Copolymerization. III. The Mechanism of Emulsion Copolymerization of Styrene and Acrylonitrile

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In a previous communication[1] from these laboratories monomer–polymer composition curves determined by mass and emulsion polymerization techniques were compared for the system styrene–acrylonitrile. It was concluded that at least during the initial stages of styrene–acrylonitrile emulsion copolymerization, the propagation reaction occurred within the oil phase but not to any appreciable extent in the aqueous phase. The present paper presents the results of an investigation to determine the validity of this oil phase mechanism for emulsion copolymerizations carried to high conversions.

Since the data do not differentiate between oil droplets and swollen micelles as the polymerization locus, the expression "oil phase mechanism" used here and in previous communications[1,2] includes both non-aqueous phase loci within its meaning.

The emulsion copolymerizations of styrene and acrylonitrile were carried out under conditions similar to those employed previously.[1] Two series of polymerizations were allowed to proceed to conversions of 42–52 and 12–17 weight per cent., respectively. The copolymer was isolated and purified, and the amount of combined acrylonitrile in the product was determined by duplicate micro Dumas analyses.

Results and Discussion

The results of the investigation are summarized in Table I. Since the analytical data were determined on high conversion copolymers, the monomer reactivity ratios for this system were calculated from the integrated form of the Mayo and Lewis[3] copolymerization equation. Their method for showing graphically the calculated r_1/r_2 relationship[4] for single experiments was employed and the results of the two series of experiments are shown in Figs. 1 and 2. From Fig. 1 (42–52 weight per cent. conversion) the following monomer reactivity ratios were obtained: styrene 0.46 ± 0.09 and acrylonitrile 0.03 ± 0.03. From Fig. 2 (12–17 weight per cent. conversion) monomer reactivity ratios of 0.52 ± 0.04 and 0.03 ± 0.03 for styrene and acrylonitrile, respectively, were found. Greater accuracy for the lower conversion series is to be expected. Mayo, Lewis and Hulse[5] have reported values of 0.41 ± 0.08 and 0.04 ± 0.04 for the mass copolymerization of styrene and acrylonitrile. The monomer reactivity ratios determined from the low conversion emulsion copolymerization curves reported previously[1] are 0.52 ± 0.03 and 0.03 ± 0.03, respectively. The values cited above for emulsion copolymerizations are calculated on the basis of monomer quantities *charged* to the reaction. In accordance with our views on emulsion copolymerization, monomer reactivity ratios calculated on this basis for emulsions are *apparent* values only and should be slightly different from the mass values due to different solubilities of the comonomers in the aqueous phase. That this is the case has already been shown.[1] Thus the present values reported for high conversion emulsion copolymerization experiments should be compared strictly with the low conversion emulsion values given above and not with the values in mass. The determination of monomer reactivity ratios at conversions of 42–52 weight per cent. is not sufficiently precise however to show this differentiation, and the values obtained include within their limits both the mass and emulsion

TABLE I

| | Moles of unreacted monomers | | | | | | | Nitrogen analyses, % | |
| | Styrene | | Acrylonitrile | | Time, | Temp., | Conversion | | |
Expt.	Initial	Final	Initial	Final	min.	°C.	wt., %	I	II
1	0.9122	0.4538	0.0942	0.0184	62	78	51.9	2.10	2.01
2	.6722	.2702	.5654	.2971	7	80	56.1	6.73	6.68
3	.3841	.1222	1.1308	.8401	12	74	42.7	9.63	9.45
4	.9122	.7990	0.0942	.0746	84	67	12.8	2.29	1.99
5	.6722	.5594	.5654	.4932	73	67	15.6	6.59	6.42
6	.0960	.0269	1.6962	1.5178	12	73	16.7	15.04	14.95

values obtained at low conversions. The results do show, on the other hand, that all of the monomer–polymer composition curves have the same shape and that they lie in close proximity to each other. This is the principal result of the investigation.

Applying arguments identical with those already advanced,[1] it is apparent that the composition of copolymer molecules forming during emulsion polymerizations carried to high conversions is determined by the relative monomer concentrations existing within the oil phase. It is there-

(1) Fordyce and Chapin, This Journal, **69**, 581 (1947).

(2) Fordyce and Ham, ibid., **69**, 695 (1947).

(3) Mayo and Lewis, ibid., **66**, 1594 (1944).

(4) Nomenclature of Alfrey, Mayo and Wall, J. Polymer Science, **1**, 581 (1946).

