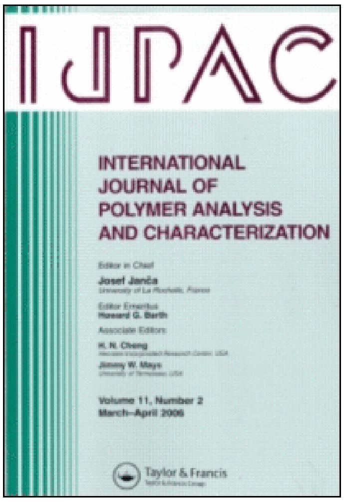

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Synthesis, Characterization, and Solution Properties of Acrylic Ester Polymers

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To cite this Article Mathakiya, Ismail , Rakshit, A. K. and Rao, P. V. C.(2003) 'Synthesis, Characterization, and Solution Properties of Acrylic Ester Polymers', International Journal of Polymer Analysis and Characterization, 8: 5, 339 — 358
To link to this Article: DOI: 10.1080/10236660304869
URL: http://dx.doi.org/10.1080/10236660304869

International Journal of Polymer Anal. Charact., 8: 339–358, 2003
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ISSN: 1023-666X print
DOI: 10.1080/10236660390226329

Synthesis, Characterization, and Solution Properties of Acrylic Ester Polymers

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Free radical solution polymerization has been employed to synthesize homopolymers of vinyl acetate (VAc), cyclohexyl acrylate (CA), benzyl acrylate (BA), and other various acrylates. The method was also used to synthesize copolymers of vinyl acetate with these various acrylates at 50:50 (v/v) feed ratio. To compute reactivity ratios of monomers in P(VAc-CA) and P(VAc-BA), a series of copolymers in the feed ratio of 80:20, 60:40, 50:50, 40:60, and 20:80 (v/v) of VAc and either CA or BA were also synthesized. Fineman-Ross and Kelen-Tudos methods were used to compute reactivity ratios from ^{1}H-NMR spectroscopic data. The homopolymers and copolymers were characterized by FTIR, ^{1}H- and ^{13}C-NMR, TGA, GPC, and viscosity measurements. The activation energy of decomposition (E_a) of the polymers was calculated from TGA analysis using the Broido method. M_n, M_w, and MWD of the polymers were evaluated from GPC data. The intrinsic viscosities of polymer, in non-theta and in theta (θ) solvents were evaluated using a capillary viscometer. Using intrinsic viscosity and GPC data, the voluminosity (V_E), shape factor (v), activation parameters of

Received 12 June 2001; accepted 3 January 2002.

One of the authors (IM) thanks CSIR, New Delhi, for the awards of Senior Research Fellowship (SRF) and (SRF-Extended). We are also thankful to Dr. A. R. Bandyopadhyay of IPCL for help.

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viscous flow, root-mean-square end-to-end distance ($\langle R^2 \rangle^{1/2}$), radius of diffusing particle (r'), and diffusion coefficient (D_o) were also computed at various temperatures.

Keywords: Synthesis; Polyacrylates; Copolymers; Properties; Theta condition

During the past three decades, acrylic copolymers have acquired prime importance for industrial applications[1]. The combination of durability, versatility, and the ability to tailor molecules relatively easily to specific applications have made acrylic and methacrylic esters main candidates for numerous and diverse applications[2]. Homo- and copolyacrylates are of great interest in many industrial applications because of the wide range of physical and chemical properties that can be covered by an appropriate choice of side groups and copolymer systems[3]. Acrylates are the most outstanding products, widely used as building blocks (poly[methyl methacrylate]) for a variety of polymers, controlled drug release matrices (poly[hydroxy methacrylate]), contact lenses (polyhydroxy acrylates), electroactive polymers (poly[phenyl acrylate]), varnishes (poly[methyl acrylate]), and many others[4,5].

A number of alkyl fumarate-vinyl acetate copolymers were reported as flow enhancers for high waxy Borhalla crude oil[6]. Graft copolymers prepared by the polymerization of poly(ethylene oxide) macromonomers with acrylic and vinyl comonomers have been extensively studied as semipermeable membranes for biomedical applications, as well as support systems for the preparation of microcapsules and nanoparticles[7]. Soundararajan et al.[8] reported co/terpolymers of butyl acrylate, styrene, and/or maleic anhydride, which have been used as top coat lacquers in the leather industry. Adhesive properties of terpolymers of ethyl acrylate, ethyl α-cyano-cinnamate, and styrene were investigated by Angelovici and Kohn[9]. However, poly(vinyl acetate) (PVAc) is one of the most important of all the synthetic thermoplastic adhesives with a wide range of industrial applications[10]. It also finds widespread use as the intermediate for the commercial production of poly(vinyl alcohol) and poly(vinyl acetal) and as a sizing material for paper and textiles. Application in chewing gum is also popular[11].

Knowledge of copolymer composition is an important step in the evaluation of its utility. The accurate estimation of the copolymer composition and the determination of monomer reactivity ratios are important for tailoring copolymers with the required physico-chemical properties. The nuclear magnetic resonance (NMR) spectroscopic technique is well established as a convenient method for determining the composition ratio of constituent monomer units in copolymers[12,13]. The viscosity of a dilute polymer solution gives an insight into the conformation adopted by polymer chains. Theories based on viscosity also account for the influences of variables such as temperature and solvent on conformational changes in a solution[14]. In this regard the present study reports synthesis and characterization of a series of vinyl acetate–acrylate copolymers. The change in properties as a function of composition and constitution of monomers and the determination of reactivity ratios of monomers were also studied and presented in detail.

EXPERIMENTAL

The monomers vinyl acetate (VAc, Fluka, Switzerland), ethyl acrylate (EA, BDS, Poole, U.K.), methyl acrylate (MA), *n*-butyl acrylate (BuA), and methyl methacrylate (MMA, National Chemicals, Baroda, India) (Figure 1) were distilled at reduced pressure. The middle fraction of the distillate was collected and used. The purity of other monomers, *n*-hexyl acrylate (HA, 99.0%), cyclohexyl acrylate (CA, 92.9%), and benzyl acrylate (BA, 99.8%) was checked by gas chromatography. These were a gift from the Indian Petrochemical Corporation Limited, Baroda, India, and were used without any further treatment. Technical grade azobisisobutyronitrile (AIBN) was recrystallized from warm methanol, and benzoyl peroxide (BPO, Fluka) was purified by dissolving it in chloroform at room temperature and reprecipitating it by adding methanol before it was used. The solvents were all freshly distilled before use.

