Synthesis and Characterization of Copolymers of Bromoacrylated Methyl Oleate

Tarik Eren, Selim H. Küsefoğlu

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

ABSTRACT: In this study, methyl oleate was bromoacrylated in the presence of *N*-bromosuccinimide and acrylic acid in one step. Homopolymers and copolymers of bromoacrylated methyl oleate (BAMO) were synthesized by free radical bulk polymerization and photopolymerization techniques. Azobisisobutyronitrile (AIBN) and 2,2-dimethoxy-2-phenyl-acetophenone were used as initiators. The new monomer BAMO was characterized by FTIR, GC-MS, ^{1}H, and ^{13}C-NMR spectroscopy. Styrene (STY), methylmethacrylate (MMA), and vinyl acetate (VA) were used for copolymerization. The polymers synthesized were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, and differential scanning calorimetry (DSC). Molecular weight and polydispersities of the copolymers were determined by GPC analysis. Ten different feed ratios of the monomers STY and BAMO were used for the calculation of reactivity ratios. The reactivity ratios were determined by the Fineman–Ross and Kelen–Tudos methods using ^{1}H-NMR spectroscopic data. The reactivity ratios were found to be $r_{sty} = 0.891$ (Fineman–Ross method), 0.859 (Kelen–Tudos method); $r_{bamo} = 0.671$ (Fineman–Ross method), 0.524 (Kelen–Tudos method). © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2475–2488, 2004

Key words: halogenated; renewable resources; photopolymerization; copolymerization

INTRODUCTION

Unsaturated fatty acids are good candidates for the preparation of biodegradable polymers. However, fatty acid double bonds cannot serve as monomers for polymerization due to their unreactivity. Figure 1 shows the functional groups that can be potentially modified to a polymerizable functionality on methyl oleate. These include the double bond, the allylic carbon, the ester group, and the carbon alpha to the ester group.

The unsaturation of the fatty acids has been used for air drying in alkyd resin technology for over a century. In industry a large amount of alkyds are produced from the alcoholysis process of triglycerides, such as soya and linseed oil. After the monoglyceride formation, the available OH groups in monoglyceride are esterified with polybasic acid such as phtalic anhydride.[1] The double bonds in the fatty acid residue are later used in crosslinking by autoxidation initiated by atmospheric oxygen. The product is industrially used as a paint binder; the common name "oil paint" is given to such paints. Alkyd resins are soft, flexible solids that are ideal as surface coatings such as varnish or paint, but they are not rigid enough to be structural polymers. One reported attempt to functionalize methyl oleate to a polymerizable monomer involves first epoxidation of the double bond, followed by opening of the epoxide with acrylic acid to yield a hydroxy acrylate derivative.[2]

In this study, the addition of bromine and acrylate to the oleate double bond of methyl oleate was achieved in one step. The chemistry is shown in Figure 2 and consists of reaction of the fatty alkene with *N*-bromosuccinimide (NBS) in the presence of acrylic acid. The bromoacrylated product should not only be able to polymerize through the reactive acrylate, but the presence of bromine should impart considerable flame resistance to the product polymer.

EXPERIMENTAL

Reagents and instruments

The methyl oleate was obtained from Henkel KgaA (Dusseldorf, Germany). *N*-bromosuccinimide (NBS) was obtained from Fluka (Buchs, Switzerland) and used without purification. Acrylic acid was obtained from Aldrich (Milwaukee, WI). $CDCl_3$ (Aldrich, Milwaukee, WI) was used for ^{1}H and ^{13}C-NMR analysis. Styrene, methyl methacrylate, and vinyl acetate were purchased from Fluka (Buchs, Switzerland). Technical-grade azobisisobutyronitrile (AIBN, Fluka, Buchs, Switzerland) was recrystallized from warm methanol.
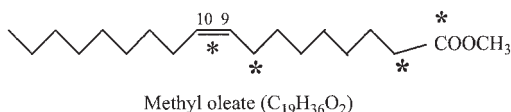
Figure 1 Chemical structure of the methyl oleate.

The photoinitiator used was 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, Aldrich, Milwaukee, WI).

^{1}H and ^{13}C-NMR spectra were recorded on a Varian 400 Mhz NMR (Varian Associates, Palo Alto CA) using TMS as the internal standard operating at 399.986 MHz for proton and 100.587 MHz for carbon. TMS was used as an internal reference and $CDCl_3$ as an internal lock. Mass spectrum was obtained using a Finnigan MAT 212-mass spectrometer (MasCom GmbH, Bremen, Germany). The IR analysis was performed on a Genesis FT-IR spectrometer (New Castle, DE) using NaCl windows. The glass-transition temperature (Tg) for homo- and copolymers were evaluated using differential scanning calorimetry (DSC). DSC measurements were carried out for the polymers at temperatures from -100 to $150°C$ using modulated differential scanning calorimetry with a TA Instrument Universal (Giancarlo Scientific, Pittsburgh PA) V2–5H system at a heating rate of $10°C/min$ under a nitrogen atmosphere. Photopolymerization was done under a UV SL-25 ultraviolet lamp operating at 366 nm and Rayonet (Southern New England UV Comp., Hamded, Connecticut) photochemical reactor. Molecular weight of the polymers were determined using a Waters GPC instrument (Massachusetts, USA) with 515 HPLC pump, calibrated with polystyrene narrow standards through 10^3, 10^4, 10^5 °A styragel columns at $30°C$ with tetrahydrofuran as solvent with a flow rate of 1 mL/min.
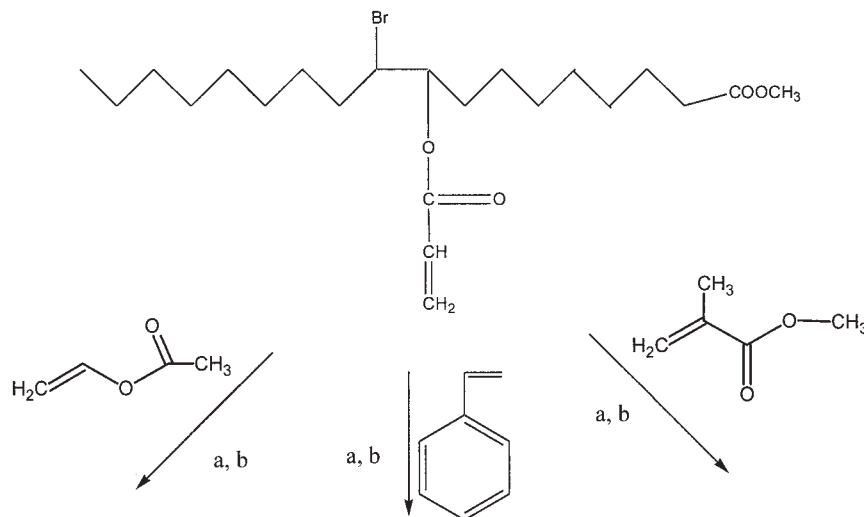
Bromoacrylation of methyl oleate

2.57 g (8.6 mmole) methyl oleate (MO) and 150 mL (2.18 mol) acrylic acid were mixed. Then 3.0 g (17 mmole) NBS was added to the reaction mixture. The flask was purged with N_2 and was well covered with aluminum foil to prevent light exposure and stoppered. After all of the NBS dissolved (it takes approximately $2-3$ min), the mixture was kept at room temperature without mixing for one 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 $Na_2S_2O_3$ (5 g/200 mL H_2O) to remove excess NBS. Unreacted acrylic acid was removed by extraction with aqueous (5%) NaOH. The ether layer was dried by Na_2SO_4 and then evaporated. 3.20 g of an orange-yellow oily residue was obtained. ^{1}H-NMR indicated 92% conversion. The product was purified by column chromatography (28 cm $\times$ 2 cm) on silica gel 60 (Merck, $70-230$ mesh) with petroleum ether/ethyl acetate (8 : 2) as eluent.

