

Monomer Reactivity Ratios for Acrylonitrile/Ammonium Itaconate during Aqueous-Deposited Copolymerization Initiated by Ammonium Persulfate

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ABSTRACT: Monomer reactivity ratios of acrylonitrile/ammonium itaconate during aqueous-deposited copolymerization initiated by ammonium persulfate were investigated. Kelen-Tudos method was used to examine the reactivity ratios. It was shown that the reactivity ratios were influenced by the conversions and temperatures of copolymerization. The reactivity ratios in aqueous-deposited copolymerization system were similar to those in the solution polymerization system at polymerization conversions of less than 5% [reactivity ratio of acrylonitrile (r_1) 0.842 ± 0.02 , reactivity ratio of ammonium itaconate (r_2) $= 3.624 \pm 0.02$].

The reactivity ratio of AN rises and that of $(\text{NH}_4)_2\text{IA}$ decreases, when the polymerization conversion increases till 13%. Aqueous-deposited copolymerization initiated by AIBN was also studied. It was found that some polymers were formed in water phase and the monomers had different reactivity ratios by comparison with those initiated by ammonium persulfate. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4645–4648, 2006

Key words: aqueous-deposited copolymerization; reactivity ratios; acrylonitrile; ammonium itaconate

INTRODUCTION

Polyacrylonitrile (PAN) based precursors are emerging as one of the best materials for making carbon fibers. It is important to select a kind of befitting comonomer incorporated in the precursors.¹ Superior mechanical properties of carbon fibers are reported when some comonomers, such as IA, AA, MA, and so on, are used.^{2–4} But there is a great deal of residuary solvent in the resulting fibers made by these copolymers. When the fibers are in the gel form, the existence of solvent will reduce the dipole interaction between the nitrile groups, resulting in the decrease of mechanical properties of carbon fibers.⁵ So we tried to find a new comonomer with excellent hydrophilicity, which may promote the diffusion between water and solvent, and effectively lessen the residuary solvent in the final fibers. Ammonium itaconate $(\text{NH}_4)_2\text{IA}$ has a relatively substantial solubility in water when compared with that of IA. According to the contact angle of the copolymers, it was confirmed that poly(AN- $(\text{NH}_4)_2\text{IA}$) possesses more excellent hydrophilicity than poly(AN-IA). The final fibers obtained by

poly(AN- $(\text{NH}_4)_2\text{IA}$) have lower residuary solvent and more excellent properties.

AN is an organic compound with high polarity and thus has a relatively substantial solubility in water (7.9 wt % at 40°C) when compared with those oil-soluble monomers.⁶ $(\text{NH}_4)_2\text{IA}$ is a kind of ammonium salt with higher substantial solubility in water, and lower solubility in organic solvent (about 0.23 wt % in DMSO at 60°C). In recent investigation, Chen and Liu had studied AN/ $(\text{NH}_4)_2\text{IA}$ suspension polymerization and the hydrophilicity of the copolymers.⁷ Using AIBN as initiator, the polymer was formed in monomer phase without almost any comonomer of AN/ $(\text{NH}_4)_2\text{IA}$. However, when using water-soluble initiator to polymerize in water phase, high concentration of $(\text{NH}_4)_2\text{IA}$ can be obtained in the resulted polymer.

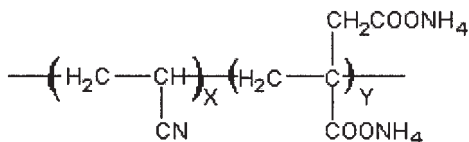
In this study, water-soluble initiator (ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$) was first used in AN/ $(\text{NH}_4)_2\text{IA}$ polymerization system. The reactivity ratios for the monomers were investigated during the polymerization in water phase.

EXPERIMENTAL

Materials

AN was purified by alkali washing, followed by distillation. Ammonium itaconate $(\text{NH}_4)_2\text{IA}$ was recrystallized in methanol. Ammonium persulfate and 2,2'-azobisisobutyronitrile (AIBN) were used as initiators

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Scheme 1. Copolymer of AN with $(\text{NH}_4)_2\text{IA}$.

and also refined before the polymerization. Deionized water was adopted as the polymerization medium.

Polymerization

Appropriate amount of AN, $(\text{NH}_4)_2\text{IA}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and deionized water was put into a glass bottle that can withstand high pressure. The bottle was closed and was wholly immersed in a temperature-controlled water bath. Ultrapure nitrogen was continuously input to the bottle. To conveniently separate the polymers produced in the monomer and water phases, the suspending agent and the agitation were not used. After a defined reaction time, a large amount of methanol was poured into the resultant mixture for precipitation. The mixture was washed several times with methanol, dried at 60°C under vacuum, and then weighed.

