

Structural Chemistry of Polymerizable Monomers. II. Polymerization and Structure of Itaconic Acid in the Solid State[†]

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ABSTRACT: The solid-state polymerization of itaconic acid (IA) was investigated with and without the catalyst (dibutyl peroxide) at 100, 120, and 150°C, respectively. The reaction products were identified as oligomers by elemental, infrared, and liquid chromatographic analyses. The relation between the crystal structure of IA and its reactivity in the solid state was also studied. It was deduced that the spacing and the angle between olefinic π -orbitals of adjacent vinyl groups, the conformation of the molecules, and the kinks of hydrogen bonds are probably the most important factors for determining the reactivity of the monomer in the solid state.

KEY WORDS Itaconic Acid / Solid-State Polymerization / Oligomerization / Solid-State Oligomerization / Crystal Structure / X-Ray Analysis /

Recently, the crystal structure of *N*-vinylcarbazole (NVC), which is one of the solid-state polymerizable monomers, was determined and the correlation between its crystal structure and its solid-state reaction was discussed.¹ The present study deals with itaconic acid (IA), which is a well-known monomer in the field of solution polymerization. It was once thought that IA does not homopolymerize in any medium. One of the present authors, T. H.,^{2,3} previously studied the copolymerization of IA and showed that its monomer reactivity ratios depend on the medium. From this point of view, its homopolymerization in an appropriate medium can be expected. Nagai, *et al.*,⁴ and Marvel⁵ reported that IA was homopolymerized with a radical initiator in an aqueous solution. However, Ishida⁶ found that the polymerization of IA by γ -irradiation in the crystal-

line state could not be successfully carried out. After our completion of the crystallographic work,[†] a paper describing the structure of IA was presented by Harlow, *et al.*,⁷ but no detailed discussion has been reported on the crystal structure of IA. In the present study the crystal structure of IA was determined and the polymerization of IA was tried at a temperature below its melting point with and without a radical initiator; its reactivity is then discussed from a crystallographic point of view.

EXPERIMENTAL

Materials

IA monomer (commercial grade made by Charles Pfizer, USA) was purified by recrystallization twice from water, mp 167.5–168.7°C. Commercially available dibutyl peroxide (DBP) was distilled under a reduced pressure, bp 40°C (23 mm).

Polymerizations

Solid-State Polymerization. The required amounts of IA and DBP were weighed in a

[†] A crystallographic part of this study was presented at the 23rd Annual Meeting of the Society of Polymer Science, Japan, at Tokyo, May, 1974. See Abstracts, p 449.

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glass tube and the tube was sealed under nitrogen atmosphere. The solid-state polymerization of IA was examined under the conditions shown in Table I. After the volatile compounds from all reaction mixtures were removed, the residues were identified by elemental, infrared, and liquid chromatographic analyses.

Solution Polymerization. According to the procedure of Nagai, IA (1.9919 g) in water (10 ml) was polymerized with $K_2S_2O_8$ (38.5 mg) at $50^\circ C$. The polyitaconic acid (PIA) was isolated by pouring the reaction mixture into 100 ml of acetone. The crude polymer was washed with acetone and then dried *in vacuo*. $[\eta]$ ($c=0.1$ g/water solution of 100 ml, $30^\circ C$)=0.945, $D_{obs}=1.248$ g·cm⁻³.

Measurements

The infrared spectra of the products were measured with a JASCO IR A-2 infrared spectrophotometer, using films obtained by evaporating a tetrahydrofuran (THF) solution of the product on KBr plates. Gel-permeation chromatograph (GPC) experiments were made on a Yanagimoto GPC Model L-1030, equipped with a continuously variable UV-visible detector M-214, using THF as eluting agent.

Crystallographic Study

The crystal is orthorhombic: $a=5.462(3)$, $b=11.573(4)$, $c=18.528(4)$ Å; $D_x=1.476$ g·cm⁻³ ($Z=8$). The space group is *Pbca*. Weissenberg intensity data ($0kl-3kl$, $h0l-h4l$, $hk0-hk2$) were collected by means of Cu K_α radiation. There were 992 independent reflections, of which 212 were too weak to be observed. The crystal structure was solved by direct methods.⁸ All the hydrogen atoms were found by a difference Fourier synthesis. The final R factor was 9.1% for the observed reflections. The X-ray photographs of products obtained during solid-state polymerization, except for PIA which is amorphous, showed clear diffraction patterns (Debye rings).