^{1}H-NMR ($CDCl_3$) δ: 0.88 (t, 3H, H-18), 1.10$-$1.30 (m, 18H, $(CH_2)_9$), 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, -HCBr-), 5.00 (dt, 1H, -HCO(C=O)CH=CH$_2$), 5.71 (d, 1H, -O(C=O)CH=C*Ha*Hb), 6.15 (dd, 1H, -O(C=O)C*H*=CHaHb), 6.34 (d, 1H, O(C=O)CH=CHa*Hb*).

^{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 (-OCH_3), [57.71, (57.75), -CHBr-], [75.33, (75.37), -CHO(C=O)CH=CH$_2$], (128.37, 131.32, -CHO(C=O)CH=CH$_2$), 165.44 (-CHO(C=O)CH=CH$_2$), 174.12 ((-C=O)OCH_3).

MS (PCI, i-Butane): 449.1 (M+H)$^+$, 369.3 [(M+H)$^+$-Br], 297 [((M+H)$^+$-Br)- CH$_2$=CH-COOH].

Scheme 1   (a) Photopolymerization by using 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) initiator; and (b) Free radical bulk polymerization by using azobisisobutyronitrile (AIBN) initiator.
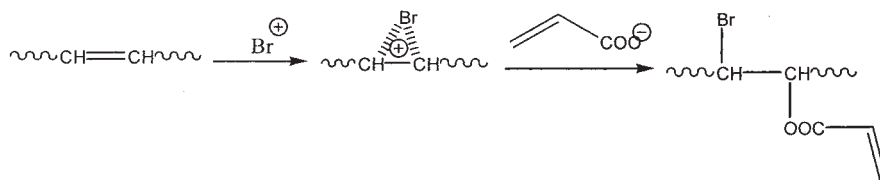
**Figure 2** Bromoacrylation of the methyl oleate double bond.

IR (Film) $\tilde{v}$ (cm^{-1}): 2952 (s, CH), 2855 (s, CH), 1741 (s, C=O), 1729 (s, C=O), 1636 (m, -HC=CH-), 1462 (m, CH$_2$, Def.), 1436 (m, CH$_3$O, Def.), 1404 (m, =CH$_2$, Def.), 1294−1264 (m, C-O-C, Def.), 1186 (m, CO, Def.; C-O-C, Def.), 984 (m, =CH, Def.), 808 (m, =CH$_2$, Def.), 724 (m, C-Br)

Homopolymerization of bromoacrylated methyl oleate (BAMO)

Bulk polymerization

0.350 g BAMO and 0.006 AIBN were mixed in a vessel and purged with nitrogen for 10 min. The mixture was
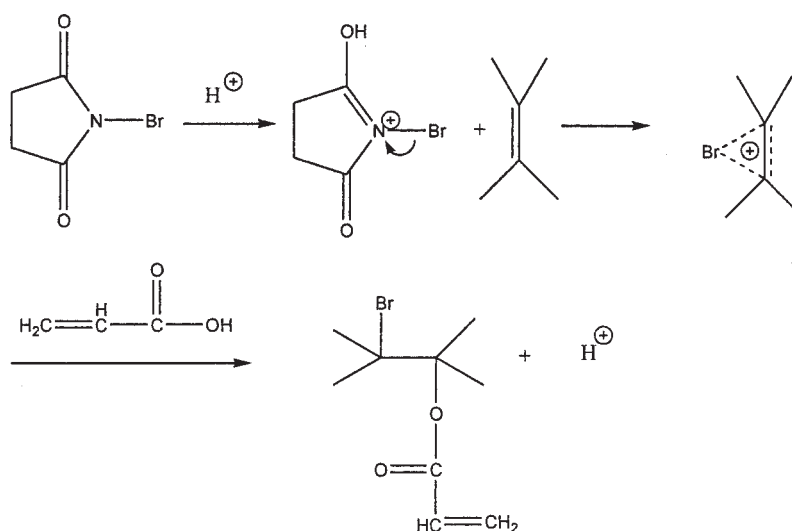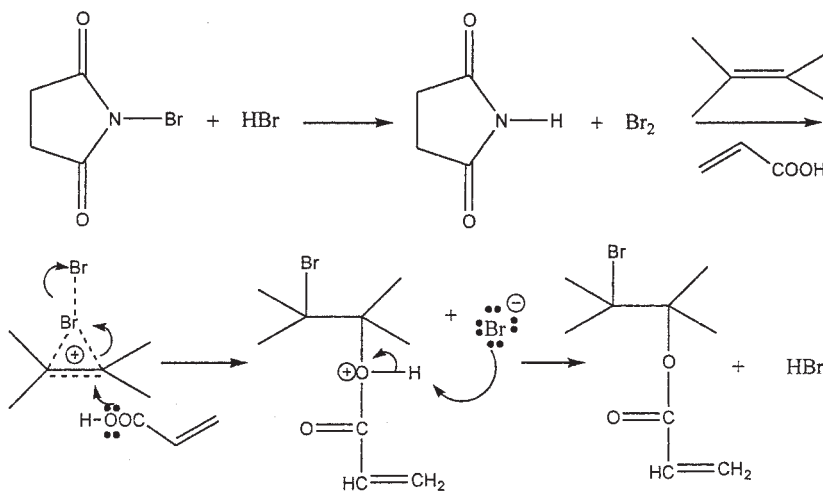

Figure 3 Mechanisms of the bromoacrylation of olefin in the presence of NBS.

then heated to 70°C in a oil bath. At the end of 24 h the homopolymer was precipitated by a large excess of methanol. The polymer was obtained as a viscous liquid (0.19 g, 55% conversion).

Photopolymerization

0.250 g BAMO and 0.002 g DMPA were dissolved in 3 mL CH$_2$Cl$_2$ and then photopolymerized by exposure of UV-Vis lamp at 366 nm for 30 min. Resulting polymer was precipitated in excess MeOH. Polymer was obtained as a viscous liquid (0.05 g, 20% conversion).

Copolymerization of bromoacrylated methyl oleate

Bulk polymerization

The polymerizations were run in a closed vial. BAMO was mixed with 35% of its own weight of styrene (STY), vinyl acetate (VA), or methyl methacrylate (MMA) to give yellow colored transparent solutions. 1.5% AIBN was used for each polymerization. The mixtures were purged with N$_2$ for 10 min and then heated in oil bath. The copolymerization with STY and BAMO was done at 80°C for 24 h. The copolymer thus obtained was purified by dissolving in CHCl$_3$ and precipitating with an excess amount of nonsolvent MeOH and finally dried in *vacuo* before characterization. The polymer was highly viscous oil. MMA copolymer was polymerized at 50°C for 24 h. The copolymer was a soft solid polymer that did not dissolve but swelled in common solvents. MMA-BAMO copolymer was also synthesized by solution polymerization. 100 parts of BAMO was mixed with 35 parts MMA and 1.5% AIBN in 3 mL tetrahydrofuran and heated at 65°C for 24 h. The mixture was poured into excess methanol to give a semirigid copolymer in 55% yield. This polymer was soluble in chloroform. Bulk polymerization of the VA copolymer was done at 65°C for 24 h. The resulting copolymer was precipitated in MeOH. The copolymer was a viscous oil, and its conversion was 40%.

