[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

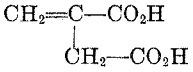
Polymerization Reactions of Itaconic Acid and Some of Its Derivatives

C. S. MARVEL AND THOMAS H. SHEPHERD[1]

Received September 24, 1958

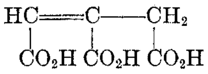
The homopolymerization of itaconic acid and dimethyl, diethyl, and di-*n*-butyl itaconate has been carried out. Copolymers of itaconic acid with acrylic acid, aconitic acid, and butadiene have been prepared, as well as copolymers of dimethyl itaconate with butadiene. Polydimethyl itaconate has been reduced to poly-2-hydroxyethylallyl alcohol. The conversion of a butadiene–dimethyl itaconate copolymer to a butadiene-2-hydroxyethylallyl alcohol copolymer has also been effected. Bis(*N*,*N*-dimethyl)itaconamide and 2-hydroxyethylallyl alcohol have been prepared; the conversion of the former to bis(*N*,*N*-dimethyl)-mesaconamide has been effected.

It has been reported in the literature[2] that itaconic acid (I) does not homopolymerize, although it has been found to enter into copolymerization reactions in numerous instances.[3-8] Since itaconic esters do homopolymerize to materials of fairly high molecular weight,[9-11] the failure to bring about polymerization of the acid appeared to be anomalous. When an aqueous solution of itaconic acid was treated with catalytic amounts of potassium persulfate, no polymerization was effected. Polymerization also failed to proceed in alkaline solution. Itaconic acid did, however, undergo homopolymerization in solution in 0.5*N* hydrochloric acid using persulfate initiation. The polymer was produced in 35 per cent conversion in 68 hours at 50°.



$CH_2{=}C(CO_2H){-}CH_2{-}CO_2H$

I



$HC(CO_2H){=}C(CO_2H){-}CH_2(CO_2H)$

II

The polyitaconic acid is extremely water soluble, and is soluble in methanol. It was found to be insoluble in other common organic solvents, including ethanol. The polymer, as obtained by freeze drying the aqueous solution, contained water of hydration which amounted to about one mole of water for each itaconic acid unit. When an attempt was made to dry the acid at 100° and 0.1 mm. pressure, this water of hydration was lost and anhydride formation occurred to some extent as indicated by a high carbon analysis. Viscosity determinations on the polyacid were not too useful in estimating its molecular size; hence the acid was esterified with ethanol to give an organic solvent–soluble material which gave viscosity data indicating a molecular weight of the order of about 5×10^4 if we estimate the molecular weight using constants determined on the related polymethyl methacrylate.[12]

The copolymerization of itaconic acid and acrylic acid was carried out in aqueous solution at 26°. Potassium persulfate initiation was used, and the polymerization required about seven days to reach 90 per cent conversion. A greater amount of itaconic acid than was initially soluble in the solution system was used, and this excess slowly dissolved as polymerization proceeded. Thus, an essentially constant concentration of itaconic acid was present in the reacting phase during the polymerization. The itaconic acid–acrylic acid copolymer is very hard and brittle, but forms a tough, flexible transparent film when a water solution of the polymer is evaporated. The copolymer is soluble in water as well as in methanol and ethanol. Analytical difficulties were encountered with this polymer because it, too, held water of hydration and further drying caused anhydride formation. It is much higher in molecular weight than the homopolymer of acrylic acid on the basis of the viscosity determined on the partial ester. The physical properties (tensile, etc.) of the polymer indicated the same thing. An estimate of the composition of the copolymer was made by determining the amount of unreacted itaconic acid in a standard polymerization. The evidence indicates that there are about two moles of itaconic acid for every three moles of acrylic acid in the

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(1) This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division. This paper is based on portions of a thesis submitted by Thomas H. Shepherd to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of doctor of philosophy.

(2) C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley and Sons, Inc., New York (1952), p. 308.

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

(4) J. Exner and Miloslav Bohdanecky, *Chem. listy*, **48**, 483 (1954).

(5) J. B. Dickey and H. W. Coover, Jr., U.S. Patent **2,533,207** (Dec. 12, 1950).

(6) G. F. D'Alelio, U.S. Patent **2,531,408** (Nov. 28, 1950).

(7) G. Pitzl, U.S. Patent **2,570,478** (Oct. 9, 1951).

(8) S. B. Lippincott and L. A. Mikeska, U.S. Patent **2,542,542** (Feb. 20, 1951).

(9) H. Stobbe and A. Lippold, *J. prakt. Chem.*, **90**, 336 (1914).

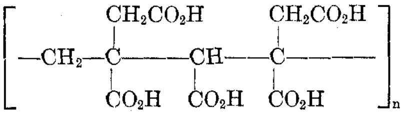
(10) E. Hope, Brit. Patent **264,550** (Oct. 26, 1925).

(11) L. W. Mixon and R. Watson, U.S. Patent **2,672,446** (March 16, 1954).

(12) P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 312.

copolymer. For each molecule of acid there is one molecule of water of hydration.

