

# Copolymerization Kinetics of Acrylonitrile with Amino Ethyl-2-Methyl Propenoate in H<sub>2</sub>O/DMSO Mixture

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**ABSTRACT:** Amino ethyl-2-methyl propenoate (AEMP) was used successfully to copolymerize with acrylonitrile (AN). This was achieved by using azobisisobutyronitrile as the initiator. Kinetics of copolymerization of AN with AEMP was investigated in H<sub>2</sub>O/dimethylsulfoxide (DMSO) mixture between 50 and 70 °C under N<sub>2</sub> atmosphere. The rate of copolymerization was measured. The kinetic equation of copolymerization system was obtained and the overall activation energy for the copolymerization system was determined. Values of monomer apparent reactivity ratios were calculated using Kelen–Tudos method. It has been found that the apparent reactivity ratios in aqueous suspension polymerization system are similar to those in solution polymerization system at polymerization conversion less than

25%. At conversion beyond 45%, the changes of monomer apparent reactivity ratios become less prominent. In water-rich reaction medium (H<sub>2</sub>O/DMSO > 70/30), monomer apparent reactivity ratios are approximately equivalent to those in aqueous suspension polymerization system. In DMSO-rich reaction medium (DMSO/H<sub>2</sub>O > 70/30), apparent reactivity ratios are similar to those in solution polymerization system. With an increase of polarity of solvent, values of apparent reaction ratios both decrease. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2095–2100, 2006

**Key words:** acrylonitrile; copolymerization; kinetics; activation energy

## INTRODUCTION

Carbon fiber composites are important construction materials in applications where high strength and modulus, high thermal and corrosion resistance, and light weight are the prime requirements.<sup>1</sup> It is well known that the properties of the final carbon fibers are determined by the nature of the precursor fibers. It is important to select a suitable technique and optimize the conditions of polymerization for the synthesis of an acrylic polymer satisfying the requirements for high-tenacity acrylic fibers.<sup>2,3</sup> Several polymerization techniques have been successfully used to synthesize homopolymers and copolymers of acrylonitrile (AN) for high-tenacity fibers. Solution, aqueous suspension, and solvent water suspension are the most common used techniques.<sup>4</sup> The solvent water suspension method is a new and promising technique that may be used in the production of high-performance acrylic

fiber, and this cleverly combines the advantages of solution and those of aqueous suspension.

Knowledge of copolymer's composition is an important step in the evaluation of its utility. The theory of radical copolymerization leads to the conclusion that the copolymer composition and its distribution are dependent on the monomer reactivity ratios. Reactivity ratio values may be evaluated by various procedures: linear procedures, nonlinear procedures, and other copolymer composition equations.<sup>5–7</sup> Kelen–Tudos method has been widely used.<sup>8</sup>

Various carboxylic acids are used as comonomers to copolymerize with AN to obtain specialty fibers for various applications.<sup>9–12</sup> Considerable information exists in the literature on the use of comonomers other than carboxylic acids for the preparation of polyacrylonitrile precursor fibers.<sup>13</sup> In the case of amino ethyl-2-methyl propenoate (AEMP), a lowering of the time of stabilization, a reduction in the thermal degradation, and a better control of heat flux during oxidative cyclization have been reported. But fewer are on kinetic study of copolymerization of AN with AEMP in H<sub>2</sub>O/dimethyl sulfoxide (DMSO) mixture systems and there is almost no report on monomer apparent reactivity ratios for AN and AEMP. In this study, H<sub>2</sub>O/DMSO suspension technique was used to synthesize AN/AEMP copolymers. For estimating polymerization rates, copolymerization experiments were

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terminated at <10% conversion.<sup>14</sup> The conversion was controlled and determined by gravimetric measurements. Kinetics of copolymerization of AN with AEMP was studied between 50 and 70 °C under N<sub>2</sub> atmosphere and a suitable kinetic scheme was proposed and the overall activation energy was evaluated. Furthermore, elemental analyses were carried out by a PE2400 microanalyzer. Kelen–Tudos method was also employed. Effects of different copolymerization conditions on monomer apparent reactivity ratios for AN/AEMP copolymer were studied for comparison.

