SHORT COMMUNICATIONS

Infrared Spectra of Some Deuterated Crystalline Polystyrenes. III. Characteristic Bands of Isotactic Polymer from Styrene-d_5

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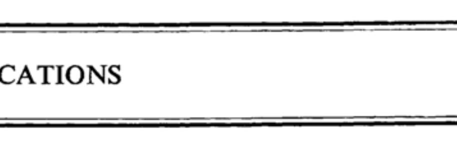
In order to interpret the absorption bands characteristic of the helical conformation of isotactic polystyrene, several deuterated derivatives in which the hydrogen atoms of the skeletal chain are substituted with deuterium, such as crystalline poly-αd_1-, poly-βd_1-, poly-$\alpha, \beta d_2$- and poly-$\beta, \beta d_2$-styrene, have been synthesized and their infrared spectra have been investigated[1,2]. It was found that the characteristic bands appearing (1) in the region of 1450∼1180 cm^{-1} (1364σ, 1314σ, 1297π and 1195π), (2) at near 1070 cm^{-1} and (3) at near 900 cm^{-1} were remarkably affected by the sites and the numbers of the substituted deuterium atoms. However, the frequency shifts of these bands on deuteration were not always so simple that it seemed difficult to assign them to simple vibrational modes. Although it seems reasonable to consider that the deformational vibrations of the skeletal CH and CH_2 groups and the stretching vibrations of the carbon chain in the helix contribute to the appearance of the characteristic bands, we could not disregard the effects of the coupling of these modes with the CH deformations of the side group, since it was known that[3] some of the characteristic bands were moderately affected by deuteration of the para position.

In order to throw some light on the problem, the infrared spectra of the polymers (both isotactic and atactic) of the monomer $C_6D_5CH=CH_2$ were investigated.

The monomer was prepared by the following scheme



$$C_6D_6 + \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O \xrightarrow[\text{in } CS_2]{AlCl_3} C_6D_5-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} C_6D_5-\underset{\underset{OH}{|}}{C}-CH_3 \xrightarrow{-H_2O} C_6D_5-CH=CH_2$$

C_6D_6 was prepared from benzene and deuterosulfuric acid, D_2SO_4, by an exchange reaction, the product contained about 85 mol.% of deuterium. The monomer thus obtained was polymerized in *n*-heptane using Ziegler type catalyst, then isotactic polystrene-d_5 was obtained. The atactic polymer was prepared by bulk polymerization using B. P. O. as a catalyst.

In Fig. 1 the spectra of the atactic and isotactic (crystallized) polymers were compared with each other.

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[1] M. Kobayashi, This Bulletin, 33, 1416 (1960).

[2] M. Kobayashi, ibid., in press.

[3] H. Tadokoro et. al., ibid., 32, 313 (1959).

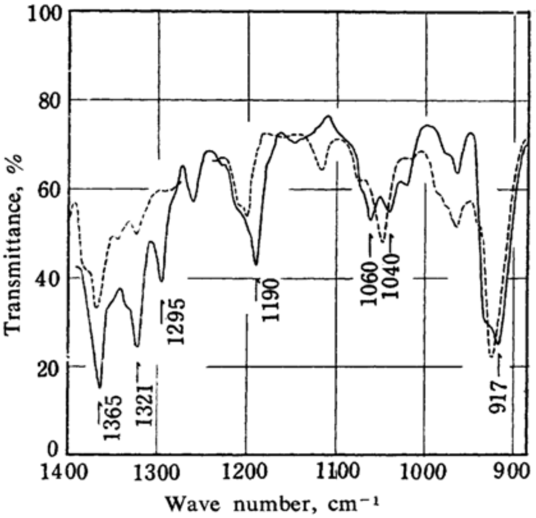

Fig. 1. Infrared spectra of polystyrene-d_5.
—— isotactic polymer at crystalline state
---- atactic polymer

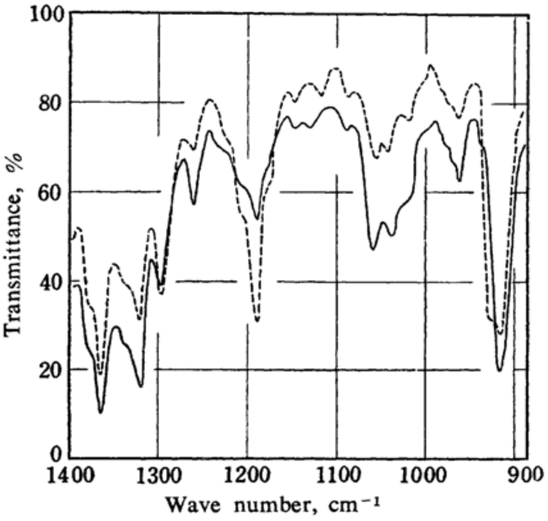

Fig. 2. Polarized infrared spectra of isotactic polystyrene-d_5.
—— electric vector perpendicular to elongation
---- electric vector parallel to elongation

A most noticeable feature is that the spectroscopic characters of isotactic polystyrene are observed also in our deuterated sample; the appearance of the bands at 1365, 1321, 1295 and 1190 cm^{-1} and the splitting of the bands at near 1070 cm^{-1} and at near 900 cm^{-1} on crystallization. Especially, the bands in the region of 1450∼1180 cm^{-1} have almost the same frequencies and relative intensities as those of polystyrene. Moreover, as shown in Fig. 2, measurements of the polarization spectra of the oriented crystallized sample show that the polarization properties of the characteristic bands coincide with those of isotactic polystyrene.

These results may support the assumption that the CH deformations of the phenyl group have little effect upon the appearance of the characteristic bands of isotactic polystyrene, especially, those in the region of 1450∼1180 cm^{-1}. Then, it may be concluded that the helical conformation of the isotactic polystyrene molecule reflects mainly on the absorption bands associated with the modes of the groups composing the skeletal chain.

The detail of this work will be reported in elsewhere.

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