Synthesis and Rheological Behavior in Aqueous Solutions of Poly(Acrylamide-co-Maleic Acid)

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SYNOPSIS

Water-soluble copolymers of acrylamide with maleic acid were synthesized in aqueous solution by using potassium persulfate with N,N,N',N'-tetramethyl ethylenediamine as initiator. The influences of synthetic variables on the copolymerization were investigated. The copolymers were characterized by IR and ^{1}H-NMR spectroscopy. The copolymeric composition was obtained by using ^{1}H-NMR method. The monomer reactivity ratios were calculated by the Kelen–Tudos method and the values of r_1 (AM) and r_2 (MA) were determined to be 11.45 and 0.0129, respectively. The rheological behavior of aqueous solution of synthetic poly(acrylamide-co-maleic acid) was determined, and flowing activation energy E was calculated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is evident from published articles that the water-soluble copolymers of acrylamide with maleic acid have shown a wide variety of applications. Its major uses are for papermaking agents, drilling additives, adhesives and flocculants, etc. The copolymer has good flocculating properties for suspension of bentonite and wastewater, and additives for paper afford excellent retention and strength.[1-3] The copolymerization of acrylamide with maleic acid using photochemical irradiation,[1] persulfate-sodium sulfite redox system,[3] ammonium persulfate,[4] and AIBN[5] as initiator, respectively, has been studied before. In addition, ammonium persulfate-tetramethyl ethylene-diamine system has been successfully used for the initiation of acrylamide polymerization.[6,7] In this article, the objective of our work was to conduct an investigation for the copolymerization of acrylamide with maleic acid in an aqueous solution using potassium persulfate-tetramethyl ethylenediamine as redox initiator. In the synthesis, the effects of reaction condition on the copolymerization, the kinetics, and the reactivity ratios were described. In addition, the rheological properties of the title copolymer in aqueous solution will be discussed. These are of practical importance for the application of enhanced oil recovery.

EXPERIMENTAL

Materials

Acrylamide (AM) was recrystallized from benzene and vacuum-dried to constant weight, mp 84.5°C. Potassium persulfate (KPS) was recrystallized from water. N,N,N',N'-tetramethyl ethylenediamine (TMEDA) was purified by distillation. Maleic acid (MA) and other chemicals were chemically pure and were used as purchased.

Copolymerization

The copolymerization of AM with MA is conducted in an aqueous solution using KPS–TMEDA as initiator under nitrogen atmosphere. Maleic acid was dissolved in water, and the solution was neutralized with alkali to adjust the pH. AM aq. was then added with stirring at room temperature, followed by bubbling nitrogen gas for 30 min; then initiator was added to the monomer solution. At the end of the reaction, the resulting product was poured into

ethanol, and copolymer was precipitated, washed, and vacuum-dried at 50°C to constant weight.

The copolymerization was carried out at various reaction conditions. Copolymerization conversion (%) was determined gravimetrically.

Characterization

1. Infrared (IR) spectra of the copolymers were recorded on a NICOLET FT-20 SX spectrometer as KBr pellets.
2. ^{1}H-NMR spectra for the copolymer were obtained using TX-90 Q spectrometer with D_2O as solvent, and tetramethyl silicone (TMS) as the internal reference. Composition analysis of copolymers was found by ^{1}H-NMR method.
3. The intrinsic viscosity of the title copolymer was measured in $1M$ $NaNO_3$ aqueous solution at 30°C by an Ubbelohde viscometer.
4. Rheological properties of the copolymer in aqueous solution were determined using NDJ-79 model rotary viscometer at various temperatures.

