

# Synthesis and Rheological Properties in Aqueous Solution of Poly(Acrylamide-co-Sodium Allylsulfonate)

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## SYNOPSIS

The copolymerization of acrylamide (AM) with sodium allylsulfonate (SAS) was studied. The copolymerization rate equation was determined,  $R_p = K[\text{KPS}]^{0.70}[\text{AM}]^{1.60}[\text{SAS}]^{-0.60}$ . The copolymeric composition obtained by nitrogen and sulfur elemental analysis, and  $^1\text{H-NMR}$  method. The reactivity ratios were calculated by the Kelen-Tudos method and the value of  $r_1(\text{AM})$ ,  $r_2(\text{SAS})$  was determined to be 2.45 and 0.060, respectively. The rheology of aqueous solution of synthetic poly(acrylamide-co-sodium allylsulfonate) was determined at different temperatures and flowing activation energy  $E_a$  were calculated.

## INTRODUCTION

It is evident from published patents,<sup>1,2</sup> that the copolymers of acrylamide-sodium allylsulfonate were prepared and used as dispersing agent, scale inhibitor, and additive for borehole drilling, but the kinetics of their copolymerization, reactivity ratios, and the rheological properties of these copolymers in aqueous solution have not been studied. In this article we conduct an experimental investigation for these because this is a technically sound study for quality control and for the application of the copolymer to thickening.

In addition, this article deals with the compositional analysis of random copolymers of acrylamide with sodium allylsulfonate utilizing the  $^1\text{H-NMR}$  method.

## EXPERIMENTAL

### Materials

Acrylamide (AM) was recrystallized from benzene and vacuum dried to constant weight. Sodium allylsulfonate (SAS) was purified by recrystallization with 90% alcohol. Potassium persulfate (KPS) was recrystallized from water.

## Copolymerization

The copolymerization of AM( $M_1$ ) with SAS( $M_2$ ) was conducted in an aqueous solution using potassium persulfate (KPS) as initiator under nitrogen atmosphere. The weighed amount of comonomers were dissolved in deionized water, and inert gas ( $\text{N}_2$ ) was bubbled through while stirring and warmed. Then initiator was added to monomers solution. After completion of the reaction, the reaction mixture was poured into ethanol and the copolymer was precipitated, washed, and dried under reduced pressure to constant weight.

The copolymerization was carried out under various reaction conditions. Conversions (%) were determined gravimetrically.

## Characterization

1. The infrared (IR) spectra of the polymers were recorded with a NICOLET FT-20 SX spectrophotometer. KBr disk.
2.  $^1\text{H-NMR}$  spectra for the polymer were obtained using FX-90 Q spectrometer with  $\text{D}_2\text{O}$  as solvent and TMS as the internal reference.
3. The intrinsic viscosity of polymers was determined at  $25^\circ \pm 0.1^\circ\text{C}$  in 0.5M NaCl solution by an Ubbelohde viscometer.
4. Composition analysis of copolymer was found from the nitrogen and sulfur estimation of

copolymer by Kjeldahl and oxygen flask method, and using the  $^1\text{H-NMR}$  method.

5. Reactivity ratios: Copolymerization for different monomer ratios ( $M_1/M_2$ ) were carried out in an aqueous solution at  $60^\circ\text{C}$  with initiator (KPS). The conversion was in all cases restricted within 10%. The Kelen-Tudos method was employed to calculate the reactivity ratios.
6. Rheology: All solution viscosities were determined by using NDJ-79 model rotary viscometer.

## RESULTS AND DISCUSSION

### Copolymerization

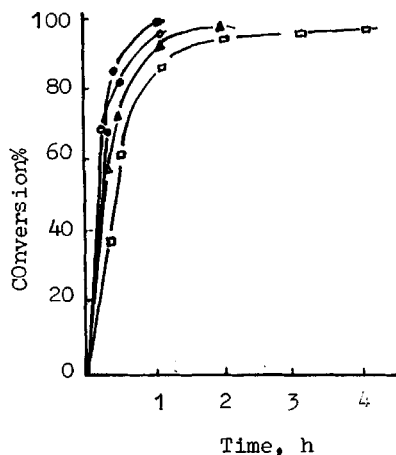
#### Effect of Initiator Concentration on Copolymerization

The primary reaction rate and conversion increase with increasing initiator concentration, results given in Figure 1. Obviously, the increase in initiator concentration brings about an increase in the numbers of radicals ( $\text{SO}_4^{\cdot-}$ ), thereby an increase in reaction rate (Fig. 2).