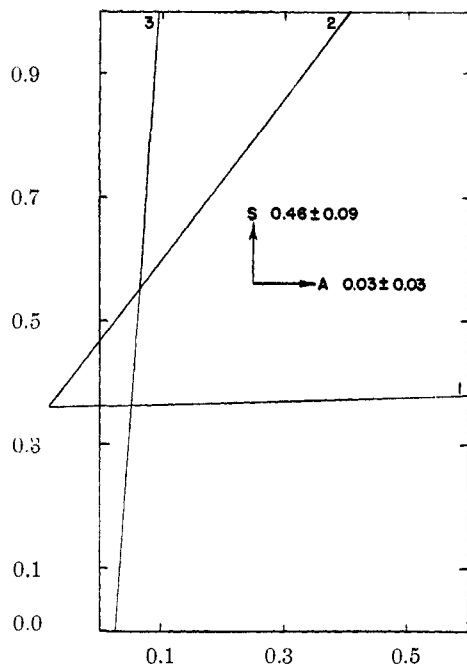(5) Mayo, Lewis and Hulse, This Journal, **67**, 1701 (1945).

Fig. 1.—Monomer reactivity ratios of styrene radical (S) and acrylonitrile radical (A): experiments 1, 2 and 3, 42–52 weight per cent. conversion.
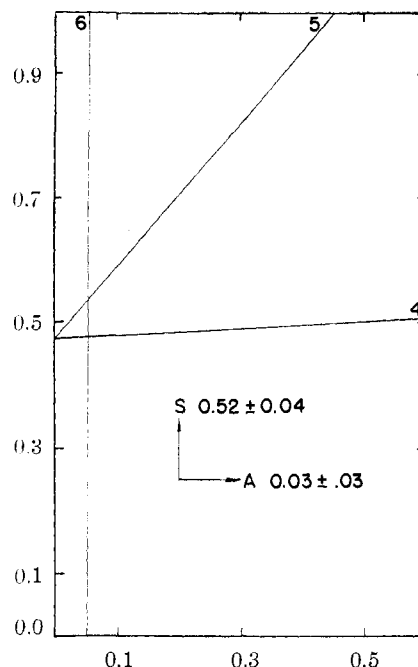

Fig. 2.—Monomer reactivity ratios of styrene radical (S) and acrylonitrile radical (A): experiments 4, 5 and 6, 12–17 weight per cent. conversion.

fore concluded that in the emulsion copolymerization of styrene and acrylonitrile, the polymerization occurs within the oil phase for at least 50% of the reaction and probably occurs there throughout the entire polymerization.

Experimental

Styrene Monomer.—Redistilled Dow Chemical Co. N-100 material was used.

Acrylonitrile.—Redistilled American Cyanamid Co. material was used.

Potassium Persulfate.—The product of the General Chemical Co. was used.

Santomerse D.—The product of Monsanto Chemical Co. was used (an alkyl aryl sodium sulfonate).

A master batch of emulsifier solution was prepared by dissolving 200 g. of Santomerse D in 4800 ml. of distilled water. The polymerizations utilized 200 g. of this emulsifier solution and 100 g. of total comonomers. The emulsifier solution, 0.1 g. of potassium persulfate and appropriate weights (Table I) of styrene and acrylonitrile were added to a 1–1, three-necked flask equipped with stirrer and reflux condenser. The reaction mixture was stirred for one and one-half hours at room temperature and then raised to the reaction temperature (Table I) during twenty minutes by means of a Glas-Col mantle. Polymerization at the reaction temperature was continued until the desired conversion (Table I) had been attained. Conver-

sions during the reaction were estimated by observing the amount of polymer precipitated when 5 ml. of the emulsion was added to 200 ml. of ethanol. Polymerization times at the reaction temperature for the compositions employed are given in Table I. The entire reaction mixture was then poured into 3000 ml. of stirred ethanol and this mixture was boiled to coagulate the product. Since there was a tendency for polymer particles to stick together after the boiling operation, the ethanol solution was decanted and the product re-comminuted by mixing in a Waring blendor with fresh alcohol. The fine powder thus obtained was boiled with 3000 ml. of fresh ethanol, filtered and the operation repeated. After the final filtration the product was dried in an evaporating dish at 60° in a circulating air oven for forty-eight hours. Conversions corrected for residue in the polymerization flask and for samples withdrawn during polymerization, were determined gravimetrically. These data and the nitrogen content of the products are given in Table I.

Summary

Data obtained from a study of the relative rates of copolymerization of styrene and acrylonitrile in emulsion polymerizations carried to high conversions are interpreted as giving support to an oil phase mechanism for emulsion polymerization.