

# NOTE

## Study on Polymerization of Acrylonitrile with Methylacrylate and Itaconic Acid in Mixed Solvent

### INTRODUCTION

It is well known that three general methods of polymerization are used commercially, namely, the solution, suspension, and emulsion methods. In actual practice, the solution and, in particular, the suspension methods are most commonly employed for acrylic fiber manufacture. A vast amount of literature is available on polymerization processes of acrylonitrile, together with other comonomers.<sup>1-4</sup> Studies on polymerization in the mixed solvent of water with an organic solvent are not described. It is conceivable that this method would combine advantages of solution and suspension (in water) polymerization and could offer more ways to change polymerization conditions and product properties.

In this article, an attempt was made to investigate systematically the effect of the mixed solvent of DMF-water on the polymerization behavior and the properties of polymers.

### EXPERIMENTAL

#### Materials

Acrylonitrile and methylacrylate (MA) were washed from the inhibitor successively with a 10% aqueous solution of NaOH and distilled water until a neutral reaction was obtained, followed by drying over anhydrous CaCl<sub>2</sub> and by fractional distillation. Hydrogen peroxide, ascorbic acid (AH<sub>2</sub>), itaconic acid (IA), dimethylformamide (DMF), etc., were of analytical grade. Water was doubly distilled over alkaline permanganate.

#### Polymerization

A calculated amount of water together with DMF was added into a reaction vessel and deaerated by sparging with nitrogen for 20 min. A known amount of comonomer mixture was added under nitrogen and heated to the ap-

propriate temperature. The calculated amounts of ascorbic acid and hydrogen peroxide were also introduced into the reaction vessel and the time was noted. After polymerization for a given time, the required amount of additional solvent was added. The polymer formed was filtered, sufficiently washed with water, and dried at 60°C under vacuum to constant weight. The conversion was determined gravimetrically.

The weight-average molecular weight of polymers was determined by viscometry in 0.1M NaSCN/DMF at 30°C and calculated with the following Mark-Houwink relationship:

$$[\eta] = 3.35 \times 10^4 M_w^{0.72}$$

Molecular weight distribution (MWD) was determined by GPC with a Waters 150C. GPC measurement was performed in DMF at 30°C. The amount of polymer solution injected was 0.3 g/dL  $\times$  0.2 mL and the elution rate was 1 mL/min.

### RESULTS AND DISCUSSION

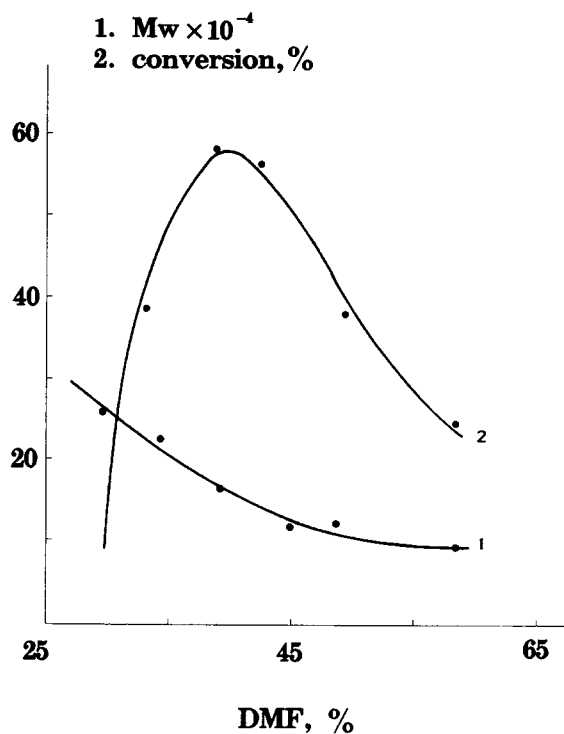
#### Effects of the Composition of Mixed Solvent

The polymerization of AN-MA-IA in a solvent mixture of DMF-water initiated by hydrogen peroxide and ascorbic acid showed the characteristics of heteroge-

**Table I** Relationship Between Maximum Monomer Concentration and Ratio of DMF to Water

DMF/H <sub>2</sub> O	M (%)					
	20	25	30	35	40	50
30/70	+	0	-	-	-	-
35/65	+	+	0	-	-	-
40/60	+	+	+	0	-	-
50/50	+	+	+	+	+	0

(+) Complete solubility; (-) partial solubility; (0) critical value for split phase.



