The Polymerization and Polymers of Itaconic Acid Derivatives. VI.[1] *The Polymerization and Copolymerization of Itaconic Anhydride*[2]

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Previous work reported in this series of papers has shown that[3] the rate constants of the polymerization of dialkyl itaconates decrease in the order of di-2-ethylhexyl> di-*n*-butyl>di-*n*-propyl≃diethyl>dimethyl, and that[4] the monomer reactivity ratios in the copolymerization with vinyl chloride are as follows: $r_1=0.053\sim0.06$ (M_1: vinyl chloride) and $r_2=5.1\sim7.0$ (M_2: dialkyl itaconates).

The purpose of the present investigation is to clarify the polymerization and copolymerization characteristics of itaconic anhydride compared with those of itaconic esters.

While many reactions of itaconic anhydride are described in the literature, its polymerization has not yet been reported* except for a few patents[5] including copolymers with styrene.

Experimental

Materials.—Itaconic anhydride (produced by the Tokyo Kasei Co.) was recrystallized from ethyl ether. M. P. 67∼68°C. Dimethyl itaconate and di-2-ethylhexyl itaconate were prepared by the method described before.[4] Vinyl chloride, supplied by the Kanegafuchi Kagaku Co., was used as a comonomer. Butyl acetate and tetrahydrofuran were distilled and used as solvents in the copolymerization.

Copolymerization.—The copolymerization of itaconic anhydride with vinyl chloride was carried out, first in butyl acetate and then in tetrahydrofuran, in both cases in a sealed glass tube at 50°C. In both cases, copolymers were found to precipitate after copolymerization. The precipitates were filtered and washed with ethyl ether before being dried. The compositions of the copolymers were determined by the analysis of their chlorine contents.

The Rate of Polymerization.—The rates of the bulk polymerization of itaconic anhydride, dimethyl itaconate and di-2-ethylhexyl itaconate were measured in a dilatometer at 75°C. It is difficult to feed a monomer as crystal or powder through the capillary tubing into the bulb of the commonly-used dilatometer. In the present study a special dilatometer, shown in Fig. 1, was used. In this apparatus the capillary tubing and the bulb were connected by ground glass joints in order to facilitate the feeding of the monomer. The height of the meniscus of the melted monomer could be controlled by means of a movable bottom of mercury, which will be described below. There are two chambers, A and B, separated by a glass stopper, C. First, with C opened, several milliliters of clean mercury was charged into the bottoms of both A and B. Then C was closed. Monomer was charged into A on the mercury, and then the initiator was charged. Assembled with the tubings, the dilatometer was attached to the vacuum line. The content of the dilatometer was degassed and flushed with nitrogen alternatively. Then the dilatometer was immersed in a thermostat set at 75°C. As soon as the monomer melted, the dilatometer was picked up quickly and inclined, with the stopper C, and D and E opened, so that the mercury in B moved over to A, sending the liquid monomer

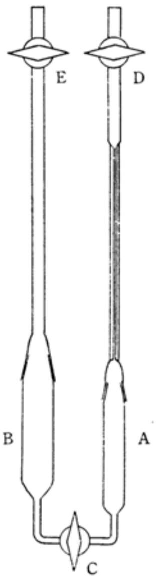

Fig. 1. The dilatometer used in the present study.

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[1] Part V of this series; S. Nagai, This Bulletin, 36, 1459 (1963).

[2] Presented at the Local Meeting of the Chemical Society of Japan, Fukuoka, October, 1961,

[3] S. Nagai and K. Yoshida, *Chem. High Polymers, Japan*, 17, 79 (1960).

[4] S. Nagai and K. Yoshida, ibid., 17, 77 (1960).

* After this paper was presented,[2] two other reports[6,7] appeared.

[5] U. S. Pat. 2625471 (1952); 2625529 (1953); etc.

[6] J. Drougas and R. L. Guile, *J. Polymer Sci.*, 55, 297 (1961).

[7] S. Ishida and S. Saito, *J. Japan Soc. of Color Material*, 35, 377 (1962).

