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COPOLYMERIZATION OF ACRYLAMIDE WITH ACRYLONITRILE BY USING AMMONIUM PERSULFATE-*N,N,N′,N′*-TETRAMETHYL ETHYLENEDIAMINE IN AQUEOUS SOLUTION

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Key Words: Copolymerization; Acrylamide; Acrylonitrile; Ammonium persulfate; *N,N,N′,N′*-Tetramethyl ethylenediamine

ABSTRACT

Studies were conducted on the copolymerization of acrylamide (AM) with acrylonitrile (AN) by utilizing ammonium persulfate-*N,N,*-*N′,N′*-tetramethyl ethylenediamine (APS-TMEDA) system as initiator in aqueous solution. The copolymerization rate equation was established as

$$R_p \propto [\mathrm{APS}]^{0.38}[\mathrm{TMEDA}]^{0.28}[\mathrm{AM}]^{0.91}[\mathrm{AN}]^{0.32}$$

The reactivity ratios were determined by both of the Fineman-Ross and Kelen-Tüdös methods, and the values of r_1 (AM) and r_2 (AN) were determined to be $r_1 = 0.738$ and $r_2 = 0.050$. The apparent activation energy (E_a) of the copolymerization was calculated to be 25.03 kJ/mol.

INTRODUCTION

It is evident from published works that the copolymer of acrylamide (AM) with acrylonitrile (AN) can be prepared by inverse emulsion copolymerization [1] and copolymerization in aqueous solution by using $Na_2S_2O_8$-$NaHSO_3$ [2] and $K_2S_2O_8$-$Na_2S_2O_3$ [3] as initiators. In addition, initiation by the persulfate-*N,N,N′,N′*-tetramethyl ethylenediamine system for the homopolymerization of acrylamide or acrylonitrile in aqueous solution has been reported [4-9]. The aliphatic diamine has a higher promoting activity in AM or AN homopolymerization when using ammonium persulfate (APS)-*N,N,N′,N′*-tetramethyl ethylenediamine (TMEDA) as initiator because this redox couple has a lower activition energy.

The main goal of the present paper is to investigate the copolymerization of AM with AN by using APS-TMEDA as initiator. We conducted an investigation for the copolymerization of AM with AN using various reaction conditions. In addition, the reactivity ratios, apparent activation energy and reaction rate equation were calculated. This information is particularly useful for quality control and practical applications. Synthetic poly(AM-*co*-AN) is of considerable importance in various industrial applications as a flocculent, a borehole drilling additive, thickener, etc.

EXPERIMENTAL

Materials

Acrylamide (AM), C.P. grade, was further purified by recrystallization from benzene, mp 84.5°C. Acrylonitrile (AN) was purified by distillation at reduced pressure (45.5°C/0.33 kPa, $n_D^{25} = 1.3889$). *N,N,N′,N′*-Tetramethyl ethylenediamine (TMEDA) was purified by distillation (22°C/1.03 kPa, $n_D^{20} = 1.4179$). Ammonium persulfate (APS) was analytically pure. All other reagent and solvents were commercially available and used as received.

Procedure

The copolymerization of AM with AN was conducted in an aqueous solution using APS-TMEDA redox as initiator.

Weighted amounts of AM and AN were dissolved in water and warmed in a bath, and an inert gas (N_2) was bubbled through with vigorous stirring. The aqueous solution was neutralized with aqueous NaOH to adjust the pH, and APS and TMEDA were introduced into the reaction mixture. The resulting copolymer was precipitated by pouring the reaction solution into 95% ethanol, washed, and the copolymer was purified by repeated precipitation and dried in vacuo. The copolymerization was carried out under various reaction conditions. Conversion (%) was calculated gravimetrically.

The compositions of the copolymer were determined by IR spectra using a Nicolet FT-20 SX spectrophotometer, KBr disk.

