Synthesis and Characterization Studies of Homopolymers of *N*-Vinylpyrrolidone, Vinyl Acetate, and Their Copolymers

ISMAIL MATHAKIYA, ANIMESH KUMAR RAKSHIT

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002, India

ABSTRACT: Homopolymers of *N*-vinylpyrrolidone (VP) and vinyl acetate (VAc) were synthesized by a free-radical solution polymerization technique. Copolymers of VP and VAc in various monomer feed ratios were also synthesized by the same procedure. They were characterized by elemental analysis, FTIR, PNMR, TGA, swelling, and viscosity measurements. The reactivity ratios of the monomers were computed by both Fineman–Ross and Kelen–Tudos methods using data from both PNMR and elemental analysis studies. The activation energy values for various stages of decomposition were calculated from TGA analysis using Broido's method. The viscosity measurements were carried out at four different temperatures: 30, 35, 40, and 45°C. The activation parameters of the viscous flow, voluminosity (V_E), and shape factor (ν) were also computed for all systems. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 91–102, 1998

Key words: TGA; PNMR; viscosity; homopolymer; copolymer; vinylpyrrolidone; vinyl acetate

INTRODUCTION

The synthesis of novel polymers with varied properties for different needs has been the focus of polymer research for many years. A wide variety of chemical or physical strategies including copolymerization, polymer blend formation, and crosslinking network formation have been explored to provide multifunctional polymers.[1] The accurate estimation of the composition of copolymers and the determination of monomer reactivity ratios are important for tailoring copolymers with the required physicochemical properties.[2] Copolymers and terpolymers containing *N*-vinylpyrrolidone (VP) find wide application in the field of hydrogels, pharmaceuticals, and cosmetics and in the food industry as well as in numerous other technical fields.[3] It was decided, therefore, to co-polymerize vinyl acetate (VAc) with VP since poly(vinyl acetate) (PVAc) is one of the most important of all the synthetic thermoplastic adhesives with wide range of industrial applications.[4] The possibility of biodegradation of the P(VP–VAc) copolymer is also a major reason for the synthesis of these copolymers. In this article, we present the results of our study of the properties of PVP, PVAc, and their copolymers P(VP–VAc). Various studies, for example, IR, NMR, thermal degradation, swelling, and solution viscosity, were done. The results of these studies are discussed in this article.

EXPERIMENTAL

N-Vinylpyrrolidone (VP, Fluka) was used as received. Vinyl acetate (VAc, SD's Lab-Chem. Industry, Bombay, India) was vacuum-distilled and the middle fraction used for polymerization. Technical-grade azobisisobutyronitrile (AIBN) was recrystallized from warm methanol and stored at

$-20°C$. The solvents, that is, benzene, n-hexane, n-heptane, n-octane, n-nonane, methanol, and chloroform, were obtained from Qualigens, India. All solvents were freshly distilled before use.

The FTIR of the films of the homopolymers and copolymers were recorded on a Bomem-MB104, Canada, FTIR spectrophotometer. The films were prepared by dissolving the polymers in chloroform and then pouring the solution over a pool of mercury. The films were obtained by vacuum evaporation of the solvent.

The NMR of the polymer solutions in $CDCl_3$ were recorded on a JEOL GSX, 400 MHz PMR at RSIC, IIT, Madras, India. The elemental analysis (viz., C and H) was carried out with a Coleman C, H analyzer and nitrogen was estimated by the Dumas method. TGA was recorded on a Shimadzu thermal analyzer DT-30B. The TGA analysis was done in the presence of air at three different heating rates: 10, 15, and 20 K min^{-1}.

The swelling behavior of the copolymers P(VP–VAc) with various compositions was studied on approximately uniform particle-size powdered samples. The swelling in different solvents was calculated using the following relation:

$$S = \% \text{ swelling} = \frac{W - W_0}{W_0} \times 100$$

where W and W_0 are weights of the swollen and dry polymers, respectively.

Viscosity measurements of the dilute solution of the homopolymers and copolymers in chloroform were carried out using an Ubbelohde dilution viscometer suspended in a thermostated bath at the required temperature ($\pm0.05°C$). Measurements for each solution were repeated five to six times. Densities of the solutions at different temperatures were assumed to be those of solvents at that temperature.[5] Polymerization of VP, VAc, and their copolymers, in various feed ratios, was carried out by the free-radical solution polymerization technique[6] described below.

Polyvinylpyrrolidone (PVP) was synthesized as follows: Twenty percent (v/v) of VP in methanol and 0.2% (w/v) of AIBN as an initiator were taken in a three-necked flask under a nitrogen atmosphere. The reaction mixture was stirred at 75°C for a period of 7 h. The three-necked flask was equipped with a water condenser and was placed in a thermostat maintained at 75°C. The reaction mixture after polymerization was poured into an excess of n-hexane to precipitate out PVP

and then purified by repeated reprecipitations from the methanol solution into the n-hexane medium.

The synthesis of poly(vinyl acetate) (PVAc) was carried out in the following way: Ten grams of VAc in 20 mL of methanol was taken in a three-necked flask. The reaction setup was similar to that used for the synthesis of PVP. AIBN, 0.1 g, was used as the initiator. The reaction mixture was stirred for a period of 5 h, under a nitrogen atmosphere, at 65°C. PVAc was obtained by pouring the reaction mixture into nonsolvent water.

Copolymerization of VP and VAc was carried out with various different feed ratios, that is, 80 : 20, 60 : 40, 40 : 60, and 20 : 80 (v/v) of the two monomers.[7] The recipe for the synthesis of a copolymer of 80 : 20 (v/v) of VP and VAc was as follows: 16 mL VP, 4 mL VAc, and 0.2 g AIBN were taken in 80 mL of benzene. The reaction was carried out under a nitrogen atmosphere at 70°C for a period of 10 h. The reaction setup of the PVP synthesis was used. The reaction mixture, after polymerization, was poured into an excess of n-hexane to precipitate out the product. The homopolymer PVP is insoluble in 2% acetone (v/v) in benzene although the copolymers are soluble. The precipitate was therefore treated with the above acetone–benzene solvent for 24 h with vigorous shaking. The residue was homopolymer PVP. The filtrate was then poured into an excess of n-hexane. The precipitated product was then Soxhlet-extracted with a toluene–cyclohexane mixture (80/20, v/v). The homopolymer PVAc is soluble in this mixture and, hence, was separated from the copolymer. The copolymer was washed well with cyclohexane and dried *in vacuo* before characterization.