RESULTS

Solid-State Polymerization

It has been reported that no polymer was obtained under γ -irradiation by the 300-Ci.⁶⁰Co source at $50-100^\circ C$ for 6 days (5.1×10^4 R/hr of

Table I. Oligomerization conditions of itaconic acid in solid state

Run no.	Monomer, g	DBP, g	Temp, °C	Reaction time, day
a	2.035	0	100	7
b	2.082	0.01	100	7
c	2.045	0	120	7
d	2.043	0.01	120	7
e	2.073	0	150	5
f	2.046	0.01	150	5

does rate) in the crystalline state.⁶ On the other hand, the thermal polymerization in a solid state has not been tried yet. Therefore, it was examined under the conditions shown in Table I.

Powdered IA was used for all the examinations. The contents of all tubes were apparently white solids at the beginning of the reaction; the contents of runs a, b, and c did not discolor but those of runs d, e, and f yellowed in the course of the reaction process. Thus, the results are more likely to be colored with increasing reaction temperature and, further, by the addition of DBP. After three days of polymerization time, a very small amount of the contents of runs e and f underwent softening. The results of elemental analysis of the reaction products showed that their observed values are similar to the calculated one of the monomer (C, 46.16; H, 4.65%) and that the maximum deviation between their values is about 1% for carbon and 0.3% for hydrogen.

The IR spectra of the monomer, the reaction products of run f, and the PIA obtained during solution polymerization are given in Figure 1. The decay of absorption due to the double bond in run f and PIA is clarified as shown in this figure.

The GPC analysis of reaction products a and b showed that their elution volume agreed with that of the monomer, 14.2 ml. In the cases of reaction products e and f, for both runs their volumes are as follows: 12.3, 13.2, 14.2 ml. It was assumed, therefore, that both products e and f will consist of monomers and low molecular oligomers. The proportion is approximately 5:2:1 for run e and 4:2:1 for run f. These situations are consistent with those for the IR test.

Polymerization and Structure of Itaconic Acid

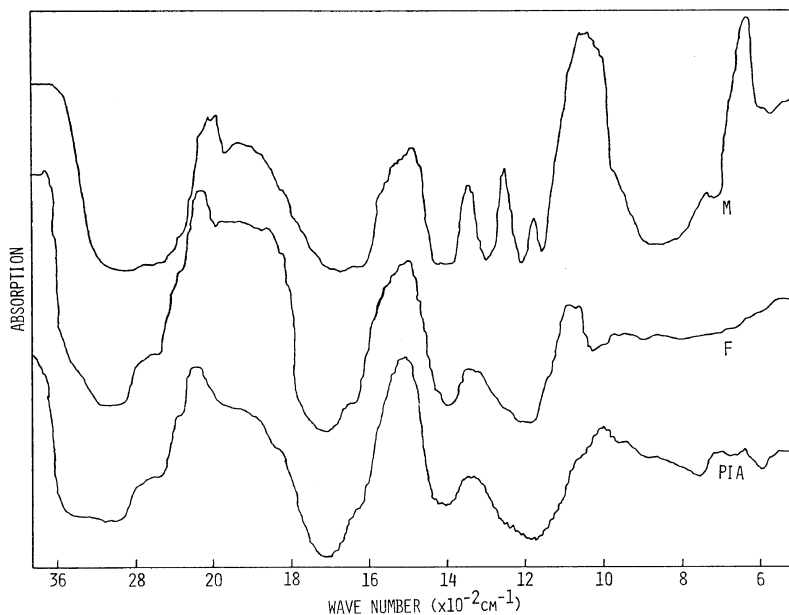


Figure 1. Infrared spectra of M, monomer (IA); F, run f; PIA, poly(itaconic acid).

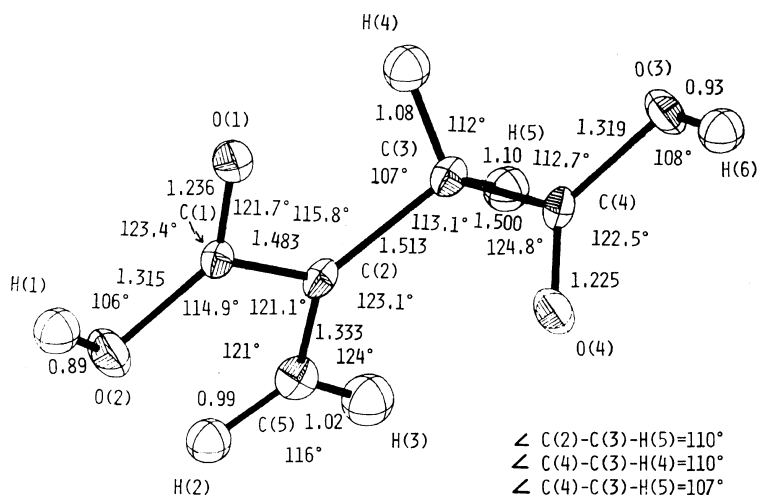


Figure 2. Molecule with the bond lengths and angles. Estimated standard deviations for these quantities concerning only heavy atoms are 0.008 Å and 0.5°, and for those concerning hydrogen atoms are 0.05 Å and 2.7–4.4°, respectively.

