

Study on acrylamide-vinyl pyrrolidone copolymer

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S U M M A R Y

The solution copolymerization of acrylamide (AAm) with N-vinyl pyrrolidone (NVP) was investigated using azobisisobutyronitrile (AIBN) as an initiator at 60°C. The study was performed by measuring the rate of the copolymerization reaction, the molecular weights and by determining the monomer reactivity ratios. In addition, the thermal properties (thermal conductivity, thermal diffusivity and volumetric heat capacity) of the resulted copolymers in aqueous solutions were investigated at various temperatures. The kinetic results and the apparent reactivity ratios indicate that NVP is more reactive than AAm towards the copolymerization process. The values of the thermal properties showed that the behaviour of such parameters depend on the polymer concentration, the temperatures and the content of vinyl pyrrolidone in the copolymeric chains.

I N T R O D U C T I O N

Acrylamide (AAm) has assumed increasing industrial importance as a monomer and as a chemical intermediate. It tends to impart the same property to homopolymers and copolymers. Polyacrylamide (PAAm) is especially useful as a flocculant for fine solids suspended in water (DIXON 1967), as a thickening agent (KOLODNY 1961, YASUO 1987), as a pigment-retention aid in paper-making (ELDRED 1968), as a heat stabilizer for polyacetal resins (FUMIHIKO and KENJIRO 1988). Anionic PAAm is used to accelerate the emergence of tomato and lettuce seedlings and increased their dry weights (ARTHUR 1987). Copolymers of AAm are being used in chemical grouts (BIKALES 1965) and for plastic electric resistors (HIROSHI 1987), and with acrylic acid in additives to increase the dry strength of paper (ELDRED 1968). There has been much interest in acrylamide-based photographic systems (OSTER 1969). Acrylamide copolymers are also useful as corrosion inhibitors (AHMAD, 1987) and for preparing thermal recording paper with good water and solvent resistances and with good antisticking properties (SHIGERU 1988). Cationized acrylamide copolymers are used as strengthening agents for neutral paper (YOSHIKI and TOSHIKI 1988).

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These interesting applications of PAAM lead us to study the copolymerization and the properties of AAm-NVP system.

EXPERIMENTAL

Copolymerization

The solution copolymerization of acrylamide (AAm) with N-vinyl pyrrolidone (NVP) in presence of dioxane at 65°C (or ethyl alcohol at 60°C) as solvent initiated by AIBN was carried out by the same method as was reported previously (ABO EL-KHAIR and MOKHTAR 1984). The copolymer compositions were calculated on the basis of the nitrogen content of the copolymers. The apparent reactivity ratios of the copolymer, r_1 and r_2 respectively, were calculated by applying the Fineman-Ross method (FINEMAN and ROSS 1950) and by Kelen-Tudös method (KELEN and TUDÖS 1975).

Thermal properties

An experimental set-up for the simultaneous absolute measurement of the thermal activity (b), thermal diffusivity (a) and volumetric heat capacity (ρc), of polymer solutions with AC heated-wire (strip) technique is used (ATALLA 1981). The measurements were carried out in water at various polymer concentrations in the temperature range 20 to 90°C.

RESULTS AND DISCUSSION

The rate and the interinsic viscosities results for solution copolymerization of acrylamide (AAm) with N-vinyl pyrrolidone (NVP) of different molar ratios in presence of AIBN as an initiator at 65°C are represented in table 1. The rates of the copolymerization reactions were observed to be higher in the system containing higher concentration of NVP in the monomer feed. Also, it is obvious that, the intrinsic viscosity, which is related directly to the molecular weight of the obtained AAm-NVP copolymer, increases with increasing the content of AAm in the reaction medium. These results indicate that the investigated polymerizing system is more efficient to produce copolymer with higher molecular weights with increasing the content of AAm in the monomer feed.