The intrinsic viscosity of the copolymer was measured by Ubbelohde viscometer. The measurements were performed on copolymers dissolved in DMF-H_2O (1:1 volume) at 30°C.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on Conversion (%)

pH

Strong acid or base conditions cause hydrolysis of AM and AN monomers. It was found that when the pH was in the 6–8.5 range, the copolymerization conversion (%) was over 80%. At pH 7.02, a significant enhancement in conversion was obtained (Fig. 1).

Initiator Concentration

Figures 2 and 3 show the effect of initiator (APS and TMEDA) concentration on conversion. It was found that conversion increased with increasing concentrations of APS and TMEDA. The highest conversion was obtained at an APS concentration of 8.0×10^{-3} mol/L and a TMEDA concentration of 6.4×10^{-3} mol/L. On the other hand, it was evident from the curves that the conversion and the polymerization rate R_p increased with increasing reaction time under various concentrations of APS and TMEDA. Conversion reached 60–70% within 1 hour and increased slowly to an ultimate conversion of over 90%.

As seen in Fig. 4, the reaction orders with respect to APS and TMEDA are

$$R_p \propto [\mathrm{APS}]^{0.38} \quad \text{and} \quad R_p \propto [\mathrm{TMEDA}]^{0.28}$$

The intrinsic viscosity $[\eta]$ of the copolymer decreased with increasing initiator concentration. TMEDA influences $[\eta]$ as does APS (see Tables 1 and 2 and Fig. 5).

Monomer Concentration

The relationship between the polymerization rate and the monomer concentration was examined at 35°C. Plots of log R_p vs log [M] are presented in Figs. 6 and 7. From the figures the reaction orders with respect to [AM] and [AN] are

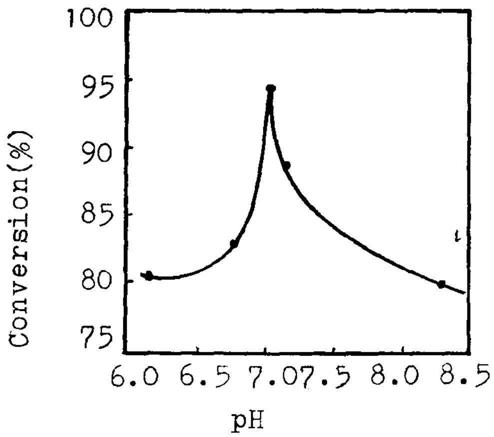

FIG. 1. Effect of pH on conversion (%). [AM] = 1.00 mol/L; [AN] = 0.5 mol/L; [APS] = 3.2×10^{-3} mol/L; [TMEDA] = 3.2×10^{-3} mol/L; 35°C; 6 hours.

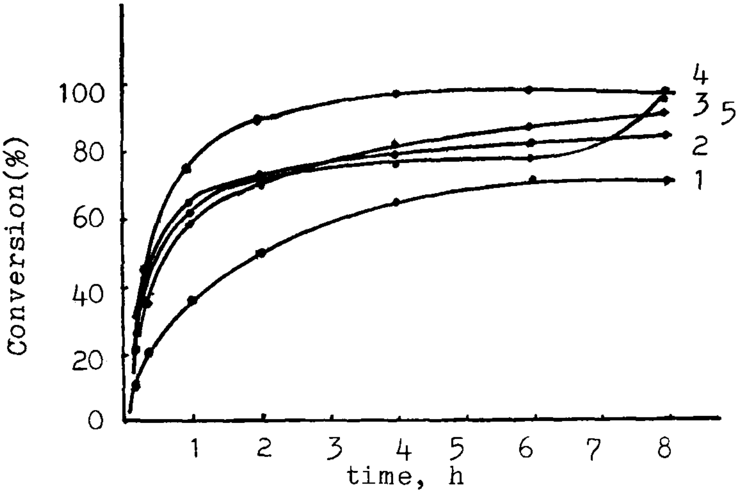

FIG. 2. Effect of APS concentration at various times on conversion (%). [AM] = 1.00 mol/L; [AN] = 0.5 mol/L; [TMEDA] = 3.2×10^{-3} mol/L; pH 7.0; 35°C; 8 hours. [APS] $\times 10^{-3}$ (mol/L): (1) 2.0, (2) 3.2, (3) 6.4, (4) 8.0, (5) 16.0.

