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COPOLYMERIZATION OF ACRYLONITRILE WITH ETHYL METHACRYLATE—I

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Abstract—This paper reports briefly the results of copolymerization of ethyl methacrylate (EMA) and acrylonitrile (AN). The effect of the medium on the reactivity ratios was investigated. It was found that the medium had no effect on the value of r for EMA whereas r for AN for solution copolymerization was different from the value for bulk or emulsion copolymerizations. The values remained constant up to about 70 per cent conversion.

INTRODUCTION

Although the copolymerization of AN and methyl methacrylate has received considerable attention [1] no similar study has been made for AN and EMA. It has been shown [2] that n-propyl and n-butyl methacrylates are appreciably different in their kinetic behavior in polymerization. Furthermore, Bevington *et al.* have shown that the ratio k_t/k_p^2, where k_t and k_p are rate termination and rate propagation constants, respectively, is significantly different for the methyl, ethyl, phenyl, benzyl and cyclohexyl methacrylates. This suggested that if the copolymerization of ethyl methacrylate with different monomers was investigated, a difference in behaviour between its copolymerization and those involving other methacrylates would be observed.

This work is an investigation into the copolymerization behaviour of AN and EMA in dimethylformamide (DMF) solution, in the bulk, and in aqueous emulsions.

RESULTS AND DISCUSSIONS

(a) *Copolymerization in dimethylformamide*

DMF was chosen as a solvent to ensure homogeneity; both monomers and resulting copolymers are soluble in this solvent. The experimental results for copolymerization at 70° are illustrated in Fig. 1. The reactivity ratios of AN and EMA, r_1 and r_2, respectively, were calculated by application of the Fineman–Ross method [3]. This method is based on the differential version of the copolymer composition equation in the form:

$$\frac{F}{f}(f-1) = r_1\frac{F^2}{f} - r_2,$$

where F represents the molar ratio of AN to EMA in the feed and f represents the molar ratio in the resulting copolymer. Thus a plot of $F/F(f-1)$ against F^2/f yields a straight line of slope r_1 and intercept $-r_2$. The least square method was used to obtain the best values of r_1 and r_2 which would fit the curve of Fig. 1. These values are, respectively, $0{\cdot}18 \pm 0{\cdot}02$ and $0{\cdot}82 \pm 0{\cdot}12$. Fig. 2 is the Fineman–Ross plot for solution copolymerization.

(b) *Copolymerization in the bulk and in an emulsion*

To determine the effect of the medium on the values of r_1 and r_2, copolymerizations were carried out in emulsion at 30° and in bulk at 70°. The results are illustrated in Fig. 1. The values for r_1 and r_2, obtained in the same way as for solution polymerization, are:

$$\left.\begin{aligned} r_1 &= 0{\cdot}33 \pm 0{\cdot}01 \\ r_2 &= 0{\cdot}33 \pm 0{\cdot}1 \end{aligned}\right\} \text{for emulsion polymerization}$$

$$\left.\begin{aligned} r_1 &= 0{\cdot}34 \pm 0{\cdot}01 \\ r_2 &= 0{\cdot}85 \pm 0{\cdot}12 \end{aligned}\right\} \text{for bulk polymerization.}$$

The Fineman–Ross plots are shown in Figs. 3 and 4. It is clear that the reactivity ratios for both AN and EMA are the same for both emulsion and bulk polymerizations; this is in agreement with other workers [4–6]. Since both AN and EMA are only sparingly soluble in water, polymerization in emulsion must take place mainly in the organic phase, especially when monomer concentrations are high.

