Effect of Emulsifier upon the Compositions of Emulsion Copolymers of Acrylonitrile and Water-soluble Monomers

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Introduction

In a previous paper[1] we reported that the compositions of emulsion copolymers of acrylonitrile and water-insoluble monomers such as vinylidene chloride or styrene depend upon the concentrations of emulsifier in aqueous solutions. In this paper, first, the relations between the compositions of emulsion copolymers of acrylonitrile and the other water-soluble monomers such as methyl methacrylate vinylacetate and methyl acrylate and the amounts of emulsifier used are given and then the deviations of monomer polymer composition curves of emulsion copolymerizations from those of bulk copolymerizations are discussed.

Experimental

Acrylonitrile (AN).—Redistilled American Cyanamide Co. material was used for all experiments.

Methyl Methacrylate (MMA).—Redistilled Mitsubishi Rayon Co, material was used.

Vinyl Acetate (VAc).—Redistilled commercial material was used.

Methyl Acrylate (MA).—Redistilled Toa Gosei Chemical Co. material was used.

Emulsifier (Sodium Dodecyl Sulfate).—Recrystallized Kao soap Co. material was used.

Emulsion polymerization procedure was the same as that used in the previous report[2].

The amount of water used was 8 times as much as that of the monomer, and 0.8% by weight of the potassium persulfate as the catalyst, and 0.8% by weight of sodium bisulfate as reductant (both based on the total monomers) were employed. The polymerization temperature was 45°C. The combined acrylonitrile in copolymer was determined by the Kjeldahl method. The composition of monomer oil phase was determined by the refractive indices method as we previously reported[1].

Results and Discussion

(1) Effect of Emulsifier upon the Compositions of Copolymers.—In the copolymerization 0, 0.1, 0.2, 0.4, 0.6, 1.0 and 1.5%

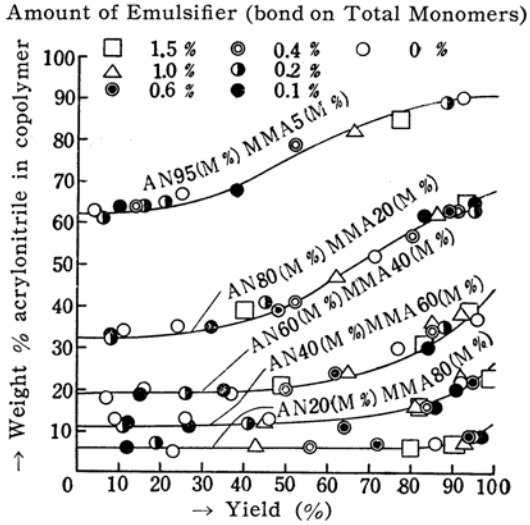

Fig. 1. Effect of emulsifier on composition of acrylonitrile methyl methacrylate copolymers.

1) M. Uchida and H. Nagao, This Bulletin, **30**, 314 (1957).
2) M. Uchida and H. Nagao This Bulletin, **29**, 928 (1956).

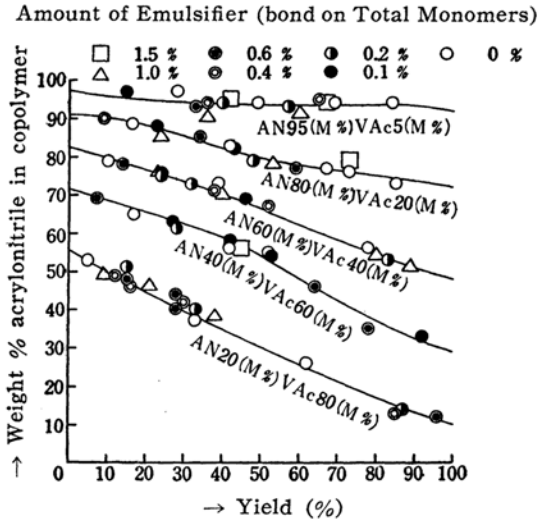

Fig. 2. Effect of emulsifier on composition of acrylonitrile vinyl acetate copolymers.

