Polymerization and Polymers of Itaconic Acid Derivatives. V. The Copolymerization Reactivity of Itaconic Acid in an Aqueous Solution[1,2]

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Studies of the copolymerization of itaconic acid have been reported by several workers.[3-7] Concerning the effect of pH value on the copolymerization reactivity of itaconic acid, however, no information has been produced in the literature available to the author.

In the preceding report[1] on the homopolymerization of itaconic acid in an aqueous solution, it was shown that an increase in the pH values of the solution caused a great decrease in the rate of polymerization. For the interpretation of this phenomenon, it was suggested that itaconic acid in the dianionic form polymerizes poorly.

Therefore it became of interest to determine whether or not itaconic acid in the dissociated state is able to copolymerize with other monomers. In the present paper, the effect of pH value on the copolymerization reactivity of the acid with acrylonitrile is described.

Experimental

Materials.—Acrylonitrile was purified by Thomas' method.[8] Itaconic acid was recrystallized two times from water. Potassium persulfate was also recrystallized from water and was used as a polymerization initiator. Deionized water, prepared by treating water with ion-exchange resin, was used as the solvent of the copolymerization.

The Copolymerization Procedure and the Treatment of the Copolymer.—Three pH values, 1.5, 4.6 and 9.5, were selected for the copolymerization systems of itaconic acid and acrylonitrile in an aqueous solution. In order to adjust the pH, hydrochloric acid or potassium hydroxide was added to the solution of itaconic acid.

Potassium persulfate, the itaconic acid solution with its pH adjusted, and acrylonitrile were charged for the polymerization into a clean glass tube. The total volume of the solution in each batch was 50 ~60 cc. After they had been flushed with nitrogen, the tubes were sealed and immersed in a water-bath regulated to the polymerization temperature of 50°C. and then kept still for several hours.

The copolymer formed was soluble or insoluble to the solution depending on both the composition of the copolymer and the pH value of the system. For the system in which the copolymer precipitated, it was easy to separate the copolymer from the unreacted monomers by filtration. When, however, the

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[1] Part IV of this series: S. Nagai and K. Yoshida, *Chem. High Polymers, Japan*, **17**, 746 (1960).

[2] Presented at the 11th Annual Meeting of the Society of Polymer Science, Japan, Nagoya, May, 1962.

[3] R. G. Fordyce and C. G. Ham, *J. Am. Chem. Soc.*, **69**, 695 (1947).

[4] J. Exner and M. Bohdanecky, *Chem. Abstr.*, **48**, 8583 (1954).

[5] M. Uchida and H. Nagao, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **60**, 494 (1957).

[6] T. Higuchi and M. Imoto, ibid., **61**, 1053 (1958).

[7] C. S. Marvel and T. Shepherd, *J. Org. Chem.*, **24**, 599 (1959).

[8] W. M. Thomas and J. J. Pellon, *J. Polymer Sci.*, **13**. 329 (1954).

copolymer did not precipitate in the copolymerization medium at the acid pH, the solution was first neutralized by the addition of potassium hydroxide to pH 7, and then an excess amount of calcium chloride solution was rapidly stirred in at about 50°C to form the calcium salts of the itaconic monomer and the copolymer.⁹⁾ The calcium salt of the copolymer obtained was a fine powder and was insoluble to the solution, while that of the monomer was soluble. The copolymer salt was so finely suspended in the solution that it was difficult to isolate the salt by suction filtration through a glass filter. Accordingly, the suspension was centrifuged to recover the precipitates, and the upper solution was then decanted. The precipitates were washed with hot water and centrifuged again. This procedure was repeated several times until no chlorine ions were found in the washings. Then the copolymer was dried.

After copolymerization at a slightly alkaline pH, the solution of this system changed its color to yellow; the addition of a calcium chloride solution caused no recovery of the copolymer. In this case, however, the addition of hydrochloric acid precipitated the copolymer, with a yellow color, at about pH 3~4. Before being dried, the precipitate was dissolved again in water and reprecipitated by the addition of hydrochloric acid.

The Analysis of the Copolymer.—The acrylonitrile content of the copolymer was determined by nitrogen analysis using Kieldahl's method. The ash obtained from the copolymer was analyzed for calcium by the titration of EDTA and for potassium by the gravimetric method or by flame photometry.* Then the itaconic acid content was calculated from that of acrylonitrile, considering the calcium and potassium content of the copolymer.