Copolymerization of VAc with CA and BA was carried out in different feed ratios of the two monomers. The ratios chosen for study were 80:20, 60:40, 50:50, 40:60, and 20:80 (v/v) of vinyl acetate and acrylate(s), respectively. The recipe for the synthesis of copolymer 80:20 (v/v) of VAc and acrylate(s) was as follows: 6.0 mL VAc, 1.5 mL acrylate(s), and 0.075 g AIBN were taken in 22.5 mL 1,4-dioxane. The polymerization reaction was carried out under nitrogen atmosphere at 85°C. The reaction setup remained the same as reported earlier[15]. The copolymerization was stopped at a low conversion (below 10%). It was then poured in an excess of double-distilled water to precipitate copolymers. The homopolymer, poly(vinyl acetate), is soluble in methanol. The precipitate was then treated with methanol to remove PVAc homopolymer. The homopolymers PCA and PBA are soluble in *p*-xylene and hence these polymers were separated from the copolymers. The copolymers were washed well with methanol and dried in vacuo before characterization.

The synthesis of homopolymers PVAc and polyacrylate(s) was done as reported earlier[10,15,16]. Copolymers of VAc with various acrylate(s),

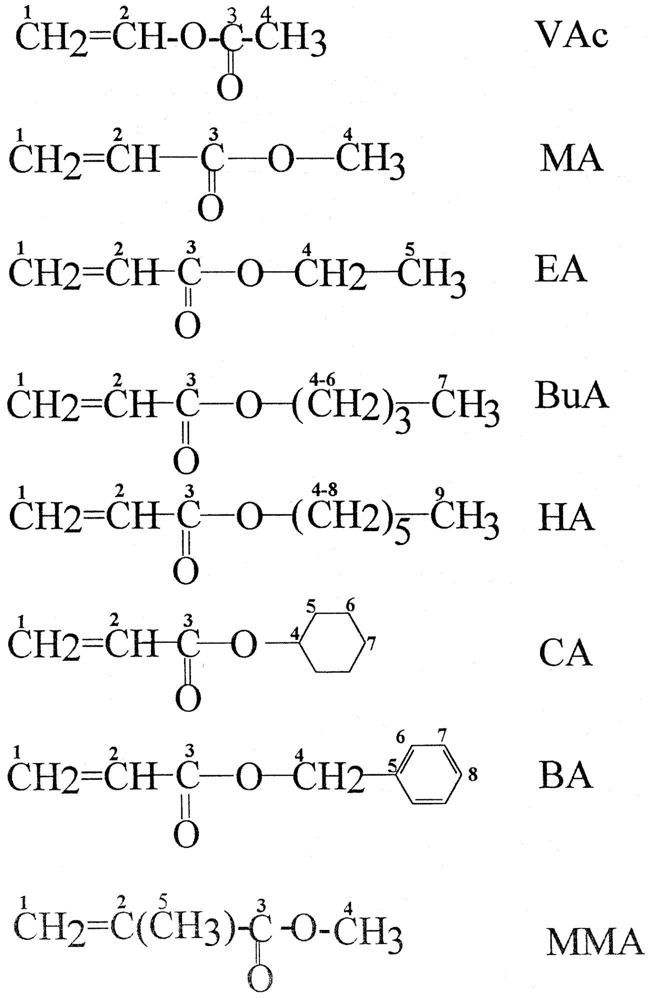

FIGURE 1 Molecular structure and carbon assignments for monomers.

namely, MA, EA, BuA, HA, CA, and BA, in initial feed ratios of 50:50 (*v*/*v*) were also prepared in dimethyl formamide (DMF) using benzoyl peroxide as the free radical initiator at 85°C. The reaction setup was the same as reported earlier[15]. The reaction mixture after polymerization was poured into an excess of double-distilled water to precipitate out the polymers. The precipitated product was further purified by removal of the respective homopolymers in a selective solvent-nonsolvent system, and dried in vacuo before characterization.

The Fourier transform infrared (FTIR) spectrum of the polymers was 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, then liquid polymers were spread over the NaCl cells and the spectra were recorded. ^{1}H and ^{13}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, for ^{1}H-NMR and ^{13}C-NMR. Tetramethylsilane (TMS) was used as an internal reference and $CDCl_3$ as an internal lock.

Thermal analyses of the polymers were made using thermogravimetric analysis (TGA) measurements. The TGA of the polymer samples was recorded on a Shimadzu Thermal Analyzer DT-30B at a heating rate of 10°C min^{-1} in the presence of air. Molecular weights (M_n and M_w) and molecular weight distribution (M_w/M_n) were determined with respect to polystyrene standard by gel permeation chromatography (GPC). The Waters Associates system used was equipped with a model 700 injector, a model 510 HPLC solvent pump, three columns packed with Styragel of nominal pore sizes of 500, 1000, and 10,000 Å connected in series, and a refractive index (RI) detector. The elusion rate of toluene was 0.8 mL min^{-1}. The GPC was calibrated with polystyrene standards of molecular weights in the range 15,000 to 4,700,000.

Viscosity measurements of the dilute solution of the homo- and copolymers in 1,4-dioxane, isopropyl alcohol (IPA), and nitromethane (NM) were carried out using an Ubbelohde dilution viscometer suspended in a thermostated bath at the required temperature ($\pm 0.05°C$). Measurements for each solution were repeated five to six times. Densities of the solutions at different temperatures were assumed to be those of solvent at that temperature[17].

