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Chain Structure of Isotactic Polyvinyl Cyclohexane

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Kurzmitteilung

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Many types of helical chains present in the crystals of different isotactic polymers have been described in the last years. They all correspond to successions of more or less distorted trans and gauche bonds[1]).

The chains of the polymers, which have an identity period along the fiber axis comprised between 6.4 and 6.7 Å, generally correspond to successions of undistorted trans ($\tau_1 = 180°$) and gauche ($\tau_2 = 60°$) bonds, repetition being achieved along a three-fold helix[2]) [$(AB)_3$ or $(AC)_3$ according to the terminology of C. W. Bunn[3])].

Surprisingly, we have recently found that the chain of isotactic polyvinyl cyclohexane, which has an identity period along the fiber axis of 6.5 Å, does not follow a three-fold helix, but a four-fold one.

Crystalline polyvinyl cyclohexane has been obtained in this Institute by polymerization of vinyl cyclohexane with the same catalysts which polymerized α-olefins, styrene and some substituted styrenes to isotactic polymers.

The isotactic structure of polyvinyl cyclohexane is also confirmed by the fact that through hydrogenation of isotactic polystyrene, and hydrogenation and dehalogenation of isotactic amorphous polychlorostyrenes we obtained products exhibiting the same X-ray diffraction lines as crystalline polyvinyl cyclohexane[4]).

All X-ray reflections given by a fiber of this polymer may be indexed on the basis of a tetragonal unit cell, with $a = 21.9$ Å. The space group is

[1]) G. Natta, P. Corradini, and I. W. Bassi, Rend. Acc. Naz. Lincei **19** (8) (1955) 404; P. Corradini and I. Pasquon, Rend. Acc. Naz. Lincei **19** (8) (1955) 453; G. Natta, P. Corradini, and I. W. Bassi, Gazz. chim. ital. **89** (1959) 784; G. Natta and P. Corradini, Nuovo Cimento, in press.

[2]) G. Natta and P. Corradini, Makromolekulare Chem. **16** (1955) 77; G. Natta, P. Corradini, and I. W. Bassi, Makromolekulare Chem. **18/19** (1955) 455, **21** (1955) 240; G. Natta, P. Corradini, and M. Cesari, Rend. Acc. Naz. Lincei **21** (8) (1956) 365; G. Natta, P. Corradini, and I. W. Bassi, Rend. Acc. Naz. Lincei **23** (8) (1957) 363.

[3]) C. W. Bunn, Proc. Roy. Soc. [London] **180** (1942) 67.

[4]) G. Natta and D. Sianesi, Rend. Acc. Naz. Lincei **26** (8) (1959) 418; G. Natta, F. Danusso, and D. Sianesi, Makromolekulare Chem. **28** (1958) 253.

I $4_1/a$, as it can be deduced from the systematic extinction of reflections hkl with $h+k+l = 2n+1$ and $hk0$ with $h = 2n+1$ and $k = 2n+1$.

The calculated density, with 16 monomeric units per unit cell, is 0.95 g./cm.^{3}, in accordance with the experimental datum. Thus, successive monomeric units along the four-fold helices result equivalent from a crystallographic point of view, because they are repeated through the operation of the 4_1 and 4_3 axes, present in the space group[5]).

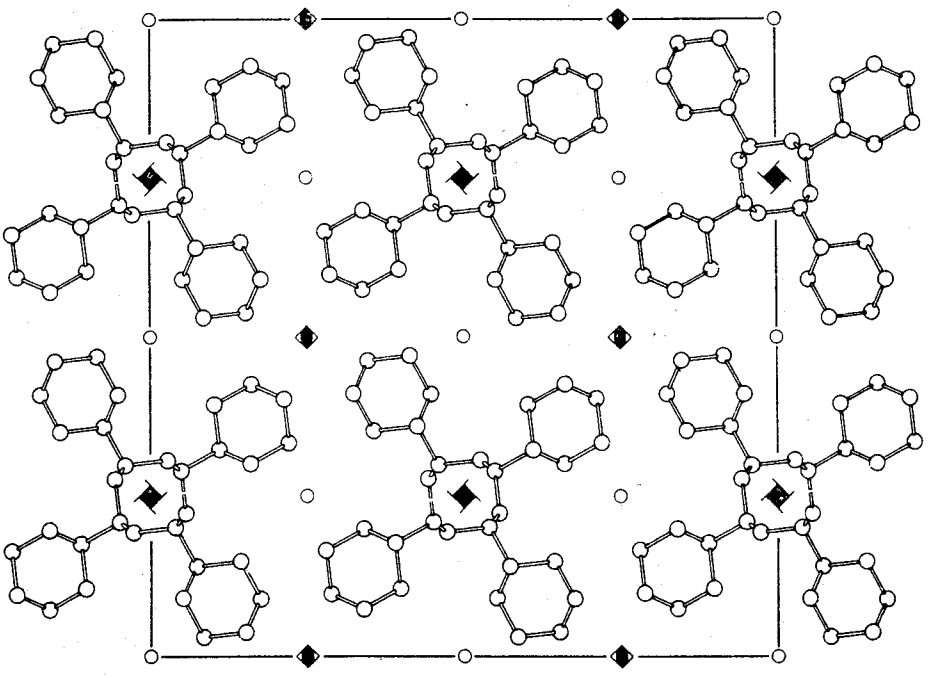

Fig. 1. Mode of packing of isotactic polyvinyl cyclohexane
(For the symbols drawn in Fig. 1, see [5]))

Each right-handed helicoidal chain is surrounded by four anticlined left-handed helicoidal chains and *vice versa* (Fig. 1). The mode of packing is slightly different from that shown by isotactic poly-o-methylstyrene, in which each four-fold helical chain is surrounded by four enantiomorphous but isoclined chains[6]). It is interesting to note that also poly-3-methylbutene possesses a four-fold chain structure, with an identity period along the fiber axis (6.85 Å) analogous but slightly longer than that of polyvinyl cyclohexane (6.50 Å). In both cases, the rather large distortion of internal rotation angles from the minimum energy values of a polymethylenic chain must be attributed to the encumbrance of the side groups. We are now performing a complete calculation of the structure of polyvinyl cyclohexane.

[5]) Int. Tabellen zur Bestimmung von Kristallstrukturen 1, 162, Gebr. Bornträger, Berlin 1935.

[6]) P. CORRADINI and P. GANIS, Nuovo Cimento, in press.