CHAPTER - 4

SYNTHESIS AND CHARACTERIZATION STUDIES OF HOMOPOLYMERS OF N-VINYLPYRROLIDONE, VINYL ACETATE AND THEIR COPOLYMERS

4.1 Preview

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 polymer.[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 tercopolymers 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] The copolymerization process in microemulsion medium (μE) has evoked considerable interest to the polymer scientist. A large amount of research work has been done on the polymerization in microemulsion medium in the last decade and a half.[4] The microemulsion has a reasonably well defined structure. The one phase microemulsion can have oil in water (o/w), water in oil (w/o) or a bicontinuous type of structure. In continuation of our studies of synthesis, characterization and properties of polymeric materials it was decided, therefore, to copolymerize 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.[5] The possibility of biodegradation of the P(VP-VAc) copolymer is also a major reason for the synthesis of these copolymers.

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We also decided to exploit the microemulsion structure to obtain the same copolymers P(VP-VAc) and compare the results with those obtained through solution polymerization. The accurate estimation of copolymer composition and determination of monomer reactivity ratios are hence important in understanding the nature of copolymerization process. In this Chapter, we present the results of our study of the properties of PVP, PVAc, and their copolymers P(VP-VAc) synthesized in solution medium. We also present the results of our study of P(VP-VAc) copolymers synthesized using microemulsion polymerization technique. It is to be noted that quite often[6] monomer(s) itself is used as oil in this type of polymerization. We, however,[7] used a fully defined microemulsion of oil, water, surfactant and cosurfactant. The monomers were dissolved in the one phase microemulsion of above constituents. We believe that under the above condition the formation of the product would not change the nature of μE which happens when product forming monomers are used as the oil. Various studies, for example, FTIR, ^{1}H- & ^{13}C- NMR, thermal degradation, swelling, and solution viscosity, were done. The results of these studies are discussed in this Chapter.

4.2 Materials

N-vinylpyrrolidone (VP, Fluka) was used are 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. SDS (Qualigens, India) was used as received. 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.

4.3 Experimental Methods

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 ^{1}H-NMR of the polymer solutions in $CDCl_3$ were recorded on a JEOL GSX, 400 MHz PMR at RSIC, IIT, Madras, India. ^{13}C-NMR spectra was also recorded for samples of homopolymers of VP, VAc and its copolymers synthesized in microemulsion medium having various initial feed ratios of monomers using 20-25% (w/v) solution in $CDCl_3$ at 50°C on a JEOL JNM FX-100 FT-NMR spectrometer in ^{13}C mode at a frequency of 25 MHz. TMS was used as an internal reference and $CDCl_3$ as an internal lock.

The elemental analysis (viz., C and H) was carried out with a Coleman C, H analyzer and nitrogen was estimated by the Dumas method. The 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 behaviour 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:

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

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

Viscosity measurements of the dilute solutions of the homopolymers and copolymers in chloroform and water were carried out using an Ubbelohde dilution viscometer suspended in a thermostated bath at the required temperature (±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 solvents at that temperature[8]. Polymerization of VP, VAc, and their copolymers, in various feed ratios, was carried out by the free-radical solution polymerization technique[9] described below.

4.4 Polymer Synthesis

(a) Using Solution Polymerization Technique :

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 three necked flask was equipped with a water condenser and was placed in a thermostat maintained at 75°C and the reaction mixture was stirred for 7 h. The reaction mixture after polymerization was poured into an excess of *n*-hexane to precipitate out PVP and then purified by repeated reprecipitations from methanol 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 set up 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 non solvent water.

Copolymerization of VP and VAc was carried out using solution polymerization process with various different feed ratios, that is, S1(80:20), S2(60:40), S3(40:60), and S4(20:80) (v/v) of the two monomers[10]. The recipe for the synthesis of a copolymer of S1(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 set up 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

(b) Using Microemulsion Polymerization Technique :

Copolymerization of VP and VAc was also carried out in microemulsion medium with various different feed ratios {i.e. NP1(80:20), NP2(60:40), NP3(40:60), and NP4(20:80) (v/v)} of the two monomers. One phase microemulsion was made up of water and benzene (1:1), sodium dodecyl sulfate + *n*-propanol (1:2) which constituted 32.5% (w/w) of the total amount[7]. The μE was o/w type. The microemulsion to total monomer ratio was 4:1 (v/v). The polymerization process was thermally initiated at 70°C using oil soluble initiator AIBN and the reaction time was 10 hours. The viscosities of the system remain low during the process providing evidence for the polymerization taking place exclusively inside the oil droplets. After polymerization, the reaction mass was dried in a bulb oven. The surfactant was removed by dissolving the polymerized mass in chloroform and filtered. Homopolymers were removed thereafter (as mentioned above). The copolymers were dried in *vacuo* before characterization.

(c) Hydrolysis of Copolymers :