RESULTS AND DISCUSSION

FTIR Analysis

The structures of vinyl acetate-co-acrylate copolymers were deduced from FTIR spectra of polymer films spread over the NaCl cell. FTIR spectra of copolymers showed a band at 610 cm^{-1}, characteristic of a vinyl acetate unit due to the out-of-plane CH_2-CO_2 bend[10]. The C=O stretching of the ester group was observed at a higher frequency (1750 cm^{-1}) than normal carboxyl absorption. C-CH_3 symmetric and asymmetric bending vibrations were observed at 1451 and 1370 cm^{-1}, respectively. Other prominent absorption peaks due to symmetrical (ν_s O-C-O) and asymmetrical stretching (ν_{as} O-C-O) vibration were observed at 1246 and 1180 cm^{-1}, respectively, whereas an out-of-plane C-H bend of acrylate moieties was observed at 773 cm^{-1}. Beside this, aliphatic stretching absorption of C-H, due to $-CH_2$ and $-CH_3$, appears at 2942 and 2861 cm^{-1}. The assignments were done with the help of the literature data[10,16,18].

^{1}H-NMR Analysis

Assignments of ^{1}H-NMR signals based on comparisons with previously published spectra of homopolymers[16–20] determined that the product contained vinyl acetate (VAc) and acrylate repeat units. The resonance signals appearing at $\delta = 1.71$–1.83 and 1.35 ppm correspond to methylene backbone protons of VAc and CA, respectively. The methine backbone protons (αCH-) of the VAc and CA monomeric units resonate as broad signals at $\delta = 4.95$–4.58 and 3.69–3.63 ppm, respectively. The methine backbone signal (αCH-) of the VAc unit overlapped with a signal associated with the proton of the $-OCH$ group of the CA unit (appeared at around 4.70 ppm) and $-CH_2$- adjacent to the phenyl group of BA (appeared at around 4.93 ppm) and hence could not be distinguished. The aromatic protons of the BA unit give a distinct signal at $\delta = 7.25$ ppm, whereas the signal around $\delta = 1.97$ ppm is associated with acetoxy protons ($-OCOCH_3$) of the VAc unit.

The average copolymer composition (mole fraction of vinyl acetate, m_{VAc}, in P[VAc-CA] copolymer) can be readily obtained by using the equation

$$m_{VAc} = \frac{I(-OCOCH_3)}{I(-OCOCH_3) + 3I(\alpha CH\text{-})} \tag{1}$$

where $I(-OCOCH_3)$ and $I(\alpha CH\text{-})$ represent the total peak intensities of the proton resonances of $-OCOCH_3$ of the VAc unit and of the αCH- of the CA unit, respectively. The acetoxy proton of VAc resonates at ~1.97 ppm, whereas the αCH- proton of CA resonates at 3.69–3.63 ppm. The composition of copolymers as determined by ^{1}H-NMR along with the feed composition is given in Table I.

The vinyl acetate mole fraction (m_{VAc}) in P(VAc-BA) copolymer was calculated using the peak intensity of the methylene group of the VAc unit and the phenyl group of the BA unit using the following relation:

$$m_{VAc} = \frac{5I(-CH_2\text{-})}{5I(-CH_2\text{-}) + 2I(Ph)} \tag{2}$$

where $I(-CH_2\text{-})$ and $I(Ph)$ represent the peak intensities of the methylene protons of the VAc unit and of the phenyl protons of the BA unit,

TABLE I Composition of monomer in feed and in copolymers and Kelen-Tudos parameters

Samples	M_1[a]	m_1[b]	$X = M_1/M_2$	$Y = m_1/m_2$	$G = X(Y-1)/X$	$F = X^2/Y$	$\varepsilon = F/\alpha + F$	$\theta = G/\alpha + F$
VCA-1	0.872	—	6.813	—	—	—	—	—
VCA-2	0.719	0.385	2.259	0.626	−0.374	8.152	0.656	−0.030
VCA-3	0.630	0.293	1.703	0.414	−0.586	7.005	0.620	−0.052
VCA-4	0.532	0.223	1.127	0.286	−0.714	4.441	0.509	−0.082
VCA-5	0.299	0.075	0.427	0.081	−0.919	2.251	0.344	−0.141
VBA-1	0.869	0.656	6.634	1.907	3.155	23.078	0.894	0.122
VBA-2	0.714	0.569	2.497	1.320	0.605	4.723	0.634	0.081
VBA-3	0.625	0.488	1.667	0.953	−0.082	2.916	0.517	−0.015
VBA-4	0.469	0.428	0.883	0.748	−0.297	1.042	0.367	−0.079
VBA-5	0.294	0.350	0.416	0.538	−0.357	0.322	0.106	−0.117

$\alpha = \sqrt{F_{min} \cdot F_{max}} = 4.28$ (for P[VAc-CA]) and 2.73 (for P[VAc-BA]); VCA represents P(VAc-CA) copolymer systems and VBA represents P(VAc-BA) copolymer systems.

[a] Mole fraction of vinyl acetate (VAc) in feed ($M_1 + M_2 = 1$).

[b] Mole fraction of vinyl acetate (VAc) in the copolymer ($m_1 + m_2 = 1$).

respectively. The mole fractions of monomers in the relevant copolymers of various compositions calculated using ^{1}H-NMR are listed in Table I.

Monomer reactivity ratios r_1 (VAc) and r_2 (CA or BA) could thus be calculated graphically using the equation proposed by Fineman and Ross (F.R.)[21]:

$$\frac{X(Y-1)}{Y} = r_1 \frac{X^2}{Y} - r_2 \tag{3}$$

where $X = M_1/M_2$ and $Y = m_1/m_2$ (as defined in Table I). On plotting $X(Y-1)/Y$ versus X^2/Y, the slope and intercept yielded r_1 (VAc) and r_2 (CA or BA). The values obtained for reactivity ratios are r_1 (VAc) $= 0.089$ and r_2 (CA) $= 1.109$ for VAc and CA in P(VAc-CA) copolymer, and r_1 (VAc) $= 0.155$ and r_2 (BA) $= 0.390$ for VAc and BA in P(VAc-BA) copolymer.

The reactivity ratios were also determined according to the Kelen-Tudos (K.T.) procedure[22]. The resulting values of reactivity ratios estimated were r_1 (VAc) $= 0.083$ and r_2 (CA) $= 1.109$ and r_1 (VAc) $=$ 0.164 and r_2 (BA) $= 0.461$, for VAc with CA and BA in P(VAc-CA) and P(VAc-BA) copolymer, respectively. The values obtained by the methods of F.R. and K.T. agree very well with each other.