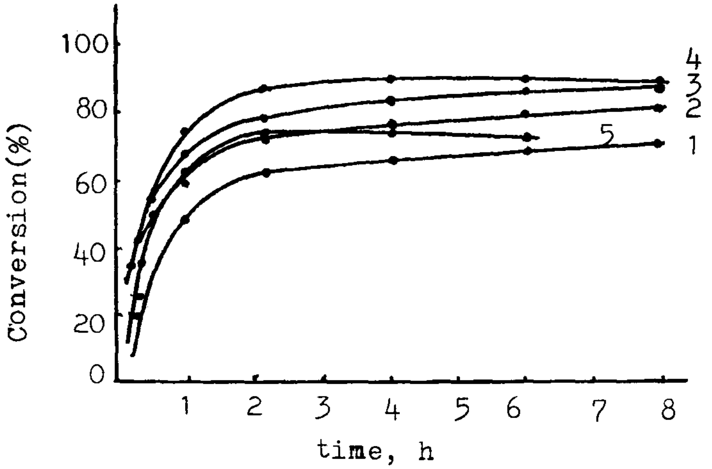

FIG. 3. Effect of TMEDA concentration at various times on conversion. [AM] = 1.00 mol/L; [AN] = 0.5 mol/L; [APS] = 3.2×10^{-3} mol/L; pH 7.0; 35°C; 8 hours. [TMEDA] $\times 10^{-3}$ (mol/L): (1) 1.6, (2) 3.2, (3) 4.8, (4) 6.4, (5) 8.0.

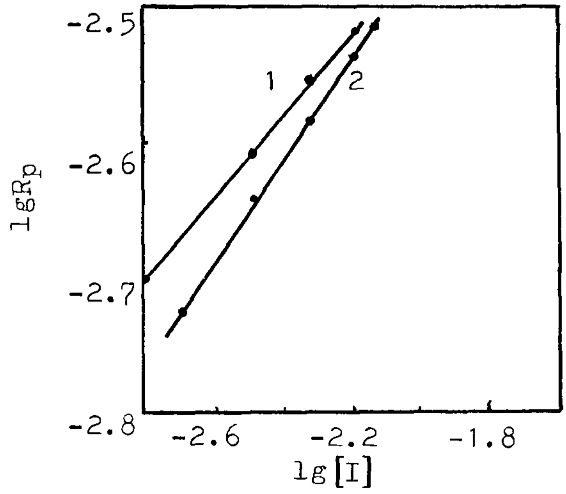

FIG. 4. Relation between lg R_p and lg [I]. Reaction conditions as in Figs. 2 and 3. [I]: (1) APS, (2) TMEDA.

TABLE 1. The Influence of APS Concentration on Conversion and Intrinsic Viscosity[a]

APS (mol/L × 10^{-3})	2.0	3.2	6.4	8.0	16.0
Conversion (%)	70.56	81.91	79.76	97.31	86.82
[η]	0.987	0.849	0.762	0.662	0.381

[a] AM/AN = 2, total monomer concentration = 10%, [TMEDA] = 3.2 × 10^{-3} mol/L, pH 7.0 at 35°C for 8 hours.

TABLE 2. The Influence of TMEDA Concentration on Conversion and Intrinsic Viscosity[a]

TMEDA (mol/L × 10^{-3})	1.6	3.2	4.8	6.4	8.0
Conversion (%)	73.87	84.92	89.09	90.01	72.65
[η]	1.102	0.849	0.766	0.762	0.647

[a] AM/AN = 2, total monomer concentration = 10%, [APS] = 3.2 × 10^{-3} mol/L, pH 7.0 at 35°C for 8 hours.