Photopolymerization

The photo-copolymerizations of BAMO were done in the presence of 1.5% DMPA and a feed ratio of 35% comonomers (i.e., STY, MMA, and VA). The mixtures were purged with N$_2$ for 10 min and then were irradiated under UV-Lamp at 366 nm. in a closed quartz tube. After 10 min all the copolymers were dissolved in CHCl$_3$ and precipitated in MeOH. The copolymers were viscous oils and were obtained in 55, 40, and 25% conversions for STY, MMA, and VA, respectively. The precipitated products were further purified by removal of the respective homopolymers in a selective solvent-nonsolvent system. For example, polystyrene
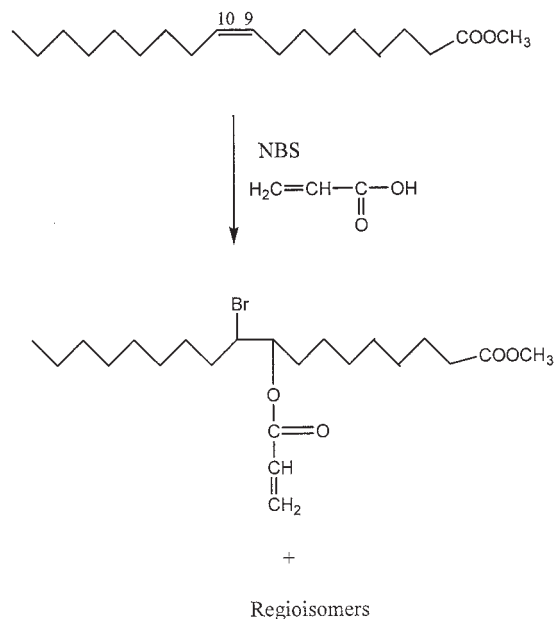

Figure 4 Bromo acrylate adduct of methyl oleate.

homopolymer was removed by extracting the BAMO-STY copolymer with acetone.

Copolymerization of styrene with bromoacrylated methyl oleate (BAMO)

Copolymerization of STY with BAMO was carried out with 10 different feed ratios (w/w) of STY and BAMO. The recipe for the synthesis of the copolymer 50 : 50 (w/w) of STY and BAMO was as follows: 0.33 g of styrene, 0.33 g of BAMO, and 0.008 g AIBN were mixed in a closed vessel. The polymerization reaction was carried out under a nitrogen atmosphere at 80°C in a oil bath. The copolymerization was stopped at a low conversion (about 10%) by cooling the samples to 0°C. Then the resulting copolymers were precipitated by adding 300 mL of cold petroleum ether. The homopolymer, PS, was insoluble in acetone although the copolymer was soluble. The precipitate was then extracted with acetone to separate the BAMO-STY copolymer from the styrene homopolymer. The copolymer was washed well with petroleum ether and dried in *vacuo* before characterization.

RESULTS AND DISCUSSION

Synthesis and characterization of the bromoacrylated monomers

Bromination of an alkene in nucleophilic solvent can lead to solvent incorporation.[3,4] N-bromoimides are the most common halogen compounds having bromine in the + 1 oxidation state. If it is desired to get a high yield of solvent incorporation, it is necessary to
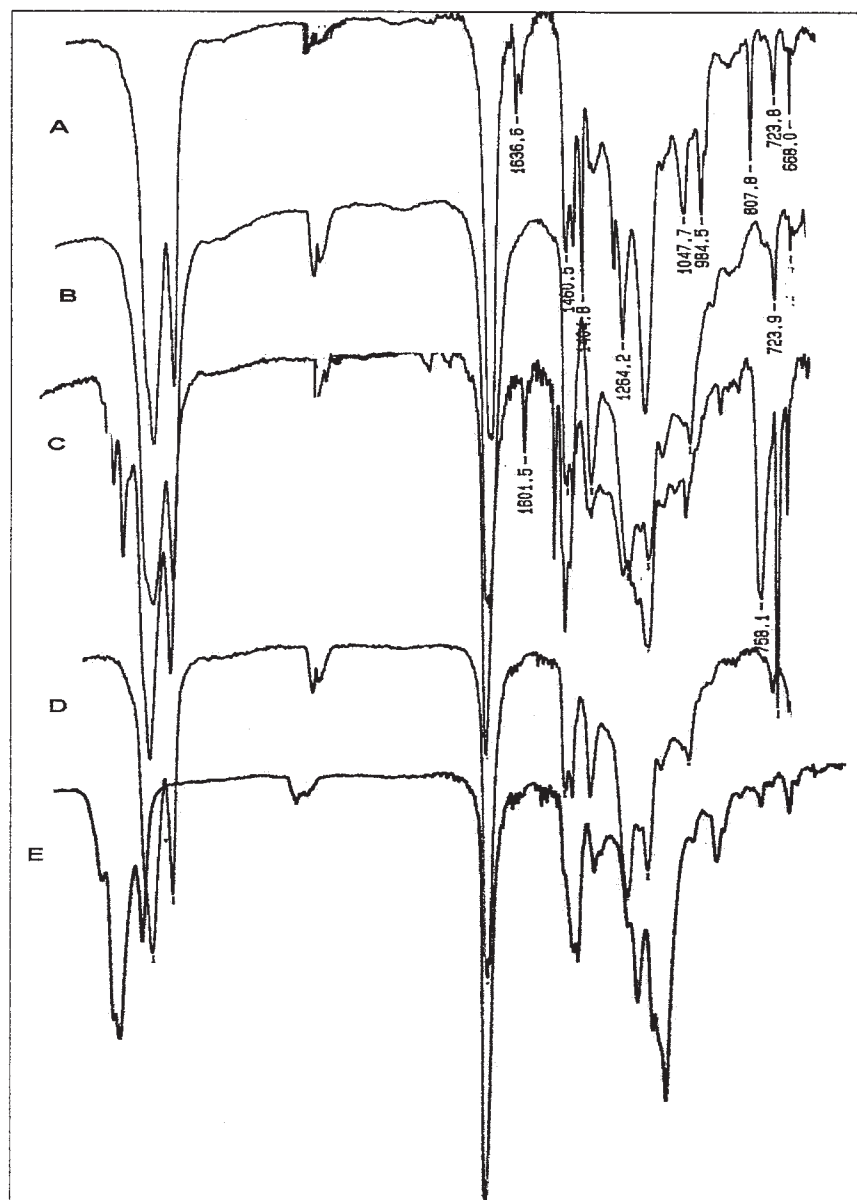
Figure 5 Representative IR spectra of: (A) Bromoacrylated methyl oleate (BAMO), (B) Homopolymer of BAMA, (C) Copolymer of BAMO with styrene, (D) Copolymer of BAMO with vinyl acetate, and (E) Copolymer of BAMO with methyl methacrylate.

keep the concentration of bromide ion as low as possible,[5] so that dibromide formation is minimized. Bromination with NBS in an acidic solvent may take place by two mechanisms. Suggested mechanisms of bromoacrylation are shown in Figure 3. In mechanism a, the heterolytic fission of the N-Br bond in NBS creates a bromonium ion and a succinimide anion. While the bromonium ion is attacked by the π system of the alkene, the succinimide anion is protonated by the acidic solvent to give a weak nucleophile succinimide.[6,7]

In mechanism b, the source of bromine is a fast ionic reaction between NBS and the HBr liberated. HBr could come from bromo acrylate adduct or from the NBS source. It is necessary to use an excess amount of acrylic acid to obtain solvent participation in meaningful amounts. Otherwise, dibromo addition takes place on the unsaturated fatty compounds. The reaction vessel should be covered well to prevent O_2 penetration and light since these can facilitate radical reactions.