Results and Discussion

The results of the copolymerization of three systems I, II and III, at different pH values are presented in Table I. In these cases, itaconic acid is designated as monomer 2, while acrylonitrile is monomer 1.

The Relationship between the pH of the System and the Dissociation of Itaconic Acid.—The copolymerization was carried out in the pH ranges of 1.0~2.2 (I), 4.7~5.3 (II) and 9.8~7.1 (III). It can be considered on the basis of Fig. 1,¹⁰⁾ which shows the relationship between the pH value and the degree of dissociation of itaconic acid, that the compositions of the acid in these systems are as follows:

(I) $IA > 97\%$

(II) $IA^{-} \simeq 80\%$, $IA \simeq IA^{2-} \simeq 10\%$

(III) $IA^{2-} > 97\%$

where IA means the undissociated form, IA^{-} means the first step dissociated monoanion, and IA^{2-} means the second-step dissociated dianion.

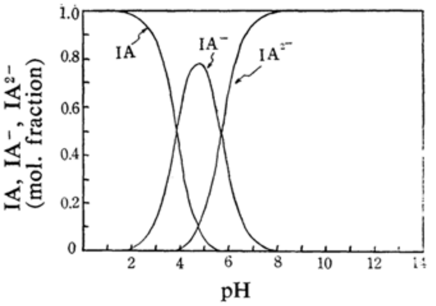

Fig. 1. Dissociation curves of itaconic acid against pH. IA, IA^{-} and IA^{2-} mean undissociated, first step dissociated and second step dissociated forms of itaconic acid, respectively.

The Precipitation of the Copolymer in the Copolymerization System.—In the cases of both I and II, the copolymer rich in acrylonitrile precipitated during the polymerization, while the copolymer rich in itaconic acid did not precipitate. The copolymer of an intermediate composition was partly precipitated and partly dissolved in the solution. (Cf., e. g., Table I, I-3.) However, in the case of III, no precipitates were found, presumably because of the great solubility of the copolymer composed, even though only in part, of itaconic dianion, whose water solubility is very large.

The Rate of Copolymerization.—In the acid pH copolymerization, a great decrease in the rate of copolymerization was observed as the composition of itaconic acid increased. This phenomenon had already been reported and explained by Uchida;⁵⁾ itaconic acid acts as a retarder in the emulsion copolymerization with acrylonitrile. Thus, itaconic acid monomers (M_2) add predominantly to the polymer radicals in competition with acrylonitrile monomers, i. e., $r_1 < 1 < r_2$. This results in a yield of polymer radicals with the itaconic units whose homopropagation ability is comparatively poor added at the growing ends.

However, in the neutrallized solution of the present work, rates of copolymerization which were rather large in comparison with those in acid pH copolymerization were observed in the range of 0.2~0.4 mol. fractions of M_2. The most probable interpretation of this phenomenon is that the relationship between r_1 and r_2 is now changed, as will be mentioned below; i. e., $r_1 > r_2 \simeq 0$, with a larger r_1

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9) This method has previously been described by H. Ito and S. Suzuki in the case of the copolymerization of acrylonitrile with acrylic acid; *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **58**, 627 (1955).

* The author wishes to thank Miss Muyo Higashiura et al. of the Inorganic Analysis Laboratory of the Institute for their kind directions for the analysis.

10) This figure has already been presented in the preceding report.¹⁾

TABLE I. RESULTS OF COPOLYMERIZATION OF ITACONIC ACID (M_2) WITH ACRYLONITRILE (M_1) AT VARIOUS pH [*1]