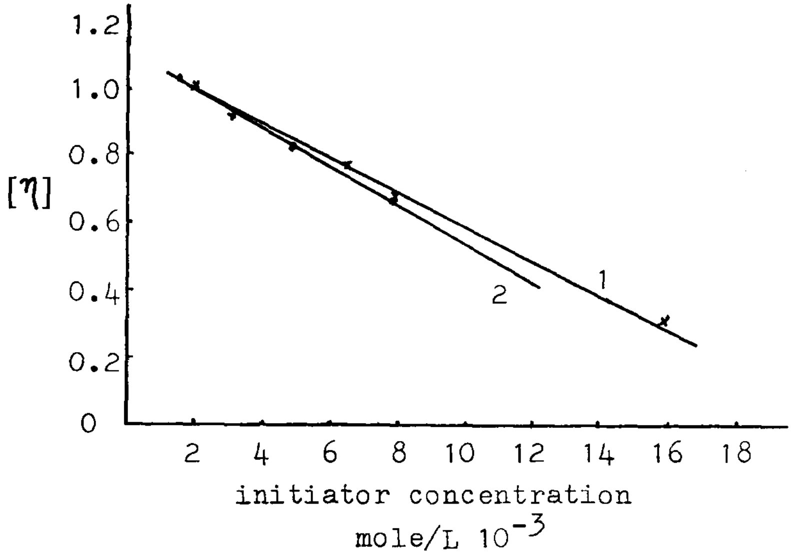

FIG. 5. Effect of APS and TMEDA concentration on [η]. [AM] = 1.00 mol/L; [AN] = 0.5 mol/L; 35°C; 8 hours. 1: [APS]. 2: [TMEDA].

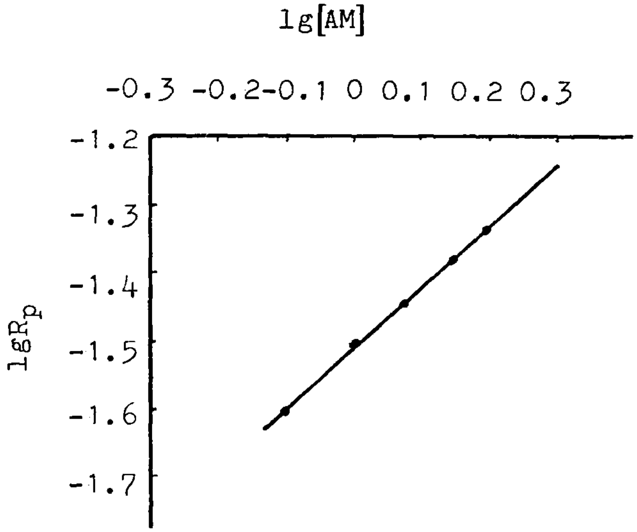

FIG. 6. Relation between lg R_p and lg [AM]. [AN] = 0.40 mol/L; [APS] = 3.2 × 10^{-3} mol/L; [TMEDA] = 6.4 × 10^{-3} mol/L; pH 7.0; 35°C; 8 hours.

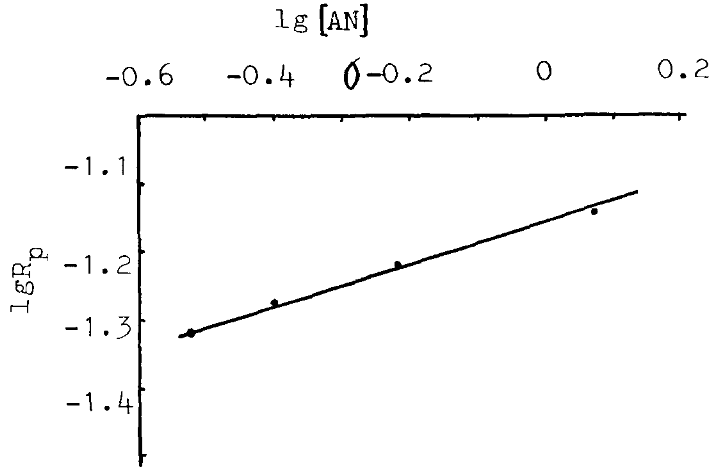

FIG. 7. Relation between lg R_p and lg [AN]. [AM] = 1.2 mol/L; reaction conditions as in Fig. 6.