Table 1: The solution copolymerization of acrylamide (AAm) with N-vinyl pyrrolidone (NVP) in dioxane initiated by azobisisobutyronitrile (AIBN) at 65°C.
[dioxane]/[AAm + NVP] = 1:1;
[AIBN] = 5×10^{-3} mole/litre.

$\frac{[AAm]^*}{[NVP]}$	Relative rate	$[\eta]^{**}$ (dl. gm ⁻¹)
100/0.0	1.00	0.550
80/20	2.60	0.492
50/50	3.33	0.418
20/80	4.25	0.244

* In mole %.

** Intrinsic viscosity at 30°C in water as solvent.

Fig. 1 illustrates the monomer-copolymer composition curve for the solution copolymerization of AAm and NVP initiated by AIBN at 60°C. These results were analysed to determine the apparent reactivity ratios of the two monomers by Fineman-Ross method and by Kelen-Tudős method and the obtained data are represented in table 2.

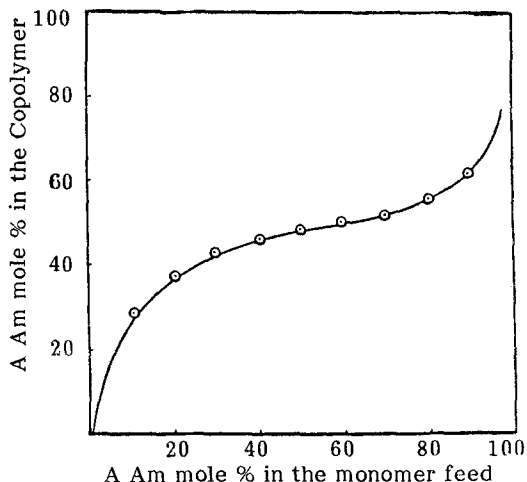


Fig. 1: Monomer/copolymer composition curve for acrylamide (AAm) with N-vinyl pyrrolidone (NVP) solution copolymerization initiated by azobisisobutyronitrile at 60°C. ($[AIBN] = 5 \times 10^{-3}$ mole/litre).

It is clear that, at the initial stages of polymerization, N-vinyl pyrrolidone monomer is more reactive than AAm towards the copolymerization process and this agrees with the obtained kinetic results.

Table 2: Apparent reactivity ratios for the solution copolymerization of acrylamide (AAm) with N-vinyl pyrrolidone (NVP) at 60°C.

Method	apparent reactivity ratios	
	r_{AAm}	r_{NVP}
Fineman-Ross	0.063	$0.157 \pm 1.7 \times 10^{-4}$
Kelen-Tudős*	0.064	$0.156 \pm 1.2 \times 10^{-4}$

* $\alpha = 1.235$

The thermal properties of acrylamide-N-vinyl pyrrolidone (AAm-NVP) copolymer solutions of different molar ratios and with various concentrations in the temperature range 20-90°C were investigated to improve their practical applications (HARUMI 1987). Fig.2 represents the variation of volumetric heat capacity for AAm-NVP copolymer solutions

