Action of Emulsifier upon Compositions of Emulsion Copolymers of Acrylonitrile and Water-insoluble Monomers

By Moriya UCHIDA and Hideo NAGAO

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Introduction

It has been reported by several investigators[1-5] that the composition of copolymer forming in a copolymerization depends upon the monomer composition at that instant. Moreover, Alfrey and Goldfinger[6], Mayo and Lewis[7], and Walling and Briggs[8] derived independently the general equation describing monomer-polymer composition relationship, with which the experimental data determined for bulk copolymerization showed agreement. However, the water solubility of a monomer can not be neglected in the copolymerization system, in case water is used as the medium.

Fordyce and Chapin[9] compared the composition of the copolymer of styrene and acrylonitrile obtained in emulsion polymerization with that of the copolymer obtained in bulk polymerization, and found that the emulsion copolymer is consistently richer in styrene, though by a small amount, than the bulk copolymer produced from the same initial monomer composition.

They have suggested that this difference may be due solely to the decrease in the content of acrylonitrile of the oil phase, which resulted from the water solubility of acrylonitrile. Smith[10] determined the

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[1] F. T. Wall, *J. Am. Chem. Soc.*, **66**, 2050 (1944).

[2] F. M. Lewis, F. R. Mayo and W. F. Hulse, ibid. **67**, 1701 (1945).

[3] T. Alfrey, Jr., and E. Lavin., ibid., **67**, 2044 (1945).

[4] T. Alfrey, Jr., E. Merz and H. Mark, *J. Polymer. Sci.*, **1**, 37 (1946).

[5] T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **14**, 115 (1946).

[6] T. Alfrey, Jr., and G. Goldfinger, ibid., **12**, 202, 322 (1944).

[7] F. R. May and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

[8] C. Walling and E. R. Briggs, ibid., **67**, 1774 (1945).

[9] R. G. Fordyce and E. C. Chapin, ibid., **69**, 581 (1947).

[10] W. V. Smith, ibid., **70**, 2177 (1948).

compositions of styrene-acrylonitrile solutions in equilibrium with water-acrylonitrile solutions and showed that Fordyce and Chapins' emulsion polymerization data were indentical with their bulk polymerization data in regard to composition of copolymer produced from a given oil phase, when the equilibrium composition was used to calculate the acrylonitrile contents of the oil phases presented in their emulsion copolymerization experiments.

However, in the system of copolymerization of water soluble monomer as acrylonitrile and water-insoluble monomer such as styrene, the copolymer compositions are not always dependent upon the monomer composition in oil phase as shown by Fordyce and Smith.

As we reported, in the copolymerization of acrylonitrile-vinylidene chloride[11] and acrylonitrile-styrene[12], the compositions of emulsion copolymers depend upon the amount of emulsifier used. This paper deals with the variation of the monomer-polymer composition curve arising from the variation of the amount of emulsifier used.

Experimental

The emulsion polymerization procedure was the same as that of previous reports[2,3]. The emulsifier is Sodium Dodecyl Sulfate.

In the case of benzoyl peroxide as a catalyst, the amount of benzoyl peroxide used was 1 weight % against total monomers and the copolymerizations were done at the temperature of 75°C. The polymerizations were allowed to proceed to low conversions (mostly <5%) and the initial polymer was isolated and purified. The amount of combined acrylonitrile in the initial copolymer was determined by the Kjeldahl analysis.

The acrylonitrile-vinylidene chloride solutions were thoroughly shaken with the given amounts of water, in a water bath maintained at 25°C and thus the solutions were separated into two phases. Then the concentrations of acrylonitrile in the partition phases were determined by the following methods.

A. Method by Acrylonitrile Analysis.—The acrylonitrile in a sample with-drawn from oil phase was analysed by n-dodecyl-mercaptan method[14] and the amount of acrylonitrile in oil phase was determined. In this case, vinylidene chloride did not injure the acrylonitrile analysis as shown in Fig. 1.

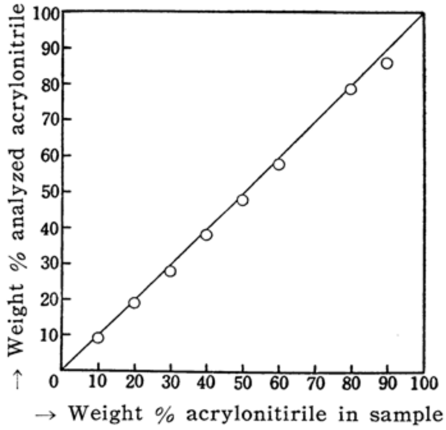

Fig. 1. Analyses of acrylonitrile in vinylidene chloride.