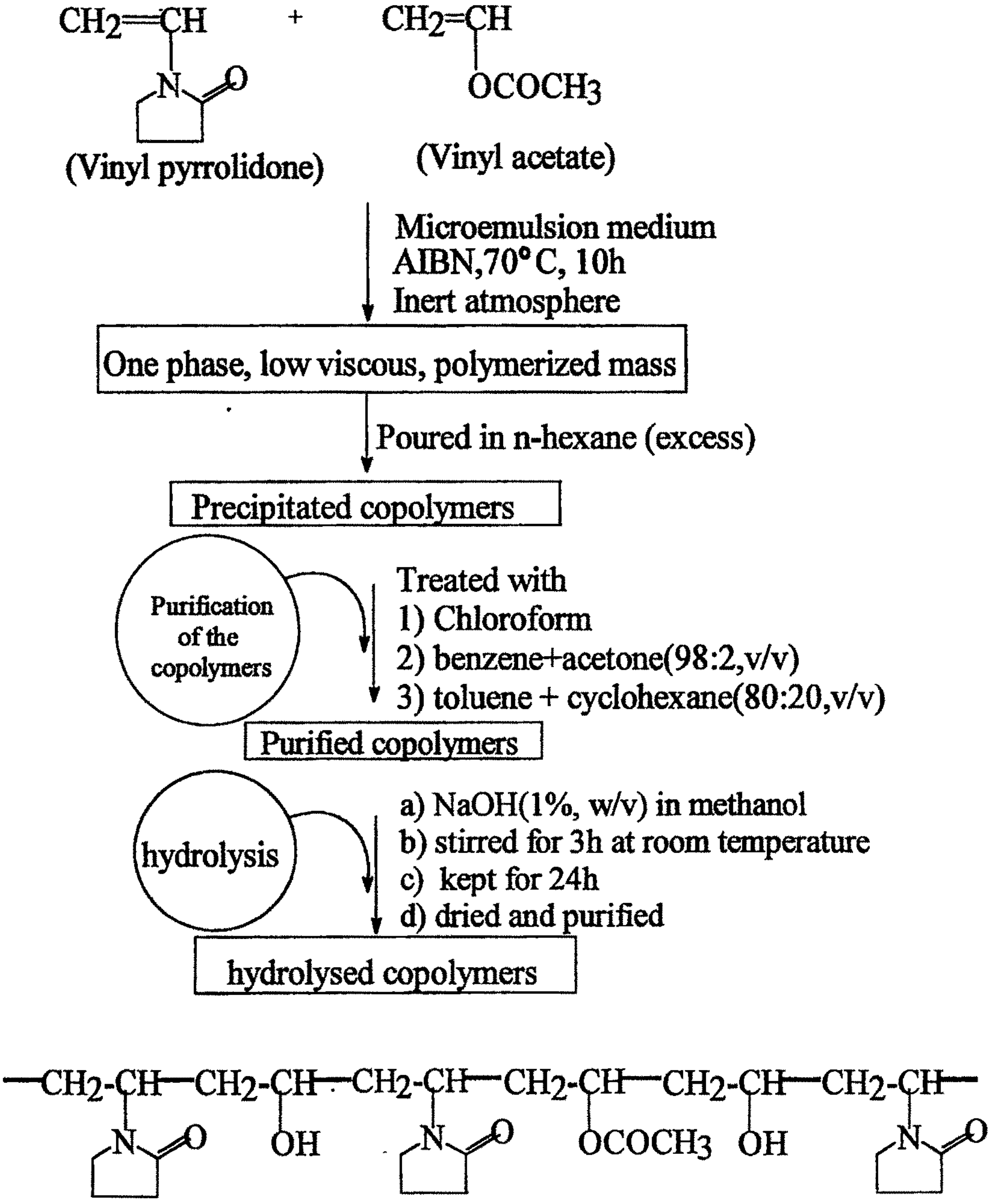
The hydrolysis of vinyl acetate (VAc) moieties present in the copolymer (synthesized in μE) were done using a method suggested by McDowell et al..[11] The polymer sample (2.0 g) was dissolved in methanol (15.0 mL) and the theoretical amount of 1% (w/v) sodium hydroxide in methanol necessary to react with the acetyl groups were added. Content of the flask was shaken for 3 hours and kept at room temperature for a period of 24 h. The solvent was evaporated in bulb oven (~50^0C) and the dried product (designated as HP 1-3) was washed twice with ice cold distilled water and then dried in *vacuo* before characterization. The synthesis and hydrolysis of the copolymers are schematicaly represented in Scheme 1.

4.5 Results and Discussion

(a) FTIR analysis :

FTIR spectroscopy is a powerful tool for structure elucidation[12]. 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[13,14] 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. 4.1(a)]. The band at 617 cm^{-1} is very characteristic of PVAc due to the

Synthesis and hydrolysis of the copolymers:



Scheme 1

out-of-plane $\mathrm{CH_2}$—$\mathrm{CO_2}$ bend. The 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 asymmetric and symmetrical bending vibrations of C—$\mathrm{CH_3}$. The asymmetric stretches (C—O—C) were seen at 1245 cm^{-1}. Aliphatic stretches of C—H, due to —$\mathrm{CH_2}$ and —$\mathrm{CH_3}$, 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.[15]

The FTIR of PVP shows characteristic absorption which agreed very well with those reported in the literature[3] and are given in Figure 4.1(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 $\mathrm{CH_2}$) in the spectra was observed at 1445 cm^{-1} due to the —$\mathrm{CH_2}$—CO-- (small ring) and —$\mathrm{CH_2}$—N (amides) groups of PVP. Besides this, the asymmetrical stretching (ν_{as} $\mathrm{CH_2}$) occurs near 2934 cm^{-1}.

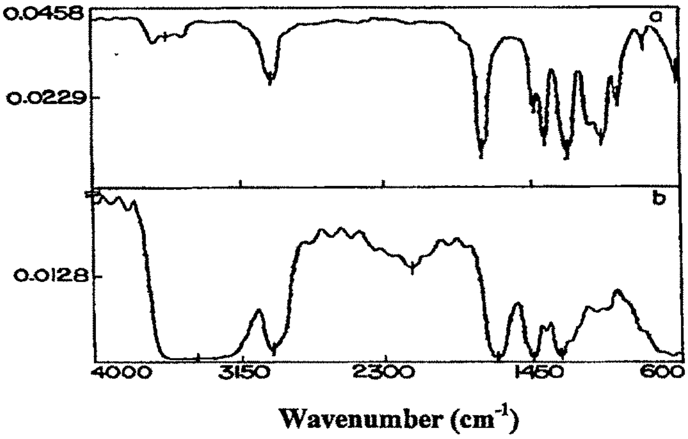


Figure 4.1: FTIR spectrum of (a) PVAc and (b) PVP

The hydrolysed (HP) and non-hydrolysed (NP) copolymers with well-defined structures were characterized by FTIR studies in detail. Figure 4.2 depicts their IR spectra, The band at 1654 cm^{-1} both in HP and NP was attributed to the carbonyl group of VP monomeric unit in the copolymers[16]. The peak at 1734 cm^{-1} for the carbonyl group in (a) and disappearance of these peak and the appearance of a very broad peak in the region 3200-3400 cm^{-1} for the hydroxyl group of vinyl alcohol (VA) in (b) confirmed the existence of NP [i.e. P(VP-VAc)] and HP [i.e. P(VP-VA)] copolymers[16]. The band at 617 cm^{-1} is very characteristic of VAc monomeric unit due to the out-of-plane CH_2-CO_2 bend and 1372 cm^{-1} due to the asymmetrical bending vibrations of C-CH_3. The disappearance of the peaks and formation of new peaks at 1285 cm^{-1} due to bending vibration of polymeric -O-H group gives clear evidence for presence of vinyl alcohol monomeric unit in the hydrolysed copolymers[16].