Jovtscheff[8] studied the bromo acetoxylation of unsaturated fatty compounds such as ricinoleic methyl ester, oleic acid, methyl oleate, linoleic acid, and methyl linoleate. Bromo acetoxylation of the unsaturated fatty compounds occurred in high yields. Our synthetic plan involves the use of acrylic acid instead of acetic acid and is shown in Figure 4.
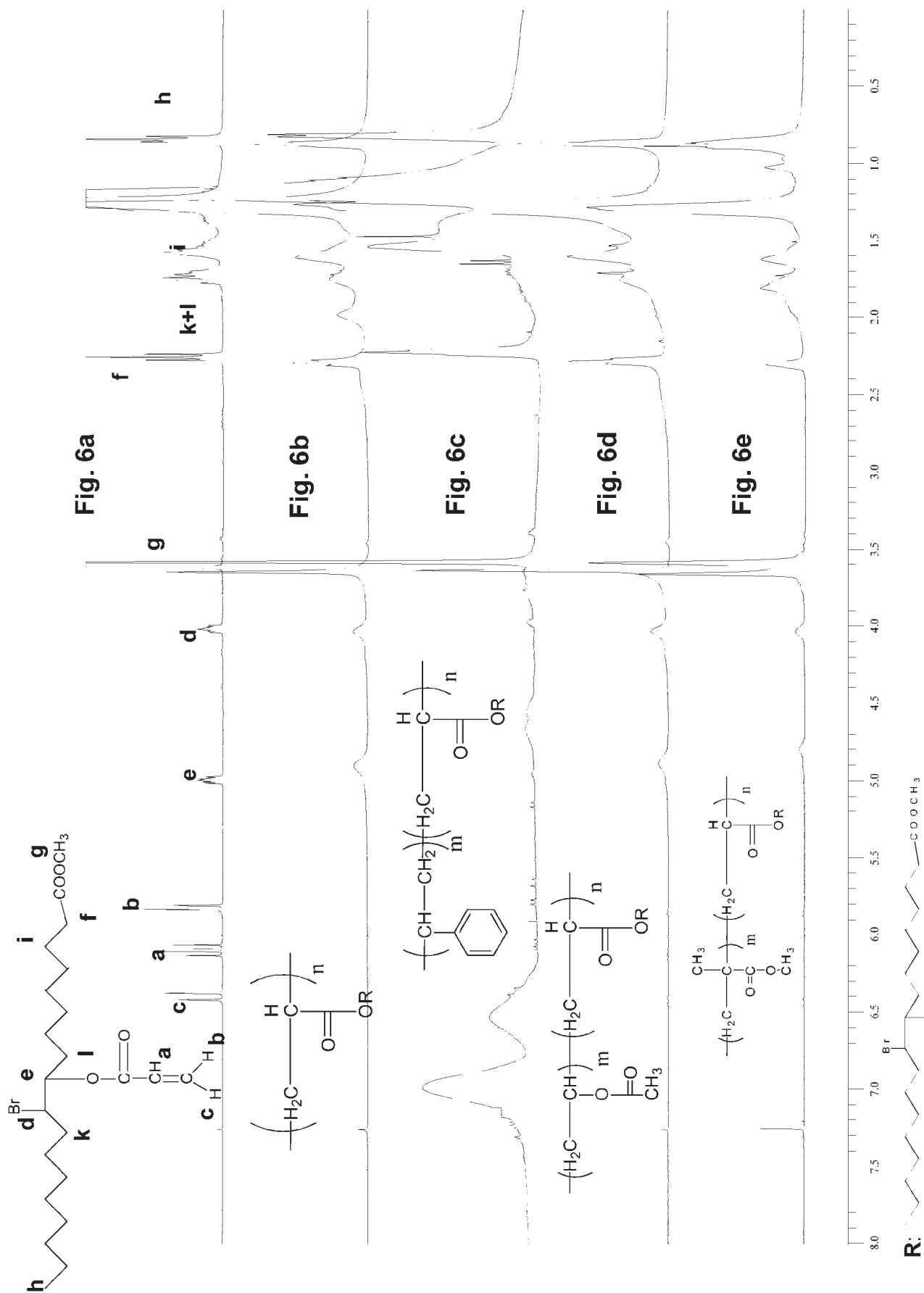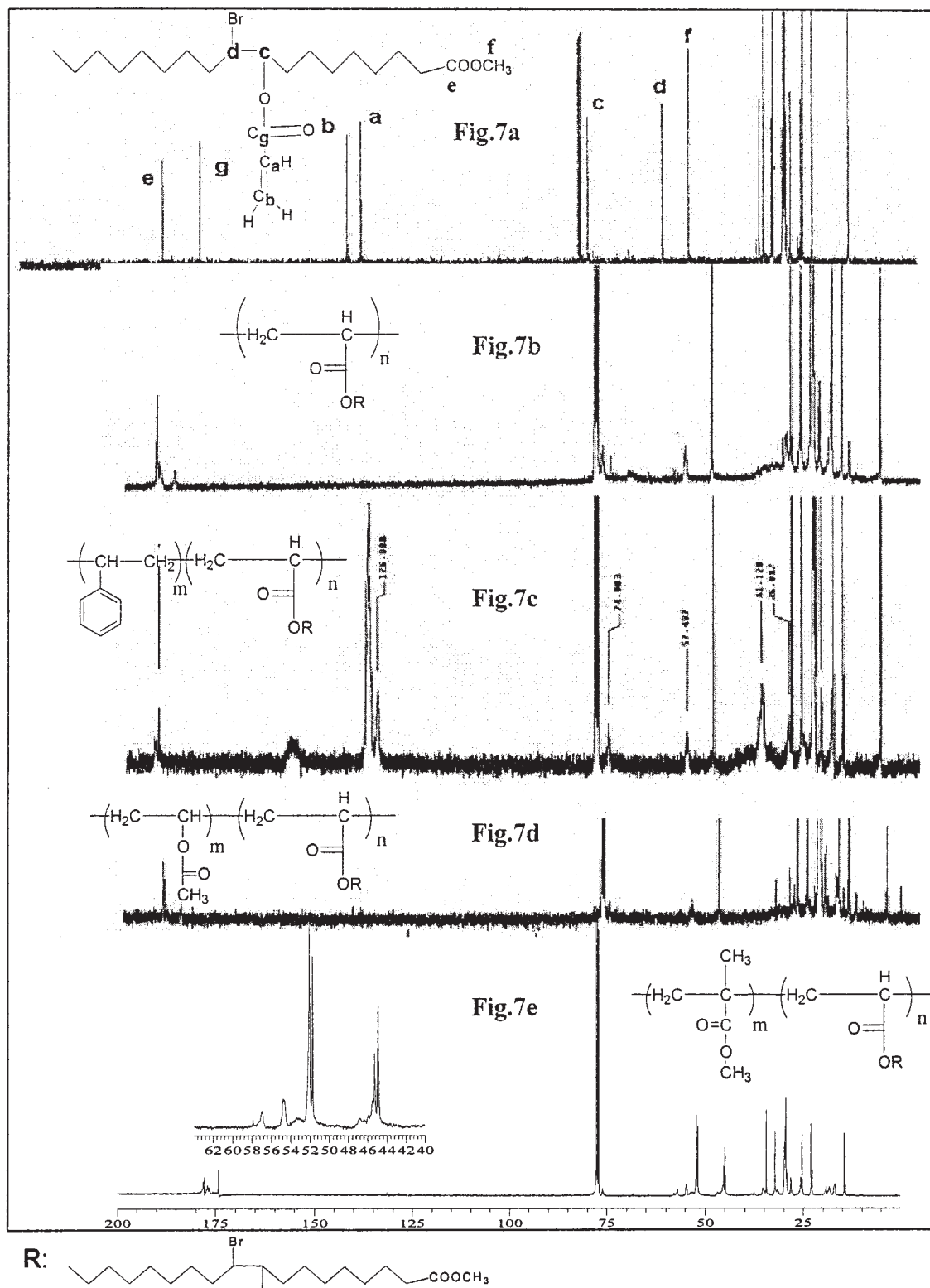
Figure 6   Representative ^{1}H-NMR spectra of: (a) BAMO and (b) its homopolymer, (c) STY copolymer, (d) VA copolymer, and (e) MMA copolymer.