RESULTS AND DISCUSSION

Influence of Various Conditions on Copolymerization

Effect of pH

As seen in Figure 1 the conversion exhibits a maximum at pH 7. Recently Guo[7] proposed that when

Figure 1   Influence of pH on conversion: [AM] = 0.83 mol/L; [MA] = 0.17 mol/L; [KPS] = 2.5 × 10^{-3} mol/L; [TMEDA] = 7.5 × 10^{-3} mol/L; at 35°C; 2.5 h.

ammonium persulfate–TMEDA is used as redox initiator for the free radical polymerization of acrylamide, the free radical $(CH_3)NCH_2(CH_3)N\dot{C}H_2$ (1) is one of the initial free radicals responsible for the initiation of vinyl polymerization in addition to sulfate free radical $(HOS\dot{O}_3)$ (2). The following mechanism represents the production of initial radical for polymerization:

APS + TMEDA →

→ $(CH_3)_2NCH_2CH_2(CH_3)N\dot{C}H_2$ + $.OSO_3H$ + $SO_4^=$
     (1)   (2)

It is clear that a lower pH and a further increase of the pH should retard the production of radical (1) and (2), or rather, pH 7 is favorable. It is in good agreement with result of Figure 1.

Effect of Initiator Concentration

It was observed that higher conversion was obtained in the concentration of KPS 2.5 × 10^{-3} mol/L and TMEDA 7.5 × 10^{-3} mol/L. As shown in Figure 2, the conversion and initial rate of the copolymerization increase with increasing KPS concentration, but the intrinsic viscosity $[\eta]$ of the copolymer decreased (Fig. 3). It was also found that the higher the concentration of TMEDA in the initiator composition, the larger the increase in conversion and in initial rate of copolymerization, but at the concentration of 10 × 10^{-3} mol/L, it is over and above what is wanted, in fact, the conversion was found to decrease markedly, as shown in Figure 4. The $[\eta]$ of the copolymer decreased as TMEDA concentration increased, too, as in Figure 5. Naturally, these results conform to the rule of the radical polymerization.

Effect of Mole Fraction of Monomers in the Feed

As shown in Figure 6, the conversion and the initial rate of the copolymerization increase with increasing the mole fraction of acrylamide in the feed; in other words, the conversion and rate decrease with increasing the mole fraction of maleic acid.
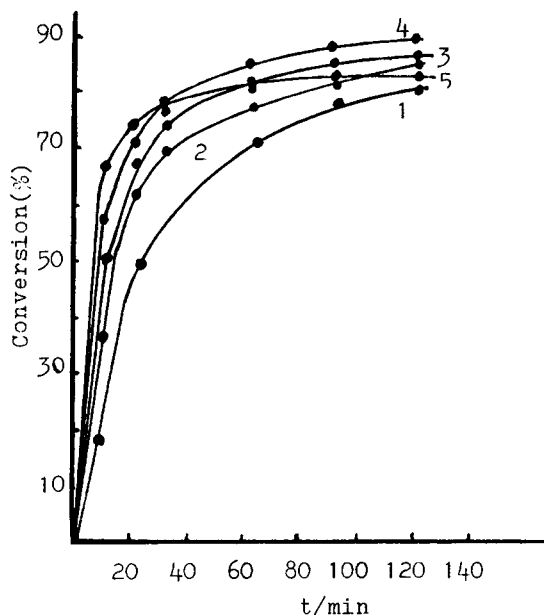
Figure 2   Influence of KPS concentration on copolymerization: [AM] = 0.83 mol/L; [MA] = 0.17 mol/L; [TMEDA] = 7.5 × 10⁻³ mol/L; at 35°C; pH 7. [KPS]: (1) 0.63 × 10⁻³ mol/L; (2) 1.25 × 10⁻³ mol/L; (3) 1.88 × 10⁻³ mol/L; (4) 2.50 × 10⁻³ mol/L; (5) 3.15 × 10⁻³ mol/L.
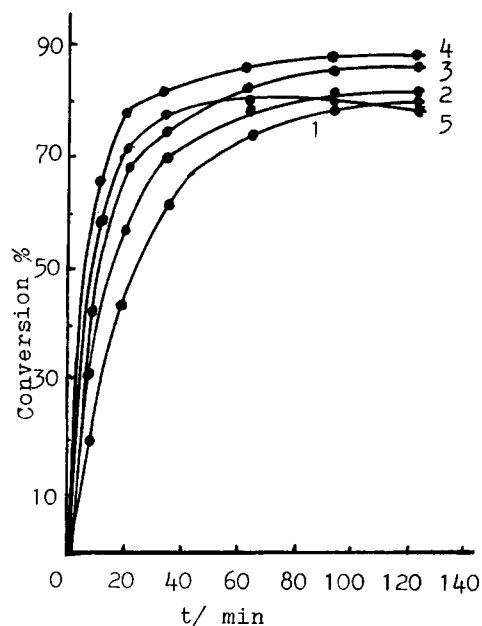
Figure 4   Influence of TMEDA concentration on copolymerization: [AM] = 0.83 mol/L; [MA] = 0.17 mol/L; [KPS] = 2.5 × 10⁻³ mol/L; at 35°C; pH 7. [TMEDA]: (1) 1.0 × 10⁻³ mol/L; (2) 2.5 × 10⁻³ mol/L; (3) 5.0 × 10⁻³ mol/L; (4) 7.5 × 10⁻³ mol/L; (5) 10 × 10⁻³ mol/L.