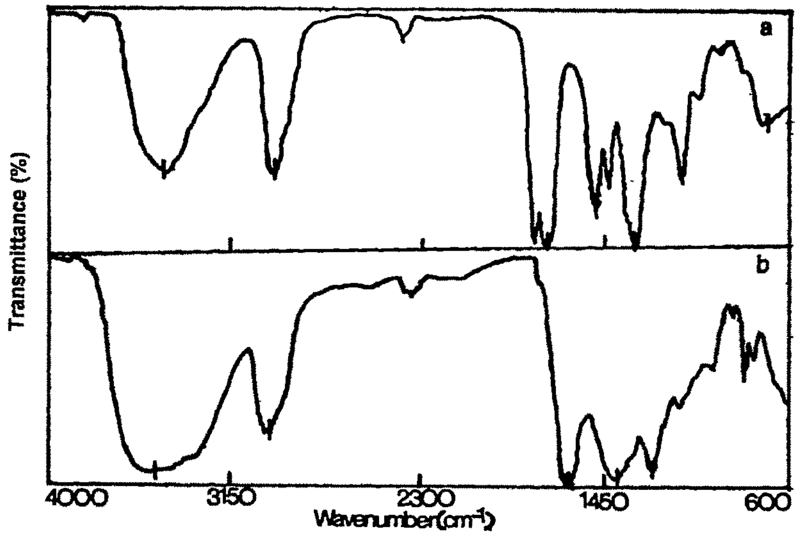


Figure 4.2 : FTIR spectra of (a) NP2 and (b) HP3 copolymers synthesized in μE medium.

(b) ^{1}H-NMR analysis :

The evidence for the two monomer units being incorporated was given by the ^{1}H-NMR spectra of the copolymers.[2,3,14,15,17] The signals appropriate to this discussion are represented in Figure 4.3 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 synthesized in solution medium. In the ^{1}H-NMR spectrum of the copolymer (S1, VP = 59.5 mol % in the copolymer, Fig. 4.4) , the signals that occur around δ = 4.77 ppm (ref.17) 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. 4.3] and methylene backbone protons (d) resonate at 1.98., 2.00, and 2.02 ppm[14]. 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.[17] Besides this, one can see from Figure 4.4 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.[15]

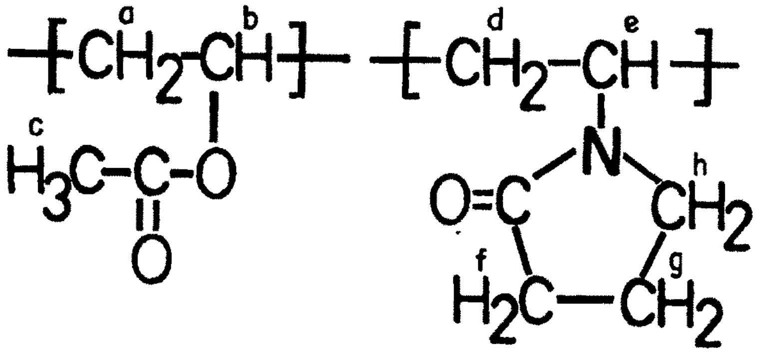


Figure 4.3 : Repeat unit in the homopolymers and/or copolymers.

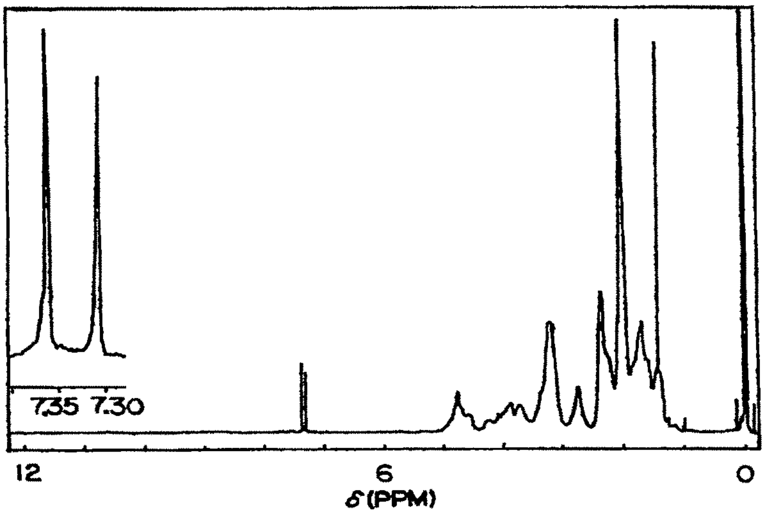


Figure 4.4 : PNMR spectrum of the copolymer S1 (VP=59.5 mol% in the copolymer) in CDCl$_3$.

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

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

The above equation can be written as[18]

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

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 4.1 and 4.2). 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 ^{1}H-NMR spectral data.

Table 4.1 : 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 (1) and Vac (2) in Copolymer		Mole Fraction[c] (ϕ) of VP (1) and VAc (2) in Copolymer	
	M_1	M_2	Nitrogen[a] (wt%)	Carbon (wt %)	Hydrogen (wt%)	m_1	m_2	ϕ_1	ϕ_2
S1 {NVP : VAc 80 : 20}	0.756	0.244	8.28	56.90	7.89	0.598	0.402	0.595	0.405
S2 {NVP : VAc 60 : 40}	0.537	0.463	7.35	56.97	7.77	0.520	0.480	0.528	0.472
S3 {NVP : VAc 40 : 60}	0.341	0.659	6.62	57.52	7.47	0.462	0.538	0.469	0.531
S4 {NVP : VAc 20 : 80}	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 4.2 : K-T Parameters for the Monomer VP (1) and VAc (2) 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

$\alpha = \sqrt{F_{max} \cdot F_{min}} = 0.68$: 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.
See Table 4.1 and text for symbols.

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

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

where I (—CH of VP) and I(—CH of VAc) represent the peak intensities of the —CH protons of VP and VAc, respectively. The —CH proton of VP resonates at $\delta = 3.75\text{-}3.95$ ppm, whereas the —CH protons of VAc resonates at $\delta = 4.77$ ppm. The mole fractions of VP and VAc in the copolymers of various compositions calculated by using ^{1}H-NMR are listed in Table 4.1.

Monomer reactivity ratios r_1 and r_2 could thus be calculated graphically by plotting $H(1\text{-}H)/h$ 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 4.3), respectively[19].

Reactivity ratios were also determined using the Kelen-Tudos (K-T) methods[20]. Equation (1) can be rewritten as

$$G/(\alpha+F) = (r_1 + r_2/\alpha)\, F/(\alpha + F) - r_2/\alpha \tag{4}$$

where G, F, and α are mathematical functions of H and h as defined in Table 4.2. 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 4.3). The calculated values were found to differ from the literature values[21,22] (Table 4.3). The values, particularly of

Table 4.3 : Monomer Reactivity Ratios for Copolymerization of VP (1) with Vac (2)

Monomer	By Elemental Analysis		By PNMR Spectroscopy		Ref. 21	Ref. 22
	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	--	--

ref.22, 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 4.1. The reactivity ratios (r) of VP and VAc in the copolymer were also determined by the F-R method[23] using elemental analysis data. The following equation was used :

$$X(Y-1)/Y = r_1X^2/Y - r_2 \qquad (5)$$

where $X = M_1/M_2$ and $Y = m_1/m_2$ (as defined in Table 4.1).

