Synthesis and Characterization of Homopolymer of 2-Ethylhexyl Acrylate and Its Copolymers with Acrylamide, Acrylonitrile, and Methyl Methacrylate

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SYNOPSIS

A homopolymer of 2-ethylhexyl acrylate (EHA) was synthesized by a free-radical solution polymerization technique. Copolymers of EHA with acrylonitrile (AN), acrylamide (AA), and methyl methacrylate (MMA) in various ratios were also synthesized by the same procedure. These were characterized by PNMR, ^{13}C-NMR, FTIR, GPC, and viscosity measurements. The reactivity ratios of various monomers were determined. The viscosity measurements were carried out in four different solvents: ethyl acetate (EA), methyl ethyl ketone (MEK), toluene (TL), and tetrahydrofuran (THF). The studies were done at three different temperatures of 30, 35, and 40°C. The activation parameters of the viscous flow were computed for different systems. The intrinsic viscosity of the copolymers increased with temperature in MEK and EA. This trend showed reversal for the other two solvents. The results are discussed in detail. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Studies on polymeric matrices and membranes are gaining much interest as potential transdermal drug-delivery systems. Celluloses, poly(ethylene glycol) (PEG), and polyvinylpyrrolidone (PVP) have been studied extensively.[1] Advances in transdermal delivery systems (TDS) and the technology involved have been rapid because of sophistication of polymer science which now allows incorporation of polymeric additives in transdermal delivery systems, in adequate quantity. A recent review article discusses some typical polymers used for this purpose.[2] The pressure-sensitive adhesive tapes, used in TDS, generally comprise acrylic polymers. Adhesive tape prepared by applying a mixture of 2-ethylhexyl acrylate (EHA), methacrylic acid, and methyl methacrylate (MMA) copolymer emulsion with other additives, on polypropylene (PP), has been reported on.[3] Copolymers of hydrophobic monomers like styrene, alkyl acrylates, and acrylonitrile (AN) and small amounts (1–10%) of polar unsaturated car-

boxylated monomers like acrylic acid, methacrylic acid, and itaconic acid are products of commercial interest due to their applications in paints, adhesives, binders, thickeners, etc.[4] Higher acrylates find application as pressure-sensitive adhesives. These acrylic adhesives are generally composed of two monomers which are copolymerized. One of the monomers, present in excess (80–98% of the total weight of the two monomers), is hydrophobic and is usually an acrylic or methacrylic ester containing 4–10 carbon atoms. The second monomer, incorporated during copolymerization, is a reinforcing monomer, present in 2–20% (of the total weight of all monomers) and generally contains 1–3 carbon atoms in the alkyl group, e.g., acrylic and methacrylic acid, their respective esters, acrylamide (AA), and methacrylamide.[5] Poly(2-ethylhexyl acrylate-g-MMA) copolymers having properties of an elastomer have been reported.[6] These materials have "hard" grafts (PMMA, T_g = 105°C) joined by a flexible, "soft" backbone (PEHA, T_g = −65°C). The copolymers of MMA with EHA of various monomer compositions have been synthesized and studied in detail.[7]

With all this in mind, as well as our interest in acrylates and ANs,[8,9] we decided to synthesize pres-

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sure-sensitive adhesives by copolymerization of EHA with various reinforcing monomers like MMA, AA, and AN. The copolymers obtained are inherently rubbery, tacky, and suitably heat- and light-stable, i.e., there is no need to add tackifiers or stabilizers. The copolymers were synthesized by free-radical solution polymerization and were thoroughly characterized. The characterization techniques were spectroscopic-^{13}C-NMR, PMR, and FTIR; molecular weight and molecular weight distribution by GPC; and viscosity measurements. The copolymers and PEHA were also then subjected to monolayer studies. The monolayer studies will be published elsewhere. This article discusses the various results obtained on characterization.

EXPERIMENTAL

2-Ethylhexyl acrylate (EHA; Union Carbide Corp.), acrylamide (AA; Mitsubishi Chemicals Ltd.), acrylonitrile (AN; BDH, India), and methyl methacrylate (MMA; National Chemicals, India) were used for the copolymerizations without any purification. The solvents, i.e., ethyl acetate (EA), methanol, methyl ethyl ketone (MEK), tetrahydrofuran (THF), and toluene (TL) were obtained from Merck, India. All solvents were freshly distilled before use.

