Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Singh, Paramjit and Sawhney, Harjot K.(1994) 'Studies on Copolymerization of Acrylamide and *N*-Vinylpyrrolidone', Journal of Macromolecular Science, Part A, 31: 5, 613 — 627

To link to this Article: DOI: 10.1080/10601329409349742

URL: http://dx.doi.org/10.1080/10601329409349742

J.M.S.—PURE APPL. CHEM., A31(5), pp. 613–627 (1994)

STUDIES ON COPOLYMERIZATION OF ACRYLAMIDE AND *N*-VINYLPYRROLIDONE

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ABSTRACT

Copolymers of acrylamide and *N*-vinylpyrrolidone were prepared using different techniques, viz., solution, precipitation, and inverse emulsion. Xylene was used as a continuous medium and sorbitane monooleate as a surfactant for the inverse emulsion technique. Acetone was used as a solvent in the precipitation technique. The initiator used in all the reactions was 2,2-azobis(2-amidinopropane)dihydrochloride. C, H, and N elemental analysis was used to determine the compositions of the copolymers formed. Reactivity ratios as determined by the Fineman and Ross method were found to be 0.61 and 0.05 for acrylamide and *n*-vinylpyrrolidone, respectively. Intrinsic viscosity measurements were made at temperatures ranging from 16 to 75°C.

INTRODUCTION

Acrylamide (AAM) copolymers with N-vinylpyrrolidone (NVP) have important applications in enhanced oil recovery processes including mobility control, polymer flooding, etc. [1, 3]. NVP is widely used as a comonomer for modifying less expensive monomers. It enhances the hydrophilicity of the copolymer system. It helps in improving adhesion to substrates such as metals, glass, nylon, etc. [4–8].

Most literature studies on the copolymerization of the AAM-NVP system relate to aqueous solution polymerization using various initiators. Stahl [2] used azo initiators at various temperatures, Azorlosa [4] used AIBN, while Moens and

Smets [5] and then Sullivan [6] used organic peroxides. Clark [9] followed the inverse emulsion technique using AAM, NVP, and sodium-2-acrylamido-2-methylpropanesulfonate monomers in the presence of redox initiators. The emulsifying agent was comprised of sorbitane fatty acid esters and ethoxylated alcohol. The reaction was carried out at 50°C for 20 hours. Rosiak et al. [10] used γ-radiation for copolymerization in aqueous solution.

Igarashi et al. [11] used the AAM-NVP copolymer in the determination of albumins, and Detwiler et al. [12] used it for the determination of bilirubin. Watson et al. [13] modified polyelectrolytes containing the anhydride group with this copolymer and subsequently used them as flocculants.

Cvetkovska et al. [14] copolymerized AAM and NVP in order to synthesize macroinitiators with surface-active characteristics. Schulz et al. [15] described the effect of NVP units on the hydrolytic stability and viscosification ability of acrylamide copolymers. Kiyotani et al. [16] used this copolymer as a hydrophilic coating agent for aluminum fins in heat exchangers.

The theory and practice of acrylamide-based copolymer synthesis [17] and their potential applications in industry and agriculture have recently been reviewed [18]. Chatterjee and Burns [8] reported reactivity ratios for aqueous solution copolymerization of AAM and NVP as 0.66 and 0.17, respectively.

Solution, precipitation, and inverse emulsion techniques were employed in this work to synthesize these copolymers, using the water-soluble initiator 2,2-azobis(2-amidinopropane)dihydrochloride, and characterized them primarily for their viscosities in the presence of salts to assess their suitability for applications in fields where appreciable salt concentrations exist, e.g., in enhanced oil recovery, agricultural applications, etc.

EXPERIMENTAL

Materials Used

N-Vinylpyrrolidone (Fluka) was purified by distillation under reduced pressure (4 mmHg at 110°C). Acrylamide (Loba); water-soluble free-radical polymerization initiator 2,2-azobis(2-amidinopropane)dihydrochloride (V-50, Wako Pure Chemicals); sorbitane monooleate (SMO, Span 80, Fluka); bis(2-ethyl hexyl) sulfosuccinate sodium salt (Aerosol OT, Fluka); sulfur-free xylene (E. Merck); EDTA (Fluka); and acetone (BDH) were all used as received. Double distilled water was used throughout.