Figure 7 Representative ^{13}C-NMR spectra of: (a) BAMO and (b) its homopolymer, (c) STY copolymer, (d) VA copolymer, and (e) MMA copolymer.

FTIR spectra of the bromoacrylated methyl oleate (BAMO) and its homopolymer are presented in Figure 5. IR spectrum indicates a new ester carbonyl stretch-ing band (-OC(═O)CH═CH$_2$) at 1729 cm^{-1}, a C-Br stretching band at 721 cm^{-1}, and acrylate double bonds are observed at 808, 1404, and 1636 cm^{-1}. Fig-

TABLE I
Mole Fraction and Properties of Copolymers

Run	w_1	M_1	w_2	M_2	Temp.	Time (h)	con. %	X_1 (%)	X_2 (%)	Mn	p	Properties
Homopolymer	0.3502	0.78	—	—	85°C	24	50	—	—	23.725	1.96	Viscous oil
Styrene copolymer	0.4041	0.90	0.2226	2.1	85°C	24	90	38	62	27.164	2.82	Highly viscous oil
Vinylacctate copolymer	0.2789	0.62	0.1750	2.0	65°C	24	40	50	50	34.704	4.35	Viscous oil
MMA copolymer[a]	0.3780	0.84	0.2011	1.9	50°C	24	100	—	—	crosslinked	—	Soft solid
MMA copolymer[b]	0.3193	0.71	0.1433	1.36	50°C	0.15	55	65	35	25.238	1.51	Soft solid

w_t: weight (g) of the bromoacrylated methyl oleate used.
M_1: moles (mmole) of the bromoacrylated methyl oleate used.
w_2: weight (g) of the respective monomers used.
M_2: moles (mmole) of the respective monomers used.
X_1: BAMO mole fraction found in copolymer composition by ^{1}H NMR.
X_2: co-monomer mole fraction found in copolymer composition by ^{1}H NMR.
Mn: Number average molecular weight as determined by GPC.
P: Polydispersity.
[a] Bulk polymerization.
[b] Solution polymerization was done in THF 1.5% AIBN is used in all polymerizations.

ure 5B agrees with the homopolymer of BAMO in that the acrylate peaks disappeared after polymerization. Retention of the C-Br stretching band during the polymerization indicates the stability of the bromide during the polymerization condition.

FTIR spectra of the copolymers of BAMO with STY, MMA, and VA are shown in Figure 5. Characteristic absorption bands for acrylate disappeared in all spectra. Additional absorptions from the benzene ring of the STY (5C) were observed at 3058, 3027, 1601, and 1492 cm^{-1}. The strong bands at 700 and 758 cm^{-1} were indications of monosubstituted aromatic ring. Characteristic peaks in the copolymer of VA (5D) are very similar to the BAMO homopolymer because very similar functional groups exist in both monomers. C-O-C symmetric and asymmetric stretches increased in intensity at 1240 and 1170 cm^{-1}. The copolymerization of MMA with BAMO in the bulk gave soft solid polymer that did not dissolve but swelled in common solvent. However, solution copolymer of BAMO with MMA gave a polymer that dissolved in CHCl$_3$. This copolymer's IR spectrum in Figure 5E shows the disappearance of acrylate peaks and broadening at the carbonyl regions.

The ^{1}H-NMR spectra of the BAMO and its homopolymer are given in Figure 6. Figure 6a shows the protons attached to bromine (-CHBr-) and acrylate (-CHOC(=O)CH=CH$_2$) as doublets of triplets at 4.00 ppm and 5.00 ppm, respectively. Acrylate double bonds are seen at 5.71, 6.15, and 6.34 ppm. Vinyl protons of methyl oleate (-CH=CH-) at 5.2 ppm and allylic hydrogens (=CH-CH_2-) at 2.00 ppm disappeared as expected. After the homopolymerization, acrylate vinyl protons also disappeared. New peaks belonging to the -CH_2-CH-C(=O)-O and –CH$_2$-CH-C(=O)-O were observed at 1.6 ppm and 1.8 ppm, respectively. Styrene copolymer[9] (Fig. 6c) showed

characteristic aromatic proton signals at 7.05–6.52. The other characteristic peaks at 1.85 (-CH benzylic) and 1.43 ppm (-CH$_2$- backbone proton) could not be assigned well because they overlapped with the BAMO signals. After polymerization the -HC-Br signal shifted to 3.9 ppm and –C(=O)-O-CH- shifted to 4.8 ppm. VA-BAMO copolymer (Fig. 6d) showed a characteris-
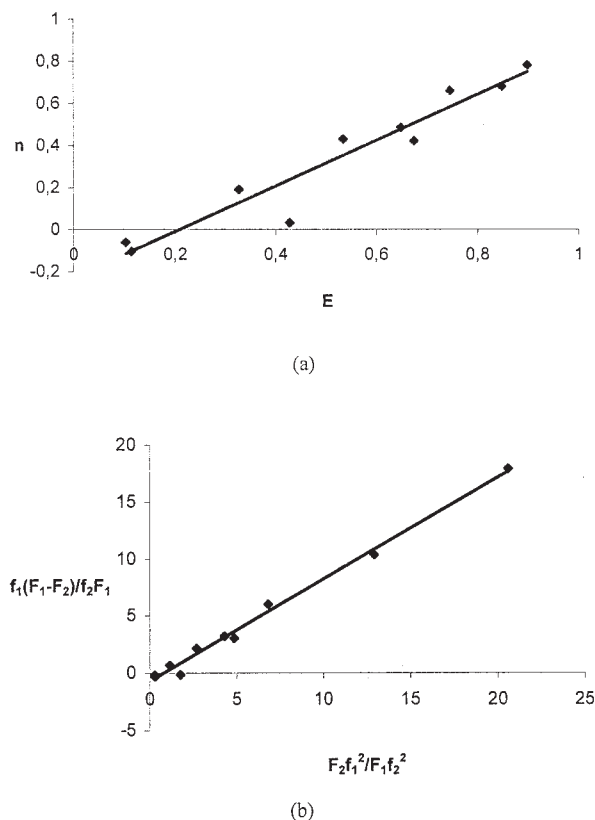

(a)

(b)

Figure 8 (a) Kelen–Tudos plot, and (b) Fineman–Ross plot for BAMO-styrene copolymer.

Styrene (1)/ Acrylates (2)	Ethyl acrylate	Octadecyl acrylate	2-ethyl hexyl acrylate	isobutyl acrylate	Acrylic acid, 2 bromo ethyl ester	BAMO[b]
r_1	0.800	0.75	0.940	0.970	0.060	$(0.859)^d$; $(0.891)^c$
r_2	0.200	0.34	0.260	0.280	0.500	$(0.524)^d$; $(0.671)^c$

[a] Polymer Handbook, 3rd ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley & Sons: New York, 1989.
[b] Bromoacrylated methyl oleate.
[c] Reactivity ratios were obtained by Finemann–Ross method.
[d] Reactivity ratios were obtained by Kelen–Tudos method.

tic resonance signal at 2.0 ppm (-O-C(=O)-CH_3) and 5.1 ppm (-CH-O-C(=O)-CH_3). The bulk copolymerization product of BAMO with MMA swelled but was not soluble in common solvents. Figure 6e shows the solution polymerization product of the two monomers. The characteristic signal for methyl hydrogens belonging to the ester group (-C(=O)- O-CH_3) of MMA was observed at 3.4 ppm.