TABLE I. THE COPOLYMERIZATION OF ITACONIC ANHYDRIDE AND VINYL CHLORIDE

Monomers in feed g.				Solvent cc.		Time hr.	Conversion wt. %	Mol. % of ItAnh	
VC	ItAnh	AIBN	BPO	BuAc	THF			in Monomers	in Copolymer
7.207	0.112	0.0828		15		3	1.5	0.86	26.9
7.120	0.111		0.1395		5	6	21	0.86	—
7.204	0.224	0.0835		15		5	1.4	1.7	47.7
6.918	0.560	0.0863		15		5	0.3	4.32	—
7.306	0.560	0.0860		15		8.25	1.9	4.10	58.3
6.258	0.562	0.0855		15		9.5	2.2	4.77	53.8
6.941	0.561		0.1395		5	6	4.8	4.31	54.6
6.055	1.125	0.0911		15		17.5	2.6	9.39	61.5
5.803	1.125		0.1294		5	12	8.5	9.75	66.2
7.541	2.245	0.0993		25		17.5	1.9	14.24	62.7
7.142	2.243		0.1694		5	6	7.2	14.8	73.3

TABLE II. RATE OF POLYMERIZATION OF ITACONIC ANHYDRIDE IN COMPARISON WITH THOSE OF ITACONIC ESTERS*

Monomer	ItAnh		DMI	DEHI
Wt. of monomer, g.	3.1798	3.1129	4.1224	3.6837
Wt. of initiator, g.	0.0173	0.0325	0.0349	0.0113
Polymerization time, min.	92	73	61	65
Yield of polymer, g.	0.9146	1.3318	0.5677	0.8557
Conversion, %	28.6	42.4	13.3	23.2
Initial volume of the system, cc.	2.55	2.51	3.95	4.10
Mol. of monomer, $\times 10^2$	2.84	2.78	2.67	1.04
[M], mol./l.	11.1	11.1	6.76	2.53
Mol. of initiator, $\times 10^4$	0.72	1.34	1.44	0.47
[I]/[M], mol. ratio	1/397	1/208	1/185	1/223
[I], mol./l. $\times 10^2$	2.80	5.34	3.65	1.14
R_p,** mol./l./min. $\times 10^2$	4.63	6.53	1.63	0.90
k_o,** $l^{1/2}$/mol$^{1/2}$/min. $\times 10^2$	2.49	2.54	1.26	3.34
$[\eta]_{\text{acetone}}$, 100 cc./g.	0.132	0.195	0.128	—

* Polymerization temperature was 75.1°C and the initiator used was benzoyl peroxide.

** R_p was calculated from the initial slope of the curve shown in each Fig. and the rate constant k_o was calculated assuming $R_p=k_o[\mathrm{M}][\mathrm{I}]^{1/2}$.

on the mercury up until the meniscus rose to a sufficient level of the capillary. Then, with all the stoppers closed, the dilatometer was again immersed into the bath. It took less than 7 min. from the first immersion to the final setting. The polymerization time was counted from this final setting, and the rate of the shrinkage of the monomer was measured with a cathetometer. After it had been polymerized for 1～2 hr., the dilatometer was taken off the bath and cooled. Polyitaconic anhydride was precipitated by pouring an acetone solution of the reaction mixture into a large excess of ethyl ether; it was then washed with fresh ether and dried in a vacuum oven at 40～50°C. for several hours. For polydimethyl itaconate and polydi-2-ethylhexyl itaconate, benzene was used as the solvent and methanol was used as the precipitant.

Viscosity Measurement.—The viscosity of the polymer solution was measured by a Ubbelohde-type viscometer at 30°C, using acetone as the solvent.

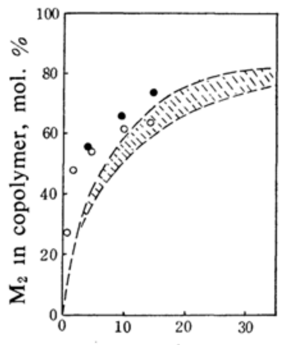
Hydrolysis.—Polyitaconic anhydride (54.1 mg.) was dissolved in 50 ml. of water at room temperature. After it had been stirred for 5 min., the pH of the solution showed 3.1; it changed no more, even after 24 hr.

Results and Discussion

Copolymerization.—The results of the copolymerization of itaconic anhydride and vinyl chloride are presented in Table I and Figs. 2 and 3.

From these results it can be seen that, when copolymerized with vinyl chloride, the anhydride always produced copolymers with considerably higher ratios of anhydride than in the feed. This tendency is quite analogous to the case of itaconic esters and vinyl chloride, as Fig. 2 shows.

