

# Synthesis and Characterization of Styrene–Acrylic Ester Copolymers

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**ABSTRACT:** Homopolymers and copolymers of styrene and different acrylic esters (i.e., acrylates) were synthesized by the free-radical solution polymerization technique. Feed ratios of the monomers styrene and cyclohexyl acrylate/benzyl acrylate were 90 : 10, 75 : 25, 60 : 40, 50 : 50, 40 : 60 and 20 : 80 (v/v) in the synthesis of copolymers. All 6 homopolymerizations of acrylic ester synthesis were carried out in *N,N*(dimethyl formamide) except for the synthesis of poly(cyclohexyl acrylate) (PCA), where the medium was 1,4-dioxane. Benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) were used as initiators. The polymers synthesized were characterized by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and viscosity measurements. The reactivity ratios were determined by the Fineman–Ross method using <sup>1</sup>H-NMR spectroscopic data. The reactivity ratios (*r*) for the copolymerization of styrene (*r*<sub>S</sub>) with cyclohexyl acrylate (*r*<sub>CA</sub>) were found to be *r*<sub>S</sub> = 0.930 and *r*<sub>CA</sub> = 0.771, while for the copolymerization of styrene with benzyl acrylate, the ratios were found to be *r*<sub>S</sub> = 0.755 and *r*<sub>BA</sub> = 0.104, respectively. The activation energies of decomposition (*E*<sub>a</sub>) and glass-transition temperature (*T*<sub>g</sub>) for various homo- and copolymers were evaluated using TGA and DSC analysis. The activation parameters of the viscous flow, voluminosity (*V*<sub>E</sub>) and shape factor (*ν*) were also computed for all systems using viscosity data. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1513–1524, 2001

**Key words:** synthesis; characterization; styrene; acrylates; copolymers

## INTRODUCTION

Homopolymers of styrene have been shown to have properties suitable for a variety of industrial applications. Of growing importance are those related to uses in packaging, molded household wares, containers, machine housing, electrical equipment, toys, water coolers, and so on.<sup>1</sup> However, molecular inflexibility leaves the pure homopolymer unable to withstand high rates of me-

chanical loading, making it brittle under impact and causing stress-cracking. By copolymerizing styrene with other monomers such as acrylates, the deficiencies of polystyrene are tempered, and desirable properties can be achieved.<sup>2,3</sup> Copolymers of hydrophobic monomers like styrene, alkyl acrylates, and acrylonitrile and small amounts (1–10%) of polar unsaturated carboxylated monomers like acrylic acid, methacrylic acid, and itaconic acid are products of commercial interest because of their applications in paints, adhesives, binders, thickeners, and so forth.<sup>4</sup> The preparation of adhesive tape by applying a mixture of 2-ethylhexyl acrylate (EHA), methacrylic acid,

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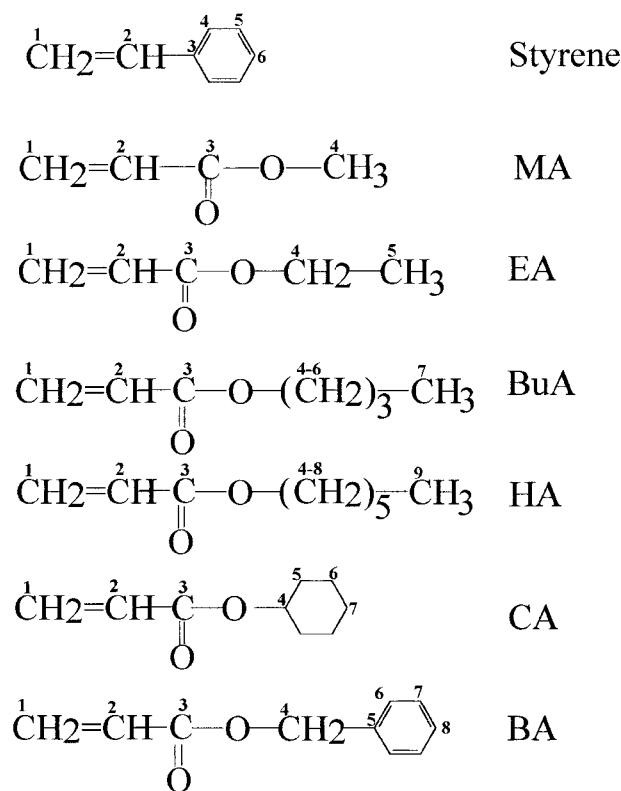
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and methyl methacrylate (MMA) copolymer emulsion with other additives, on polypropylene (PP) has been reported.<sup>5</sup> The terpolymerization of maleic anhydride–methyl methacrylate–styrene has been extensively studied, including its modification by tributyltin oxide to yield terpolymers of biological interest.<sup>6</sup>

A wide variety of chemical or physical strategies including copolymerization, polymer blend formation, and crosslinking network formation have been explored to provide multifunctional polymers.<sup>7</sup> The combination of durability and versatility and the ability to tailor molecules relatively easily to specific applications have made acrylic polymers prime candidates for numerous applications.<sup>8</sup> Acrylate homopolymers along with their copolymers are used in various fields, such as thin films, fibers, filaments, coatings, lithography, lacquers, adhesives, printing inks, binders, and so forth.<sup>9–12</sup> The ability to produce polymers containing long sequences of two or more different monomers has led to new products with unique and valuable properties, depending on the constitution and ratio of monomeric units and also on the method of preparation.<sup>13,14</sup> Free-radical copolymerization is a method of modifying the properties of polymers. The aim of our present investigation was to synthesize and characterize the copolymers of styrene with different acrylate monomers with wide variations in composition. The changes in the physical and chemical properties as functions of chemical composition and the unique combination of the pendant and main chain are also studied and presented in detail.

## EXPERIMENTAL

The monomers styrene (S; Fluka, Switzerland), ethyl acrylate (EA; BDS, Poole, England), methyl acrylate (MA), *n*-butyl acrylate (BuA; National Chemicals, Baroda, India; Fig. 1) were distilled at reduced pressure. The middle fraction of distillate was collected and used. The other monomers, *n*-hexyl acrylate (HA; 99.0%), cyclohexyl acrylate (CA; 92.9%), and benzyl acrylate (BA; 99.8%, purity checked by gas chromatography) were donated by Indian Petrochemicals Corporation Limited, Baroda, India. Technical-grade azobisisobutyronitrile (AIBN) was recrystallized from warm methanol, and benzoyl peroxide (BPO; Fluka) was purified before use by dissolving it in chloroform at room temperature and then reprecipitating it



**Figure 1** Molecular structures for the monomers used in the experiments.

by adding methanol. The solvents were all freshly distilled before use.