The FTIR of the homopolymers and copolymers were recorded on a Perkin-Elmer PC-16 spectrophotometer. The NMR of the polymer solutions in CDCl$_3$ were recorded on a Varian XL, 300 MHz for PMR and 75 MHz for ^{13}C-NMR, at the RSIC, IIT, Bombay, India. The GPC of the polymers was run in THF at ambient conditions ($\sim 27°$C) on a TO-SOH, Japan, with a TOSOH 8010 refractive index detector. Viscosity studies of different solutions were carried out with the help of an Ubbelohde viscometer that was placed vertically in a thermostat at the required temperature ($\pm0.05°$C).

The copolymer comprising EHA and AA was prepared using a solution polymerization technique as follows: EHA, 9.3 g; AA, 0.7 g; benzoyl peroxide, 30 mg; and solvent EA, 20 mL, were mixed in a three-necked flask under a nitrogen atmosphere. The reaction mixture was stirred at 79–80°C for a period of 6 h. The three-necked flask was equipped with a water condenser and placed in a thermostat which was maintained at the desired temperature.

Similar conditions were maintained for the copolymerization of EHA with AN and EHA with MMA and for the synthesis of homopolymer poly(2-ethylhexyl acrylate) (PEHA). The ratios main-

tained were 93 : 7, 80 : 20, and 60 : 40 (w/w) for EHA : AN and EHA : MMA copolymerizations. The mol fractions of each component in the feed as well as in the copolymers are given in Table I. The EHA : AA copolymers having a higher content of AA (i.e., more than 7% w/w AA) could not be synthesized under the present conditions. The products obtained under these conditions were in the form of a gel, probably due to the high reactivity of AA. These were difficult to dissolve in common organic solvents and were therefore not studied. The reaction mixtures, after polymerization, were poured into an excess of methanol to precipitate out the product. The product was Soxhlet-extracted with water to remove polyacrylamide and dried and dissolved in acetone. The homopolymer of EHA remained insoluble in acetone. The copolymer EHA : AA, soluble in acetone, was reprecipitated in methanol, dried, and used for characterization and monolayer studies. The homopolymer of AN was insoluble in acetone and, hence, could be separated from the acetone-soluble copolymer EHA : AN. The copolymer was reprecipitated from methanol. The homopolymer of MMA was soluble in acetic acid although the copolymer EHA : MMA was not. The acetic acid-insoluble copolymer was dissolved in acetone and reprecipitated from methanol. All the copolymers and homopolymers obtained in the pure form were dried *in vacuo* and characterized.

RESULTS AND DISCUSSION

FTIRs of PEHA, EHA : AA (93 : 7), and EHA : AN (93 : 7) are given in Figures 1–3. The polymers were spread over the NaCl cells and the spectra were recorded. The FTIR of PEHA (Fig. 1) shows the characteristic peak due to the ester group at 1732 cm^{-1}. Other prominent absorption peaks were at 1454 and 1400 cm^{-1}. These are due to asymmetrical and symmetrical bending vibrations of C — CH$_3$.

Table I Copolymer Composition for EHA : AN Copolymers*

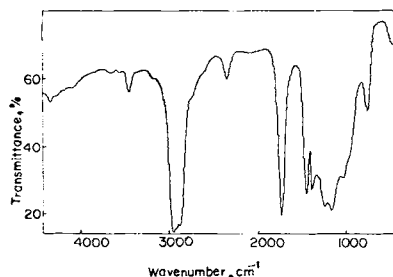| Feed Ratio EHA : AN (w/w)	M_1	M_2	m_1	m_2	H	h
93 : 7	0.21	0.79	0.19	0.81	0.27	0.23
80 : 20	0.46	0.54	0.40	0.60	0.85	0.67
60 : 40	0.70	0.30	0.66	0.34	2.33	1.94

* For symbols, see text.

Figure 1 FTIR spectrum of homopolymer PEHA.

The asymmetric and symmetric stretches $(C—O—C)$ were seen at 1246 and 1170 cm^{-1}, respectively. Aliphatic stretches, $C—H$, due to $—CH_2$ and $—CH_3$, were also observed at 2948 and 2880 cm^{-1}. An out-of-plane $C—H$ bend was seen at 766 cm^{-1}. These account for all the main absorption bands. The assignments were done with the help of the literature data.[10,11]

In Figure 2, additional absorptions due to the $—CONH_2$ group were also seen. The $N—H$ stretches at 3440 cm^{-1} and $N—H$ bending at 1674 cm^{-1} were observed.