Itaconic acid copolymerized with aconitic acid (II) in aqueous solution, yielding a polymer which is believed to have a regular structure (III), resulting from alternation of monomer units in the polymer chain. Analysis of the copolymer and analysis of the acid mixture recovered from polymerization confirm the opinion that this alternating structure (III) is the correct one. This itaconic acid–aconitic acid copolymer is hard and brittle, and forms a rather weak transparent film. The copolymer is soluble in water and methanol, but not in ethanol. Inherent viscosity measurements on dilute solutions of the partially esterified polymer indicated a molecular weight of the order of 3 × 10^4 if calculated using the constants previously employed.[12]



$$\left[-CH_2-\overset{CH_2CO_2H}{\underset{CO_2H}{C}}-\underset{CO_2H}{CH}-\overset{CH_2CO_2H}{\underset{CO_2H}{C}}-\right]_n$$

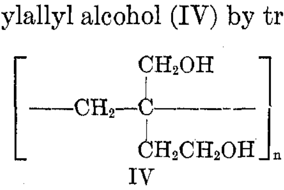
III

Emulsion polymerization of a vinyl monomer is favored by water insolubility and oil solubility of the monomer.[13] Since itaconic acid is very water soluble and exhibits only insignificant oil solubility, its copolymerization with butadiene in an emulsion system is quite surprising. The recipe used was similar to that employed for the copolymerization of butadiene and acrylic acid.[14] When a 3:1 ratio of butadiene over itaconic acid was used, a polymer with 20 per cent incorporation of the acid was produced. This copolymer had an inherent viscosity of 1.4 in tetrahydrofuran solution. The polymer was completely soluble in tetrahydrofuran, but only partially soluble in benzene. The polymer dispersed in methanol and alkaline water. It was not soluble in water, but became tacky when moist.

Since it was desired to investigate the feasibility of preparing polyalcohols by reduction of polyesters, the homopolymerization of itaconic esters was investigated. Homopolymers of dimethyl, diethyl, and di-*n*-butyl itaconate were prepared. The use of emulsion systems in the polymerizations gave polymers of higher inherent viscosity than those reported in the literature, which were prepared in bulk systems.[11,15] The homopolymers are thermoplastic materials, forming clear melts at temperatures ranging from about 125° for polydimethyl itaconate and 85° for polydiethyl itaconate to about 50° for polydi-*n*-butyl itaconate. The latter polymer exhibits cold flow at room temperature, but shatters under a sudden impact. It is thought that the lower melting point, and observable cold flow of the polydi-*n*-butyl itaconate, is caused by internal plasticization by the butyl groups.

The failure of itaconic acid, and its esters, to homopolymerize to materials having molecular weights of the order of those found in the polyacrylates is attributed to the presence of allylic hydrogen atoms in the molecules. Such hydrogen atoms act as chain transfer agents according to Bartlett,[16,17] thus a situation where "self-modification" can occur exists in the polymerization of itaconic acid and its esters.

Polydimethyl itaconate was reduced to the poly-2-hydroxyethylallyl alcohol (IV) by treating it with lithium aluminum hydride in tetrahydrofuran solution. Microanalysis of the product indicated that reduction was about 97 per cent complete; however, a weak carbonyl band remained in the infrared spectrum. The poly-2-hydroxyethylallyl alcohol is soluble in a dioxane-water mixture, but was insoluble in all other solvents. When the polyalcohol was allowed to stand in water which was only slightly acidic (*p*H of 5), cross linking occurred. It is thought that these are ester cross links, resulting from transesterification reactions involving unchanged ester groups in the polymer. The polyalcohol is hard and brittle, but can be ground into a white powder.



$$\left[-CH_2-\overset{CH_2OH}{\underset{CH_2CH_2OH}{C}}-\right]_n$$

IV

Although a copolymerization of dimethyl itaconate with butadiene in an emulsion system has been reported in the literature,[18,19] a study of the copolymerization was made to determine conditions for the preparation of a copolymer containing desired amounts of the ester.

The copolymerization was carried out at 50° using persulfate initiation in an ORR soap emulsion. The composition of copolymers produced with high monomer conversion (100 per cent) approached that of the monomer charge. When the polymerization was stopped at about 60 per cent conversion, the resultant copolymer contained a larger proportion of dimethyl itaconate than was present in the monomer charge. This indicated that the butadiene radical adds to dimethyl itaconate at a faster rate than it adds to butadiene, since the addition of the dimethyl itaconate radical to dimethyl itaconate is relatively slow at 50°. The butadiene–dimethyl itaconate copolymers exhibit inherent

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

(14) C. S. Marvel, R. M. Potts, J. Economy, G. P. Scott, W. K. Taft, and B. G. Labbe, *Ind. Eng. Chem.*, **47**, 2221 (1955).

(15) C. J. Knuth and P. F. Bruins, *Ind. Eng. Chem.*, **47**, 572 (1955).

(16) P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

(17) P. D. Bartlett and R. Altschul, *J. Am. Chem. Soc.*, **67**, 816 (1945).

(18) G. F. D'Alelio, U.S. Patent **2,366,495** (Jan. 2, 1945).

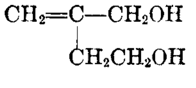
(19) J. W. Meier, U.S. Patent **2,748,027** (May 29, 1956).

viscosities of about 2.3, and have typical elastomeric properties.

Butadiene–dimethyl itaconate copolymers were reduced to the alcohol copolymers in tetrahydrofuran solution with lithium aluminum hydride using a modification of a procedure previously described.[14] When a copolymer containing about 20 per cent of the ester was reduced, no carbonyl band appeared in the infrared spectrum of the product in 10 per cent chloroform solution. However, another spectrum obtained on the alcohol copolymer in 40 per cent chloroform solution revealed a weak carbonyl band. A comparison of absorption intensities in the infrared spectra of the reduced copolymer and the ester copolymer indicated that reduction was about 90 per cent complete. Thus the copolymer contains about one per cent unchanged dimethyl itaconate recurring units.