Polymerization and Characterization

Acrylamide and *N*-vinylpyrrolidone were copolymerized at temperatures ranging from 40 to 56°C by using polymerization techniques such as solution, precipitation, and inverse emulsion. The monomers were taken in different molar ratios, viz., 90:10, 70:30, 50:50, 30:70, and 10:90, with concentrations ranging from 5 to 15 wt%. The initiator concentrations used varied from 0.5 to 4 mmol/L of the reaction mixture. Xylene was used as the continuous phase in batch inverse emulsion copolymerizations. Span 80 (5 wt% of the oil phase) and Aerosol OT (1 wt% of the oil phase) were used as surfactants. The water-to-oil ratio was varied from 60:40 to

40:60. Acetone was used as the polymerization medium in the precipitation method. The samples withdrawn periodically were precipitated in acetone, filtered, and dried in vacuum oven at 35–40°C for 48 hours. The conversions were estimated by C, H, and N analysis. Various reaction conditions are presented in Table 1.

An Ubbelohde viscometer was used for the determination of intrinsic viscosities in the 16 to 75°C ± 0.01 temperature range. The initial concentration of the sample taken was 0.7 g/100 mL, and the concentration after the final dilution was not allowed to be below 0.05 g/100 mL. Viscosity determinations were made in water, 0.1 N HCl, 0.1 N NaCl, and 1.0 N NaCl.

RESULTS AND DISCUSSION

Emulsion Stability

Acrylamide and *N*-vinylpyrrolidone in molar ratios varying from 10:90 to 90:10 and at an overall monomer concentration of 7.5% were dissolved in water. This water phase was slowly poured into the oil phase containing xylene and Span 80. Stable emulsions were obtained after stirring for about 20 minutes. Various phase ratios were tried to improve the stability of the emulsions, and it was found that the stability decreased with an increasing proportion of water in the emulsion. Thus, the stability was the best for a water:oil phase ratio of 40:60, and it decreased progressively as the phase ratio was increased to 50:50 or 60:40. The conversions were predominantly lowered in the presence of Aerosol OT as the cosurfactant.

Reactivity Ratios

The reactivity ratios were estimated by the Fineman and Ross method using a least-squares fit to yield $r_1 = 0.61$ for AAM and $r_2 = 0.05$ for NVP, with a correlation coefficient of 0.99. The data are tabulated in Table 2 and plotted in Fig. 1.

Conversion–Time Curves

The conversion–time data for the system AAM-NVP for the molar ratios 10:90, 30:70, and 70:30 are plotted in Fig. 2. In the inverse emulsion copolymerization of AAM and NVP in a molar ratio of 90:10, the system was inverted after about 20 minutes. The system yielded 71% of the product after 3 hours of reaction time when the monomers were taken in a molar ratio of 70:30, while 58 and 13% conversions were obtained at molar ratios of 30:70 and 10:90, respectively, in the same reaction time.

Conversion–Composition Data

Instantaneous copolymer compositions (F_1) were calculated for assumed discrete values of comonomer composition (f_1) from the reactivity ratios derived experimentally. Similarly, F_1 was calculated using reactivity ratios obtained from the literature for corresponding values of f_1. The experimental values of F_1 at time t for conversions of less than 10% for various monomer molar ratios were obtained from C, H, and N analysis, making the assumption that in this low conversion range the

TABLE 1. Reaction Conditions for Copolymerization of AAM with NVP

No.	Reaction type	Molar ratio, AAM:NVP	Monomer concentration, %	Temperature, °C	Initiator, mmol/L	Comments
1	Solution	70:30	5.0	40	1.0	Viscous solution
2	Solution	70:30	5.0	40	1.0[c]	Viscous solution
3	Inverse emulsion[a]	10:90	7.5	50	1.0	Stable emulsion
4	Inverse emulsion	30:70	7.5	50	1.0	Stable emulsion
5	Inverse emulsion	70:30	7.5	50	1.0	Stable emulsion
6	Inverse emulsion	90:10	7.5	50	1.0	Coagulum (26.8%)
7	Inverse emulsion	70:30	10.0	40	0.5	Coagulum (31.1%)
8	Inverse emulsion	70:30	10.0	40	0.5[d]	Coagulum (21.8%)
9	Inverse emulsion	70:30	10.0	40	1.0[d]	Coagulum (7.3%)
10	Inverse emulsion	90:10	15.0	40	1.0	Gel (37.9%)
11	Inverse emulsion	50:50	15.0	50	1.0	Gel (37.9%)
12	Precipitation[b]	70:30	15.0	50	4.0[e]	Precipitates, 40% conversion
13	Precipitation	70:30	15.0	56	4.0[e]	Precipitates, 82% conversion

[a] Water:oil phase ratio, 60:40.
[b] Water:acetone phase ratio, 40:60.
[c] Buffer used: 0.1 mol/L.
[d] Buffer used: 0.05 mol/L.
[e] Buffer used: 0.01 mol/L.