Then the amount of acrylonitrile in water phase was determined by the procedure.

B. Method by Specific Gravity Measurement.—The relationship between specific gravity and composition was established by preparing acrylonitrile-vinylidene chloride solutions of known compositions and measuring the specific gravity with pycnometer.

The results used to establish the relationship are given in Table I. All compositions were determined by linear interpolation of the data in Table I.

TABLE I

SPECIFIC GRAVITIES AND REFRACTIVE INDICES OF ACRYLONITRILE VINYLIDENE CHLORIDE SOLUTIONS

Composition of solution		Specific gravity	Refractive index
Acrylonitrile (weight %)	Vinylidene chloride (weight %)	25°C	n_D^{25}
100.00	0.00	0.8002	1.3888
90.00	10.00	0.8264	1.3908
80.00	20.00	0.8554	1.3918
70.00	30.00	0.8855	1.3945
60.00	40.00	0.9199	1.3976
50.00	50.00	0.9542	1.3999
40.00	60.00	0·9905	1.4018
30.00	70.00	1.0410	1.4077
20.00	80.00	1.0879	1.4113
10.00	90.00	1.1438	1.4163
0.00	100.00	1.2074	1.4215

The relationship between specific gravity and acrylo-nitrile concentration in its aqueous solution was established by the same procedure as above. The results thereof are given in Table II.

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[11] H. Nagao, M. Uchida and T. Yamaguchi, *J. Chem. Soc. Japan*, in press "Emulsion Copolymerization of Acrylonitrile and Vinylidene chloride."

[12] H. Nagao, M. Uchida and T. Yamaguchi, ibid., in press "Heat Stability of Emulsion Copolymer of Acrylonitrile and Vinylidene chloride."

[13] M. Uchida and H. Nagao, This Bulletin, **29**, 928 (1956).

[14] D. W. Beesing, W. P. Tyler, D. M. Kurtz and S. A. Harrison, *Anal. Chem.*, **21**, 1073 (1949).

TABLE II
SPECIFIC GRAVITIES AND REFRACTIVE INDICES OF ACRYLONITRILE AQUEOUS SOLUTION

Composition of solution		Specific gravity	Refractive index
H_2O (weight %)	Acrylonitrile (weight %)	25°C	n_D^{25}
100.00	0.00	0.9971	1.3325
99.00	1.00	0.9965	1.3329
98.00	2.00	0.9950	1.3337
97.00	3.00	0.9941	1.3341
96.00	4.00	0.9931	1.3348
95.00	5.00	0.9915	1.3363
94.00	6.00	0.9911	1.3375
93.00	7.00	0.9898	1.3376

Then the compositions of partition phases were determined by measuring their specific gravities, respectively.

C. Method by Refractive Index Measurement.—The relationship between refractive index and composition was established by preparing monomer solution and acrylonitrile aqueous solutions of known compositions and measuring the refractive index with Pulfrich refractometer. The results are given in Table I, II and III.

TABLE III
REFRACTIVE INDICES OF ACRYLONITRILE-STYRENE SOLUTIONS

Composition of solution		Refractive index	Refractive index of solution saturated with water
Acrylonitrile (mol. %)	Styrene (mol. %)	n_D^{25}	n_D^{25}
100.00	0.00	1.3888	1.3881
95.00	5.00	1.4027	1.3996
80.00	20.00	1.4385	1.4356
60.00	40.00	1.4750	1.4726
40.00	60.00	1.5019	1.5028
20.00	80.00	1.5276	1.5252
0.00	100.00	1.5464	1.5460

Then the compositions of oil and water phases were determined by measuring their refractive indices.

The composition of Acrylonitrile in styrene phase was determined by refractive index measurement and by calculating from analytical value of acrylonitrile in water phase.

Results and Discussion

(1) Acrylonitrile-Vinylidene chloride Copolymerization.—The various equilibrium compositions of oil and water phases were measured. The results are given in Figs. 2 and 3.