FTIR spectroscopy is a powerful tool for structure elucidation.[8] The position, intensity, and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers at the molecular level. It is well known[9,10] that the infrared spectrum of PVAc exhibits changes with tacticity. The band at 1061 cm^{-1} is associated with the isotactic structure of the polymer [Fig. 1(a)]. The band at 617 cm^{-1} is very characteristic of PVAc due to the out-of-plane CH_2—CO_2 bend. The $\diagdown$C$=$O band of PVAc was observed at 1734 cm^{-1}. Other prominent absorption peaks were at 1372 and 1431 cm^{-1}. These are due to the asymmetrical and symmetrical bending vibrations of C—CH_3. The asymmetric stretches
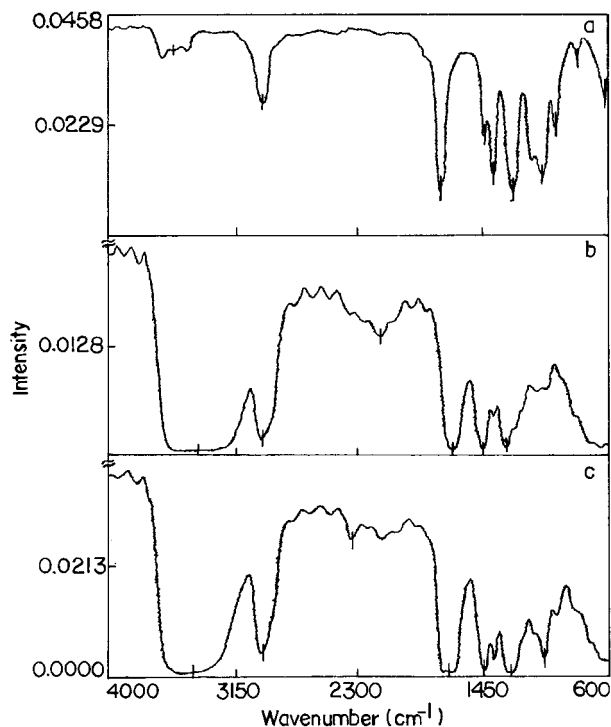
Figure 1 FTIR spectrum of (a) PVAc, (b) PVP, and (c) sample S2.

(C—O—C) were seen at 1245 cm^{-1}. Aliphatic stretches of C—H, due to —CH$_2$ and —CH$_3$, were also observed at 2951 cm^{-1}. These account for all the main absorption bands of PVAc. The assignments were done with the help of the literature data.[11]

The FTIR of PVP showed characteristic absorptions which agreed very well with those reported in the literature[3] and are given in Figure 1(b). The strong absorption at 1654 cm^{-1} is associated with the C=O absorption of tertiary amide and of the five-membered ring. This C=O band occurs at a longer wavelength than normal carbonyl absorption due to the resonance effect. The C—N stretching absorption appears at 1283 cm^{-1}. This is at higher frequency than the corresponding absorption of normal aliphatic amine because the force constant of the C—N bond is increased by resonance with the ring C=O groups. The scissoring band (δ_s CH$_2$) in the spectra was observed at 1445 cm^{-1} due to the
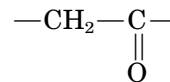
$$-CH_2-\underset{\underset{O}{\|}}{C}-$$

(small ring) and —CH$_2$—N$\diagup^{\diagdown}$ (amides) groups of PVP. Besides this, the asymmetrical stretching (ν_{as}CH$_2$) occurs near 2934 cm^{-1}.

Figure 1(c) shows the FTIR of the P(VP–VAc) copolymer (S2). It is similar to the FTIR of PVP [Fig. 1(b)]. The VAc group incorporated could not be very well distinguished by FTIR, but was supported by PNMR spectroscopy as shown below.

The evidence for the two monomers being incorporated was given by the PNMR spectra of the copolymers.[2,3,10–12] The signals appropriate to this discussion are represented in Figure 2 as (a–c), corresponding to protons on the VAc in the copolymer, and signals (d–h) corresponding to protons on the VP moiety in the copolymer. In the PNMR spectrum of the copolymer (S1, VP = 59.5 mol % in the copolymer, Fig. 3), the signals that occur around δ = 4.77 ppm (ref. 12) are associated with the methine backbone protons (b), whereas methine backbone protons (e) appear as a broad peak at δ = 3.75–3.95 ppm.[2,3] It was shown that the three peaks of the acetoxy proton signals [3H, (c) in Fig. 2] and methylene backbone protons (d) resonate at 1.98, 2.00, and 2.02 ppm.[10] Various resonances in this area cannot be distinguished because of the overlap due to spin–spin coupling and the sensitivity of methyl protons toward tacticity and the monomer sequence.[12] Besides this, one can see from Figure 3 that signals from protons (a) and (g) overlap and give a broad peak at around 1.427–1.695 ppm, whereas protons (f) resonate at around δ = 3.08–3.42 ppm.[11]

The change in the composition of the copolymer of VP (1) on the copolymerization with VAc (2) is expressed by the following relations:
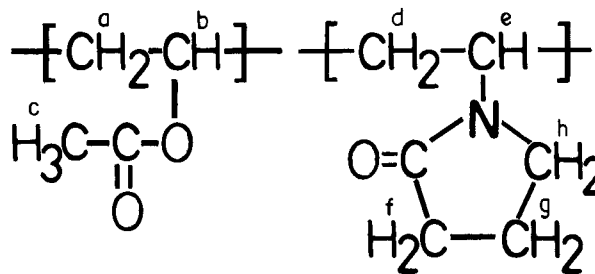

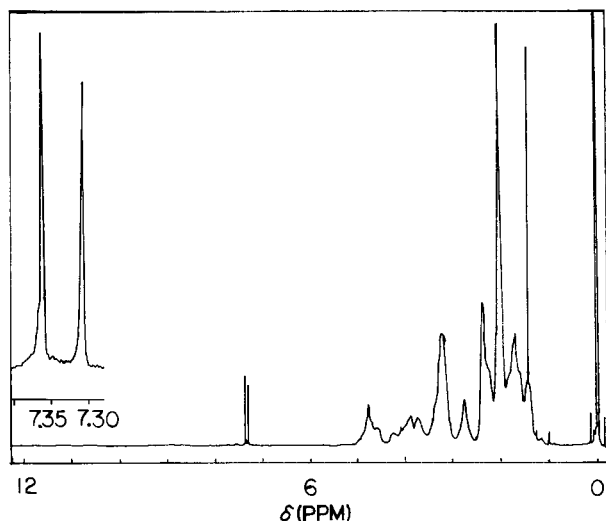**Figure 2** Repeat unit in the homopolymers and/or copolymers.