On plotting $X(Y-1)/Y$ against X^2/Y, a straight line was obtained, whose slope was r_1 and intercept yielded r_2. The values obtained for r_1 and r_2 are 0.184 and 0.168, respectively (Table 4.3).

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

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

where β, ε and α are mathematical functions of G and F as defined in Table 4.4. The β versus ε plot was linear (Fig. 4.5) 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 4.3) indicate that the copolymers should have a random distribution of the monomer units with a tendency toward alternation[24]. It is to be noted that the estimated nitrogen in PVP is somewhat lower (Table 4.1) 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.[22,25,26] The compositions of the copolymers were computed by assuming

Table 4.4 : K-T Parameters for the Monomer VP (1) and VAc (2) Using Elemental Analysis Data

Polymer Samples	$X = \frac{M_1}{M_2}$	$Y = \frac{m_1}{m_2}$	$G = \frac{X(Y-1)}{Y}$	$F = \frac{X^2}{Y}$	$\beta = \frac{G}{\alpha + F}$	$\varepsilon = \frac{F}{\alpha + F}$
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 fractions of VAc in the feed. m_1 and m_2 are their respective experimental mole fractions in the copolymer, obtained from elemental analysis data.

See Table 4.1 and text for symbols.

a theoretical nitrogen value of 12.6% in PVP. The copolymer compositions computed from the nitrogen estimation as well as from ^{1}H-NMR are almost the same, indicating that the nitrogen estimated in the copolymers is probably correct. Why there has always been an error in the estimation of nitrogen in PVP is not understood, although high hygroscopicity may be the reason[26].

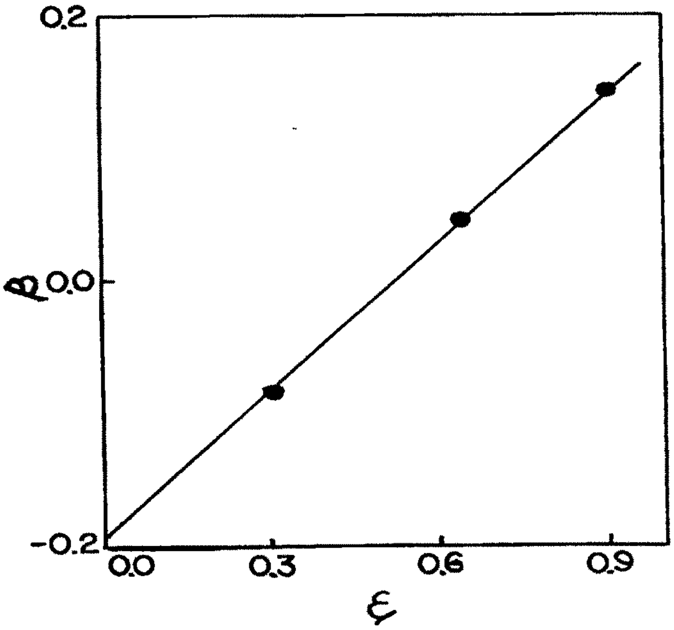


Figure 4.5 : K-T plot for coolymerization of VP with VAc.

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[27-29] :

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

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

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

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 ^{1}H-NMR spectroscopic technique. The mole fractions of 1-1, 2-2 and 1-2 sequences, that is, the blockiness, are designated by X', Y' and Z' respectively (Table 4.5). The mean sequence lengths μ_1 and μ_2 were calculated utilizing the reactions

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

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

where the r_1 and r_2 values used were from Table 4.3 (K-T method).

The intermonomer linkages and mean sequence length distributions for the P(VP-VAc) copolymers are listed in Table 4.5. 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.

(c) ^{13}C-NMR analysis :

^{13}C-NMR of PVAc [Fig. 4.6(a)] has four main signals : The methine carbon multiplet from δ=38.7-39.9 ppm show well resolved splitting due to stereo-chemical sensitivity.[17,30,31] The methine signals at δ=68.22, 67.15 and 67.05

Table 4.5 : 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

See Table 4.1 and text for symbols.

ppm represent triad sequences. The methyl carbon of Vac monomeric unit resonate at δ=20.7 ppm. Besides this the resonance signal of the carbonyl carbon of VAc appears at δ=170.2 ppm.

^{13}C-NMR spectrum of PVP is shown in Fig. 4.6(b). The resonance signal of the carbonyl appears at δ=175.4 ppm. One of the methylene carbon of the pyrrolidone ring is overlapped by the α-methine carbon of the PVP backbone.[32] The appearance of a multiplet at δ=42.6-45.0 ppm for this reason is sensitive to configurational sequences. The β-CH_2 carbon appears at δ=34.7 ppm. Besides this various methylene groups of the pyrrolidone ring appear in the regions δ=18.3 and 31.4 ppm respectively.

The two monomers incorporated were clearly observed in ^{13}C-NMR spectrum of copolymers. A representative ^{13}C-NMR spectrum of P(VP-VAc) copolymer (synthesized in μE medium, NP1, VP = 16.2 mole % in feed) is shown in Fig. 4.6(c). The resonance signals of the carbonyl carbon of VP and VAc monomeric units appear in the region δ=175.28-175.63 ppm and δ=169.81-171.58 ppm respectively. As the ratio of VP and VAc varies, the intensity of peak heights varies in the expected direction. The multiplet resonance signal of the carbonyl carbon in VAc units appear in the region δ=169.8-171.6 ppm provide information regarding the VAc centred compositional triads.[33] The -αCH carbon of the VP and VAc monomeric units also appears as a multiplet and broad peak at around δ=41.91-44.59 ppm and δ=67.05-68.55 ppm, showing its sensitivity to copolymer tacticity. Furthermore, all the methylene and methyl carbons of VP and VAc units appear at their respective chemical shift position [Fig. 4.6(c)].