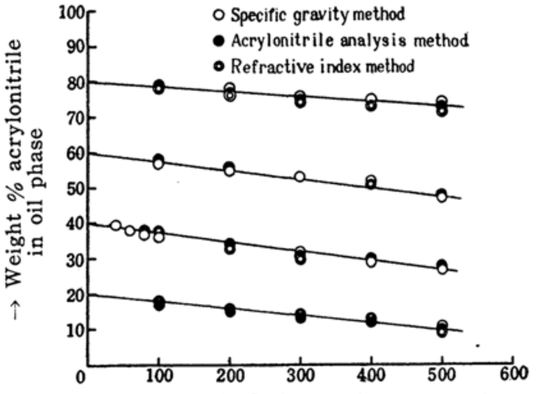

Fig. 2. Partition of acryronitrile in vinylidene chloride.

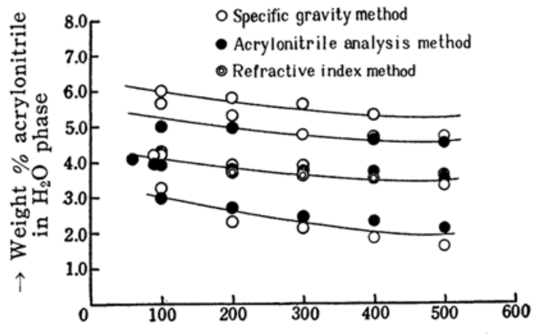

Fig. 3. Partition of acrylonitrile in water.

In the emulsion copolymerization of acrylonitrile-vinylidene chloride, the composition of copolymer was dependent upon the amount of emulsifier used; the composition of the compolymer forming either no emulsifier or very dilute emulsifier solutions, containing much acrylonitrile. The monomer-polymer composition curves are shown in Fig. 4.

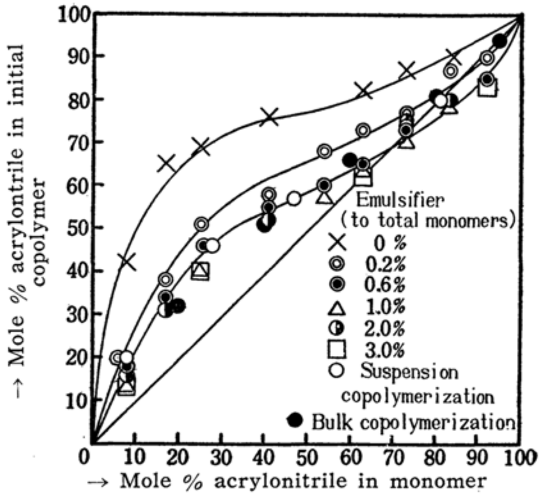

Fig. 4. Monomer-polymer composition curves for acrylonitrile-vinylidene chloride (I).

The compositions of copolymers became richer in styrene along with the increase in the amount of emulsifier used.

The relative reactivity between acrylonitrile and vinylidene chloride has been found in bulk polymerization²⁾.

r_1 (Acrylonitrile)	r_2 (Vinylidene chloride)	Temperature.
0.91±0.10	0.37±0.10	60°C

When the monomer-polymer composition curve is drawn in Fig. 4 from above r_1, r_2 values, it will be seen that this curve comes between that of emulsifier-free copolymerization and that of emulsion copolymerizations. If polymerization occurs in oil phase as was asserted by Fordyce, Chapin⁹⁾ and Smith¹⁰⁾, the monomer-polymer composition curves will be dependent upon the composition of oil phase. The amounts of acrylonitrile in oil phase are shown in Fig. 5. As we substituted the compositions of oil phase in aqueous polymerization instead of the charged compositions, the monomer-polymer composition curves thereof are shown in Fig. 6.

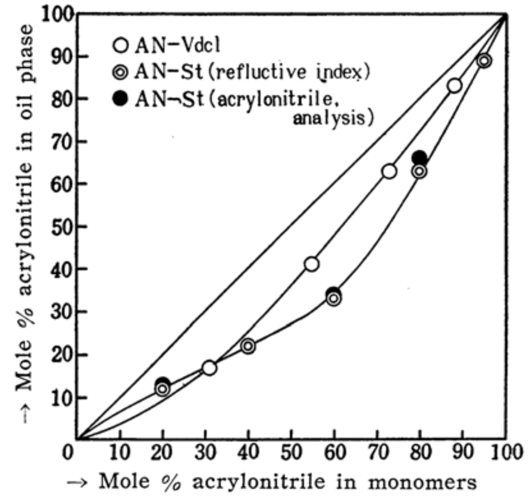

Fig. 5. Relation between composition of monomer and that of oil phase.