Fourier transform infrared (FTIR) spectra of the polymers were recorded on a Nicolet FTIR Impact 400D spectrophotometer. For FTIR spectra, the solid polymers and KBr (spectroscopic grade) were thoroughly mixed, and this mixture was pressed to form a pellet, whereas liquid polymers were spread over the NaCl cells and their spectra were recorded. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of homo- and copolymers were recorded under standard conditions at room temperature in deuterated chloroform on a JEOL JNM FX-100 FT-NMR spectrometer operating at 100 and 25 MHz respectively. TMS was used as an internal reference and CDCl<sub>3</sub> as an internal lock.

Thermal analysis of the polymers was conducted using TGA and DSC measurements. TGA was recorded on a Shimadzu thermal analyzer DT-30B at a heating rate of 10°C/min in the presence of air. DSC measurements were carried out for the polymers at temperatures from –75 to 200°C using modulated differential scanning calorimetry with a MDSC™ (TA Instruments Inc.,

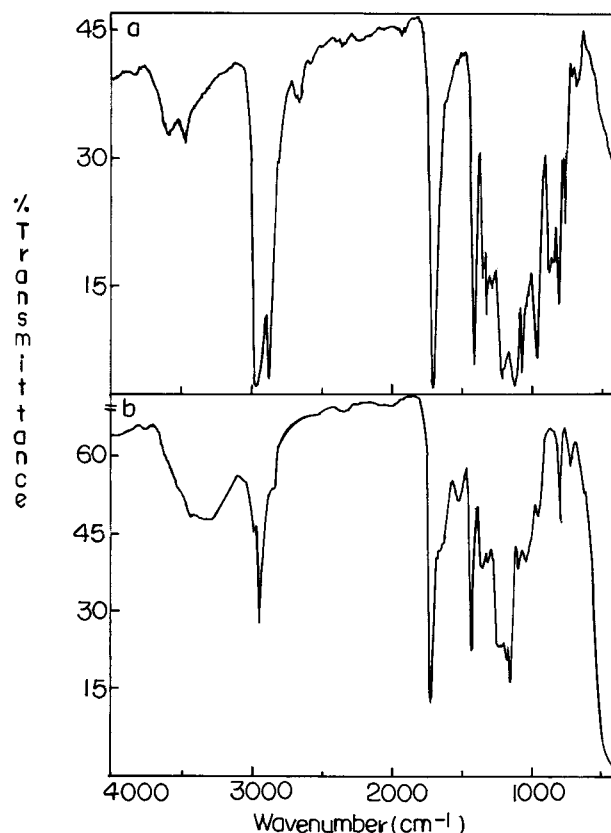
New Castle, DE) DSC 2910 system at a heating rate of 10°C/min under a nitrogen atmosphere).

Viscosity measurements of the dilute solution of the homopolymers and copolymers in 1,4-dioxane were carried out using an Ubbelohde dilution viscometer suspended in a thermostated bath at the required temperature ( $\pm 0.05^\circ\text{C}$ ). Measurements for each solution were repeated five to six times. Densities of the solutions at different temperatures were assumed to be those of a solvent at that temperature.<sup>15</sup>

Homopolymer polyacrylate(s) were synthesized as follows: 20.0 mL of acrylate(s) in 60.0 mL of DMF (except cyclohexyl acrylate where solvent was 1,4-dioxane) and 0.1% (w/v) of BPO as an initiator were put in a three-necked flask under a nitrogen atmosphere. The reaction mixture was stirred at 85°C for a period of 9 h. The three-necked flask was equipped with a water condenser and was placed in a thermostated water bath at 85°C. The reaction mixture after polymerization was poured into an excess of doubly distilled water to precipitate out the polymer(s). The polymer thus obtained was purified by reprecipitation from a solvent system into a nonsolvent system and finally dried *in vacuo* before characterization.

Synthesis of styrene homopolymer and styrene-acrylate copolymers was carried out in a benzene medium: 20.0 mL [50 : 50 (v/v) of styrene and an acrylate] of total monomer in 30.0 mL of benzene was taken in a three-necked flask. The reaction setup was similar to that used for the synthesis of polyacrylate(s). AIBN (0.2 g) was used as the initiator. The reaction mixture was stirred for 9 h under a nitrogen atmosphere at 70°C. Polymers were obtained by pouring the reaction mixture into the nonsolvent, methanol, except for poly(styrene-co-methyl acrylate) and poly(styrene-co-ethyl acrylate), that is, poly(S-MA) and poly(S-EA), respectively. These polymers were precipitated in excess of *n*-hexane. The precipitated product was further purified by removal of the respective homopolymers in a selective solvent-nonsolvent system.

Copolymerization of styrene (S) with cyclohexyl acrylate (CA) and benzyl acrylate (BA) was also carried out with different feed ratios—90 : 10, 75 : 25, 60 : 40, 40 : 60, and 20 : 80 (v/v)—of styrene and acrylate(s), respectively. The recipe for the synthesis of the copolymer 75 : 25 (v/v) of styrene and acrylate(s) was as follows: 7.5 mL of styrene, 2.5 mL of acrylate(s), and 0.1 g of AIBN were added to 15.0 mL of benzene. The polymer-

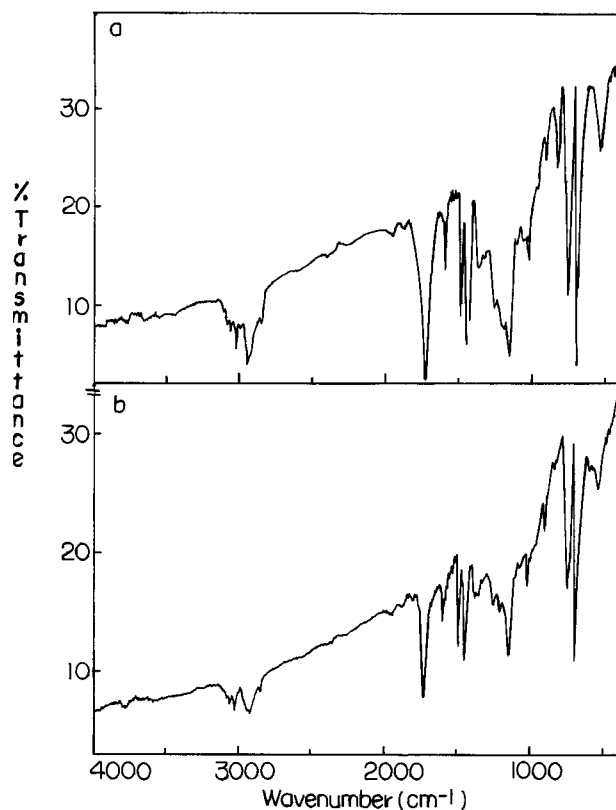


**Figure 2** Representative FTIR spectrum of homopolymers (a) PCA and (b) PMA.

ization reaction was carried out under a nitrogen atmosphere at 70°C. The reaction setup was the same as described earlier. The copolymerization was stopped at a low conversion (below 10%). Then the resulting copolymers were precipitated by a large quantity of methanol. The homopolymer, PS, was insoluble in acetone although the copolymers were soluble. The precipitate was then treated with acetone to remove polystyrene homopolymer. The homopolymers PBA and PCA were soluble in warm nitromethane; hence, these polymers were separated from the copolymers using warm nitromethane. The copolymers were washed well with methanol and dried *in vacuo* before characterization.

