

Action of Emulsifier upon the Copolymerization of Acrylonitrile and Styrene

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Introduction

The mechanism of emulsion polymerizations of water-insoluble monomers as styrene and isoprene has been shown by Harkins¹⁾ and Smith²⁾. However, the mechanism of emulsion polymerizations of water-soluble monomers as acrylonitrile seems to be different from that of styrene and isoprene. It has been known that the polymerization rate of acrylonitrile in water increases as the polymer forms³⁾. It appears to be due to diffusion and adsorption of monomer to polymer precipitated in water⁴⁾. It has been known that in heterogeneous polymerization the loci of polymer propagation reaction are the polymers adsorbed with monomers and the appearance of this polymerization looks like that

of emulsion polymerization. It was already reported that the compositions of emulsion copolymers of water-soluble monomer as acrylonitrile and water-insoluble monomer as vinylidenechloride depended on the concentrations of emulsifier used in copolymerization⁵⁾. The reactivity of acrylonitrile and styrene in emulsion copolymerization was studied by Fordyce and Chapin⁶⁾ and Smith⁷⁾. Although they proved that the composition of formed copolymer depended on the composition of oil phase, the action of emulsifier has not been cleared up yet. In the present paper, in the first place, some observations in emulsifier-free copolymerization, and then the action of anionic emulsifier upon the rate of polymerization, the degree of polymerization and the composition of formed copolymer are given.

1) W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).

2) W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

3) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press (1953), p. 208.

4) H. Nagao, M. Uchida and T. Yamaguchi, *J. Chem. Soc. Japan* (in Japanese) **59**, 695 (1956).

5) H. Nagao, M. Uchida and T. Yamaguchi, *J. Chem. Soc. Japan*, in press.

6) R. G. Fordyce and E. C. Chapin, *J. Am. Chem. Soc.*, **69**, 581 (1947).

7) W. V. Smith, *J. Am. Chem. Soc.*, **70**, 2177 (1948).

Experimental

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

Styrene Monomer (St).—Redistilled commercial material was employed.

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

Polymerization Procedure.—A stirred 1-liter, four-necked-flask placed in a water bath maintained at $45 \pm 0.1^\circ\text{C}$ was charged by the additions of the required emulsifier aqueous solution and monomers. The air in the flask was purged by the introduction of nitrogen. Then the catalyst (potassium persulfate) 0.8 weight % and the reductant (sodium bisulfite) 0.8 weight % were added after the flask had attained thermal equilibrium. These weight % concentrations were based on total monomers. The mixer of the flask was rotated at 300 revolution per minute. The latex was coagulated in water or in a calcium chloride solution which contained hydroquinone as an inhibitor. Conversion data were based on total solid determinations. η_{sp}/c was measured in 2 g./l. dimethylformamide solution at 25°C . The combined acrylonitrile in copolymer was determined by Kjeldahl analysis.

Results and Discussion

(1) Rate of Polymerization in Emulsifier-free Copolymerization

The mixture of water-soluble monomer as acrylonitrile and water-insoluble monomer as styrene in the presence of suitable water-soluble redox initiating reagents is capable of undergoing copolymerization in water without the assistance of emulsifying agents. The relation between conversion and polymerization times is shown in Fig. 1.

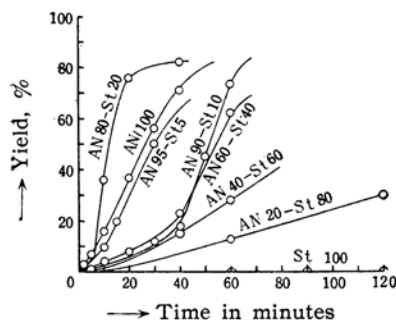


Fig. 1. Rate of polymerization of acrylonitrile and styrene in aqueous solution.