TABLE 2. Variation of Copolymer Composition with Comonomer Composition [component 1 = acrylamide (AAM), component 2 = *N*-vinylpyrrolidone (NVP)]

Experimental		Theoretical	
		$r_1 = 0.61$ $r_2 = 0.05$	$r_1 = 0.66$ $r_2 = 0.17$
f_1	F_1	F_1	F_1
0.1	0.44	0.42	0.29
0.3	–	0.53	0.48
0.5	0.64	0.61	0.58
0.7	0.71	0.70	0.70
0.9	–	0.87	0.87

average copolymer composition is about the same as the instantaneous copolymer composition. The data have been summarized in Table 2 for AAM:NVP molar ratios of 10:90, 30:70, 50:50, 70:30, and 90:10 and plotted in Fig. 3. Both F_1 and $<F_1>$, computed as a function of conversion corresponding to the reactivity ratios determined in this work for the monomer molar ratios 30:70, 70:30, and 90:10, have been plotted in Figs. 4 and 5. The experimental values of $<F_1>$ for molar ratios 30:70 and 70:30 were directly obtained from C, H, and N analysis. The overall average copolymer composition $<F_1>$ decreases with conversion for the

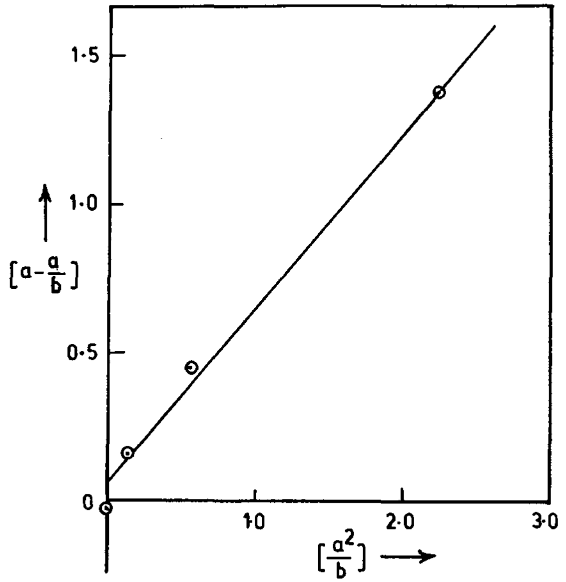

FIG. 1. Fineman and Ross plot for the system AAM and NVP. $a = f_1/f_2$; $b = F_1/F_2$.

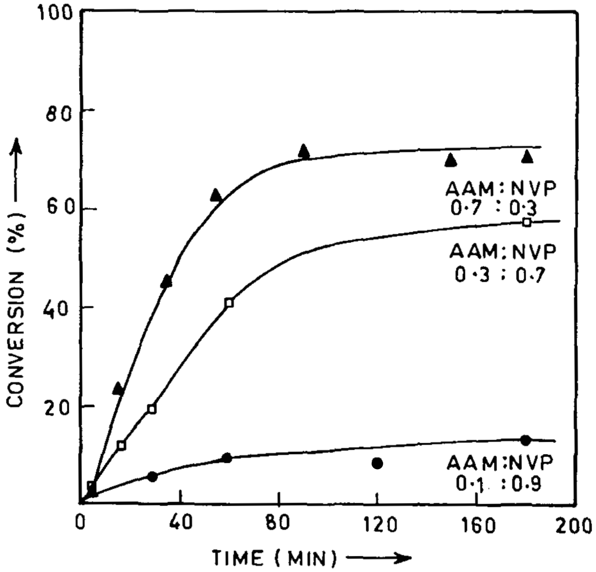

FIG. 2. Conversion-time curves for AAM and NVP system. Reaction conditions: temperature = 50°C, monomer concentration = 7.5%, and initiator concentration = 1 mmol/L.