## RESULTS AND DISCUSSION

FTIR spectra of various homopolymers (Fig. 2; PMA and PCA) and copolymers [Fig. 3; poly(S-MA) and poly(S-BA)] are presented. All the polymers showed characteristic IR absorptions that



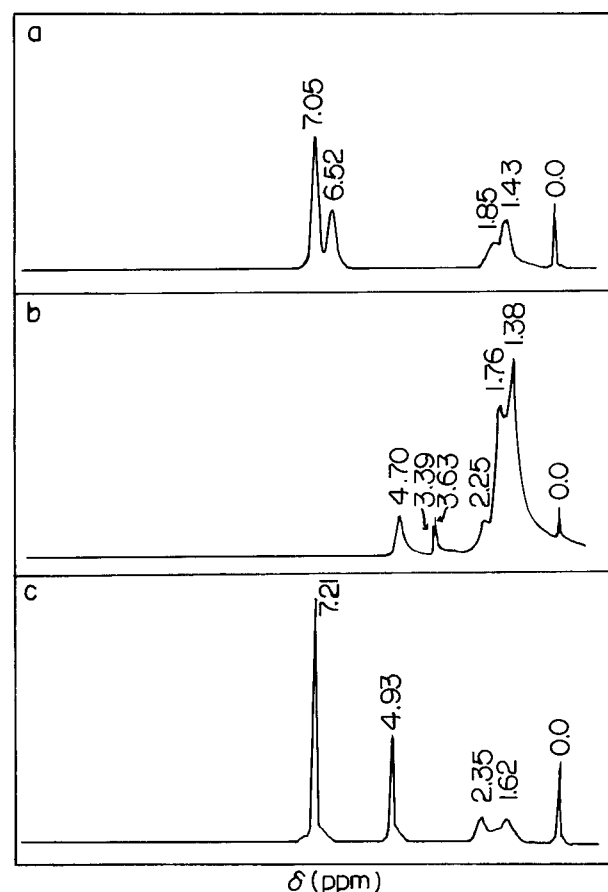
**Figure 3** Representative FTIR spectrum of copolymers (a) poly(S-MA) and (b) poly(S-BA).

agreed very well with those reported in the literature.<sup>16,17</sup> The homopolymers (Fig. 2) showed characteristic absorption bands due to an ester group ( $\text{C}=\text{O}$  stretch) at  $1733\text{ cm}^{-1}$ .  $\text{C}-\text{O}-\text{C}$  symmetric and asymmetric stretches were observed at  $1266$  and  $1176\text{ cm}^{-1}$ , respectively. Symmetrical and asymmetrical bending vibrations of  $\text{C}-\text{CH}_3$  were also seen at  $1452$  and  $1374\text{ cm}^{-1}$ , respectively, while an out-of-plane  $\text{C}-\text{H}$  bend was observed at  $760\text{ cm}^{-1}$ . Other prominent absorption peaks were at  $2937$  and  $2860\text{ cm}^{-1}$ . These are due to aliphatic ( $\text{C}-\text{H}$ ) stretches of  $-\text{CH}_2-$  and  $-\text{CH}_3$ . The FTIR spectra of various copolymers (Fig. 3) showed characteristic absorption bands because of their respective acrylate monomer units. Additional absorptions from the benzene ring of the styrene monomer units were also observed at  $1501$ ,  $1602$ , and  $3037\text{ cm}^{-1}$ .<sup>17,18</sup>

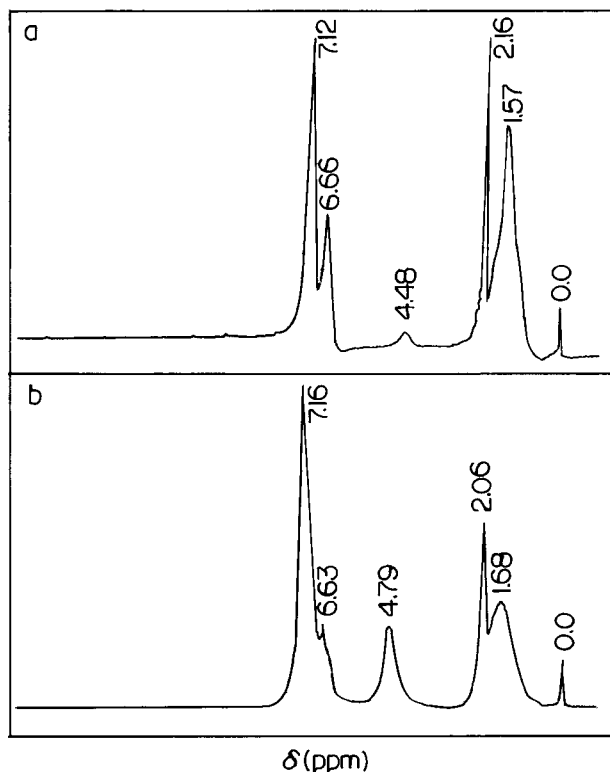
The  $^1\text{H-NMR}$  spectra of the homopolymers [(a) PS, (b) PCA, and (c) PBA] and copolymers [(a) SCA-2 and (b) SBA-5], along with assignments of various resonance signals, are shown in Figures 4 and 5, respectively.  $^1\text{H-NMR}$  spectra show the resonance signals corresponding to their structures (Fig. 1).

Polystyrene homopolymer [Fig. 4(a)] resonance signals appeared at  $7.05$ – $6.52$  (benzene ring),  $1.85$  ( $-\text{CH}$  connected with benzene ring), and  $1.43$  ppm ( $-\text{CH}_2-$  backbone protons),<sup>18</sup> while  $7.21$  (benzene ring),  $4.93$  ( $-\text{CH}_2-$  adjacent to phenyl group),  $2.35$  ( $-\text{CH}-$ ), and  $1.62$  ppm ( $-\text{CH}_2-$ ) are the resonance signals corresponding to poly(benzyl acrylate) [PBA; Fig. 4(c)]. Figure 4(b) represents the signal, around  $\delta = 4.70$  ppm, associated with protons of the  $-\text{OCH}$  group, and those between  $\delta = 3.69$ ,  $3.63$ , and  $2.25$  ppm are a result of five methylene groups. The methine backbone proton ( $-\text{CH}-$ ) and backbone methylene proton ( $-\text{CH}_2-$ ) resonate at  $1.76$  and  $1.38$  ppm, respectively.<sup>16</sup>

The copolymer compositions were determined by  $^1\text{H-NMR}$  spectra [Fig. 5(a,b)]. The distribution of protons in the two units is important in distinguishing the monomers in the copolymer chain.<sup>19</sup> The  $-\text{CH}-$  and  $-\text{CH}_2-$  protons of styrene, CA,



**Figure 4** Representative  $^1\text{H-NMR}$  spectrum of homopolymers (a) PS, (b) PCA, and (c) PBA in  $\text{CDCl}_3$ .