Effect of Reaction Temperature

The relationships between the copolymerization and reaction temperature are shown in Figure 7. It can be seen that the conversion and the reaction rate increase with increasing temperature; however,

temperatures above 55°C showed decreased conversion. The reaction temperature of 35°C facilited the conversion. The plot of $\log R_p$ vs. $1/T$, according to the Arrhenius equation from the slope of the $\log R_p$ $- 1/T$ straight line (Fig. 8), the apparent activation energy E_a was calculated to be 12.04 kJ/mol. A low

Figure 3   Influence of KPS concentration on [η] (continued from Fig. 2).
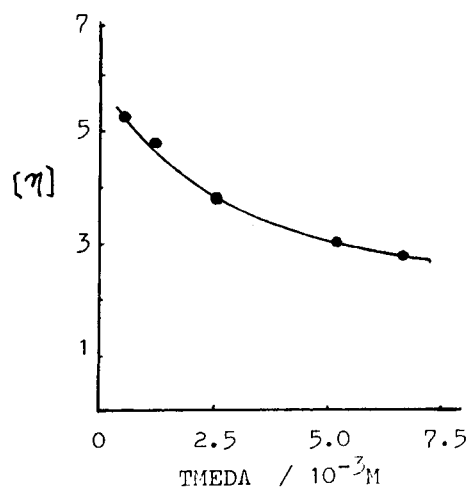
Figure 5   Influence of TMEDA concentration on [η] (continued from Fig. 4).
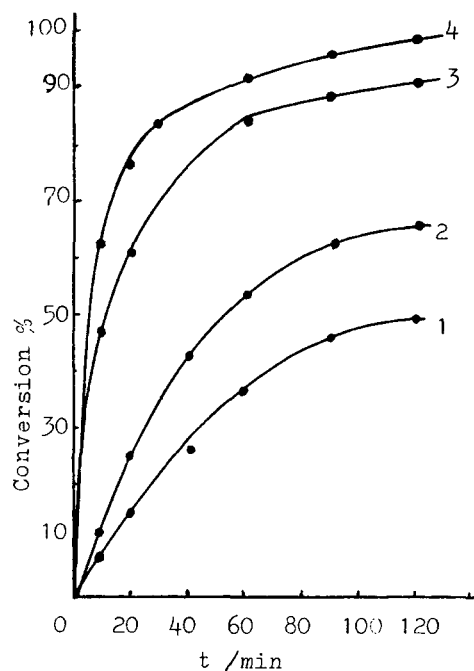
Figure 6   Influence of monomer mole fraction in the feed on copolymerization: [KPS] = 2.5 × 10⁻³ mol; [TMEDA] = 7.5 × 10⁻³ mol/L; at 35°C; pH 7. Monomer mole fraction in the feed: (1) AM = 0.4, MA = 0.6; (2) AM = 0.5, MA = 0.5; (3) AM = 0.8, MA = 0.2; (4) AM = 0.9, MA = 0.1.
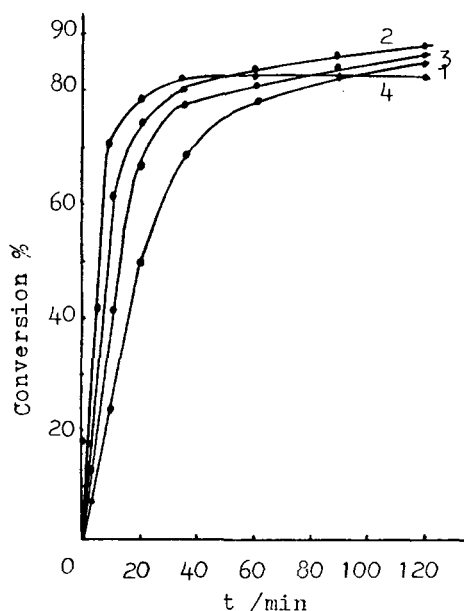
Figure 7   Influence of reaction temperature on copolymerization: [AM] = 0.83 mol/L; [MA] = 0.17 mol/L; [KPS] = 2.5 × 10⁻³ mol/L; [TMEDA] = 7.5 × 10⁻³ mol/L; pH 7. Temperature: (1) 28°C; (2) 35°C; (3) 45°C; (4) 55°C.
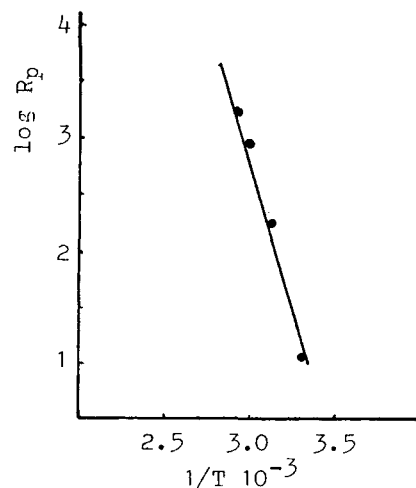
Figure 8   Plot of log R_p vs. $1/T$ (continued from Fig. 7).

