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Kurzmitteilung

Chain Conformation of Polypropylenes having a Regular Structure

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Chain Conformation of Polypropylenes having a Regular Structure

By G. NATTA, P. CORRADINI, and P. GANIS

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In previous papers, two postulates fit for defining the most probable chain conformation of a tactic polymer in the crystalline state, were enunciated: that is the postulate of geometric equivalence of the monomeric units of a tactic chain with regard to an axis, and the postulate that the conformation is such that the potential energy of the chain, considered as not subjected to external forces, is the lowest1).

It has been possible, starting from these postulates, and in connection with analogous work carried out by A. M. Liquori2) on many other polymers such as polyisobutylene and polyvinylidene chloride, to justify in a simple way the chain conformations experimentally found by us for different crystalline polymers.

In this communication, we briefly refer on some preliminary calculations effected by us, in order to foresee from the two above postulates the possible chain conformations of isotactic and syndiotactic polypropylenes and to compare them with the known ones.

To gratify the equivalence postulate, the repetition along the axis of the monomeric units of isotactic polypropylene must take place along a helix (succession of isoclined isomorphous units). The succession of internal rotation angles*) along the chain is generally bound to be of the type $\sigma_1, \sigma_2, \sigma_1, \sigma_2, \ldots$ (σ_1 and σ_2 = any value; $\sigma_1 + \sigma_2 \neq 2\pi$, except in the case that $\sigma_1 = \pi = \sigma_2$).

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*) The convention used to measure the internal rotation angle $\widehat{l_1 l_2 l_2 l_3}$ concerning a l_2 bond of the chain in respect to l_1 and l_3 is as follows: The internal rotation angle is π for a *trans* conformation, whereas it is $<\pi$, if looking along l_2 from l_3 (l_1) it is necessary to rotate l_3 (l_1) by an angle lower than π to make it superpose the l_1 (l_3)3).

1) G. Natta and P. Corradini, J. Polymer Sci. **39** (1959) 29. G. Natta and P. Corradini, Suppl. Nuovo Cimento **15** (1960) 9.

2) A. M. Liquori – Paper presented at the Summer School in Advanced Inorganic Chemistry, Varenna 1959; to be published in a book by the Accad. Naz. Lincei.

3) E. B. Wilson jr., J. C. Decins and P. C. Croos, Molecular Vibrations, McGraw-Hill Book Comp., Inc., New York, Toronto, London 1955, p. 60.

The repetition of the monomeric units of syndiotactic polypropylene may take place according to two different chain types:

a) along a glide plane, the glide defining thus the direction of the axis (succession of enantiomorphous isoclined units). In that case the succession of the internal rotation angles must be of the type:

$$\sigma_1, \pi; \ -\sigma_1, \pi; \ \sigma_1, \pi \cdots\cdots$$

$$(\sigma_1 = \text{any value})$$

b) along a helix associated with twofold axes perpendicular to the axis of the chain itself (succession of isomorphous anticlined units). The most general succession of the internal rotation angles is

$$\sigma_1, \sigma_1, \sigma_2, \sigma_2, \ \times \ \sigma_1, \sigma_1, \sigma_2, \sigma_2$$

$$(\sigma_1, \sigma_2 = \text{any value}; \ \sigma_1 + \sigma_2 \mp 2\pi \text{ except in the case that } \sigma_1 = \pi = \sigma_2).$$

The couples σ_1, σ_1 (σ_2, σ_2) are adjacent to the same CH_2 group, through which the twofold axis necessarily passes.

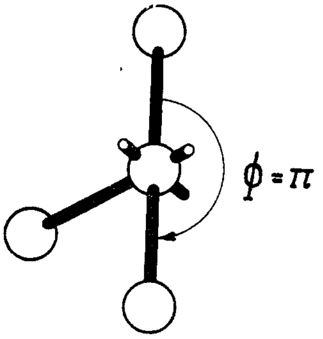

Fig. 1. Convention used to measure φ angles of relation (1)

An approximate calculation of the potential energy of an isolated chain, when varying the internal rotation angles allowed by the equivalence postulate, has been performed in the following way:

With reference to Fig. 1, the energy due to the interaction between carbon atoms which are separated by three bonds (and between hydrogen atoms belonging to them) has been approximated to be of the form (taking the energy difference between a *trans* and a *gauche* conformation equal to 1 Kcal[4])

$$(1) \qquad V(\varphi) = \frac{3}{2}(1 + \cos 3\varphi) + \frac{2}{3}\left\{2 + \cos\varphi + \cos\left(\varphi + \frac{2\pi}{3}\right)\right\} \text{ Kcal./bond}$$

The energy (in Kcal/m. u.) due to VAN DER WAALS contacts between carbon atoms (and between the hydrogen atoms belonging to them) separated by 4 bonds has been assumed in the simplified form (due to MASON and KREEVOY and function of the carbon-carbon distance)[5]:

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[4] S. MIZUSHIMA and I. SHIMANOCHI, J. Amer. chem. Soc. **21** (1949) 1320.