**Figure 5** Representative  $^1\text{H-NMR}$  spectrum of copolymers (a) poly(S-CA) (CA = 20.0 mol % in the feed) and (b) poly(S-BA) (BA = 75.0 mol % in the feed) in  $\text{CDCl}_3$ .

and BA, as well as phenyl protons of styrene and BA, are almost indistinguishable. Hence, in the present study aromatic protons ( $\sim 7$  ppm) of styrene and  $-\text{OCH}$  protons ( $\sim 4.48$  ppm) of CA were chosen for the estimation of styrene composition in the poly(S-CA) copolymer. The mole fraction of styrene ( $m_1$ ) in the copolymer poly(S-CA) was determined using the following relation:

$$m_1 = \frac{A_{\text{ph}}}{A_{\text{ph}} + 5A_{-\text{OCH}}} \quad (1)$$

where  $A_{\text{ph}}$  and  $A_{-\text{OCH}}$  represent the  $^1\text{H-NMR}$  resonance peak areas of protons on the phenyl and  $-\text{OCH}$  groups, respectively. The styrene composition in the poly(S-BA) copolymer was evaluated using the distinct peaks of methylene protons ( $\sim 4.57$  ppm, adjacent to phenyl group), and the peak intensity corresponds to the total number of protons of a particular group. The mole fraction of the copolymer was calculated by the following equation<sup>19</sup>:

$$\frac{\text{Intensity of methylene protons } (I_{\text{CH}_2})}{\text{Intensity of total protons } (I_{\text{T}})} = \frac{2m_2}{10m_2 + 8m_1} \quad (2)$$

The eq. (2) is based on the 10 protons in BA and the 8 protons in styrene and BA, with 2 methylene protons, produces a distinct resonance peak for the methylene group, at 4.57 ppm. From this and  $m_1 = 1 - m_2$ , the following equation was derived.

$$m_2 = \frac{4I_{\text{CH}_2}}{I_{\text{T}} - I_{\text{CH}_2}} \quad (3)$$

Integrated peak intensities were employed for this calculation. So,  $m_2$  is the mole fraction of BA and  $m_1 (= 1 - m_2)$  is that of styrene. Based on eq. (3), the mole fraction of styrene was calculated by measuring the intensities of methylene protons and total protons from the spectra of all copolymer samples. The mole fraction calculated for styrene in the poly(S-CA) and poly(S-BA) copolymers of various compositions are listed in Table I. The reactivity ratios  $r_1$  (styrene) and  $r_2$  (CA or BA) were determined by the Fineman-Ross method.<sup>20</sup> The following equation was used.

$$X(Y - 1)/Y = r_1(X^2/Y) - r_2 \quad (4)$$

where  $X$  is  $M_1/M_2$  and  $Y$  is  $m_1/m_2$  (Table I). On plotting  $G$  versus  $F$  (Table I), a straight line (Fig. 6) was obtained whose slope and intercept yielded  $r_1$  and  $r_2$ , respectively. The values obtained for  $r_1$  and  $r_2$  are  $r_1(\text{S}) = 0.930$  and  $r_2(\text{CA}) = 0.771$  for styrene and CA in poly(S-CA) copolymers, while  $r_1(\text{S}) = 0.755$  and  $r_2(\text{BA}) = 0.104$  for styrene and BA in the poly(S-BA) copolymer.

The  $r_1r_2$  value (Table II) of the S-CA copolymer is 0.717, indicating that the copolymer should have a random distribution of monomeric units with a tendency toward alternation, while the low value, 0.079, of  $r_1r_2$  for the S-BA system indicates an alternate distribution of monomeric units.<sup>21</sup> Several values of  $r_1$  and  $r_2$ , depending on temperature and reaction conditions, are reported in the literature<sup>22</sup> for the various monomer pairs and are presented in Table II. However, our computed data for  $r_1$  and  $r_2$  (Table II) are different from that available in the literature.<sup>22</sup> The literature values are also scattered. We do not



**Table I** Composition of Monomers in Feed and in Copolymers and Fineman-Ross Parameters

Samples	$M_1^a$	$m_1^b$	$X = M_1/M_2$	$Y = m_1/m_2$	$G = X(Y - 1)/Y$	$F = X^2/Y$
SCA-1	0.925	0.927	12.33	12.70	11.98	11.36
SCA-2	0.804	0.740	4.10	2.85	5.91	2.66
SCA-3	0.672	0.675	2.05	2.08	2.02	1.06
SCA-4	0.477	0.596	0.91	1.48	0.56	0.29
SCA-5	0.255	0.457	0.34	0.84	0.14	-0.06
SBA-1	0.923	0.909	11.99	9.99	14.39	10.79
SBA-2	0.800	0.798	4.00	3.95	4.05	2.99
SBA-3	0.667	0.670	2.00	2.03	1.98	1.02
SBA-4	0.471	0.642	0.89	1.79	0.44	0.39
SBA-5	0.250	0.575	0.33	1.35	0.11	0.12

<sup>a</sup>  $M_1$  is the mole fraction of styrene in feed.

<sup>b</sup>  $m_1$  is the mole fraction of styrene in the copolymer, determined by <sup>1</sup>H-NMR spectroscopy.

SCA is the copolymer of styrene with cyclohexyl acrylate, and SBA is the copolymer of styrene with benzyl acrylate.

presently have any reasonable explanation for such scattering of reactivity ratio values.