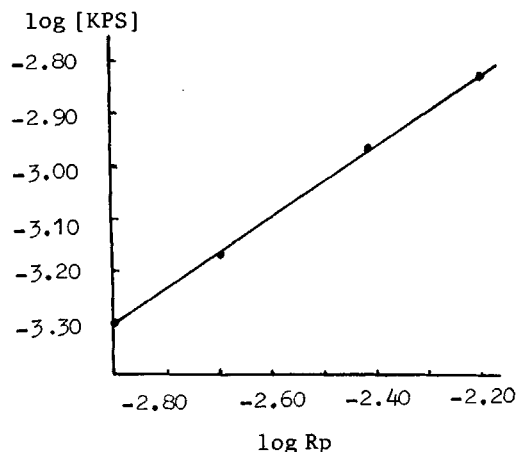
From Figure 2 order of reaction with respect to KPS concentration was found to be 0.70.

#### Effect of Acrylamide Concentration on Copolymerization

As shown in Figure 3 the conversion and the rate increase with increasing acrylamide concentration.



**Figure 1** Effect of KPS concentration on conversion:  $[\text{AM}] = 0.98\text{M}$ ,  $[\text{SAS}] = 0.02\text{M}$ , at  $t^\circ\text{C} = 60 \pm 0.2$ ;  $[\text{KPS}]$ : (1)  $2.0 \times 10^{-3}\text{M}$  ( $\square$ ); (2)  $3.7 \times 10^{-3}\text{M}$  ( $\Delta$ ); (3)  $5.0 \times 10^{-3}\text{M}$  ( $\circ$ ); (4)  $6.0 \times 10^{-3}\text{M}$  ( $\bullet$ ).



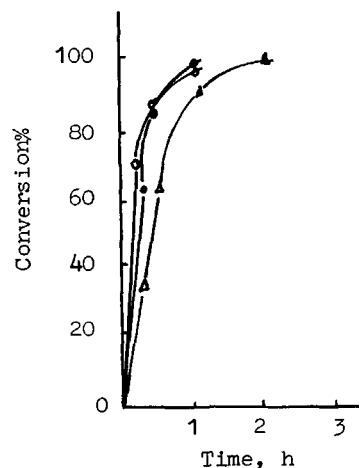
**Figure 2** Plot of  $\log R_p$  vs.  $\log [\text{KPS}]$  (continued from Fig. 1).

The effect of concentration was studied in 0.8–1.2 mol/L range. We could attribute this increase in the conversion and the rate with increasing AM in the feed to the reason that the increase in acrylamide molecules of availability for copolymerization.

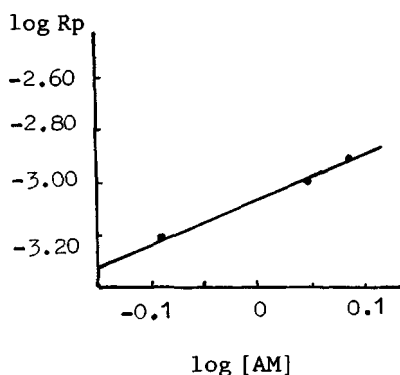
Order of reaction with respect to acrylamide concentration was found to be 1.60 (from Fig. 4).

#### Effect of Sodium Allylsulfonate Concentration on Copolymerization

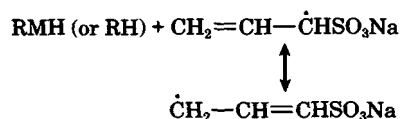
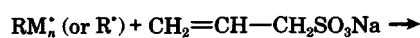
Primary rate and conversion decrease with increasing sodium allylsulfonate concentration (Fig. 5). That may be due to chain translation as following:



**Figure 3** Effect of AM concentration on conversion:  $[\text{SAS}] = 0.02\text{M}$ ,  $[\text{KPS}] = 3.7 \times 10^{-3}\text{M}$ , at  $t^\circ\text{C} = 60 \pm 0.2$ ;  $[\text{AM}]$ : (1)  $0.8\text{M}$  ( $\Delta$ ); (2)  $1.1\text{M}$  ( $\circ$ ); (3)  $1.2\text{M}$  ( $\bullet$ ).