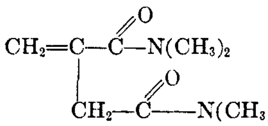
This copolymer, however, when dried free from solvent, failed to dissolve. This insolubility is not due to oxidative cross linking since the copolymer, after being saturated with antioxidant, only swelled in solvents after drying, but remained completely soluble if not completely dried. It is thought that the cross linking was due to transesterification reactions involving unchanged ester groups in the polymer.

In the course of the investigation, 2-hydroxyethylallyl alcohol (V) was prepared by the reduction of dimethyl itaconate with lithium aluminum hydride, and bis(N,N-dimethyl)itaconamide (VI) was prepared by treating itaconyl chloride with dimethylamine. Since neither of these compounds has been reported, their preparation is given in the experimental section.



$CH_2{=}\underset{\displaystyle CH_2CH_2OH}{\underset{|}{C}}{-}CH_2OH$

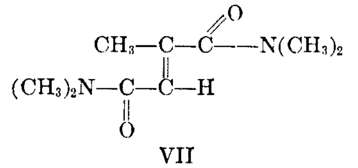
V



$CH_2{=}\underset{\displaystyle CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-N(CH_3)_2}{\underset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-N(CH_3)_2$

VI

In an attempt to cause homopolymerization of VI by treating it with sodium in liquid ammonia, a rearrangement occurred. The product was subsequently identified as bis(N,N-dimethyl)mesaconamide (VII)



$$\begin{array}{l} CH_3-C-\overset{\displaystyle O}{\overset{\|}{C}}-N(CH_3)_2 \\ \qquad\qquad \| \\ (CH_3)_2N-\underset{\displaystyle O}{\underset{\|}{C}}-C-H \end{array}$$

VII

The elemental composition and molecular weight of VII were the same as that of VI. The rearrangement product exhibited a λ_{max} of 235 mμ with an extinction coefficient of 8700, while neither itaconamide, acrylamide nor bis(N,N-dimethyl)itaconamide showed an absorption maximum in the ultraviolet region. The nuclear magnetic resonance spectrum of VII had peaks corresponding to an olefinic hydrogen, an olefinic methyl group, and four N-methyl groups. The characteristic band for methylene hydrogens was absent.

Hydrolysis of VII with dilute sodium hydroxide yielded mesaconic acid after acidification of the hydrolyzate. This was identified by a mixed melting point with an authentic sample of mesaconic acid. Treatment of maleic acid and fumaric acid with base under the same conditions caused no isomerization of these acids, thus it is likely that no isomerization occurred in the hydrolysis of VII.

In the treatment of bis(N,N-dimethyl)itaconamide with sodium in liquid ammonia, 0.04 g. (0.0017 g.-atom) of sodium yielded 1.8 g. (0.01 mole) of the rearrangement product, indicating that a chain reaction occurred.

EXPERIMENTAL[20]

All polymerizations were carried out in 4-oz. screw-capped bottles sealed with Buna-N gaskets. Prior to sealing the bottles, air was removed by flushing with nitrogen, except when butadiene was employed as a comonomer. Butadiene was added in excess and allowed to boil away until the proper weight was reached, thus flushing air from the system.

Water employed in the polymerizations was distilled in an all-glass apparatus, and freed from air by heating it to boiling and bubbling nitrogen through the liquid until it cooled to room temperature. Reagents were added to the polymerization vessels in the order listed in the recipes. All liquid monomers were redistilled, and solid monomers were recrystallized to a constant melting point before use.

Inherent viscosities were determined on dilute solutions of the polymers in a modified Ostwald viscometer at 25 ± 0.2°.

Homopolymerization of itaconic acid. A solution of 20 g. of itaconic acid, 50 ml. of 0.5N hydrochloric acid, and 0.10 g. of potassium persulfate was allowed to stand at 50° for 68 hr. Some itaconic acid remained undissolved. The solution was then dripped slowly into acetone and polymer precipitated. The polymer was removed by filtration, redissolved in water, reprecipitated from acetone, and dried under diminished pressure. An analytical sample was freeze-dried from aqueous solution. Seven g. (35%) of a white powder was obtained.

Anal. Calcd. for $[(C_5H_6O_4)_5(H_2O)_4]_n$: C, 41.56; H, 5.30; for $(C_5H_6O_4)_n$: C, 46.16; H, 4.65. Found: C, 41.89; H, 5.32. When this polymer was further dried over phosphorus pentoxide at 100° and 0.1 mm. pressure, anhydride formation occurred as indicated by the analysis, C, 48.16; H, 4.73. This corresponds to about 30% anhydride–70% acid.

Results of the viscosity determination on dilute aqueous solution of the hydrated polymer are given in Figure 1.

Copolymerization of itaconic acid and acrylic acid. Six polymerization bottles were charged with 10 g. of itaconic acid, 50 ml. of water, 10 g. of redistilled acrylic acid, and 0.10 g. of potassium persulfate. The polymerization was allowed to proceed 8 days at 26°. Not all the itaconic acid was initially soluble in the system, but gradually dissolved as the polymerization proceeded. The viscous solutions were then triturated with acetone to precipitate the polymer. The poly-

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(20) We are indebted to Mr. Jozsef Nemeth, Miss Claire Higham, Mrs. Maria Stingl, and Mrs. Ruby Ju of the Microanalytical Laboratory of the University of Illinois for the microanalyses, to Mr. James Brader and Mr. Paul McMahom, University of Illinois, for the infrared data, and to Mr. Jen Chiu of the University of Illinois for the ultraviolet analyses.