The monomer reactivity ratios are approximately 5～10 for r_2 (M_2: ItAnh) and 0.01 for r_1. However, it is rather difficult to determine their definite values for each solvent system,



M$_2$ in monomer mixture, mol. %

Fig. 2. Relationship between monomer compositions and copolymer compositions in the copolymerization of vinyl chloride (M$_1$) and itaconic derivatives (M$_2$).
○ M$_2$: ItAnh (in BuAc), ● M$_2$: ItAnh (in THF), dotted line zone: M$_2$: DMI, DEI, DiPI and DEHI (bulk)

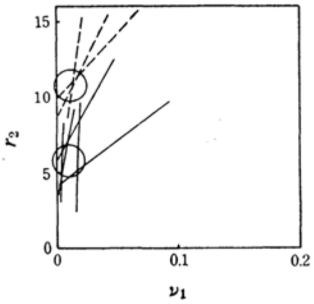
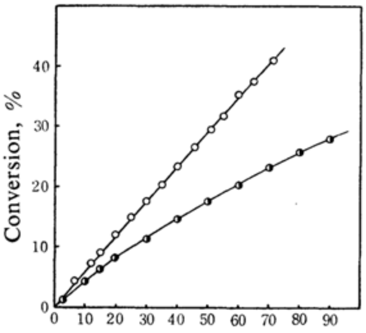
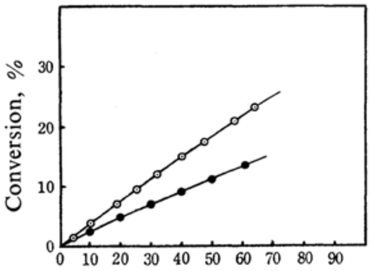


Fig. 3. Diagram of calculation for r_1 and r_2.
---- VC-ItAnh (in THF)
—— VC-ItAnh (in BuAc)



Time, min.

Fig. 4. Relationship between time and conversion in the bulk polymerization of ItAnh, at 75°C, by dilatometry.
—○— $[I]=5.34\times10^{-2}$ mol./l.
—◑— $[I]=2.80\times10^{-2}$ mol./l.



Time, min.

Fig. 5. Relationship between time and conversion in the bulk polymerization of itaconic esters, at 75°C, by dilatometry.
—⊙— DEHI, $[M]=2.53$ mol./l.
$[I]=1.14\times10^{-2}$ mol./l.
—●— DMI, $[M]=6.76$ mol./l.
$[I]=3.65\times10^{-2}$ mol./l.

since a large difference exists between r_1 and r_2 values; on the other hand, in the case of itaconic anhydride and styrene Drougas and Guile[6] determined somewhat different values for r_1 and r_2 depending on the different solvent systems.

The Rate of Polymerization.—The copolymerization data obtained above suggest that itaconic anhydride homopolymerizes quite readily. For the preliminary test the bulk polymerization in a sealed glass tube was carried out at 75°C, using 5 wt. % benzoyl peroxide as the initiator. After the polymerization had continued for 140 min., the conversion of the monomer to the polymer was about 76%.

Detailed results of the dilatometry are shown in Figs. 4 and 5 and in Table II.

It is of interest to note that the rate constant of the polymerization (k_o) of itaconic anhydride is larger than that of dimethyl itaconate but smaller than that of di-2-ethylhexyl itaconate. As for the viscosity data, although the intrinsic viscosity of the polyitaconic anhydride obtained was somewhat larger than that of polydimethyl itaconate, these small values of both polymers, at any rate, represent very low $\bar{P}$ values.

The above facts might be partly explained qualitatively by considering the propagation reactivity as well as the chain transfer reactivity of the anhydride in comparison with those of dialkyl itaconates.[3] It is thought that the double bond of itaconic anhydride is in the most free state from the steric effect, if any, of the adjacent carboxylate groups among the double bonds of itaconic derivatives. This advantage might serve somewhat to increase k_o. On the contrary, it is also considered that the anhydride has the most exposed active methylene among the itaconic derivatives. This might increase the anhydride's susceptibility to the chain transfer reaction and, hence, decrease k_o to some degree. Perhaps the observed rate of polymerization can be determined from a balance of these factors. Of course, however, it is not possible at present to come to any definite conclusion.

Infrared Spectra.—Infrared absorption spectra of the monomer and polymer are presented in Fig. 6. The bands near 1665 cm^{-1} (CH_2=C< stretching), 1408 cm^{-1} (CH_2=C< in plane deformation) and 925 cm^{-1} (CH_2=C< out plane deformation) in the monomer disappeared in the polymer, while the bands near 1850 and 1760 cm^{-1} (C=O stretching) and 1220 cm^{-1} (C–O–C stretching) in the monomer remained, slightly shifting to 1860, 1775 and 1225 cm^{-1} respectively after polymerization.