[5] E. A. MASON and M. M. KREEVOY, J. Amer. chem. Soc. **77** (1955) 5808.

$$(2) \quad V(r) = 2.390\cdot 10^4/r.^{7.37} \qquad (2.7 \leqslant r \leqslant 3.2\,\text{Å})$$

$$V(r) = 2.739\cdot 10^5 \exp(-3.329\,r) - 2.942\cdot 10^3/r^6 \qquad (r > 3.2\,\text{Å})$$

Contacts between atoms separated by more than 4 C–C bonds have not been taken into consideration (though important for some values of σ_1 and of σ_2), because they are negligible in the regions of minimum found energies. The C–C–C angles (112 °) and the C–C distances (1.54 Å) have been furthermore assumed constant. The convention used to label the σ angles is shown in Fig. 2. For the chain conformation of isotactic crystalline polypropylene only two minima of energy are allowed respectively corresponding to a threefold right and left-handed helix, as it has been experimentally found (Fig. 3)[6].

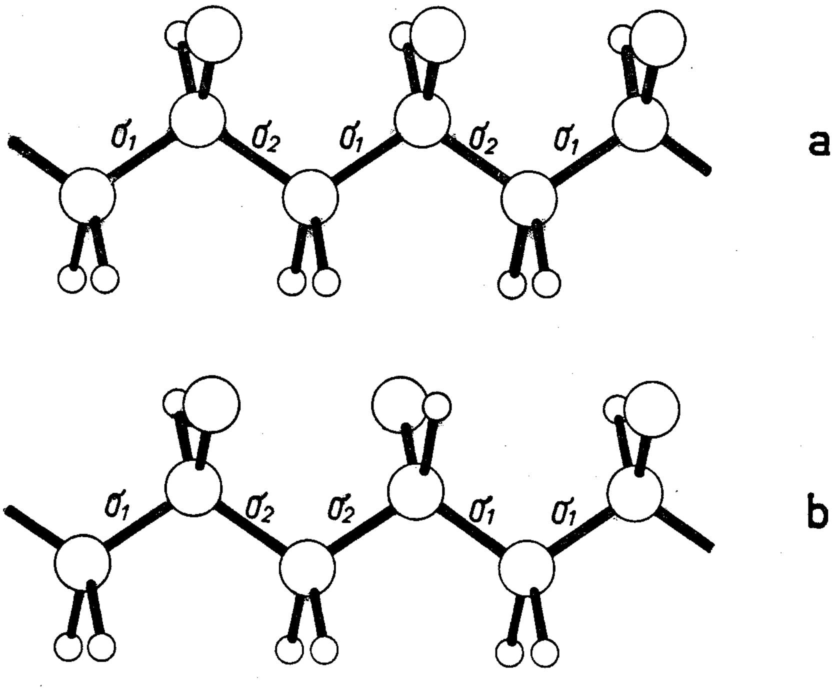

Fig. 2. Convention used to label σ angles for isotactic polypropylene (a) and syndiotactic helicoidal polypropylene (b) (chains arbitrarily stretched on a plane)

For the conformation of the chain of syndiotactic polypropylene, three equal minima of energy exist corresponding respectively to $\sigma_1 = 180°$, $\sigma_2 = 60°$; $\sigma_1 = 300°$, $\sigma_2 = 180°$; $\sigma_1 = 180°$, $\sigma_2 = 180°$ (Fig. 4, 5).

The two first conformations correspond to those found for the right and left-handed helix of syndiotactic polypropylene[7].

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[6] G. NATTA and P. CORRADINI, Suppl. Nuovo Cimento **15** (1960) 40.

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

[8] G. NATTA and P. CORRADINI, J. Polymer Sci. **20** (1956) 251.