TABLE I

RESULTS OF COPOLYMERIZATION OF ITACONIC ACID AND ACONITIC ACID

No.	Itaconic Acid, G.	Aconitic Acid, G.	Initiator,[a] G.	Activator,[b] G.	Water, Ml.	Time, Days	Temp., °C.	Polymer, G.	Inherent[c] Viscosity
1	5.0	5.00	0.05		50.0	6	25	1.5	1.60
2	3.75	5.00	0.05		50.0	6	26	0.9	1.30
3	3.75	5.00	0.05		50.0	7	26	1.3	
4	3.75	5.00	0.05		50.0	8	26	1.5	
5	3.75	5.00	0.05		50.0	9	26	1.5	
6	3.75	5.00	0.05		50.0	10	26	1.4	
7	3.75	5.00	0.05		50.0	11	26	1.7	1.25
8	8.2	5.00	0.05		50.0	2	26	1.0	0.30
9	8.2	10.0	0.05		50.0	2	−5	1.5	0.28
10	7.5	10.0	0.05	0.0276	50.0	3	26		
11	7.5	10.0	0.05	0.0276	50.0	3	50	3.1	0.62
12	7.5	10.0	0.15	0.0276	25.0	4	26	7.0	0.24
13	7.5	10.0	0.05	0.0276	50.0	3	26	3.1	0.62
14	7.5	10.0	0.10	0.0276	50.0	3	26	3.6	0.55
15	7.5	10.0	0.15	0.0276	50.0	3	26	3.7	0.54
16	7.5	10.0	0.20	0.0276	50.0	3	26	3.7	0.56
17	7.5	10.0	0.10	0.0276	50.0	7	26	6.0	0.50
18	7.5	10.0	0.10	0.0552	50.0	7	26	6.1	0.40

[a] Ammonium persulfate. [b] Sodium sulfite.[21] [c] Determined on 0.25 g./100 ml. aqueous solutions.

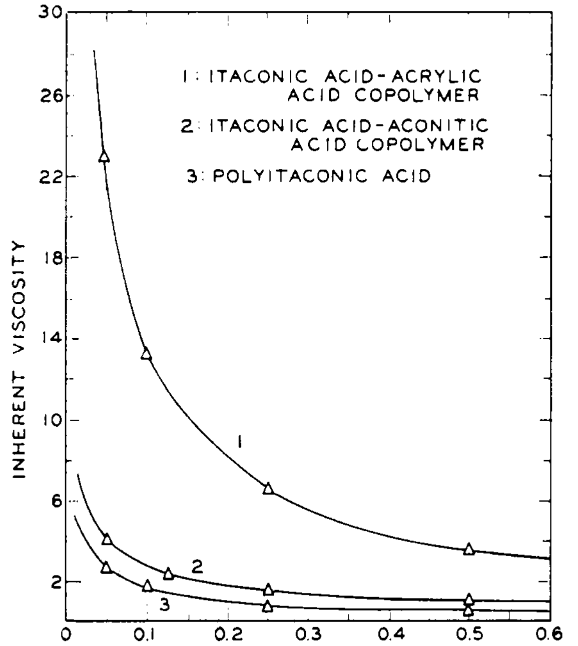

Fig. 1. Viscosity-concentration relationships for dilute aqueous solutions of polyacids

mer was redissolved in water and was reprecipitated by slowly adding the aqueous solution to 8 times its volume of acetone. The polymer was then dried to a constant weight under diminished pressure. An 88% conversion (105 g.) was realized. An analytical sample was freeze-dried from aqueous solution, and then dried at 78° under a pressure of 0.05 mm. Hg.

Anal. Found: C, 46.55; H, 5.53.

Results of inherent viscosity determinations on dilute aqueous solutions of this polymer are given in Figure 1. An attempt to carry out the above polymerization at 0° failed to yield any polymer.

A polymerization mixture containing 10 g. of itaconic acid, 45 ml. of water, 5 g. of acrylic acid, and 0.05 g. of potassium persulfate was allowed to stand 72 hr. at 25°. At this time some itaconic acid was still present as a solid phase. The contents of the bottle were slowly added to 1 l. of acetone, and the precipitated polymer was removed. One g. of hydroquinone was added to the acetone solution, and the solution was evaporated to dryness under vacuum to remove water and acrylic acid. The crystalline residue was then washed with a few milliliters of benzene to remove hydroquinone and acrylic acid. Itaconic acid (7.8 g., m.p. 146–161°) was recovered. The polymer was dried under diminished pressure and 3.9 g. of polymer was obtained. The inherent viscosity of a solution of 0.25 g. of polymer in 100 ml. of water was 3.1. A portion of the copolymer was reprecipitated, freeze-dried from aqueous solution, and dried under a pressure of 0.05 mm. Hg. On the basis of the polymer yield and the recovered itaconic acid this copolymer would be expected to contain 2 moles of itaconic acid for every 3 moles of acrylic acid. From previous experience with these polyacids, about one molecule of water for each molecule of acid would also be anticipated.

Anal. Calcd. for $[(C_5H_6O_4)_2(C_3H_4O_2)_3 5H_2O]_n$: C, 44.01; H, 6.50. Found: C, 44.39; H, 5.59.

Copolymerization of itaconic acid and aconitic acid. The bottles were charged with the recipes listed in Table I and the solutions were allowed to stand for the desired time at the desired temperature. The polymers were isolated by pouring the solutions into acetone to precipitate the polymers which were then dried under diminished pressure.