The nature of the copolymer sequence of P(VAc-CA) and P(VAc-BA) copolymer systems is alternating[23]. The systems are in the range of $0 < r_1r_2 < 1$. Since the product r_1r_2 (0.092 and 0.076 for P[VAc-CA] and P[VAc-BA] copolymer, respectively; r_1 and r_2 were used from the K.T. method) is closer to zero than to unity, there is a great tendency for M_1 and M_2 to alternate in the polymeric chain[10,23]. The copolymer composition versus initial monomer composition plot (Figure 2) for the P(VAc-BA) copolymer was sigmoidal and crossed the ideal line at the point where $M_1 = m_1 = 0.390$, indicating the azeotropic copolymer composition[23]. Theoretically, the value was obtained from the following equation and was very close (0.392) to the experimental value:

$$M_{1\text{critical}} = m_{1\text{critical}} = \frac{1 - r_2}{2 - r_1 - r_2} \tag{4}$$

The Q and e values of the Alfrey-Price Q,e scheme[23] for CA and BA were determined by using experimentally obtained values of the corresponding reactivity ratios. The values of $e_2 = -0.88$ and $Q_2 = 0.026$ from the literature were used for VAc, and e_1 and Q_1 were evaluated for CA and BA using the following equations:

$$e_1 = e_2 \pm (|\ln\ r_1r_2|)^{1/2} \tag{5}$$

$$Q_1 = Q_2/r_2 \exp\ [e_2(e_1 - e_2)] \tag{6}$$

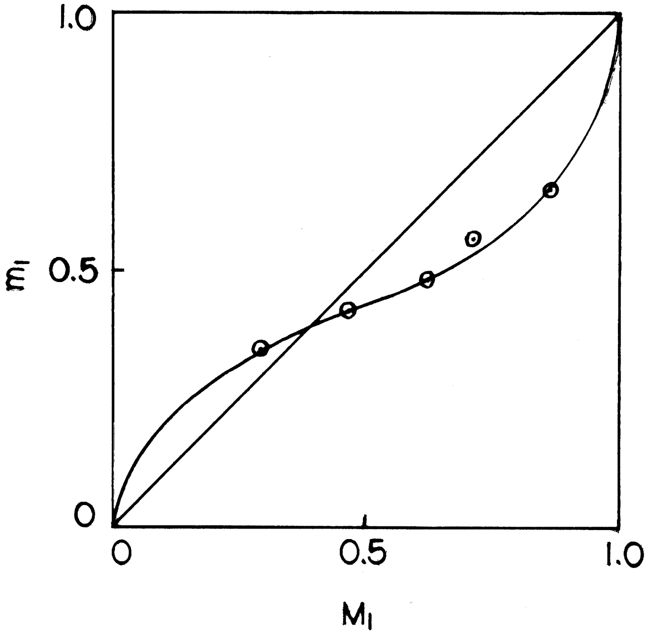

FIGURE 2 Copolymer composition (m_1) vs. initial monomer composition (M_1) plot for P(VAc-BA) copolymers.

The values were found to be $e_1 = 0.665$ and $Q_1 = 0.075$ for cyclohexyl acrylate (CA) and $e_1 = 0.725$ and $Q_1 = 0.035$ for benzyl acrylate (BA), respectively.

^{13}C-NMR Analysis

The proton decoupled ^{13}C-NMR spectrum of all the polymers shows characteristic resonance signals at their positions corresponding to their constituent monomeric units. The representative ^{13}C-NMR spectrum of the VAc-acrylate copolymers (in 1:1 [*v*/*v*] of the two monomers) was recorded in $CDCl_3$ at room temperature. The assignments of various resonance peaks due to different carbon atoms were made using the literature data[18–20] as well as comparison with the previously published spectra of homopolymers[24]. The chemical shift values corresponding to various carbon atoms present in the homopolymers and copolymers are listed in Tables II and III respectively.

As shown in Table III, ^{13}C-NMR spectra of all the copolymers showed two distinct and well-resolved carbonyl carbon resonances of the VAc

TABLE II Chemical shifts (δ_{ppm}) of the carbon peaks in ^{13}C-NMR for the various homopolymers

PVAc	PMA	PEA	PBuA	PHA	PCA	PBA	PMMA
C_1 170.26	C_3 174.65	C_3 174.31	C_3 174.26	C_3 174.55	C_3 174.16	C_3 174.11	C_3 177.77
							176.84
C_2 67.05	C_4 51.56	C_4 60.33	C_4 64.27	C_4 64.68	C_4 72.95	C_5 135.56	C_1 54.24
67.15							
68.22							
C_1 39.67	C_2 41.13	C_2 41.23	C_2 41.37	C_2 41.61	C_2 41.62	C_{6-8} 128.55	C_4 51.75
C_4 21.05	C_1 34.74	C_1 34.99	C_1 35.28	C_1 35.57	C_1 35.62	C_4 66.41	C_2 44.88
							44.54
							43.81
		C_5 13.99	C_5 30.51	C_5 31.53	C_5 31.77	C_2 41.47	C_5 18.81
							16.37
			C_6 19.01	C_6 28.60	C_6 25.58	C_1 35.57	
			C_7 13.60	C_7 25.58	C_7 24.02		
				C_8 22.61			
				C_9 14.03			

TABLE III Chemical shifts (δ_{ppm}) of the carbon peaks in ^{13}C-NMR for the various P(VAc-acrylates) copolymers