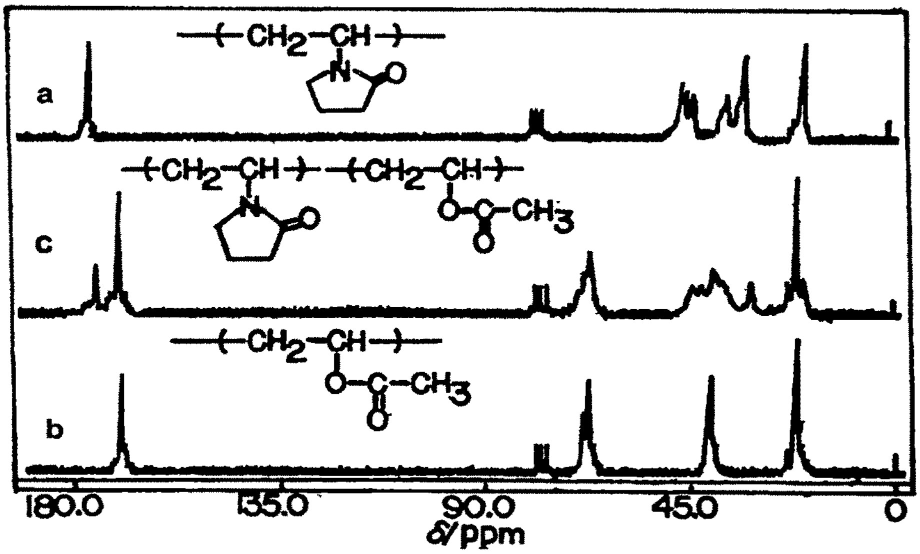


Figure 4.6 : Representative ^{13}C-NMR of (a) PVP, (b) PVAc and (c) copolymer P(VP-VAc) 20:80 (v/v) feed ratio.

The copolymer compositions have been calculated from the relative intensities of the carbonyl carbons (C=O) resonance of VP and VAc using the expression :

$$n_1 = \frac{\mathrm{I\ (C{=}O\ of\ VP)}}{[\mathrm{I\ (C{=}O\ of\ VP) + I\ \ (C{=}O\ of\ VAc)}]}$$

where, n_1 is the mole fraction of VP in the copolymer, I (C=O of VP) and I(C=O of VAc) represent the peak intensities of carbonyl carbons of VP and VAc monomeric units respectively. The reactivity ratios were determined by using well known Finemann-Ross (F-R) and Kelen-Tudos (K-T) methods[18,20,23]. The reactivity ratios (r) for the copolymerization of VP and VAc were found to be r_1=0.844 and r_2=0.343 respectively by K-T method. F-R method yielded a value of r_1 = 0.799 and r_2 = 0.303 respectively. The reactivity ratios r_1 and r_2 of VP and VAc in the copolymers obtained by the solution polymerization were found to be 0.189 and 0.169 (Table 4.3) respectively by ^{1}H-NMR spectroscopy. The change in the values of r_1 and r_2 indicate that the reaction mechanism of the polymerization by both the processes are quite different. However, the errors in r_1 and r_2 are generally high and hence more research is needed before a definite conclusion is arrived. The value of r_1r_2 by μE polymerization is ~0.25 indicating a reasonably random distribution of the monomeric molecules in the copolymer, whereas, the copolymer showed tendency towards alternate arrangement when synthesized through solution polymerization, where value of r_1r_2 is ~0.03. For the case of solution polymerization, both the monomers are in the same phase and hence availability of the monomers to react with each other are equal. Beside low and nearby values of r_1 and r_2 can allow both the monomers to react in the alternate fashion. While in the case of microemulsion polymerization, the monomers are either in droplet or in bulk phase and hence availability of both the monomers to form copolymers are not equal which leads to formation of random copolymers.

(d) TGA analysis :

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 4.7. 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 stability. 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.[34,35] The equation used for the calculation of the activation energy (E_a) was

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

where

$$Y'' = (W_t - W_\infty) / (W_o - W_\infty) \qquad (13)$$

that is, Y" is the fraction of the number of initial molecules not yet decomposed; W_t is the weight at any time '*t*' is W_∞ is the weight at infinite time (=zero); and W_0 is 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 4.8. The values for the activation energy of decomposition were evaluated at three different heating rates of 10, 15 and 20°C min^{-1} in air and are listed in Table 4.6.

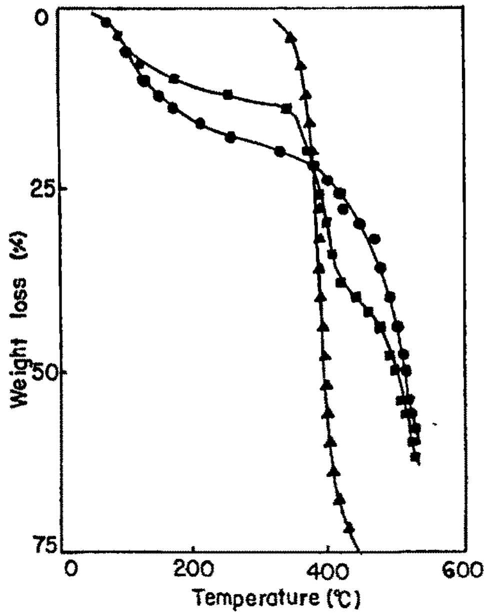


Figure 4.7 : Representative TGA plots of (▲) PVAc, (●) PVP, and (■) copolymer S3 at heating rate of 10K min^{-1} in air.

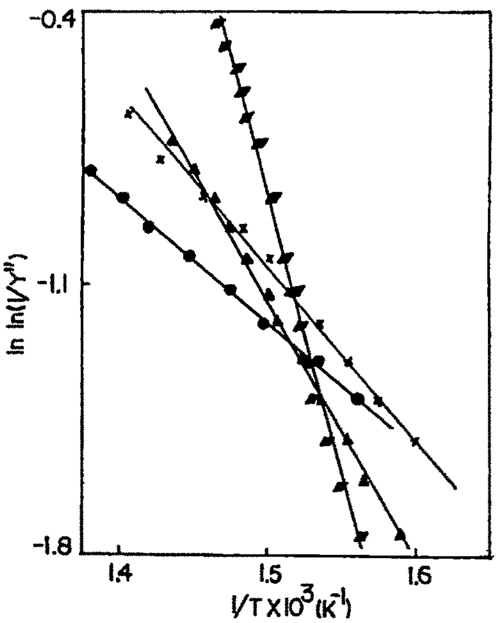


Figure 4.8 : Activation energy plot for the copolymers : (●) S1; (X) S2; (▲) S3; (■) S4.

Table 4.6 : 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.

See Table 4.1 and text for symbols.