Exp. No.	Monomer composition $M_2/(M_1+M_2)$ mol. fraction	Time hr. : min	pH	Conversion[*2]	Rate of copolymerization %/hr.	Copolymer composition $m_2/(m_1+m_2)$ mol. fraction
I-1	0.0574	1 : 0	1.20∼1.40	6.2	6.2	0.0476[*3]
I-1′	0.0627	2 : 0	1.33∼1.70	13.0	6.5	0.070[3*]
I-2	0.127	2 : 0	1.31∼2.20	2.8	1.4	0.180[3*]
I-3	0.176	4 : 40	1.37∼2.00	4.4	0.94	0.32∼0.35[*4]
I-4	0.252	6 : 15	1.35∼2.10	5.2	0.84	0.452
I-5	0.308	12 : 40	1.20∼1.40	8.8	—	0.488
I-6	0.342	16 : 50	1.33∼2.00	9.1	—	0.551
I-7	0.543	16 : 50	1.31∼2.00	4.5	—	0.692
I-8	0.705	4 : 20	1.00∼1.15	3.1	0.72	0.785
I-9	0.844	5 : 30	1.00∼1.20	1.8	0.33	0.890
II-1	0.0661	1 : 37	4.80∼5.25	14.0	8.75	0.037[*3]
II-2	0.115	1 : 37	4.70∼5.10	12.0	7.5	0.042[*3]
II-3	0.187	2 : 35	4.70∼5.12	4.0	1.6	0.221[*3]
II-4	0.290	6 : 00	4.70∼4.80	—	—	0.390
II-5	0.426	4 : 20	4.70∼4.89	3.3	0.76	0.532
II-6	0.565	5 : 30	4.70∼4.66	4.5	0.82	0.594
II-7	0.713	6 : 00	4.70∼5.00	—	—	0.672
II-8	0.789	3 : 55	4.70∼4.80	1.3	0.33	0.775
III-1	0.0671	1 : 25	9.20∼7.40	7.6	5.35	0.0137
III-2	0.184	2 : 30	9.20∼7.33	13.0	5.2	0.26
III-2′	0.194	5 : 05	9.00∼7.20	25.5	5.0	—
III-3	0.227	7 : 30	8.30∼7.98	28.0	—	0.330
III-4	0.328	2 : 30	9.77∼7.64	11.8	4.75	0.327
III-4′	0.307	12 : 40	8.68∼7.40	25.1	—	0.332
III-5	0.394	2 : 30	9.57∼7.50	7.5	3.0	0.405
III-5′	0.379	15 : 35	8.00∼7.10	20.5	—	—
III-6	0.456	2 : 35	9.35∼8.40	2.3	0.9	0.421
III-7	0.736	7 : 45	9.20∼8.40	very low		0.522
III-8	0.803	4 : 20	9.43∼8.51	very low		0.652

[*] The initiator, potassium persulfate, was used in concentrations of 1/200 mol. per monomers.

[*2] The conversion data represent the copolymers of AN and IA recalculated from those for the experimentally-obtained copolymers containing Ca and K.

[*3] The copolymer is insoluble to the aqueous solution.

[*4] Some of the copolymers are insoluble.

TABLE II. COPOLYMERIZATION PARAMETERS OBTAINED[*]

Series	pH	M_2	r_1	r_2	Q_2	e_2
I	1.0∼2.2	IA >97%	0.25	1.57	0.55	0.22
II	4.7∼5.3	IA^- ≃max.	0.30	0.60	—	—
III	9.8∼7.1	IA^{2-} >97%	0.43	0.1	0.12	−0.58

[*] The *Q* and *e* values of acrylonitrile used for this calculation are 0.41 and 1.2 respectively.

and a smaller r_2 than those for the acid pH copolymerization, thus accelerating the consumption of M_1 and increasing the rate of copolymerization.

When more than a 0.4 mol. fraction of itaconic acid was used, the rate of conversion became very small.

The Composition of the Copolymer and the Copolymerization Parameters.—The calculation of the monomer reactivity ratios was carried out according to Lewis and Mayo's method, as shown in Fig. 2, except for runs which yielded precipitated copolymers, because the unexpected absorption of the unreacted monomers to the precipitated polymers might have occurred.

Figures 3—5 show the relationship between the monomer and the copolymer compositions. The curve represents the calculated values for

r_1 and r_2, while the points represent the experimentally-determined compositions. Each curve rides sufficiently on the respective experimental points, except for those systems excluded from the calculation.

Figure 3 shows that when itaconic acid is undissociated, copolymers with acrylonitrile always contain an excess fraction of itaconic acid compared with the fraction of the acid in the monomer mixtures. On the other hand, when itaconic acid is ionized to the second step dissociated form, the "azeotropic" points are observed on a composition of about 0.4 mol. fraction of M_2, as shown in Fig. 5. Figure 4 shows an example of the results obtained by the copolymerization at intermediate pH values when IA, IA^- and IA^{2-} are all involved in the reaction.