E_a implies that the copolymerization of AM with MA using KPS–TMEDA initiator occurs at room temperature. It is obvious that the TMEDA accelerated the redox reaction. This result is shown in Figure 4.

Spectra

IR Spectrum (Fig. 9)

IR spectroscopy was used to analyze the synthetic copolymer. IR absorbances at 1577 and 1400 cm⁻¹ can be attributed to carboxyl absorption, and the absorbences at 1661 and 1641 cm⁻¹ are of the —$CONH_2$ group absorption. These data indicated that synthetic copolymer was poly(AM-co-MA).
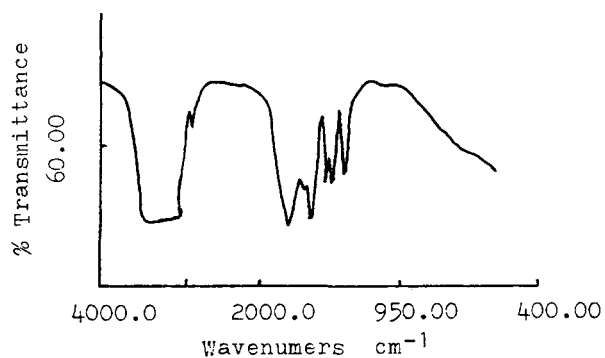
Figure 9   IR spectrum for poly(acrylamide-co-maleic acid) KBr disks.

¹H-NMR Spectrum and Compositional Quantitation

In the ¹H-NMR spectrum (Fig. 10), the distinct peak assignments for copolymer are

$$\begin{array}{cc} \overset{a}{-}CH_2\overset{b}{-}CH\overset{}{-} & \overset{b}{-}CH\overset{b}{-}CH\overset{}{-} \\ | & | \quad | \\ CONH_2 & COOHCOOH \end{array}$$
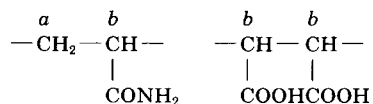
for the chemical shift values (ppm) (Fig. 10): H_a = 1.66 and H_b = 2.19.