**Figure 1** The effect of DMF content on conversion and molecular weight: AN : MA : IA = 95 : 4 : 1 (mol %),  $[M] = 30\%$  (wt %),  $[AH_2] = 0.15\%M$ ,  $[H_2O_2] = 0.15\%M$ ,  $t = 1$  h,  $T = 30^\circ C$ . (1)  $M_w$ ; (2) conversion.

neous polymerization. The reaction system, though homogeneous before initiation of polymerization, became heterogeneous as soon as polymerization started due to the insolubility of the polymer in the solvent mixture. However, it is important to note the influence of adding DMF on the physical state of the reaction system. The addition of DMF enhanced monomer solubility in the polymerization medium, which regulated the physical characteristics of polymerizing slurries and the occlusion level of growing chain radicals, thereby controlling the polymerization rate and polymer properties. Figure 1 shows the effects of compo-

**Table II** Conversion and Molecular Weight at Maximum Monomer Concentration Responding to Ratio of DMF to Water

DMF/H <sub>2</sub> O	$[M]$ (%)	$M_w \times 10^{-4}$	Conversion (%)
50/50	50	37.9	36
40/60	35	37.3	19.8
35/65	30	45.4	20
30/70	25	46.9	14

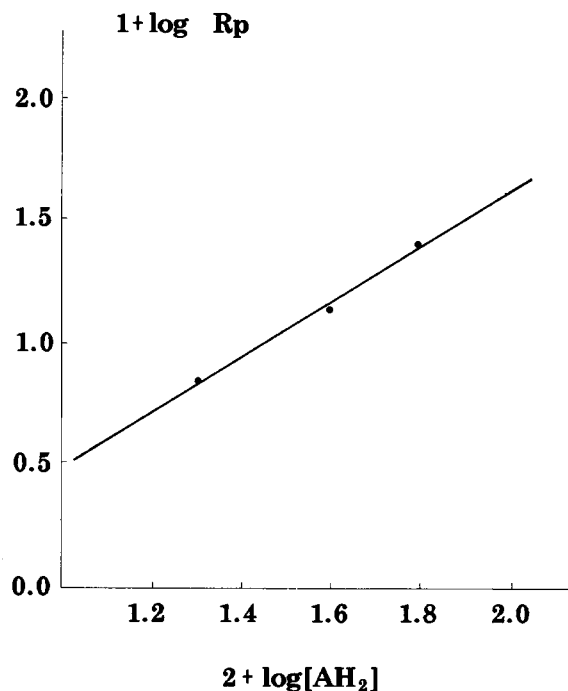
AN : MA : IA = 97 : 2 : 1 mol %;  $[AH_2] = 0.1\% M$ ;  $[H_2O_2] = 0.05\% M$ ;  $t = 1$  h.

**Table III** Relationship Between MWD and DMF/H<sub>2</sub>O

DMF/H <sub>2</sub> O	$[M]$ (%)	MWD
50/50	50	2.62
40/60	35	3.95
35/65	30	3.67
30/70	25	3.53

AN : MA : IA = 97 : 2 : 1 mol (%);  $[AH_2] = 0.094\% M$ ;  $[H_2O_2] = 0.047\% M$ ;  $T = 30^\circ C$ ;  $t = 4$  h.

sition of the solvent mixture on the conversion and molecular weight of the polymers. It is found that the molecular weight of the resulting polymers decreases with an increase in concentration of DMF and the conversion increases initially and then decreases with a further rise in DMF content of the solvent mixture. The lowering of molecular weight due to the addition of DMF may be explained by the chain-transfer mechanism and biradical termination being more available, especially at higher DMF content. The maximum conversion at 40% of DMF content is attributed mainly to higher monomer concentration, because in the reaction carried out under 30% of monomer concentration, all the monomers could dissolve in the mixed solvent (see Table I). When the content of DMF is below 40%, only partial monomers could dissolve in