The product from polymerization No. 1 in Table I was purified by dissolving it in water and reprecipitating it from acetone. The polymer was then freeze-dried from aqueous solution.

Anal. Calcd. for itaconic acid ($C_5H_6O_4$): C, 46.16; H, 4.65; for aconitic acid ($C_6H_6O_6$): C, 41.39; H, 3.47; for $[(C_5H_6O_4)(C_6H_6O_6)]_n$: C, 43.72; H, 4.02. Found: C, 43.83; H, 4.43.

The results of inherent viscosity determinations on solutions of this polymer are plotted in Figure 1.

From the acetone used to precipitate polymer No. 7 (Table I), 6.12 g. of unchanged monomer was isolated. Two-tenths g. of this monomer mixture required 32.70 ml. of 0.1000*N* sodium hydroxide for neutralization to a phenolphthalein end point, for a neutralization equivalent of 61.2. This figure corresponds to a 50/50 molar composition of ita-

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(21) R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140(1946).

conic and aconitic acids. Carbon analysis also corroborated this composition of the recovered acids.

Anal. Calcd. for a 50/50 molar mixture of itaconic and aconitic acids: C, 43.43; H, 3.98. Found for mixture: C, 43.41; H, 4.11.

Neut. Equiv. Calcd. for 50/50 molar mixture: 61.5. Found: 61.2.

Esterification of polyitaconic acid and the itaconic acid–aconitic acid copolymer. The following procedure was used for the preparation of the ethyl ester of both polyitaconic acid and the itaconic acid–aconitic acid copolymer. The transesterification was necessary, since these polymers are insoluble in ethanol.

A 100-ml., three-necked flask was fitted with a dropping funnel and a 12 × $^1/_2$ inch column packed with glass helices and fitted with a distillation head. In the flask were placed 1.5 g. of the polymer and 50 ml. of methanol. The solution was heated until distillation began. *p*-Toluenesulfonic acid (0.5 g.) was introduced, and ethanol was added until the distillation temperature reached 78°. The solution was then heated under reflux overnight. The reaction mixture was cooled and poured into 300 ml. of water. The polymer precipitated, was removed, and dried *in vacuo.*

Anal. Calcd. for polydiethyl itaconate ($C_9H_{14}O_4$): C, 58.05; H, 7.58. Found: C, 50.39; H, 6.11. Thus, esterification of polyitaconic acid proceeded to the extent of about 40%.

Anal. Calcd. for ethyl ester of the itaconic–aconitic acid copolymer: C, 53.70; H, 7.30. Found: C, 48.24; H, 6.05. Thus the itaconic acid–aconitic acid copolymer was about 45% esterified.

Esterification of the itaconic acid–acrylic acid copolymer. Into a 500-ml., one-necked flask fitted with a fractionating column equipped with a Dean-Stark reflux trap and condenser were placed 1.5 g. of the copolymer, 200 ml. of benzene, and 100 ml. of ethanol. About 0.2 g. of *p*-toluenesulfonic acid was added, and the solution was heated under reflux until the ternary azeotrope ceased to separate (about 3 days). The benzene-ethanol solution was then decanted from the polymer which was insoluble in the reaction mixture. The polymer was dissolved in ethanol, reprecipitated from water, and dried under diminished pressure.

Anal. Calcd. for ethyl ester of the itaconic acid–acrylic acid copolymer: C, 58.62; H, 7.85. Found: C, 55.66; H, 7.59. Thus about 75% esterification was achieved.

TABLE II

INHERENT VISCOSITIES OF DILUTE SOLUTIONS OF THE PARTIALLY ESTERIFIED POLYACIDS IN ETHANOL

Partially Esterified Polymer	Concentration of Solution G./100 Ml.	Inherent Viscosity
Polyitaconic acid	0.25	0.23
	0.125	0.22
Itaconic acid–aconitic acid	0.20	0.18
copolymer	0.10	0.15
Itaconic acid–acrylic acid	0.25	1.72
copolymer	0.125	1.73

Copolymerization of itaconic acid and butadiene. Two polymerization bottles were charged with 5 g. of itaconic acid, 1 g. of Triton X-301,[22] 0.02 g. of *n*-decyl mercaptan, 35.0 ml. of water, 0.05 g. of potassium persulfate, and 15 g. of butadiene. The bottles were tumbled for 23 hr. at 50° and then cooled and opened. After unchanged butadiene had evaporated, the contents were slowly added to 150 ml. of alum coagulant. White polymer coagulated. The material was washed with water to which a few milliliters of hydrochloric acid had been added, and then was dissolved in tetrahydrofuran and reprecipitated from acidified water. The polymer was washed with methanol, redissolved in tetrahydrofuran in which 1 g. of *N*-phenyl-β-naphthylamine had been dissolved, and reprecipitated from water. The polymer was dried *in vacuo.* Eight g. of polymer (20% conversion) was obtained. The polymer was 100% soluble, and had an inherent viscosity of 1.41 in tetrahydrofuran solution. Analysis shows the copolymer contains 20 wt. % of the itaconic acid.

Anal. Calcd. for butadiene (C_4H_6): C, 88.81; H, 11.18; for itaconic acid ($C_5H_6O_4$): C, 46.10; H, 4.61. Found: C, 79.65; H, 10.02.