Figure 3 shows a triple-bond stretch, $C≡N$, at 2240 cm^{-1}. The intensity of this peak increases with increase in AN content. The FTIR of EHA : MMA is similar to the FTIR of PEHA (Fig. 1). The MMA group incorporated could not be distinguished by FTIR, but was supported by NMR spectroscopy as shown below. The band at 2350 cm^{-1} is due to atmospheric CO_2. ^{1}H-NMR spectra of PEHA, EHA : MMA (93 : 7), and EHA : AN (93 : 7) are shown in Figures 4–6.

The signals that occur around $\delta = 0.9$ ppm are associated with protons of methyl groups and those between $\delta = 1.2$ and 1.4 ppm are due to methylene groups. The locations of these peaks depend upon configuration of the nearest neighbors. The two $—CH_3$ groups [6 H, Fig. 7(a) and (b)] resonate at 0.844, 0.867, and 0.887 ppm. Various resonances in this area cannot be distinguished because of overlap due to spin–spin coupling and sensitivity of methyl
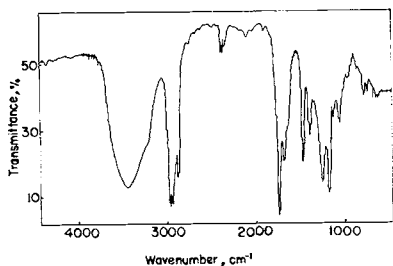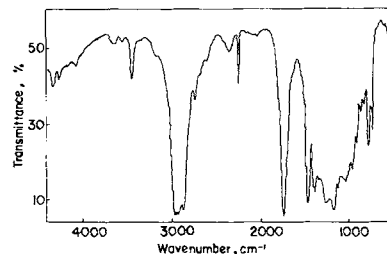

Figure 2 FTIR spectrum of copolymer EHA : AA.

Figure 3 FTIR spectrum of copolymer EHA : AN.

protons toward tacticity and monomer sequence. The four $—CH_2$ groups [(c)–(e) and (f)] and one methine proton, $—CH$ (g) resonate between 1.270 and 1.395 ppm, giving a multiplet. The methine backbone proton (i) and backbone $—CH_2$ (j) resonate at 2.280 and 1.562 ppm, respectively. The pendant $—CH_2$ of the PEHA backbone (h) gives a doublet at 3.941 and 3.922 ppm.[6] The $—OCH_3$ group of MMA incorporated (Fig. 5) resonates at 3.585 ppm. The peak at 0.879 arises from the methyl of the syndiotactic triad, while the peak at 1.032 ppm is due to the heterotactic triad.[8] The occurrence of a single methylene peak at 1.82 ppm is indicative of the racemic dyads. The change in the composition of the copolymer of EHA on copolymerization with AN or MMA is expressed by the following relation:

$$\frac{m_1}{m_2} = \frac{r_1 M_1^2 + M_1 M_2}{r_2 M_2^2 + M_1 M_2} \qquad (1)$$

The above equation can be rewritten as[12]

$$r_2 = r_1 H^2/h + H(1-h)/h \qquad (2)$$

where $H = M_1/M_2$ and $h = m_1/m_2$. M_1 and M_2 are mol fractions of the monomers in the feed, and m_1 and m_2 are the mol fractions of the monomers in the relevant copolymer. r_1 and r_2 are the reactivity
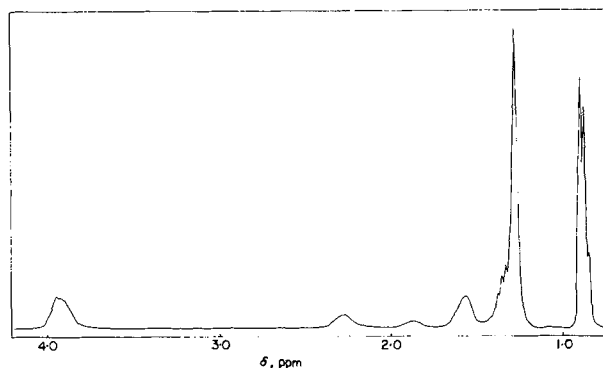

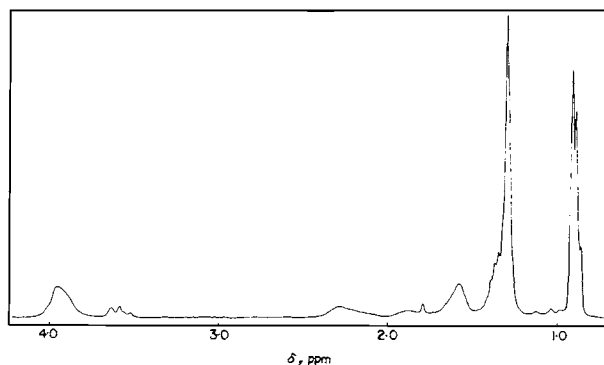**Figure 4** ^{1}H-NMR spectrum of PEHA.