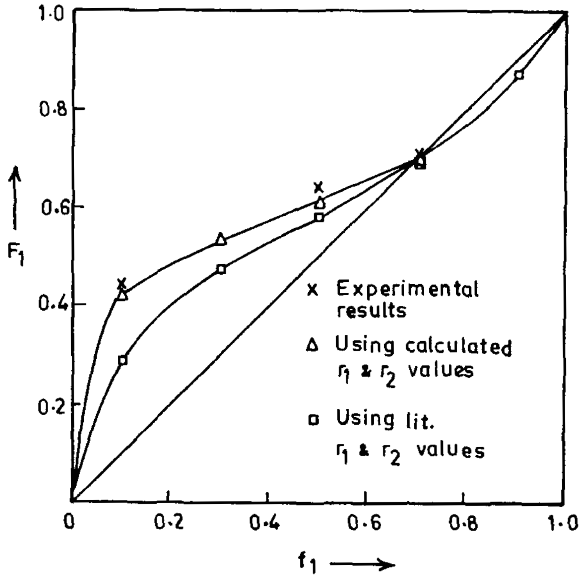

FIG. 3. Variation of copolymer composition with comonomer composition. Component 1 = AAM, component 2 = NVP.

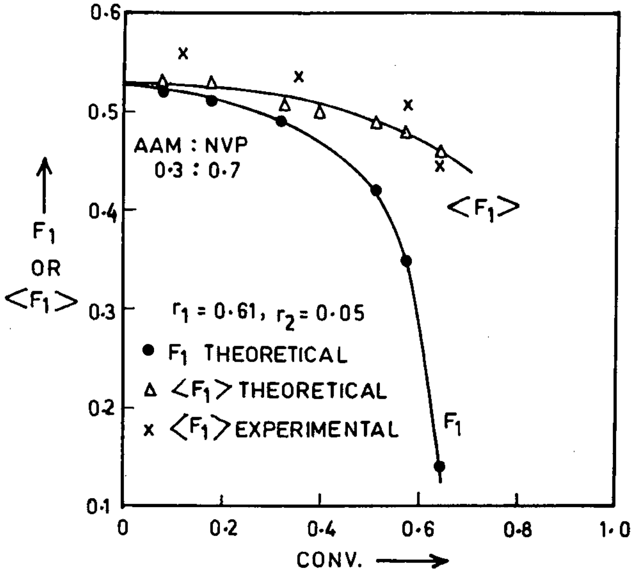

FIG. 4. Variation of overall average $<F_1>$ and instantaneous copolymer composition F_1 with conversion for comonomer ratio AAM:NVP = 30:70.

comonomer composition 30:70, while it is almost constant at all conversions when the initial comonomer composition taken is 70:30, thereby showing the azeotropic behavior of the system.

Effect of pH on Reaction

It was observed in all cases studied that the pH of the system falls as soon as the initiator is added and remains constant thereafter. In the copolymerization of AAM and NVP, some of the pyrrolidone units hydrolyze to give aldehyde or acid, thus causing lowering of the system pH. This effect is predominant at lower conversions and in acidic medium. The buffer helps to maintain the electroneutrality of the medium [19]. Figure 6 depicts the effect of pH on the reaction with or without buffer. In solution polymerization, the pH of the mixture remained at approximately 7 throughout the reaction when buffer was used; conversion after 6 hours was 100%. In the absence of buffer, the pH remained less than 5 and the yield after the same reaction time was only 65%.

Precipitation Technique for Polymer Isolation

Nonsolvents such as *t*-butanol, methanol, and acetone were tried for the precipitation of the copolymer. The polymer was precipitated in the form of a cluster when *t*-butanol was used as the nonsolvent. Monagle [19], however, obtained beads of the copolymer by suspension polymerization using *t*-butanol as the continuous medium. Very fine precipitates were recovered with methanol, but the yield was poor. Finely divided powderous precipitates with high yield were obtained when acetone was poured into the polymer solution/emulsion with continuous stirring.

