[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Copolymerization. II. The Mechanism of Emulsion Copolymerization of Styrene and Itaconic Acid

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In a previous paper from these laboratories,[1] monomer–polymer composition curves determined by mass and emulsion polymerization techniques for the system styrene–acrylonitrile were compared. It was concluded that at least during the early stages of styrene–acrylonitrile emulsion copolymerization, the propagation reaction occurred within the oil droplet or at its interface but not to any appreciable extent in the aqueous phase. If this oil phase mechanism were generally valid, it was also predicted that a wide spread would be observed between the mass and the emulsion monomer–polymer composition curves for the case of a comonomer having a partition coefficient in favor of the water phase. This paper presents data obtained on such a system.

Styrene and itaconic acid were chosen as comonomers since the latter has a high solubility in water and a very low solubility in styrene. In determining the normal or mass type monomer–polymer curve, it was therefore necessary to carry out the copolymerization in a mutual solvent, dioxane.[2] Emulsion copolymerizations were carried out in the conventional way. All copolymerizations were allowed to proceed to low conversions (mainly < 4%) and this initial copolymer was isolated and purified. The composition of the product was then determined by duplicate carbon and hydrogen analyses.

Results and Discussion

The results of the investigation are summarized in Table I, from which the monomer–copolymer composition curves, Fig. 1, were drawn.

TABLE I

Monomer mole% itaconic acid	Time at polymerization temp.	Wt. % conversion	Analyses, % Carbon I	Carbon II	Hydrogen I	Hydrogen II	Copolymer mole% itaconic acid
Emulsion polymerization, 70°, no catalyst							
16.67	3.5	0.2	90.81	90.75	8.06	7.72	2.6
34.80	4.8	2.2	92.25	91.91	7.82	7.54	0.3
54.56	9.5	0.4	91.21	91.02	7.48	7.39	2.0
Dioxane solution polymerization, 70°, 0.1% Bz_2O_2							
8.17	4.0	5.1	80.72	80.44	7.52	7.23	21.4
16.68	4.0	4.8	77.20	77.15	6.91	6.88	28.0
34.80	4.0	4.0	70.16	70.12	6.88	6.48	42.5
54.56	5.0	4.6	66.88	67.29	7.18	6.97	49.0

The composition of the copolymer samples was determined with fair accuracy by carbon analysis, since the carbon content of polystyrene is 92.26% and that of polyitaconic acid is 46.16%.

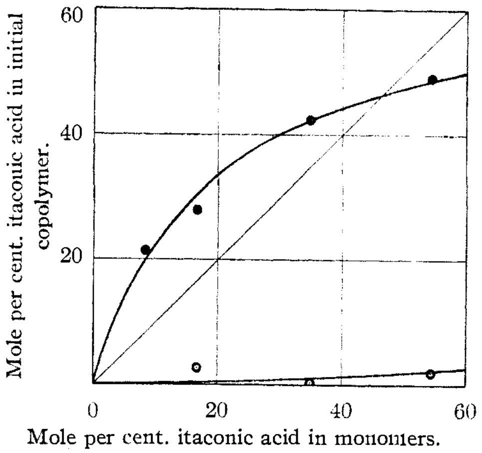

Fig. 1.—Monomer–polymer composition curves for styrene-itaconic acid: solution polymerization ●——; emulsion polymerization ○——.

The procedures employed for isolating and purifying the samples of initial copolymer formed are based on the solubility characteristics of the various products involved. Thus, itaconic acid is only slightly soluble in hexane but has the following solubilities in 100 g. of water: 8.3 g. at 20°, 29.2 g. at 50°, 45.9 g. at 60° and 72.6 g. at 70°. To clarify further the procedures involved, it should be mentioned that copolymers containing more than 20 mole per cent. itaconic acid are alcohol soluble, and those containing less than 80 mole per cent. itaconic acid are water insoluble.

The monomer reactivity ratios for the two radicals which fit the data of Table I are styrene 0.301 and itaconic acid 0.201. These constants represent the ratio of the rate constants for the reaction of the given radical with the corresponding monomer and with the other monomer, respectively.

In a previous publication,[1] arguments were presented in favor of an oil phase mechanism for the emulsion copolymerization of styrene–acrylonitrile during the first stages of polymerization. It was predicted that if an oil phase mechanism were generally operative, then the monomer–polymer composition curves for mass and emulsion polymerization should be widely divergent in the case where one comonomer had a partition coefficient in favor of water. Attempts were made to measure the partition of itaconic acid between styrene and water by titration of the two phases. The results, cited elsewhere, showed that virtually

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(1) R. G. Fordyce and E. C. Chapin, THIS JOURNAL, **69**, 581 (1947).

(2) Results, to be published later, have been obtained at these laboratories on several comonomer systems wherein the mass monomer–polymer composition curve has been shown to be coincident with the dioxane solution curve.

all of the itaconic acid was present in the water phase and that the amount dissolved in the styrene was too small to be measured by this method. These results indicate that the relative concentration of itaconic acid to styrene monomer in the oil droplets of the emulsion would be very much lower than the relative amounts initially charged to the reaction, hence the initial copolymer formed in emulsion should contain far less combined itaconic acid than the corresponding solution copolymer. The data in Table I and Fig. 1 are in agreement with this prediction and further strengthen the argument that in emulsion copolymerizations at least the initial polymerization proceeds within the oil droplet or at its interface.

