

# Kinetics of Copolymerization of Acrylonitrile with Ammonium Itaconate in a H<sub>2</sub>O/Dimethyl Formamide Mixture

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**ABSTRACT:** Kinetics of copolymerization of acrylonitrile (AN) with ammonium itaconate (AI) initiated by azobisisobutyronitrile (AIBN) were investigated in a H<sub>2</sub>O/dimethyl formamide (DMF) mixture between 50 and 70°C under a N<sub>2</sub> atmosphere. The rate of copolymerization and particle size were measured. The kinetic equation of copolymerization system is obtained and the overall activation energy for the copolymerization system was computed. Values of monomer apparent reactivity ratios were calculated by the Kelen–Tudos method. It was found that in DMF-rich

reaction medium (DMF/H<sub>2</sub>O > 80/20), monomer apparent reactivity ratios are similar to those in the solution polymerization system. Effect of hydroquinone and dioxane additives on copolymerization was discussed. The polymerization is retarded by hydroquinone and accelerated by dioxane, which confirms the free-radical copolymerization of AN with AI. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1151–1155, 2004

**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, 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. Several polymerization techniques have been successfully used to synthesize polymers and copolymers of acrylonitrile for high-tenacity fibers. Solution, aqueous suspension, and solvent water suspension are the most common useful techniques.<sup>2</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 specialty fibers for various applications. To our knowledge, there are only a few reports on ammonium itaconate (AI) as comonomer, but fewer are on kinetic study of

copolymerization of AN with AI in H<sub>2</sub>O/dimethyl formamide (DMF) mixture systems. In this study, the solvent water suspension technique was used to synthesize AN/AI copolymers. For estimating polymerization rates, copolymerization experiments were terminated at <10% conversion.<sup>3</sup> The conversion was controlled and determined by gravimetric measurements. The kinetics of copolymerization of AN/AI were studied between 50 and 70°C under N<sub>2</sub> atmosphere, and a suitable kinetic scheme was proposed. Furthermore, the overall activation energy was evaluated. Values of monomer apparent reactivity ratios were calculated by Kelen–Tudos method.<sup>4</sup>

## EXPERIMENTAL

### Materials

Industrial grade monomer AN was supplied by Tianjin Chemical Resin Industry (Tianjin, China) and was distilled to remove inhibitors before use. AI was obtained by neutralization of itaconic acid supplied as extra pure grade by Tianjin Chemical Resin Industry (Tianjin, China) and NH<sub>3</sub>. Azobisisobutyronitrile (AIBN), supplied by Shanghai Chemical Resin Industry (Shanghai, China), was used as an initiator and was recrystallized from ethanol before use. Poly(vinyl alcohol) (PVA) was obtained from Shanghai Chemical Resin Industry and was used as a suspending agent. Deionized water (self-made) and DMF supplied by

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Shanghai Chemical Resin Industry (Shanghai, China) were adopted as the polymerization media.

### Copolymerization

Required amounts of AN, AI, PVA, AIBN, and different ratios of H<sub>2</sub>O/DMF mixture were placed in different flasks, respectively, which were continuously flushed with ultrapure nitrogen. The flasks were wholly immersed in a temperature-controlled water bath and were shaken from time to time. After a definite reaction time, copolymerization was terminated at <10% conversion. The solvent and unreacted monomer in the resultant mixture were removed by the suction pump. 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

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 was measured at 35°C in dimethyl formamide by using a Ubbelohde viscometer,<sup>5</sup> and the molecular weight was calculated from<sup>6</sup>

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

Elemental analyses of the copolymers were carried out by using a PE2400 microanalyzer to determine the oxygen content of these copolymers. The monomer reactivity ratios for copolymerization of AN and AI were determined from the monomer feed ratios and the copolymer composition. The apparent reactivity ratios of AN and AI were calculated by Kelen-Tudos method from

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

TABLE I  
Effect of Initiator Concentration on Copolymerization

Initiator concentration		Conversion (%)	$M_w/10^4$
wt %	mol/L		
0.08	0.00500	5.02	61.2
0.10	0.00625	5.94	51.3
0.12	0.00750	6.85	39.1
0.15	0.00938	8.09	32.8

Conditions:  $C_{AN} = 4.15$  mol/L,  $C_{AI} = 0.04$  mol/L,  $C_{PVA} = 0.22$  g/L, H<sub>2</sub>O/DMSO = 80/20,  $T = 60^\circ\text{C}$ ,  $t = 15$  min.