## EXPERIMENTAL

### Materials

AN (Shanghai Chemical Reagents, AR grade) was vacuum distilled from CaH<sub>2</sub> just before polymerization. AEMP (Shanghai Chemical Reagents, AR grade) was used as a comonomer. Azobisisobutyronitrile (AIBN) was used as an initiator and recrystallized from ethanol before use. Polyvinyl alcohol (PVA) (polymerization degree = 1800) was used as suspending agent. Deionized water and DMSO were adopted as the polymerization medium.

### Copolymerization

A typical example of the general procedure was as follows. Required amounts of AN, AEMP, PVA, AIBN, deionized water, and DMSO were placed in a flask, which was continuously flushed with ultrapure nitrogen. The flask was wholly immersed in a temperature-controlled water bath and was shaken from time to time. All the experimental conditions have been provided in Tables I–VI. After a definite reaction time, copolymerization was terminated at <10% conversion by cooling the flask in the ice water. The resultant mixture was poured into a large amount of methanol for precipitation, washed with methanol several times, dried at 60 °C in vacuum until the constant weight, and then weighed.

### Characterization

Conversion and the rate of polymerization were calculated from the weight of polymer obtained. The molecular weight ( $M_w$ ) of the purified polymers was determined by viscosity measurements. Intrinsic viscosity  $[\eta]$  of the polymers were measured at 35 °C in dimethyl formamide using an Ubbelohde viscometer,<sup>15</sup> and the molecular weight was calculated from<sup>16</sup>

$$[\eta] = 2.78 \times 10^{-4} M_w^{0.76} \quad (1)$$

Elemental analyses of the copolymers were carried out with PE2400 microanalyzer to determine the oxygen content of these copolymers. The monomer reactivity ratios for copolymerization of AN with AEMP were determined from the monomer feed ratios and the copolymer composition. The apparent reactivity ratios of AN and AEMP were calculated by Kelen–Tudos method from eq. (2)

$$\frac{x(y-1)}{ay+x^2} = \frac{(r_{AN} + r_{AEMP}/a)x^2}{ay+x^2} - \frac{r_{AEMP}}{a} \quad (2)$$

$$x = \frac{M_{AN}}{M_{AEMP}} \text{ (mol/mol)}, y = \frac{dM_{AN}}{dM_{AEMP}} \text{ (mol/mol)}$$

where  $x$  is the ratio of molar fractions of monomer AN and monomer AEMP in the monomer feed,  $y$  is the ratio of molar fractions of monomer AN and monomer AEMP in the copolymer, and  $a$  is an equation parameter. The equation parameter can be computed according to eq.(3):

$$a = \frac{x_{\min}x_{\max}}{\sqrt{y_{\min}y_{\max}}} \quad (3)$$

where  $x_{\min}$ ,  $x_{\max}$  are minimal and maximal molar fractions in the monomer feed, and  $y_{\min}$ ,  $y_{\max}$  are minimal and maximal molar fraction in the copolymer.

Transform eq. (2) into the form:

$$\tau = (r_{AN} + r_{AEMP}/a)\delta - \frac{r_{AEMP}}{a} \quad (4)$$

$$\tau = \frac{x(y-1)}{ay+x^2}, \delta = \frac{x^2}{ay+x^2}$$

The plot of  $\tau$  versus  $\delta$  gives a straight line. Extrapolation of the line to  $\delta=1$  gives  $r_{AN}$  and  $\delta=0$  gives  $r_{AEMP}/a$ .

## RESULTS AND DISCUSSION

### Kinetic equation of different copolymerization system

Aqueous suspension technique was used to synthesize AN/AEMP copolymer. Effect of AIBN concentration

TABLE I  
Effect of Initiator Concentration on Copolymerization

AIBN concentration (mol·L <sup>-1</sup> )	Conversion (%)	$M_w$ (10 <sup>4</sup> )
0.0045	4.01	55.3
0.0060	4.92	40.2
0.0075	5.82	30.1
0.0090	6.67	19.8

Conditions:  $C_{AN} = 4.5 \text{ mol}\cdot\text{L}^{-1}$ ,  $C_{AEMP} = 0.04 \text{ mol}\cdot\text{L}^{-1}$ ,  $C_{PVA} = 0.22\text{g}\cdot\text{L}^{-1}$ , H<sub>2</sub>O/DMSO (w/w) = 100/0,  $T = 60 \text{ }^\circ\text{C}$ ,  $t = 15 \text{ min}$ .