Solubility Test.—Ten milligrams of itaconic anhydride did not dissolve in 4 cc. portions of petroleum ether, ligroin, *n*-hexane, cyclohexane, benzene, toluene or carbon tetrachloride at room temperature. The monomer dissolved in ethyl ether and chloroform, but the polymer did not dissolve. The solvents for both the monomer and the polymer so far tested are acetone, cyclohexanone, ethyl methyl ketone, dioxane, glacial acetic acid, tetrahydrofuran and ethyl ether. Water, alcohols, dimethyl sulfoxide, dimethyl formamide, and pyridine may be classified as reactive solvents. The anhydride dissolved rapidly in methyl alcohol, but it did so slowly in ethyl and propyl alcohols. It is considered that the corresponding monoesters were partly formed. When the anhydride was dissolved in dimethyl sulfoxide, dimethyl formamide and pyridine respectively, a yellow or brownish yellow color appeared, and this became deeper with time. Perhaps some complex was formed, but this has not yet been confirmed. In the case of the polymer solution, the color was slight and did not become deeper with heating.

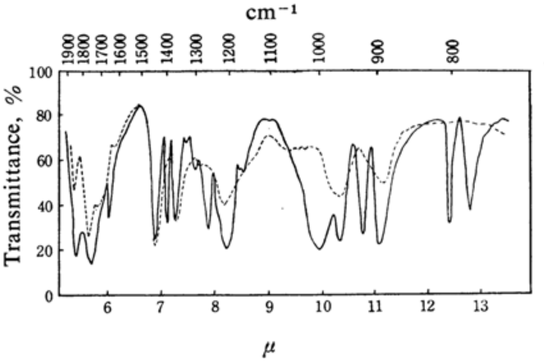


Fig. 6. Infrared spectra of monomer (——) and polymer (----). (Nujol).

The Hydrolysis of the Polymer.—The hydrolysis of polyitaconic anhydride was carried out with ease, yielding polyitaconic acid or its copolymer structure with the unreacted anhydride, if any. The viscosity measurement of the aqueous solution of polyitaconic anhydride showed a concentration-viscosity curve similar to that of polyitaconic acid, as Fig. 7 shows.

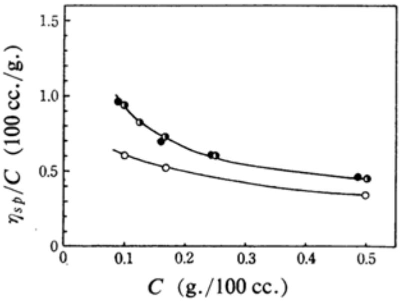


Fig. 7. Viscosity of aqueous solution of polyitaconic anhydride polymerized in bulk with $[I]=2.80\times10^{-2}$ mol./l. (◑) and $[I]=5.34\times10^{-2}$ mol./l. (○) at 75°C compared with that of polyitaconic acid obtained previously by polymerization of itaconic acid with $[M]=1.5$, $[I]=1.0\times10^{-2}$ mol./l. at 50°C (●).

It is of much interest that polyitaconic acid is easily obtained (in the form of an aqueous solution) in the course of the polymerization of itaconic anhydride, followed by a simple isolation process and further hydrolysis,* while the direct polymerization of itaconic acid itself has been stated to occur only rarely in bulk, in acetone and methyl alcohol, but chiefly in water.**

Summary

The copolymerization of itaconic anhydride and vinyl chloride has yielded copolymers with itaconic anhydride much richer than that in the feed. The rate of the homopolymerization of itaconic anhydride has been compared with the rates of itaconic esters, obtaining the following order: di-2-ethylhexyl ester>anhydride>dimethyl ester. The infrared spectra and solubility character of the polymer have been shown in comparison with those of the monomer. Further, polyitaconic acid has been obtained by the hydrolysis of polyitaconic anhydride with some ease.

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* Although the preparation of polyitaconic acid by means of the hydrolysis of polyitaconic anhydride might easily follow from the knowledge of the reactivity of anhydride, the homopolymerization of itaconic anhydride itself had been an untouched problem before the beginning of the present study.

** It was rather tedious to isolate the polymer from the solution of the reaction mixture in this case (Ref. S. Nagai and K. Yoshida, *Chem. High Polymers, Japan*, **17**, 748 (1960)).

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