**Figure 2** Double logarithmic plot of initial  $R_p$  vs. concentration of ascorbic acid.

**Table IV** Dependence of MWD on Composition and Method of Addition of Solvent

DMF/H <sub>2</sub> O	Additional Solvent	Method of Addition	$M_w \times 10^{-4}$	MWD
40/60	H <sub>2</sub> O	Once	45	3.24
40/60	H <sub>2</sub> O	Multi-adding	47.6	3.95
40/60	DMF/H <sub>2</sub> O	Multi-adding	30.1	3.24
40/60	DMF/H <sub>2</sub> O	Once	21.1	2.85

AN : MA : IA = 97 : 2 : 1 mol %; [AH<sub>2</sub>] = 0.094% M; [H<sub>2</sub>O<sub>2</sub>] = 0.047% M; T = 30°C; t = 4 h.

the medium, and if the content of DMF is beyond 40%, then the monomers are diluted and the system viscosity is reduced, thereby weakening the occlusion level of growing chain radicals and the tendency of mutual termination of the polymer chain increases. These facts might tend to decrease the rate of polymerization ( $R_p$ ). It is considered reasonable that the composition of the mixed solvent influences the  $R_p$  in two ways: One is by changing the monomer concentration in the reaction medium, and the other is by changing the viscosity of the system.

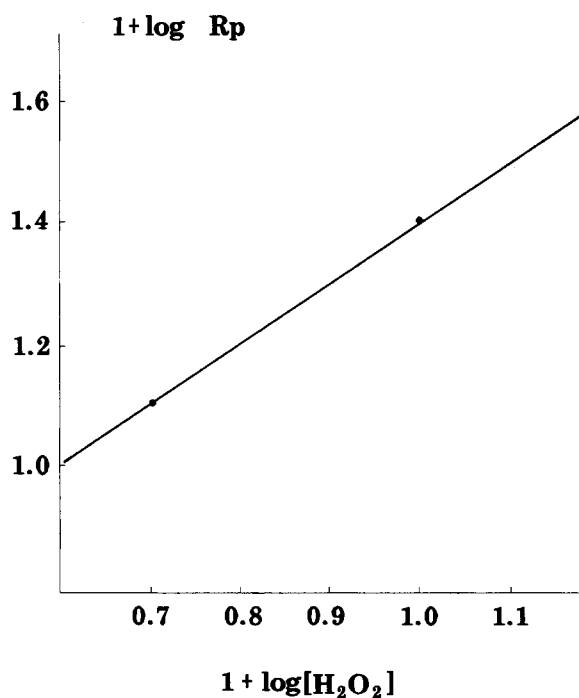
Table I presents maximum monomer concentrations in the corresponding solvent mixtures. Table II points out the conversion and molecular weight at the maximum monomer concentration as shown in Table I. It is observed from Table II that the decrease of DMF content in the solvent mixture results in higher molecular weight and lower conversion.

Table III gives the molecular weight distribution of polymers formed at the maximum monomer concentration. It can be seen from Table III that the MWD increases slightly with an increasing ratio of DMF to water but reduces significantly at a 50 : 50 ratio of DMF to water.

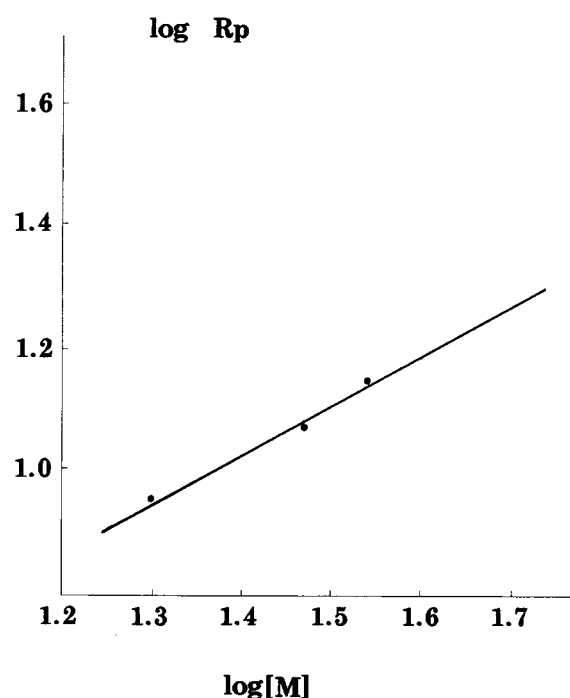
The ratio of DMF to water at 1 : 1 should be noted. It was reported<sup>5</sup> that water and DMF form a stable complex at the ratio of 1 : 1 and that this complex is a transfer agent with much less reactivity than that of anhydrous DMF.