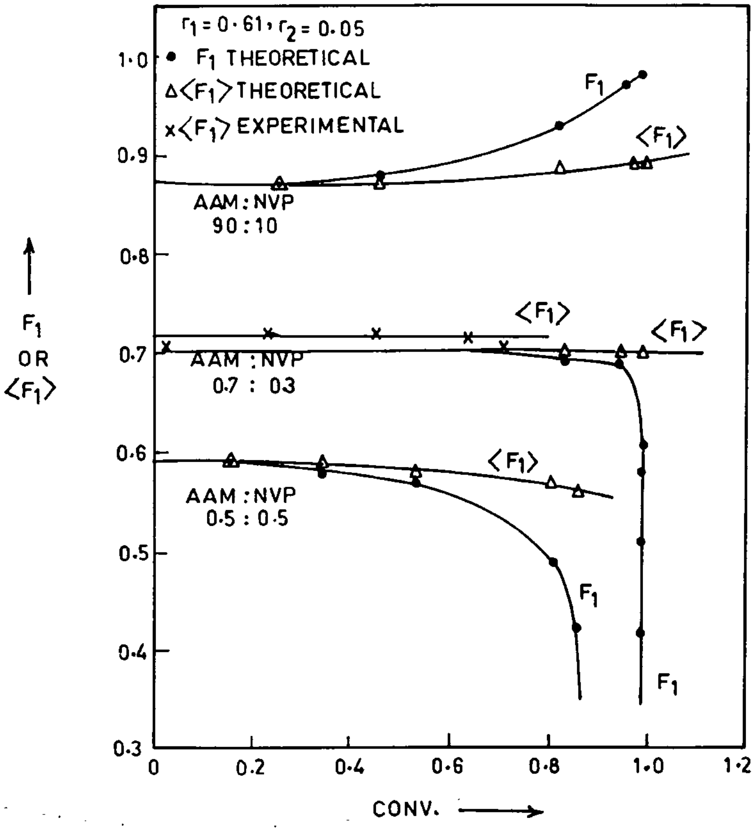

FIG. 5. Variation of overall average $<F_1>$ and instantaneous copolymer composition f_1 with conversion for different comonomer ratios.

Gel Formation

The monomers AAM and NVP in molar ratios of 90:10 and 50:50 with an overall monomer concentration of 15% were copolymerized by inverse emulsion at 40°C in an inert atmosphere for 3 hours. The gels so obtained had equilibrium water contents [EWC = (weight of hydrated gel − weight of dehydrated gel) × 100/weight of hydrated gel] equal to 97.6 and 95.8%, respectively, while the swelling ratio (SR = weight of hydrated gel/weight of dehydrated gel) was equal to 41.8 and 22.2 for the two cases at 25°C. The water loss per day [(weight of hydrated gel − weight of dehydrated gel)/number of days] was about 1 g, which gradually diminished. Percent water retained in the gel as a function of time is plotted in Fig. 7.

Intrinsic Viscosity

Intrinsic viscosities of AAM and NVP copolymers, prepared under different conditions and measured in water and other solvents at 25°C, are tabulated in Tables 3 and 4, and are independent of overall conversion. Viscosities in water at

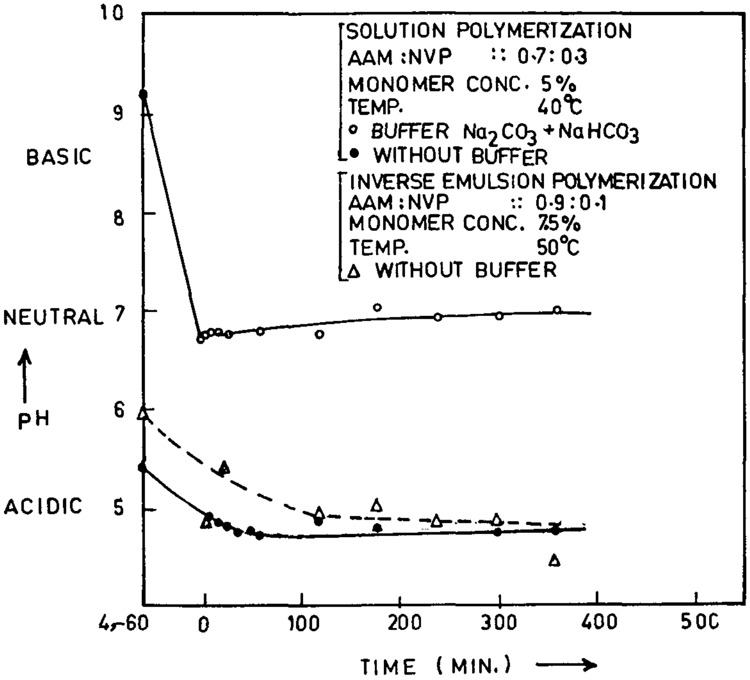

FIG. 6. Variation of pH with time.