On the basis of the results of the analyses mentioned above, it was understood that IA, which is not polymerized in a solid state below 100°C, would react 120°C and result in the formation of oligomers. This behavior may be attributed to the formation of radicals and the movement of molecules in this crystal lattice.

Hence, the crystallographic study and discussion were carried out as described below.

Crystal Structure

It was recognized that IA propagated to oligomers in the present experiment. This behavior of the IA molecules in the propagation reaction can be interpreted on the basis of the crystal

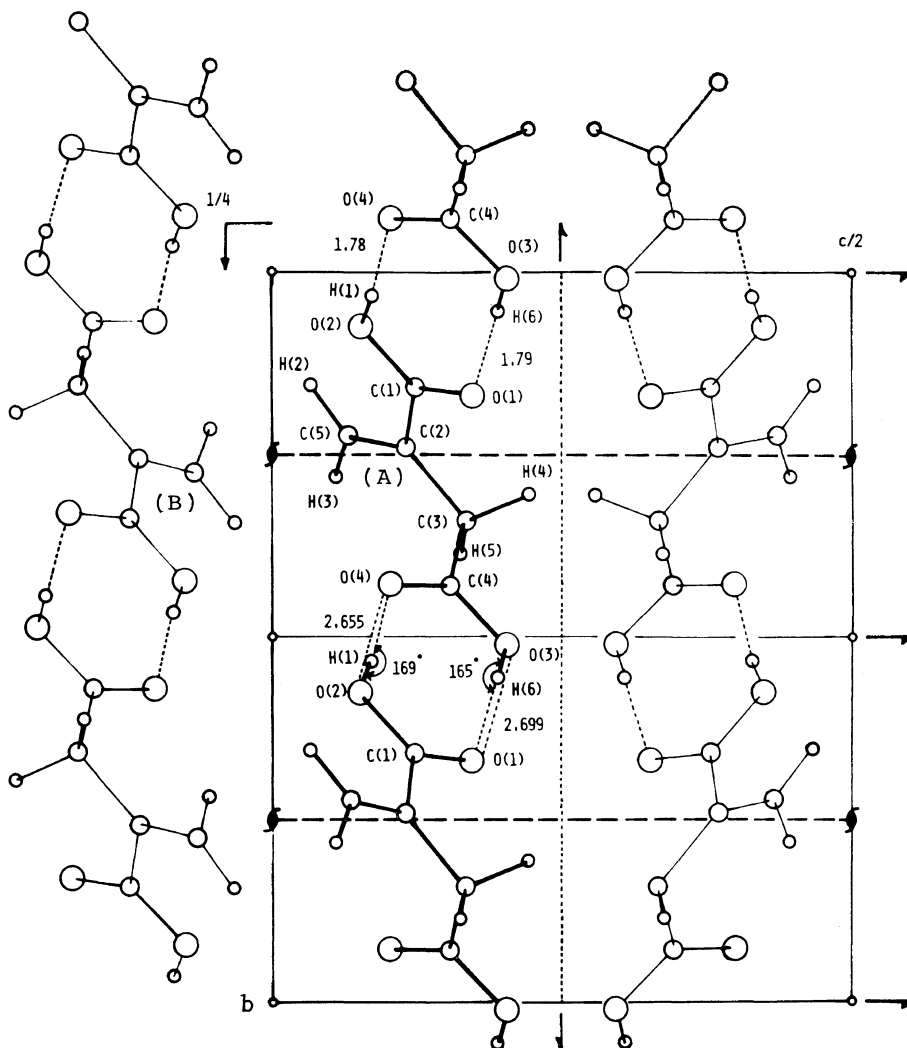


Figure 3. Molecular arrangement in crystal viewed along the a axis.

and the molecular structure of IA.

The IA molecule, as shown in Figure 2, consists of two planar parts: that is, part (I) involving C(1), C(2), C(3), C(5), O(1), and O(2) atoms, and part (II) involving C(3), C(4), O(3), and O(4) ones. Part (I) is plane within 0.05 Å. Part (II) is also planar, within 0.002 Å, and makes the dihedral angle of 106.1° with part (I). Figure 3 illustrates the molecular arrangement in the crystal viewed along the a axis. Molecules are adjoined by hydrogen bonds of a ribbon type in the b axis direction. Such modes of hydrogen bondings are characteristic

for many aliphatic dicarboxylic acids,⁹ but interestingly in the case of the present crystal the two hydrogen bonds in the ribbon type are not related by any symmetry. The crystallographic description given above agrees closely with Harlow's data.⁷