Figure 3   PNMR spectrum of the copolymer S1 (VP = 59.5 mol % in the copolymer) in CDCl$_3$.

$$\frac{\phi_1}{\phi_2} = \frac{r_1 M_1^2 + M_1 M_2}{r_2 M_2^2 + M_1 M_2} \quad (1)$$

The above equation can be rewritten as[13]

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

where $H = M_1/M_2$ and $h = \phi_1/\phi_2$. M_1 and M_2 are mole fractions of the monomers in the feed, and

ϕ_1 and ϕ_2 are the mole fractions of the monomers in the relevant copolymer (as defined in Tables I and II). r_1 and r_2 are the reactivity ratios of the two monomers. The mole fractions of the monomers in the copolymers were determined from the PNMR spectral data.

The mole fraction of VP(ϕ_1) in the copolymer was determined using the following relation:

$$\phi_1 = \frac{I(-\text{CH of VP})}{I(-\text{CH of VAc}) + I(-\text{CH of VP})} \quad (3)$$

where $I(-\text{CH of VP})$ and $I(-\text{CH of VAc})$ represent the peak intensities of the $-$CH protons of VP and VAc, respectively. The $-$CH proton of VP resonates at 3.75–3.95 ppm, whereas the $-$CH proton of VAc resonates at 4.77 ppm. The mol fractions of VP and VAc in the copolymers of various compositions calculated by using PNMR are listed in Table I.

Monomer reactivity ratios r_1 and r_2 could thus be calculated graphically by plotting $H(1 - h)/h$ versus H^2/h [Fineman–Ross (F–R) method]. The slope and intercept yielded r_1 (=0.174) and r_2 (=0.137) for VP and VAc (Table III), respectively.[14]

Reactivity ratios were also determined using the Kelen–Tudos (K–T) methods.[15] Equation (1) can be rewritten as

Table I   Composition of VP (1) and VAc (2) in the Feed and in the Copolymers

Polymer Samples	Mole Fraction (M) of VP and VAc in Feed		Elemental Analysis Data			Mole Fraction[b] (m) of VP and VAc in Copolymer		Mole Fraction[c] (ϕ) of VP and VAc in Copolymer	
	M_1	M_2	Nitrogen[a] (wt %)	Carbon (wt %)	Hydrogen (wt %)	m_1	m_2	ϕ_1	ϕ_2
S1 $\begin{Bmatrix} \text{NVP–VAc} \\ 80 : 20 \end{Bmatrix}$	0.756	0.244	8.28	56.90	7.89	0.598	0.402	0.595	0.405
S2 $\begin{Bmatrix} \text{NVP : VAc} \\ 60 : 40 \end{Bmatrix}$	0.537	0.463	7.35	56.97	7.77	0.520	0.480	0.528	0.472
S3 $\begin{Bmatrix} \text{NVP : VAc} \\ 40 : 60 \end{Bmatrix}$	0.341	0.659	6.62	57.52	7.47	0.462	0.538	0.469	0.531
S4 $\begin{Bmatrix} \text{NVP : VAc} \\ 20 : 80 \end{Bmatrix}$	0.162	0.838	4.88	57.54	7.45	0.329	0.671	0.341	0.659
PVP	—	—	11.23	55.51	8.29	—	—	—	—
PVAc	—	—	—	55.28	6.96	—	—	—	—

[a] Average of two pairs of duplicate analysis on each preparation.
[b] Calculated using elemental analysis data.
[c] Calculated using PNMR spectroscopic data.

Table II   K–T Parameters for the Monomer VP and VAc Using PNMR Spectroscopic Data

Polymer Samples	$H = \dfrac{M_1}{M_2}$	$h = \dfrac{\phi_1}{\phi_2}$	$G = \dfrac{H(h-1)}{h}$	$F = \dfrac{H^2}{h}$	$\beta = \dfrac{G}{\alpha + F}$	$\varepsilon = \dfrac{F}{\alpha + F}$
S1	3.10	1.47	0.99	6.53	0.90	0.14
S2	1.16	1.12	0.12	1.20	—	—
S3	0.52	0.88	−0.07	0.30	0.31	−0.07
S4	0.19	0.52	−0.18	0.07	0.09	−0.24

$\alpha = \sqrt{F_{\max} F_{\min}} = 0.68$: M_1 is the mole fraction of VP and M_2 is the mole fraction of VAc in the feed. ϕ_1 and ϕ_2 are their respective experimental mole fractions in the copolymer, obtained from PNMR spectroscopic data.

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

where G, F, and α are mathematical functions of H and h as defined in Table II. 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 0.189 and 0.169 for VP and VAc, respectively (Table III). The calculated values were found to differ from the literature values[16,17] (Table III). The values, particularly of ref. 17, are far from the values obtained by us. We are not in a position to explain these discrepancies.

The experimental feed ratios of the various monomers as well as the composition of the resulting copolymers, obtained by elemental analysis, are also summarized in Table I. The reactivity ratios (r) of VP and VAc in the copolymer were also determined by the F–R method[18] using elemental analysis data. The following equation was used:

$$X(Y - 1)/Y = r_1 X^2/Y - r_2 \quad (5)$$

where $X = M_1/M_2$ and $Y = m_1/m_2$ (as defined in Table I).

On plotting $X(Y - 1)/Y$ against X^2/Y, a straight line was obtained, whose slope was r_1 and inter-cept yielded r_2. The values obtained for r_1 and r_2 are 0.184 and 0.168, respectively (Table III).