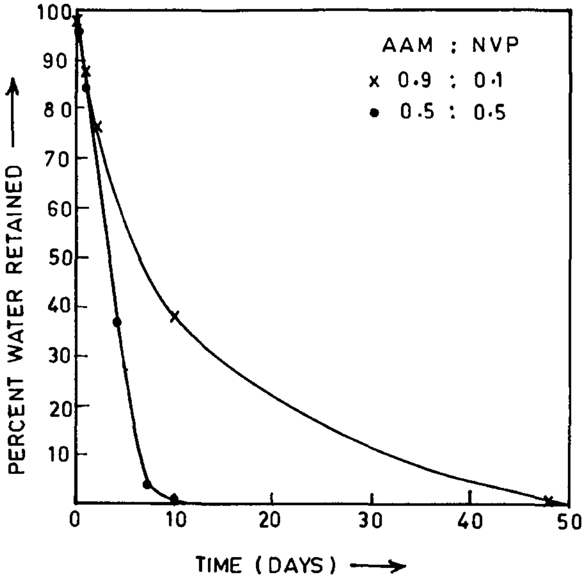

FIG. 7. Percent water retained in the gel over a period of time.

TABLE 3. Intrinsic Viscosities of the Copolymers Prepared from AAM and NVP in a Molar Ratio of 70:30 and a Monomer Concentration of 7.5% at 50°C Using the Inverse Emulsion Technique

No.	Time, minutes	Conversion, %	$[\eta]_{H_2O}^{25°C}$
1	15	21.6	1.64
2	35	45.2	2.43
3	55	62.5	2.47
4	90	71.4	2.45

25°C increase as the proportion of acrylamide in the monomer feed is increased, as seen in Fig. 8. There is no significant difference in viscosities of the copolymer aqueous solutions and salt solutions except when it is prepared by the precipitation technique. On the other hand, in the case of ionic systems such as the copolymer of acrylamide and diallyldimethylammonium chloride, the viscosities in salt solutions exhibit a very significant fall when compared to those in aqueous solutions [20]. The viscosities of the copolymer obtained by the precipitation method are much higher than the copolymer obtained by other techniques, thereby showing that the method of preparation has an effect on intrinsic viscosity.

There is a decrease in the intrinsic viscosity as well as in the specific viscosity of the copolymers in 0.1 N NaCl as the temperature is increased to 75°C. Figures 9 and 10 show, however, that the effect is not pronounced. The trend remains the same when the salt concentration is increased while keeping the sample concentration constant (Fig. 11). The effect of salt concentration in the solvent on the intrinsic

TABLE 4. Intrinsic Viscosities of Copolymers from AAM and NVP Synthesized by Different Techniques and in Various Molar Ratios at 25°C in Water, 0.1 N HCl, and 0.1 N NaCl

Polymerization technique	Feed molar ratio, AAM:NVP	$[\eta]_{H_2O}$	$[\eta]_{HCl}$	$[\eta]_{NaCl}$
Inverse emulsion	10:90	1.43	–	–
	30:70	1.62	–	–
	70:30	2.45	–	–
	90:10	5.43	–	–
Inverse emulsion	70:30	2.45	1.73	2.15
Solution (without buffer)	70:30	2.78	–	2.39
Solution (with buffer)	70:30	4.44	–	–
Precipitation	70:30	6.00	5.44	2.56

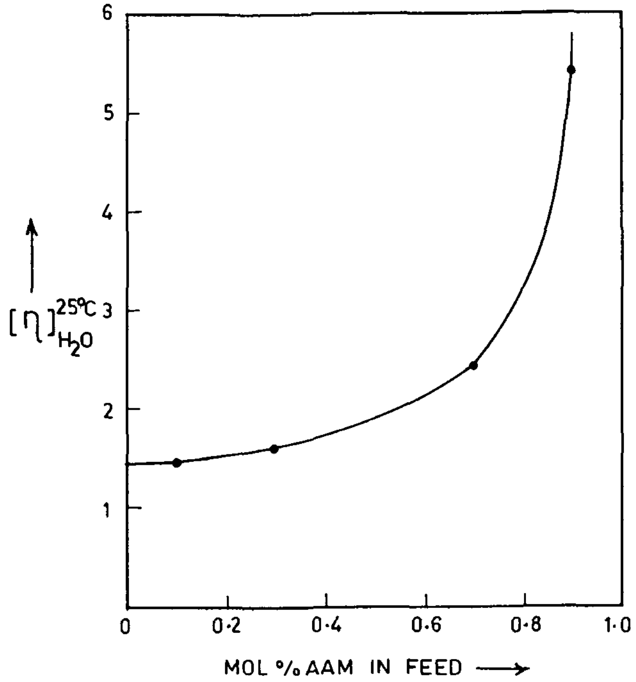

FIG. 8. Intrinsic viscosity of the copolymer (70 mol% AAM, 30 mol% NVP) in water at 25 °C with respect to mol% AAM in feed.

