

# Kinetic Study of Copolymerization of Acrylonitrile with Ammonium Acrylate

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**ABSTRACT:** Ammonium acrylate was first used to successfully copolymerize with acrylonitrile. Kinetics of copolymerization of acrylonitrile with ammonium acrylate was investigated in a H<sub>2</sub>O/dimethylsulfoxide (DMSO) mixture. The rate of copolymerization and particle size were measured. Kinetic equation of the copolymerization was obtained. Effect of copolymerization systems on monomer apparent reactivity ratios for acrylonitrile/ammonium acrylate copolymers was studied in comparison. Values of monomer apparent reactivity ratios were calculated by Kelen-Tudos method. It has been found that monomer apparent reactivity

ratios in water-rich reaction medium [H<sub>2</sub>O/DMSO > 80/20] are approximately equivalent to those in aqueous suspension polymerization system. In DMSO-rich reaction medium (DMSO/H<sub>2</sub>O > 80/20), apparent reactivity ratios are similar to those in solution polymerization system. With an increase in polarity of solvent, values of apparent reaction ratios both decrease. The values of apparent reaction ratios gradually tend to 1 with increase in the copolymerization temperature.

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**Key words:** copolymerization; kinetics; monomers

## INTRODUCTION

It is important to select a suitable technique and optimize the conditions of polymerization for the synthesis of high performance acrylic polymers.<sup>1,2</sup> Several polymerization techniques have been successfully used to synthesize homopolymers and copolymers of acrylonitrile (AN). Solution, aqueous suspension, and solvent/water suspension are the most common useful techniques.<sup>3</sup> The solvent/water suspension method is a new and promising technique that may be used in the production of high-performance acrylic fiber, which cleverly combines the advantages of solution and those of aqueous suspension. Various comonomers are used to copolymerize with AN to obtain speciality fibers for various applications.<sup>4</sup> To our knowledge, there are only few reports on ammonium acrylate (AAT) as a comonomer, but there is almost no reports on kinetic study of copolymerization of AN with AAT in H<sub>2</sub>O/dimethylsulfoxide (DMSO) mixture systems. In this study, H<sub>2</sub>O/DMSO suspension technique was used to synthesize

AN/AAT copolymers. For estimating polymerization kinetics, copolymerization experiments were terminated at less than 10% conversion.<sup>5</sup> The suitable kinetic schemes were proposed. Reactivity ratio values may be evaluated by various procedures: linear procedures, nonlinear procedures, and other copolymer composition equations.<sup>6–9</sup> Kelen-Tudos method has been widely used.<sup>10</sup> Values of monomer apparent reactivity ratios were calculated by Kelen-Tudos method in this paper. Effects of different copolymerization conditions on monomer apparent reactivity ratios for AN/AAT copolymer were also studied in comparison. Thus, the kinetic information obtained in this study in turn can be used to elucidate the optimum copolymerization conditions of AN/AAT copolymers and to evaluate the copolymer composition and utility.

## EXPERIMENTAL

### Materials

AN (Shanghai Chemical Reagents Co., A.R. grade) was vacuum distilled from CaH<sub>2</sub> just before polymerization. Comonomer AAT was obtained by neutralization of acrylic acid supplied as extra pure grade by Tianjin Chemical Resin Industry (Tianjin, China) and NH<sub>3</sub>. Azobisisobutyronitrile (AIBN) was used as the initiator and recrystallized from ethanol before use. Polyvinyl alcohol (PVA) was used as the suspending agent. Deionized water and dimethyl sulfoxide

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**TABLE I**  
Effect of Initiator Concentration on Copolymerization

| Initiator concentration (mol/L) | Conversion (%) | $M_w$ ( $10^{-4}$ ) |
|---------------------------------|----------------|---------------------|
| 0.0050                          | 6.07           | 56.5                |
| 0.0065                          | 7.19           | 44.6                |
| 0.0075                          | 7.84           | 39.8                |
| 0.0095                          | 9.06           | 24.1                |

Conditions:  $C_{AN} = 4.5$  mol/L,  $C_{AAT} = 0.04$  mol/L,  $C_{PVA} = 0.22$  g/L,  $H_2O/DMSO$  (w/w) = 80/20,  $T = 60^\circ\text{C}$ ,  $t = 20$  min.

(DMSO) or dimethyl formamide (DMF) were adopted as the polymerization medium.

