# Acrylonitrile/Ammonium Itaconate Aqueous Deposited Copolymerization

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**ABSTRACT:** Acrylonitrile/ammonium itaconate [AN/$(NH_4)_2IA$] aqueous deposited polymerizations were studied in this work. It shows that the polymerizations were influenced by various factors, especially the water solubility of AN. In the polymerization process, the system was as separated monomer and water phases, and AN transferred from monomer phase to water phase until the monomer phase disappeared. Because of the solubility of AN in water, the reactivity ratios of monomer calculated by Kelen-Tudos method were different in various monomer contents. Although $(NH_4)_2S_2O_8$ was a water-soluble initiator, there was a short amount of polymer formed in monomer phase. To inhibit the polymerization in monomer phase, two additives were used in the polymerization and experiment data indicated that the two inhibitors exert inhibitory role effectively in monomer phase. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 904–908, 2006

**Key words:** acrylonitrile; ammonium itaconate; copolymerization; water solubility

## INTRODUCTION

Polyacrylonitrile (PAN) based precursors are emerging as one of the best materials for making carbon fibers. Superior mechanical properties of carbon fiber are reported when some comonomers are usually used.[1] Poly(acrylonitrile/ammonium itaconate) [poly(AN-$(NH_4)_2IA$)] (Scheme 1) has excellent hydrophilicity, and the final fibers made by the polymer have excellent properties than those of other fibers.[2–4] $(NH_4)_2IA$ has low solubility in organic solvent (about 0.23 wt % in DMSO at 60°C); using oil-soluble initiator, the great mass of polymer is formed in monomer phase. The concentration of $(NH_4)_2IA$ of the polymer is very low. Chen et al. had studied the viscosity behavior of poly(AN-$(NH_4)_2IA$) and kinetics of their copolymerization in a $H_2O$/DMSO mixture initiated by oil-soluble initiator.[5,6]

AN has a relatively substantial solubility in water (7.9 wt % at 40°C)[7] and $(NH_4)_2IA$ has huge substantial solubility also. Thus, AN and $(NH_4)_2IA$ can be polymerized in aqueous deposited copolymerization initiated by water-soluble initiator. During polymerizations, AN partition between the monomer phase and the water phase takes place, and transfers from monomer phase to water phase.[8] So, the water solubility of AN greatly influences polymerization. However, the effects of water solubility on aqueous deposited polymerization have been ignored. In aqueous deposited copolymerization, polymerization in the monomer phase is unpleasant; using suitable oil-soluble inhibitors can decrease the polymer formed in monomer phase.

In this study, water-soluble initiator (ammonium persulfate $(NH_4)_2S_2O_8$) was first used for AN/$(NH_4)_2IA$ aqueous deposited polymerization system. Polymerization in different systems, the effect of AN solubility and inhibitors on polymerization were investigated.

## EXPERIMENTAL

### Materials

AN was purified by alkali washing followed by distillation. $(NH_4)_2IA$ was recrystallized in methanol. $(NH_4)_2S_2O_8$ was used as initiator and also refined before use. Deionized water was adopted as the polymerization medium. Di-*t*-butyl-hydroxylamine (DTBHA) and *p*-hydroxyanisole (MEHQ) were used in the aqueous deposited polymerization.

### Polymerization

Required amounts of AN, $(NH_4)_2IA$, $(NH_4)_2S_2O_8$, deionized water were carried out in closed glass bottles which can withstand high pressure. Ultrapure nitrogen was flushed into the bottle. After a defined reaction time, the resultant mixture was poured into a large amount of methanol for precipitation, washed
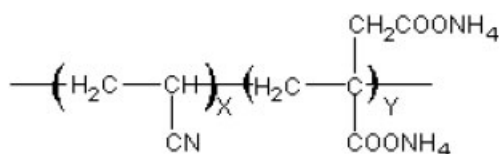
**Scheme 1** The chemical structure of AN/(NH$_4$)$_2$IA copolymer.

with methanol several times, dried at 60°C under vacuum, and then weighed.

## Measurement of AN and (NH$_4$)$_2$IA phase partitions

Abbe refractometry was the simplest method to measure AN phase partition. However, the method could not be applied successfully to the aqueous phase,[9] when it contained commoner ((NH$_4$)$_2$IA) or initiator ((NH$_4$)$_2$S$_2$O$_8$). The gas chromatographic (GC) method was adopted to determine the concentration of AN in aqueous phase and then to obtain the phase partition of AN. Type 103 GC meter (Shanghai Analytical Apparatus Factory of China), whose columns were filled with GDX10 (crosslinked polystyrene) microspheres, was used. In this experiment, hydrogen with the flow rate of about 21 mL/min was used as the carrier gas. The temperature of the injection block, column, and detector assembly were set at about 160, 130, and 130°C, respectively.[8]