As shown in Figure 10, it may be divided into two absorbing areas (A and B); H_a and H_b belong with A and B, respectively. m_1 is mole of acrylamide units in the copolymer and m_2 is mole of maleic acid units in the copolymer. Therefore,

$$2m_1 = KA$$

$$m_1 + 2m_2 = KB$$

where K is the constant, and

$$m_1/m_2 = A/(2B - A)$$

where m_1/m_2 represents the mole ratio of copolymer composition. The values of A and B were determined by the integratal values of the absorbing areas, respectively. Thus, the mole fraction of each units in the copolymer can be determined.

Reactivity Ratios

Copolymerization for different monomer mole ratios (M_1/M_2) was carried out in an aqueous solution with free-radical initiator (KPS-TMEDA). The conversion was in all cases restricted within 10%. The copolymer composition was determined by nuclear magnetic resonance (NMR) method. The Kelen–
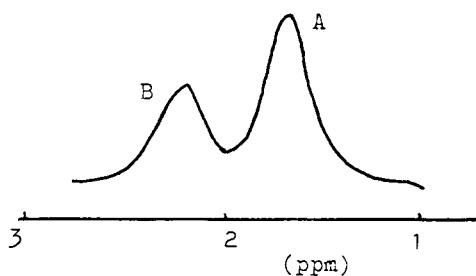
Figure 10 ¹H-NMR spectrum for poly(acrylamide-co-maleic acid); D_2O as solvent and TMS as the internal reference, 89.6 MH₂.
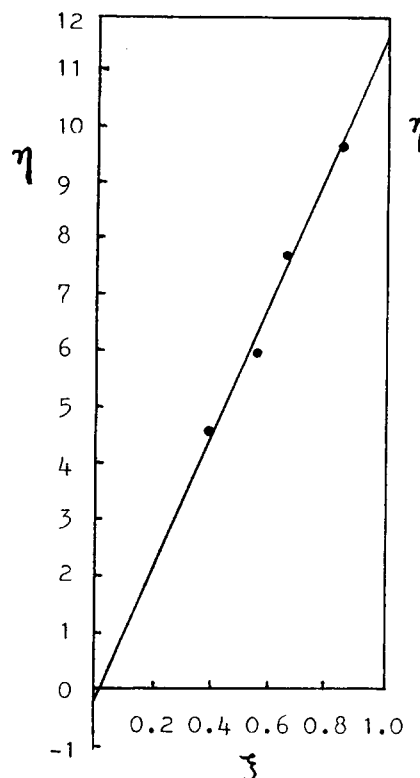

Figure 11 Kelen–Tudos plot for the determination of reactivity ratios for copolymerization of AM and MA, η vs. ζ; a = 0.0460.

Tudos method[8] was employed to calculate the reactivity ratios.

The Kelen–Tudos equation is expressed as
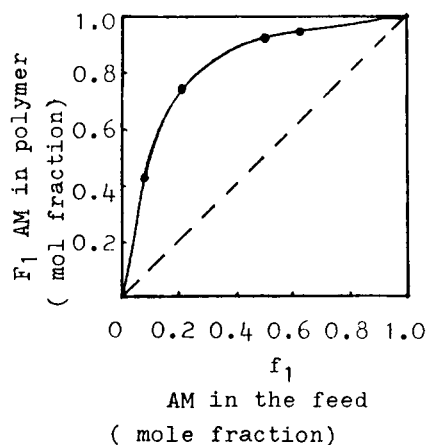
$$\eta = (r_1 + r_2/a)\xi - r_2/a \qquad (1)$$

