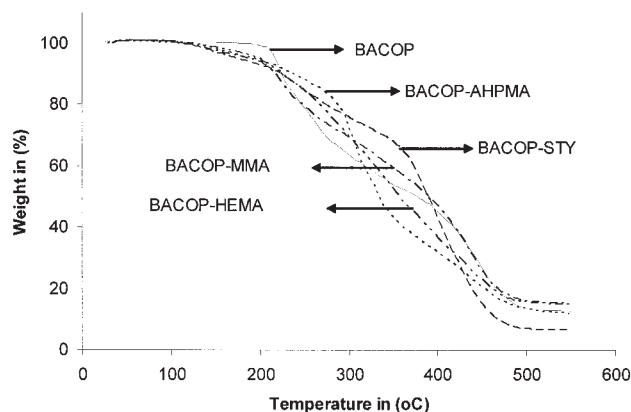**Figure 7** DMTA graph of STY-BACOP.

Figure 8 TGA data of the SINs.

Thermal stability of SINs

The bromine atom in the structure of the polymers is expected to increase polarity and impart fire resistance to the polymers, but it may also reduce thermal stability, as the carbon–bromine bonds are easily broken. Figure 8 shows that TGA analysis of the samples and indicates that all the SINs decomposed with 6–10% weight loss, in the temperature range of 25–240°C. Elimination of HBr from BACO could be responsible for the process. Between 300°C and 350°C, scission of the ester bond of BACO and urethane bond breaking were responsible for 20–35% weight loss.[18] Polyurethane degradation usually starts with the dissociation of the urethane bond and leads to carbon dioxide and isocyanate evaporation. This was observed by Rao et al., during the thermogravimetric analysis of castor oil polyurethane-polystyrene simultaneous IPN networks.[19] There is a sharp weight loss from 40% to 92%, in the temperature range of 400–500°C. This can be due to the decrosslinking of SINs.[20] Polystyrene weight loss at 450°C is 100% and degree of intermixing of BACOP resulted in the enhancement of thermal stability at the same temperature (80% weight loss). This may be due to the synergism of the components during their polymerization. BACOP-STY copolymer showed higher thermal stability between 300–400°C with respect to other synthesized SINs because of the presence of aromatic rings in STY, while other SINs consist of only aliphatic units. Weight loss around 550°C for MMA-type SINs was lower than that for the others and there remained 15% char residue at the end of the run.

In general, for better flame retardation, the decomposition of the flame retardant (in this case, bromine) should occur before the polymer decomposition. It is known that halogen-containing polymers are flame retardant, because halogen radicals act as radical scavengers in the vapor phase, which inhibit combustion. Also, the production of char protects the polymer surface from the combustion in the condensed phase;

thus, it is partly responsible for the flame retardancy.[21] 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

Castor oil was bromoacrylated by a one-step route. The acrylate and the hydroxyl functionalities on this molecule were used to prepare SINs, with reactive diluents STY, MMA, HEMA, and AHPMA, which underwent free radical polymerization, and with TDI, which underwent condensation polymerization. SINs with BACOP-MMA had the highest glass-transition temperature. AHPMA showed the lowest glass-transition temperature and the lowest modulus among the synthesized SINs. The SINs were stable up to 200°C but lost weight rapidly around 500°C. The cured BACOP-vinyl polymers may be used as coating materials or adhesives on iron or steel and also as reinforced rubber for toughened plastics. The composition of the SINs systems needs to be optimized for each specific end use of the products.

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