The Polymerization and Polymers of Itaconic Acid Derivatives. VIII. A Cation Exchange Resin from Itaconic Anhydride[1,2]

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A cation exchange resin prepared from itaconic acid may be expected to have a large ion exchange capacity. The resins obtained by Akashi[3] and Sugihara[4], however, showed relatively low ion exchange capacities. The resins prepared by the solution copolymerization of itaconic acid and divinylbenzene in methyl alcohol, ethyl alcohol and acetone showed exchange capacities of 4.3—7.6, 7.86 and 9.57 meq./g. respectively. The resin obtained by the bulk copolymerization of the two materials at 160°C showed 7.35 meq./g. The pearl copolymerization in a sodium chloride solution resulted in a low-capacity resin, and an attempt to saponify the dimethyl itaconate-divinylbenzene copolymer did not succeed.

It might be due to the poor homopropagation reactivity of itaconic acid that a high-capacity resin was not obtained under these preparation conditions.

The authers have succeeded in the synthesis of a high-capacity ion exchange resin by using itaconic anhydride as the monomer and diallyl itaconate as the cross-linking agent.

Results and Discussion

In order to prepare a copolymer rich in itaconic acid, the copolymerization system must be considered to be preferable to the homopropagation of itaconic acid. First, it is recognized that itaconic acid homopolymerizes only in an aqueous solution.[5] However, the application of the aqueous system seems unsuitable, for it requires a water-soluble cross-linking agent. Second, it is of interest to apply the finding reported by Higuchi that itaconic acid shows different copolymerization reactivities against styrene in such different solvents as methyl alcohol, pyridine and aniline.[6] Pyridine and aniline seem to promote the homopropagation of itaconic acid. However, these solvents are not only expensive, but they are also capable of some side reactions with itaconic acid. Third, it should be noticed that, when copolymerized with styrene, itaconic anhydride shows a larger reactivity ratio than that of styrene.[7] The author has also reported that itaconic anhydride readily homopolymerizes in bulk and that the polymer is rapidly hydrolyzed as soon as it is dissolved in water.[8] These facts suggest the probability of preparing the ion exchange resins with large capacity. The results obtained by means of the third method are described below.

The polymerization of itaconic anhydride was carried out in tetrahydrofuran, using divinylbenzene as the cross-linking agent. When the charged composition of divinylbenzene was 20 per cent, the polymerization product consisted exclusively of itaconic anhydride, showing much solubility to an alkaline solution as well as to acetone. Both runs, charged with 40 and 60 % divinylbenzene, on the contrary, yielded cross-linked polymers containing no carboxylic group.

These results suggest that cross-linking agents with an almost "ideal"[9] copolymerization reactivity against itaconic anhyride should be used instead of divinylbenzene. Therefore, we tried to use diallyl itaconate as the cross-linking agent.

The results of the copolymerization of itaconic anhydride and diallyl itaconate are shown in Table I.

The ion exchange resins thus obtained showed a satisfactorily large ion exchange capacity, though their swelling ratios (R-COONa/R-COOH) were relatively high.

There is a question of whether or not this type of resin, consisting of ester cross-linkage, is resistant to alkali and acid for a long time. The resin, afterward immersed both in alkali and acid (1 N) for one month, did not show as much decrease in weight as the commercial resin of the weak-acid type (Duolite CS 101).

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[2] Presented at the 13th Annual Meeting of the Society of Polymer Science, Japan, Kyoto, June, 1964.

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TABLE I. THE COPOLYMERIZATION OF ITACONIC ANHYDRIDE AND DIALLYL ITACONATE IN AN ATTEMPT TO PREPARE THE CATION EXCHANGE RESIN

No.	ItAnh	DAI	BPO	$\frac{\text{DAI}}{\text{ItAnh+DAI}}$	Yield*	Ion exchange capacity meq./g.			Swelling ratio
	g.	g.	g.	mol. %	g.	Found	Theor.	%	
I	3.628	0.258	0.080	3.65	2.5	12.9	14.5	89	~1.8
II	3.804	0.515	0.077	6.73	2.5	12.2	13.8	88	~1.6
III	3.246	0.787	0.080	11.45	2.5	11.7	12.8	92	~1.7
IV	3.034	1.006	0.079	15.0	2.2	11.2	12.0	93	~1.8

ItAnh: Itaconic anhydride; DAI: diallyl itaconate; BPO: benzoyl peroxide

* After they had been copolymerized for 1 hr. at 75°C, followed by an after cure for 3 hr. at 110°C, the copolymers were treated by the routine method of conditioning. The yield indicates the weight of the dry ion exchange resin obtained in this way, including no unreacted monomers or water-soluble polymers.

Experimental

Materials. — Itaconic anhydride was synthesized by the reaction of itaconic acid and acetyl chloride. It was recrystallized twice from anhydrous ethyl ether. M. p. 67—68°C. Commercial divinylbenzene was used as supplied, composed of 50 per cent divinylbenzene and 50 per cent ethylstyrene. Diallyl itaconate was prepared by the esterification of itaconic acid with allyl alcohol in the presence of a catalytic amount of sulfuric acid. B. p. 130—132°C (~7 mmHg).

The Copolymerization with Divinylbenzene.— When the charged amount of divinylbenzene (net) was 20 mol. %, a mixture of 4.481 g. of itaconic anhydride, 2.853 g. of 50% divinylbenzene, 20 ml. of tetrahydrofuran, and 0.269 g. of benzoyl peroxide was copolymerized in a glass tube at 60°C. After 44 hr., the homogeneous solution was poured into water in order to precipitate the powdery polymer. The polymer precipitated in the water, however, expanded and dissolved when alkali was added to the system, though it reprecipitated when hydrochloric acid was added. The polymer was also soluble in acetone, though it was insoluble in ethyl ether. The yield was 2.9 g. The alkaline solution of the polymer sample indicated no sign of the existence of benzene derivatives in the ultraviolet spectrum. When charged with 40 and 60 mol. % of net divinylbenzene, the cross-linked, alkali-insoluble polymers were obtained. However, their ion exchange capacities were almost zero.

The Copolymerization with Diallyl Itaconate.— The four runs of the bulk copolymerization, in which the charged compositions of diallyl itaconate ranged from 3.65 to 15.0 mol. %, were carried out in glass tubes at 75°C. After 15—20 min., the reaction mixtures of all four runs solidified and then small cracks occurred in them. After one hour the solid products were discharged from the reaction tubes and were postcured for 3 hr. at 110°C. The products were crushed, poured into water, and then immersed in 1 N sodium hydroxide for about 24 hr. Then they were washed with water and immersed in 1 N hydrochloric acid. After the alternative immersions in alkali and acid had been repeated two more times, they were dried for 4 hr. at 105—110°C. The swelling ratio of the wet volume of the resin in the form of R-COONa against that of R-COOH was measured roughly by means of a graduated cylinder.

The Determination of the Ion Exchange Capacity.—About 0.5 g. of the resin was exactly weighed in a beaker. Then 30 ml. of 0.1 N sodium hydroxide and 40 ml. of 0.1 N sodium chloride were pipetted into the beaker. After about 20 hr., 10 ml. of the upper solution in the beaker was pipetted out and back-titrated with 0.1 N hydrochloric acid.

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