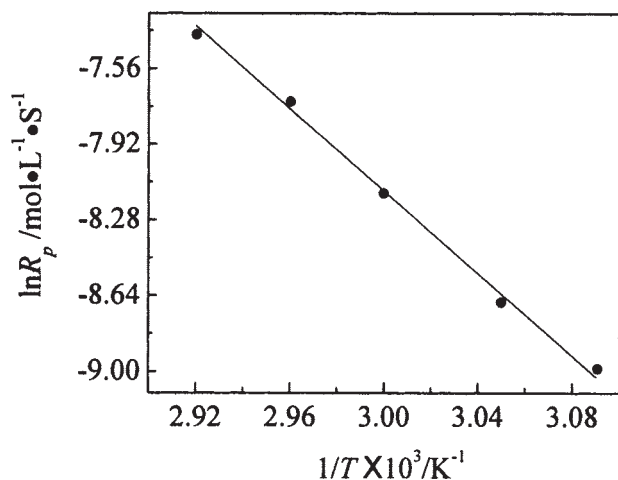


Figure 1 Relationship between  $\ln R_p$  and  $\ln[\text{AIBN}]$ .

on copolymerization was studied. Table I shows the variation in percentage conversion and molecular weight as a function of initiator concentration. According to the results summarized in Table I, it is clear that conversion increases quickly and  $M_w$  reduces quickly as AIBN concentration increases. The rate of polymerization ( $R_p$ ) was calculated from the slope of a plot of conversion versus time. Figure 1 is a logarithmic plot of  $R_p$  versus  $[\text{AIBN}]$ . The reaction order estimated from the slope is 0.735.

Effects of AN and AEMP concentrations on  $R_p$  were also studied. The reaction orders from the slope of the plot were 1.92 and 1.39, respectively. The overall rate of copolymerization is  $R_p \propto [\text{AIBN}]^{0.735}[\text{AN}]^{1.92}[\text{AEMP}]^{1.39}$ . This is different from the reaction order reported. Pan<sup>17</sup> revealed that reaction orders of initiator and monomer are 0.5 and 1 when the solution technique was used to synthesize polyacrylonitrile. Zou<sup>18</sup> also studied the kinetics of polymerization of AN initiated by the redox system using the aqueous suspension technique, and a kinetic equation  $R_p \propto [\text{initiator}]^{0.7}[\text{AN}]^2$  was proposed.

TABLE II  
Effect of Ratio of H<sub>2</sub>O/DMSO on the Kinetic Equation

H <sub>2</sub> O/DMSO (w/w)	$R_p$ (mol·L <sup>-1</sup> ·s <sup>-1</sup> )
100/0	$[\text{AIBN}]^{0.735}[\text{AN}]^{1.92}[\text{AEMP}]^{1.39}$
90/10	$[\text{AIBN}]^{0.722}[\text{AN}]^{1.84}[\text{AEMP}]^{1.35}$
80/20	$[\text{AIBN}]^{0.703}[\text{AN}]^{1.78}[\text{AEMP}]^{1.31}$
70/30	$[\text{AIBN}]^{0.683}[\text{AN}]^{1.69}[\text{AEMP}]^{1.25}$
60/40	$[\text{AIBN}]^{0.651}[\text{AN}]^{1.61}[\text{AEMP}]^{1.18}$
50/50	$[\text{AIBN}]^{0.639}[\text{AN}]^{1.51}[\text{AEMP}]^{1.13}$
40/60	$[\text{AIBN}]^{0.624}[\text{AN}]^{1.45}[\text{AEMP}]^{1.11}$
30/70	$[\text{AIBN}]^{0.613}[\text{AN}]^{1.39}[\text{AEMP}]^{1.08}$
20/80	$[\text{AIBN}]^{0.591}[\text{AN}]^{1.33}[\text{AEMP}]^{1.07}$
10/90	$[\text{AIBN}]^{0.551}[\text{AN}]^{1.26}[\text{AEMP}]^{1.04}$
0/100	$[\text{AIBN}]^{0.532}[\text{AN}]^{1.19}[\text{AEMP}]^{1.01}$

Conditions:  $T = 60\text{ }^\circ\text{C}$ ,  $t = 15\text{ min}$ .