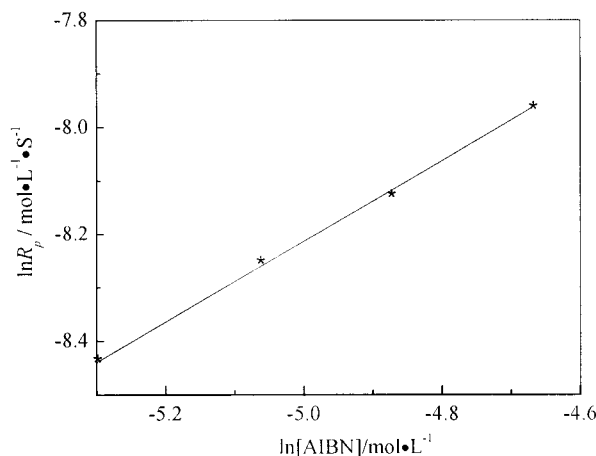


Figure 1 Relationship between  $\ln R_p$  and  $\ln[\text{AIBN}]$ .

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

where  $x$  is the ratio of mole fractions of monomer AN and monomer AI in the monomer feed,  $y$  is the ratio of mole fractions of monomer AN and monomer AI in the copolymer, and  $a$  is an equation parameter. The equation parameter can be computed according to

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

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

Equation (2) transforms into the form

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

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

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

## RESULTS AND DISCUSSION

### Kinetic equation of different copolymerization system

Solvent water suspension technique was used to synthesize the AN/AI copolymer.<sup>7</sup> The 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-

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

H <sub>2</sub> O/DMF (w/w)	$R_p/\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
100/0	$R_p \propto [\text{AIBN}]^{0.813}[\text{AN}]^{2.03}[\text{AI}]^{1.37}$
90/10	$R_p \propto [\text{AIBN}]^{0.773}[\text{AN}]^{1.92}[\text{AI}]^{1.32}$
80/20	$R_p \propto [\text{AIBN}]^{0.755}[\text{AN}]^{1.84}[\text{AI}]^{1.23}$
70/30	$R_p \propto [\text{AIBN}]^{0.746}[\text{AN}]^{1.82}[\text{AI}]^{1.19}$
60/40	$R_p \propto [\text{AIBN}]^{0.731}[\text{AN}]^{1.75}[\text{AI}]^{1.17}$
50/50	$R_p \propto [\text{AIBN}]^{0.718}[\text{AN}]^{1.70}[\text{AI}]^{1.11}$
40/60	$R_p \propto [\text{AIBN}]^{0.689}[\text{AN}]^{1.62}[\text{AI}]^{1.09}$
30/70	$R_p \propto [\text{AIBN}]^{0.651}[\text{AN}]^{1.58}[\text{AI}]^{1.07}$
20/80	$R_p \propto [\text{AIBN}]^{0.581}[\text{AN}]^{1.42}[\text{AI}]^{1.05}$
10/90	$R_p \propto [\text{AIBN}]^{0.524}[\text{AN}]^{1.21}[\text{AI}]^{1.04}$
0/100	$R_p \propto [\text{AIBN}]^{0.514}[\text{AN}]^{1.19}[\text{AI}]^{1.01}$

Conditions: T = 60°C, t = 15 min

duces quickly as the initiator 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  $C_{\text{AIBN}}$ . The reaction order estimated from the slope is 0.755.

The effect of AN and AI concentrations on  $R_p$  was also studied. The reaction orders from the slope of the plot were 1.84 and 1.23, respectively. The overall rate of copolymerization is  $R_p \propto C_{\text{AIBN}}^{0.755} C_{\text{AN}}^{1.84} C_{\text{AI}}^{1.23}$ . This is different from the reaction order reported. Pan<sup>8</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>9</sup> also studied the kinetics of polymerization of AN initiated by the redox system by using the aqueous suspension technique and a kinetic equation  $R_p \propto C_{\text{initiator}}^{0.7} C_{\text{AN}}^2$  was proposed.