The rate of polymerization was very slow in only styrene and became faster as the mixture of monomer contained much acrylonitrile. The polymerization of water-insoluble monomer as styrene without soap or with a very small amount of soap was very slow, and the degree of polymerization of the

formed polymer was low⁸⁾. The water-soluble monomer as acrylonitrile was absorbed remarkably in the initial polymer in water⁹⁾, so that the rate of polymerization would be fast and the degree of polymerization of the formed polymer would be high even if the emulsifier was not used. The difference of the property as above existed between the two monomers used. The copolymerization rate of these monomers was dependent upon the average water-solubility of their mixture. It has been known that the rate of polymerization is roughly proportional to the solubility of the monomer in water in case of polymerization of water-soluble monomer such as methyl-methacrylate, vinylacetate or acrylonitrile⁸⁾. Consequently, the solubilized amount of monomer in water must depend on the rate of polymerization. Whitby, Gross, Miller and Costanza⁹⁾ found that the addition of a small amount of acrylonitrile in copolymerization of styrene and butadiene accelerated the rate of reaction and the polymerization rate of styrene containing 5–10% methacrylonitrile was faster than that of only styrene.

It has been known that the initiation of polymerization occurs in water phase in these polymerization systems. When a layer of styrene is placed on a column of a dilute potassium persulfate solution in water and the system is allowed to stand for several days, the aqueous phase slowly becomes cloudy. If substances with greater solubility in water, e.g., methacrylic ester, vinyl acetate or acrylonitrile, are used, the cloudiness appears much more rapidly although the area of the interface is the same as before. Moreover, if a small amount of an inhibitor is added to monomer phase, the course of the polymerization in the aqueous phase is not noticeably affected; if, however, the same amount is added to the aqueous phase, the appearance of the cloudiness is considerably delayed.

This is an indication that at least the formation of active nuclei takes place in the aqueous phase.

Fryling and Harrington¹⁰⁾ observed that, in the case of the layer polymerization of acrylonitrile on top of an aqueous potassium persulfate solution, the aqueous phase remains clear and transparent for a distance of about five millimeters below the interface, indicating that no polymer is actually being formed at

8) W. P. Hohenstein and H. Mark, *J. Polymer Sci.*, **1**, 549 (1946).

9) G. S. Whitby, M. D. Gross, J. R. Miller and A. J. Costanza, *J. Polymer Sci.*, **16**, 549 (1955).

10) C. F. Fryling and E. W. Harrington, *Ind. Eng. Chem.*, **36**, 114 (1944).

the interface itself but that the dissolved monomer is the principal center for the formation of polymer. Moreover, the active center produced by interaction of monomer and potassium persulfate in water, can grow in the aqueous phase without being in any direct contact with liquid monomer and the adsorption rate of monomer to active center is greater than the consumption rate of monomer as we reported⁴⁾, so the propagation reaction seems to occur in the polymer adsorpted monomer.

It has been found that the polymer of water-insoluble monomer as styrene was slowly formed in the aqueous phase outside of the droplet by the observation of the behavior of small droplets of styrene in aqueous solutions of peroxides under the microscope³⁾. The interface between monomer and aqueous solution of catalyst seems not to be appropriate locus for the initiation and propagation of polymer. Consequently, it is thought that the initiation of polymer occurs also in aqueous phase in copolymerization of acrylonitrile and styrene, and is remarkable because of the increase of active centers in water as the amount of acrylonitrile is great in the mixture of monomer so that the rate of polymerization increases.

At the same time the reactivity of monomers must also be taken into account. The monomer reactivity ratios in the copolymerization of acrylonitrile and styrene were the following¹¹⁾.

r_1	r_2
(Styrene)	(Acrylonitrile)
0.41 ± 0.08	0.04 ± 0.04 60°C

Consequently, the rate of addition of acrylonitrile to styrene radical is faster than that to acrylonitrile radical, and the rate of addition of styrene to acrylonitrile radical is faster than that to styrene radical. The rate of propagation reaction must be maximum in the mixture of equal molecules of monomers according to the above-mentioned concept.

This concept will be applied to the copolymerization of acrylonitrile (r_1 , 0.91 ± 0.10) and vinylidenechloride (r_2 , 0.34 ± 0.10). It has been reported that the maximum rate of polymerization related to the compositions of monomer mixtures appears in the mixture of almost equal molecules of acrylonitrile and vinylidenechloride⁵⁾. Accordingly the maximum of the rate in the emulsifier-free copolymerization of acrylonitrile and styrene seems to be due to the effect of monomer reactivity which

overlapped the effect of average water-solubility of the mixture of monomer and appears in the acrylonitrile richer composition.