The plot of copolymer composition versus initial monomer composition (Fig. 7) was sigmoidal, and it crossed the ideal line at the point where  $M_1 = m_1 = 0.766$  and  $0.785$  for the poly(S-CA) and poly(S-BA) copolymers, respectively, indicating the azeotropic copolymer composition of these two systems. Theoretically, the values were obtained

from the following equation, which was very close to the experimental value:

$$m_{1 \text{ critical}} = M_{1 \text{ critical}} = \frac{1 - r_2}{2 - r_1 - r_2} \quad (5)$$

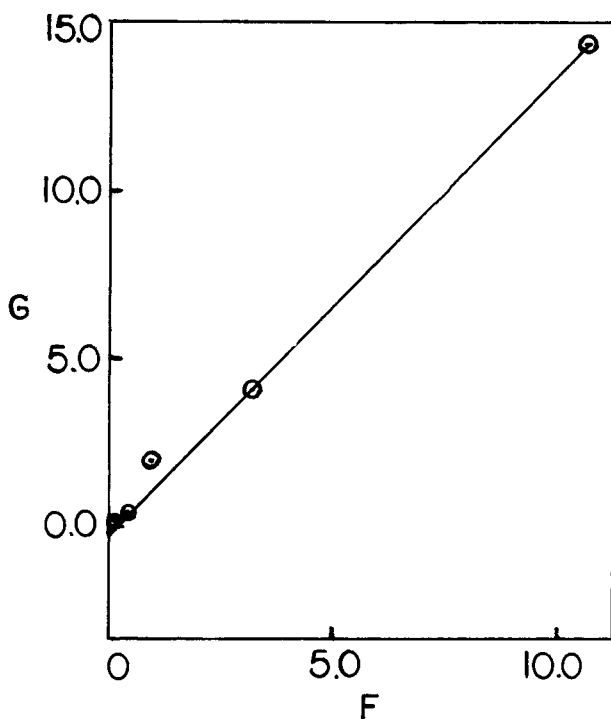
The  $Q$  and  $e$  values of the Alfrey-Price  $Q, e$  scheme<sup>9</sup> for CA and BA were determined by using experimentally obtained values of the corresponding reactivity ratios. The values of  $e_2 = -0.8$  and  $Q_2 = 1.0$ , obtained from the literature, were used for styrene, and  $e_1$  and  $Q_1$  were evaluated for CA and BA using the following equations:

$$e_1 = e_2 \pm (|\ln r_1 r_2|)^{1/2} \quad (6)$$

$$Q_1 = Q_2 / r_2 \exp[e_2(e_1 - e_2)] \quad (7)$$

The values of CA were found to be  $e_1 = 1.38$  and  $Q_1 = 0.19$  and of BA were  $e_1 = 0.80$  and  $Q_1 = 0.37$ .

The proton-decoupled <sup>13</sup>C-NMR spectrum of all the polymers shows characteristic resonance signals at their respective positions corresponding to their constituent monomeric units. The <sup>13</sup>C-NMR spectrum of homopolymers recorded in CDCl<sub>3</sub> at room temperature are shown in Figure 8. In <sup>13</sup>C-NMR, signals from the carbons of the long alkyl side chains were observed in the region of 14–42 ppm. The assignment of various resonance peaks, themselves the result of different carbon atoms, was done using the additive shift parameters for hydrocarbons.<sup>16,23</sup> In doing such calculations, an assumption was made that ester groups do not influence the chemical shifts of methylene groups



**Figure 6** Fineman-Ross plot for copolymerization of styrene with benzyl acrylate.

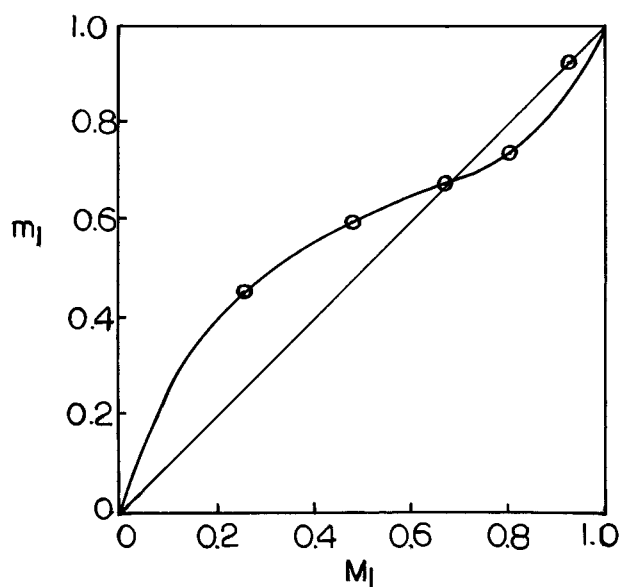
**Table II** Reactivity Ratios of Styrene ( $r_1$ ) with Different Acrylates ( $r_2$ )

Styrene (1)/ Acrylates (2)	Methyl Acrylate (MA)	Ethyl Acrylate (EA)	Butyl Acrylate (BuA)	Cyclohexyl Acrylate (CA)	Benzyl Acrylate (BA)
$r_1$	0.750 <sup>a</sup>	0.800 <sup>a</sup>	0.698 <sup>a</sup>	0.930 (0.885) <sup>a</sup>	0.755 (0.534) <sup>a</sup>
$r_2$	0.180 <sup>a</sup>	0.200 <sup>a</sup>	0.164 <sup>a</sup>	0.771 (0.254) <sup>a</sup>	0.104 (0.248) <sup>a</sup>
$r_1 r_2$	—	—	—	0.717	0.079

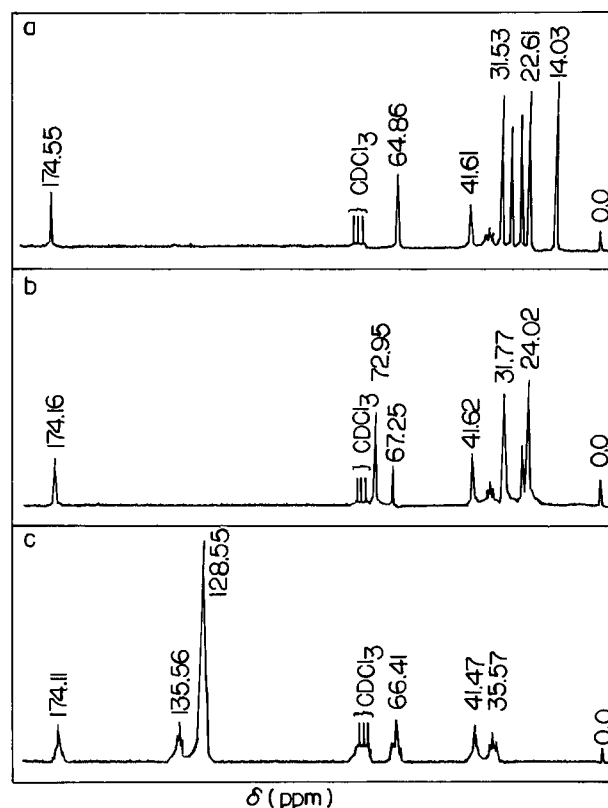
<sup>a</sup> Reference 22.

but are only affected by substitutions as far removed as the  $\delta$  position (i.e., effects of  $\alpha + 9.1$ ,  $\beta = +9.4$ ,  $\gamma = -2.5$ , and  $\delta = +0.3$  ppm). The calculations of shift were done using the formula for the predicted shift parameter,  $\delta = 2.5 + \sum nA$ , where  $A$  is the additive shift parameter and  $n$  is the number of carbon atoms for each shift parameter (methane adsorbs at 2.5 ppm upfield from TMS whereas alkane groups, unsubstituted by heteroatoms, absorb downfield from TMS to about 60 ppm).

