

# Monomer Apparent Reactivity Ratios for Acrylonitrile/Ammonium Itaconate Radical Copolymerization Systems

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**ABSTRACT:** Ammonium itaconate was first used to copolymerize with acrylonitrile. This was achieved by using azobisisobutyronitrile as the initiator and dimethyl sulfoxide as the solvent. Effects of copolymerization systems on monomer apparent reactivity ratios for acrylonitrile/ammonium itaconate copolymers were studied. The values of monomer apparent reactivity ratios were calculated by Kelen-Tudos method. The apparent reactivity ratios in the aqueous suspension polymerization system are similar to those in the solution polymerization system at polymerization conversions of less than 18% [reactivity ratio of acrylonitrile ( $r_{AN}$ ) =  $0.47 \pm 0.01$ , reactivity ratio of ammonium itaconate ( $r_{AIA}$ ) =  $3.08 \pm 0.01$ ]. At conversions of more than 50%, the changes of monomer apparent reactivity ratios

become less prominent ( $r_{AN} = 0.68 \pm 0.01$ ,  $r_{AIA} = 2.47 \pm 0.01$ ). In water-rich reaction medium [(H<sub>2</sub>O/dimethylsulfoxide (DMSO) > 80/20)], the monomer apparent reactivity ratios are approximately equivalent to those in the aqueous suspension polymerization system. In DMSO-rich reaction medium (DMSO/H<sub>2</sub>O > 80/20), the apparent reactivity ratios are similar to those in the solution polymerization system. With an increase in the polarity of the solvent, the values of apparent reaction ratios both decrease. The values of apparent reaction ratios gradually tend to 1 with increasing the copolymerization temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3920–3923, 2007

**Key words:** copolymerization; kinetics; fibers

## INTRODUCTION

Carbon fiber composites are important construction materials in applications where high strength and modulus, high thermal and corrosion resistance 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 polyacrylonitrile precursor fibers.<sup>2</sup> It is crucial to select a suitable comonomer and optimize the polymerization conditions for synthesis of acrylonitrile (AN) polymers satisfying the requirements for high-tenacity polyacrylonitrile fibers. Interaction of a few percent of comonomers generally enhances the spinnability and depresses the onset of cyclization temperature during the thermal stabilization process of carbon fibers.<sup>3–5</sup> Several polymerization techniques

have been successfully used to synthesize AN polymers. Solution, aqueous suspension, and solvent water suspension are the most common useful techniques.<sup>6</sup> The solvent water suspension method is a new and promising technique that may be used in the production of high-performance polyacrylonitrile fiber, which cleverly combines the advantages of the solution and those of the aqueous suspension. The most widely used comonomers are itaconic acid,<sup>7</sup> acrylamide,<sup>8</sup> and methyl acrylate.<sup>9</sup> Acidic comonomers help in lowering the onset temperature of cyclization, presence of ammonium increases the solubility of the polymer in the spinning solvent and modifies the fiber morphology, and to our knowledge, there are no reports on ammonium itaconate (AIA) as a comonomer, thus AIA was first used to as a comonomer to copolymerize with AN in this study. Knowledge of copolymer's composition is an important factor in the evaluation of its utility. The theory of radical copolymerization leads 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>10–12</sup> Although the values of monomer apparent reactivity ratios calculated by Kelen-Tudos method are only approximate, Kelen-

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Tudos method has been widely used.<sup>13</sup> It is evident from published articles that the medium affects the reactivity ratios in some free radical polymerization, for example, in acrylonitrile-methyl methacrylate systems,<sup>14</sup> but they are not systematic studies. In this article, different polymerization techniques were used to synthesize AN/AIA copolymers to compare the reactivity ratios. Kelen-Tudos method was employed to estimate the monomer reactivity ratios. The copolymerization experiments were terminated at less than 10% conversion. Effects of different copolymerization conditions on monomer apparent reactivity ratios for AN/AIA copolymer were studied for contrast. The most optimum copolymerization conditions for AN/AIA copolymers can be obtained by the monomer apparent reactivity ratios.

## EXPERIMENTAL

### Materials

AN (Shanghai Chemical Reagents, A.R. grade) was vacuum distilled from  $\text{CaH}_2$  just before polymerization. Comonomer AIA was obtained by neutralization of itaconic acid supplied as extra pure grade by Tianjin Chemical Resin Industry (Tianjin, China) and  $\text{NH}_3$ . Azobisisobutyronitrile (AIBN) was used as the initiator and recrystallized from ethanol before use. Poly(vinyl alcohol) (PVA) was used as the suspending agent. Deionized water and dimethyl sulfoxide (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, AIA, 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. The copolymerization experiments were terminated at less than 10% conversion. 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°C under vacuum, and then weighed.