(2) Rate of Polymerization in Emulsion Copolymerization

The results of emulsion copolymerization rate which used emulsifier 0, 0.1, 0.2, 0.4, 0.6, 1.0, 1.5 weight % to total monomer are given in Figs. 2, 3, 4, 5, 6, 7, 8 and 9.

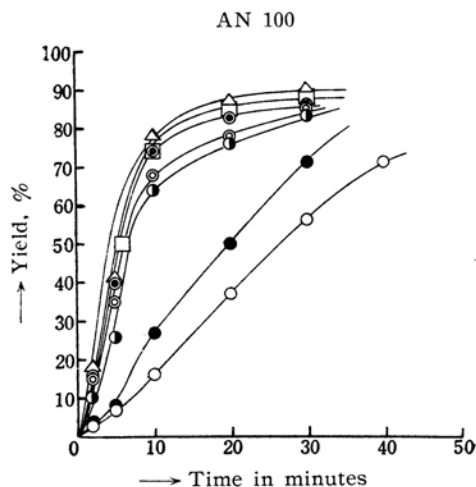


Fig. 2. Rate of emulsion polymerization, No. 1.

Emulsifier (to Total Monomers)		
□ 1.5%	△ 1.0%	⊙ 0.6%
⊗ 0.4%	⊖ 0.2%	● 0.1%
○ 0%		

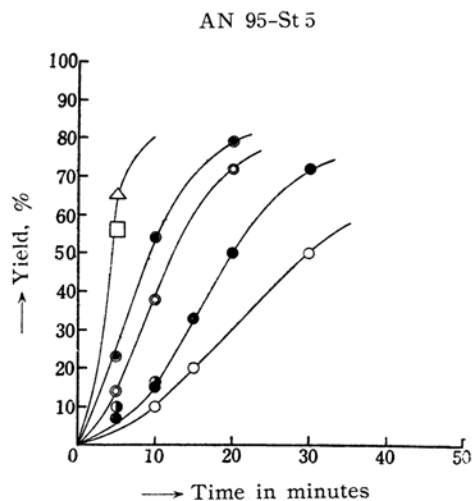


Fig. 3. Rate of emulsion polymerization, No. 2.

Emulsifier (to Total Monomers)		
□ 1.5%	△ 1.0%	⊙ 0.6%
⊗ 0.4%	⊖ 0.2%	● 0.1%
○ 0%		

11) F. M. Lewis, F. R. Mayo and W. F. Hulse, *J. Am. Chem. Soc.*, **67**, 1701 (1945).

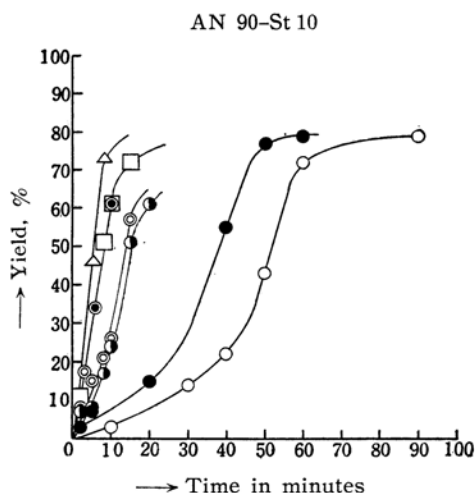


Fig. 4. Rate of emulsion polymerization, No. 3.

Emulsifier (to Total Monomers)

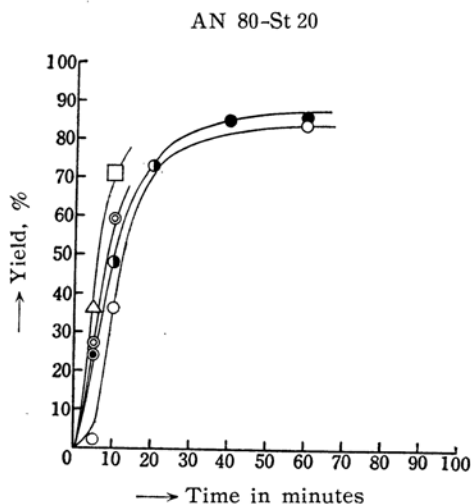
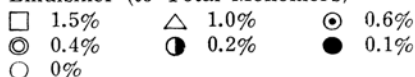
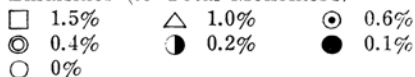


Fig. 5. Rate of emulsion polymerization, No. 4.