For PHA  $\delta$  should be predicted for all five side-chain carbon atoms. Beginning with the terminal methyl, the predicted shift parameters were 13.8, 22.9, and 32.0 ppm. The  $-\text{OCH}_2$  group absorbed at 64.9 ppm. The observed values are in good agreement with the calculated values. The  $\delta_5$  and  $\delta_6$  showed only small downfield values because of the influence of the heteroatoms. In addition to


**Figure 7** Copolymer composition ( $m_1$ ) versus initial monomer composition ( $M_1$ ) plot for poly(S-CA) copolymer.

these absorptions, the methine ( $-\text{CH}-$ ) absorbed at 41.6 ppm and the methylene ( $-\text{CH}_2-$ ) group at 35.6 ppm, while the  $\text{C}=\text{O}$  resonated at 174.4 ppm.<sup>4,24</sup> In all these polyacrylates, the carbonyl carbons do not show any splitting, but the methylene carbons show splitting because of configurational effects (Fig. 8). In the cases of PS and PBA, the methylene and methine carbons of the phenyl ring resonated at 126.0, 128.6, 132.0, and 135.6 ppm, while the cyclohexyl group methylene and methine of PCA also absorbed at their respective positions, as shown in Figure 8.


**Figure 8** Representative  $^{13}\text{C}$ -NMR spectrum of homopolymers (a) PHA, (b) PCA, and (c) PBA in  $\text{CDCl}_3$ .

In copolymers because of the various carbon atoms in the copolymer, the assignment of peaks was done according to the corresponding homopolymer spectra. These peaks are listed in Table III. Unlike with the homopolymers of acrylates the carbonyl carbons in all these copolymers show splitting. Also various splitting patterns can be observed in the resonances of the backbone methylenes and methines. The splitting is influenced by the composition of the copolymers and is a result of configurational and sequence distribution effects.

The thermal behavior of the homopolymers and copolymers was studied with thermogravimetry. The thermograms of all the homopolymers and copolymers were found to have a similar nature, showing a one-step decomposition (Fig. 9). Most polymer samples were stable up to 300°C and started to lose weight above this temperature (Table IV). The decomposition observed in the temperature range 320°C–590°C is perhaps a result of the breakdown of polymer initiated from the weak sites (e.g., unsaturated chain ends, branching, head-to-head linkages, etc.), as observed earlier.<sup>25</sup> The activation energy ( $E_a$ ) of decomposition values (Table IV) shows that PMA exhibits a lower thermal stability than PEA, while the other polymers—PBuA and PHA—exhibited higher thermal stability at a heating rate of 10°C/min. All the copolymers also followed a similar pattern, that is, with increasing linear chain length of the pendant group in the copolymers, thermal stability increases. The data listed in Table IV give the initial decomposition temperature (IDT), maximum rate of decomposition ( $T_{max}$ ), complete decomposition temperature (FDT), and the activation energies ( $E_a$ )<sup>26</sup> calculated using standard relations suggested by Broido.<sup>27</sup>

$$\ln \ln(1/Y') = -E_a/R(1/T) + \text{constant} \quad (8)$$

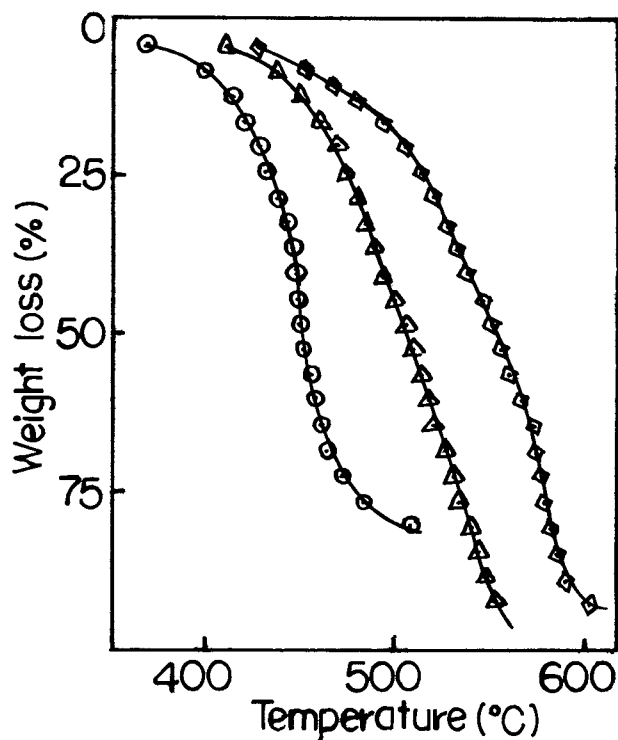
where  $Y'$  [=  $(W_o - W_t)/(W_o - W_\infty)$ ] is the fraction of the number of initial molecules not yet decomposed; and  $W_t$ ,  $W_\infty$  (= 0), and  $W_o$  are the weight at time  $t$ , the weight at infinite time, and the initial weight, respectively. A plot of  $\ln \ln(1/Y')$  versus  $(1/T)$  (eq. 8) provides an excellent approximation to a straight line over a range of 0.999  $\langle Y' \rangle$  0.001. The slope is related to the activation energy. Representative plots are shown in Figure 10.

DSC curves for PS and polyacrylates are shown in Figure 11. From the DSC curves, the glass-