$R_p \propto [AM]^{0.91}$ and $R_p \propto [AN]^{0.32}$

We obtained the total reaction rate equation:

$$R_p \propto [APS]^{0.38}[TMEDA]^{0.28}[AM]^{0.91}[AN]^{0.32}$$

The experimental results show that the apparent index of initiator concentration deviated from 1/2, reducing the probability of termination by a bimolecular reaction of the propagating radicals and raising the probability of termination of the primary radical at higher system viscosities. Apparent indexes with respect to AM and AN are less than 1 for the monomer when the copolymerization is more complex, the initiation rate of redox copolymerization is related to the monomer concentration.

Temperature

The effect of temperature on conversion was examined over the 30-60°C range. Conversion increased with increasing reaction temperature; however, conversion decreased above 40°C (Fig. 8). The suitable temperature is 35°C. The plot of lg R_p vs $1/T$ is recorded in Fig. 9. According to the Arrhenius equation, from the slope of the lg R_p-$1/T$ straight line, the apparent activition energy E_a was calculated to be 25.03 kJ/mol. A lower E_a implies that the copolymerization of AM with AN with APS-TMEDA initiator occurs at room temperature. It is obvious that TMEDA accelerated the redox reaction. This result is shown in Figs. 2 and 3. It is also observed that the induction period is shorter (see also Figs. 2 and 3). The intrinsic viscosity $[\eta]$ of the copolymer decreases with increasing reaction temperature (Fig. 10), in agreement with the conventional rule of radical polymerization.

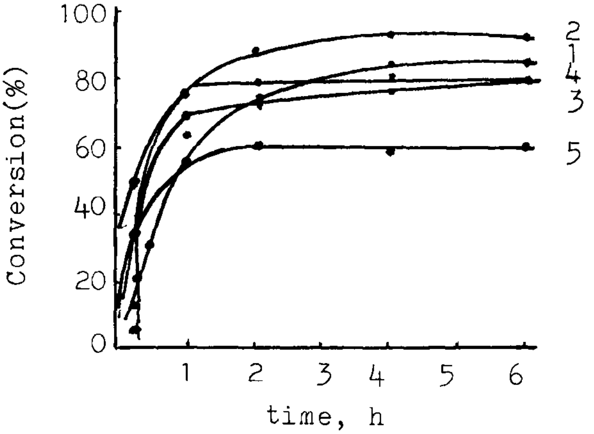

FIG. 8. Effect of temperature on conversion (%). [AM] = 1.00 mol/L; [AN] = 0.50 mol/L; [APS] = 3.2 × 10^{-3} mol/L; [TMEDA] = 6.4 × 10^{-3} mol/L; pH 7.0; 6 hours. Temperature (°C): (1) 30, (2) 35, (3) 40, (4) 50, (5) 60.

IR Spectra

Figure 11 shows the IR spectra of copolymers of AM and AN with various compositions. For the copolymer, $\gamma_{C=O}$ ($-\underset{\underset{O}{\|}}{C}-NH_2$) and $\gamma_{C\equiv N}$ ($-C\equiv N$) characteristic peaks at 1615-1658 and 2244 cm^{-1} were observed, respectively.

Reactivity Ratio

The copolymer composition was determined from the ratio of the characteristic peak areas of —AM— and —AN— units. The absorbance peak ratios A_{1663}/A_{2244} were determined for a series of mixed polymers of polyacrylamide (PAM) and polyacrylonitrile (PAN), and plotted as a function of X_{AM}/X_{AN} (Fig. 12).