**Figure 4** Plot of  $\log R_p$  vs.  $\log [AM]$ , (continued from Fig. 3).

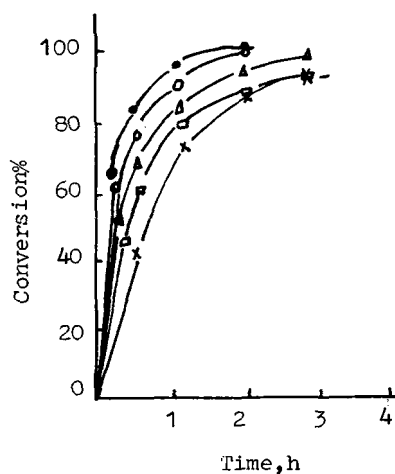


The radical abstract hydrogen atom from  $\alpha$ -carbon of allylsulfonate molecule involves the rearrangement of electrons to form a stable radical, thereby copolymerization is unfavored.

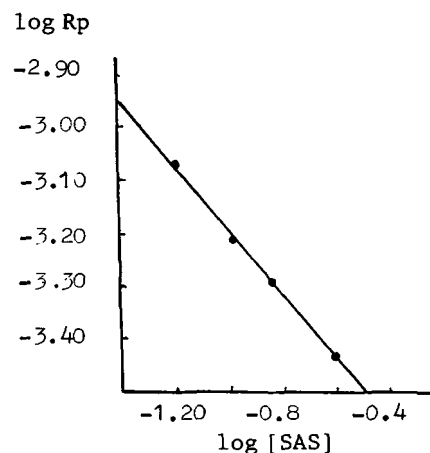
Order of reaction with respect to SAS concentration was found to be  $-0.60$  (from Fig. 6).

From before, we obtained the reaction rate equation:

$$R_p = [KPS]^{0.70} [AM]^{1.60} [SAS]^{-0.60}$$



**Figure 5** Effect of SAS concentration on conversion:  $[AM] = 0.98M$ ,  $[KPS] = 3.7 \times 10^{-3}M$ , at  $t^\circ C = 60 \pm 0.2$ ;  $[SAS]$ : (1)  $0.24M$  (X); (2)  $0.14M$  ( $\square$ ); (3)  $0.10M$  ( $\Delta$ ); (4)  $0.06M$  ( $\circ$ ); (5)  $0.02M$  ( $\bullet$ ).



**Figure 6** Plot of  $\log R_p$  vs.  $\log [SAS]$ , (continued from Fig. 5).

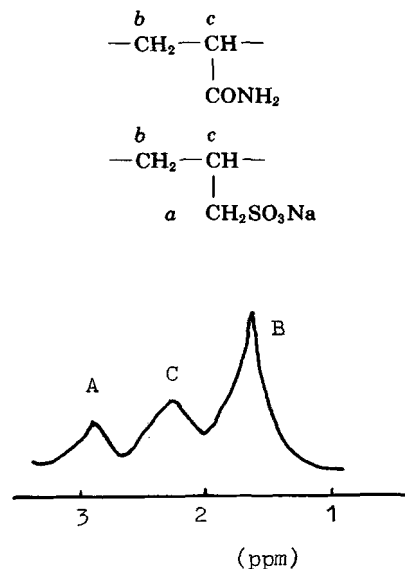
## Spectra

### IR Spectra

The absorbance at  $1664.74 \text{ cm}^{-1}$ , attributed to  $C=O$  stretching, is present in AM units. Similarly, the absorbance at  $3360.898$  (NH) and  $1041.40 \text{ cm}^{-1}$  ( $S=O$ ) were characteristic peak for AM and SAS units, respectively.

### $^1H$ -NMR Spectrum and Compositional Quantitation

In the  $^1H$ -NMR spectrum (Fig. 7) the distinct peak assignments for copolymer are



**Figure 7**  $^1H$ -NMR for poly(acrylamide-co-sodium allylsulfonate).

For the chemical shift values (ppm) (Fig. 7):

$$H_a = 2.86$$

$$H_b = 1.66$$

$$H_c = 2.19$$

As shown in Figure 7, it may be divided into three absorbing areas (A, B, and C),  $H_a$ ,  $H_b$ , and  $H_c$  belong with A, B, and C, respectively.