Figure 5 ^{1}H-NMR spectrum of EHA : MMA.

ratios of the two monomers. The mol fractions of monomers in the copolymers were determined from NMR spectral data.

The mol fraction of AN (m_1) in the copolymer was determined using the following relation:

$$m_1 = \frac{2I(-\mathrm{CHCN})}{I(-\mathrm{OCH}_2) + 2I(-\mathrm{CHCN})} \quad (3)$$

where $I(-\mathrm{OCH}_2)$ and $I(-\mathrm{CHCN})$ represent the peak intensities of $-\mathrm{OCH}_2$ and $-\mathrm{CHCN}$ protons. The $-\mathrm{CHCN}$ proton resonates at 2.60 ppm. The mol fractions calculated for AN and EHA, in copolymers of various compositions, are listed in Table I.

Monomer reactivity ratios r_1 and r_2 could thus be calculated graphically by plotting $H(1-h)/h$ vs. H^2/h (graphical method). The slope and intercept yielded r_1 and r_2, respectively.[10] r_1 and r_2 were found to be 0.83 and 1.23, respectively, for AN and EHA.

Reactivity ratios were also determined using the Kelen–Tudos method.[13] Equation (1) can be rewritten as

$$G/(\alpha + F) = (r_1 + r_2/\alpha)F/(\alpha + F) - r_2/\alpha \quad (4)$$
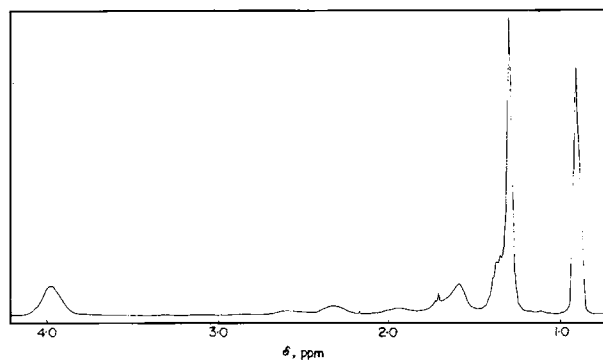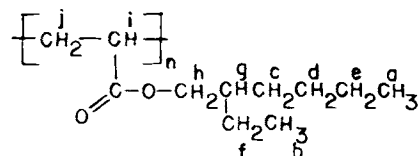

Figure 7 Repeat unit of PEHA.

where $G = H(h-1)/h$, $F = H^2/h$, and $\alpha = \sqrt{F_m F_M}$. F_m and F_M stand for the lowest and highest values of F calculated for the series of copolymeric systems. On plotting $G/(\alpha + F)$ as a function of $F/(\alpha + F)$, a straight line was obtained. This, when extrapolated to $F/(\alpha + F) = 0$ and $F/(\alpha + F) = 1$, gave $-r_2/\alpha$ and r_1 (both as intercepts), respectively. r_1 and r_2 were found to be 0.72 and 1.18, respectively, for AN and EHA.

The reactivity ratios for the monomers EHA and MMA were calculated similarly. The peak intensities due to $-\mathrm{OCH}_3$ protons were taken for the calculation of mol fractions of MMA and EHA in the respective copolymers.[14] The values of r_1 and r_2 were found to be 1.90 and 0.96, respectively (graphical method), for MMA and EHA.