^{13}C-NMR

The ^{13}C-NMR spectra of the copolymers and the homopolymer are shown in Figure 7. All acrylate vinyl carbons are consumed, and the methine (-CH-) attached to the acrylate group absorbs at around 40 ppm as a shoulder. The methylene (-CH$_2$-) groups gave signals at 35.2 ppm, but this signal coincides with the carbons of the long alkyl side chains of the BAMO. In styrene copolymer (Fig. 7b), the aromatic carbons showed splitting around 125, 127, and 128 ppm. Quaternary carbon of the phenyl ring gave a signal at 145 ppm. Figure 7c belongs to the VA-BAMO copolymer, and this spectrum was similar to that of BAMO homopolymer as the monomers have almost the same structure. Figure 7d shows the MMA-BAMO copolymer. In this spectrum the methyl peak (-C(=O)-

OCH_3) of MMA coincides with the methyl peak of fatty ester at 51 ppm. The carbonyl carbon at 174 ppm belongs to BAMO, but the carbonyl carbons splitting at around 176, 177, and 178 ppm belong to the polymerized MMA.

In all of the spectra, bromine bearing carbon (-CHBr-) is observed at 57 ppm and acrylate bearing carbon (-CH-OC(=O)-) is observed at 75 ppm, indicating that bromine is intact under the reaction conditions. The carbonyl carbons in all of these copolymers and homopolymers showed splitting. Configuration and random sequence distribution of the monomers during the polymerization resulted in the splitting and broadening of the ^{13}C spectra shown in Figure 7e.

Copolymer composition

The copolymer compositions were determined by ^{1}H-NMR spectra. To distinguish the monomers in the copolymer chain, their unique resonance signals were used. For STY copolymer, aromatic protons, for VA (-O-C(=O)-CH_3), and for MMA (-C(=O)- O-CH_3) signals were compared with the BAMO methyl signal at 3.6 ppm (-C(=O)- O-CH_3). Mole fraction of the respective monomers were determined by the peak intensities. For instance, mole fraction of styrene in the copolymer composition was found by the following equation:[9]

$$Mole\ fraction = \frac{3Iphenyl}{3Iphenyl + 5Imethyl}$$

The feed and copolymer monomer ratios of all the polymers are given in Table I. The number average molecular weight (Mn) for homo and copolymers ranged from 20,000 to 35,000, as estimated by GPC. These low molecular weights were probably due to chain transfer to the bromine group attached to the BAMO or due to steric inhibition of the long alkyl chains of the fatty ester of BAMO.
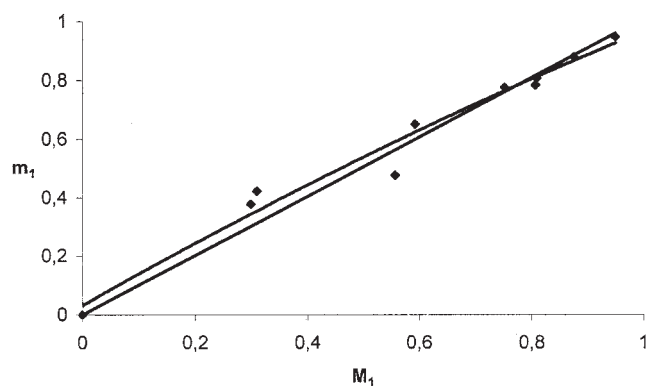

Figure 9 Copolymer composition (m_1) versus initial monomer composition (M_1) plot for BAMO-styrene copolymer.

Determination of reactivity ratios

The composition of a copolymer is usually different from the composition of the feed because the reactivity of each monomer is different.[10,11] The reactivity ratios were obtained at about 10% conversion. The polymerization was stopped by cooling the samples to 0°C, and the polymers were precipitated using petroleum ether as nonsolvent. Precipitated polymers were extracted with acetone, which dissolved the copolymer but not the STY homopolymer.

The reactivity ratio r_1 (styrene) and r_2 (BAMO) were determined by the Fineman–Ross Method[12] and the Kelen–Tudos[13] method. The Fineman–Ross plot is shown in Figure 8b. A plot of the $f_1/f_2\{F_1\text{-}F_2/F_1\}$ versus $F_2/F_1\{f_1^2/f_2^2\}$ gives a straight line with slope equal to r_1 and intercept equal to $-r_2$. F_1 and F_2 are the instantaneous compositions (mole fractions) of the monomers in the copolymer, and f_1 and f_2 are the mole fractions of the monomers. The slope, (r_1) corresponding to styrene reactivity ratio, is 0.859. The intercept, BAMO reactivity ratio ($-r_2$), is 0.524. Srinivasan et al.[14] rearranged the method of Finemann–Ross and Kelen–Tudos and use the equations:
Equation used for Fineman–Ross method:

$$\frac{f_1\{F_1-F_2\}}{f_2F_1} = \frac{F_2}{F_1}\{\frac{f_1^2}{f_2^2}\}r1 - r2$$

Equation used for Kelen–Tudos method:

$$\eta = (r_1+r_2/\alpha)\xi + r_2/\alpha$$

where η and ξ are functions of the molar ratio of the monomers in the copolymer and the monomer mixture. The Kelen–Tudos plot is shown in Figure 8a, and corresponding reactivity ratios are $r_{1(styrene)} = 0.891$ and $r_{2(bamo)} = 0.671$.

The reactivity ratios determined by both the methods were found to be very close to each other. The r_1r_2 value (Kelen–Tudos methods used) of the copolymer is 0.45, indicating that the copolymer has some tendency toward alternation. The copolymer equation

was proposed by Mayo and Lewis,[11] that the parameters r_1 and r_2 are defined by:

$$r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21}$$

The parameters r_1 and r_2 are defined as monomer reactivity ratios. r_1 is the ratio of the rate constant for a reactive propagating species (M_1^*, STY) adding its own type (M_1, STY) of monomer to the rate constant for its addition of the other monomer (M_2^*, BAMO). r_2 is similarly defined for the other monomer. The r_1/r_2 value is 1.63, which indicates that styrene is about twice as reactive as BAMO, thus styrene will be incorporated into the copolymer faster. Hence, during the polymerization, although both monomers are being consumed, the styrene monomer is being consumed almost twice as fast as BAMO. Table II shows the several values of r_1 and r_2 reported in the literature for various acrylate type monomers and styrene.

The reactivities of acrylic monomers depend on the polar, resonance, and steric effects of the substituents. For example, acrylate monomers having α-alkyl substituents larger than methyl show poor or no polymerizability under free radical conditions due to steric effect.[15,16] It was expected that long alkyl groups of BAMO would inhibit the polymerization to some extent, but the presence of the bromine group at beta position increased the reactivity of BAMO as compared to octadecyl acrylate, as shown in Table II.

Figure 9 shows the plot of copolymer composition versus feed composition. It is sigmoidal and at the intersection (crossover point) of F_1 (instantaneous copolymer composition) = f_1 (initial comonomer feed composition), the copolymer and feed composition are the same and copolymerization occurs without a change in the feed composition. The crossover point was at $M_1 = m_1 = 0771$. Theoretically, the value (0785) was obtained from the following equation, which was very close to the experimental value.