### Characterization

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 AIA were determined from the monomer feed ratios and the copolymer composition. The apparent reactivity ratios

of AN and AIA were calculated by Kelen-Tudos method eq. (1)

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

$$x = \frac{M_{\text{AN}}}{M_{\text{AIA}}}(\text{mol/mol}),$$

$$y = \frac{dM_{\text{AN}}}{dM_{\text{AIA}}}(\text{mol/mol}) \quad (1)$$

where  $x$  is the ratio of molar fractions of monomer AN and comonomer AIA in the monomer feed,  $y$  is the ratio of molar fractions of monomer AN and comonomer AIA in the copolymer, and  $a$  is an equation parameter. The equation parameter can be computed according to eq. (2):

$$a = \frac{x_{\text{min}}x_{\text{max}}}{\sqrt{y_{\text{min}}y_{\text{max}}}} \quad (2)$$

where  $x_{\text{min}}$  and  $x_{\text{max}}$  are minimum and maximum molar fractions in the monomer feed, respectively.  $y_{\text{min}}$  and  $y_{\text{max}}$  are minimum and maximum molar fraction in the copolymer.

Equation (1) transforms into the form

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

$$\tau = \frac{x(y-1)}{ay+x^2} \bar{\delta} = \frac{x^2}{ay+x^2} \tau \quad (3)$$

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

## RESULTS AND DISCUSSION

### Reactivity ratios in solution polymerization system

Solution polymerization technique was used to synthesize AN/AIA copolymer. The copolymerization experiments were terminated at less than 10% conversion. Table I shows some important parameters and the polymerization conditions of the copolymer. Kelen-Tudos method gave monomer apparent reactivity ratios for AN and AIA of  $r_{\text{AN}} = 0.47$  and  $r_{\text{AIA}} = 3.08$  (Fig. 1), which is a criteria to judge other results. The higher reactivity ratio value of AIA confirms its high reactivity compared with that of AN. The polymer radical with an AIA unit at the chain end is considerably more active than with an AN unit, and the probability of AIA entry into the chain is greater than that of AN entry, which leads to an increase of

TABLE I  
Solution Copolymerization Parameters  
of AN/AIA in DMSO

$x/$ (mol/mol)	Conversion/ wt %	Content of oxygen/wt %	$y/$ (mol/mol)
90	6.55	2.65	42.48
80	6.85	2.98	37.46
70	7.01	3.41	32.33
60	7.26	3.73	29.31
40	8.43	5.56	18.61
30	8.55	7.55	12.89
20	9.67	10.1	8.901

Condition: [AN], 4.15 mol/L; [AIBN], 0.008 mol/L; temperature, 60°C.

polymerization conversion with the addition of AIA comonomer.

### Apparent reactivity ratios in aqueous suspension polymerization system

The reactivity ratios of AN and AIA in aqueous suspension polymerization system was also calculated by Kelen-Tudos method. The experimental results are given in Figure 2. At the monomer conversions of less than 18%, the values of monomer reactivity ratios in the aqueous suspension polymerization system are similar to those in the solution polymerization system ( $r_{AN} = 0.47 \pm 0.01$ ,  $r_{AIA} = 3.08 \pm 0.01$ ). With increasing polymerization conversion, reactivity ratio for AN rises rapidly and that for AIA reduces quickly. When the conversion is more than 50%, the changes of monomer reactivity ratios become less prominent ( $r_{AN} = 0.68 \pm 0.01$ ,  $r_{AIA} = 2.47 \pm 0.01$ ). The reactivity ratios determined are called the apparent reactivity ratios as a function of different conversion. The apparent reactivity ratios of monomers in a system depend on the technique of polymerization. When AN/AIA copolymer is synthesized using aqueous suspension technique, oligomeric radicals may be formed in the initial stages of polymerization, which precipitate out after a

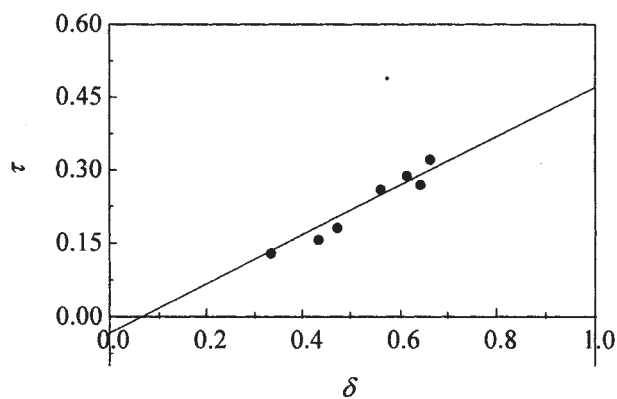


Figure 1 Relationship between  $\tau$  and  $\delta$ .