Further evidence for the various comonomers incorporated was given by ^{13}C-NMR spectra of the polymers (Figs. 8–10). Sequence determinations of the copolymer of MMA and ethyl methacrylate[14] and the copolymer of AN and EA[14] have been reported. In ^{13}C-NMR, signals due to the carbons of long alkyl side chains were observed in the region 10–40 ppm. The assignments for these carbons were done using the additive shift parameters for hydrocarbons.[11] In such calculations, an assumption was made that the ester groups do not influence the chemical shifts of the methylene groups. The calculations were done using the formula $\delta = -2.5 + nA$, where A is the additive shift parameter; n, the number of carbon atoms for each shift parameter (methane absorbs at 2.5 ppm upfield from TMS); and δ, the predicted

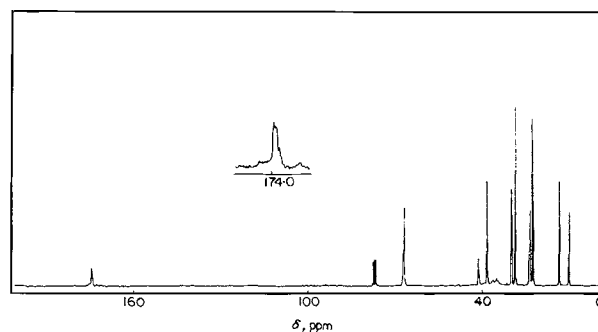**Figure 6** ^{1}H-NMR spectrum of EHA : AN.

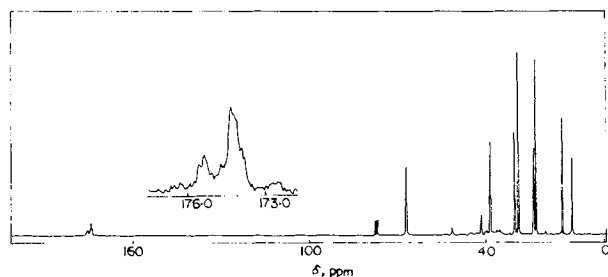**Figure 8** Proton decoupled ^{13}C-NMR spectrum of PEHA.

Figure 9 Proton decoupled ^{13}C-NMR spectrum of EHA : MMA.

shift parameter. For PEHA (Fig. 8), δ could be predicted for all the seven side-chain carbon atoms. Beginning with terminal methyl (δ_a), the predicted shift parameters were $\delta_a = 14.0$, $\delta_e = 23.3$, $\delta_d = 29.8$, $\delta_c = 36.4$, $\delta_g = 34.0$, $\delta_f = 29.9$, and $\delta_b = 11.4$ ppm. The calculated and observed values were in good agreement. Besides these absorptions, the methine ($-$CHCOO) of the backbone absorbs at 41.508 ppm and the $-$OCH$_2$ group at 66.885 ppm. The carbonyl carbon $\diagdown$C$=$O appears as a multiplet at

$\delta = 172.610$–174.359 ppm, demonstrating that $\diagdown$C$=$O in PEHA is configurationally sensitive.

The ^{13}C-NMR of EHA : MMA (93 : 7), as shown in Figure 9, shows an additional $-$CH$_3$ signal at 19.545 ppm, and for the quarternary carbon, at 45.357 ppm. The methoxy carbon appears as a singlet at 51.494 ppm, while the signal at $\delta = 175.341$–176.953 ppm is due to ester carbonyl carbon. The nitrile carbon (Fig. 10) appears as a well-resolved multiplet, centered at 119.969 ppm, showing sensitivity toward different monomer placements.[15] Some of the signals could not be used for such analysis due to poor resolution. All these absorptions support the structures of the copolymers prepared. However, NMR was not useful in the analysis of the EHA–AA copolymer.

The DSC measurements were carried out for the polymers from -50 to 200°C. Neither an endotherm nor an exotherm was observed for copolymers in ratio 93 : 7, indicating that the T_g is below -50°C for all of them.

The molecular weights and molecular weight distributions are listed in Table II. The copolymers EHA : MMA and PEHA are somewhat more polydisperse when compared to the other two copolymers.

The viscosities for the above polymers were determined in four solvents (THF, MEK, TL, and EA) at 30, 35, and 40°C. The intrinsic viscosities were

computed by a well-known procedure, at different temperatures and in different solvents.[16] The values are listed in Table III. The accuracy of the data was checked by calculating K' and K'', and their difference was 0.5, as expected (Fig. 11).[12] The intrinsic viscosities of all the copolymers in EA and MEK increased with increase in temperature. However, in TL and THF, the intrinsic viscosities decreased with increase in temperature. The increase in temperature generally leads to an increase in solvent power, i.e., solubility of the polymer in a solvent, which results in uncoiling of the polymer chains. This results in an increase in $[\eta]$ with temperature, which was observed for these polymers in MEK and EA solutions. On the other hand, an increase in temperature may lower the rotational barrier, thereby enhancing the degree of rotation about a skeletal bond, forcing the molecular chains to assume a more compact coiled configuration. This results in a decrease in $[\eta]$ with increase in temperature as was seen in toluene and THF solutions. Thus, an increase in temperature of a polymer solution generates two effects opposing one another. The variation of $[\eta]$ with temperature will be dependent upon the relative importance of these two properties.[17]