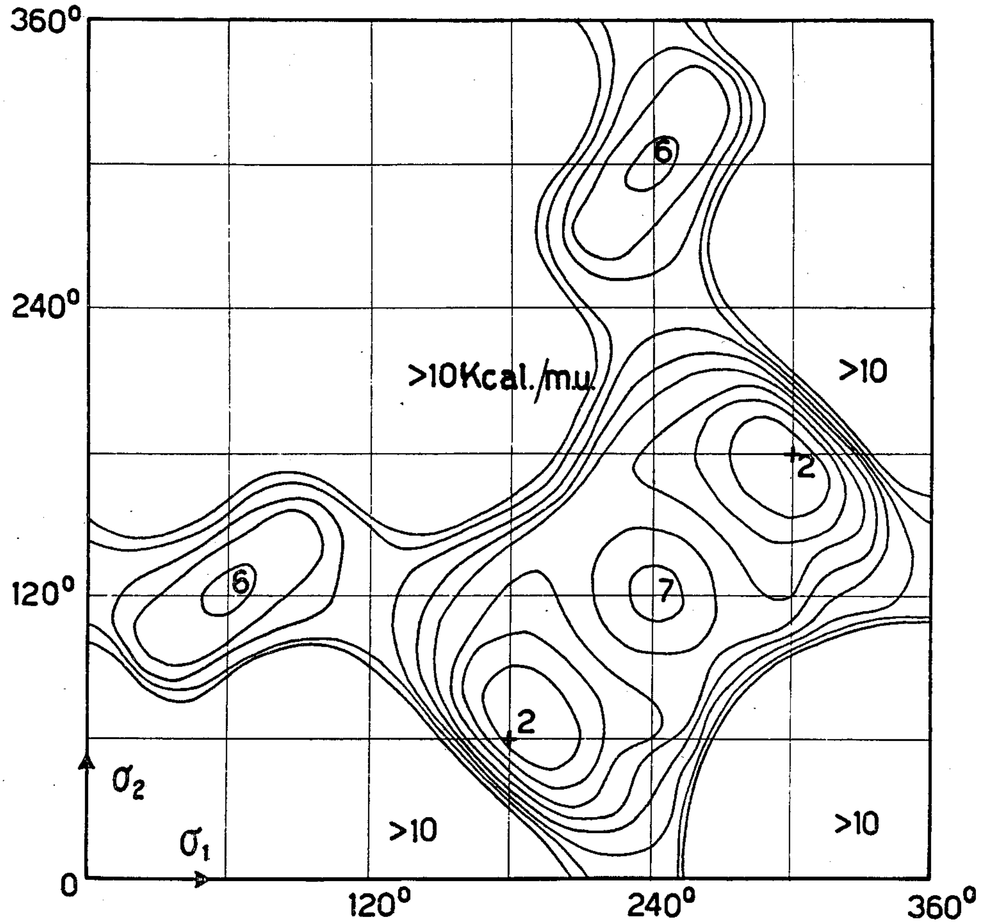

Fig. 3. Internal energy of an isotactic polypropylene chain for different helicoidal conformations ($\sigma_1, \sigma_2 \ldots$)

