Polymorphism of Bis-β-hydroxyethyl Terephthalate

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In the course of a study of the infrared spectra of various derivatives of terephthalic acid, it was found that bis-β-hydroxyethyl terephthalate has several modifications. The crystal of bis-β-hydroxyethyl terephthalate prepared by the usual method, recrystallization from water or slow cooling of the melt, is obtained in the most stable form, which is called α-form in this paper. Besides this α-form, at least three other forms can be obtained by rapid cooling of the melt. These three modifications are tentatively called β-, γ- and δ-forms. The infrared spectra of these modifications are shown in Fig. 1, and the x-ray diffraction patterns in Fig. 2. There are some remarkable differences between the infrared spectra of these modifications; it seems that these differences offer some valuable information for the interpretation of the infrared spectrum of polyethylene terephthalate.

Method of Preparation

α-Form.—This form is the common one. Recrystallization from water generally gives this form. It is the most stable form and cannot be changed to any other form unless remelted.

β-Form.—Molten mixture of bis-β-hydroxyethyl terephthalate and ethylene glycol (ca. 1:1) kept at a temperature of ca. 100°C, is quenched dropwise on the surface of an ice-cooled metal plate. Removing ethylene glycol from the solidified drops at a temperature below ca. 20°C by means of filter papers or a porous plate, β-form is obtained. It is essentially important to maintain this at a low temperature; otherwise, the δ-form is obtained. This form changes to the α-form when washed with water or alcohol. It converts to in the δ-form at ca. 40°C, and to the α-form above ca. 45°C. These transition temperatures become lower as the atmospheric humidity becomes higher.

γ-Form.—This form is obtained by rapid cooling of the melt. Washing with water, it changes to the α-form. It also changes gradually above ca. 60°C, to the α-form.

δ-Form.—Molten mixture of bis-β-hydroxyethyl terephthalate and ethylene glycol is quenched dropwise. Ethylene glycol is removed from the solidified drops by filter papers, as in the case of β-form, at a temperature of 30°C to 40°C. Once formed, this form is rather stable; it does not change when washed with water, nor when kept at 100°C for an hour.

It was ascertained that all these modifications are chemically the same. The analytical values of C and H conform to the formula $C_6H_4(CO_2CH_2CH_2OH)_2$, and determination of the ethylene glycol content by periodic acid after saponification of each modification, also agrees with the above formula.

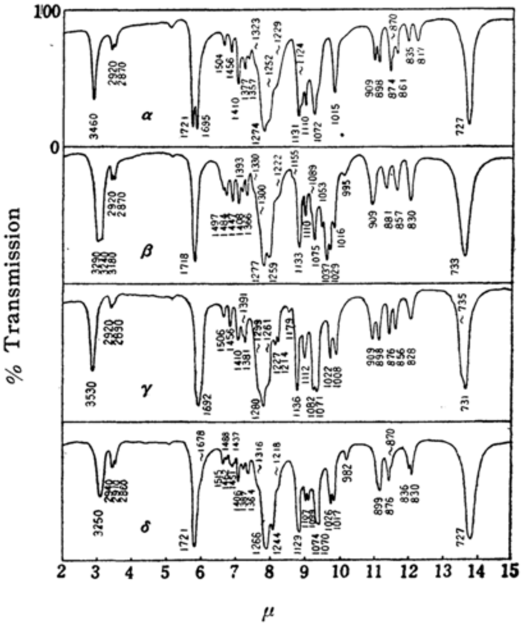

Fig. 1. Infrared spectra of four polymorphic forms.

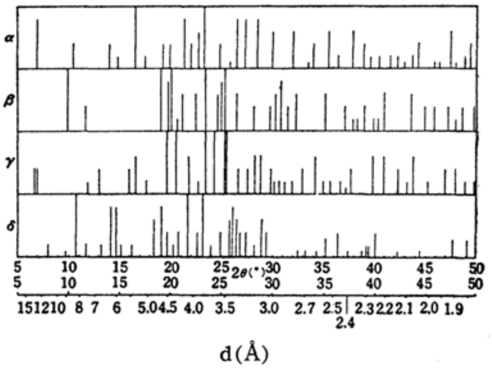

Fig. 2. X-ray diffraction patterns of four polymorphic forms.

Infrared and X-ray Measurements

The infrared spectra were obtained with a Perkin-Elmer Model 21 Spectrometer using NaCl prism. Samples were measured as nujol mulls except in the C—H frequency region. For this region, hexachlorobutadiene or low molecular weight polytrifluorochloroethylene oil was used as the mulling agent.

X-ray diffraction patterns were obtained with a Norelco Geiger counter x-ray diffractometer. Nickel filtered radiation from a copper target was used. In the case of the β-form which is easily transformed into the δ-form under the influence of atmospheric moisture, the specimen shield assembly was covered with cellophane and desiccated with phosphorous pentoxide.