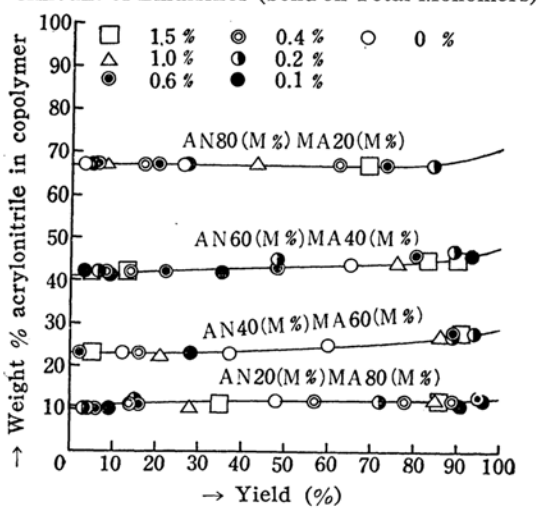

Fig. 3. Effect of emulsifier on composition of acrylonitrile methyl acrylate copolymers.

by weight of emulsifier based on total monomers were used. The compositions of copolymers thus formed in various degrees of conversion for the copolymerization of acrylonitrile and methyl methacrylate are given in Fig. 1, Fig. 2 and Fig. 3 show the corresponding results for the copolymerization of acrylonitrile and vinyl acetate and that of acrylonitrile and methyl acrylate respectively. In these copolymerizations, the compositions of copolymers are independent of the concentrations of emulsifier.

(2) Monomer-polymer Composition Curves.—The monomer-polymer composition curves obtained from the compositions of copolymers extrapolated to 0 conversion are given in Figs. 4, 5 and 6. As to the relative reactivities between acrylonitrile and the other monomers for the bulk copolymerization, the data hitherto known are cited as follows.

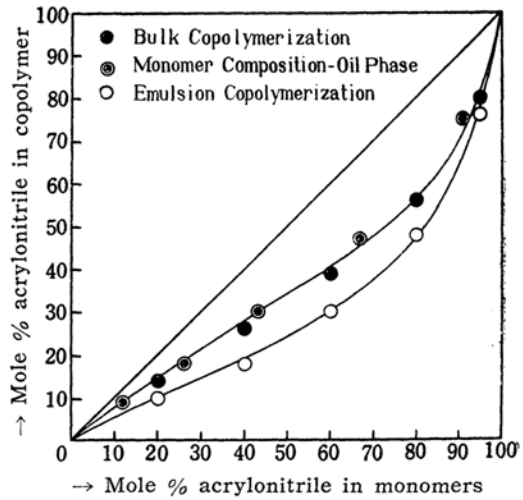

Fig. 4. Monomer-polymer composition curves for acrylonitrile methyl methacrylate copolymerization.

Monomer		Relative Reactivity	
M_1	M_2	r_1	r_2
Methyl methacrylate	Acrylonitrile	1.35±0.1	0.18 ±0.1[3]
Acrylonitrile	Vinyl acetate	4.05±0.3	0.061±0.013[4]
Acrylonitrile	Methyl acrylate	0.67±0.1	1.26 ±0.1[5]

From the monomer-polymer composition curves given in Figs. 4, 5 and 6, it will be seen that while the curve of acrylonitrile methyl methacrylate emulsion copolymerization is not superposed on that of the bulk copolymerization, those of the other copolymerizations fall on the latter. For the purpose of determining monomer oil phase compositions, the refractive indices of monomer mixture of known compositions saturated with water and monomer oil phases were measured. The results are given in Table I, II and III.

3) F. M. Lewis, F. R. Mayo, and W. F. Hulse, *J. Am Chem. Soc.*, **67**, 1701 (1945).
4) F. R. Mayo, C. Walling, F. M. Lewis and W. F. Hulse, ibid., **70**, 1523 (1948).
5) S. Okamura, "Outlook of High Polymer" Vol. 5, Association of High polymer Chemistry, Kyoto, Japan (1952), p. 42.

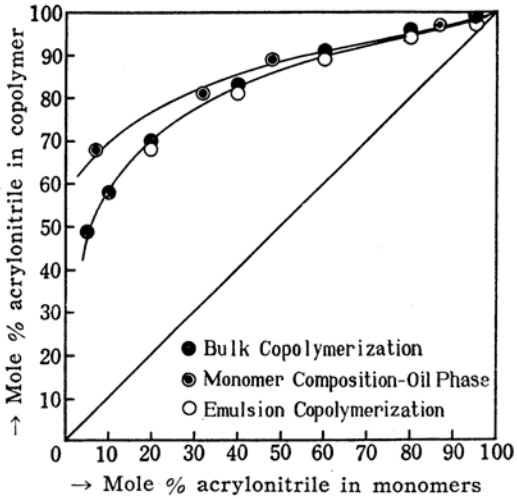

Fig. 5. Monomer-polymer composition curves for acrylonitrile vinyl acetate copolymerization.