The reactivity ratios r_1 and r_2 of VP and VAc, respectively, in the copolymers were also estimated by the method of K–T:

$$\beta = r_1\varepsilon - r_2(1 - \varepsilon)/\alpha \quad (6)$$

where β, ε, and α are mathematical functions of G and F as defined in Table IV. The β versus ε plot was linear (Fig. 4) and r_1 and r_2 were found to be 0.182 and 0.142, respectively, for VP and VAc. The r_1r_2 values (Table III) indicate that the copolymers should have a random distribution of the monomer units with a tendency toward alternation.[19] It is to be noted that the estimated nitrogen in PVP is somewhat lower (Table I) than the expected value of 12.6%. Our repeated determination on fresh samples did not improve the value. However, this discrepancy in the estimated nitrogen value was also reported earlier.[17,20,21] The compositions of the copolymers were computed by assuming a theoretical nitrogen value of 12.6% in PVP. The copolymer compositions computed from the nitrogen estimation as well as from PNMR are almost the same, indicating that that the nitrogen estimated in the copolymers is probably correct. Why there has always been error in the estimation of nitrogen in PVP is not understood, although high hygroscopicity may be the reason.[21]

Table III   Monomer Reactivity Ratios for Copolymerization of VP with VAc

Monomer	By Elemental Analysis		By PNMR Spectroscopy		Ref. 16	Ref. 17
	F–R Methods	K–T Methods	F–R Methods	K–T Methods		
VP (r_1)	0.184	0.182	0.174	0.189	0.44	2.28
VAc						
(r_2)	0.168	0.142	0.137	0.169	0.38	0.24
r_1r_2	0.031	0.026	0.024	0.032	—	—

Table IV   K–T Parameters for the Monomer VP and VAc Using Elemental Analysis Data

Polymer Samples	$X = \dfrac{M_1}{M_2}$	$Y = \dfrac{m_1}{m_2}$	$G = \dfrac{X(Y-1)}{Y}$	$F = \dfrac{X^2}{Y}$	$\beta = \dfrac{G}{\alpha + F}$	$\varepsilon = \dfrac{F}{\alpha + F}$
S1	3.10	1.49	1.02	6.45	0.14	0.90
S2	1.16	1.08	0.09	1.24	0.05	0.64
S3	0.52	0.86	−0.09	0.31	−0.09	0.31
S4	0.19	0.49	−0.20	0.08	—	—

$\alpha = \sqrt{F_{max}F_{min}} = 0.70$: M_1 is the mole fraction of VP and M_2 is the mole fraction of VAc in the feed. m_1 and m_2 are their respective experimental mole fractions in the copolymer, obtained from elemental analysis data.

Further, as both r_1 and r_2 values are almost same, we can conclude that the composition of the copolymer does not vary with time and, therefore, the equations used to compute the reactivity ratios are justified. The low r_1r_2 values (~ 0.03) indicate that the copolymer is more an alternating copolymer rather than a completely random copolymer.

The statistical distributions of the monomer sequence, 1–1, 2–2, and 1–2, were calculated using the following relations[22–24]:

$$X' = \phi_1 - 2\phi_1\phi_2/\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1\phi_2]^{1/2}\} \quad (7)$$
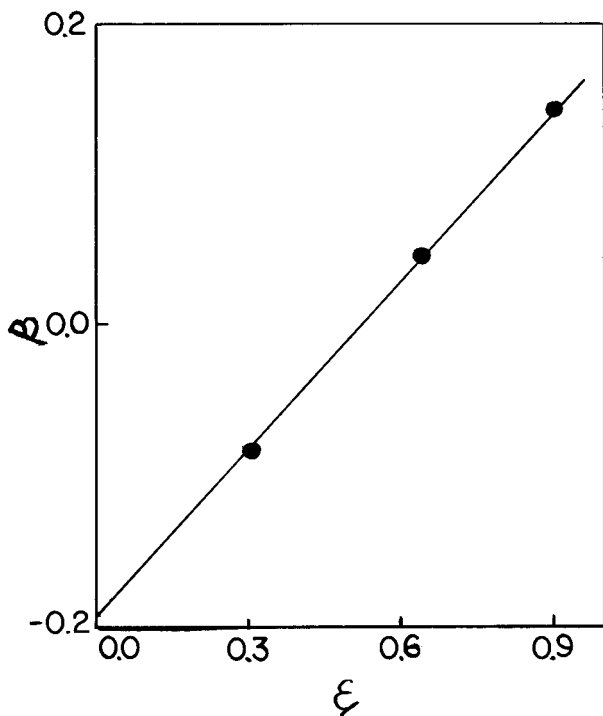

Figure 4   K–T plot for copolymerization of VP with VAc.

$$Y' = \phi_2 - 2\phi_1\phi_2/\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1\phi_2]^{1/2}\} \quad (8)$$

$$Z' = 4\phi_1\phi_2/\{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1\phi_2]^{1/2}\} \quad (9)$$

where r_1 and r_2 are the reactivity ratios of VP and VAc, respectively. ϕ_1 and ϕ_2 are the mole fractions of VP and VAc in the copolymer, obtained from the PNMR spectroscopic technique. The mole fractions of the 1–1, 2–2, and 1–2 sequences, that is, the blockiness, are designated by X', Y', and Z', respectively (Table V). The mean sequence lengths μ_1 and μ_2 were calculated utilizing the relations

$$\mu_1 = 1 + r_1(\phi_1/\phi_2) \quad (10)$$

$$\mu_2 = 1 + r_2(\phi_2/\phi_1) \quad (11)$$

where the r_1 and r_2 values used were from Table III (K–T method).

The intermonomer linkages and mean sequence length distributions for the P(VP–VAc) copolymers are listed in Table V. For the series of P(VP–VAc) copolymers, μ_1 varied from 2.278 to 1.098 as the mole ratio of VP/VAc decreased. The calculated mole fraction of 1–2 linkages obtained in each copolymer was relatively high, indicating an alternating tendency of the copolymer formation, which was also concluded from the reasonably low values (~ 0.03) of r_1r_2.