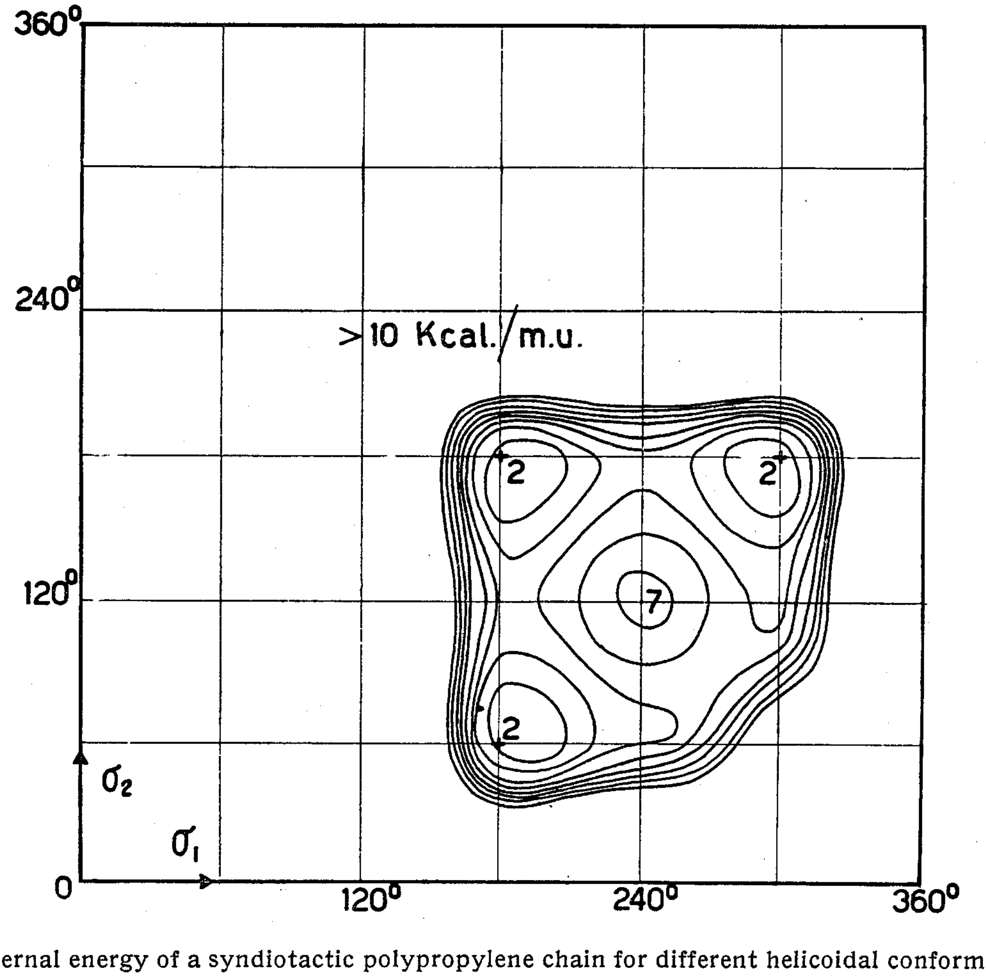

Fig. 4. Internal energy of a syndiotactic polypropylene chain for different helicoidal conformations ($\sigma_1, \sigma_1, \sigma_2, \sigma_2 \ldots$)

The third one corresponds to the conformation found for syndiotactic polybutadiene[8]). It is interesting to point out that the helices of different isotactic polymers correspond to values of σ_1 and σ_2 very near to those of minimum potential energy for polypropylene[9]).

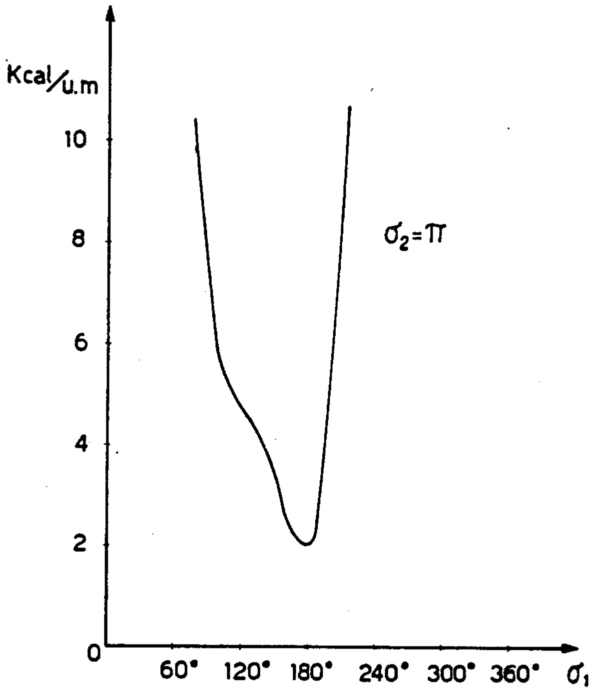

Fig. 5. Internal energy of a syndiotactic polypropylene chain for different glide-plane conformations ($\sigma_1, \pi, -\sigma_1, \pi\ldots$)

Detailed calculations are being made for the 4 crystalline polybutadienes, for the crystalline polymers of alkenyl ethers and for other polymers, and confirm the results obtained for polypropylene.

We wish to thank Prof. A. M. LIQUORI for the helpful advices he gave us, when preparing this work.

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[9]) G. NATTA, P. CORRADINI, and I. W. BASSI, Makromolekulare Chem. **33** (1959) 247; P. CORRADINI and P. GANIS, Suppl. Nuovo Cimento **15** (1960) (10) 96; P. CORRADINI and P. GANIS, J. Polymer Sci. **43** (1960) 311; P. CORRADINI and I. PASQUON, Rend. Acc. Naz. Lincei **19** (1955) 453.