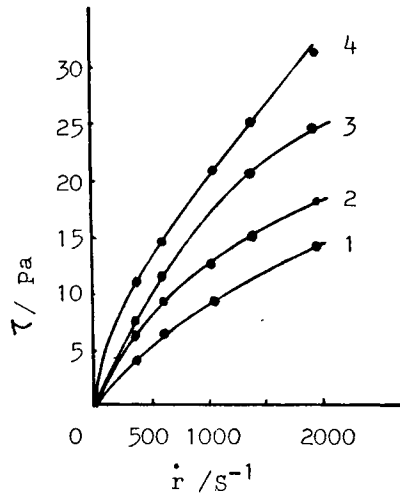**Figure 12** Copolymer composition as a function of feed composition of AM and MA.

Figure 13 Rheogram of copolymer solution as a function of concentration, τ vs. $\dot{r}$, at 30°C; solution concentration (%): (1) 1.5; (2) 2.0; (3) 2.5; (4) 3.0.

where $\eta = G/(a + F)$, and $\zeta = F/(a + F)$

$$F = X^2/Y \qquad G = X(Y - 1)/Y$$
$$X = M_1/M_2 \qquad Y = m_1/m_2$$

Parameter a is obtained from $a = \sqrt{(F_m F_M)}$ = 0.0460, where F_m and F_M are the lowest and highest F from the experimental data. By plotting η versus ζ according to Eq. (1), we obtain directly r_1 = 11.45 and r_2 = 0.0129 from the intercept (Fig. 11) at $\zeta = 1$ and $\zeta = 0$, respectively.
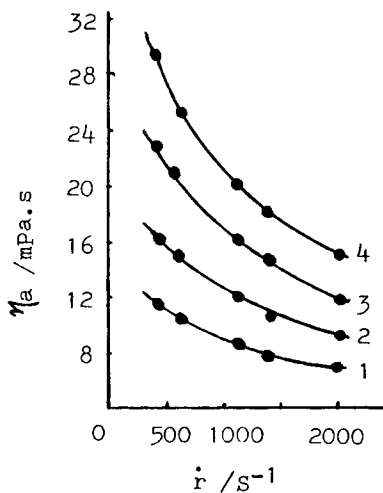
The copolymer composition as a function of feed

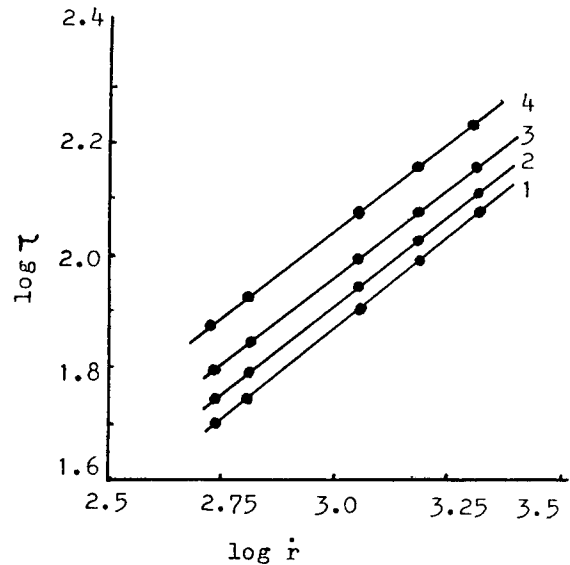**Figure 15** Plot of $\log \tau$ vs. $\log \dot{r}$ (2% aq. solution); temperature (°C): (1) 60; (2) 40; (3) 30; (4) 13.

composition for the copolymerization of acrylamide with maleic acid is shown in Figure 12. The curve was derived from the copolymerization equation using the experimentally determined reactivity ratios. Because $r_1 > 1$, $r_2 < 1$, the copolymer composition is different from the monomer composition in the feed, i.e., $F_1 > f_1$.