**Table III** Chemical Shifts ( $\delta$ ) of Carbon Peaks in <sup>13</sup>C-NMR for Various Poly(S-Acrylate) Copolymers

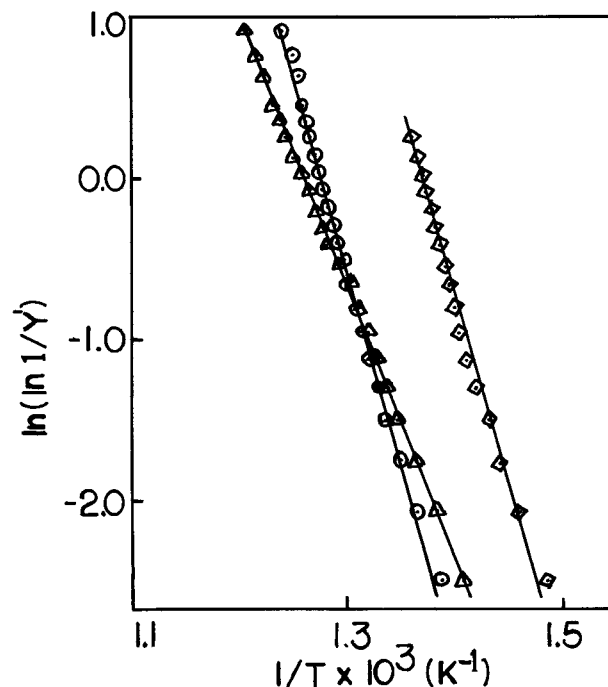
	Poly(S-MA)	Poly(S-EA)	Poly(S-BuA)	Poly(S-HA)	Poly(S-CA)	Poly(S-BA)
C <sub>3</sub> (MA)	175.96	175.43	C <sub>3</sub> (BuA)	C <sub>3</sub> (HA)	C <sub>3</sub> (CA)	C <sub>3</sub> (BA)
	175.43	174.89	175.63	174.77	174.85	174.11
C <sub>3</sub> (S)	142.78	143.36	144.06	C <sub>3</sub> (S)	C <sub>3</sub> (S)	174.55
C <sub>4-6</sub> (S)	128.16	128.01	127.96	C <sub>4-6</sub> (S)	C <sub>4-6</sub> (S)	143.99
	126.21	126.02	126.11	127.96	128.11	143.27
C <sub>4</sub> (MA)	51.17	59.34	C <sub>4</sub> (BuA)	C <sub>4</sub> (HA)	C <sub>4</sub> (CA)	C <sub>4</sub> (BA)
			63.79	64.13	72.22	135.91
C <sub>2</sub> (S + MA)	41.03	40.79	C <sub>2</sub> (S + BuA)	C <sub>2</sub> (S + HA)	C <sub>2</sub> (S + HA)	C <sub>4-6</sub> (S) +
C <sub>1</sub> (S + MA)	39.52	38.79	C <sub>2</sub> (S + EA)	C <sub>1</sub> (S + HA)	C <sub>1</sub> (S + HA)	C <sub>6-8</sub> (BA)
			30.55	31.38	31.58	128.06
			19.05	28.41	25.44	126.02
			13.69	25.53	23.83	41.03
				22.51	17.94	39.96
				C <sub>7</sub> (HA)		
				C <sub>5</sub> (HA)		
				C <sub>6</sub> (HA)		
				C <sub>8</sub> (HA)		
				C <sub>9</sub> (HA)		
						65.54





**Figure 9** Representative TGA plots of ( $\diamond$ ) poly(S-EA), ( $\Delta$ ) poly(S-CA), and ( $\square$ ) PCA at a heating rate of  $10 \text{ K min}^{-1}$  in air.

transition temperatures ( $T_g$ ) of the polymers were obtained. Polyacrylates have low values of  $T_g$ , but as the styrene unit is incorporated into the copolymers of acrylates, their  $T_g$  values increase (Table IV). The  $T_g$  values obtained for all



**Figure 10** Representative Brido plots for: ( $\diamond$ ) PCA, ( $\square$ ) poly(S-BA), and ( $\Delta$ ) poly(S-CA).

these polymers agree well with those reported in the literature.<sup>23,28</sup> The onset  $T_g$ ,  $T_g$  at point of inflection, and peak  $T_g$  values of PS, which are 93.5, 100.2, and 104.7°C, respectively, are shown in Figure 11.

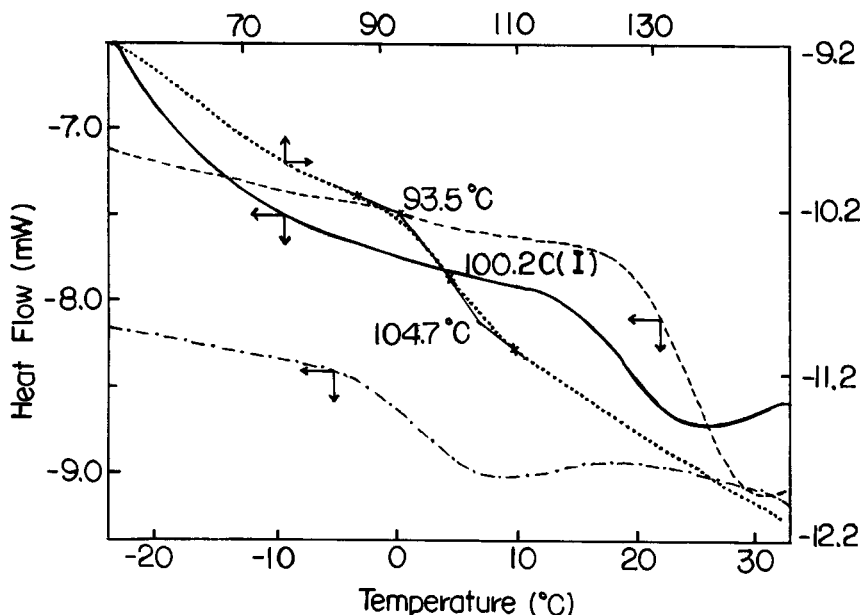
Intrinsic viscosity  $[\eta]$ , one of the most important sources of information on the size and shape of polymer molecules,<sup>27</sup> can be obtained by the use of the Huggins and Kraemer equations

**Table IV** Thermal Analysis Results for Various Homopolymers and Copolymers

Polymer Samples	IDT (°C)	$T_{\max}$ (°C)	FDT (°C)	Weight Loss (%)	$E_a^b$ (kJ mol <sup>-1</sup> )	$T_g$ (°C)
PMA <sup>a</sup>	320	—	500	89	92.0	19.5
PEA <sup>a</sup>	380	—	510	87	136.3	-3.0
PBuA <sup>a</sup>	360	—	530	90	141.3	—
PCA	400	445	508	80	174.8	12.6
PBA	435	503	535	80	188.2	12.5
PS	408	501	553	80	124.7	100.2
Poly(S-MA)	430	518	567	92	129.3	48.0
Poly(S-EA)	481	546	589	92	141.0	17.4
Poly(S-BuA)	428	519	549	84	153.2	-0.3
Poly(S-HA)	460	515	558	88	153.3	—
Poly(S-CA)	438	505	557	92	139.9	46.4
Poly(S-BA)	435	510	535	80	188.2	—

<sup>a</sup> Ref. 26.

<sup>b</sup> Calculated using Brido's method at a heating rate of  $10^\circ\text{C}/\text{min}$  in air.