If

$m_1$  = mole of acrylamide units in the copolymer

$m_2$  = mole of sodium allylsulfonate units  
in the copolymer

Therefore

$$2m_2 = KA$$

$$3m_1 + 3m_2 = K(B + C)$$

where,  $K$  is a constant

resolvent:

$$m_1/m_2 = \frac{2(B + C)}{3A} - 1 = Y$$

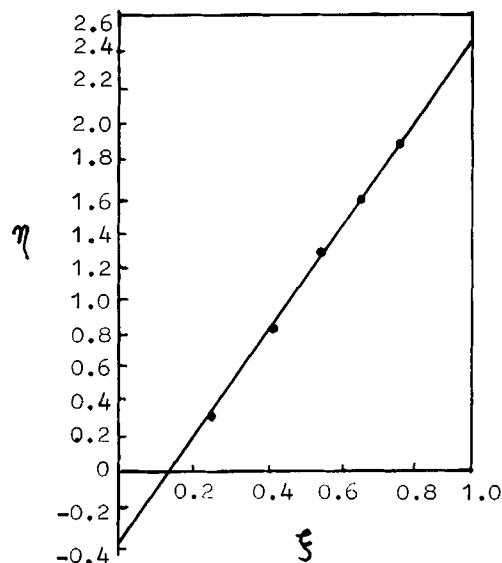
where  $Y$  is a mole ratio ( $m_1/m_2$ ) in the copolymer, and we obtain the values of  $A$ ,  $B$ , and  $C$  with integrated curvilinear level. The calculated results with NMR method and elemental analysis were found to be in good agreement (see Table I).

### Reactivity Ratios

The reactivity ratios were calculated by the Kelen-Tudos (K-T) method.<sup>3</sup> The K-T equation is expressed as

**Table I** Mole Ratios of Monomeric Units in Copolymer

No.	Mole Ratios in Feed ( $M_1/M_2$ )	Y ( $m_1/m_2$ )	
		NMR Method	Elemental Analysis
1	1.50	4.49	4.50
2	1.00	3.25	3.30
3	0.67	2.48	2.48
4	0.43	1.83	1.82
5	0.25	1.25	1.24



**Figure 8** Kelen-Tudos plot for the determination of reactivity ratios for copolymerization of AM with SAS,  $a = 0.158$ .

$$\eta = (r_1 + r_2/a)\xi - r_2/a \quad (1)$$

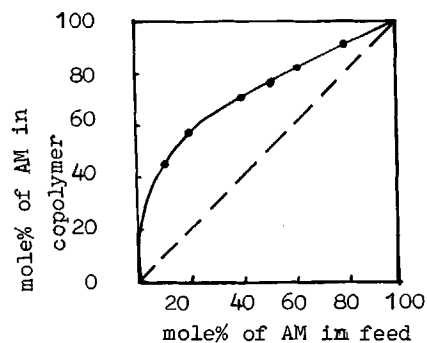
where,  $\eta = G/(a + F)$ ,  $\xi = F/(a + F)$