Before measuring AN percentage, a calibration curve of AN concentration was first set up by measuring a series of aqueous solutions with known AN concentration. Using the calibration curve, the percentage of AN in the aqueous phase from the AN/
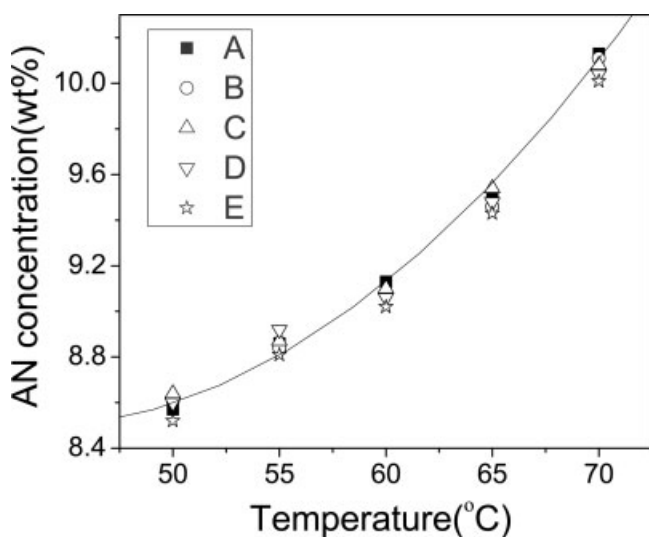
**TABLE I**
**Effect of the Concentration of (NH$_4$)$_2$IA on the Water Solubility of AN at 60°C**

| (NH$_4$)$_2$IA concentration (wt %) | AN Concentration (wt %) |
|---|---|
| 0.0 | 9.14 |
| 1.0 | 9.08 |
| 2.0 | 9.12 |
| 3.0 | 9.04 |

Condition: AN/(NH$_4$)$_2$IA = 95:5, 60, 30 min.

(NH$_4$)$_2$IA/H$_2$O system could be determined by GC. The AN concentration in the monomer phase was calculated by the AN in the aqueous phase and in the copolymer.

## Characterization

Oxygen content of the copolymers was measured by element analyzer (Vario ELIII). The molecular weight of (NH$_4$)$_2$IA is 164, and the molecular weight of AN is 53. Thus (NH$_4$)$_2$IA concentration (mol/mol) was calculated by eq. (1):

$$[(NH_4)_2IA] = \frac{\dfrac{Co}{4 \times 16}}{\dfrac{1 - \dfrac{Co}{4 \times 16} \times 164}{53} + \dfrac{Co}{4 \times 16}} = \frac{53Co}{64 - 111Co} \tag{1}$$

Therefore, the (NH$_4$)$_2$IA content in aqueous phase could be calculated by the concentration in copolymer, and this content in monomer phase could be ignored.



**Figure 1** AN partition in water phase with different temperature. A: in deionized water; B: using (NH$_4$)$_2$S$_2$O$_8$ as initiator; C: using AIBN as initiator; D: the concentration of (NH$_4$)$_2$IA is 2 wt % in monomer feed; E: the concentration of (NH$_4$)$_2$IA is 10 wt % in monomer feed.
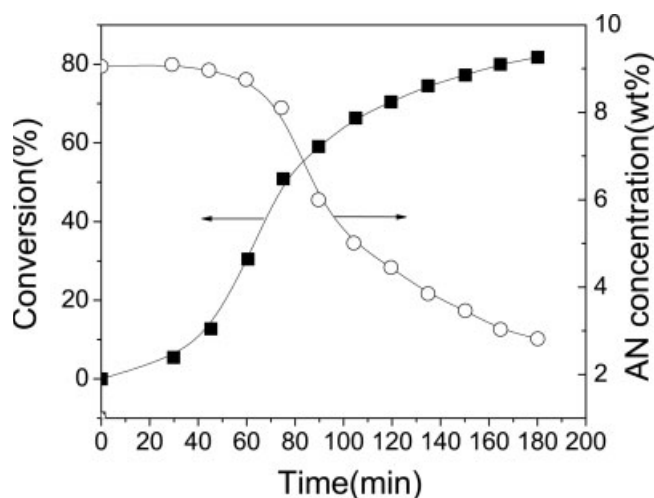