When AN/AI copolymer is synthesized by using solvent water suspension technique,<sup>10,11</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 in H<sub>2</sub>O phase, the DMF phase, or at the interface of DMF–H<sub>2</sub>O mixture depending on the solubility of monomers. In water-rich reaction medium (H<sub>2</sub>O/DMF > 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 (i.e., H<sub>2</sub>O phase and primary radical phase). The chain termination mainly results from single free radicals, 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 AI is greater than AN in DMF, so the departure from 1 of the reaction order is smaller. In DMF-rich reaction medium (DMF/H<sub>2</sub>O > 80/20), copolymerization is more likely to follow the way of solution polymerization. The kinetic equation of is  $R_p \propto C_{\text{AIBN}}^{0.524} C_{\text{AN}}^{1.21} C_{\text{AI}}^{1.04}$  when the ratio of H<sub>2</sub>O/DMF is

TABLE III  
Effect of Temperature on Copolymerization

T/°C	Conversion/%	$M_w/10^4$	D/mm
50	2.55	69.8	0.05–0.10
55	3.96	54.6	0.10–0.20
60	6.85	39.1	0.15–0.25
65	10.6	34.5	0.25–0.45
70	16.5	26.5	0.30–0.55

Conditions:  $C_{\text{AN}} = 4.15 \text{ mol/L}$ ,  $C_{\text{AI}} = 0.04 \text{ mol/L}$ ,  $C_{\text{AIBN}} = 0.00750 \text{ mol/L}$ , H<sub>2</sub>O/DMSO = 80/20,  $C_{\text{PVA}} = 0.22 \text{ g/L}$ , t = 15 min.

10/90 (Table II). The extent of active free radicals embedded becomes less prominent. The chain termination mainly results from double free radicals, 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.

Effect of temperature on polymerization was also studied, which is given in Table III. AN/AI copolymer was synthesized at 50, 55, 60, 65, and 70°C. The rate of polymerization and particle size of copolymer increase 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 DMF is  $28.4 \times 10^{-5}$  at 50°C<sup>12</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 (Figure 2), is 91.4 kJ/mol. Moreover, the overall activation energy computed is 89.5 kJ mol<sup>-1</sup> when AN concentration is 4.25 mol L<sup>-1</sup> instead of 4.15 mol L<sup>-1</sup>; the overall activation energy computed is 80.1 kJ mol<sup>-1</sup> when AI concentration is 0.05 mol L<sup>-1</sup> instead of 0.04 mol L<sup>-1</sup>.

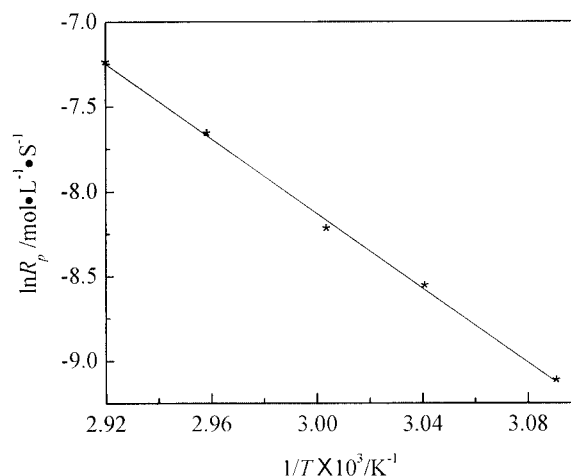


Figure 2 Relationship between  $R_p$  and T.

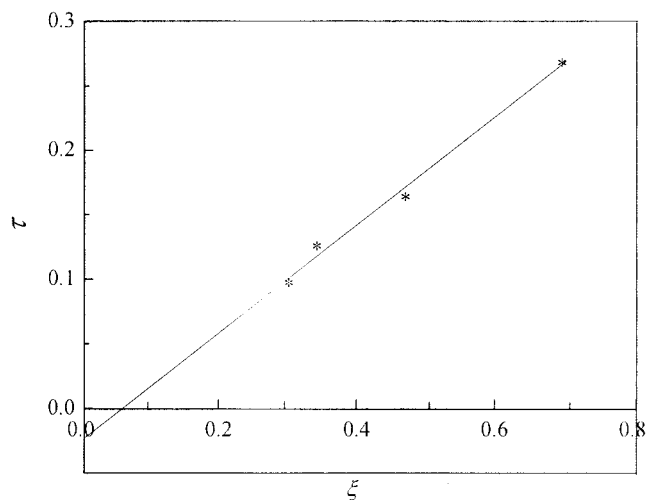


Figure 3 Relationship between  $\tau$  and  $\xi$ .

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.