#### Effect of Composition of Additional Solvent

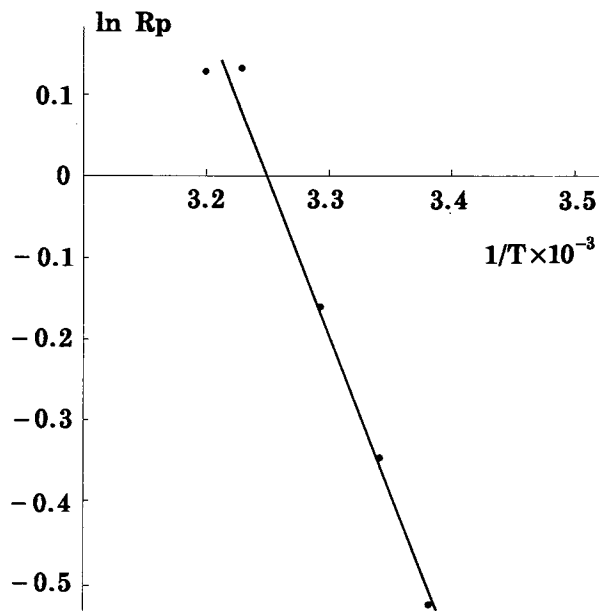
After polymerization for a given time, additional solvent was added. Table IV indicates that the molecular weight and its distribution depend strongly on the composition



**Figure 3** Double logarithmic plot of initial  $R_p$  vs. concentration of hydrogen peroxide.



**Figure 4** Double logarithmic plot of initial  $R_p$  vs. initial monomer concentration.



**Figure 5** Arrhenius plot relative to the  $R_p$ . AN : MA : IA = 97 : 2 : 1 mol %, DMF/H<sub>2</sub>O = 40/60, [M] = 30%, [AH<sub>2</sub>] = 0.2 mol % M, [H<sub>2</sub>O<sub>2</sub>] = 0.2 mol % M.

of additional solvent and could be regulated by the number of aliquots added. Clearly, the MWD is narrower in the case of adding water-DMF than when adding only water. It is also seen from Table IV that in the case of both adding water and water-DMF the MWD is narrower with one addition than with multiple additions.

### Kinetics of Polymerization

The polymerization was carried out in 40 : 60 DMF-water at varying concentrations of ascorbic acid (AH<sub>2</sub>). As can be seen in Figure 2, the dependence of the concentration of ascorbic acid on the rate is first order. The polymerization was also carried out with varying concentrations of hydrogen peroxide and a constant ratio of DMF-water and constant concentrations of AH<sub>2</sub> and comonomer. As seen in Figure 3,  $R_p$  is proportional to the 0.80 power of [H<sub>2</sub>O<sub>2</sub>]. Furthermore, the polymerization was carried out at varying comonomer concentrations under otherwise constant conditions, as shown in Figure 4; the initial rate of polymerization  $R_p$  is proportional to 0.98 power of the concentration of co-

monomers. Therefore, the following relationship is obtained for the initial concentration of hydrogen peroxide, ascorbic acid, and comonomers:

$$R_p = K [\text{H}_2\text{O}_2]^{0.8} [\text{AH}_2]^{1.0} [\text{M}]^{0.98}$$

This means, from the polymerization-rate equation, that the termination of the growing polymer chains would have both monoradical and biradical termination mechanisms; which of them would dominate depends on the content of DMF in the medium.

The effect of temperature on the  $R_p$  was investigated over 20–40°C. From the Arrhenius plot of  $\log R_p$  against  $1/T$  (Fig. 5), the overall activation energy was calculated as 8.126 kcal/mol, which is close to the usual redox system.<sup>1</sup>

In conclusion, the DMF used in this study's system enhances the solubility of monomers in water and weakens the occlusion level of growing chain radicals and, accordingly, influences the polymerization behavior, thereby offering a variety of ways to regulate the product properties for end-use.

### REFERENCES

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