In Brandrup's work [7] on the copolymerization of AN and ethyl acrylate, the results for heterogeneous and homogeneous conditions were quite different. This was because in his emulsion polymerization, due to the

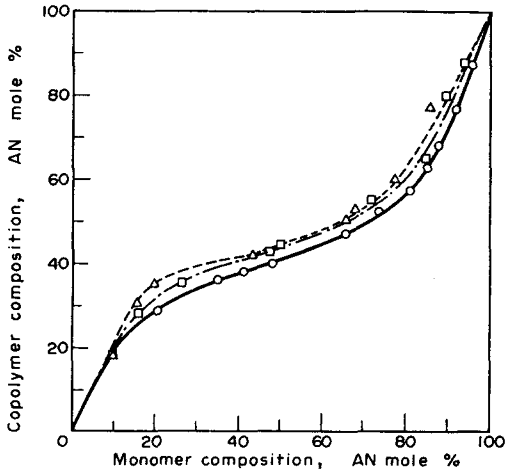

Fig. 1. Plots of copolymer composition against monomer composition for acrylonitrile and ethyl methacrylate. -·-□-·- Copolymerization in bulk; —○— copolymerization in DMF; ---△--- copolymerization in aqueous medium.

low initial concentrations, he started with homogeneous copolymerization and adsorption effects were negligible. However, in the present work, the initial concentrations of AN were large and therefore adsorption of monomer on to polymer is important and conditions are more similar to bulk polymerization conditions.

The value for r_1 in solution (DMF) copolymerization is different from the other values of r_1, whereas r_2 is essentially the same in all systems. The lower value of r_1 in DMF could be due to either a decrease in k_{11} (the rate constant for interaction of AN monomer with a growing radical $\cdots CH_2—\underset{\displaystyle C\equiv N}{\underset{|}{\dot{C}H}}$) or to an increase in k_{12} (the rate constant for interaction of EMA monomer with a growing radical $\cdots CH_2—\underset{\displaystyle C\equiv N}{\underset{|}{\dot{C}H}}$).

The growing AN radical is polarized by the electron-withdrawing nitrile group; this polarization should be increased by increasing the polarity of the solvent. In order to detect polarization effect, the i.r. spectra of acrylonitrile in dimethylformamide and in benzene were studied. It was found that the position of the C≡N band remained constant but that its intensity varied with the solvent (see Table 1).

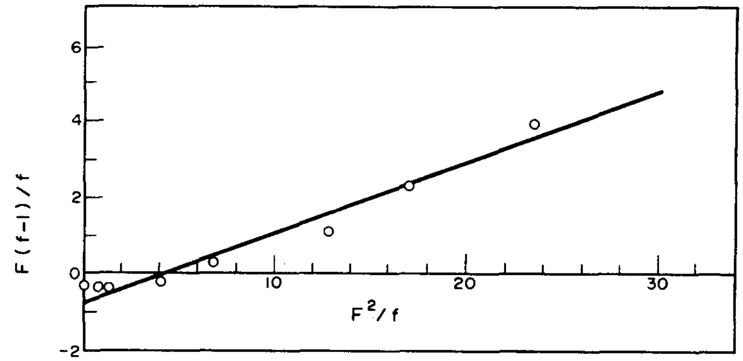

Fig. 2. Copolymerization in solution. Plots used to determine relative reactivity ratios for AN and EMA.

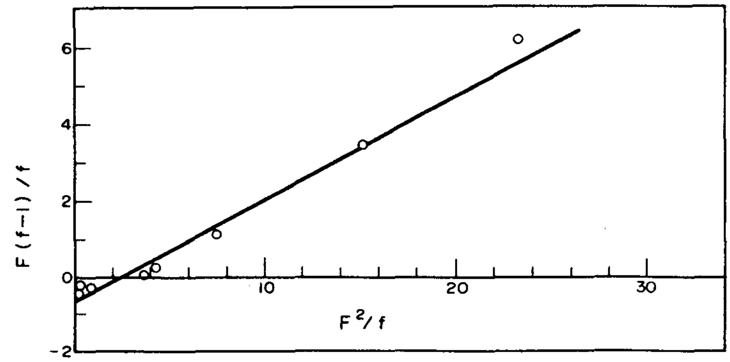

Fig. 3. Copolymerization in aqueous medium.