Cases may be found where a reactive water soluble comonomer present in high concentrations will actively polymerize or copolymerize in the aqueous phase by ordinary solution polymerization. In such cases it is possible that oil phase emulsion polymerization may proceed simultaneously to produce copolymers in both phases. Instances of this special case will normally be rare since monomers of the greatest interest for emulsion copolymerization are not highly water soluble. Moreover, it is questionable that reactions of this kind can strictly be termed emulsion polymerizations.

Experimental

Itaconic Acid.—Charles Pfizer and Co. material was used as received.

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

Solution Polymerizations.—The dioxane employed was refractionated Carbide and Carbon Chemical Co. product. Benzoyl peroxide was obtained from the Lucidol Corp. A solution comprising 50 g. of total monomers, 200 g. of dioxane and 0.05 g. of benzoyl peroxide was added to a 12-ounce French square bottle. Air above the solution was swept from the bottle with oxygen-free nitrogen and a metal cap screwed tightly on the bottle mouth. The relative monomer concentrations employed are summarized in Table I. Polymerization was carried out in an air oven regulated to 70 ± 1° until a slight increase in viscosity was observed. The reaction times are summarized in Table I. The crude polymer was isolated by pouring the solution with stirring into 1000 ml. of hexane. The granular precipitate was filtered on a Buchner funnel and washed with three 1000 ml. portions of fresh hexane. After drying in an air oven at 50° for twenty-four hours, the product was boiled with 1000 ml. of distilled water, to remove residual itaconic acid, and then washed on a Buchner funnel with three 1000-ml. portions of boiling water. After air drying at 50° for twenty-four hours, the copolymer was boiled with 1000 ml. of hexane, filtered and washed as before with fresh hexane. Final drying in an air oven at 50° for forty-eight hours preceded the analysis for carbon and hydrogen.

Emulsion Polymerizations.—Santomerse D used was the product of Monsanto Chemical Co. (an alkyl aryl sodium sulfonate). A master batch of emulsifier solution was prepared by dissolving 10 g. of Santomerse D in 1990 ml. of distilled water. All emulsion polymerizations utilized 200 g. of this solution and 100 g. of total monomers. The emulsifier solution was added to a stirred 2-liter three-necked flask and appropriate weights (Table I) of itaconic acid and styrene were charged. The reaction mixture was stirred for one and one-half hours at room temperature and then raised to 70 ± 2° during fifteen minutes by means of a Glas-Col mantle. Polymerization at this temperature was continued until a low conversion had been attained. Conversions during the reaction were approximated by estimating turbidity when 5 ml. of the emulsion was added to 200 ml. of ethanol. Polymerization times at 70° for the compositions employed are summarized in Table I. To interrupt polymerization, the entire reaction mixture was then poured into 1500 ml. of denatured (2B) ethanol in a large evaporating dish and evaporated to dryness at room temperature in a circulating air oven. Since ethanol does not coagulate the product, drying was necessary to isolate the crude copolymer and to remove styrene monomer, alcohol and water under conditions which precluded further polymerization. The residue was leached with three fresh 500-ml. portions of ethanol. A 10-ml. sample of the combined filtered leaching solution was added to 200 ml. of distilled water and in no case was any turbidity observed, indicating the absence of any polymer dissolved in the leaching solution.[3] The alcohol insoluble residue was dissolved in 80 ml. of dioxane, the solution concentrated to 8 ml. total volume and the copolymer precipitated by adding to 300 ml. of stirred ethanol. The fibrous precipitate was boiled with three fresh 200-ml. portions of ethanol, filtered and dried at 60° in a circulating air oven for forty-eight hours prior to analysis for carbon and hydrogen. Conversions corrected for samples withdrawn during polymerization were determined gravimetrically. These data and the analyses are summarized in Table I.

Solubility of Itaconic Acid in Water.—Solubility data were determined in the usual way by preparing saturated solutions at 20, 50, 60 and 70°.

Partition of Itaconic Acid between Styrene and Water.—A mixture comprising 40.0205 g. of water, 18.0125 g. of styrene and 4.0202 g. of itaconic acid was shaken for two hours at 70°. The layers were allowed to separate and 1-ml. samples of each titrated with 0.1061 *N* sodium hydroxide. Less than 0.05 ml. of base was required for the styrene layer, indicating less than 0.163 mg. of acid per gram of styrene. Titration of the water layer showed 0.1008 g. of itaconic acid per gram of water.

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Summary

The wide divergence between the monomer–copolymer composition curves for the system styrene–itaconic acid determined in solution and in emulsion is interpreted in terms of an oil phase mechanism for emulsion polymerization.

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[3] This test does not rigorously exclude the possibility of having leached a high (>80 mole per cent.) itaconic acid copolymer which would not precipitate in water. To show the complete absence of any copolymer, a blank experiment was performed in which an emulsion identical with the 34.8 mole per cent. itaconic acid experiment was prepared at room temperature and immediately precipitated, dried and leached. Leaching solutions of the blank and of the polymerization run were diluted to 2000 ml. Viscosity measurements at 25 ± 0.02° showed a specific viscosity of 0.0670 ± 0.0002 for the blank and 0.0670 ± 0.0002 for the actual experiment. Dissolving 0.01% of the 42.5 mole per cent. itaconic acid copolymer in the solutions raised the specific viscosity to 0.0712 ±0.0002.