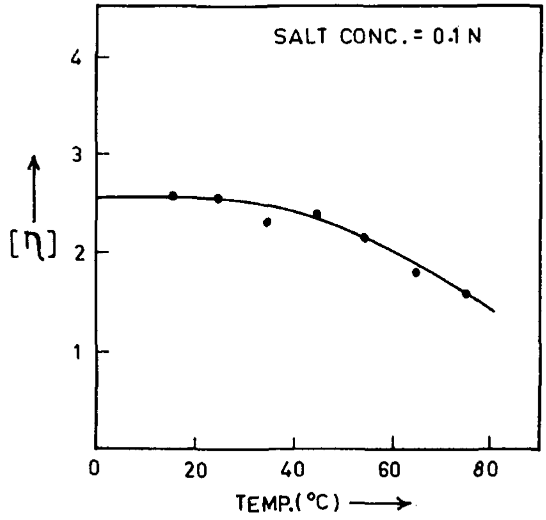

FIG. 9. Change of intrinsic viscosity of the copolymer (70 mol% AAM, 30 mol% NVP) in salt solution with temperature.

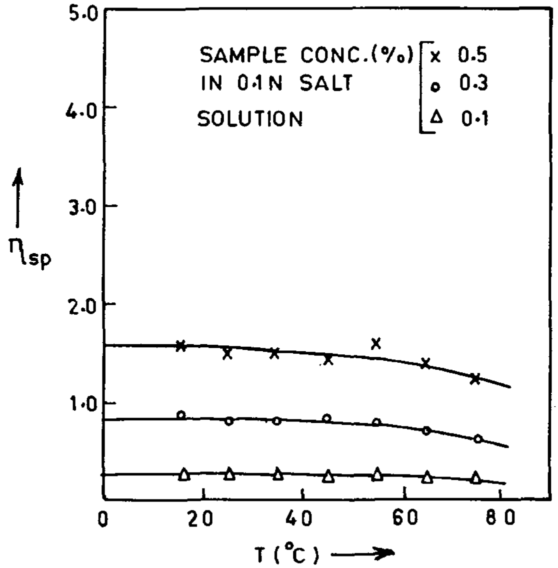

FIG. 10. Variation of specific viscosity of copolymer sample (70 mol% AAM, 30 mol% NVP) with different concentrations in 0.1 N salt solution at various temperatures.

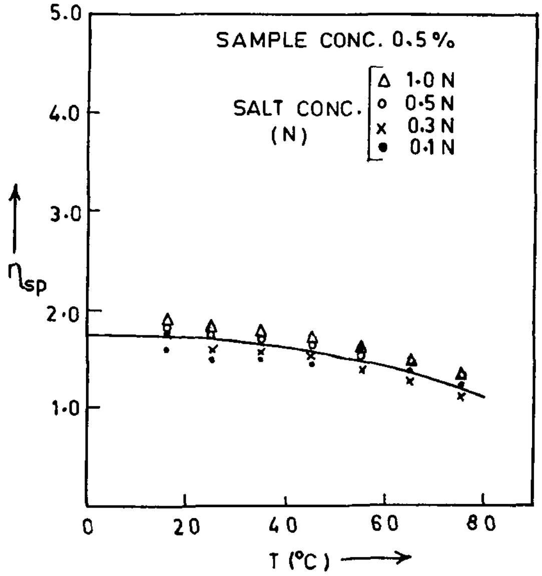

FIG. 11. Variation of specific viscosity of 0.5% copolymer sample (70 mol% AAM, 30 mol% NVP) in different salt concentrations at various temperatures.