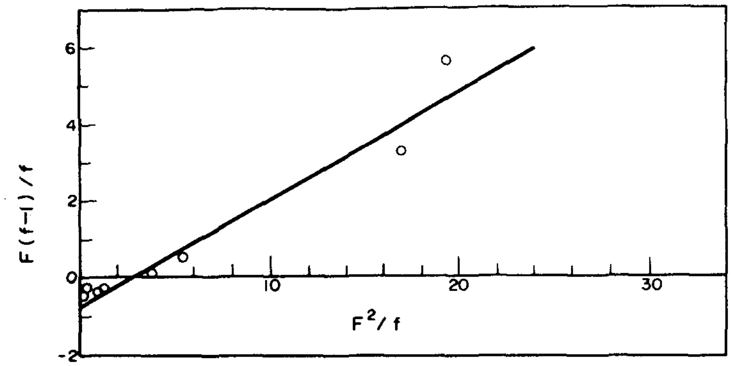

Fig. 4. Copolymerization in bulk. Plots used to determine relative reactivity ratios for acrylonitrile and ethyl methacrylate by the method of Fineman and Ross.

Table 1

Solvent	Wt % of AN	Absorbance	Frequency (cm^{-1})
Benzene	10	0·138	2220
DMF	10	0·235	2220
Benzene	25	0·360	2220
DMF	25	0·480	2220
Benzene	50	0·68	2220
DMF	50	0·78	2220

The C═C band could not be investigated due to overlap with solvent bands. It is clear from the table that AN is polarized in DMF relative to its polarization in benzene since it is known that a more polar $C\equiv N$ group gives a more intense absorption [8]. Therefore the decreased value of r_2 in DMF is probably due to polarization of both the AN monomer molecules and of the growing radical $\sim CH_2\text{—}\underset{C\equiv N}{\underset{|}{\dot{C}H}}$ which would result in a decrease of k_{11}.

Other workers [9] have attributed a similar variation in reactivity ratios to changes in polarization of carbonyl or amide groups in the monomers brought about by different polarities of the solvents. The monomers involved were methyl methacrylate, acrylamide and styrene and the change in polarization was detected by measuring a change in i.r. stretching frequencies of the double bonds of the monomers in various solvents. Yet another group of workers [10] found that, although there was a change in reactivity ratio in going from one solvent system to another, there was no detectable change in stretching frequencies, the monomers involved being styrene and methacrylonitrile. However, these workers attributed the change in r_1 with solvent to a change in polarization of the growing radical.

(c) *Fractionation of copolymers*

The validity of r_1 and r_2 values was also confirmed by fractionation of the copolymer. An AN–EMA copolymer containing 66 per cent by weight of AN and having an intrinsic viscosity of 0·52 dl g^{-1} was fractionated (see Table 2).

Table 2. Fractionation of AN–EMA copolymer in acetone–water system at 25°

No.	Wt of fraction	AN (wt %)	$[\eta]$ (dl g^{-1})
1	0·0566	82·0	0·820
2	0·2020	78·0	0·755
3	0·2004	71·5	0·695
4	0·2074	74·5	0·640
5	0·2128	72·5	0·620
6	0·2990	69·0	0·590
7	0·2660	64·0	0·545
8	0·2074	62·0	0·500
9	0·1490	61·0	0·485
10	0·1578	61·0	0·450
11	0·1250	55·0	0·380
12	0·1350	57·0	0·350
13	0·1482	69·0	0·305
14	0·1260	76·0	0·265
15	0·0736	76·0	0·225

$\sum W_i = 2{\cdot}556$ g.

These results show no correlation between the change in molecular weight and the composition of each fraction. This is to be expected for a copolymer made by a radical process and carried out to moderate conversion (about 25 per cent). Results relevant to these were obtained by Baines and Bevington [11] by the fractionation of copolymers of styrene and methyl methacrylate, using a tracer technique for analysis of the fractions.