The viscosities of the polymer solutions were determined in different temperatures for different concentrations. The well-known Frenkel–Eyring equation [Eq. (5)] for the viscous flow was used to evaluate various activation parameters of the viscous flow[18]:

$$\eta = Nh/V \exp(\Delta G^{\ddagger}_{vis}/RT) \tag{5}$$

where V is the molar volume of the solution; N, the Avogadro's number; h, the Planck's constant; R, the gas constant; T, the temperature; and $\Delta G^{\ddagger}_{vis}$, the activation free-energy change of the viscous flow. The above equation can be rewritten as
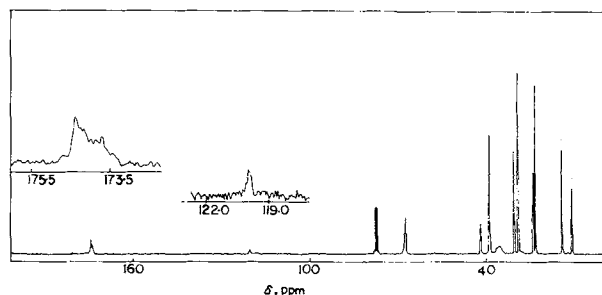

Figure 10 Proton decoupled ^{13}C-NMR spectrum of EHA : AN.

Table II **Molecular Weights and Molecular Weight Distribution for Different Copolymers and the Homopolymer as Obtained from GPC[a]**

Sample No.	Polymer	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-5}$	MWD
S1	PEHA	4.08	1.77	4.3
S2	EHA : AN	7.51	2.06	2.7
S3	EHA : AA	9.65	2.75	2.8
S4	EHA : MMA	3.27	1.50	4.6

[a] Feed ratio in copolymers were 93 : 7 w/w of EHA : comonomer.

$$\ln(\eta V / Nh) = \Delta G^{\ddagger}_{\text{vis}} / RT$$

$$= \Delta H^{\ddagger}_{\text{vis}} / RT - \Delta S^{\ddagger}_{\text{vis}} / R \quad (6)$$

where $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ are the activation enthalpy and the entropy change for the viscous flow, respectively. The molar volume V of the solution was taken to be that of the solvent. The linearity was observed by plotting $\ln(\eta V / Nh)$ against T^{-1} with correlation coefficients of .99 or better for all systems. The slope and intercept gave $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$, respectively. The values of $\Delta G^{\ddagger}_{\text{vis}}$, $\Delta H^{\ddagger}_{\text{vis}}$, and $\Delta S^{\ddagger}_{\text{vis}}$ for some representative systems are listed in Table IV.

The activation parameters for viscous flow $\Delta H^{\ddagger 0}_{\text{vis}}$ and $\Delta S^{\ddagger 0}_{\text{vis}}$ at infinite dilution were obtained by plotting $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ against concentration and extrapolating to $C = 0$ (Fig. 12).[19,20] All these acti-

vation parameters at infinite dilution are compiled in Table V. Using the values of $\Delta H^{\ddagger 0}_{\text{vis}}$ and $\Delta S^{\ddagger 0}_{\text{vis}}$ in Table V, it is possible to plot one against the other to see if a linear compensation effect exists. The plot was linear following the relationship[21,22]

$$\Delta H^{\ddagger 0}_{\text{vis}} = K_1 + K_2 \Delta S^{\ddagger 0}_{\text{vis}} \quad (7)$$

where K_1 and K_2 were obtained from the intercept and slope, respectively. Combining this relation with the thermodynamic equation

$$\Delta G^{\ddagger 0}_{\text{vis}} = \Delta H^{\ddagger 0}_{\text{vis}} - T \Delta S^{\ddagger 0}_{\text{vis}}$$

we get

$$\Delta G^{\ddagger 0}_{\text{vis}} = K_1 + (K_2 - T) \Delta S^{\ddagger 0}_{\text{vis}} \quad (8)$$