The thermogravimetric analysis (TGA) was done to study the thermal decomposition of polymers and also to determine the activation energy for decomposition. TGA curves of PVP, PVAc, and a copolymer (S3) are given in Figure 5. The thermogram of the copolymer (S3) falls in between those of the homopolymers, indicating a somewhat intermediate thermal stability. Other copolymers also show intermediate thermal stabil-

Table V   Structural Data for the Copolymers of VP (1) with VAc (2)

Polymer Samples	Composition[a] (Mole Fraction)		Blockiness[b] (Mole Fraction)		Alternation[b] (Mole Fraction)	Mean Sequence Length		$\frac{\mu_1}{\mu_2}$
	ϕ_1	ϕ_2	1–1 (X′)	2–2 (Y′)	1–2 (Z′)	μ_1	μ_2	
S1	0.595	0.405	0.212	0.022	0.766	2.278	1.115	2.043
S2	0.528	0.472	0.108	0.052	0.840	2.211	1.151	1.921
S3	0.469	0.531	0.050	0.112	0.838	1.167	1.191	0.980
S4	0.341	0.569	0.010	0.329	0.661	1.098	1.327	0.827

[a] From PNMR spectra.
[b] Statistically calculated using reactivity ratios.

ity. Two-stage decomposition was observed in all cases, except for PVAc, which showed one-stage decomposition. The activation energy associated with each stage of decomposition was evaluated by the well-known Broido method.[25,26] The equation used for the calculation of the activation energy (E_a) was

$$\ln \ln(1/Y'') = (-E/R)(1/T) + \text{constant} \quad (12)$$

where
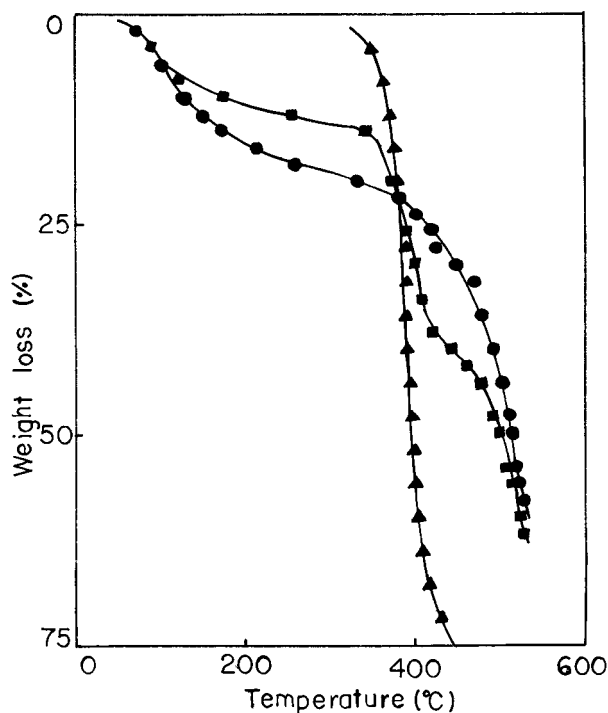
$$Y'' = (W_t - W_\infty)/(W_0 - W_\infty) \quad (13)$$

that is, Y'' is the fraction of the number of initial molecules not yet decomposed; W_t, the weight at any time "t"; W_∞, the weight at infinite time (= zero); and W_0, the initial weight.

A plot of $\ln \ln(1/Y'')$ versus $(1/T)$ [eq. (12)] gives an excellent approximation to a straight line over a range of $0.999 > Y'' > 0.001$. The slope is related to the activation energy. Representative plots are shown in Figure 6. The values for the activation energy of decomposition were evaluated at three different heating rates of 10, 15, and 20°C/min in air and are listed in Table VI.

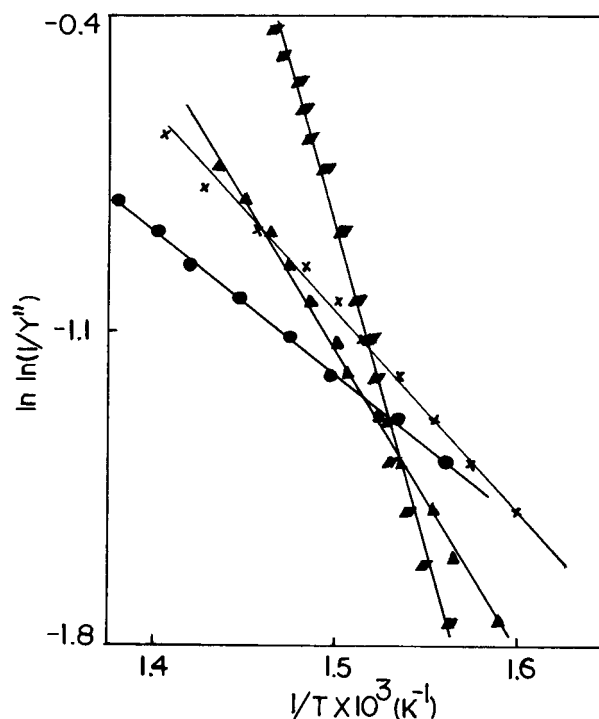The swelling is a measure of interaction be-

Figure 5   Representative TGA plots of (▲) PVAc, (●) PVP, and (■) copolymer S3 at heating rate of 10 K min⁻¹ in air.

Figure 6   Activation energy plot for the copolymers: (●) S1; (×) S2; (▲) S3; (■) S4.

Table VI   Activation Energy (E_a) of Decomposition for Various Homopolymers and Copolymers in Different Ratios by Thermogravimetric Analysis

Polymer Samples	Decomposition Temperature[a] Range (°C)	Weight Loss (%)[a]	$E_a{}^b$ (kJ mol^{-1})		
			10°C min^{-1}	15°C min^{-1}	20°C min^{-1}
PVP	103–380	22	6.2	13.7	6.8
	400–523	56	59.6	33.2	24.8
S1	68–153	14	40.7	36.3	15.7
	368–525	52	27.5	33.1	36.4
S2	68–139	12	34.5	15.0	34.3
	335–513	62	31.4	32.9	34.1
S3	70–123	08	38.7	34.7	11.9
	356–526	62	36.1	61.9	91.5
S4	39–336	08	6.6	26.0	8.9
	352–414	50	109.8	118.4	125.9
PVAc	351–416	68	203.2	234.5	259.8

[a] Heating rate, 10°C min^{-1}.
[b] Calculated using the Broido method at a heating rates of 10, 15, and 20°C min^{-1} in air.