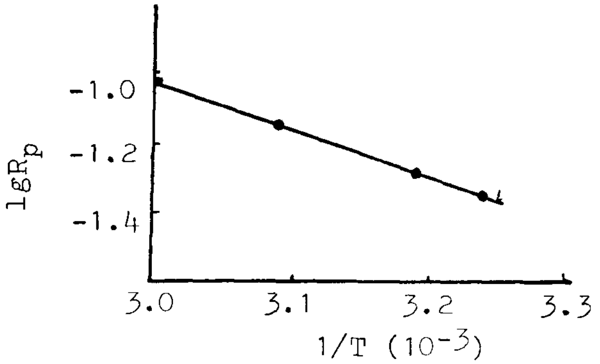

FIG. 9. Plot of lg R_p vs 1/T. [AM] = 1.00 mol/L; [AN] = 0.50 mol/L; [APS] = 3.2 × 10 mol/L; [TMEDA] = 6.4 × 10 mol/L; pH 7.0; 6 hours.

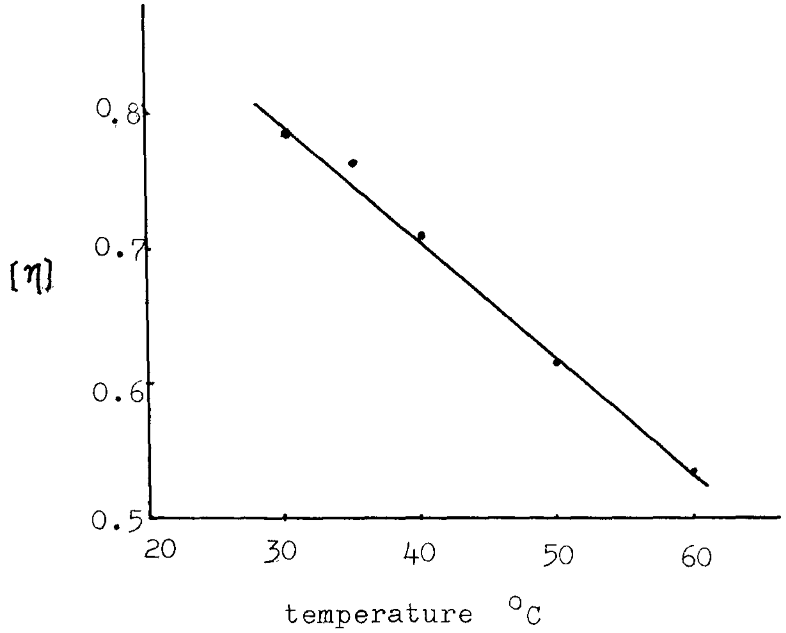

FIG. 10. Effect of temperature on [η]. [AM] = 1.00 mol/L; [AN] = 0.50 mol/L; [APS] = 3.2×10^{-3} mol/L; [TMEDA] = 6.4×10^{-3} mol/L; pH 7.0; 6 hours.

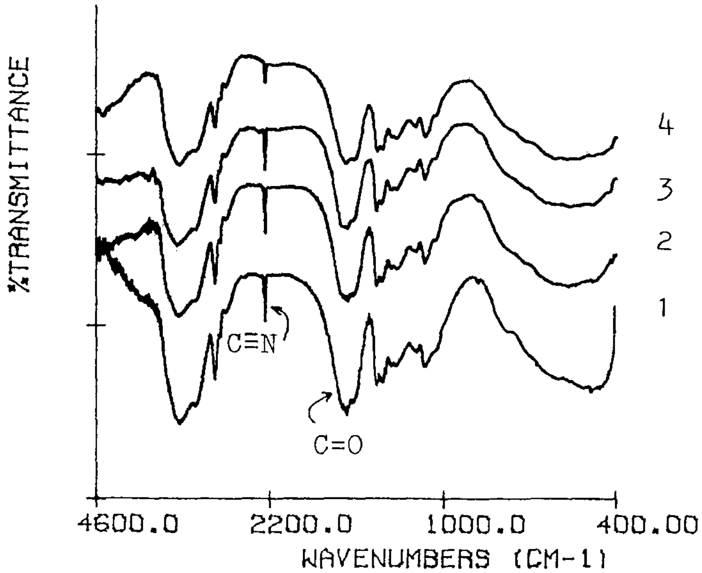

FIG. 11. Infrared spectra for copolymer of AM with AN. [AM]/[AN] (mole ratio): (1) 1, (2) 2, (3) 3, (4) 4.