### Copolymerization

A typical example of the general procedure was as follows. Required amounts of AN, AAT, 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. After a definite reaction time, the resultant mixture was poured into a large amount of methanol for precipitation, washed with methanol several times, dried at  $60^\circ\text{C}$  under vacuum, 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. Viscosity [ $\eta$ ] of the polymers were measured at  $35^\circ\text{C}$  in DMF using an Ubbelohde viscometer,<sup>11</sup> and the molecular weight was calculated from the following eq. (1)<sup>12,13</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 and AAT were determined from the monomer feed ratios and the copolymer composition. The apparent reactivity ratios of AN and AAT were calculated by Kelen-Tudos method from eq. (2)

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

$$x = \frac{M_{AN}}{M_{AAT}} (\text{mol/mol}), \quad y = \frac{dM_{AN}}{dM_{AAT}} (\text{mol/mol}) \quad (2)$$

where  $x$  is the ratio of molar fractions of monomer AN and comonomer AAT in the monomer feed,  $y$  is the ratio of molar fractions of monomer AN and comonomer AAT 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  $x_{\min}$  and  $x_{\max}$  are minimal and maximal molar fractions in the monomer feed, respectively.  $y_{\min}$  and  $y_{\max}$  are minimal and maximal molar fractions in the copolymer.

Transform eq. (2) into the form:

$$\bar{\tau} = (r_{AN} + r_{AAT}/a)\delta - \frac{r_{AAT}}{a}$$

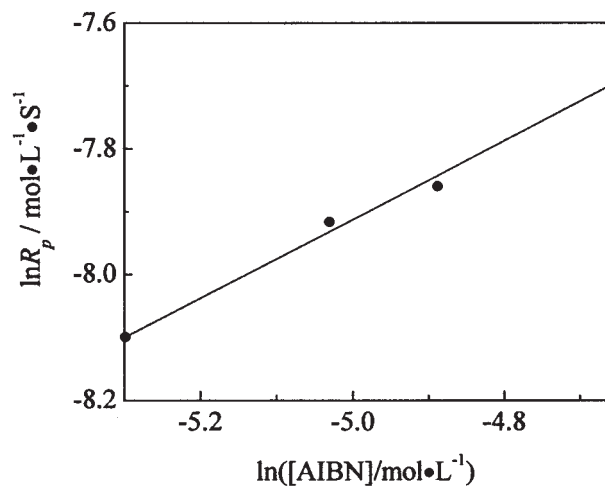
$$\bar{\tau} = \frac{x(y-1)}{ay+x^2}, \quad \delta = \frac{x^2}{ay+x^2} \quad (4)$$

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

## RESULTS AND DISCUSSION

### Kinetic equation of different copolymerization system

Solvent/water suspension technique was used to synthesize AN/AAT copolymer.<sup>14</sup> Effect of initiator concentration 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  $M_w$  re-



**Figure 1** Relationship between  $\ln R_p$  and  $\ln[AIBN]$ .

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

| H <sub>2</sub> O/DMSO<br>(w/w) | R <sub>p</sub> (mol/Ls)   |
|--------------------------------|---|
| 100/0                          | R <sub>p</sub> ∝ [AIBN] <sup>0.715</sup> [AN] <sup>1.81</sup> [AAT] <sup>1.41</sup> |
| 90/10                          | R <sub>p</sub> ∝ [AIBN] <sup>0.682</sup> [AN] <sup>1.75</sup> [AAT] <sup>1.33</sup> |
| 80/20                          | R <sub>p</sub> ∝ [AIBN] <sup>0.625</sup> [AN] <sup>1.69</sup> [AAT] <sup>1.28</sup> |
| 70/30                          | R <sub>p</sub> ∝ [AIBN] <sup>0.603</sup> [AN] <sup>1.61</sup> [AAT] <sup>1.19</sup> |
| 60/40                          | R <sub>p</sub> ∝ [AIBN] <sup>0.589</sup> [AN] <sup>1.51</sup> [AAT] <sup>1.15</sup> |
| 50/50                          | R <sub>p</sub> ∝ [AIBN] <sup>0.574</sup> [AN] <sup>1.47</sup> [AAT] <sup>1.13</sup> |
| 40/60                          | R <sub>p</sub> ∝ [AIBN] <sup>0.569</sup> [AN] <sup>1.39</sup> [AAT] <sup>1.11</sup> |
| 30/70                          | R <sub>p</sub> ∝ [AIBN] <sup>0.558</sup> [AN] <sup>1.36</sup> [AAT] <sup>1.08</sup> |
| 20/80                          | R <sub>p</sub> ∝ [AIBN] <sup>0.551</sup> [AN] <sup>1.29</sup> [AAT] <sup>1.06</sup> |
| 10/90                          | R <sub>p</sub> ∝ [AIBN] <sup>0.548</sup> [AN] <sup>1.21</sup> [AAT] <sup>1.04</sup> |
| 0/100                          | R <sub>p</sub> ∝ [AIBN] <sup>0.532</sup> [AN] <sup>1.17</sup> [AAT] <sup>1.01</sup> |

Condition: T = 60°C.

duces quickly as the initiator concentration increases. The rate of polymerization (R<sub>p</sub>) was calculated from the slope of a plot of conversion versus time. Figure 1 is a logarithmic plot of R<sub>p</sub> versus [AIBN]. The reaction order estimated from the slope is 0.625.