Characterization of AN/ $(\text{NH}_4)_2\text{IA}$ copolymerization

Elemental analyses (EA) for oxygen and sulfur contents in the copolymers were conducted by element analyzer (Vario EL Ø). The structure of poly(AN- $(\text{NH}_4)_2\text{IA}$) copolymer is given in Scheme 1.

The percentage of AN in the AN/ $(\text{NH}_4)_2\text{IA}$ / H_2O system could be determined by GC (type 103 gas chromatographic meter). AN and $(\text{NH}_4)_2\text{IA}$ reactivity ratios during the copolymerization were determined by the monomer feed ratios and the copolymer composition. Using Kelen-Tudos method,^{8,9} the reactivity ratios of acrylonitrile (r_1) and ammonium itaconate (r_2) were calculated by the following eq. (1):

$$x(y-1)/(ay+x^2) = (r_1 + r_2/a)x^2/(ay+x^2) / \times (ay+x^2) - r_2/a \quad (1)$$

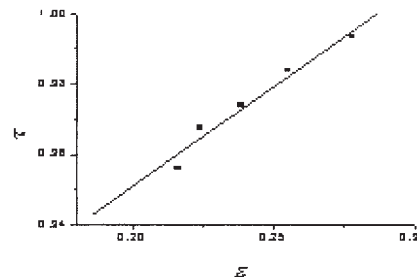


Figure 1. Kelen-Tudos plot of τ versus ϵ .

where x is the ratio of molar fractions for AN and $(\text{NH}_4)_2\text{IA}$ monomers in the monomer feed, and y , in the copolymer. a is an equation parameter. The equation parameter can be computed according to eq. (2):

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

where x_{\min} and x_{\max} are the minimal and maximal molar fractions in the monomer feed, respectively, and y_{\min} and y_{\max} , in the copolymer. Equation (1) can be changed into the following form:

$$\tau = r_1(r_2/a)\epsilon - r_2/a$$

$$\tau = x(y-1)/(ay+x^2), \quad \epsilon = x^2/(ay+x^2) \quad (3)$$

The plot of τ versus ϵ is a straight line. Extrapolation of the line to $\epsilon = 1$ gives r_1 , and to $\epsilon = 0$ gives r_2/a .

RESULTS AND DISCUSSION

Reactivity ratios in aqueous deposited polymerization system

The reactivity ratios of AN and $(\text{NH}_4)_2\text{IA}$ in the aqueous deposited polymerization system were calculated by the Kelen-Tudos method. Table I shows some important parameters and the copolymerization conditions. Figure 1 is the plot of τ versus ϵ , from which the monomer reactivity ratios are $r_1 = 1.308$ and $r_2 = 3.085$. This method can also be used as criteria to judge other results. The higher reactivity ratio of $(\text{NH}_4)_2\text{IA}$

TABLE I
Parameters for Aqueous-Deposited Polymerization of AN and $(\text{NH}_4)_2\text{IA}$ at 60°C

AN/ $(\text{NH}_4)_2\text{IA}$ (w/w)	x (mol/mol)	Conversion (%)	Elementary content (wt %)		y (mol/mol)
			Oxygen	Sulfur	
98/2	151.62	8.3	2.673	0.038	43.403
95/5	58.79	8.0	6.325	0.0372	16.225
92/8	35.58	7.9	9.504	0.0379	9.713
90/10	27.85	8.1	11.532	0.0389	7.448
85/15	17.53	7.8	14.984	0.0394	4.498

Condition: $[\text{AN}] = 3.21$ mol/L; $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.006$ mol/L.

reveals the higher reactivity with AN. The polymer radical with a (NH₄)₂IA unit at the chain end is more active than that with an AN unit, and the (NH₄)₂IA is more likely to enter the chain than AN, leading to an increase in the polymerization conversion with the addition of (NH₄)₂IA comonomer (Table I).

Effect of polymerization conversions on the reactivity ratios

The monomer reactivity ratios were also investigated at different polymerization conversions, as presented in Table II. When the polymerization conversion is less than 5%, the reactivity ratios have hardly any changes ($r_1 = 0.842 \pm 0.02$, $r_2 = 3.624 \pm 0.02$). With increasing polymerization conversions, the reactivity ratio for AN rises rapidly, and that for (NH₄)₂IA decreases. When the conversions were more than 13%, these changes become less prominent ($r_1 = 1.564 \pm 0.02$, $r_2 = 2.621 \pm 0.02$). The changes can be attributed to the following two factors. First, the reactivity ratios of the monomers in a system depend on the polymerization technique. When the AN/(NH₄)₂IA copolymer is synthesized by the aqueous-deposited polymerization technique, oligomeric radicals may form at the initial stages of polymerization, and precipitate after a certain critical molecular weight is achieved, and then acts as primary particles. Propagation will occur in either the water phase or the oligomeric radicals phase.^{10,11} When the conversion is less than 5%, polymerization is analogous to the solution polymerization technique. As polymerization conversion increases, chain propagation occurs mostly in the oligomeric radicals phase. AN units are more easily absorbed by polymer radicals than (NH₄)₂IA units. Second, there are two phases in the polymerization system, monomer and water phases. The concentration of AN in the water phase is maintained at constant (about 9.1 wt %), until the monomer phase disappears. At the lower polymerization conversions, the (NH₄)₂IA content in the water phase is also kept unchanged oppositely. The molar fractions in the monomer feed have hardly any changes. When the poly-