P(VAc-MA)	P(VAc-EA)	P(VAc-BuA)	P(VAc-HA)	P(VAc-CA)	P(VAc-BA)	P(VAc-MMA)
C_3(MA) 174.79	C_3(EA) 174.35	C_3(BuA) 174.50	C_3(HA) 174.50	C_3(CA) 173.77	C_3(BA) 174.07	C_3(MMA) 177.57
						176.69
C_3(VAc) 170.07	C_3(VAc) 170.02	C_3(VAc) 170.11	C_3(VAc)170.11	C_3(VAc)169.97	C_3(VAc) 170.11	C_3(VAc) 169.58
C_2(VAc) 69.73	C_2(VAc) 69.54	C_2(VAc) 69.78	C_2(VAc) 69.75	C_2(CA) 72.75	C_5(BA) 135.56	C_2(VAc) 66.71
C_4(MA) 51.56	C_4(EA) 60.43	C_4 (BuA) 64.42	C_4(HA) 64.76	C_2(VAc) 69.49	$C_{6–8}$(BA)128.31	C_1(MMA) 54.33
C_2(MA) 41.08	C_2(EA) 41.23	C_2(BuA) 41.37	C_2(HA) 41.27	C_2(CA) 41.57	C_2(VAc) 69.63	C_4(MMA) 51.61
C_1(VAc) 39.13	C_1(VAc) 39.27	C_1(VAc) 39.52	C_1(VAc) 38.01	C_1(VAc) 40.01	C_4(BA) 66.32	C_2(MMA) 44.65
						44.34
						43.81
C_1(MA) 36.89	C_1(EA) 36.79	C_1(BuA) 37.43	C_1(HA) 35.59	C_1(CA) 36.50	C_2(BA) 41.32	C_1(VAc) 39.72
34.65	35.13	35.28	35.13	35.67		
C_4(VAc) 20.66	C_4(VAc) 20.66	C_5(BuA) 30.55	C_5(HA) 31.29	C_5(CA) 31.38	C_1(VAc) 39.37	C_4(VAc) 20.91
	C_5(EA) 13.94	C_4(VAc) 20.81	C_6(HA) 28.36	C_6(CA) 25.24	C_1(BA) 37.13	C_5(MMA) 18.81
					35.18	16.42
		C_6(BuA) 19.05	C_7(HA) 25.34	C_7(CA) 23.68	C_4(VAc) 20.71	
		C_7(BuA) 13.64	C_8(HA) 22.57	C_4(VAc) 20.69		
			C_4(VAc) 20.71			
			C_9(HA) 13.84			

as well as the acrylate monomeric units appearing, respectively, at δ = 169.97–170.11 and 174.07–174.79 ppm. These are singlets and do not show any tacticity or sequence distribution effect. However, for P(VAc-MMA), triplet peaks showing compositional and configurational sensitivities are observed. The quaternary carbon of the MMA unit also appears as a multiplet at around δ = 43.81–44.65 ppm, showing its sensitivity to copolymer tacticity[19]. All the methylene, methine, methyl, and methoxy carbons resonate at their respective positions as presented in Tables II and III for various homopolymers and for copolymers, respectively.

TGA Analysis

The thermogravimetric analysis (TGA) was done to study the thermal decomposition of polymers and also to determine the activation energy for decomposition. The TGA studies under air provide information useful for industrial processing needs (e.g., extrusion, injection, molding, calendering, etc.). Furthermore, the presence of air/oxygen introduces some "leveling" effect and hence shows significant differences in the stability of homo- and copolymers of the same family. TGA curves of P(VAc-CA), P(VAc-BA), and P(VAc-EA) copolymers are given in Figure 3. The natures of the thermograms of all the copolymers were found to be similar, showing single-step decomposition. Most of the copolymers were stable up to 380°C, although PVAc and PMA homopolymers showed lower initial decomposition temperatures[10]. The thermal degradation of PVAc results in the formation of acetic acid and thereby forms a double bond in the main polymer chain. Subsequent degradation leads to color development due to polyene (conjugated double bond) formation[25]. On further heating, the polyenes decompose, giving hydrogen, methane, C_2-hydrocarbons, carbon dioxide, and carbon monoxide. The decomposition of copolymers observed in the temperature range of 320°–590°C is perhaps due to the breakdown of polymer initiated from the weak sites (e.g., unsaturated chain ends, branching, head-to-head linkages, etc.) as observed earlier[26]. The activation energy of the decomposition (E_a) was determined using the well-known Broido method[22]. A straight line was obtained on plotting ln ln $(1/Y')$ versus $(1/T)$ (Figure 4). The slope of the linear plot gives activation energy of decomposition[22]. The data listed in Table IV gives the initial decomposition temperature (IDT), temperature of the maximum rate of decomposition (T_{max}), the complete decomposition temperature (FDT), and the activation energy of decomposition (E_a). The activation energy (E_a) of decomposition values (Table IV) shows that both the homopolymers and copolymers synthesized from new monomers, namely BA and CA, exhibited higher thermal stability

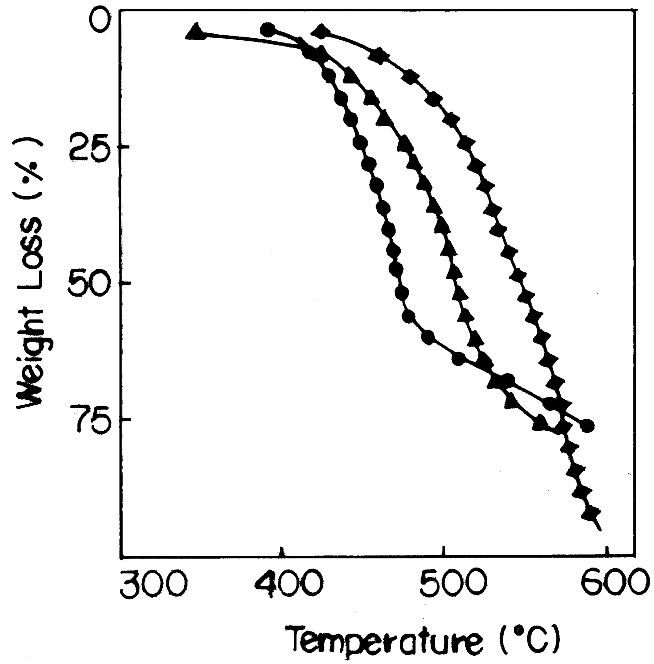

FIGURE 3 Representative TGA plots of (•) P(VAc-CA), (▲) P(VAc-BA), and (◆) P(VAc-EA) at heating rate of 10 K·min^{-1} in air.

than methyl and ethyl acrylate polymers. The higher stability of these polymers could be due to the presence of phenyl and cyclohexyl groups in the polymers. Additionally, PVAc shows higher thermal stability than the respective acrylate copolymers.

GPC Analysis

The approximate number-average (M_n), weight-average (M_w), z-average (M_z), and viscosity-average (M_v) molecular weights of homopolymers polycyclohexyl acrylate (PCA) and polybenzyl acrylate (PBA), determined by gel permeation chromatography, are 2.24×10^5, 2.42×10^5, 2.59×10^5, and 2.42×10^5 for PCA and 8.72×10^4, 1.67×10^5, 2.62×10^5, and 1.67×10^5 for PBA, respectively. The molecular weight distributions (MWD) were found to be 1.08 and 1.91 for PCA and PBA, respectively.