Rheology

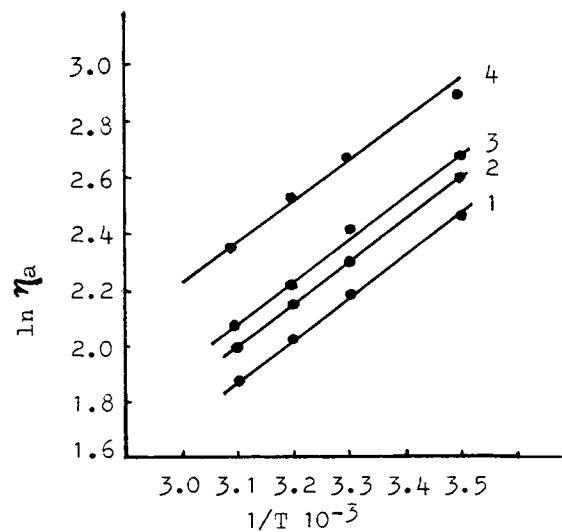The rheological parameters of the title copolymer in aqueous solution have been determined. These

Figure 14 Rheogram of copolymer solution as a function of concentration, η_a vs. $\dot{r}$, at 30°C; solution concentration (%): (1) 1.5; (2) 2.0; (3) 2.5; (4) 3.0.

Figure 16 Plot of $\ln \eta_a$ vs. $1/T$ (2% aq. solution); shear rate (s^{-1}): (1) 2028; (2) 1403; (3) 1092; (4) 624.

Table I *E* **Value, 2% Aqueous Solution of Poly (AM-co-MA)**

$\dot{r}$ (s^{-1})	624	1092	1403	2028
E (Kj/mol)	14.78	14.83	14.82	14.82

solutions have viscosities and are shear thinning. That can be predicted by the power law equation:

$$\eta_a = \tau/\dot{r} = K\dot{r}^{n-1} \quad \text{or} \quad \log \tau = \log K + n \log \dot{r}$$

$$n = d \log \dot{r}$$

where η_a is the apparent viscosity, τ the shear stress, $\dot{r}$ the shear rate, K the shearing viscosity coefficient, and n is the power law exponent.

Rheological test curve measured at 30°C of solution is given in Figures 13 and 14. These plots show that the η_a and τ increase with increasing solution concentration; however, the solutions are thinning with degree of shear thinning, increasing as concentration increases. It is clear that solutions are characterized by a pseudoplasticity, i.e., non-Newtonian behavior, shearing stress is not directly proportional to shear rate. The $\log \tau - \log \dot{r}$ curves at various temperatures, shown in Figure 15. It can be seen that the power law exponent ($n = 0.81$) is not changed with increasing temperature, but the viscosity of solution decreases as temperature and shear rate increase (see Fig. 16). According to the following equation:

$$\eta_a = Ae^{E/RT} \quad \text{or} \quad \ln \eta_a = \ln A + E/RT$$

where η_a is the apparent viscosity, A the active factor, E the flowing activation energy, R the gas constant, and T is temperature (Kelvin).

A plot of $\ln \eta_a$ vs. $1/T$ allows the determination of E and A from slope and intercept, respectively. From the preceding, E is listed in Table I.

The essential constancy of E for all shear rate range (624–2028 s^{-1}) upon changing the temperature from 13 to 60°C indicates the stability of the vis-

cosity–temperature coefficient of poly(AM-co-MA) in aqueous solution for given shear rate range.

CONCLUSION

The copolymerization of acrylamide with maleic acid was induced by using KPS–TMEDA as initiator, and the influences of various factors on the copolymerization were investigated. The reactivity ratios were determined to be $r_1 = 11.45$ and $r_2 = 0.0129$ using the Kelen–Tudos method. The apparent activition energy E_a was calculated to be 12.04 Kj/mol.

The rheological behavior of poly(acrylamide-co-maleic acid) in aqueous solution has shown to be effective for thickening, and these solutions are pseudoplastic fluids. The flowing activation E was calculated and the essential constancy of E upon changing the temperature from 13 to 60°C indicates the stability of viscosity–temperature coefficient of poly(acrylamide-co-maleic acid) aqueous solution in given shear rate range (624–2028 s^{-1}).

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