Emulsifier (to Total Monomers)



The situation changes significantly if soap solutions are used instead of pure water. Hess and his co-workers^{12,13,14} found the presence of lamellar soap micelles from the observation of the diffraction of X rays by soap solutions. The increase of average distance of adjacent lamellae due to solubilization of hydrocarbon was observed by McBain and

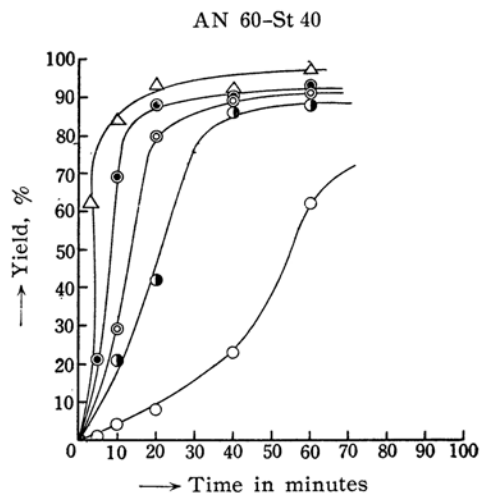
12) K. Hess and J. Gundermenn, *Ber.*, 70, 1800 (1937).13) K. Hess and W. Philippoff, *Ber.*, 70, 1808 (1937).14) K. Hess, W. Philippoff and H. Kiessig, *Naturwissenschaften*, 26, 184 (1938).

Fig. 6. Rate of emulsion polymerization, No. 5.

Emulsifier (to Total Monomers)

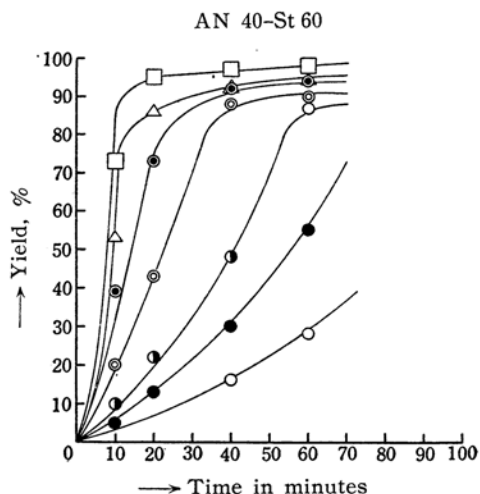
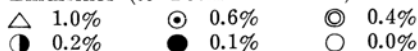
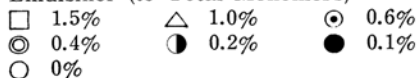


Fig. 7. Rate of emulsion polymerization, No. 6.

Emulsifier (to Total Monomers)



Harkins¹⁵⁻²⁰). The water-soluble initiator is allowed free-diffusion and the formation of active center seems to occur mainly in micelles for these micelles contained monomer

15) J. W. McBain, *Trans. Faraday Soc.*, 9, 99 (1913).16) W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Am. Chem. Soc.*, 68, 220 (1946); *J. Colloid Sci.*, 1, 105 (1946).

17) J. W. McBain, "Advance in Colloid Science" Interscience Publishers, Inc., New York, N. Y. (1942), Vol. 1, p. 124.

18) W. D. Harkins, *J. Chem. Phys.*, 13, 381 (1945).19) W. D. Harkins, *J. Chem. Phys.*, 14, 47 (1946).20) W. D. Harkins and R. S. Stearns, *J. Chem. Phys.*, 14, 215 (1946).

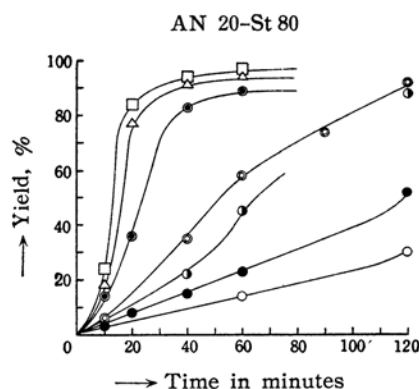


Fig. 8. Rate of emulsion polymerization, No. 7.
Emulsifier (to Total Monomers)
□ 1.5% △ 1.0% ⊙ 0.6%
⊗ 0.4% ◐ 0.2% ○ 0%