$$F = X^2/Y \quad G = X(Y - 1)/y$$

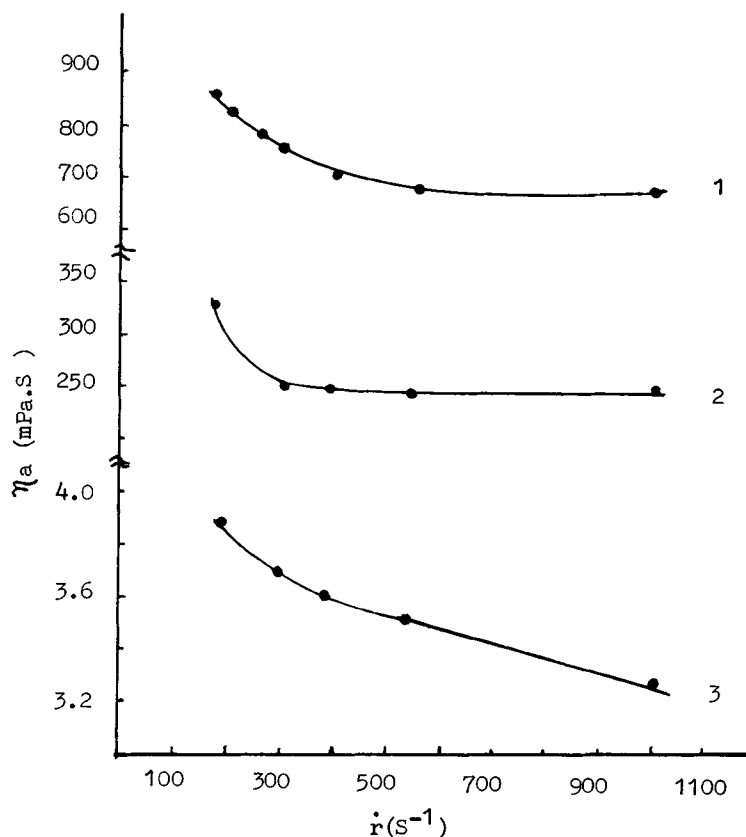
$$X = M_1/M_2 \quad Y = m_1/m_2$$

Parameter  $a$  is obtained from  $a = \sqrt{F_m F_M}$ , where  $F_m$  and  $F_M$  are the lowest and highest  $F$  from the experiment data. By plotting  $\eta$  versus  $\xi$  according to Eq. (1), we obtain directly  $r_1 = 2.45$  and  $r_2 = 0.060$  from the intercepts (Fig. 8) at  $\xi = 1$  and  $\xi = 0$ , respectively.

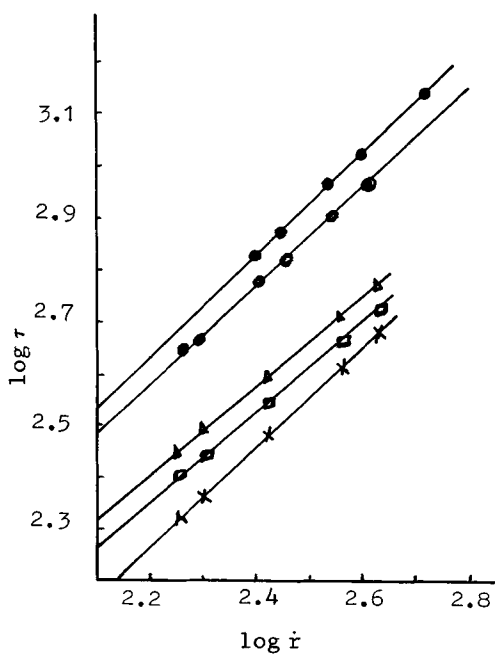
The curve was derived from the copolymerization equation using the experimentally determined reac-



**Figure 9** Copolymer composition as a function of feed composition of AM with SAS.

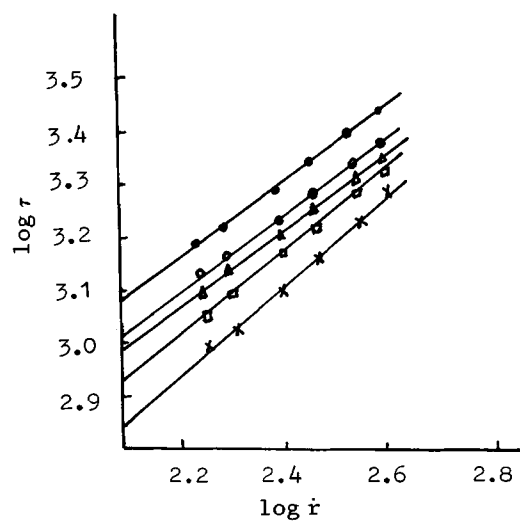


**Figure 10** Solution viscosity  $\eta_a$  vs.  $\dot{r}$ , at 30°C: (1) 15% (g/100 mL); (2) 10% (g/100 mL); (3) 3% (g/100 mL).



**Figure 11** Plot of  $\log \tau$  vs.  $\log \dot{r}$  for concentrated solution (10%) at various temperatures ( $t^\circ\text{C}$ ): (1) 60 (X); (2) 50 (□); (3) 45 (Δ); (4) 40 (O); (5) 30 (●).

tivity ratios. Because  $r_1 > 1$ ,  $r_2 < 1$ , composition is different from monomer composition in the feed (Fig. 9).



**Figure 12** Plot of  $\log \tau$  vs.  $\log \dot{r}$  for concentrated solution (15%) at various temperatures ( $t^\circ\text{C}$ ): (1) 60 (X); (2) 50 (□); (3) 45 (Δ); (4) 40 (O); (5) 30 (●).