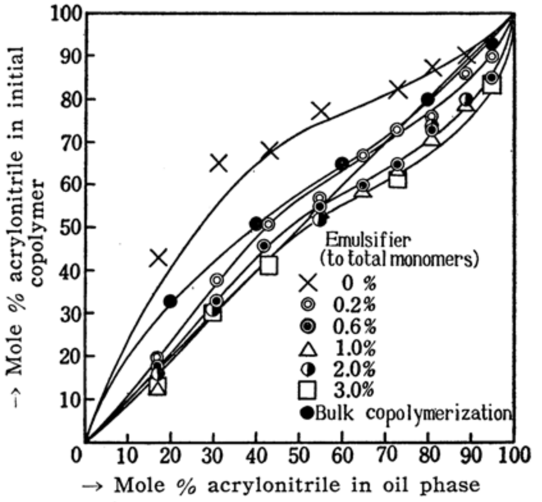

Fig. 6. Monomer-polymer composition curves for acrylonitrile vinylidene chloride (2).

It is seen that these corrections of the compositions of the emulsion oil phases make the emulsion and bulk copolymerization composition curves identical only in case of the emulsion polymerization using the emulsifier of the critical micell concentration¹¹⁾. Moreover, the monomer-polymer composition curve in aqueous suspension copolymerization using benzoyl peroxide as an oil soluble catalyst is shown in Fig. 7.

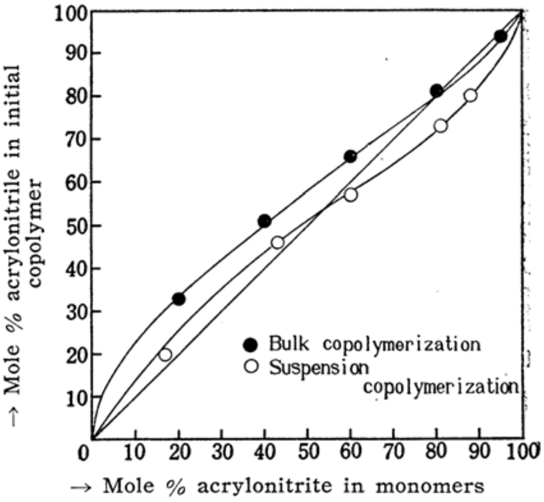

Fig. 7. Monomer-polymer composition curves for acrylonitrile-styrene (1).

It will be observed that the aqueous suspension copolymers consistently contain less combined acrylonitrile than the corresponding bulk copolymers. The copolymer composition values for suspension copolymerization were plotted on the basis of monomer concentrations charged to the reaction system, the most of the reacted monomers exist in the oil droplets of the dispersed phase.

With the oil phase compositions, the composition curve of the aqueous suspension copolymerization is identical with that of the bulk copolymerization and also with that of emulsion copolymerization using thicker emulsifier solution. Although these identities coinside with Smith's theory of oil phase mechanism of emulsion polymerization as Fordyce and Chapin[9] reported about acrylonitrile-styrene emulsion copolymerization, it does not seem to be reasonable that the composition of emulsion copolymers is dependent only upon the oil phase composition, for the copolymer composition varies by emulsifier concentrations as showed in Fig. 6.

(2) Acrylonitrile -Styrene Copolymerization.—As in the case of acrylonitrile-vinylidene chloride emulsion copolymerization, the monomer-polymer composition curve in acrylonitrile-styrene emulsion copolymerization depended upon the amount of the used emulsifier. The results are shown in Fig. 8.

The relative reactivity in bulk copolymerization is shown as follows.