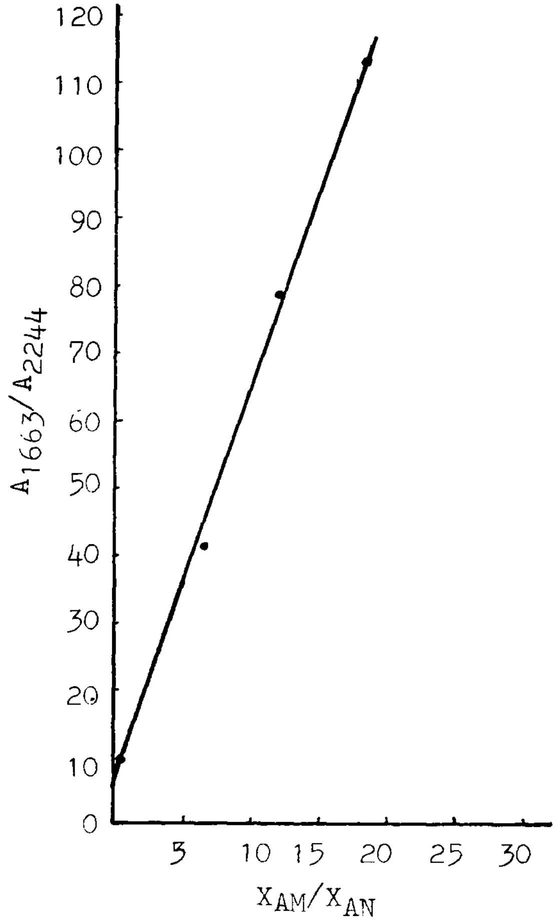

FIG. 12. Plot of A_{1663}/A_{2244} vs $X_{\mathrm{AM}}/X_{\mathrm{AN}}$ for the mixed polymer of PAM and PAN.

The results may be represented mathematically as

$$A_{1663}/A_{2244} = 5.881Y + 3.50$$

where 5.881 is derived from the slope of the line while 3.50 is derived from the intercept. $Y = X_{\mathrm{AM}}/X_{\mathrm{AN}}$ represents the mole ratio of copolymer composition. The mole fraction of each unit in the copolymer can be determined (Table 3).

TABLE 3. Data for the Examined Copolymer Composition

X = (AM)/(AN) (mole ratio in the feed)	1	2	2.5	3	4
A_{1663}/A_{2244}	44.30	18.21	21.27	22.12	26.58
$Y = X_{\mathrm{AM}}/X_{\mathrm{AN}}$	6.938	2.501	3.022	3.166	3.924

The Fineman-Ross method [10] and Kelen-Tüdös method [11] were employed to calculate the reactivity ratio.

The Fineman-Ross copolymerization equation is

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

Figure 13 is the Fineman-Ross plot for AM and AN. The reactivity ratio r_1 was determined to be 0.738 from the slope of the line and r_2 was 0.05 from the intercept.

The Kelen-Tüdös equation is

$$\eta = (r_1 + r_2/a)\zeta - r_2/a$$

where $\eta = G/(a + F)$ and $\zeta = F(a + F)$. In these expressions, $F = X^2/Y$ and $G = X(Y - 1)/Y$, $a = \sqrt{F_m \cdot F_M} = 2.554$. F_m and F_M are the lowest and the highest F values, respectively, from the experimental data.

By plotting η versus ζ according to the linear equation, we found $r_2 = 0.051$ and $r_1 = 0.738$ from the intercept (Fig. 14). The reactivity ratios calculated by both methods are in good agreement.

The copolymer composition as a function of the feed composition for the copolymerization of AM and AN is shown in Fig. 15. The curve was derived from the copolymerization using the experimentally determined Kelen-Tüdös reactivity ratios.