Table III **Intrinsic Viscosities of Various Copolymers and the Homopolymers at Different Temperatures in Various Solvents; Solubility Parameters of the Solvents Are Given in Parentheses**

| Solvent	Polymer	$[\eta]$ (dL g^{-1})		
		30°C	35°C	40°C
Ethyl acetate (EA)	S1	0.176	0.187	0.193
($\delta = 9.1$)	S2	0.372	0.384	0.388
	S3	0.409	0.439	0.441
	S4	0.284	0.290	0.294
Tetrahydrofuran (THF)	S1	0.271	0.250	0.250
($\delta = 9.1$)	S2	0.475	0.456	0.454
	S3	0.569	0.541	0.518
	S4	0.395	0.386	0.378
Toluene (TL)	S1	0.299	0.283	0.266
($\delta = 8.9$)	S2	0.577	0.572	0.562
	S3	0.520	0.518	0.505
	S4	0.351	0.344	0.345
Methyl ethyl ketone (MEK)	S1	0.188	0.189	0.192
($\delta = 9.3$)	S2	0.360	0.370	0.376
	S3	0.403	0.415	0.425
	S4	0.286	0.291	0.299
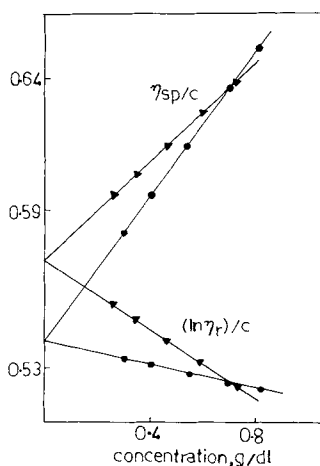
Figure 11 Representative plots of inherent and reduced viscosity vs. concentration: (▲) S3 in THF; (●) S2 in toluene at 35°C.

Figure 12 Representative plots of $\Delta H^{\neq}_{\text{vis}}$ and $\Delta S^{\neq}_{\text{vis}}$ vs. concentration: (●, ▲) S2 in MEK; (■, X) S1 in EA.

Such a linear free-energy relationship has been reported previously for many systems. At $K_2 = T$, $\Delta G^{\neq 0}_{\text{vis}}$ becomes totally independent of the structural
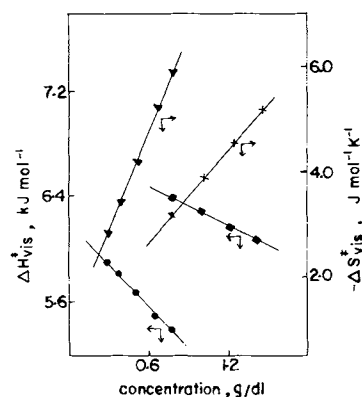
changes in the system. The value of K_2 was found to be around 300 K, its exact value depending on the solvent system (Table V).

Relative viscosity data at different concentrations were also used to calculate the voluminosity, V_E, of the polymer solutions at different temperatures in

Table IV Free Energy $\Delta G^{\neq}_{\text{vis}}$, Enthalpy $\Delta H^{\neq}_{\text{vis}}$, and Entropy $\Delta S^{\neq}_{\text{vis}}$ of the Viscous Flow at Various Concentrations in Different Solvents (Some Representative Data)

% Concentration	$\Delta G^{\neq}_{\text{vis}}$ (35°C) (kJ mol^{-1})	$\Delta H^{\neq}_{\text{vis}}$ (kJ mol^{-1})	$\Delta S^{\neq}_{\text{vis}}$ (J mol^{-1} K^{-1})
Sample S1: solvent, THF			
1.272	7.61	6.78	2.68
1.018	7.45	6.76	2.26
0.763	7.30	6.62	2.22
0.587	7.20	6.57	2.03
Sample S2: solvent, EA			
1.234	8.11	6.39	5.60
1.080	8.00	6.41	5.16
0.864	7.82	6.53	4.19
0.480	7.48	6.83	2.12
Sample S3: solvent, MEK			
0.647	7.17	5.35	5.91
0.503	7.03	5.51	4.93
0.377	6.90	5.72	3.82
0.283	6.81	5.82	3.20
Sample S4: solvent, TL			
1.006	8.67	6.98	5.49
0.836	8.55	7.21	4.35
0.503	8.25	7.64	1.99
0.377	8.14	7.77	1.20