**Table II**  $n$  Exponent of the Copolymer Solution

Concentration (%)	10					15				
	30	40	45	50	60	30	40	45	50	60
Temperature (°C)										
$n$	0.92	0.91	0.91	0.91	0.92	0.80	0.78	0.78	0.80	0.81

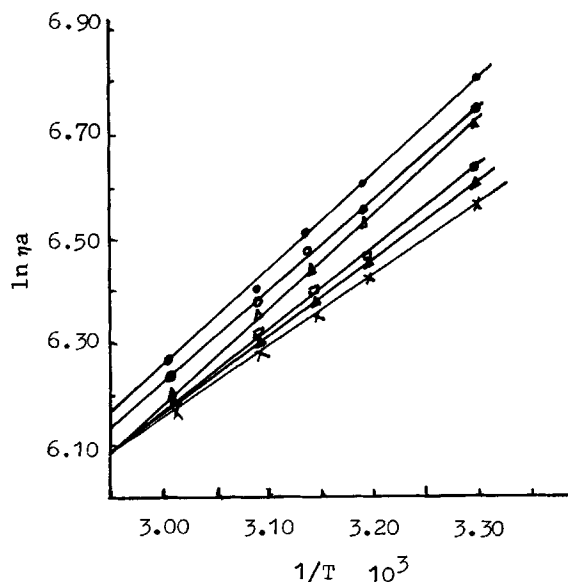
### Rheology

The rheological properties of the copolymer in aqueous solution have been determined by using NDJ-79 model rotary viscometer under various temperatures. These solutions of the copolymers are shear thinning and have viscosities that are predicted by the power law equation:

$$\tau = \eta_a \dot{\gamma} = K \dot{\gamma}^{n-1}$$

$$n = dl \, g\tau / dl \, g\dot{\gamma}$$

where  $\eta_a$  is the apparent viscosity,  $\dot{\gamma}$  is the rate of shear,  $\tau$  is shearing stress,  $K$  is shearing viscosity coefficient, and  $n$  is the power law exponent. Fluids with the  $n$  value of 1.0 are Newtonian flowing; those with the  $n$  value less than 1.0 are shear thinning (non-Newtonian) and become more shear thinning as  $n$  decreases toward zero.



**Figure 13** Plot of  $\ln \eta_a$  vs.  $1/T$  for 15% concentrated solution  $\dot{\gamma}$  ( $s^{-1}$ ): (1) 391 (X); (2) 344 (▲); (3) 282 (□); (4) 251 (Δ); (5) 185 (O); (6) 176 (●).

Viscosity measured at 30°C of solution of the copolymer is given in Figure 10. These plots show that copolymer solutions are thinning with the degree of shear thinning increasing as copolymer solution concentration increases.

Figures 11 and 12 are the plots of  $\log \tau$  vs.  $\log \dot{\gamma}$  of polymer concentrated solution (10, 15%). The data of Table II shows that the  $n$  exponent in the same concentration is not changed with increasing temperature but decrease with increasing concentration under the same temperature.

Figure 13 shows the plot of  $\ln \eta_a$  versus  $1/T$  at various shear rates. According to the following equation,

$$\eta_a = A e^{\Delta E_n / RT} \quad \text{or} \quad \ln \eta_a = \ln A + E_n / RT$$

where  $\eta_a$  is an apparent viscosity,  $A$  is a constant, and  $E_n$  is a flowing activation energy.

From the preceding,  $E_n$  is calculated in Table III.

Thus  $E_n$  decreases as  $\dot{\gamma}$  increases, and it is a positive value, so the viscosity of poly(AM-co-SAS) solution decreases with increasing temperature and shear rate.

### CONCLUSION

The synthetic water-soluble poly(AM-co-SAS) was prepared, the effects of various factors on the copolymerization were studied in detail, and the results were kinetically investigated. The copolymerization rate equation was determined:

**Table III**  $E_n$  Value, 15% Polymer Concentrated Solution

$\dot{\gamma}$ ( $s^{-1}$ )	176	195	251	282	344	391
$E_n$ (kJ/mol)	15.1	14.9	13.9	13.4	12.4	11.9

$$R_p = K[\text{KPS}]^{0.70}[\text{AM}]^{1.60}[\text{SAS}]^{-0.60}$$

The reactivity ratios  $r_1$  and  $r_2$  were determined to be 2.45 and 0.060, respectively.

The rheological behavior of the copolymer in aqueous solution has shown to be effective for thickening (e.g., polymer flooding for enhanced oil recovery), and these solutions are pseudoplastic fluids (non-Newtonian). The flowing activity energy  $E_\eta$  was calculated such that  $E_\eta$  decreases as the shear rate increases. The viscosity of poly(AM-co-SAS)

solution decreases with increasing temperature and shear rate.

## REFERENCES

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