TABLE II
Effect of Conversions on the Reactivity Ratios

Conversion (%)	r_1	r_2
3.7	0.839	3.626
4.8	0.842	3.624
6.2	1.034	3.423
8.3	1.308	3.085
10.5	1.426	2.879
13.1	1.564	2.621
14.3	1.57	2.607

Condition: [AN] = 3.21 mol/L; [(NH₄)₂S₂O₈] = 0.006 mol/L; temperature, 60°C.

TABLE III
Effect of Polymerization Temperatures on the Reactivity Ratios

Temperature (°C)	[AN] ^a (wt %)	r_1	r_2
55	8.9	0.802	3.857
60	9.1	0.842	3.624
65	9.5	0.915	3.005
70	10.1	0.986	2.795

Condition: [AN] = 3.21 mol/L; [(NH₄)₂S₂O₈] = 0.006 mol/L.

^a [AN] is the concentration of AN in water phase, which was determined by GC.

merization conversion is more than 5%, the concentration of (NH₄)₂IA in water phase decreases, and that of AN is not changed. The molar fraction in unpolymerized monomer increases. AN units have more chances to polymerize with radical groups, giving rise to the increase of the reactivity ratio for AN. Both of these two factors results in the rapid rise of r_1 .

Effect of temperatures on the reactivity ratios

The effect of the polymerization temperatures on the monomer reactivity ratios was also studied (Table III). (NH₄)₂IA can be polymerized with AN in aqueous deposited polymerization system at different temperatures with a conversion around 5%. The reactivity ratio of AN rise and that of (NH₄)₂IA decrease with elevating the polymerization temperature. The reactivity ratios of the two monomers have a tendency to 1, and the copolymerization is approaching to the "ideal" one. With increasing the temperature, the concentration of AN in water phase rises, resulting in an increase of the reactivity ratio of AN. From Table III, r_1 increases from 0.802 to 0.986 and r_2 decreases from 3.857 to 2.795 when the polymerization temperature rises from 55 to 70°C, which was consistent with the theoretic derivation (the characterizing definition of reactivity ratio).¹²

Effect of initiators on the reactivity ratios

Different initiator (ammonium persulfate) concentrations hardly changes the reactivity ratios of the monomers. During the aqueous-deposited copolymerization initiated by ammonium persulfate, polymer can be almost fully formed in the water phase. Table IV shows that a considerable amount of polymer is formed in the water phase when AIBN is used as initiator. Although AIBN is regarded as an oil-soluble initiator, its solubility reported in water is up to 1×10^{-3} mol/L in the presence of AN.¹³ The formation of polymer in the water phase is perhaps initiated by AIBN in water. (NH₄)₂IA group can hardly be exam-

TABLE IV
Parameters for Aqueous-Deposited Polymerization with Different Initiators

Initiator	Polymer formed (wt %)		r_1	r_2
	Monomer phase	Water phase		
(NH ₄) ₂ S ₂ O ₈	0	100	0.842	3.624
AIBN	90.9	9.1	0.826	3.862

Condition: [AN] = 3.21 mol/L; [Initiator] = 0.006 mol/L; conversion = 5%; temperature = 60°C.

ined in the polymer formed in monomer phase, confirming that (NH₄)₂IA cannot be dissolved in AN phase. The reactivity ratios obtained by the polymer formed in water phase were calculated (as Table IV). The reactivity ratio of (NH₄)₂IA initiated by (NH₄)₂S₂O₈ is lower, and the reactivity ratio of AN is higher than that initiated by AIBN. An explanation is that the comonomer have less chances to polymerize with radical groups because of the repulsion between (NH₄)₂S₂O₈ and (NH₄)₂IA.

CONCLUSIONS

The reactivity ratios of monomer in the aqueous-deposited copolymerization system depend on the conversions, the initiators, and the temperatures of polymerization of AN with (NH₄)₂IA. At smaller polymer-

ization conversion (<5%), the monomer reactivity ratios are unchanged. The reactivity ratio of AN rises and that of (NH₄)₂IA decreases, when the polymerization conversion increases till 13%. As the temperature increases, the polymerization has a tendency to the ideal copolymerization, and the reaction ratios tend to 1. When the polymerization is initiated by AIBN in water phase, the reactivity ratio of (NH₄)₂IA rises and that of AN decreases when compared with that initiated by (NH₄)₂S₂O₈.

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