Effects of AN and AAT concentrations on R<sub>p</sub> were also studied. The reaction orders from the slope of the plot were 1.69 and 1.28, respectively. The overall rate of copolymerization is R<sub>p</sub> ∝ [AIBN]<sup>0.625</sup>[AN]<sup>1.69</sup>[AAT]<sup>1.28</sup>. This is different from the reaction order reported. Pan<sup>15</sup> revealed that reaction orders of initiator and monomer are 0.5 and 1 when the solution technique was used to synthesize polyacrylonitrile. Zou et al.<sup>16</sup> also studied the kinetics of polymerization of AN initiated by the redox system, using the aqueous suspension technique and a kinetic equation R<sub>p</sub> ∝ [initiator]<sup>0.7</sup>[AN]<sup>2</sup> was proposed.

When AN/AAT copolymer is synthesized using solvent/water suspension technique,<sup>17,18</sup> oligomeric radicals may form quickly in the initial stages of polymerization, which precipitate out after attaining a critical molecular weight and then act as primary particles. Propagation would then occur either in H<sub>2</sub>O phase, the DMSO phase, the oligomeric radicals phase, or at the interface of DMSO–water–oligomer mixture, depending on the solubility of monomers. In water-rich reaction medium (H<sub>2</sub>O/DMSO > 80/20), propagation is more likely to follow the way of suspension polymerization because of the insoluble primary radicals. A two-loci polymerization mechanism is assumed, H<sub>2</sub>O phase and primary radicals phase. The chain termination is mainly resulted from the one-radical reaction, and so that the reaction order of initiator tends to be 1. The rate of initiation is influenced by monomer concentration, and so the reaction order of monomer is much larger than 1. Solubility and reactivity of AAT is greater than AN in DMSO, so the deviation from one of the reaction order is smaller. In DMSO-rich reaction medium (DMSO/H<sub>2</sub>O > 80/20), copolymerization is more likely to follow the way of solution polymerization. The kinetic equation is R<sub>p</sub>

TABLE III  
Solution Copolymerization Parameters of AN/AAT in DMSO

| x   | Conversion<br>(wt %) | Content of oxygen<br>(mol %) | y    |
|-----|----------------------|------------------------------|------|
| 100 | 6.25                 | 4.74                         | 41.2 |
| 80  | 6.78                 | 6.19                         | 31.3 |
| 60  | 7.16                 | 7.61                         | 25.3 |
| 40  | 7.65                 | 11.8                         | 15.9 |
| 30  | 8.12                 | 15.2                         | 12.2 |
| 10  | 9.34                 | 41.2                         | 3.86 |

Conditions: C<sub>AN</sub> = 4.5 mol/L, C<sub>AIBN</sub> = 0.008 mol/L, T = 60°C, t = 20 min.

∝ [AIBN]<sup>0.548</sup>[AN]<sup>1.21</sup>[AAT]<sup>1.04</sup> when the ratio of H<sub>2</sub>O/DMSO is 10/90 (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 reactivity ratios

Solution polymerization technique was used to synthesize AN/AAT copolymer. Table III shows some important parameters and the polymerization conditions of the copolymer. It has been found that AN/AAT copolymers have been obtained successfully. Kelen-Tudos method gave monomer apparent reactivity ratios for AN and AAT of r<sub>AN</sub> = 0.412, r<sub>AAT</sub> = 3.11 (Fig. 2), the higher reactivity ratio value of AAT confirms its high reactivity compared with that of AN. The polymer radical with a AAT unit at the chain end is considerably more active than with an AN unit, and the probability of AAT entry into the chain is greater than that of AN entry, which leads to an increase of polymerization conversion with the addition of AAT comonomer.

Apparent reactivity ratios of AN and AAT in aqueous suspension polymerization system were also cal-

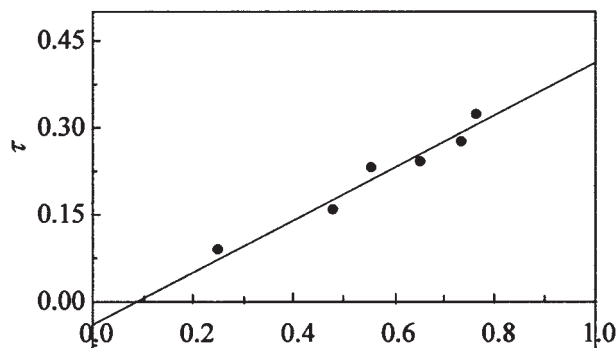


Figure 2 Relationship between  $r$  and  $\delta$ .

culated by Kelen-Tudos method,  $r_{AN} = 0.565$ ,  $r_{AAT} = 2.27$ , which is a criteria to judge other results. When AN/AAT copolymer is synthesized using the aqueous suspension technique, oligomeric radicals may be formed in the initial stages of polymerization, propagation would then mostly occur in oligomeric radicals phase.<sup>19</sup> AN units are more easily copolymerized with oligomeric radicals than that of AAT units. The value of reactivity ratio for AN rises rapidly.