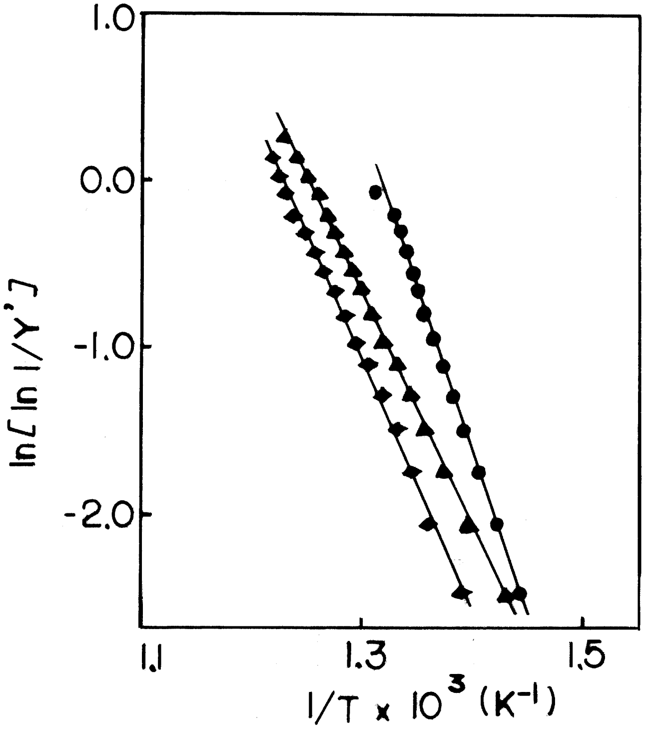

FIGURE 4 Representative Broido plot of (●) P(VAc-CA), (▲) P(VAc-BA), and (◆) P(VAc-EA).

Viscosity Studies

The conformation properties of polymer chains can be determined in dilute solutions[10]. The intrinsic viscosity $[\eta]$ can be obtained by using the well-known Huggins and Kraemer equations[10]. The $[\eta]$ values of all the polymers are presented in Table V. It can be seen that $[\eta]$ decreases as the temperature increases, and $[\eta]$ versus T plots are linear with a negative slope. The decrease in $[\eta]$ with increasing temperature indicates a decrease in hydrodynamic volume of polymer molecules. This is due to conformational and solvent association changes with increasing temperature[27]. Increase in temperature of a polymer solution generates two antagonistic effects[27]. First, increase in solvent power, i.e., solubility of the polymer in a solvent increases. This results in uncoiling of the polymer chains, leading to increase in $[\eta]$ with temperature. Second, increase in temperature may lower the rotational barrier, thereby enhancing the

TABLE IV Thermal analysis results for various (VAc-acrylate) copolymers (50:50, *v*/*v* feed ratio)

Samples	IDT[a] (°C)	T_{max} (°C)	FDT[b] (°C)	Weight loss (%)	E_a[c] (kJ mol^{-1})
PVAc	351	378	416	68	203.2
PMA	320	415	500	89	92.0
PEA	380	441	510	87	136.3
PCA	400	445	508	80	174.8
PBA	435	503	535	80	188.2
P(VAc-MA)	390	468	538	76	114.5
P(VAc-EA)	446	503	567	68	114.0
P(VAc-CA)	388	455	490	60	142.0
P(VAc-BA)	426	497	533	62	149.5

[a] Initial decomposition temperature.

[b] Final decomposition temperature.

[c] Calculated using Broido method at a heating rate of 10°C min^{-1} in air.

degree of rotation about a skeletal bond, forcing the molecular chains to assume a more compact, coiled configuration. This leads to a decrease in $[\eta]$ with increase in temperature. In the present case, the second phenomenon probably predominates over the first and thus a decrease in $[\eta]$ with a rise in temperature is observed. It is found that isopropyl alcohol (IPA) is a theta (θ) solvent for PCA at 29.6° C and nitromethane (NM) is a θ-solvent for PBA at 46.6° C. The intrinsic viscosities $[\eta]$ of PCA and PBA were also determined over a wide temperature range above the θ-temperature in IPA and NM, respectively. The $[\eta]_\theta$ values for PCA and PBA were determined by extrapolating $[\eta]$ versus T plot up to the θ-temperature.

The intrinsic viscosity expansion factor is determined by

$$\alpha_\eta^3 = [\eta]_T/[\eta]_\theta \tag{7}$$

where $[\eta]_T$ and $[\eta]_\theta$ represent the intrinsic viscosities in ordinary and θ-solvents, respectively. The values obtained for PCA and PBA are 1.08 and 1.49, respectively. This indicates that PBA is more swollen than PCA in their respective θ-solvents.

The intrinsic viscosity data were used to compute activation parameters of the viscous flow using the procedure suggested by Frenkel and Eyring[28]. The values obtained for change in the free energy ($\Delta G^{\neq}_{vis}$), enthalpy ($\Delta H^{\neq}_{vis}$), and entropy ($\Delta S^{\neq}_{vis}$) of activation for the viscous flow are listed in Table V. It is observed that $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ of all the systems calculated at 0.8 g dL^{-1} concentration in 1,4-dioxane are more or less constant quantities, independent of temperature, and the averages were

TABLE V Intrinsic viscosity ([η]), hydrodynamic volume (V_E), and various activation parameters for viscous flow of the P(VAc-acrylates) copolymers at different temperatures in 1,4-dioxane