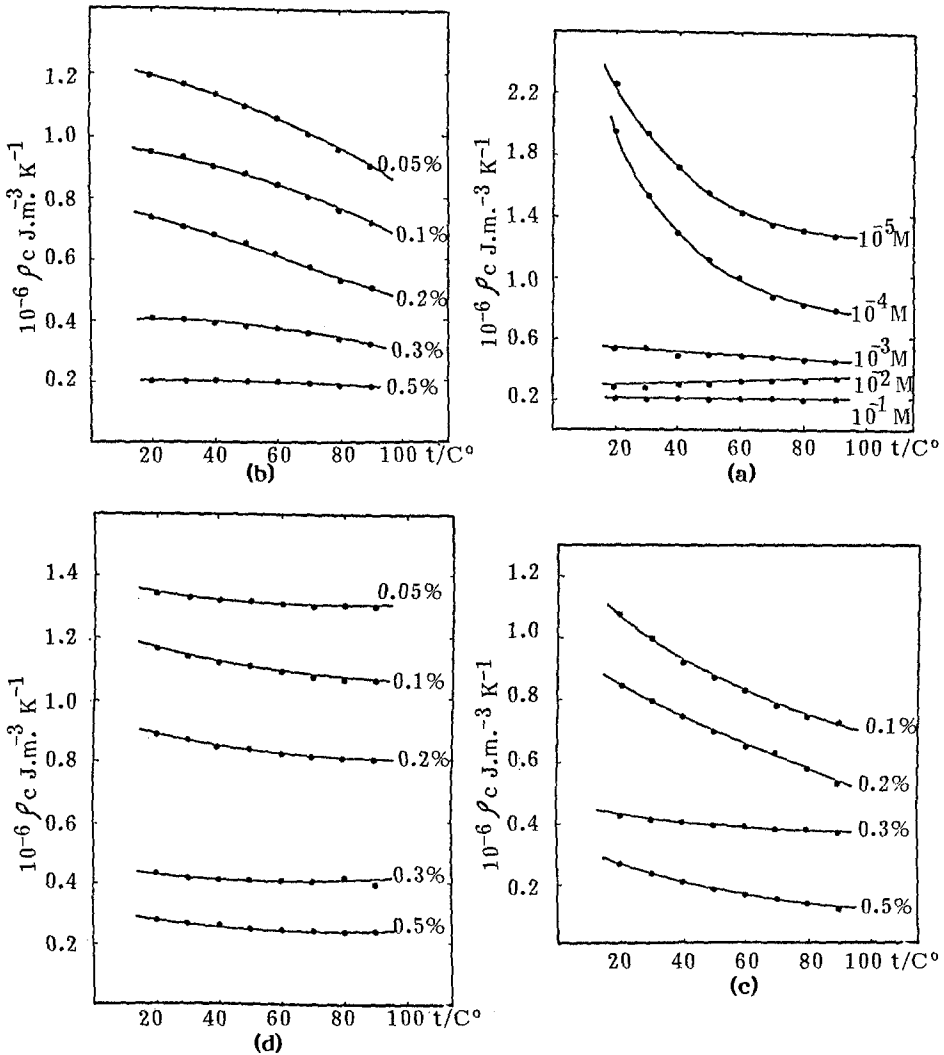


Fig. 2: Variation of volumetric heat capacity of AAm-NVP copolymer solutions (in aqueous media) with temperature:
 (a) [AAm]/[NVP] = 100/0.0; (b) [AAm]/[NVP]* = 70/30;
 (c) [AAm]/[NVP]* = 60/40; and (d) [AAm]/[NVP]* = 50/50.
 * mole % in monomer feed.