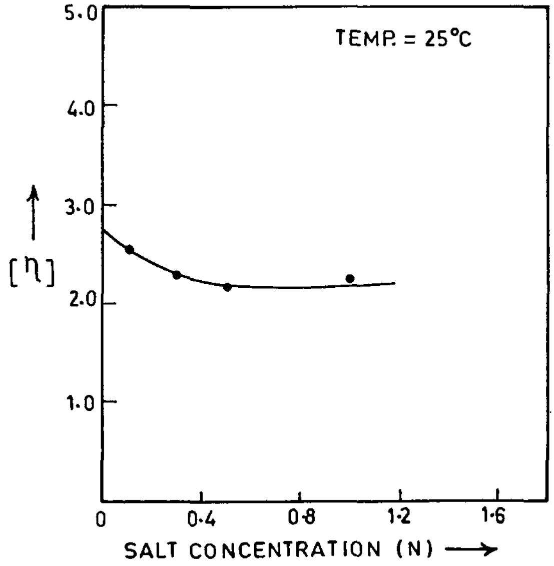

FIG. 12. Intrinsic viscosity of copolymer sample (70 mol% AAM, 30 mol% NVP) in different salt concentrations at 25°C.

viscosity is plotted in Fig. 12. The viscosity initially decreases with enhanced salt concentration, after which it is independent of both the amount of salt added to the system and the aging time in the studied range (Fig. 13). Heating of copolymer in a

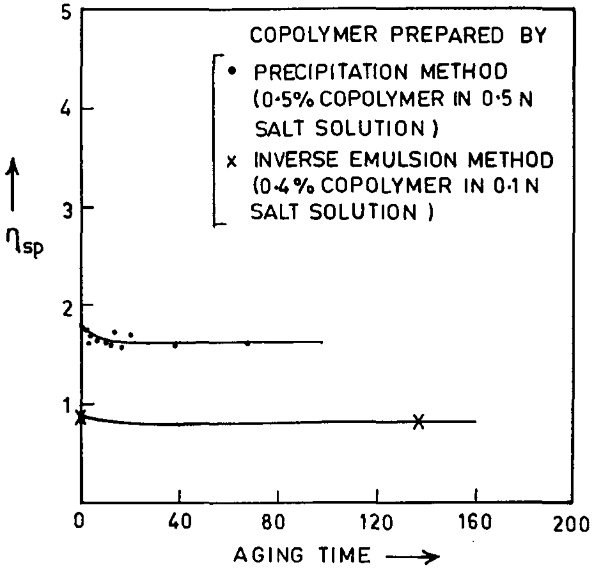

FIG. 13. Specific viscosity of the copolymer (70 mol% AAM, 30 mol% NVP) in salt solution versus aging time.

salt solution at 75°C and refluxing at 120°C for 9 hours caused no precipitation or any other visible change in the solution, and no change in viscosity was observed when it was measured again at 25°C. The trend is also independent of the method of copolymer synthesis.

CONCLUSIONS

1. Solution polymerization was carried out at 5% monomer concentration. The effect of pH on the reaction was studied. Complete conversions were obtained at 5% monomer concentrations.
2. The inverse emulsion technique was used in order to overcome the difficulty of a steep viscosity rise in solution polymerization. Stable emulsions were formed for monomer concentrations ranging from 7.5 to 15%, beyond which the stability decreased and the coagulum formation increased.
3. The reactivity ratios of the system were less than 1, and the values were found to be r_1 (AAM) = 0.61 and r_2 (NVP) = 0.05. Azeotropic formation was observed when monomers AAM and NVP were taken in a molar ratio of 70:30 as predicted by the reactivity ratios.
4. The reaction was successfully run at 15% monomer concentration with the precipitation technique which required a smaller amount of nonsolvent.
5. No significant falls in the viscosities of these copolymers were observed when measured in water or salt solutions at 25 or 75°C and even after refluxing at 120°C, thereby suggesting the suitability of these copolymers for use in more harsh conditions such as in enhanced oil recovery, agricultural applications for water retention, etc.

NOMENCLATURE

AAM	acrylamide (taken as monomer 1)
NVP	*N*-vinylpyrrolidone (taken as monomer 2)
f_1	instantaneous mole fraction of monomer 1 in feed
f_2	instantaneous mole fraction of monomer 2 in feed
F_1	instantaneous mole fraction of monomer 1 in copolymer
F_2	instantaneous mole fraction of monomer 2 in copolymer
$<F>$	average composition of the copolymer formed

ACKNOWLEDGMENTS

The financial support of the Department of Science and Technology (DST), Government of India, and the facilities extended by the Department of Chemical Engineering and Technology, Panjab University, are gratefully acknowledged.

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Received February 11, 1993
Revision received August 24, 1993