V. N. NIKITIN, N. V. MIKHAILOVA

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Abstract

Full Text

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MANIFESTATION OF THE CRYSTALLINE STRUCTURE OF ISOTACTIC POLYMETHYL METHACRYLATE IN INFRARED ABSORPTION SPECTRA

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The study of the crystalline structure of isotactic polymethyl methacrylate (PMMA) by the X-ray method (^{1}) showed that this polymer crystallizes in the form of a 5_2 helix with an identity period of 10.55 Å.

It could be expected that the helical structure of PMMA would manifest itself in the IR absorption spectrum, as, for example, was observed in isotactic polypropylene (^{2}).

Fig. 1. X-ray patterns of amorphous *(I)* and crystallized *(II)* isotactic polymethyl methacrylate.

The appearance of absorption bands upon crystallization of a polymer may be caused by two reasons—intermolecular order in the elementary crystalline cell and order along the polymer chain, which exists in the helical structure of the chain. In the first case one speaks of "crystallinity" bands, since they disappear upon transition to the amorphous state or upon dissolution of the crystalline polymer ($^{3–5}$). Absorption bands caused by intramolecular order—"helical bands" —may also persist upon dissolution of the polymer, if helical portions of the chain are then partially retained. In theoretical works (^{6,7,8}) it was shown that in statistically coiled molecules one-dimensional short-range order, corresponding to one-dimensional long-range order in the crystal, should be preserved. In other words, in solution there exist segments of chains having the same conformation as in the crystal. We note that the existence of a helical conformation in solution has been established experimentally for synthetic polypeptides and proteins.

The question of the physical cause leading to the appearance of crystallinity bands in polymers and monomers is at present under study. It may be considered

Fig. 2. IR absorption spectra

Figure 2: Fig. 2. IR absorption spectra

that one of the reasons leading to the appearance of these bands is the influence of intermolecular interaction on the vibrating bonds in the elementary crystalline cell; analogously, "helical bands" are associated with intramolecular interaction of vibrating bonds.

The isotactic PMMA investigated in the present work was obtained by the method described in ([9])* by homogeneous catalytic polymerization of methyl methacrylate in toluene with butyllithium ($t = -60^\circ$). The IR spectrum of isotactic PMMA was recorded on a double-beam spectrometer IKS-14 with a NaCl prism; film thickness $\sim 10\,\mu$. The films were prepared from a solution of PMMA in chloroform ($\sim 2\%$) by casting onto NaCl plates. Crystallization of PMMA was carried out by swelling the film in 4-heptanone for 16 h at 20°. After removal of the solvent, the polymer was crystallized, which was confirmed by the X-ray method* (see Fig. 1).

Fig. 2. IR absorption spectra of films of amorphous isotactic PMMA (*I*), crystallized PMMA (*II*), crystallized PMMA heated to 220° (*III*). Spectrum of preliminarily crystallized PMMA dissolved in chloroform (*IV*). Cell thickness $d = 0.250$ mm, concentration $\sim 1.27\%$.

Figure 2 presents the spectrograms of isotactic PMMA in the amorphous and crystalline states, as well as of crystallized PMMA dissolved in chloroform. In the latter case, chloroform absorption was excluded with the aid of a second compensating cell. Amorphous isotactic PMMA has the following absorption bands: 755, 840, 955, 995, 1150, 1192, 1263, 1390, 1445, $\sim$ 1580, 1730 cm^{-1}. The absorption spectrum obtained for PMMA agrees with the data of work [10], except for the weak band at 1580 cm^{-1}, which we detected in sufficiently thick specimens.

As can be seen from Fig. 2, in the spectrum of crystallized isotactic PMMA two sharp absorption bands are observed at 1580 and 1560 cm^{-1}, absent in the amorphous specimen. After heating the crystallized film at 220° for 2 h, the spectrum of this specimen, recorded at +20°, showed only one broad absorption band with a minimum at $\sim$ 1580 cm^{-1}. The X-ray diffraction pattern of such a preheated film indicated a sharp decrease in crystallinity, which was restored only by repeated swelling of the specimen in 4-heptanone. In this case the absorption bands at 1580 and 1560 cm^{-1} reappeared, and the

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X-ray diffraction pattern had the form of curve II in Fig. 1. Thus, heating a crystallized specimen above the melting temperature (m.p. ~ 160°) destroys the crystalline structure, which is not restored upon cooling the specimen.

Curve IV in Fig. 2 is the absorption spectrum of a crystallized specimen dissolved in chloroform. As can be seen, the two sharp bands at 1580 and 1560 cm^{-1} are retained in the dissolved specimen, decreasing in intensity. Films cast from such a solution were crystalline and did not require preliminary treatment in 4-heptanone. Their X-ray diffraction patterns and spectrograms practically did not differ from the X-ray diffraction pattern and spectrogram of the initial specimen crystallized by swelling in 4-heptanone. The data obtained make it possible to suppose that the bands at 1580 and 1560 cm^{-1}, which appear upon crystallization and are retained when the specimen is dissolved, characterize the helical conformation of isotactic PMMA.

Such an assumption would be valid if we were dealing with a molecular solution of the polymer in chloroform. However, a study of birefringence in a flow of solutions of isotactic PMMA in benzene, as well as of the Kerr effect[11], showed that the solution of this polymer is not true and contains a small quantity of insoluble crystallites. This circumstance does not permit one to state unambiguously that the bands at 1580 and 1560 cm^{-1}, observed also in solution, can be associated only with one-dimensional helical order and are not associated with three-dimensional order. At the same time, the high intensity of these bands in a dilute polymer solution in chloroform (see Fig. 2, IV), as well as the stability of these bands that we observed upon heating above the crystallization temperature (b.p. 160°), rather permits these bands to be associated with the helical structure of isotactic PMMA.

Institute of High-Molecular Compounds
Academy of Sciences of the USSR

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