**Figure 11** Representative DSC thermograms of homopolymers (· · · · ·) PS, (—) PCA, (---) PMA, and (- · · · -) PEA at a heating rate  $10 \text{ K min}^{-1}$  in a  $\text{N}_2$  atmosphere.

$$(\eta_r - 1)/C = [\eta] + k'[\eta]^2C \quad (9)$$

$$\ln \eta_r/C = [\eta] - k''[\eta]^2C \quad (10)$$

where  $k'$  and  $k''$  are usually referred to as the Huggins and Kraemer constants. The accuracy of the data was checked by calculating  $k'$  and  $k''$  and their difference, which was 0.5 as expected. The

intrinsic viscosity values of all the polymers are presented in Table V. It can be seen that  $[\eta]$  decreases as the temperature increases, and the plots of  $[\eta]$  versus  $T$  plots are linear with negative slopes.<sup>29</sup> This indicates that the swelling of polymer chains is limited in these systems, and the critical solution temperatures are lower for these polymer solutions because of decreased thermo-

**Table V** Intrinsic Viscosity ( $[\eta]$ ) Hydrodynamic Volume ( $V_E$ ), and Shape Factor ( $\nu$ ) of Various Polymers at Different Temperature in Dioxane

Polymer Samples	30°C			40°C			50°C		
	$[\eta]$ (dL g <sup>-1</sup> )	$V_E$ (dL g <sup>-1</sup> )	$\nu$	$[\eta]$ (dL g <sup>-1</sup> )	$V_E$ (dL g <sup>-1</sup> )	$\nu$	$[\eta]$ (dL g <sup>-1</sup> )	$V_E$ (dL g <sup>-1</sup> )	$\nu$
PMA	0.330	0.1302	2.5	0.326	0.1288	2.5	0.323	0.1268	2.5
PEA	0.226	0.0898	2.5	0.224	0.0844	2.5	0.222	0.0880	2.5
PBuA	0.224	0.0893	2.5	0.223	0.0888	2.5	0.220	0.0879	2.5
PHA	0.161	0.0639	2.5	0.159	0.0629	2.5	0.157	0.0628	2.5
PCA	0.136	0.0540	2.5	0.135	0.0539	2.5	0.134	0.0532	2.5
PBA	0.478	0.1846	2.6	0.472	0.1828	2.6	0.466	0.1808	2.6
PS	0.188	0.0745	2.5	0.185	0.0740	2.5	0.182	0.0722	2.5
Poly(S-MA)	0.187	0.0747	2.5	0.185	0.0740	2.5	0.183	0.0728	2.5
Poly(S-EA)	0.188	0.0747	2.5	0.185	0.0728	2.5	0.183	0.0726	2.5
Poly(S-BuA)	0.197	0.0779	2.5	0.194	0.0774	2.5	0.192	0.0766	2.5
Poly(S-HA)	0.202	0.0800	2.6	0.200	0.0794	2.5	0.197	0.0785	2.5
Poly(S-CA)	0.162	0.0642	2.5	0.160	0.0631	2.5	0.158	0.0626	2.5
Poly(S-BA)	0.230	0.0920	2.5	0.226	0.0898	2.5	0.223	0.0885	2.5

dynamic affinity with increased temperature.<sup>29</sup> Moreover, as shown in Table V, it can be recognized that the intrinsic viscosities of all the copolymers having a linear pendant group increased with increasing chain length of the pendant group. However, in the case of homopolymers, the intrinsic viscosities decreased with an increase in chain length of the pendant group. From the values of intrinsic viscosity (Table V), it can be observed that the intrinsic viscosity in a solvent is dependent on the interaction between polymer and solvent as well as the interaction among the polymer chains. In addition to this, the chemical composition and constitution, the homogeneity, and the length of sequences of chemically identical monomer units also affect the  $[\eta]$  value.<sup>29</sup>

The well-known Frenkel-Eyring equation for viscous flow can be written as

$$\eta = (Nh/V)\exp(\Delta G_{\text{vis}}^{\ddagger}/RT) \quad (11)$$

where  $V$  is the molar volume of the solution. But the molar volume of a polymer solution is an enigma; hence, the molar volume of the solvent was used in the calculations because the densities of the polymer solution and of the solvent are generally the same.<sup>26</sup> The other quantities have their usual meaning. This equation can be rewritten as

$$\ln(\eta V/Nh) = (\Delta H_{\text{vis}}^{\ddagger}/RT) - (\Delta S_{\text{vis}}^{\ddagger}/RT) \quad (12)$$

where  $\Delta H_{\text{vis}}^{\ddagger}$  and  $\Delta S_{\text{vis}}^{\ddagger}$  are the enthalpy and entropy of the viscous flow. Polystyrene, polyacrylates, and all copolymers at a concentration of 0.8 g dL<sup>-1</sup> in 1,4-dioxane showed a linear relationship with a correlation coefficient of 0.99 or better. It can be observed that  $\Delta H_{\text{vis}}^{\ddagger}$  values of all the systems in 1,4-dioxane are more or less constant, and the average was found to be 15.6 ± 0.2 kJ mol<sup>-1</sup>. This low value and the constancy indicate the polymers were not crosslinked.<sup>26</sup> The entropies of activation of the viscous flow ( $\Delta S_{\text{vis}}^{\ddagger}$ ) were also low and positive—22 ± 1 J mol<sup>-1</sup> K<sup>-1</sup>, indicating the polymer structures were reasonably ordered in 1,4-dioxane. Therefore, the  $\Delta G_{\text{vis}}^{\ddagger}$  values can be computed and were found to decrease with an increase in temperature.

The relative viscosity data were used to calculate the equivalent hydrodynamic volume (voluminosity,  $V_E$ ), a measure of size of a solvated polymer molecule at infinite dilution.  $V_E$  was cal-

culated by plotting  $\psi$  against concentration (in g dL<sup>-1</sup>), where

$$\psi = (\eta_r^{0.5} - 1)/C(1.35\eta_r^{0.5} - 0.1) \quad (13)$$

The straight line obtained was then extrapolated to C=O, and the intercept yielded  $V_E$ . The voluminosity values (Table V) are a function of temperature. As the temperature increases, the solvation decreases, and hence,  $V_E$  decreases.<sup>20</sup> The shape factor ( $\nu$ ) was obtained from the equation

$$[\eta] = \nu V_E \quad (14)$$

The shape factor gives an idea about the shape of the polymer molecule in solution.<sup>30</sup> The values of shape factors in different temperatures were found to be 2.5 ± 0.1, suggesting that the macromolecules acquire spherical conformation in dioxane. Moreover, the  $\nu$  values were found to be independent of temperature, suggesting that conformation is not dependent on temperature (Table V).

## CONCLUSIONS

It is clearly seen from the data in this study that free-radical copolymerization reaction of styrene with the acrylic ester systems studied follows classical copolymerization theory. FTIR and <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy provided information regarding structure, conformation, and composition of the polymers. The reactivity ratios of the monomers obtained by <sup>1</sup>H-NMR spectroscopy showed a relatively higher reactivity of the styrene than that of respective acrylic esters. Single-stage decomposition was observed for all polymers. The activation energy of the decomposition increases as the linear alkyl chain length of the pendant group increased. These increase in pendant-group chain length have opposite effects on the intrinsic viscosity of homopolymers and copolymers with styrene—for the former it decreases, whereas for the latter it increases.

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