	30°C		40°C		50°C				
Samples	[η] (dL g^{-1})	V_E (dL g^{-1})	[η] (dL g^{-1})	V_E (dL g^{-1})	[η] (dL g^{-1})	V_E (dL g^{-1})	$\Delta H^{\neq}{}_{vis}$ (kJ mol^{-1})	$\Delta S^{\neq}{}_{vis}$ (J mol^{-1} K^{-1})	$\Delta G^{\neq}{}_{vis}$ (40°C) (kJ mol^{-1})
P(VAc-MA)	0.167	0.066	0.165	0.065	0.163	0.064	10.2	2.6	9.4
P(VAc-EA)	0.178	0.071	0.175	0.070	0.172	0.068	10.3	2.7	9.5
P(VAc-BuA)	0.158	0.064	0.156	0.063	0.154	0.161	10.2	2.6	9.4
P(VAc-HA)	0.428	0.165	0.421	0.164	0.415	0.161	10.4	1.7	10.3
P(VAc-CA)	0.110	0.044	0.108	0.043	0.106	0.042	10.2	2.9	9.3
P(VAc-BA)	0.144	0.058	0.142	0.056	0.139	0.055	10.3	2.9	9.3
P(VAc-MMA)	0.135	0.058	0.134	0.053	0.132	0.052	10.2	2.7	9.5
PCA	0.136	0.054	0.135	0.054	0.134	0.053	10.9	2.6	9.4
PBA	0.478	0.185	0.472	0.183	0.466	0.181	10.5	1.5	10.0

found to be 10.3 ± 0.1 kJ mol^{-1} and 2.5 ± 0.2 J mol^{-1} K^{-1}, respectively. These low and constant values of $\Delta H^{\neq}_{vis}$ signify that the systems are not cross-linked, whereas low and positive values of $\Delta S^{\neq}_{vis}$ indicate that the polymer structures were reasonably ordered in 1,4-dioxane. The $\Delta G^{\neq}_{vis}$ values can hence be computed and were found to decrease with increase in temperature.

Voluminosity, V_E (i.e., a measured volume of solvated polymer), was evaluated by plotting y against concentration c in g dL^{-1} where

$$y = \frac{[\eta_r^{0.5} - 1]}{[c\ (1.35\ \eta_r^{0.5} - 0.1)]} \tag{8}$$

and η_r is the relative viscosity of the polymer solution.

The plot was linear and extrapolated to $c = 0$, and the intercept yielded V_E. It can be seen that V_E decreases with increase in temperature due to the desolvation effect (Table V)[10].

The shape factor, v (which suggests conformation of macromolecules in solution), was obtained from

$$[\eta] = v\ V_E \tag{9}$$

The v values were found to be 2.5 ± 0.1 for all the systems at three temperatures, indicating that polymer coils are spherical in nature in 1,4-dioxane and are not affected by temperature[22].

Some of the molecular parameters of polymers were calculated using solution viscosity data. The root-mean-square, end-to-end distances of homopolymers PCA and PBA chains were determined using[29]

$$[\eta] = \phi_0 \langle R^2 \rangle^{3/2} / M_n \tag{10}$$

where ϕ_0 is the universal constant, commonly known as the Flory-Fox constant. The relative viscosities of these polymers are not much higher than unity. Hence, the solvent is assumed to be a θ-solvent and $\langle R^2 \rangle^{1/2}$ can be calculated. The calculated values of $\langle R^2 \rangle^{1/2}$ obtained at various temperatures are presented in Table VI. As temperature increases, $\langle R^2 \rangle^{1/2}$ values decrease, indicating coiling of the polymer chain in solution.

The radius of the diffusing particle (r′) was calculated from[14,30]

$$[\eta] = 10\pi\ N\ r'^3 / 3M_n \tag{11}$$

where N is Avogadro's number. The values of r′ thus obtained for PAC and PAB homopolymers at different temperatures are listed in Table VI and were found to be independent of temperature.

The quantitative relationship between the coefficient of diffusion D_0 and the radius of particles was obtained by[14,31]

TABLE VI Root-mean-square, end-to-end distance ($\langle R^2\rangle^{1/2}$), radius of the diffusion particle (r'), and diffusion coefficient (D_0) of homopolymers in 1,4-dioxane

	30°C			40°C			50°C			Values at θ condition		
Polymers	$\langle R^2\rangle^{1/2} \cdot 10^7$ (cm)	$r' \cdot 10^7$ (cm)	$D_0 \cdot 10^7$ ($cm^2 \cdot Sec^{-1}$)	$\langle R^2\rangle^{1/2} \cdot 10^7$ (cm)	$r' \cdot 10^7$ (cm)	$D_0 \cdot 10'$ ($cm^2 \cdot Sec^{-1}$)	$\langle R^2\rangle^{1/2} \cdot 10^7$ (cm)	$r' \cdot 10^7$ (cm)	$D_0 \cdot 10^7$ ($cm^2 \cdot Sec^{-1}$)	$\langle R^2\rangle^{1/2} \cdot 10^7$ (cm)	$r' \cdot 10^7$ (cm)	$D_0 \cdot 10^7$ ($cm^2 \cdot Sec^{-1}$)
PCA	21.97	1.69	119.7	21.92	1.69	144.6	24.20	1.68	166.1	20.35[a]	1.57[a]	128.0[a]
PBA	24.40	1.88	107.3	24.30	1.87	130.7	24.20	1.86	150.0	16.23[b]	1.25[b]	199.6[b]

[a] Values at 29.6°C in isopropyl alcohol.

[b] Values at 46.6°C in nitromethane.

$$D_0 = R\ T/6\pi\ \eta_s r'\ N \tag{12}$$

where η_s is the viscosity of solvent. The values of D_0, tabulated in Table VI, show that D_0 increases as the temperature increases.

CONCLUSIONS

The free radical copolymerization reaction of VAc with CA/BA systems follows classical copolymerization theory. FTIR and ^{1}H and ^{13}C-NMR spectroscopy provided evidence for the structure and composition of the copolymers. The reactivity ratios measured via ^{1}H-NMR and calculated by Fineman-Ross and Kelen-Tudos methods agree very well with each other. The values of r_1r_2 suggested a strong tendency for monomers to alternate in the polymeric chain. Single-stage decomposition was observed for all copolymers. The viscosity activation parameters indicate that the polymers in 1,4-dioxane solution are not cross-linked and have reasonably ordered structures.

REFERENCES

[1] Narasimhaswami, T., B. S. R. Reddy, S. C. Sumathi, and S. Rajadurai. (1989). Reactivity ratios of phenyl-methacrylate and N-vinyl-2-pyrrolidone copolymer system by ^{1}H-NMR. *J. Polym. Mater.* **6**, 209–212.