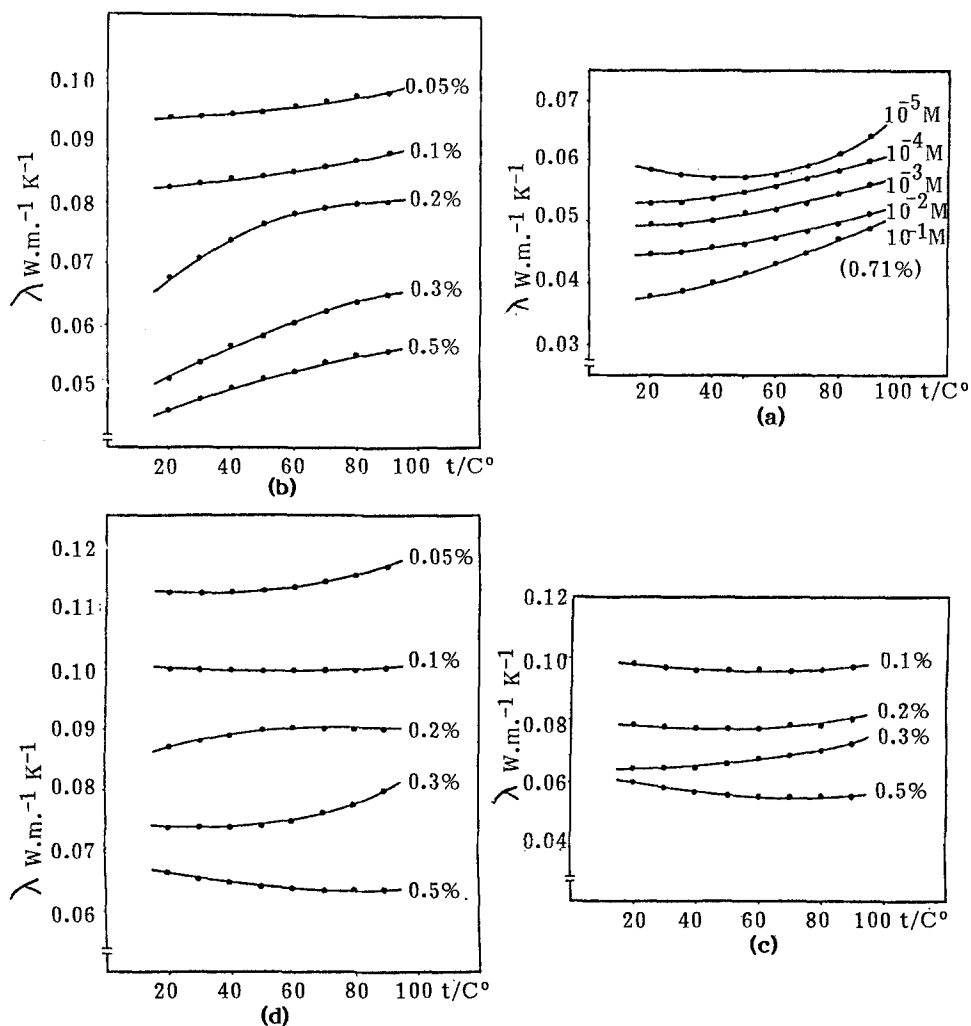


Fig. 3: Variation of thermal conductivity of AAm-NVP copolymer solutions (in aqueous media) with temperature: (a) $[AAm]/[NVP] = 100/0.0$; (b) $[AAm]/[NVP]^* = 70/30$; (c) $[AAm]/[NVP]^* = 60/40$; and (d) $[AAm]/[NVP]^* = 50/50$. * mole % in monomer feed.

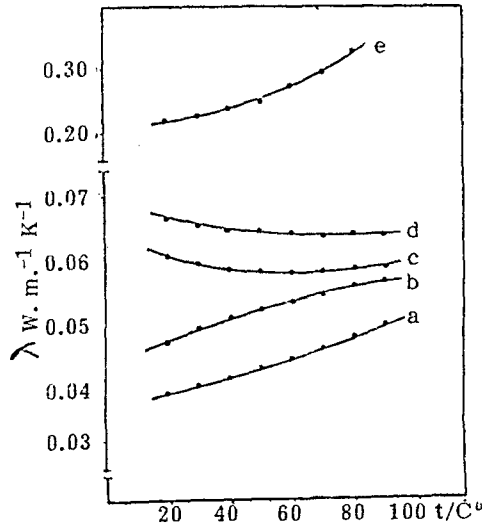


Fig. 4: Variation of thermal conductivity of AAm-NVP copolymer solutions with temperature (the copolymer concentration is 0.5 wt% in H₂O ; except for pure polyacrylamide is 0.71%):

- (a) [AAm]/[NVP] = 100/0.0;
 - (b) [AAm]/[NVP]* = 70/30;
 - (c) [AAm]/[NVP]* = 60/40;
 - (d) [AAm]/[NVP]* = 50/50; and
 - (e) [AAm]/[NVP]** = 0.0/100 (pure polyvinyl pyrrolidone).
- * mole % in monomer feed.
 ** DAKROURY 1990 (Fig.5, p. 519).