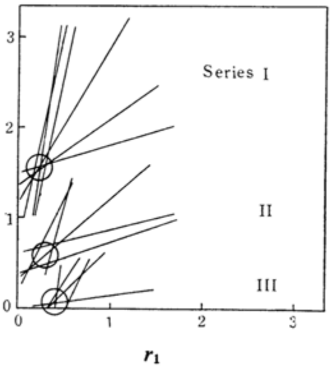

Fig. 2. Calculation diagram of reactivity ratios.

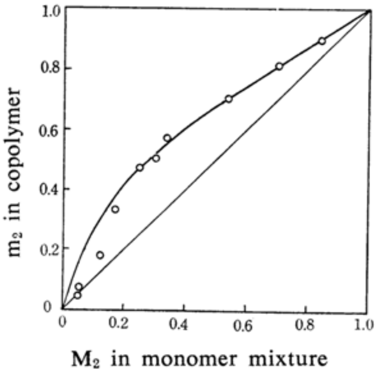

Fig. 3. Relationship between monomer composition and the initial copolymer composition. (Series I)

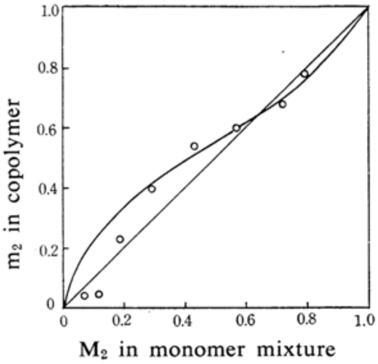

Fig. 4. Relationship between monomer composition and the initial copolymer composition. (Series II)

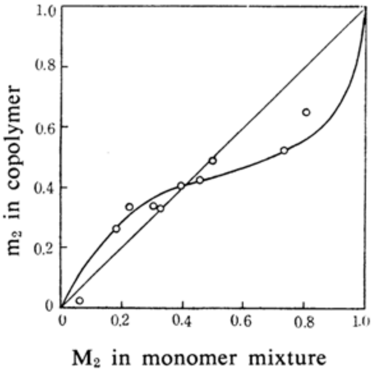

Fig. 5. Relationship between monomer composition and the initial copolymer composition. (Series III)

The monomer reactivity ratios and the Q-e values calculated according to the method of Alfrey and Price are summarized in Table II.

As for the monomer reactivity ratios, it is observed that r_2 decreases from 1.57 to 0.1 according as itaconic acid changes from the undissociated form to the second-step dissociated anion. This fact suggests that, in accordance with the finding reported in the previous paper,[1] for all practical purposes the second-step dissociated itaconic dianion does not homopolymerize.

During the considerable change in r_2 above mentioned, however, a comparatively small change is observed in r_1, one ranging from 0.25 to 0.43. This finding demonstrates that the itaconic dianion has yet a considerable reactivity to copolymerization.

Concerning the corresponding changes in Q and e values, Q_2 varies from 0.55 to 0.12, while e_2 varies from 0.22 to -0.58, according as itaconic acid changes from IA to IA^{2-}. If this finding is compared with that of acrylic acid, some interesting facts are observed. In the case of acrylic acid, Ito and Suzuki reported[9] that Q varies from 0.40 to 0.11, while e varies from 0.25 to -0.15, according as the acid changes from the undissociated form to the anion. It may be due to the similar structures of acrylic and itaconic acid from the point of view of resonance stabilization that the two monomers have similar Q values, showing similar changes in response to the changes in the dissociation degree. Further, probably responsible for the second step dissociation of itaconic acid against the only one step dissociation of acrylic acid is the fact that the change in the e value of itaconic acid is much larger than the change of that of acrylic acid.

Summary

The copolymerization of itaconic acid with acrylonitrile has been carried out in aqueous solutions of three different pH values. From the composition data obtained, the monomer reactivity ratios and the Q-e values have been calculated. The results indicate that itaconic acid, when ionized to the second-step dissociated form, is able to copolymerize with other monomers, while it is almost completely unable to homopolymerize.

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