Effects of ratios of H<sub>2</sub>O/DMSO on the kinetic equation were shown in Table II. AIBN cannot dissolve in water easily, when AN/AEMP copolymer is synthesized using solvent water suspension technique,<sup>19,20</sup> oligomeric radicals may form quickly in the initial stages of polymerization. The oligomeric polymers precipitate out at the different critical molecular weight depending on the solvent/water ratio and then act as primary particles. In water-rich reaction medium (H<sub>2</sub>O/DMSO > 80/20), propagation of the oligomeric polymers is more likely to follow the way of suspension polymerization because of the insoluble primary radicals. The chain termination is mainly resulted from the one-radical reaction, so that the reaction order of initiator tends to be 1. The rate of initiation is influenced by monomer concentration, so the reaction order of monomer is much larger than 1. Solubility and reactivity of AEMP is greater than AN in DMSO, so the departure from 1 of the reaction order is smaller. In DMSO-rich reaction medium (DMSO/H<sub>2</sub>O > 80/20), there is no oligomeric polymers precipitating out and the copolymerization follows the way of solution polymerization. The kinetic equation of is  $R_p \propto [\text{AIBN}]^{0.532}[\text{AN}]^{1.19}[\text{AEMP}]^{1.01}$  when the ratio of H<sub>2</sub>O/DMSO is 0/100 (Table II). The extent of active free radicals embedded becomes less prominent. The chain termination mainly results from the two-radical reaction, so that the reaction order of initiator is close to 0.5. Efficiency of initiator increases and almost all the radicals are used to initiate the monomers. The reaction order of monomers tends to be 1.

#### Determination of the overall activation energy

Effect of temperature on polymerization was also studied, which is given in Table III. AN/AEMP copolymer was synthesized at 50, 55, 60, 65, and 70 °C. The rate of polymerization of copolymer increases and the molecular weight decreases as temperature increases. The drop in the molecular weight may be attributed to the swift termination rate, which results from the high chain transfer coefficient. It is reported that the high chain transfer coefficient of DMSO is  $7.95 \times 10^{-5}$  at 50

TABLE III  
Effect of Temperature on Copolymerization

$T$ (°C)	Conversion (%)	$M_w$ (10 <sup>4</sup> )
50	2.41	56.8
55	3.57	46.7
60	5.82	30.1
65	8.61	24.6
70	12.8	18.9

Conditions:  $C_{\text{AN}} = 4.5\text{ mol L}^{-1}$ ,  $C_{\text{AEMP}} = 0.04\text{ mol L}^{-1}$ ,  $C_{\text{AIBN}} = 0.0075\text{ mol L}^{-1}$ , H<sub>2</sub>O/DMSO (w/w) = 100/0,  $C_{\text{PVA}} = 0.22\text{ g L}^{-1}$ ,  $t = 15\text{ min}$ .

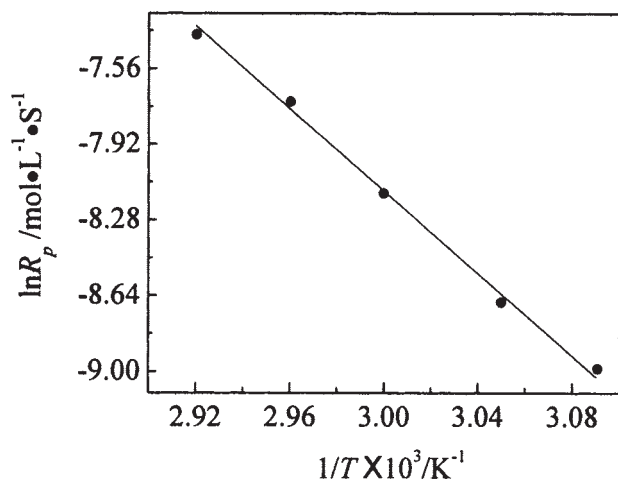


Figure 2 Relationship between  $R_p$  and  $T$ .

$^{\circ}\text{C}$ ,<sup>21</sup> and the extent of chain transfer reaction increases with temperature. The overall activation energy of polymerization, calculated from the slope of linear Arrhenius plot (Fig. 2) is  $81.5 \text{ kJ mol}^{-1}$ .

#### Effect of monomer concentration on the overall activation energy

Moreover, the overall activation energy computed is  $82.2 \text{ kJ mol}^{-1}$  when AN concentration is  $4.4 \text{ mol L}^{-1}$  instead of  $4.5 \text{ mol L}^{-1}$ ; the overall activation energy computed is  $80.5 \text{ kJ mol}^{-1}$  when AEMP concentration is  $0.05 \text{ mol L}^{-1}$  instead of  $0.04 \text{ mol L}^{-1}$  (Table IV). From these experiments, we can conclude that influence of monomer concentration on the overall activation energy is less obvious. The overall activation energy is mainly determined by the activation energy of pyrolytic reaction of the initiator.