DISCUSSION

The closest contact (Figure 3) between the ethylenic C(2)=C(5) bonds is found between molecules, for example (A) and (B), related by the two-fold screw axis parallel to a axis; the

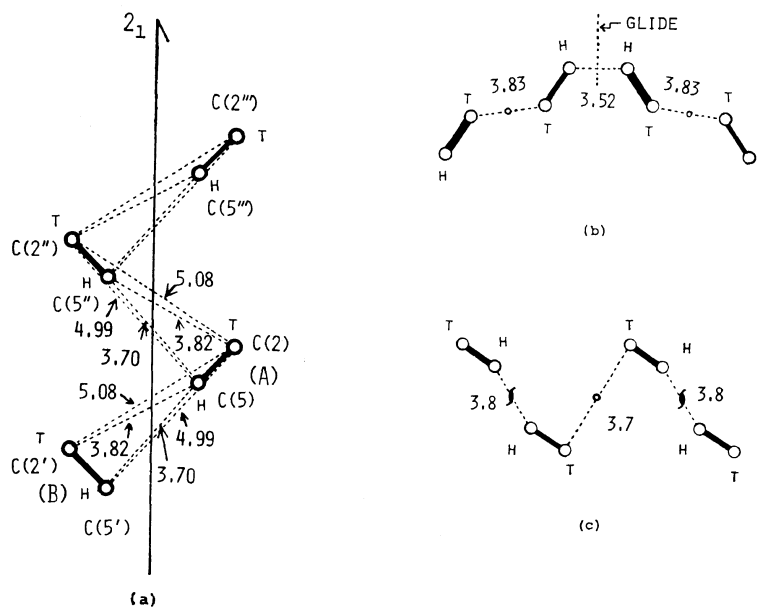


Figure 4. Geometry of contacts between neighbouring $\text{CH}_2=\text{C}<$ groups: (a) itaconic acid; (b) acrylic acid; (c) acrylamide.

center-to-center distance is 4.35 Å. The two vinyl groups of molecules (A) and (B) make a dihedral angle of 113.2° . Figure 4(a) shows this contact viewed along the b axis together with the distances between these $\text{CH}_2=\text{C}<$ groups. The symbols H and T in this figure refer to the head ($\text{CH}_2=$) and tail ($=\text{C}<$) respectively of the $\text{CH}_2=\text{C}<$ group. The inter-centric distance is somewhat longer than those of α -class (3.6–4.1 Å) and β -class (3.9–4.1 Å) of cinnamic acid derivatives,¹⁰ which photodimerize in a solid state, but it is shorter than that of NVC (4.9 Å),¹ which is polymerizable in a solid state, and corresponds to that of α -bromo-*cis*-cinnamic acid (4.4 Å).¹¹ The short inter-atomic distances in Fig. 4(a), 3.70 Å (H—H) and 3.82 Å (H—T), correspond to those in the crystals of solid-state polymerizable compounds, acrylic acid (AA)^{12,13} and acrylamide (AAM),^{14–16} and not to most of those in NVC.¹ Thus, it is presumed that IA will be solid-state polymerizable. However, polymerization of IA under γ -irradiation could not be carried out. As seen in Figure 4, both the AA and the AAM molecules are arranged more favorably than the IA molecule for a solid-state polymerization. Further, the olefinic π -orbitals between adjacent molecules of both

AA and AAM are parallel or nearly parallel and can overlap easily through the process of reaction, while it is hard for those of IA to overlap. The adjacent vinyl groups, including H atoms, in the IA crystal made a dihedral angle of 113.2° and their π -orbitals meet at approximately a right angle to each other, whereas that of NVC made an angle of 140.3° . AAM molecules are joined by two kinds of N—H—O hydrogen bonds and form a two-dimensional network. AA molecules are also joined by O—H—O hydrogen bonds, related by a center of symmetry, and make a dimer. As compared with AA and AAM, the IA molecule has an additional bulky part, *i.e.*, part (II) mentioned above, which makes a dihedral angle of 106.1° with part (I), thus disturbing the transfer and rotation of a monomer molecule. In the crystal of IA, furthermore, the monomer molecules connected by O—H—O hydrogen bonds of the ribbon type form an endless chain and can hardly move and rotate as compared with AA. The melting point of IA is somewhat higher than those of the three others: IA (167–168) > AAM (84.5) > NVC (64–66) > AA (13–14°C). The matters mentioned above support the conclusion that it is difficult for IA to polymerize in the solid

state even under γ -irradiation at 50–100°C. Thus, at the process of thermal polymerization in the solid state above 120°C the hydrogen bonds in the lattice come loose and the rotation and translation of molecule may occur somewhat more readily than predicted at the low temperature. It can therefore be presumed that IA molecules make an oligomer through the approach and the rotation. However, the additional propagation occurs rarely, because of the crystal structure of IA mentioned above.

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