Homopolymerization of diethyl itaconate. A mixture of 7.2 g. of diethyl itaconate, 20 g. of ORR soap solution,[23] 0.05 g. of lauryl mercaptan (Hooker Electrochemical Co.), and 0.05 g. of potassium persulfate was placed in 2 bottles which were tumbled at 50° for 65 hr. The contents of 2 such polymerization charges were poured into 100 ml. of sodium chloride–sulfuric acid coagulant to coagulate the polymer. The polymer was shredded and thoroughly washed with water. The polymer was then dissolved in acetone and the solution was filtered to remove soap. The polymer was then reprecipitated with water. The polymer was dried, dissolved in benzene, reprecipitated from petroleum ether, and dried under diminished pressure. Twelve g. of polymer, having an inherent viscosity of 0.11 in ethanol solution, was obtained.

A small portion of the polymer was redissolved in benzene, freeze-dried, and submitted for analysis.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.62; H, 7.82.

When the polymerization was attempted at 0° and at 26° using this recipe, no polymer was obtained.

In a similar manner polymerization bottles were charged with 40 g. of ORR soap solution, 14 g. of dimethyl itaconate, a drop of lauryl mercaptan (Hooker Electrochemical Co.), and 0.045 g. of potassium persulfate and tumbled at 50°. The contents of each bottle were then poured into 50 ml. of sodium chloride coagulant solution to coagulate the polymers. The polymer was shredded, washed with water, and dried. The polymer was then dissolved in benzene and reprecipitated with pentane, and then dried under reduced pressure. Analytical samples were freeze-dried from benzene solution. The results of these experiments are given in Table III.

Somewhat better conversions were obtained when the following recipe was used: 10 g. of dimethyl itaconate, 1 g. of Triton X-301, 35 g. of water, a drop of lauryl mercaptan (Hooker Electrochemical Co.) and 0.045 g. of potassium persulfate. The contents of each bottle were then added to 40 ml. of alum coagulant. The polymer coagulated as a fine

TABLE III

EMULSION HOMOPOLYMERIZATION OF DIMETHYL ITACONATE

Time, Hr.	Modifier, G.	Conversion, %	Inherent Viscosity[a]
		ORR Soap Recipe	
50	0.025	43	0.15
70	0.01	50	0.35
72	0.00	50	0.28
		Triton X-301 Recipe	
46	0.01	100	0.22
48	0.00	94	0.25

[a] 0.25 g./100 ml. of benzene.

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(22) A 20% solution of sodium alkyl aryl polyether sulfate supplied by Rohm & Haas Co.

(23) A special soap made to Office of Synthetic Rubber specifications from tallow fatty acids by Procter and Gamble Co. Used as a 2.8% aqueous solution.

powder and was removed by filtration. The polymers were dissolved in chloroform and reprecipitated from a solution of 500 ml. of methanol and 100 ml. of water. The products were redissolved in chloroform, reprecipitated from petroleum ether, and dried under diminished pressure. These experiments are also summarized in Table III.

Anal. Calcd. for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.40; H, 6.29.

Similarly charges of 10 g. of di-*n*-butyl itaconate, 35 g. of ORR soap solution, 0.01 g. of lauryl mercaptan (Hooker Electrochemical Co.) and 0.06 g. of potassium persulfate were used in the soap recipe, and of 10 g. of ester, 1 g. of Triton X-301, 35 ml. of water, 0.01 g. of lauryl mercaptan (Hooker Electrochemical Co.) and 0.06 g. of potassium persulfate were used in the Triton X-301 recipe.

The bottles were allowed to tumble at 50° for 44 hr. The polymers were isolated and purified by the same procedure used before. The results on the butyl esters are recorded in Table IV.

TABLE IV

EMULSION HOMOPOLYMERIZATION OF DI-*n*-BUTYL ITACONATE

Recipe	Polymer, G.	Conversion, %	Inherent Viscosity
Triton X-301	7.2	72	0.23
ORR soap	10.0	100	0.26

Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.25; H, 9.08.

TABLE V

EMULSION COPOLYMERIZATION OF DIMETHYL ITACONATE WITH BUTADIENE

Sample No.	Monomer[a] Ratio	Time, Hr.	Conversion, %	% Incorp. of Ester	Solubility, %	Inherent Viscosity[b]
1	10/10	20	100	48.7	14.6	6.1
2	15/5	20	93	29.2	10.0	8.3
3	17.5/2.5	7	95	17.6	100.0	1.4
4	17.5/2.5	5	60	19.7	100.0	2.2
5	18.4/1.6	5.5	75	10.9	100.0	2.4

[a] Butadiene/dimethyl itaconate. [b] Determined on soluble portions only.

Reduction of polydimethyl itaconate. In a 2-l. flask fitted with a Vibrostirrer, gas inlet tube, and Soxhlet extractor was placed a solution of 10.0 g. (0.0635 mole) of polydimethyl itaconate in 1200 ml. of tetrahydrofuran.[24] In the thimble of the extractor was placed 9.8 g. (0.26 mole) of lithium aluminum hydride. Stirring was commenced, and the reaction mixture was heated under reflux while a slow stream of nitrogen was passed through the apparatus. The first extraction resulted in a vigorous reaction. The reaction was continued 11 hr. and a finely divided gel precipitated in the reaction flask. Heating was then discontinued, and the reaction mixture was allowed to stir overnight. About 50 ml. of ethyl acetate was then added to decompose excess hydride. About 300 ml. of 2*N* sulfuric acid was then slowly added, causing the reaction mixture to separate into 2 phases. The polymer adhered to the walls of the flask. The solutions were removed by decantation and the polymer was dissolved in a water-dioxane mixture. The polymer was insoluble in tetrahydrofuran, chloroform, acetone, dioxane, and water, but dissolved in the mixture of water and dioxane. The polymer was purified by precipitating from solution in acetone, washing with water to remove aluminum salts, redissolving in a dioxane-water mixture, and reprecipitating from acetone. The polymer was dried *in vacuo*. Four and two-tenths g. (70%) of polymer was obtained.