(e) Swelling studies :

The swelling is a measure of interaction between 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[13,36]. The swelling data of P(VP-VAc) copolymers in various hydrocarbons as solvents, are shown in Figure 4.9. 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 4.7, 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 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 following equation[13] :

$$Q = \frac{W - W_0}{W_0} \frac{1}{d} \qquad (14)$$

where Q is the swelling coefficient; W is the weight of the swollen polymer; W_0 is the initial weigh of the polymer prior to swelling; and d is the density of the solvent used. The values obtained for the swelling and the swelling coefficients are shown in Tables (4.7 & 4.8). All measurements were in duplicate. It is observed from Tables 4.7 and 4.8 that the percent swelling shows same trend in copolymers obtained by both solution and μE processes. However, the copolymers synthesized in μE medium show relatively higher values than that of the corresponding copolymers synthesized in solution. This could be due to random distribution of monomeric units in μE copolymers which lead to more porous structure and hence higher swelling. The random distribution of the monomers will necessarily make the packing of the molecules in the copolymer a bit loose making porosity high. Alternate distribution will help in close packing. Hence high swelling in μE polymerization product (loose packing) and less swelling in solution polymerization product (close packing).

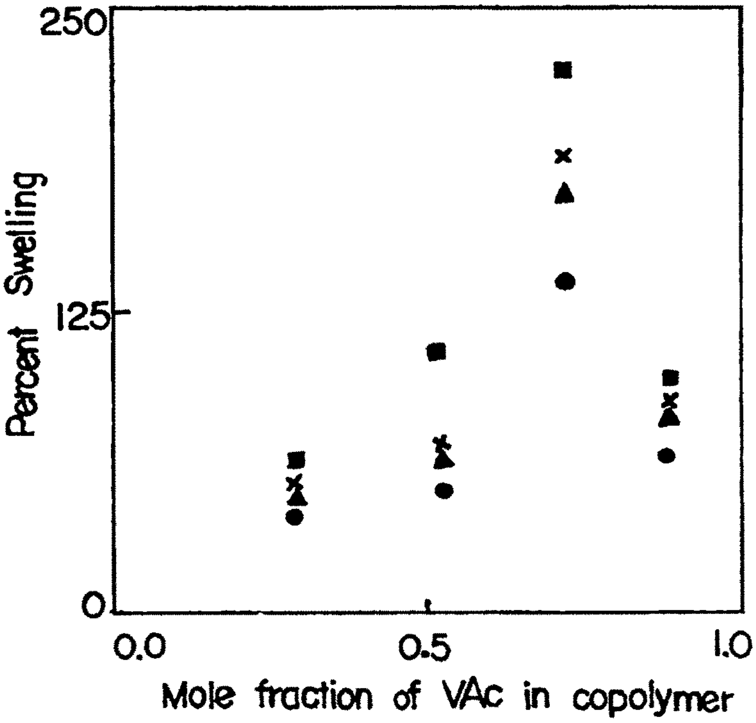


Figure 4.9 : Swelling behavior of copolymers in solvents : (●) *n*-hexane; (▲) *n*-heptane; (X) *n*-octane; (■) *n*-nonane.

Table 4.7 : Swelling Measurements of P(VP-VAc) Copolymers Synthesized in Solution Using Different Solvents at Room Temperature

Polymer Samples	Swelling Time (h)	Density of the Polymer ρ (g mL^{-1})	Solvent Used							
			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

See Table 4.1 and text for symbols.

Table 4.8 : Swelling Measurements of Nonhydrolysed Copolymers Synthesized in µE Medium Using Different Solvents at Room Temperature for Period of 25 Hours

Polymer Samples	Solvent Used							
	n-hexane (0.659)[a] (7.30)[b]		*n*-heptane (0.684)[a] (7.45)[b]		*n*-octane (0.703)[a] (7.55)[b]		*n*-nonane (0.718)[a] (7.65)[b]	
	S[c]	Q[d]	S[c]	Q[d]	S[c]	Q[d]	S[c]	Q[d]
NP1 (VP:VAc) (60 : 40)	81.5	1.237	98.1	1.434	107.1	1.523	129.8	1.808
NP2 (VP:VAc) (40 : 60)	138.8	2.091	154.3	2.255	169.0	2.404	225.7	3.143
NP3 (VP:VAc) (20 : 80)	120.6	1.829	149.8	2.190	164.6	2.341	185.1	2.578

[a]solvent density; [b]solubility parameter; [c]percent swelling; [d]swelling coefficient

(f) Viscosity measurements :

In Table 4.9, the intrinsic viscosities [η] of all systems at various temperatures are given. They were computed by the well known procedure.[37] The accuracy of the data was checked by calculating K' and K", and their differences were 0.5, as expected (Fig. 4.10).[38] The correlation coefficient was always 0.99 or better. It can be seen that [η] decreases as the temperature increases and [η] 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.

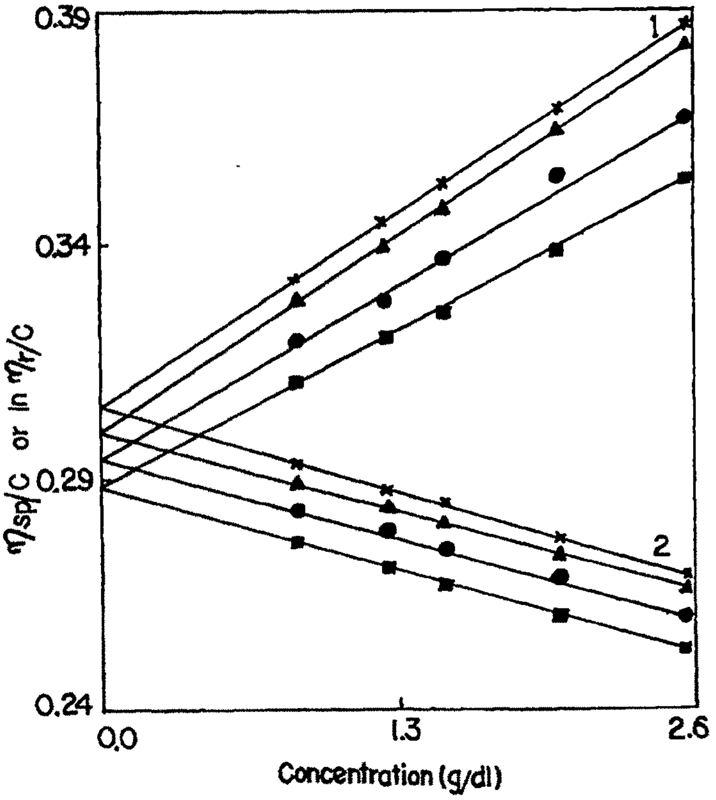


Figure 4.10 : Typical plot of (1) η_{sp}/C and (2) $\ln \eta_r/C$ against concentration for copolymer S3 : (X) 30°C; (▲) 35°C; (●) 40°C; (■) 45°C.