Because the reactivity ratios are $r_1 < 1$ and $r_2 < 1$, there is a constant point ($A = 0.78$) on the plot (Fig. 15). From the reactivity ratios, it can be seen that the copolymers possess an alternating structure (see Table 4, $r_1 r_2 \sim 0$).

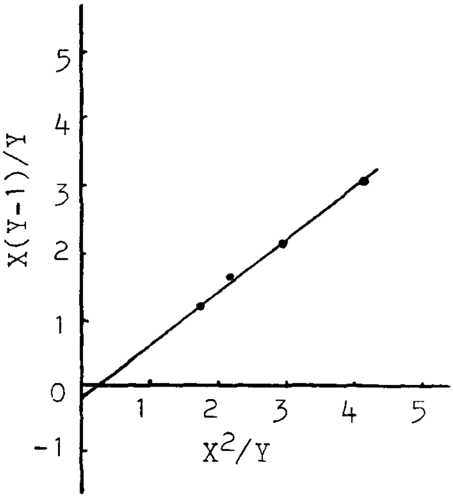

FIG. 13. Fineman-Ross plot for the determination of the reactivity ratios for the copolymerization of AM with AN.

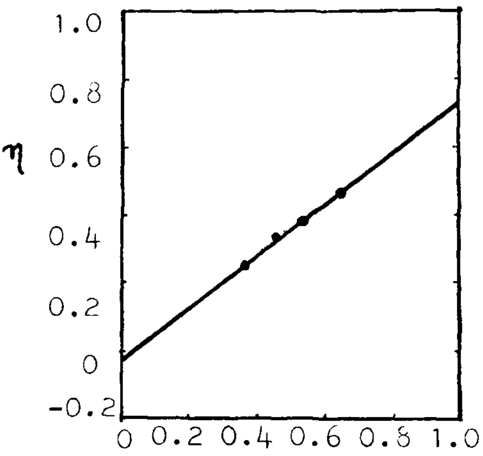

FIG. 14. Kelen-Tüdös plot for the determination of the reactivity ratios for the copolymerization of AM with AN. $\alpha = 2.554$.

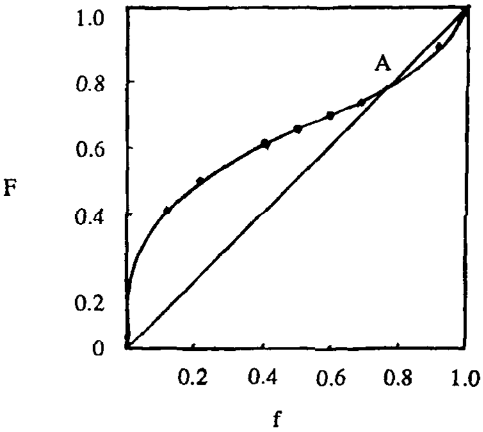

FIG. 15. Relationship between the copolymer composition and comonomer feed composition. Point *A* is a constant point ($A = 0.78$).

TABLE 4. Reactivity Ratios for the Copolymerization of [AM] with [AN]

Method	r_1	r_2	r_1r_2
Fineman-Ross	0.738	0.05	0.0369
Kelen-Tüdös	0.738	0.051	0.0376

CONCLUSIONS

The preparation of AM-AN copolymers by using the APS-TMEDA redox couple in aqueous solution and the effects of reaction conditions on conversion are described in detail. The results were investigated kinetically. The copolymerization rate equation was determined to be

$$R_p \propto [\mathrm{APS}]^{0.38}[\mathrm{TMEDA}]^{0.28}[\mathrm{AM}]^{0.91}[\mathrm{AN}]^{0.32}$$

The monomer reactivity ratios from both the Fineman-Ross and Kelen-Tüdös methods were calculated to be $r_1 = 0.738$ and $r_2 = 0.050$. Because the monomer reactivity ratios are $r_1 < 1$ and $r_2 < 1$, $r_1 r_2 = 0.037$, and the copolymers are generally random in nature, possessing a slight alternating tendency. The apparent activation energy E_a of copolymerization of AM-AN is 25.03 kJ/mol.

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