#### Effect of mixture solution on reactivity ratios

Solution polymerization technique was used to synthesize AN/AEMP copolymer. Table V shows some important parameters and the polymerization conditions of the copolymer. It has been found that pure AN/AEMP copolymers have been obtained successfully. Kelen–Tudos method gave monomer apparent

TABLE IV  
Effect of Monomer Concentration on the Activation Energy

$C_{\text{AN}}$	$C_{\text{AEMP}}$	$\Delta E_a \text{ (kJ}\cdot\text{mol}^{-1}\text{)}$
4.5	0.04	81.5
4.5	0.05	80.5
4.4	0.04	82.2

Conditions:  $C_{\text{AIBN}} = 0.0075 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}/\text{DMSO}$  (w/w) = 100/0,  $C_{\text{PVA}} = 0.22 \text{ g L}^{-1}$ ,  $t = 15 \text{ min}$ .

TABLE V  
Solution Copolymerization Parameters of AN/AEMP in DMSO

$x$ (mol/mol)	Conversion (wt %)	Content of oxygen (mol %)	$y$ (mol/mol)
100	5.99	4.49	42.5
80	6.56	4.68	40.7
40	7.84	8.62	21.2
20	8.24	16.1	10.4

Condition:  $C_{\text{AN}} = 4.5 \text{ mol L}^{-1}$ ,  $C_{\text{AIBN}} = 0.0075 \text{ mol L}^{-1}$ ,  $T = 60 \text{ }^{\circ}\text{C}$ .

reactivity ratios for AN and AEMP of  $r_{\text{AN}} = 0.485$ ,  $r_{\text{AEMP}} = 2.69$  (Fig. 3), which is a criteria to judge other results. The higher reactivity ratio value of AEMP confirms its high reactivity compared with that of AN. The polymer radical with a AEMP unit at the chain end is considerably more active than with an AN unit, and the probability of AEMP entry into the chain is greater than that of AN entry, which leads to an increase of polymerization conversion with the addition of AEMP comonomer.

Apparent reactivity ratios of AN and AEMP in aqueous suspension polymerization system was also calculated by Kelen–Tudos method. The experimental results are given in Figure 4. At monomer conversion less than 25%, the values of monomer apparent reactivity ratios in aqueous suspension polymerization system are similar to those in solution polymerization system,  $r_{\text{AN}} = 0.485 \pm 0.002$ ,  $r_{\text{AEMP}} = 2.69 \pm 0.02$ . With an increase of monomer conversion, reactivity ratio for AN rises rapidly and that for AEMP reduces quickly. When conversion is more than 45%, the changes of monomer reactivity ratios become less prominent,  $r_{\text{AN}} = 0.669 \pm 0.002$ ,  $r_{\text{AEMP}} = 2.24 \pm 0.02$ . Apparent reactivity ratios of monomers in a system depend on the technique of polymerization. When AN/AEMP copolymer is synthesized using aqueous suspension technique, oligomeric radicals may be

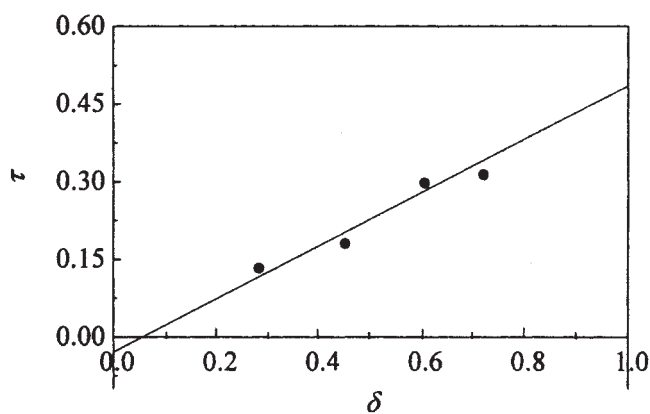


Figure 3 Relationship between  $\tau$  and  $\delta$ .