Table 4.9 : Intrinsic Viscosities of Various Copolymers and the Homopolymers at Different Temperatures in Chloroform

Polymer Samples	$[\eta]$ (dL g^{-1})				K'-K"
	30°C	35°C	40°C	45°C	(35°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

See Table 4.1 and text for symbols.

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

$$\eta = \frac{Nh}{V} \exp\left(\Delta G^{\neq}_{vis}/RT\right) \qquad (15)$$

was used to evaluate various activation parameters of the viscous flow[39] where V is the molar volume of the solution; N is Avogadro's number; h is Planck's constant; R is the gas constant; T is the temperature; and $\Delta G^{\neq}_{vis}$ is the activation free-energy change of the viscous flow. The above equation can be rewritten as

$$\begin{aligned} \ln(\eta V/Nh) &= \Delta G^{\neq}_{vis}/RT \\ &= \Delta H^{\neq}_{vis}/RT - \Delta S^{\neq}_{vis}/R \qquad (16) \end{aligned}$$

where $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ are the activation enthalpy and the entropy change for the viscous flow, respectively. V is the molar volume of the solution and was taken as equal to the molar volume of the solvent[40]. The plot of $\ln(\eta V/Nh)$ against T^{-1} shows linearity with correlation coefficients of 0.99 or better for all systems (Fig. 4.11). The slope and intercept gave $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$, respectively. The calculated values of $\Delta G^{\neq}_{vis}$, $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ for some representative systems at a concentration of 0.5 g dL^{-1} are listed in Table 4.10. The $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ 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 4.10). 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 $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ of this system seem to be almost same for all copolymers and both homopolymers with an average value

Table 4.10 : Free Energy $\Delta G^{\neq}_{vis}$, Enthalpy $\Delta H^{\neq}_{vis}$ and Entropy $\Delta S^{\neq}_{vis}$ of Activation for Viscous Flow of the P(VP-VAc) Copolymers and Respective Homopolymers in Chloroform

Polymer Samples	$\Delta G^{\neq}_{vis}$ (kJ mol^{-1})				$\Delta H^{\neq}_{vis}$ (kJ mol^{-1})	$\Delta S^{\neq}_{vis}$ (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}.
See Table 4.1 and text for symbols.

of 5.9 ± 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 $\Delta G^{\neq}_{vis}$ at all temperatures can, hence, be calculated.

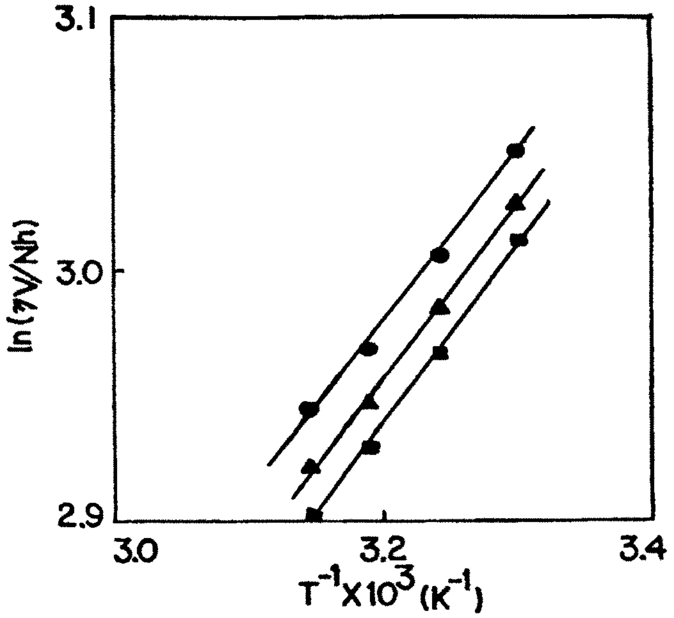


Figure 4.11 : Plots of ln(ηV/Nh) against 1/T for 0.5 g dL^{-1} solutions in $CHCl_3$: (●) PVP; (▲) S2; (■) S4.

The viscosity of a reasonably dilute polymer (synthesized in microemulsion medium) solutions is also related to the polymer concentration by the Huggins and Kreamer equations (Fig.4.12). The viscosity average molecular weights (Table 4.11) were evaluated by using the Mark-Houwink relationship, $[\eta]=KM^{\alpha}$. The reported values of K and α in chloroform for PVP at 25°C were used[41], as K and α for copolymers are not available[42]. The intrinsic viscosities of all the copolymers (NPs & HPs) in chloroform increase with increase in temperature. However, in water, the intrinsic viscosity decreases 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

Table 4.11 : The Viscosity Parameters viz. Intrinsic Viscosity '[η]', Hydrodynamic Volume 'V_E', Shape Factor 'ν' and Viscosity Average Molecular Weight 'M_v' of Various Polymers at 30°C in Chloroform and Water

CHCl$_3$						H$_2$O				
Polymer Samples	[η] dLg^{-1}	ν	V_E dLg^{-1}	K'-K"	Mol. Wt.^{b} (M_v x 10^{-4})	Polymer Samples	[η] dLg^{-1}	ν	V_E dLg^{-1}	K'-K"
PVP^a	0.368	2.6	0.145	0.51	13.24	PVP^a	0.352	2.6	0.138	0.51
NP1 {(VP:VAc) (60 : 40)}	0.293	2.5	0.116	0.48	9.27	NP1	0.256	2.5	0.101	0.50
NP2 {(VP:VAc) (40 : 60)}	0.215	2.5	0.086	0.50	5.72	HP1	0.297	2.5	0.118	0.50
NP3 {(VP:VAc) (20 : 80)}	0.335	2.5	0.133	0.52	11.43	NP3	0.322	2.5	0.126	0.46
PVA^b	0.366	2.6	0.232	0.49	7.11^c	HP3	0.242	2.5	0.100	0.50

[a] Polymers were obtained by solution polymerization technique.

[b] Calculated using K and α values for PVP at 25°C in chloroform. The values are 19.4 x 10^{-3} and 0.64 respectively.

[c] K and α values for PVAc at 25°C in chloroform are 16.2 x 10^{-3} and 0.74 respectively.

results in uncoiling of the polymer chains and hence increase in [η] with temperature[18] (as observed in chloroform solution, Fig. 4.13). 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 [η] with increase in temperature (as observed in water solutions, Fig. 4.13). Thus an increase in temperature of a polymer solution generally generates two effects opposing one another. The variation of [η] with temperature will be dependant on the relative importance of these two effects[18]. The intrinsic viscocities of non hydrolysed copolymers (NPs) and hydrolysed copolymers (HPs) are presented (Table 4.11). The intrinsic viscosities in a solvent is a function of interaction between polymer and solvent as well as among the polymer chains. Due to hydrolysis, the copolymers have VP, VAc and VA moieties. Depending upon the interaction of these moieties with water as well as among themselves, the intrinsic viscosity values do change as seen from Table 4.11. The PVP and NPs have higher [η] in $CHCl_3$ than in water indicating that relatively speaking nonhydrolysed polymers do not favour water as solvent.