tween polymer chains and the solvent molecule. It is a process of sorption/diffusion of a low molecular weight solvent by/in a polymer but it is accompanied by a change in the polymer structure. The penetration of a solvent into the interstructural space of a polymer causes the super-molecular structures of polymers to expand.[9,27] The swelling data of P(VP–VAc) copolymers, as uncrosslinked, linear, and semicrystalline polymers in various hydrocarbons as solvents, are shown in Figure 7. It is observed that the percent swelling increases with increase of the VAc content in the copolymer up to around a 0.7 mole fraction before its decrease in all solvents. In Table VII, we present the densities of all copolymers. The notable point is that as the concentration of VAc in the copolymer increases the density decreases up to about a 0.7 mole fraction. In other words, the polymer structure becomes highly porous with increasing VAc. This, in turn, accepts more solvent and, hence, higher swelling. With further increase in the VAc concentration, the copolymer structure becomes more condensed and, hence, there is less swelling. The swelling coefficient also shows the same trend, which was calculated using the following equation [9]:

$$Q = \frac{W - W_0}{W_0} \frac{1}{d} \tag{14}$$

where Q is the swelling coefficient; W, the weight of the swollen polymer; W_0, the initial weight of the polymer prior to swelling; and d, the density of the solvent used. The values obtained for the swelling and the swelling coefficient are shown in Table VII. All measurements were in duplicate.
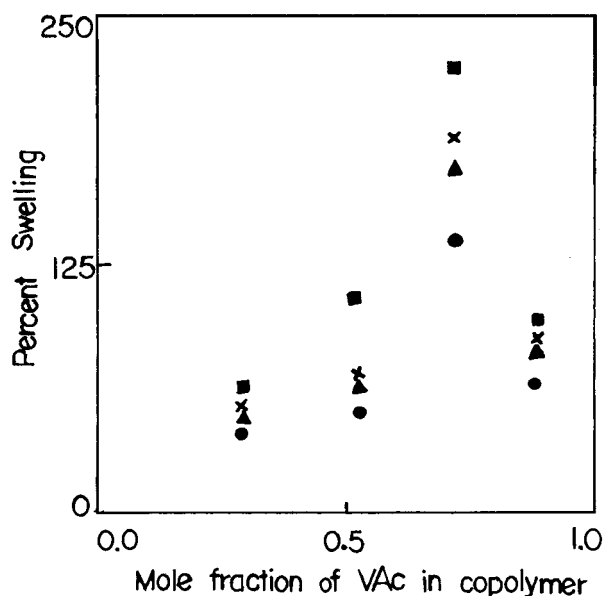

Figure 7   Swelling behavior of copolymers in solvents: (●) n-hexane; (▲) n-heptane; (×) n-octane; (■) n-nonane.

Table VII   Swelling Measurements of P (VP–VAc) Copolymers Using Different Solvents at Room Temperature

Polymer Samples	Swelling Time (h)	Density of the Polymer ρ (g/mL)	n-Hexane		n-Heptane		n-Octane		n-Nonane	
			S^a	Q^b	S^a	Q^b	S^a	Q^b	S^a	Q^b
S1	25	0.9790	41.6	0.6313	49.0	0.6979	56.7	0.8284	67.5	0.9398
S2	25	0.9581	52.0	0.7891	63.4	0.9018	69.8	1.0211	129.8	1.8078
S3	25	0.9103	139.3	2.1138	173.8	2.4723	190.1	2.7797	226.0	3.1476
S4	25	0.9881	67.5	1.0240	82.2	1.1693	84.4	1.2345	84.3	1.3131

[a] Percent swelling.
[b] Swelling coefficient.

In Table VIII, the intrinsic viscosities $[\eta]$ of all systems at various temperatures are given. They were computed by the well-known procedure.[28] The accuracy of the data was checked by calculating K' and K'', and their differences were 0.5, as expected (Fig. 8).[29] The correlation coefficient was always 0.99 or better. It can be seen that $[\eta]$ decreases as the temperature increases and $[\eta]$ versus T plots were always linear with a negative slope. This result is because a temperature increase 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.

The viscosities of the polymer solutions were determined at different temperatures. The well-known Frenkel–Eyring equation

$$\eta = \frac{Nh}{V} \exp(\Delta G_{vis}^{\ddagger}/RT) \qquad (15)$$

was used to evaluate various activation parameters of the viscous flow[30] and where V is the molar

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

$$\ln(\eta V/Nh) = \Delta G_{vis}^{\ddagger}/RT$$
$$= \Delta H_{vis}^{\ddagger}/RT - \Delta S_{vis}^{\ddagger}/R \qquad (16)$$

where $\Delta H_{vis}^{\ddagger}$ and $\Delta S_{vis}^{\ddagger}$ are the activation enthalpy and the entropy change for the viscous flow, respectively. V is the molar volume of the
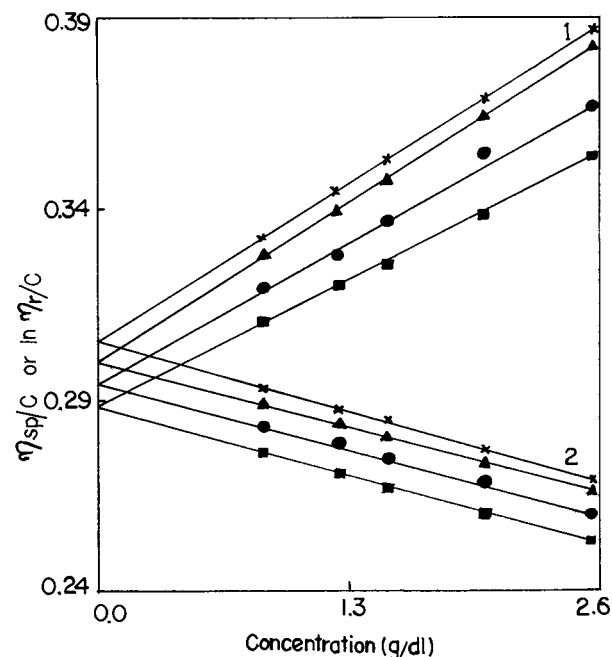
Table VIII   Intrinsic Viscosities of Various Copolymers and the Homopolymers at Different Temperatures in Chloroform

Polymer Samples	$[\eta]$ (dL g^{-1})				$K' - K''$ (35°C)
	30°C	35°C	40°C	45°C	
PVP	0.368	0.366	0.363	0.358	0.51
S1	0.316	0.310	0.301	0.294	0.51
S2	0.318	0.314	0.310	0.308	0.51
S3	0.305	0.299	0.294	0.288	0.50
S4	0.290	0.276	0.269	0.266	0.51
PVAc	0.632	0.614	0.612	0.608	0.49