Anal. Calcd. for dimethyl itaconate ($C_7H_{10}O_4$): C, 53.16; H, 6.37; for alcohol ($C_5H_{10}O_2$): C, 58.80; H, 9.87. Found: C, 58.46; H, 8.84.

A slight residue was obtained on ignition which could arise from incomplete hydrolysis of alkoxy-aluminum bonds, which could account for the low hydrogen analysis. A weak carbonyl band was present in the infrared spectrum.

Copolymerization of dimethyl itaconate with butadiene. A modified mutual recipe[25] consisting of 40 g. of ORR soap solution, 0.025 g. of lauryl mercaptan (Hooker Electrochemical Co.), 0.06 g. of potassium persulfate, and 20 g. of monomers was used. The polymerizations were carried out at 50° in a tumbling bath. Ten ml. of methanolic *N*-phenyl-β-naphthylamine was added to each before coagulation of the latex was effected with sodium chloride–sulfuric acid coagulant. The polymers were then shredded, washed thoroughly with water, and dried to a constant weight under diminished pressure. Polymers to be used in subsequent reduction reactions were dissolved in benzene and reprecipitated from methanol. Analytical samples were purified 3 times by this process and dried *in vacuo*. The results are recorded in Table V.

The infrared spectra of these polymers, determined in chloroform, exhibited the following bands: 2980, 2900, 1725, 1635, 1440, 1200, 1020, 975, and 915 cm.$^{-1}$.

Preparation of a butadiene-2-hydroxyethylallyl alcohol copolymer. The procedure used for this reaction is similar to the one used for the reduction of a butadiene–methyl acrylate copolymer.[26]

TABLE VI

RESULTS OF ELEMENTAL ANALYSES OF BUTADIENE–DIMETHYL ITACONATE COPOLYMERS

Anal. Calcd. for butadiene (C_4H_6): C, 88.82; H, 11.18; for dimethyl itaconate ($C_7H_{10}O_4$): C, 53.16; H, 6.37.

Found:

Sample No.	% Carbon	% Hydrogen	% Incorporation of Ester
1	71.28	8.99	48.7
2	78.49	9.69	29.2
3	83.85	11.01	17.6
4	81.75	10.29	19.6
5	84.94	10.63	10.9

In a 5-l. flask fitted with a Vibrostirrer, gas inlet tube, and Soxhlet extractor was placed 12.0 g. of the dimethyl itaconate–butadiene copolymer (Sample No. 4, 80% butadiene–

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[24] Purified by passing through a column of Linde Molecular Sieves, No. 13X.

[25] R. L. Frank, J. R. Blegen, G. E. Inskeep, and P. V. Smith, *Ind. Eng. Chem.*, **39**, 893 (1947).

[26] C. S. Marvel, R. M. Potts, and C. King, *J. Am. Chem. Soc.*, **77**, 177 (1955).

20% dimethyl itaconate). To this was added 1500 ml. of pure tetrahydrofuran, and the mixture was stirred until the the solution of the polymer was complete. In the thimble of the extractor was placed 6.0 g. of lithium aluminum hydride. Nitrogen was bubbled through the system, and the solution was heated under reflux with stirring to extract the lithium aluminum hydride into the reaction mixture. The first extraction resulted in a vigorous reaction as did the second; however, the reaction subsided thereafter. The mixture was heated under reflux 6 hr. About 40 ml. of ethyl acetate was then added to the gelled mixture to decompose excess lithium aluminum hydride. Then 1*N* sulfuric acid was added to the reaction mixture until the *p*H reached 4 (about 200 ml.). The mixture was then stirred 16 hr. Additional acid was added during this time to keep the *p*H at the mentioned level. The polymeric material had not dissolved, so the solution was decanted, and the polymer was stirred with a chloroform-dioxane mixture. A portion of the material dissolved. The gel solution was spun in a centrifuge and then filtered through a 100-mesh screen. A portion of the filtrate was slowly added to methanol, and polymer precipitated. The polymer was pressed as free as possible from solvent and was redissolved in chloroform (10% solution) and submitted for infrared spectral analysis. No carbonyl band appeared in the spectrum. A second spectrum was obtained on this material in 40% chloroform solution, and a weak carbonyl band appeared.

Another portion of the dioxane-chloroform solution of the polymer was precipitated from a saturated methanolic solution of *N*-phenyl-β-naphthylamine. The polymer was allowed to stand in this solution until the amine began to crystallize. The polymer was then removed and dried *in vacuo*. This material only swelled when allowed to stand in a 50% chloroform-dioxane solution. The addition of a small portion of ethanol to this solution did not aid dispersion. The remainder of the polymer which was precipitated and dried without the antioxidant also remained insoluble.