Table V Free Energy $\Delta G_{vis}^{\neq 0}$, Enthalpy $\Delta H_{vis}^{\neq 0}$, and Entropy $\Delta S_{vis}^{\neq 0}$ of Activation for the Viscous Flow at Infinite Dilution of Copolymers and the Homopolymer in Various Solvents

Solvent/Polymer	$\Delta G_{vis}^{\neq 0}$ (35°C) (kJ mol^{-1})	$\Delta H_{vis}^{\neq 0}$ (kJ mol^{-1})	$-\Delta S_{vis}^{\neq 0}$ (J mol^{-1} K^{-1})	K_2 (K)
EA				
S1	7.04	6.77	0.88	
S2	7.08	7.09	−0.04	
				310
S3	7.04	6.44	1.96	
S4	7.05	7.62	−1.86	
THF				
S1	6.85	6.38	1.52	
S2	6.85	6.27	1.88	
				298
S3	6.88	5.49	4.52	
S4	6.83	5.88	3.09	
TL				
S1	7.78	7.96	−0.58	
S2	7.84	8.05	−0.67	
				315
S3	7.87	10.41	−8.25	
S4	7.83	8.26	−1.39	
MEK				
S1	6.52	6.34	0.58	
S2	6.50	6.20	0.99	
				309
S3	6.52	6.19	1.03	
S4	6.52	6.17	1.15	

Table VI Voluminosity V_E at Various Temperatures, for the Copolymers and the Homopolymer in Different Solvents

Solvent	Polymer	V_E (mL g^{-1})		
		30°C	35°C	40°C
EA	S1	6.98	7.42	7.65
	S2	14.62	15.16	15.23
	S3	16.29	17.40	17.54
	S4	11.38	11.52	11.71
THF	S1	10.71	9.94	9.99
	S2	18.97	18.12	18.15
	S3	22.28	21.48	20.50
	S4	15.72	15.29	14.81
TL	S1	11.91	11.24	10.57
	S2	22.83	22.52	22.31
	S3	20.78	20.50	20.22
	S4	13.84	13.69	13.73
MEK	S1	7.48	7.51	7.68
	S2	14.36	14.87	14.99
	S3	16.10	16.53	16.90
	S4	11.36	11.59	11.88

all solvent systems (Table VI). Recently, it was used to determine the shape of protein molecules.[23] V_E was calculated by plotting Y against concentration (in g/mL), where

$$Y = (\eta_r^{0.5} - 1)/C(1.35\eta_r^{0.5} - 0.1) \tag{9}$$

The straight line obtained was then extrapolated to $C = 0$ and the intercept yielded V_E. The shape factor was obtained from the equation[8,19,20,22,23]

$$[\eta] = \nu V_E \tag{10}$$

The shape factor gives an idea about the shape of the polymer molecules in solution.[24] Values of shape factors in different solvents and temperatures were found to be 2.51 ± 0.02, suggesting that the macromolecules acquire spherical conformation.[25] Moreover, the ν values were found to be independent of temperature, suggesting that the conformation was not dependent on temperature. The voluminosity (Table VI) values are a function of temperature. V_E is a measure of volume of solvated polymer molecules. As the temperature increases, the sol-

vation decreases; hence, V_E decreases. This was observed for the solvents toluene and THF. MEK and EA showed a reverse trend for all the polymers. The $\Delta S_{vis}^{\neq 0}$ values (Table IV) are always very low, sometimes even negative, implying poorly ordered structures of the homopolymer and copolymers in solution.

CONCLUSIONS

The structural elucidation of copolymers EHA : AA, EHA : AN, and EHA : MMA was done by FTIR, PMR, and ^{13}C-NMR. FTIR showed characteristic absorption peaks due to the ester group at 1732 cm^{-1}, N — H stretch at 3440 cm^{-1}, and — C$\equiv$N at 2240 cm^{-1}. High-field PMR and ^{13}C-NMR further supported the structure. The PMR study was used to find the reactivity ratios. Monomer reactivity ratios for AN and EHA were 0.83 and 1.23, respectively, and 1.90 and 0.96 for MMA and EHA, respectively. The assignments for the chemical-shift values, in ^{13}C-NMR, were done using additive shift parameters for hydrocarbons and they were in agreement with experimentally obtained values. The intrinsic viscosities of all the copolymers in EA and MEK increased with temperature, whereas they decreased with temperature in toluene and THF. The shape factor for the copolymers was around 2.5, in all solvents and at all temperatures, indicating a spherical conformation. An enthalpy–entropy compensation effect was observed for all systems.

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