Figure 8   Typical plot of (1) η_{sp}/c and (2) $\ln \eta_r/c$ against concentration for copolymer S3: ($\times$) 30°C; ($\blacktriangle$) 35°C; ($\bullet$) 40°C; ($\blacksquare$) 45°C.
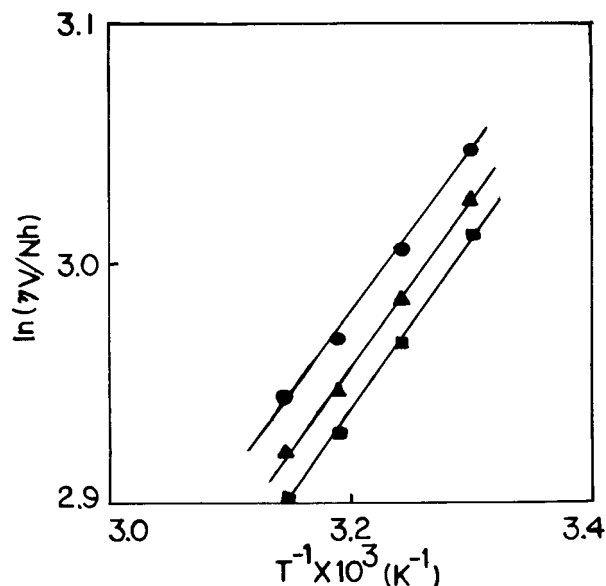
Figure 9 Plots of $\ln(\eta V/Nh)$ against $1/T$ for 0.5 g dL solutions in CHCl$_3$: (●) PVP; (▲) S2; (■) S4.

solution and was taken as equal to the molar volume of the solvent.[31] The plot of $\ln(\eta V/Nh)$ against T^{-1} shows linearity with correlation coefficients of 0.99 or better for all systems (Fig. 9). The slope and intercept gave $\Delta H_{vis}^{\ddagger}$ and $\Delta S_{vis}^{\ddagger}$, respectively. The calculated values of $\Delta G_{vis}^{\ddagger}$, $\Delta H_{vis}^{\ddagger}$, and $\Delta S_{vis}^{\ddagger}$ for some representative systems at a concentration of 0.5 g dL^{-1} are listed in Table IX. The $\Delta H_{vis}^{\ddagger}$ and $\Delta S_{vis}^{\ddagger}$ for all systems are constant quantities, independent of temperature, which signifies that the systems are not crosslinked. It is also observed that the heats of activation of viscous flow are positive (Table IX). The values are not large: The highest value observed was around 6.10 kJ mol^{-1} for S4 at a 0.5 g dL^{-1} concentration. The entropies of activation of the

viscous flow are also low and negative, indicating that the polymer structures are poorly ordered in chloroform. The $\Delta H_{vis}^{\ddagger}$ and $\Delta S_{vis}^{\ddagger}$ of this system seem to be almost same for all copolymers and both homopolymers with an average value of 5.9 $\pm$ 0.1 kJ mol^{-1} and -6.0 ± 0.3 J mol^{-1} K^{-1}, respectively. This constancy indicates that the structures of the solutions are similar in all respects. The $\Delta G_{vis}^{\ddagger}$ at all temperatures can, hence, be calculated.

Relative viscosity data at different concentrations were also used to calculate the voluminosity, V_E, of the polymer solutions at different temperatures in chloroform (Table X). V_E was calculated by plotting ψ against the concentration (in g dL^{-1}), where

$$\psi = (\eta_r^{0.5} - 1)/C(1.35\eta_r^{0.5} - 0.1) \quad (17)$$

The straight line obtained was then extrapolated to C=O and the intercept yielded V_E (Fig. 10). The shape factor was obtained from the equation[27,31–33]

$$[\eta] = \nu V_E \quad (18)$$

The shape factor gives an idea about the shape of the polymer molecules in solution.[34] The shape factors in different temperatures were found to be 2.5 $\pm$ 0.2, suggesting that the macromolecules acquire a spherical conformation.[35] Moreover, the ν values were found to be independent of temperature, suggesting that the conformation was not dependent on temperature. The voluminosity (Table X) is a function of temperature. V_E is a measure of volume of solvated polymer molecules.[36] As the temperature increases, desolvation takes place and, hence, V_E decreases. In our systems,

Table IX   Free Energy $\Delta G_{vis}^{\neq}$, Enthalpy $\Delta H_{vis}^{\neq}$, and Entropy $\Delta S_{vis}^{\neq}$ of Activation for Viscous Flow of the P (VP–VAc) Copolymers and Respective Homopolymers in Chloroform

Polymer Samples	$\Delta G_{vis}^{\neq}$ (kJ mol^{-1})				$\Delta H_{vis}^{\neq}$ (kJ mol^{-1})	$\Delta S_{vis}^{\neq}$ (J mol^{-1} K^{-1})
	30°C	35°C	40°C	45°C		
PVP	7.66	7.70	7.73	7.76	5.69	−6.51
S1	7.61	7.64	7.67	7.70	5.78	−6.03
S2	7.62	7.65	7.68	7.71	5.72	−6.26
S3	7.59	7.62	7.65	7.68	5.83	−5.82
S4	7.58	7.61	7.63	7.65	6.10	−4.89
PVAc	7.98	8.01	8.04	8.08	5.97	−6.62

Concentration of the solution was 0.5 g dL^{-1}.

Table X   Hydrodynamic Volumes (V_E) and Shape Factor (ν) of Various Polymers at Different Temperatures

Polymer Samples	30°C		35°C		40°C		45°C	
	V_E (dL g^{-1})	ν	V_E (dL g^{-1})	ν	V_E (dL g^{-1})	ν	V_E (dL g^{-1})	ν
PVP	0.145	2.6	0.144	2.5	0.141	2.6	0.140	2.5
S1	0.121	2.6	0.120	2.5	0.118	2.5	0.116	2.5
S2	0.122	2.6	0.121	2.5	0.121	2.5	0.121	2.5
S3	0.118	2.5	0.117	2.5	0.114	2.5	0.114	2.5
S4	0.112	2.6	0.108	2.5	0.106	2.6	0.105	2.5
PVAc	0.232	2.7	0.227	2.7	0.230	2.6	0.288	2.6

the V_E also decreases with increase in temperature, indicating desolvation (Table X). The biodegradative nature of these copolymers is presently being tested.

CONCLUSIONS

On the basis of the above-mentioned results, it can be concluded that the free-radical copolymerization reaction of VP with VAc systems studied follows the classical copolymerization theory. FTIR and PNMR spectroscopy provided evidence for the structure of the copolymers. The reactivity ratios of the monomers were obtained by both ele-

mental analysis and PNMR spectroscopy and did show relatively higher reactivity of VP than of VAc. The monomer units in the copolymer show a tendency toward alternation and the composition of the copolymer does not seem to vary with time. The activation energy of decomposition, viscosity activation parameters, and shape factors were obtained by TGA and solution viscosity studies. The viscosity activation parameters indicate that the polymers in chloroform solutions are not crosslinked and the structure of homopolymer and copolymer solutions are similar.