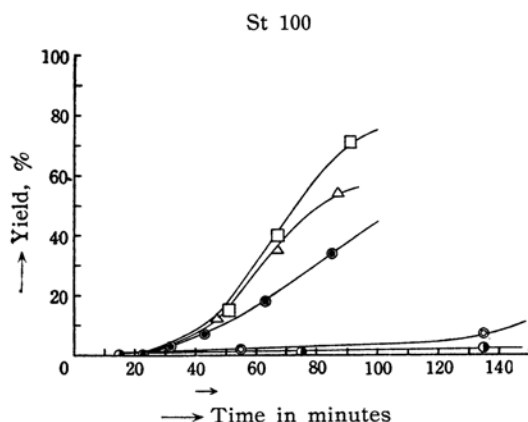


Fig. 9. Rate of emulsion polymerization, No. 8.
Emulsifier (to Total Monomers)
□ 1.5% △ 1.0% ⊙ 0.6%
⊗ 0.4% ◐ 0.2%

and swelled by water in the soap concentrations of our polymerization systems as Fikentscher²¹⁾ and Hohenstein²²⁾ have shown. The rate of polymerization increased as the emulsifier was used much, for the formation of an active center in a micelle increased as above mentioned. Moreover, it seemed to depend upon the average water-solubility of mixture of monomers, for it increased as the mixture contained much acrylonitrile. If the initiation occurs by the interaction between the radical of catalyst and monomers solubilized in micelles, according to Harkins' theory, the reaction rate will vigorously increase in the critical micelle concentration of emulsifier. The critical micelle concentration of Sodium Dodecyl Sulfate used as emulsifier has been

known to be 0.05–0.2% aqueous solution^{23,24)}. It has been known that the critical micelle concentration becomes low by the addition of polar organic materials²⁵⁾, so that 0.1–1.0 weight % (to total monomer) solution of emulsifier corresponds to about 0.01–0.15 weight % aqueous solution, that is to say, critical micelle concentration. In fact, the increase of reaction rate was found in this concentration range. The rate of polymerization seems also to depend upon the average water-solubility of monomer mixture, for it depends upon the solubilized volume of monomer in emulsion polymerization. Accordingly, it increases as the mixture of monomers contains much acrylonitrile having good ability of solubilization²⁶⁾.

The rates of polymerization shown in about 40% conversion in various system are given in Table I.

TABLE I
RATE OF POLYMERIZATION (%/min.)

Amount of Emulsifier % to Total Monomer	Acrylonitrile mol. % in Monomer Mixture							
	100	95	90	80	60	40	20	0
1.5	16	16	9.0	7.1	—	7.0	5.0	1.7
1.0	19	16	9.0	7.1	9.0	5.0	4.2	1.2
0.6	14	6.0	7.0	—	8.1	3.5	3.2	0.7
0.4	12	4.8	6.0	6.8	4.8	2.2	1.1	0.3
0.2	8.6	—	5.0	6.6	2.9	1.4	0.6	0.02
0.1	2.4	3.5	3.0	6.1	—	1.2	0.4	0.01
0	2.0	2.1	2.8	6.1	2.0	0.7	0.3	0.0

Its maximum appeared in the composition of acrylonitrile 80 mol. % and styrene 20 mol. %. This seems to depend upon the effect of the monomer reactivity which overlapped that of the average water-solubility of monomer mixture as above described. The rate of acrylonitrile rich polymerization shows maximum in the concentration nearly 1% (to total monomer) of emulsifier. The emulsifier acts less upon the polymerization of water-soluble monomer than that of water-insoluble monomer, for the initiation of water-soluble monomer is easy even in emulsifier-free polymerization. It appears to be the cause of rate maximum related to emulsifier aqueous concentration that the monomer solubilized in water makes critical micelle concentration lower and in more high concentration of emulsifier the radical diffusion into micelle

23) R. Goto, "Outlook of High Polymer", Association of High Polymer Chemistry, Kyoto, Japan (1951), Vol. 5, p. 47.

24) K. A. Wright, A. D. Abbott, V. Sivertz and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 549 (1939).

25) K. Schinoda, *J. Phys. Chem.*, **58**, 1136 (1954).

21) H. Fikentscher, *Angew. Chem.*, **51**, 433 (1934).
22) W. Hohenstein, S. Siggia and H. Mark, *India Rubber World*, **111**, 173 (1944).