Some Remarks on the Infrared Spectra

From the differences in the infrared spectra, it might be possible to obtain some information about the molecular form or the crystal structure of the four modifications. In this respect, there are at least three characteristic points. The first of these is the absorption band at 3500-3200 cm⁻¹. The position of this band shows that the O—H terminal groups are all hydrogen bonded in these modifications; however the type of hydrogen bond is different between each modification. The next point is the C=O band at 1720 cm^{-1} and 1695 cm^{-1}. The former shows the existence of free ester carbonyl groups, the latter hydrogen bonded carbonyl groups. Accordingly, β- and δ-form have only free ester groups, while γ-form has hydrogen bonded carbonyls, α-form has both of them in equal amount. The third point is concerned with the four absorption bands which appear at 910 to 850 cm^{-1}. The vibrations expected to appear in this region are the CH_2 rocking vibrations and certain vibrations of the benzene ring. For the determination of the latter, the comparison with the spectra of other terephthalic acid esters is useful. In Fig. 3, three such esters are given; comparing these spectra with that of bis-β-hydroxyethyl terephthalate, it becomes apparent that there exists only one band 875 cm^{-1} which seems to be a benzene ring vibration, so long as it is assumed that the benzene ring vibrations have almost constant frequencies in such series. Thus the absorption bands chosen in Table I can be assigned to the CH_2 rocking vibrations.

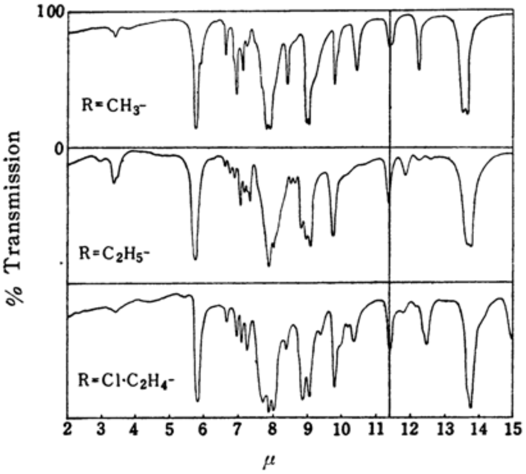

Fig. 3. Infrared spectra of $ROOC\cdot C_6H_4\cdot COOR$.

TABLE I
FREQUENCIES OF THE CH_2 ROCKING VIBRATION (cm^{-1})

α	909	898	~870	861
β	909			857
γ	909	898	876	856
δ		899	~870	

The absorption band 876 cm^{-1} of the γ-form is assumed to be composed of two components, benzene ring vibration and CH_2 rocking vibration. The frequencies given in Table I consist of two pairs, (909, ~857) and (899, ~870). β-Form has only the former pair, δ-form only the latter, while α-and γ-form have both.

Nakagawa1) has shown that CH_2 rocking frequencies in a molecule of the type $X—CH_2—CH_2—X$ depends profoundly on the angle of internal rotation, and their values decrease in the following order: B_g (*trans*) > A (*gauche*) > B (*gauche*) > A_u (*trans*). In the light of this conception, the former pair (909, ~857) can be considered as the CH_2 rocking frequencies arising from *trans* configuration of the $O—CH_2CH_2—O$ group. The latter pair (899, ~870) represents the existence of *gauche* configuration. Thus, the configuration of the $O—CH_2CH_2—O$ group in β-form is *trans*, in δ-form *gauche*, in α- and γ-form both *trans* and *gauche*.

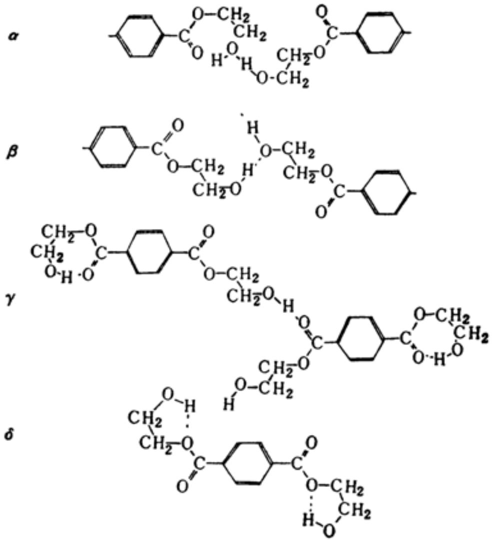

Fig. 4. Structures of four polymorphic forms.

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1) I. Nakagawa, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **76**, 813 (1955).

It might be too speculative to derive structural conceptions from only the arguments made above; the four modifications may be considered to have the structures something like those shown in Fig. 4 at the present time.

Summary

It is found that bis-β-hydroxyethyl terephthalate shows polymorphism, and there exist at least four different modifications. From the infrared spectra of these modifications, differences between the molecular forms are elucidated to some extent. These differences occur mainly from the difference in configuration of the side chain attached to the benzene ring.

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