Figure 5 illustrates the integral compositional curve for this copolymer. This curve was constructed starting with fractions of lower AN content followed by fractions with increasing AN content. Thus the points were obtained by using data from Table 2 whereas the line was calculated from the equation proposed by Kruse [12] using fixed values of $r_1 = 0{\cdot}18$ and $r_2 = 0{\cdot}82$. It is

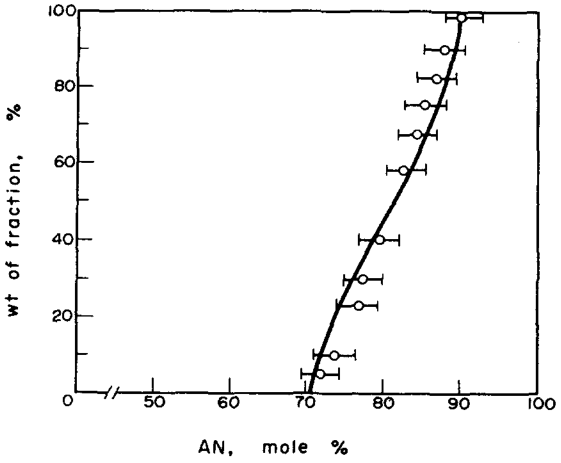

Fig. 5. Integral compositional distribution curve; the points were obtained from the experimental results of fractionation.

clear that the theoretical curve is in good agreement with the experimental values, indicating that the values of r_1 and r_2 are constant during the copolymerization.

In order to support this conclusion, a parallel investigation was carried out in which the composition of the copolymer at different conversions was followed kinetically by the conventional ampoule technique. Figure 6 illustrates the experimental points, and the calculated line using the same values of r_1 and r_2 up to 70 per cent conversion.

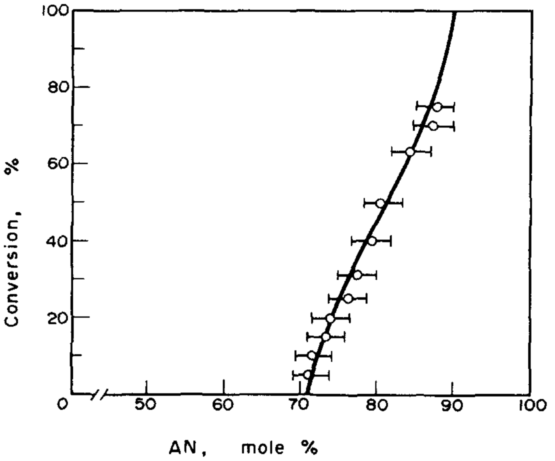

Fig. 6. Integral compositional curve; the line is the calculated curve, the points are the experimental data.

EXPERIMENTAL

Ethyl methacrylate (Koch-Light Labs. Ltd.) was washed several times with 5 per cent aqueous sodium hydroxide and then repeatedly with distilled water. It was then dried and fractionated under nitrogen. The fraction distilling at 117·5° was used.

Acrylonitrile. (B.D.H. Ltd.) was distilled under nitrogen (b.p. 76·5–77·5°).

Bulk and solution copolymerizations were performed at 70° ± 0·1° in a nitrogen atmosphere using pyrex tubes and the reaction was allowed to proceed to about 10 per cent. The initiator was azobisisobutyronitrile at 0·2 per cent by weight of the two monomers. The copolymers were recovered by precipitation and were then vacuum dried. Nitrogen was determined by Kjeldahl's procedure.

Heterogeneous copolymerizations were carried out at 30° ± 0·1° with stirring in conical flasks; the reaction was allowed to proceed to less than 10 per cent conversion. The initiator system was a mixture of potassium persulphate, potassium metasulphate and Mohr's Salt in a weight ratio of 10:15:2, respectively. Sodium lauryl sulphate was used as an emulsifying agent and the pH was kept at 2·5 with hydrochloric acid. Copolymers were filtered, washed repeatedly with ethanol–water mixtures and vacuum dried.

Fractionation was performed at about 25° by addition of water to dilute solutions of polymers in acetone.

Generally about 3 g of copolymer were used in about 300 ml of acetone. The procedure described by Baines and Bevington [11] was then carried out and at least 12 fractions were collected. Each fraction was dissolved in acetone and completely precipitated by adding a large excess of water. It was filtered off, washed with water and dried thoroughly in vacuum.

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