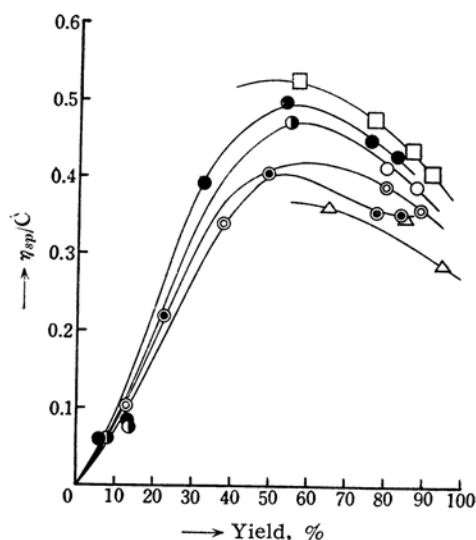
26) S. Okamura and T. Motoyama, *J. Chem. Soc. Japan*, **57**, 930 (1954).

becomes difficult due to the fact that the wall of micelle is thick or the solubilized amount of monomers decrease because of the excess of emulsifier²⁷⁾. Consequently, the maximum will easily appear in the polymerization of acrylonitrile rich monomer mixtures.

(3) Degree of Polymerization

The relations between η_{sp}/c and conversion are given in Figs. 10, 11, 12, 13 and 14.

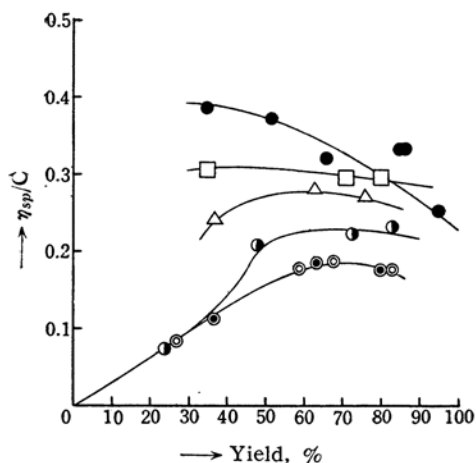
AN 95-St 5

Fig. 10. η_{sp}/C vs. yield of copolymer, No. 1.

Emulsifier (to Total Monomers)

□ 1.5% △ 1.0% ⊙ 0.6%
 ⊙ 0.4% ● 0.2% ● 0.1%

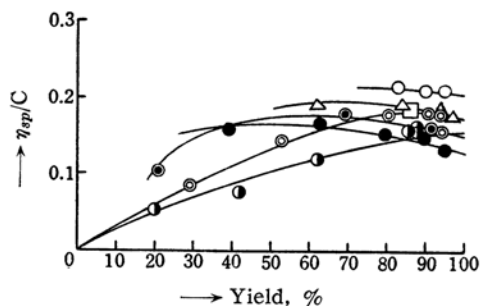
AN 80-St 20

Fig. 11. η_{sp}/C vs. yield of copolymer, No. 2.

Emulsifier (to Total Monomers)

□ 1.5% △ 1.0% ⊙ 0.6%
 ⊙ 0.4% ● 0.2% ● 0.1%

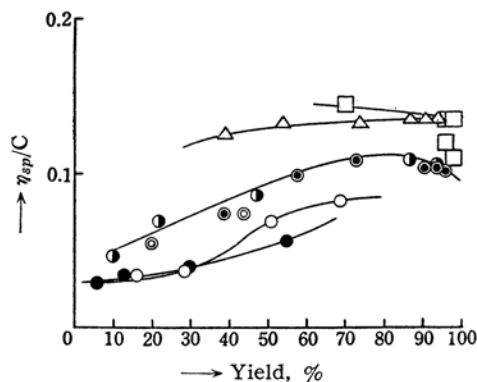
AN 60-St 40

Fig. 12. η_{sp}/C vs. yield of copolymer, No. 3.