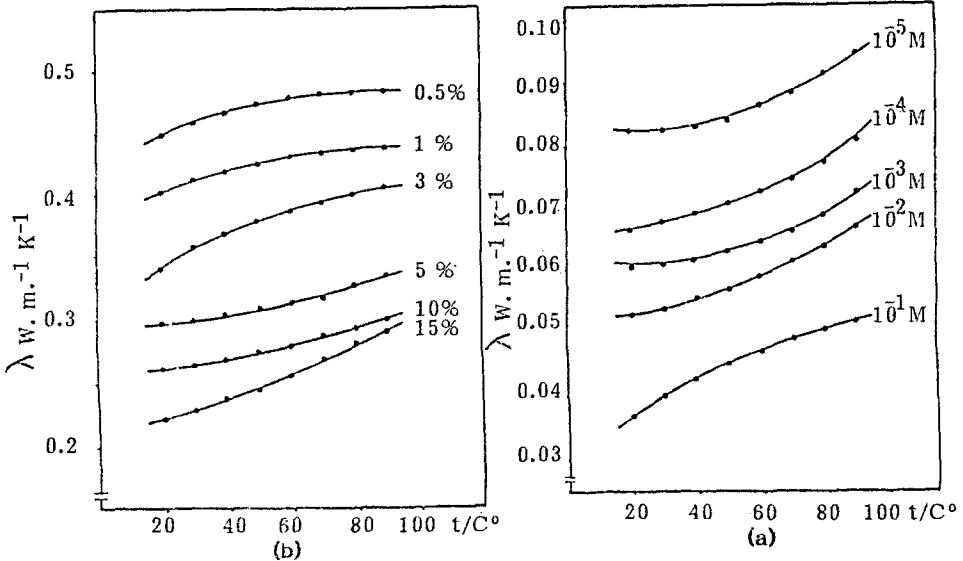


Fig. 5: Variation of thermal conductivity of acrylamide (a) and N-vinyl pyrrolidone (b) solutions (in aqueous media) with temperature.

with different concentrations of the polymer at various temperatures. As could be seen from Fig.2 that the volumetric heat capacity decreases with increase in polymer concentration. It also decreases with temperatures.

The results of the thermal diffusivity of AAm-NVP copolymer solutions with temperature showed that it increases as the temperature increases. Also, it increases with increasing the concentration of AAm-NVP copolymer in the system.

The thermal conductivity results for AAm-NVP copolymer solutions with different concentrations of the copolymer in the temperature range 20-90°C are illustrated in Fig.3. As shown, the values of thermal conductivity decrease with polymer concentration and increase with temperatures. These results may be due to the increase in the solution viscosity (η) with increasing the concentration of the copolymer in the medium and this leads to a decrease in the values of λ according to the following equation (BERMAN 1958):

$$\eta \lambda = \text{constant}$$

The effect of different molar ratios of AAm-NVP copolymer solutions on the behaviour of their thermal conductivities can be observed from Fig.4. It is clear that (Fig.4), the values of thermal conductivity increase with increasing the content of vinyl pyrrolidone monomeric units in the polymeric chains, since higher values of such parameter was previously observed for pure polyvinyl pyrrolidone (DAKROURY 1990). These results indicate that the pyrrolidone ring of NVP and its content in the copolymeric chains play an important role on the behaviour of the thermal properties of the investigated system. Such data can be confirmed from the study of the thermal properties of acrylamide (AAm) and N-vinyl pyrrolidone (NVP) monomers. As could be seen from Fig.5 that NVP monomer is more conductor than AAm monomer. This means that the pyrrolidone ring of vinyl pyrrolidone monomer affects the values of the thermal properties than the amide groups of acrylamide. The above results indicate that the obtained values of the thermal properties depend mainly on the polymer concentration, the temperatures and the content of vinyl pyrrolidone in the copolymeric chains.

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