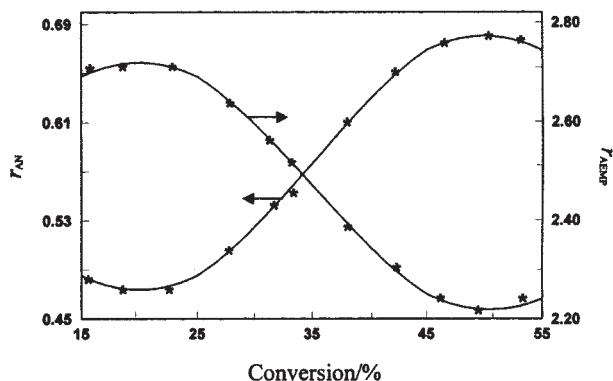


formed in the initial stages of polymerization, which precipitate out after attaining a certain critical molecular weight and then act as primary particles. Propagation would then occur either in water phase or the oligomeric radicals phase.<sup>22</sup> When conversion is less than 25%, polymerization follows more of the solution polymerization technique, reactivity ratios calculated are similar to those in solution polymerization system. As polymerization conversion increases, propagation would then mostly occur in oligomeric radicals phase. AN units are more easily absorbed by polymer radicals than AEMP units. The value of reactivity ratio for AN rises rapidly.

Effect of mixture solution on apparent reactivity ratios of monomers was also studied. AN/AEMP copolymer was synthesized by solvent water suspension polymerization technique. According to the results summarized in Table VI, in water-rich reaction medium ( $H_2O/DMSO > 70/30$ ), values of monomer apparent reactivity ratios are similar to those in aqueous suspension polymerization system; in DMSO-rich reaction medium ( $DMSO/H_2O > 70/30$ ), values of monomer reactivity ratios are similar to those in solution polymerization system. When AN/AEMP copolymer is synthesized using solvent water suspension technique, after a definite time, propagation would then occur either in water phase, the DMSO phase, the oligomeric radicals phase, or at the interface of DMSO–water–oligomer mixture, depending on the solubility of monomers.<sup>23</sup> In water-rich reaction medium, because of the insolubility oligomeric radicals, propagation follows the suspension polymerization technique more. In DMSO-rich reaction medium, copolymerization follows the solution polymerization technique more.

#### Effect of solvent polarity on reactivity ratios

To study the effect of solvent polarity on apparent reactivity ratios of monomers, AN/AEMP copolymer



**Figure 4** Effect of conversion on monomer reactivity ratios in aqueous suspension polymerization system. Condition:  $C_{AN} = 4.5 \text{ mol L}^{-1}$ ,  $C_{AIBN} = 0.0075 \text{ mol L}^{-1}$ ,  $C_{PVA} = 0.22 \text{ g L}^{-1}$ ,  $T = 60 \text{ }^\circ\text{C}$ .

**TABLE VI**  
Reactivity Ratios Parameters in  $H_2O/DMSO$  Mixture Solvent Medium

$H_2O/DMSO$ (w/w)	$r_{AN}$	$r_{AEMP}$
90/10	0.479	2.78
80/20	0.489	2.67
70/30	0.484	2.71
60/40	0.529	2.62
50/50	0.558	2.59
40/60	0.604	2.39
30/70	0.667	2.25
20/80	0.671	2.29
10/90	0.668	2.21

Condition:  $C_{AN} = 4.5 \text{ mol L}^{-1}$ ,  $C_{AIBN} = 0.0075 \text{ mol L}^{-1}$ ,  $C_{PVA} = 0.22 \text{ g L}^{-1}$ ,  $T = 60 \text{ }^\circ\text{C}$ .

was synthesized in DMF by solution polymerization technique. Previous articles reported that effect of solvent polarity on reactivity ratios may be not obvious.<sup>24</sup> But in this study, different conclusions are drawn,  $r_{AN} = 0.462$ ,  $r_{AEMP} = 2.42$ . Both  $r_{AN}$  and  $r_{AEMP}$  decrease compared with those in DMSO. Solubility and activity of monomer AN, AEMP, and the polymer radicals are different in different polar solvent. The concentrations of AN and AEMP in local area are lower than those in the monomer feed. The reactivity ratios of AN and AEMP were calculated using concentrations in the monomer feed instead of those in local area. In fact, what we calculated are called the apparent reactivity ratios.

## CONCLUSIONS

Laboratory kinetic studies of different copolymerization systems reveal that AIBN successfully initiates the free radical copolymerization of AN with AEMP. The kinetic schemes are proposed. The overall activation energy is mainly determined by the activation energy of pyrolytic reaction of the initiator.

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