Emulsifier (to Total Monomers)

□ 1.5% △ 1.0% ⊙ 0.6% ⊙ 0.4%
 ● 0.2% ● 0.1% ○ 0%

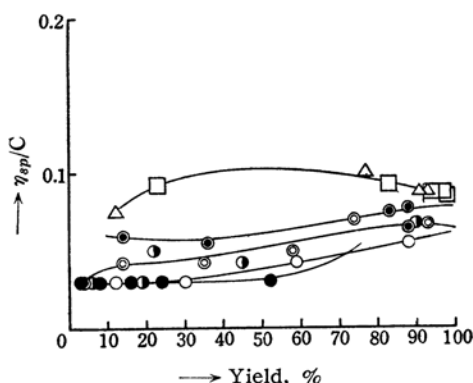
AN 40-St 60

Fig. 13. η_{sp}/C vs. yield of copolymer, No. 4.

Emulsifier (to Total Monomers)

□ 1.5% △ 1.0% ⊙ 0.6% ⊙ 0.4%
 ● 0.2% ● 0.1% ○ 0%

AN 20-St 80

Fig. 14. η_{sp}/C vs. yield of copolymer, No. 5.

Emulsifier (to Total Monomers)

□ 1.5% △ 1.0% ⊙ 0.6% ⊙ 0.4%
 ● 0.2% ● 0.1% ○ 0%

In the polymerization of styrene rich monomer η_{sp}/c increases with much using of

27) K. Kanamaru et al., *J. Chem. Soc. Japan*, 58, 221 (1955).

emulsifier and is proportional to the tendency of polymerization rate and it seems that the increase of the active center also brings the increase of the degree of polymerization according to its rate. However, η_{sp}/c in the polymerization of the monomer containing acrylonitrile decreases, shows the minimum and increases as the concentration of emulsifier becomes thick. The used amounts of emulsifier when η_{sp}/c becomes minimum are given in the following Table.

TABLE II

The Composition of Monomer Mixture		The Amount of Emulsifier Minimized η_{sp}/c
Acrylonitrile (mol. %)	Styrene (mol. %)	(weight %)
0	100	0
20	80	0.1
40	60	0.1
60	40	0.2
80	20	0.4-0.6
95	5	1.0
100	0	1.0

It has been known that the initiation of styrene occurs in micelle, so the increase of emulsifier brings the increase of polymerization rate due to the increase of active center and the increase of the degree of polymerization due to the decrease of termination. But the diffusion of water-soluble monomer as acrylonitrile in water is very faster than that of styrene, so that the degree of polymerization of monomers containing acrylonitrile becomes high even in emulsifier-free polymerization. The second radical can be more easy to diffuse into polymer swelled by water and to combines with polymer radical as the concentration of emulsifier becomes thick, so that the polymerization degree of formed polymer becomes low. In thicker concentration, the diffusion of the second radical may be hindered by the thick wall of emulsifier, so that the degree of polymerization seems to be large. In any case, the degree of polymerization of formed polymer depends upon the state of water in micelles and the affinity between monomer, polymer, emulsifier and radical due to the water-solubility of monomer. η_{sp}/c decreased as the monomer mixture contained much acrylonitrile. It has been known that the relation between η_{sp}/c and the degree of polymerization varies with the composition of the copolymer, but η_{sp}/c of copolymer becomes great even in the same molecular weight as the used solvent becomes poor solvent to copolymer as Maeda, Kawai and Yamaguchi⁽²⁸⁾

mentioned in regard to the copolymer of vinylchloride and vinylacetate. Dimethylformamide which is used for the measurement of η_{sp}/c in this paper is a good solvent for the copolymers containing much acrylonitrile unit in their structure. Consequently, the degree of polymerization becomes greater because of the increase of the solubilized amount of monomer due to its containing richer acrylonitrile.

(4) Composition of Copolymer on the Process of Polymerization

The compositions of copolymers formed in various conversions are given in Figs. 15, 16 and 17.

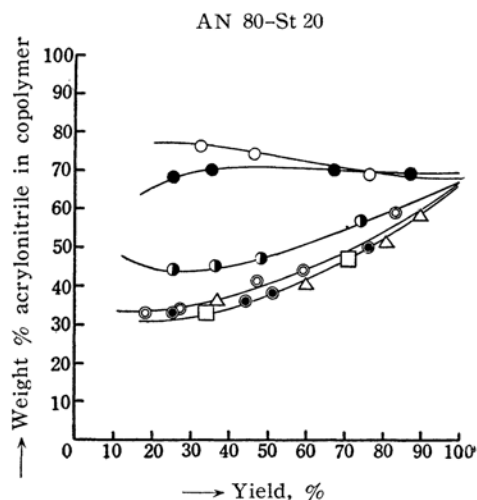


Fig. 15. Variation of copolymer composition with yield, No. 1.