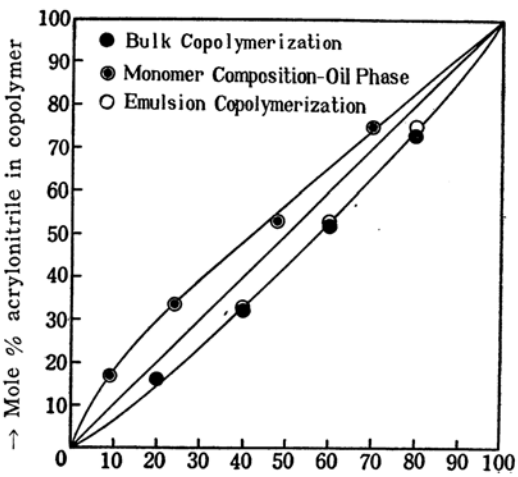

Fig. 6. Monomer-polymer composition curves for acrylonitrile methyl acrylate copolymerization.

TABLE I

REFRACTIVE INDICES OF ACRYLONITRILE-METHYL METHACRYLATE SOLUTIONS

Composition of solution		Monomer saturated with water	Oil phase
AN (M%)	MMA (M%)	n_D^{45}	n_D^{45}
95	5	1.3780	1.3795
80	20	1.3830	1.3860
60	40	1.3882	1.3919
40	60	1.3930	1.3965
20	80	1.3975	1.3991
0	100	1.4009	1.4009

TABLE II

REFRACTIVE INDICES OF ACRYLONITRILE-VINYL ACETATE SOLUTIONS

Composition of solution		Monomer saturated with water	Oil phase
AN (M%)	VAc (M%)	n_D^{45}	n_D^{45}
100	0	1.9769	—
95	5	1.3777	1.3779
80	20	1.3780	1.3787
60	40	1.3800	1.3804
40	60	1.3807	1.3808
20	80	1.3813	1.3814
0	100	1.3820	1.3820

TABLE III

REFRACTIVE INDICES OF ACRYLONITRILE-METHYL ACRYLATE SOLUTIONS

Composition of solution		Monomer saturated with water	Oil phase
AN (M%)	MA (M%)	n_D^{45}	n_D^{45}
95	5	1.3776	1.3779
80	20	1.3799	1.3816
60	40	1.3830	1.3846
40	60	1.3852	1.3867
20	80	1.3872	1.3882
0	100	1.3885	1.3885

If polymerization occurs in oil phase as Fordyce, Chapin[6] and Smith[7] asserted, the monomer-polymer composition curves will be dependent upon the composition of oil phase.

The amounts of acrylonitrile in oil phase were estimated from their refractive indices. The composition of oil phase was used in place of the monomer compositions. The monomer-polymer composition curves thus represented are shown in Figs. 4, 5 and 6.

It is seen that this correction of the compositions of emulsion oil phases makes the emulsion and bulk copolymerzation composition curves identical only in the case of acrylonitrile-methyl methacrylate copolymerization. Consequently, it seems that the water solubility of the monomer affects the compositions of copolymers formed in emulsion copolymerization. The water solubility of this monomer is as follows.

6) R. G. Fordyce and E. D. Chapin, *J. Am. Chem, Soc.*, **69**, 581 (1947).
7) W. V. Smith, ibid., **70**, 2177 (1948).

TABLE IV
WATER SOLUBILITY OF THE MONOMER

Monomer	Solubility (%)	Temperature (°C)
Styrene	0.28	25[8]
Methyl methacrylate	1.5	30[8]
Vinyl acetate	2.5	20[9]
Methyl acrylate	5.2	[9]
Acrylonitrile	7.4	25[10]

In the emulsion copolymerizations of monomers having good water solubility, the composition curves are identical with those of the bulk copolymerizations, that is to say, such emulsion copolymerizations behave just like a solution copolymerization, even if the monomer oil phase exists.

8) F. A. Bovey, I. M. Kolthoff, A. I. Medalia and E. J. Beehan, "Emulsion polymerization," (1955) p. 157.
9) E. R. Blout, W. P. Hohenstein and H. Mark, "Monomer," Inerscience Inc. New York (1949). p. 23 in chapter on "Vinyl Acetate," p. 23 in chapter on "Esters of Acrylic Acid."
10) H. S. Davis, and O. F. Wiedeman, *Ind. Eng. Chem.* **37**, 482 (1945).

Summary

The following facts are found from emulsion copolymerizations of acrylonitrile and water soluble monomers such as methyl methacrylate, vinyl acetate and methyl acrylate.

(1) The compositions of copolymer are independent of the concentration of the emulsifiers used.

(2) The monomer-polymer composition curve of emulsion copolymerization of acrylonitrile and methyl methacrylate is made consistent with that of bulk copolymerization, when the composition of emulsion oil phace is used in place of that of the monomer.

(3) The monomer-polymer composition curves of emulsion copolymerization of acrylonitrile and vinyl acetate or methyl acrylate fall on that of bulk copolymerization.

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