Solution polymerization technique was used to synthesize AN/AI copolymer in DMF. For estimating monomer reactivity ratios, copolymerization experiments were terminated at <15% conversion. Table I shows some important parameters and polymerization conditions of the copolymer. Kelen–Tudos method gave monomer apparent reactivity ratios for AN and AI of  $r_{AN} = 0.395$ ,  $r_{AI} = 2.60$  (Figure 3), which is a criterion to judge other results. The higher reactivity ratio value of AI confirms its high reactivity compared with that of AN. The polymer radical with an AI unit at the chain end is considerably more active than with an AN unit, and the probability of AI entry into the chain is greater than that of AN entry, which leads to the increase of polymerization conversion with the addition of AI comonomer (Table IV).

Effect of mixture solution on apparent reactivity ratios of monomers was also studied. AN/AI copoly-

TABLE IV  
Solution Copolymerization Parameters of AN  
with AI in DMSO

AN/AI/ (w/w)	$x$ / (mol/mol)	Content of oxygen in copolymer/ wt %	$y$ / (mol/mol)
98/2	102.62	2.769	40.52
95/5	39.79	6.428	15.69
92/8	24.08	9.598	9.487
90/10	18.85	11.49	7.418

Conditions:  $C_{AN} = 4.15$  mol/L,  $C_{AIBN} = 0.00750$  mol/L,  $T = 60^\circ\text{C}$ ,  $t = 15$  min.

TABLE V  
Reactivity Ratios Parameters in H<sub>2</sub>O/DMF Mixture  
Solvent Medium

H <sub>2</sub> O/DMF (w/w)	$r_{AN}$	$r_{NVP}$
90/10	0.650	1.96
80/20	0.647	1.94
60/40	0.601	2.05
50/50	0.535	2.21
40/60	0.488	2.38
20/80	0.403	2.59
10/90	0.398	2.62
0/100	0.395	2.60

Conditions:  $C_{AN} = 4.15$  mol/L,  $C_{AIBN} = 0.00750$  mol/L,  $T = 60^\circ\text{C}$ ,  $t = 15$  min.

mer was synthesized by H<sub>2</sub>O/DMF suspension polymerization technique. According to the results summarized in Table V, in DMF-rich reaction medium (DMF/H<sub>2</sub>O > 80/20), values of monomer reactivity ratios are similar to those in the solution polymerization system. In DMF-rich reaction medium, copolymerization follows more of the solution polymerization technique.<sup>13</sup>

#### Effect of additives

Effects of hydroquinone and dioxane on the rate of copolymerization have been studied by varying concentrations from  $1.0 \times 10^{-2}$  to  $3.0 \times 10^{-2}$  mol/L while keeping other parameters constant.<sup>14</sup> From Table VI, it is clear that the rate of copolymerization decreases with an increase of hydroquinone concentration. Table VI also reveals that the polar solvent dioxane accelerates the rate of copolymerization. The effect of additives on the rate of copolymerization indicates the presence of free radicals in this system and confirms the free-radical polymerization of AN with AI.

#### CONCLUSION

Experimental kinetic studies of different copolymerization systems reveal that AIBN initiates the free-

TABLE VI  
Effect of Additive on Copolymerization

Additive	Additive concentration (mol · L <sup>-1</sup> )	Conversion (%)	$R_p/10^{-4}$ (mol · L <sup>-1</sup> · s <sup>-1</sup> )
None	0	6.85	3.16
Hydroquinone	$1 \times 10^{-2}$	5.54	2.55
	$3 \times 10^{-2}$	3.92	1.81
Dioxane	$1 \times 10^{-2}$	8.12	3.74
	$3 \times 10^{-2}$	9.78	4.23

Conditions:  $C_{AN} = 4.15$  mol/L,  $C_{AI} = 0.04$  mol/L,  $C_{AIBN} = 0.00750$  mol/L,  $C_{PVA} = 0.22$  g/L, H<sub>2</sub>O/DMSO = 80/20,  $T = 60^\circ\text{C}$ ,  $t = 15$  min.

radical copolymerization of AN with AI. A kinetic scheme is proposed and the overall activation energy of copolymerization is calculated. In DMF-rich reaction medium, values of the monomer apparent reactivity ratios are similar to those in the solution copolymerization system. The copolymerization rate is retarded by the addition of hydroquinone and accelerated by the addition of dioxane.

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