REFERENCES

1. X. Jin, C. Carfagna, L. Nicolasis, and R. Lanzetta, *Macromolecules,* **28,** 4785 (1995).
2. T. Narasimhaswamy, B. S. R. Reddy, S. C. Sumathi, and S. Rajadurai, *J. Polym. Mater.,* **6,** 209 (1989).
3. F. Haaf, A. Sanner, and F. Straub, *Polym. J.,* **17,** 143 (1985).
4. C. D. Han, Y.-J. Ma, and S. G. Chu, *J. Appl. Polym. Sci.,* **32,** 5597 (1986).
5. H. Tompa, *Polymer Solutions,* Butterworth, London, 1956, p. 287.
6. K. Noro, in *Poly Vinyl Alcohol: Properties and Applications,* C. A. Finch, Ed., Wiley-Interscience, New York, 1973, p. 68.
7. D. H. Lorenz, in *Encyclopedia of Polymer Science and Technology,* Vol. 14, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley, New York, 1964, p. 241.
8. W. K. Lee and C. S. Ha, *Polymer (Korea),* **18,** 935 (1994); *Chem. Abstr.,* **122,** 56997 k (1995).
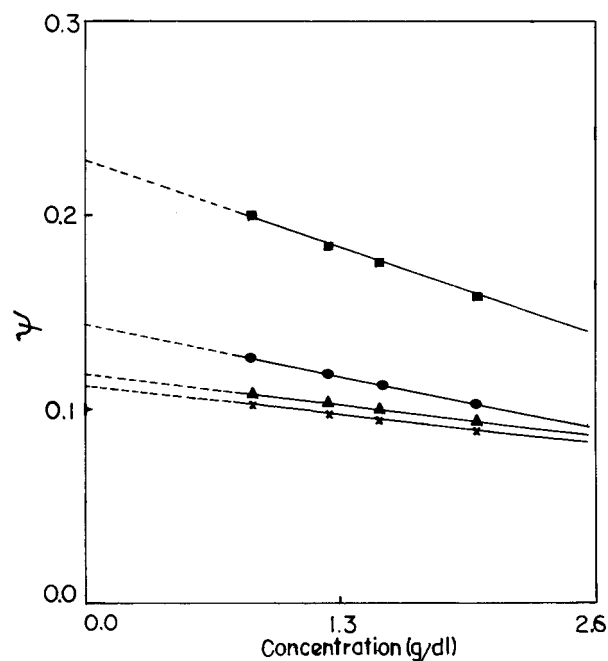
Figure 10   Plot of ψ versus concentration for polymers: (■) PVAc; (●) PVP; (▲) S3; (×) S4.

9. S. K. Verma, P. Arvindakshan, and S. C. Bisarya, *J. Appl. Polym. Sci.,* **46,** 707 (1992).

10. M. K. Lindemann, in *Encyclopedia of Polymer Science and Technology,* Vol. 15, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley, New York, 1964, pp. 546, 549.

11. R. M. Silverstien, R. G. Bessler, and T. C. Morrill, *Spectroscopic Identification of Organic Compounds,* 4th ed. Wiley, New York, 1981.

12. A. S. Brar and S. Charan, *J. Appl. Polym. Sci.,* **53,** 1813 (1994).

13. V. Vangani and A. K. Rakshit, *J. Appl. Polym. Sci.,* **60,** 1005 (1996).

14. I. K. Varma, M. V. Nair, and V. K. Karan, *J. Therm. Anal.,* **35,** 989 (1989).

15. T. Kelen and F. Tudos, *J. Macromol. Sci. Chem.,* **9,** 1 (1975).

16. K. Hayashi and G. Smets, *J. Polym. Sci.,* **27,** 275 (1958).

17. D. J. Khan and H. H. Horowitz, *J. Polym. Sci.,* **54,** 363 (1961).

18. M. Fineman and S. Ross, *J. Polym. Sci.,* **5,** 259 (1980).

19. N. A. Granem, N. A. Massiha, N. E. Ikladious, and A. F. Shaaban, *J. Appl. Polym. Sci.,* **26,** 97 (1981).

20. M. A. Al-Issa, T. P. Davis, M. B. Huglin, and D. C. F. Yip, *Polymer,* **26,** 1869 (1985).

21. S. Wen, Y. Xiaonan, and W. T. K. Stevenson, *Polym. Int.,* **27,** 81 (1992).

22. C. L. McCormick and G. S. Chen, *J. Polym. Sci.,* **22,** 3633, 3649 (1984).

23. C. L. McCormick and K. P. Blackmon, *Polymer,* **27,** 1971 (1986).

24. S. Igarshi, *J. Polym. Sci. Polym. Lett. Ed.,* **1,** 359 (1963).

25. A. Broido, *J. Polym. Sci.,* **7,** 1761 (1969).

26. R. Joseph, S. Devi, and A. K. Rakshit, *J. Appl. Polym. Sci.,* **50,** 173 (1993).

27. A. K. M. Asaduzzaman, A. K. Rakshit, and S. Devi, *J. Appl. Polym. Sci.,* **47,** 1813 (1993).

28. A. Tager, *Physical Chemistry of Polymers,* Mir, Moscow, 1978, p. 456.

29. E. A. Collins, J. Bares, and F. W. Billmeyer, *Experiments in Polymer Science,* 1st ed., Wiley, New York, 1970, p. 20.

30. G. V. Vinogradov and A. Ya. Malkin, *Rheology of Polymers,* Mir, Moscow, 1980.

31. R. Joseph, S. Devi, and A. K. Rakshit, *Polym. Int.,* **26,** 89 (1991).

32. A. S. Narang and U. C. Garg, *J. Ind. Chem. Soc.,* **66,** 214 (1989).

33. V. Vangani and A. K. Rakshit, *J. Appl. Polym. Sci.,* **45,** 1165 (1992).

34. R. Simha, *J. Phys. Chem.,* **44,** 25 (1940).

35. H. H. Kohler and J. Strand, *J. Phys. Chem.,* **94,** 7628 (1990).

36. S. Ajitkumar, D. Prasadkumar, S. Kansara, and N. K. Patel, *Eur. Polym. J.,* **31,** 149 (1995).