Preparation of 2-hydroxyethylallyl alcohol. A slurry of 13.3 g. (0.35 mole) of lithium aluminum hydride in 500 ml. of ether was placed in a 1-l., three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. Stirring was started, and a solution of 50.0 g. (0.27 mole) of diethyl itaconate in 100 ml. of ether was slowly added at such a rate that a gentle reflux was maintained (3 hr. were required for the addition). The reaction mixture was allowed to stir for an additional 30 min., and 50 ml. of ethanol was carefully added to decompose excess hydride. About 100 ml. of 1*N* sulfuric acid was then added, and aluminum hydroxide precipitated. This was removed by filtration and the filtrate was dried over a mixture of anhydrous sodium carbonate and sodium sulfate. The precipitate was placed in water and acid was added until it dissolved. The solution was extracted twice with 100-ml. portions of ether, and the extract was added to the filtrate. The filtrate was concentrated *in vacuo*, and the residue was distilled under reduced pressure. Five and two-tenths g. (20%) of material, b.p. 125-126°/16 mm. Hg, was obtained; however, 22 g. of polymeric material was present in the distillation pot. The distillate was redistilled through a 6-in. Holtzmann column, with a copper coil placed in the pot to inhibit polymerization. Four and six-tenths g. of product, b.p. 62–63°/0.01 mm. Hg, n_D^{20} 1.4689, was obtained.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.80; H, 9.87. Found: C, 58.74; H, 10.02.

An infrared spectrum of this product exhibited the following bands: 3600, 3350, 2900, 1645, 1450, 1430, 1210, 1025, 910, and 855 cm.$^{-1}$.

Preparation of bis(N,N-dimethyl)itaconamide. Itaconyl chloride was prepared by the method of Feuer and Pier.[27] When molar quantities of reactants were used, the yield was 98 g. (60%) of clear liquid, b.p. 98–100°/16 mm. Hg.

A solution of 44.4 g. (0.26 mole) of itaconyl chloride in 200 ml. of chloroform was placed in a 300-ml. flask fitted with a stirrer and gas inlet tube, and cooled in an ice bath. Anhydrous dimethylamine was bubbled into the agitated solution for 7 hr. At the end of this time the reaction mixture was filtered to remove precipitated salt. The solution was then diluted with twice its volume of diethyl ether to precipitate dimethylamine hydrochloride. The mixture was again filtered and concentrated. The residue was distilled through a 6-in. Vigreux column. The yield was 33 g. or 68% of the theoretical amount, b.p. 105–115°/0.05 mm. Hg. The distillate was fractionally distilled through a 12-in. Vigreux column. The main fraction (30 g.) boiled at 105°/ 0.01 mm. Hg, n_D^{20} 1.5018.

Anal. Calcd. for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.54; H, 8.88; N, 15.27.

The infrared spectrum of this product, determined in chloroform solution, exhibited the following bands: 3000, 1690, 1650–1620, 1500, 1450, 1400, 1260–1200, 1150, 1100, and 925 cm.$^{-1}$

Anionic rearrangement of bis(N,N-dimethyl)itaconamide. In an attempt to cause homopolymerization of the amide, a rearrangement was effected by the following procedure.

In 100 ml. of liquid ammonia in a 200-ml. flask cooled to −78° in a Dry Ice–acetone bath was dissolved 0.04 g. of clean sodium. A deep blue color prevailed in the solution. To the solution was quickly added 9.1 g. of bis(*N*,*N*-dimethyl)itaconamide. The blue color was discharged immediately. The solution was allowed to warm to room temperature to remove the ammonia by evaporation. A brownish red residue remained. This was washed with ether to remove monomer, and dried *in vacuo*. A light tan solid (1.8 g.) was obtained. The solid crystallized to white needles from heptane. After 3 recrystallizations from heptane, the material (VII) melted at 83–84°.

Anal. Calcd. for $(C_9H_{16}N_2O_2)$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.86; H, 8.63; N, 15.12; C, 58.84; H, 9.00; N, 15.21.

Mol. wt. calcd.: 186. Found: 198 (Rast).

The rearrangement product (VII) only slowly decolorized bromine solution, and slowly gave a Von Baeyer test. Bis(*N*,*N*-dimethyl)itaconamide reacts instantaneously with bromine and potassium permanganate. An ultraviolet absorption spectrum determined on VII in ethanol solution showed a λ_{max} at 235 mμ with a molar extinction coefficient of 8700. Ultraviolet spectra of bis(*N*,*N*-dimethyl)itaconamide, itaconamide, or acrylamide in ethanol solution at similar concentrations exhibited no absorption maxima in the 200–350 mμ region. A nuclear magnetic resonance spectrum determination of VII in chloroform solution at 41.08 m.c. gave the following Δ c.p.s. values relative to chloroform: 64.4 (olefinic hydrogen, triplet); 182.1 (amide methyl groups, 3 peaks—2 shifted); 218.0 (methyl group attached to olefin, doublet). The infrared spectrum of VII (chloroform) exhibited the following bands: 2965, 2910, 1655, 1625, 1500, 1450, 1420, 1405, 1335, 1265, 1150, 1110, 1060, 1040, 940, 850, and 660 cm.$^{-1}$.

Alkaline hydrolysis of VII. In a 25-ml. flask was placed 0.5 g. of VII, 15 ml. of water, and 0.5 g. of sodium hydroxide. The solution was heated on a steam bath for 11 hr. The odor of dimethylamine was present in the hydrolyzate. The solution was cooled and acidified to a *p*H of 2 with dilute hydrochloric acid. The solution was evaporated slowly to dryness. The white residue was extracted with chloroform to remove any dimethylamine hydrochloride. The residue was recrystallized twice from water, m.p. 200-202° (corr.). A mixture of the crystals with an authentic sample of mesaconic acid melted at 201–203° (corr.).

After treatment of both maleic acid and fumaric acid with base under the conditions employed in the hydrolysis, no isomerization was noted. Thus it is likely that no isomerization occurred in the hydrolysis.

URBANA, ILL.

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(27) H. Feuer and S. M. Pier, *Org. Syntheses*, **33**, 41 (1953).