**Figure 2** The changes of AN concentration and conversion during polymerization.

| Recipe | | | Polymer (g) | | $(NH_4)_2IA$ content (wt %) | |
|---|---|---|---|---|---|---|
| Initiator (g) | Monomer (g) | Water (g) | Monomer phase | Water phase | Monomer phase | Water phase |
| 0.1418 $(NH_4)S_2O_8$ | 40 | 160 | 0.0292 | 1.9483 | 0.0 | 8.162 |
| 0.1205 $(NH_4)S_2O_8$ | 34 | 166 | 0.0209 | 1.6869 | 0.0 | 7.335 |
| 0.1064 $(NH_4)S_2O_8$ | 30 | 170 | 0.0182 | 1.4739 | 0.0 | 6.546 |
| 0.0922 $(NH_4)S_2O_8$ | 26 | 174 | 0.0165 | 1.2334 | 0.0 | 5.981 |

The reactivity ratios of AN ($r_1$) and $(NH_4)_2IA$ ($r_2$) were calculated by the K-T method, as follows[10]:

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

where $x$ is the ratio of the molar fractions of the AN and $(NH_4)_2IA$ monomers in the monomer feed, $y$ is the ratio of molar fractions of the AN and $(NH_4)_2IA$ monomers in the copolymer, and $a$ is an equation parameter. The equation parameter can be computed according to eq. (3):

$$a - \sqrt{x_{min}x_{max}/y_{min}y_{max}} \quad (3)$$

where $x_{min}$ and $x_{max}$ are the minimal and maximal molar fractions in the monomer feed, respectively, and $y_{min}$ and $y_{max}$ are the minimal and maximal molar fractions in the copolymer, respectively. Equation (2) transforms into the form:

$$\tau = r_1(r_2/a)\varepsilon - r_2/a$$
$$\tau = x(y-1)/(ay+x^2), \quad \varepsilon = x^2/(ay+x^2) \quad (4)$$

The plot of $\tau$ versus $\varepsilon$ gives a straight line. Extrapolation of the line to $\varepsilon = 1$ gives $r_1$ and to $\varepsilon = 0$ gives $r_2/a$.
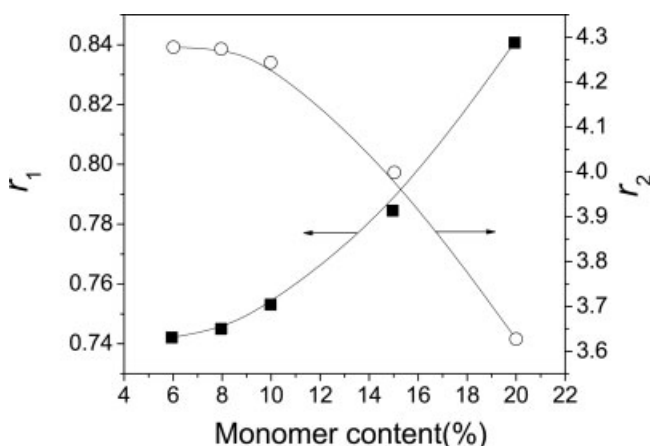


**Figure 3** The reactivity ratio of monomers with different monomer content.

## RESULTS AND DISCUSSION

### AN phase partition between monomer and aqueous phase

Because of different densities of monomer and water, the $AN/(NH_4)_2IA/H_2O$ system was separated into two phases: monomer phase (AN phase) and water phase (containing AN, initiator, and comonomer). AN phase partitions between the monomer and water phase at different temperatures are shown in Figure 1. With the increase of temperature, the water solubility of AN rose. When $(NH_4)_2IA$ or $(NH_4)_2S_2O_8$ was used, the AN phase partitions had hardly any change, and indicated that AN partitions had not been affected obviously by various systems.

In the deposited polymerization process, the concentration of comonomer was decreased gradually. The influence of the concentration of $(NH_4)_2IA$ on aqueous phase partition was studied and the results are presented in Table I. It was shown that the water solubility of AN did not have any change also. Thus, the effect of the concentration of $(NH_4)_2IA$ on the water solubility of AN could be neglected.

### Transport of AN between monomer and water phase

The changes of AN concentration in the water phase and monomer conversion with polymeric time are shown in Figure 2. It could be seen that the concentration of AN decreased with the increase of time, and the conversion was increased. The speed of the decrease and the increase were not constant, and they expressed different changes at different reaction stages. At the beginning of the polymerization, the monomer conversion was low. Because of the transport of AN from monomer phase to water phase, the concentration of AN had hardly any change. With the increase of polymeric time, the monomer conversion rose rapidly, whereas the concentration of AN decreased slowly. Two factors had been attributed to the slow decrease of AN concentration: (1) AN transferred from monomer phase to water phase, which complemented the polymerized AN in water phase. (2) Plenty of polymer was formed and suspended in water. The polymer impeded AN transport between