$$f1 = \frac{1 - r2}{2 - r1 - r2}$$

The Q and e values of the Alfrey–Price method[17] were determined by using the reactivity ratios obtained experimentally by the Kelen–Tudos method. We used the following two equations:

$$R_2 = Q_2/Q_1 \exp[- e_2(e_2 - e_1)]$$

$$R_1 = Q_1/Q_2 \exp[- e_1(e_1 - e_2)]$$

The values of $e_2 = (-0.8)$ and $Q_2 = 1.0$ were used for styrene, and the values of BAMO were found to be $e_1 = 0.09$ and $Q_1 = 0.57$. As the electron-attracting character of a substituent increases, both Q and e values
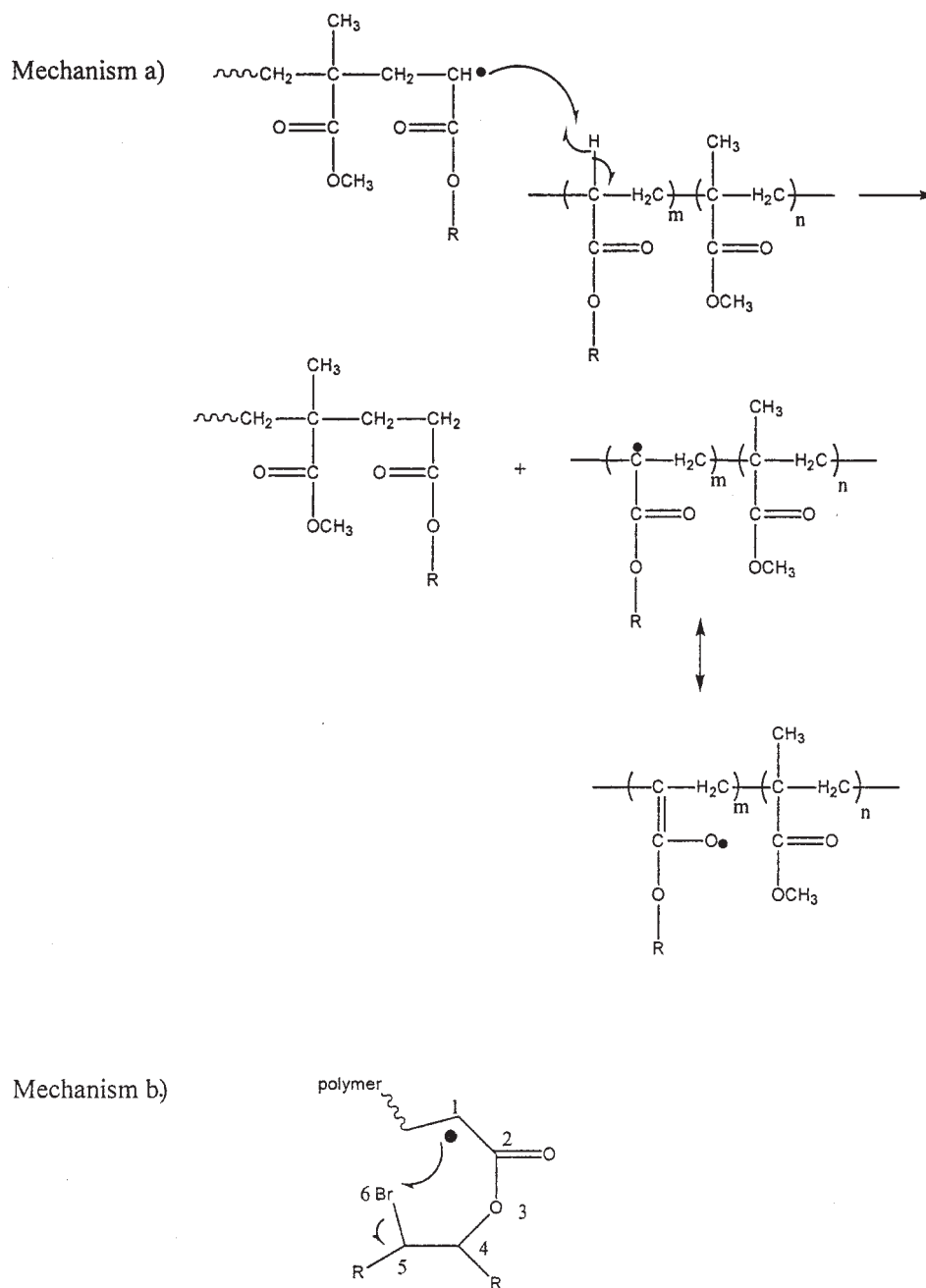
R: fatty part of the bromoacrylated methyl oleate

Figure 10 Mechanisms of (a) hydrogen abstraction from the growing chain, and (b) backbiting the bromine atom.

increase.[18] An electron releasing substituent results in decrease of Q value as well as e value. Parameter Q describes the resonance and steric factors. The length of the alkyl group part of BAMO chains shows a slight effect in the Q value (0.56) as compared with the hydrocarbon homologues shown in Table III and indicate that the steric effect of the alkyl group in BAMO does not play a significant role in its reactivity. Constant e is the measure of the polarity of the monomer. The electron withdrawing effect of bromine at the beta position and the electron donating power of the long alkyl group of BAMO causes the e value to be 0.09. It is well known that the tendency toward alternation is greatest for monomers having the same Q values with
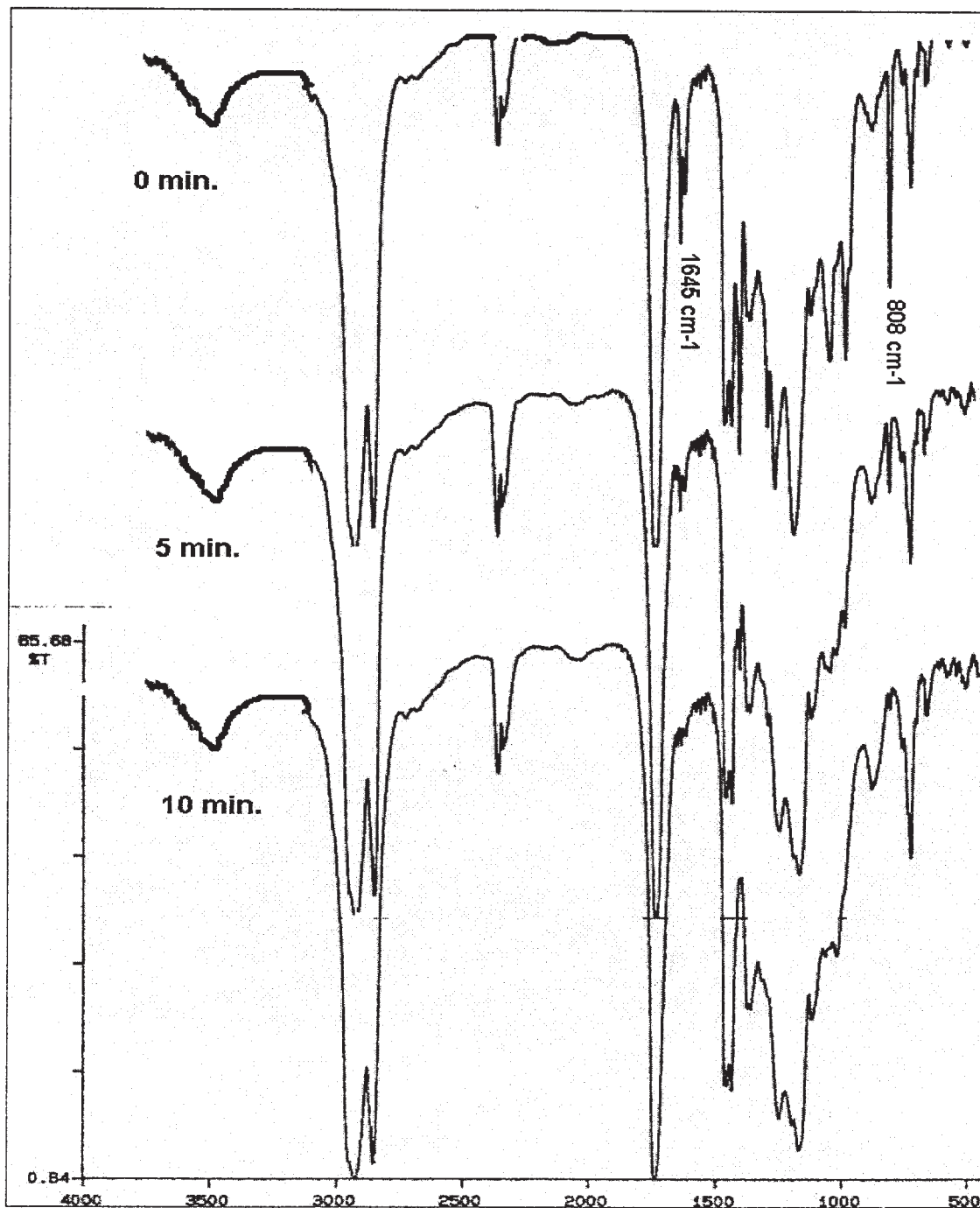
Figure 11 IR spectra of the photopolymerized bromoacrylated methyl oleate at different stages of its synthesis.

high e values of the opposite sign. The Q value of styrene is 1.0 and the Q value of BAMO is 0.56, so that tendency toward alternation is not so great, and this coincides with the r_1r_2 value, which was 0.45.