[2] Arshady, R., B. S. R. Reddy, and M. H. George. (1986). Chemical modifications of copoly(styrene-2,4,5-trichlorophenyl acrylate) to give polymers which are potentially electroactive. *Polymer* **27**, 769–775.

[3] Brar, A. S. and K. Datta. (1999). Microstructural characterization of acrylonitrile/pentyl acrylate copolymers by one and 2-D-NMR spectroscopy. *J. Polym. Sci. Part A, Polym. Chem.* **37**, 533–543.

[4] Yang, Z., A. J. Mesiona, S. Venkatasubramanian, S. H. Gross, J. M. Harris, and A. J. Russell. (1995). Activity and stability of enzymes incorporated into acrylic polymers. *J. Am. Chem. Soc.* **117**, 4843–4850.

[5] Arshady, R. (1983). Synthesis of new macromolecular phosphine ligands. *Makromol. Chem. Rapid Commun.* **4**, 237–241.

[6] Borthakur, A., N. C. Laskar, R. K. Mazumdar, K. V. Rao, and B. Subramanyam. (1995). Synthesis and evaluation of alkyl fumarate-vinyl acetate copolymers in combination with alkyl acrylates as flow improvers for crude oil. *J. Chem. Technique. Biotechnol.* **65**, 75–80.

[7] Eguiburu, J. L., M. J. Fernandez-Berridi, and J. S. Roman. (1996). Graft copolymers for biomedical applications prepared by free radical polymerisation of poly(1-lactide) macromonomers with viny and acrylic monomers. *Polymer*, **37**, 3615–3622.

[8] Soundararajan, S., B. R. S. Reddy, S. Rajadurai, and G. Thyyagarajan. (1987). Synthesis and characterization of lacquers based on styrene-acrylic copolymers for applications in leather industry. *J. Appl. Polym. Sci.* **34**, 247–259.

[9] Angelovici, M. M. and D. H. Kohn. (1991). Terpolymerization studies. IV: Terpolymerization of ethyl acrylate, ethyl α-cynocinnamate and styrene. *J. Appl. Polym. Sci.* **42**, 1121–1124.

[10] Mathakiya, I. and A. K. Rakshit. (1998). Synthesis and characterization studies of homopolymers of N-vinyl pyrrolidone, vinyl acetate, and their copolymers. *J. Appl. Polym. Sci.* **68**, 91–102.

[11] Ghosh, P. (1990). *Polymer Science and Technology of Plastic and Rubber*. New Delhi: Tata McGraw-Hill Publishing Co. Ltd.

[12] Aerdts, A. M., A. L. German, and G. P. M. Vander Velden. (1994). *Magn. Reson. Chem.* **32**, S80.

[13] Pachha, R. R., R. T. Patel, and R. D. Patel. (1995). Methylmethacrylate-acrylonitrile copolymers: Effect of copolymer composition on molecular weight and thermal properties. *J. Polym. Mater.* **12**, 281–284.

[14] Bhagat, M., S. Joshi, S. S. Kansara, and N. K. Patel. (1997). Viscosity behaviour of poly(ethylene glycol) initiated polyacrylamide. *J. Polym. Mater.* **14**, 159–164.

[15] Mathakiya, I., P. V. C. Rao, and A. K. Rakshit. (2001). Synthesis and characterization of styrene-acrylic ester copolymers. *J. Appl. Polym. Sci.* **79**, 1513–1524.

[16] Vangani, V. and A. K. Rakshit. (1996). Synthesis and characterization of homopolymer of 2-ethylhexyl acrylate and its copolymers with acrylamide, acrylonitrile and methyl methacrylate. *J. Appl. Polym. Sci.* **60**, 1005–1013.

[17] Tompa, H. (1959). *Polymer Solutions*. London: Butterworths.

[18] Silverstein, R.M., R. G. Bessler, and T. C. Morrill. (1981). *Spectroscopic Identification of Organic Compounds*, 4th ed. New York: Wiley.

[19] Brar, A. S. and S. Charan. (1996). Reactivity ratios and microstructure determination of vinyl acetate–ethyl methacrylate copolymers. *Polymer* **34**, 2451–2457.

[20] Brar, A. S. and S. Charan. (1994). Sequence determination of vinyl acetate-methyl acrylate copolymers by NMR spectroscopy. *J. Appl. Polym. Sci.* **53**, 1813–1822.

[21] Fineman, M. and S. D. Ross. (1950). Linear method for determining monomer reactivity ratios in copolymerization. *J. Polym. Sci.* **A1.5**, 259–262.

[22] Mathakiya, I., V. Vangani, and A. K. Rakshit. (1998). Terpolymerization of acrylamide, acrylic acid, and acrylonitrile: Synthesis and properties. *J. Appl. Polym. Sci.* **69**, 217–228.

[23] Balasubramanian, S. and B. S. R. Reddy. (1995). Synthesis and characterization of 4-acetamidophenyl acrylate-methyl acrylate copolymers: Determination of reactivity ratios by ^{1}H-NMR spectroscopy and thermal studies. *J. Polym. Mater.* **12**, 55–62.

[24] Langu, A. and D. C. Neckers. (1995). Solution and solid C^{13} NMR studies of multifuntional polyol-acrylate. *J Coat. Technol.* **67**, 29–35.

[25] Lindemann, M. K. (1964). In: *Encyclopedia of Polymer Science and Technology*, vol. 15. New York: Wiley, p. 645.

[26] Sharma, P., V. K. Karan, I. K. Varma, and A. K. Bhatnagar. (1989). Characterization of poly(aklyl methacrylates). *J. Polym. Mater.* **6**, 245–255.

[27] Rangaraj, A., V. Vangani, and A. K. Rakshit. (1997). Synthesis and characterization of some water soluble polymers. *J. Appl. Polym. Sci.* **66**, 45–56.

[28] Vinogradov, G. V. and A. Ya. Malkin. (1980). *Rheology of Polymers*. Moscow: Mir Publishers.

[29] Flory, P. J. and T. G. Fox. (1951). Treatment of intrinsic viscosities. *J. Am. Chem. Soc.* **73**, 1904–1908.

[30] Tager, A. (1978). *Physical Chemistry of Polymers*. Moscow: Mir Publishers, p. 460.

[31] Tager, A. (1978). *Physical Chemistry of Polymers*. Moscow: Mir Publishers, p. 501.