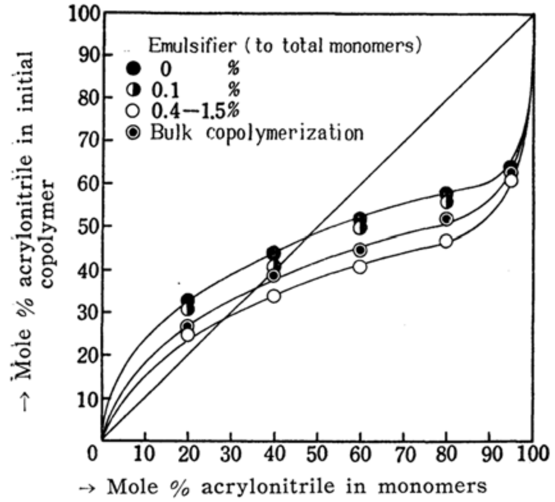

Fig. 8. Monomer-polymer composition curves for acrylonitrile-styrene. (2).

author	r_1 (styrene)	r_2 (acrylo-nitrile)	Temperature °C
Lewis, Mayo and Hulse[4]	0.41±0.08	0.04±0.04	60
Fordyce and Chapin[9]	0.41±0.08	0.03±0.03	75
Simha and Wall[15]	0.37±0.02	0.05±0.02	50
Fordyce[16]	0.52±0.04	0.03±0.03	67–80
Goldfinger and Steidlitz[17]	0.38±0.03	0.05±0.02	41.5
〃	0.45±0.03	0.02±0.02	65
〃	0.47±0.03	0.02±0.02	86.5

The values of r_1 and r_2 are mostly independent of the temperature of polymerization with the inrange of 40–80°C. Although our copolymerization temperature was 45°C, the monomer-polymer composition curve in bulk copolymerization was drawn from the data of Lewis, Mayo and Hulse in Fig. 8. This curve comes between the curve of emulsifier-free copolymerization and that of emulsion copolymerization. In this case, the above described emulsion oil phases make the composition curves of emulsion copolymerization using thick concentrations of emulsifier and that of bulk copolymerization identical, but emulsifier-free copolymers contain less combined styrene than the corresponding bulk copolymer.

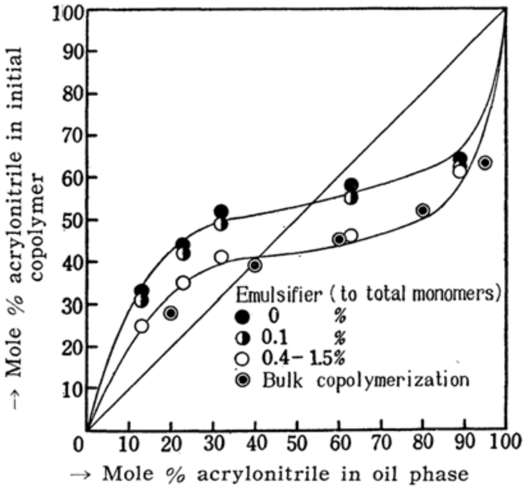

Fig. 9. Monomer-Polymer composition curves for acrylonitrile-styrene (3).

It seems that the water solubility of monomer affects the compositions of forming copolymers in aqueous copolymerizations of water soluble monomer as acrylonitrile and water insoluble monomer as styrene and vinylidene chloride using water soluble catalyst. The initiation of polymerization occurs by reaction between catalyst and monomer in water phase, since in the case of emulsifier-free copolymerization the water phase contains acrylonitrile, so the initial copolymer seems to contain much acrylonitrile. The water phase will contain more water insoluble monomer solubilized in micell, and the initial copolymer seems to contain less acrylonitrile, as the amount of emulsifier.

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[15] R. Simha and L. A. Wall., *J. Research Natl. Bur. Standards*, **41**, 521 (1948).

[16] R. G. Fordyce, *J. Am. Chem. Soc.*, **69**, 1903 (1947).

[17] G. Goldfinger and G. I. Carothers, *J. Polymer Sci.*, **4**, 97, (1949).

Summary

The following are the facts found from the monomer-polymer composition curves of aqueous copolymerization of the water soluble monomer as acrylonitrile and the water insoluble monomers as vinylidene chloride and styrene using the water soluble catalyst.

(1) The emulsifier-free aqueous copolymers contained consistently much more combined acrylonitrile than the corresponding bulk and emulsion copolymer.

(2) The emulsion copolymer contained less acrylonitrile as the amount of used emulsifier increased.

(3) The monomer-polymer composition curves of emulsion copolymerizations were identical with that of bulk copolymerization, only when critical micell concentration of emulsifier was in use.

Research Institute of Teikoku
Rayon Co, Ltd., Iwakuni