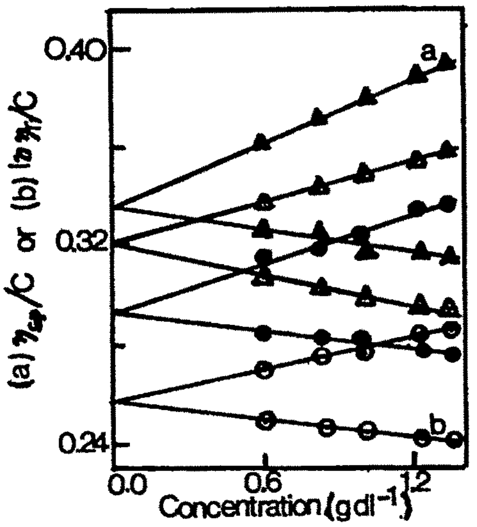


Figure 4.12 : Plot of η_{sp}/C or $\ln\eta_r/C$ vs concentration for : (□) NP2 & (Δ) NP4 in H_2O; (●) HP2 & (▲) HP4 in $CHCl_3$

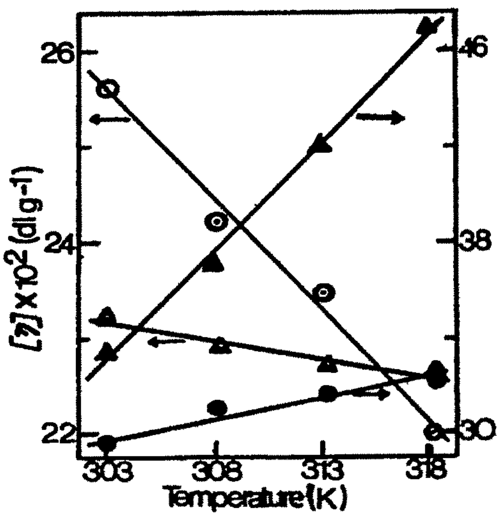


Figure 4.13 : Plot of [η] vs temperature for (□) NP2 & (Δ) NP4 in H_2O; (●) HP2 & (▲) HP4 in $CHCl_3$

Relative viscosity data at different concentrations were also used to calculate the voluminosity, V_E, of the polymer solutions at different temperatures in chloroform (Tables 4.11 & 4.12). V_E was calculated by plotting ψ against the concentration (in g dL^{-1}), where

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

The straight line obtained was then extrapolated to C=O and the intercept yielded V_E (Fig. 4.14). The shape factor (ν) was obtained from the equation[33,40-42]

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

Table 4.12 : Hydrodynamic Volumes (V_E) and Shape Factors (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

See Table 4.1 and text for symbols.

The shape factor gives an idea about the shape of the polymer molecules in solution.[43] The shape factors in different temperatures were found to be 2.5 ± 0.2, suggesting that the macromolecules acquire a spherical conformation.[44] Moreover, the ν values were found to be independent of temperature, suggesting that the conformation was not dependent on temperature. The voluminosity (Table 4.12) is a function of temperature. V_E is a measure of volume of solvated polymer molecules.[45] As the temperature increases, desolvation takes place and, hence, V_E decreases. In our systems, the V_E also decreases with increase in temperature, indicating desolvation (Table 4.12).

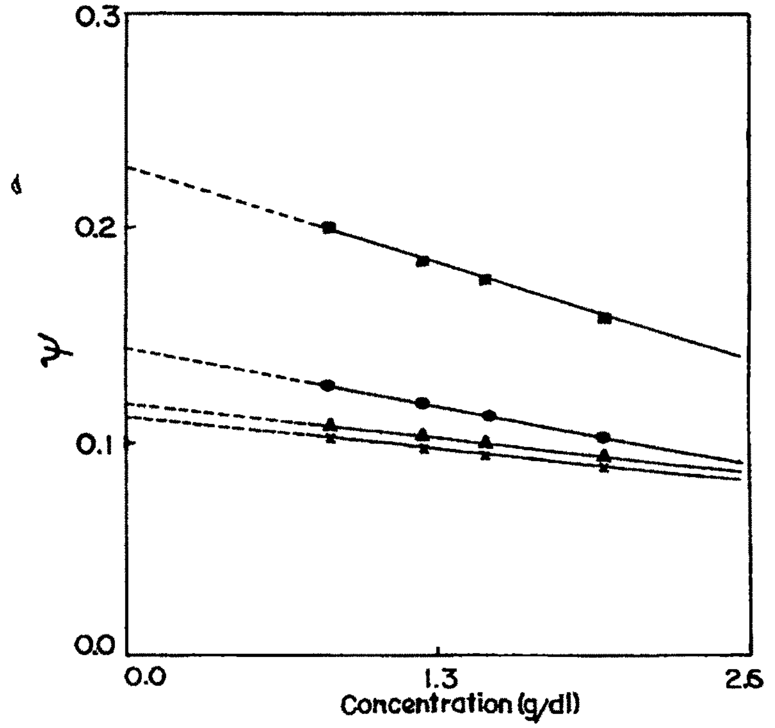


Figure 4.14 : Plot of ψ versus concentration of polymers : (■) PVAc; (●) PVP; (▲) S3; (X) S4.

4.6 Conclusion

On the basis of the above mentioned results, it can be concluded that the free-radical copolymerization reaction of VP and VAc systems follows the classical copolymerization theory. FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy provided evidence for the structure of the copolymers. The reactivity ratios of the monomers were obtained by both elemental analysis and NMR spectroscopy and did show relatively higher reactivity ratio of VP from that of VAc. The monomer units in the copolymer (synthesized in solution) show a tendency toward alternation and the composition of the copolymer does not seem to vary with time. The change in the values of r_1 and r_2 (for solution and microemulsion medium) indicate that the reaction mechanism of the polymerization by both the processes may be quite different. The activation energy of decomposition, viscosity activation parameters, and shape factors were obtained by TGA and solution viscosity studies respectively. The viscosity activation parameters indicate that the polymers in chloroform solutions are not crosslinked and the structure of homopolymer and copolymer solutions are similar.

4.7 References

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