**TABLE III**
**Amounts of Polymer Formed in Monomer and Water Phases**
**Using Different Inhibitions**

| Polymer (g) | None | DTBHA (g) | | | | MEHQ (g) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 0.01 | 0.02 | 0.03 | 0.04 | 0.01 | 0.02 | 0.03 | 0.04 |
| Monomer phase | 0.0292 | 0.0116 | 0.0098 | 0.0083 | 0.0076 | 0.0139 | 0.0121 | 0.0107 | 0.0092 |
| Water phase | 8.3008 | 1.9065 | 1.9144 | 1.8971 | 1.9089 | 1.9012 | 1.8433 | 1.8057 | 1.7104 |

Condition: monomer/water = 20:80, AN/(NH$_4$)$_2$IA = 95:5, 60, 30 min.

the monomer and water phases, which brought the decrease of AN concentration in water phase. At the time of 75 min, the monomer phase disappeared, and the concentration of AN decreased quickly. With the progress of the polymerization, more and more polymer was formed in water phase, the conversion increased and the concentration of AN decreased accordingly.

### Polymerization parameters in different systems

To study the polymerization in the two phases, the monomer phase and the water phase were separated before polymerization. Then the two phases were carried out in closed glass bottles and polymerized. After 30 min, the polymer was washed, dried, and weighed. The parameters of the polymerization are presented in Table II. Because of low solubility of (NH$_4$)$_2$S$_2$O$_8$ in AN, the amounts of polymer formed in monomer phase were much lower than those formed in water phase. Elemental analyses were used for determining oxygen content of the copolymers produced in monomer and water phases. The contents of (NH$_4$)$_2$IA were calculated and listed in Table II. It was found that almost all of the polymer formed in monomer phase was PAN homopolymer. This confirmed that suspension polymerizations cannot achieved suitable AN/(NH$_4$)$_2$IA copolymers. The (NH$_4$)$_2$IA content of the polymer formed in water phase was higher than monomer feed at low conversion, and the (NH$_4$)$_2$IA content became more with the increase of the ratios of monomer and water. This should be attributed to the following reasons: (1) In the start of the polymerization, all of (NH$_4$)$_2$IA and part of AN dissolved in water, which made the fraction of (NH$_4$)$_2$IA increase in water phase. (2) With the ratios of monomer increased, in the water phase, the concentration of (NH$_4$)$_2$IA increased but that of AN hardly changed. That is to say, the ratios of (NH$_4$)$_2$IA and AN increased in monomer feed, thus the content of (NH$_4$)$_2$IA of the polymer also increased.

For estimating monomer reactivity ratios, polymerization experiments were terminated at <10% conversion. The reactivity ratios of the polymerizations

in water phase were calculated (Fig. 3). With increase of monomer contents of the polymerization system, the reactivity ratios of AN increased and those of (NH$_4$)$_2$IA decreased. We attributed the phenomena to the different solubility of AN and (NH$_4$)$_2$IA. When monomer contents were higher than 10%, part of AN but all of (NH$_4$)$_2$IA had participated in polymerization. When monomer contents were less than 9%, the monomer phase disappeared, and the $r_1$ and $r_2$ did not change. So, the monomer reactivity ratios should be determined under monomer contents less than 9%.

### Effect of inhibitors on polymerization

Polymerization in the monomer phase was undesirable in aqueous deposited copolymerization. From the preceding study, we know that polymerization in the monomer phase could influence the composition of the polymer. To eliminate this polymerization, two oil-soluble inhibitors DTBHA and MEHQ were used to the aqueous deposited polymerization. Effects of the inhibitors on the copolymerization have been studied by varying concentrations. Table III lists the water and the monomer phases after the addition of inhibitors. The polymer produced in the monomer phase obviously decreased after DTBHA was used, whereas the polymer formed in water phase did not change with an increase of DTBHA usage, thus indicating that DTBHA exerts no inhibitory role in water phase. When MEHQ was used, the polymer produced in the monomer phase was still considerable; however, the polymer in water phase decreased with increased MEHQ usage, the reason for which may be that part of MEHQ had dissolved in the water phase. Thus, MEHQ was not a good oil-soluble inhibitor for the AN/(NH$_4$)$_2$IA aqueous deposited copolymerization system.

### CONCLUSIONS

Experimental studies on aqueous deposited copolymerization systems of AN with (NH$_4$)$_2$IA showed that AN phase partition takes place between the monomer and the water phases. The water solubility of AN was

not affected either by initiator or by the comonomer ratio, but it was increased as temperature increased. During polymerization, AN monomer transferred from monomer phase to water phase, but the polymer, which was in water phase, could impede this transport. Because of different solubilities of AN and $(NH_4)_2IA$, the value of the AN reactivity ratios were less than ''real'' value; however those of $(NH_4)_2IA$ were higher. Polymerization in monomer phase was not welcomed in $AN/(NH_4)_2IA$ aqueous deposited copolymerization. It can be effectively inhibited by the oil-soluble inhibitor DTBHA, which exerts less influence on polymerization in the water phase.

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