Emulsifier (to Total Monomers)
 □ 1.5% △ 1.0% ● 0.6% ⊙ 0.4%
 ◐ 0.2% ● 0.1% ○ 0%

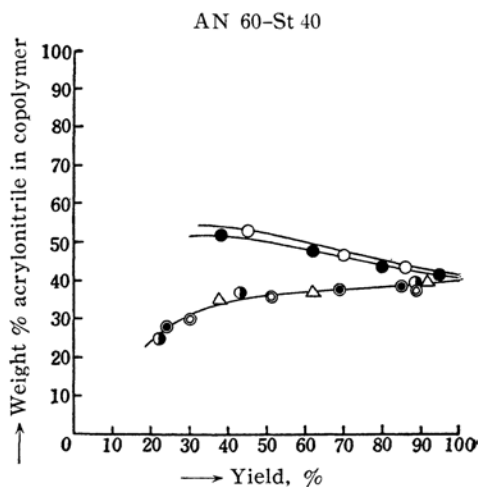


Fig. 16. Variation of copolymer composition with yield, No. 2.

Emulsifier (to Total Monomers)
 △ 1.0% ⊙ 0.6% ⊙ 0.4%
 ◐ 0.2% ● 0.1% ○ 0%

(28) K. Maeda et al., *J. Chem. Soc. Japan*, 58, 502 (1955).

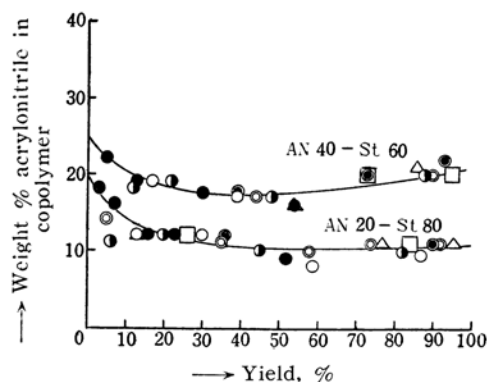


Fig. 17. Variation of copolymer composition with yield, No. 3.

Emulsifier (to Total Monomers)

- | | | |
|--------|--------|--------|
| □ 1.5% | △ 1.0% | ⊙ 0.6% |
| ⊙ 0.4% | ● 0.2% | ● 0.1% |
| ○ 0% | | |

It has been reported that in emulsion copolymerization of acrylonitrile and vinylidene chloride, the compositions of formed copolymers depended upon the concentration of emulsifier used and the copolymer produced in low concentration of emulsifier contained much acrylonitrile^{5,29)}.

The same phenomena were observed in the copolymerization of acrylonitrile and styrene. It is supposed that the water-solubility of monomer depends upon the compositions of copolymer, for these copolymerizations are those of water-soluble monomer and water

insoluble monomer. The variation of the composition is especially great in the copolymerization of almost equal weight water-soluble and water-insoluble monomer.

Conclusion

From the copolymerization of acrylonitrile and styrene done in emulsion and suspension, the following facts were found.

1. The polymerization rate becomes fast as the mixture of monomer contains much acrylonitrile and reaches the maximum in the mixture of acrylonitrile 80 mol.% and styrene 20 mol.%.

2. The polymerization rate becomes generally fast as the concentration of emulsifier becomes thick; however, it is maximum at about 1.0 weight % emulsifier (to total monomer) in the copolymerization of monomers containing above 80 mol.% acrylonitrile.

3. η_{sp}/c becomes great as the mixture of monomers contains much acrylonitrile.

4. η_{sp}/c becomes small, reaches the minimum and then becomes great as the concentration of emulsifier becomes thick.

The concentration of emulsifier giving η_{sp}/c minimum becomes thick as the mixture of monomers contains much acrylonitrile.

5. The composition of copolymer depends upon the concentration of emulsifier and it contains less acrylonitrile as the concentration becomes thick.

Research Institute of Teikoku
Rayon Co. Ltd., Iwakuni

29) H. Nagao, M. Uchida and T. Yamaguchi, *J. Chem. Soc. Japan*, in press.