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Kurzmitteilung

Crystalline Modification of Syndiotactic Polypropylene Having a Zig-zag Chain Conformation.

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In preceding papers^{1, 2)} the conformations of lowest energy of a syndiotactic polypropylene chain have been discussed. They were represented by the twofold helix conformation described by the successions of internal rotation angles:

$$\dots[-180^\circ -180^\circ - 60^\circ -60^\circ]_n \dots$$

or by its equivalent enantiomorphous conformation; and by the approximately isoenergetic zig-zag planar conformation:

$$[-180^\circ -180^\circ]_{2n} \text{ (see Figs. 2, 3 and 4 of ref. 1)}$$

A crystal form of syndiotactic polypropylene has already been found by us³⁾ to correspond to the helix conformations. We wish to refer here about a new crystal form in which the polymer chains closely approach the zig-zag shape.

The new crystal form of syndiotactic polypropylene results to be present, as is proved by infrared and X-ray evidences, in samples obtained by cold-stretching the polymer quenched from the melt, the twofold helix type structure being completely absent.

The stretched samples showing the new crystal form can be converted to the twofold-helix type structure without losing the orientation of the chains along the stretching direction. This transformation results to be practically complete in a few hours at about 100 °C. It is to be noted that ~~the rubberlike quenched samples, if not stretched, at room temperature undergo rapid hardening, showing the crystallinity of the twofold helix type.~~

The original product^{*)} showed a fairly high stereoregularity degree, and an intrinsic viscosity of about 0.65.

The infrared spectrum in polarized light of the stretched samples showing the new form, can be characterized, in the 7.5 – 14 μ range, by fairly strong bands at 8.11; 8.84; 10.38 and 12.03 μ , parallel to the

^{*)} Prepared in this Institute by Dr. A. ZAMBELLI.

stretching direction, a perpendicular, well isolated weak band at 7.56μ and a medium one at 12.08μ . The band at 8.84μ is less overlapped than the others by weaker absorption bands of amorphous polypropylene.

The rotating-fibre X-ray pattern obtained hereafter on the above samples appear to be very poor of sharp reflections; the observed intensities decrease very quickly with decreasing values of the interplanar spacings d and, moreover, a very intense non-oriented halo is observed at about $d = 5.1 \text{ \AA}$. These features seem to be connected with a high degree of structural disorder, in the observed samples.

Nevertheless, in addition to three equatorial reflections at about 5.2 ; 3.0 ; 2.65 \AA in decreasing order of intensity, which seem to be related to a pseudo-hexagonal equatorial packing of the chains, another sharp reflection is observed belonging to a layer with a periodicity of $5.05 \pm 0.10 \text{ \AA}$. Undoubtedly this reflection must be due to a nearly planar zig-zag conformation of the chains, although a long range spiralization cannot be excluded at present, owing to the probable presence of some weak reflections, which would be related to a greater periodicity along the chain.

It seems worth noting that a possible long range spiralization would not be in disagreement with the prediction of calculus; in fact, if the actual chain conformation is described by (σ_1, σ_2) values not exactly corresponding to $(180^\circ, 180^\circ)$ (see Fig. 4 of ref. ¹), a definite deviation from planarity giving rise to a long range spiralization could occur.

The existence of the zig-zag planar modification of syndiotactic polypropylene now demonstrated, is another experimental proof of the importance of the methods adopted by us to foresee the most probable conformations in the crystal state on the basis of the calculation of the internal potential energy of tactic polymer chains^{1, 2}).

¹) G. NATTA, P. CORRADINI, and P. GANIS, *Makromolekulare Chem.* **39** (1960) 238.

²) G. NATTA, P. CORRADINI, and P. GANIS, *J. Polymer Sci.* **58** (1962) 1191.

³) G. NATTA, I. PASQUON, P. CORRADINI, M. PERALDO, M. PEGORARO, and A. ZAMBELLI, *Rend. Acc. Naz. Lincei* **28** (1960) 539.