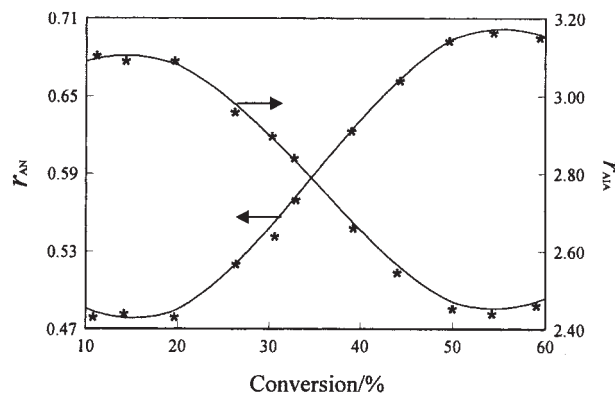


Figure 2 Relationship between reactivity ratios and conversion in aqueous suspension polymerization system, Condition: [AN], 4.15mol/L; [AIBN], 0.008mol/L; [PVA], 0.22g/L; temperature, 60°C.

certain critical molecular weight was attained and then act as primary particles. Propagation would then occur either in water phase or in the oligomeric radicals phase.<sup>15,16</sup> When conversion is less than 18%, polymerization follows more of the solution polymerization technique, reactivity ratios calculated are similar to those in solution polymerization system. As the polymerization conversion increases, propagation would then mostly occur in oligomeric radicals phase. AN units are more easily absorbed by polymer radicals than AIA units. The value of reactivity ratio for AN rises rapidly.

### Effect of reaction medium on reactivity ratios

Effect of reaction medium on apparent reactivity ratios of monomers was also studied. AN/AIA copolymer was synthesized by the solvent water suspension polymerization technique. The copolymerization experiments were terminated at less than 10% conversion. According to the results summarized in Table II, in water-rich reaction medium ( $H_2O/DMSO > 80/20$ ), values of monomer apparent reactivity ratios are similar to those in the aqueous suspension polymer-

TABLE II  
Reactivity Ratios Parameters in  $H_2O/DMSO$   
Reaction Medium

$H_2O/DMSO$ (w/w)	$r_{AN}$	$r_{AIA}$
90/10	0.67	2.48
80/20	0.65	2.58
60/40	0.64	2.72
50/50	0.59	2.83
40/60	0.55	2.88
20/80	0.51	2.95
10/90	0.49	3.01

Condition: [AN], 4.15 mol/L; [AIBN], 0.008 mol/L; [PVA], 0.22 g/L; temperature, 60°C.

**TABLE III**  
Effect of Polymerization Temperature  
on Reactivity Ratio

Temperature/°C	$r_{AN}$	$r_{AIA}$
58	0.45	3.24
60	0.47	3.08
65	0.52	2.82
70	0.58	2.64
75	0.62	2.18

Condition: [AN], 4.15 mol/L; [AIBN], 0.008 mol/L.

ization system at conversion values greater than 50%; in DMSO-rich reaction medium (DMSO/H<sub>2</sub>O > 80/20), values of monomer reactivity ratios are similar to those in the solution polymerization system. When AN/AIA copolymer is synthesized using the solvent water suspension technique, after a defined 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>17,18</sup> In water-rich reaction medium, because of the insolubility of 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/AIA copolymer was synthesized in DMF by the solution polymerization technique. The copolymerization experiments were terminated at less than 10% conversion. Previous articles reported that effect of solvent polarity on reactivity ratios may be not obvious.<sup>19,20</sup> However, in this study, we draw different conclusions ( $r_{AN} = 0.43$ ,  $r_{AIA} = 2.42$ ). Both  $r_{AN}$  and  $r_{AIA}$  decrease compared with those in DMSO. Solubility and activity of monomer AN, AIA, and the polymer radicals are different in different polar solvent. The concentrations of AN and AIA in local area are lower than those in the monomer feed. The reactivity ratios of AN and AIA 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 (see Table III). AN/AIA copolymer was synthesized in DMSO at different temperature by the solution polymerization technique. The copolymerization experiments were terminated at less than 10% conversion. According to

the characterizing definition of reactivity ratio,<sup>20</sup> copolymerization tends to ideal copolymerization as the polymerization temperature rises. Table III shows that  $r_{AN}$  increases from 0.45 to 0.62 and  $r_{AIA}$  decreases from 3.24 to 2.18 when polymerization temperature rises from 58 to 75°C, which is consistent with theoretic derivation.

## CONCLUSIONS

Laboratory studies of different copolymerization systems of AN with AIA have shown that monomer apparent reactivity ratios in a system depend on the method of polymerization, the medium, and temperature of polymerization. Monomer apparent reactivity ratios in the aqueous suspension polymerization system are similar to those in the solution polymerization system at polymerization conversions of less than 18%. When the polymerization conversion is more than 50%, the changes of monomer reactivity ratios become less prominent. In water-rich reaction medium, monomer reactivity ratios are about equivalent to those in the aqueous suspension polymerization system. With increasing polarity of the solvent, values of reaction ratios both decrease. The copolymerization tends toward ideal copolymerization as the copolymerization temperature increase.

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