#### Effect of mixture solution on reactivity ratios

Effects of mixture solution on apparent reactivity ratios of monomers were studied. AN/AAT copolymer was synthesized by solvent/water suspension polymerization technique. According to the results summarized in Table IV, in water-rich reaction medium ( $H_2O/DMSO > 80/20$ ), values of monomer apparent reactivity ratios are similar to those in aqueous suspension polymerization system; in DMSO-rich reaction medium ( $DMSO/H_2O > 80/20$ ), values of monomer reactivity ratios are similar to those in solution polymerization system. In water-rich reaction medium, because of the insolubility oligomeric radicals, propagation follows the suspension polymerization technique more. Reactivity ratios calculated are similar to those in aqueous suspension polymerization system. In DMSO-rich reaction medium, copolymerization follows the solution polymerization technique more. Reactivity ratios calculated are similar to those in solution polymerization system.

#### Effect of solvent polarity on reactivity ratios

To study the effect of solvent polarity on apparent reactivity ratios of monomers, AN/AAT copolymer was synthesized in DMF by solution polymerization technique. Previous articles reported that effect of solvent polarity on reactivity ratios may be not obvious.<sup>20,21</sup> But in this study, different conclusions are

TABLE IV  
Reactivity Ratios Parameters in  $H_2O/DMSO$  Mixture Medium

| $H_2O/DMSO$<br>(w/w) | $r_{AN}$ | $r_{AAT}$ |
|----------------------|----------|-----------|
| 100/0                | 0.565    | 2.27      |
| 90/10                | 0.566    | 2.29      |
| 80/20                | 0.564    | 2.31      |
| 60/40                | 0.533    | 2.40      |
| 50/50                | 0.488    | 2.56      |
| 40/60                | 0.468    | 2.82      |
| 20/80                | 0.417    | 3.03      |
| 10/90                | 0.414    | 3.07      |
| 0/100                | 0.412    | 3.11      |

Conditions:  $C_{AN} = 4.5$  mol/L,  $C_{AIBN} = 0.008$  mol/L,  $C_{PVA} = 0.22$  g/L,  $T = 60^\circ C$ .

TABLE V  
Effect of Polymerization Temperature on Reactivity Ratio

| Temperature<br>( $^\circ C$ ) | $r_{AN}$ | $r_{AAT}$ |
|-------------------------------|----------|-----------|
| 58                            | 0.401    | 3.18      |
| 60                            | 0.412    | 3.11      |
| 65                            | 0.457    | 2.69      |
| 70                            | 0.523    | 2.28      |
| 75                            | 0.579    | 1.98      |

Conditions:  $C_{AN} = 4.5$  mol/L,  $C_{AIBN} = 0.008$  mol/L.

drawn,  $r_{AN} = 0.398$ ,  $r_{AAT} = 2.87$ . Both  $r_{AN}$  and  $r_{AAT}$  decrease compared with those in DMSO. Solubility and activity of monomer AN, AAT, and the polymer radicals are different in different polar solvent. The concentrations of AN and AAT in local area are lower than those in the monomer feed. The reactivity ratios of AN and AAT 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.

#### Effect of polymerization temperature on reactivity ratios

Effect of polymerization temperature on comonomer reactivity ratios was also examined, which is given in Table V. AN/AAT copolymer was synthesized in DMSO at different temperature by solution polymerization technique. According to the characterizing definition of reactivity ratio,<sup>22,23</sup> the values of reactivity ratios tend to 1, and copolymerization tends to ideal copolymerization as polymerization temperature rising. Table V shows that  $r_{AN}$  increases from 0.401 to 0.579 and  $r_{AAT}$  decreases from 3.18 to 1.98 when polymerization temperature rises from 58 to 75 $^\circ C$ , which is consistent with the trend of the theoretic derivation.

## CONCLUSIONS

Laboratory studies of different copolymerization systems reveal that AIBN successfully initiates the free radical copolymerization of AN with AAT. The kinetic schemes are proposed. In water-rich reaction medium, monomer reactivity ratios were about equivalent to those in aqueous suspension polymerization system. In DMSO-rich reaction medium, apparent reactivity ratios were similar to those in solution polymerization system. With an increase of polarity of solvent, values of reaction ratios both decreased. The copolymerization tended toward ideal copolymerization and values of reaction ratios gradually tended toward 1, as the copolymerization temperature increased.

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