Copolymers of MMA-BAMO

Bulk copolymerization of MMA with BAMO produced a crosslinked soft solid polymer, although the polymerization was done at 50°C in oil bath under controlled heating. The heat of polymerization (ΔHp) is 13.1 kcal/mol for the methacrylate double bond and 20.6 kcal/mol for the acrylate double bond.[19] Autoacceleration could be the main factor for the crosslinking of the MMA copolymer. Autoacceleration or the Thormsdoff effect is known as an increase in the polymerization rate at high conversions. The viscosity increases rapidly, which affects the mobility of the
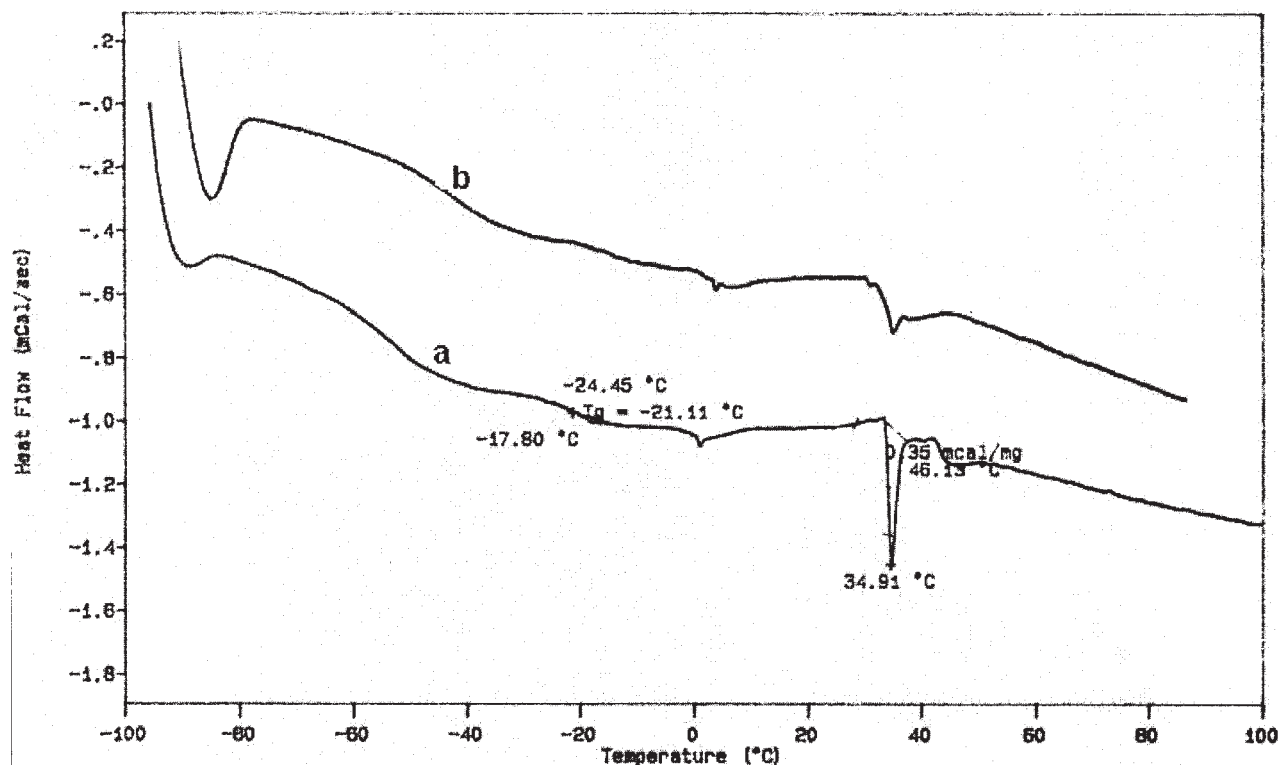
Figure 12 DSC diagram of the BAMO homopolymer (a) first run, and (b) second run.

polymer radical. The rate of termination is then reduced so that overall polymerization rate increases. Bowman et al.[20] explained that radicals propagate through the unreacted double bonds in the system until they encounter another radical chain end. After the polymerization reaches its maximum rate, it starts to decrease due to autodeceleration, where crosslinking restricts and stops the propagation reaction altogether. The high viscosity may cause extensive branching or crosslinking. These can form abstractions of 3°H from the polymer chain, as shown in Figure 10a[1]. Bromine abstraction by the growing chain and branching may also be responsible for the observed insolubility of the BAMO-MMA bulk polymer. One should note that radical attack at the acrylate system produces a new radical that is capable of backbiting the bromine atom through a six membered transition state, as shown in Figure 10b. Photoinitiated radical polymerization and solution radical polymerization of MMA with BAMO produced polymers that were soluble in CHCl₃.

Photoinitiated radical polymerization of BAMO

Photopolymerization of BAMO was done by using 1 wt % photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone (DMPA). The mixture of CH_2Cl_2 and BAMO was applied as a uniform thin film onto an NaCl crystal. Photopolymerization was done under a UV SL-25 ultraviolet lamp operating at 366 nm for 10 min under a stream of nitrogen. The extent of photopolymerization was followed by IR spectroscopy. Figure 11 shows the decrease of the peaks centered at 808 and 1643 cm^{-1} corresponding to acrylate double bonds, upon irradiation. The photohomopolymer was a viscous oil.

DSC analysis

DSC spectra of the copolymers showed that the MMA-BAMO copolymer (bulk and solution polymer) has a higher Tg ($-10°C$) than the other copolymers. The α-methyl group present in the methacrylates reduces chain flexibility by increasing packing and also prevents rotation about the C-C bond in the main chain. This may also be due to partial crosslinking. The homopolymer of BAMO has a low Tg($-22°C$), but its STY copolymer has a higher Tg (at $-13.5°C$). The VA repeating unit is not as stiff as the STY or MMA repeating units, so the BAMO-VA copolymer has a Tg of ($-17°C$). The copolymer of VA with BAMO produced higher Tg than the homopolymer of BAMO but lower than the other copolymers. DSC spectra of the homopolymer of BAMO shows a melting point in the first run, but the melting peak disappears in the second run. This may be due to some degradation produced in the first run, which disrupts crystallinity. The same observation was observed for the DSC diagram

of copolymers as well (not shown). Figure 12 shows the DSC diagram of BAMO and its homopolymer.

CONCLUSION

New acrylate monomers with large fatty, β-bromo alkyl groups were synthesized. The substitution of the bromine atom at the β position increased the reactivity of the large alkyl acrylates towards polymerization. Homopolymerization of BAMO by free radical and photopolymerization techniques was carried out successfully. MMA, STY, and VA copolymers of BAMO were also obtained. The reactivity ratios of the BAMO-STY comonomer couple were obtained by ^{1}H-NMR spectroscopy and showed a relatively higher reactivity of the styrene than BAMO. The Q and e values of BAMO were obtained by using the Alfrey–Price method. The weight average molecular weight (Mw) of the homo and copolymers of BAMO were obtained by GPC, and Mw were between the range of 45,000–120,000.

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