JOURNAL OF POLYMER SCIENCE VOL. 58, PAGES 1191–1199 (1962)

Prediction of the Conformation of the Chain in the Crystalline State of Tactic Polymers

G. NATTA, *Istituto di Chimica Industriale del Politecnico, Milan, Italy,* P. CORRADINI, and P. GANIS, *Istituto di Chimica Generale, Università, Cagliari, Italy**

All the crystallizable linear homopolymers, of which the crystal structures have been studied in the crystal state, have chain conformations satisfying the condition of being formed by chain repetition of structural units geometrically equivalent with respect to an axis.[1]

Let the conformation of a given structural unit with respect to an axis be characterized by a set of cylindrical coordinates (ρ_i, φ_i, z_i).

Then, as may be seen in Figure 1, the structural units characterized by the indicated coordinates are all geometrically equivalent to the given unit with respect to the same axis, whatever the value of ϕ and z.

The terms isomorphous and enantiomorphous (Fig. 1) do not need any explanation. The terms isoclined and anticlined refer to the possible change of sign of all the z_i coordinates, in symmetry-related units.

A regular succession of equivalent structural units may be obtained in one of the following four ways:

(*1*) Adjacent structural units are isomorphous isoclined. Their repetition may be effected only through the operation of a screw axis, that is, through the combined operation of a translation plus a rotation around the chain axis. The symmetry of the chain is helicoidal. Incidentally, we may note that as recognized in many excellent papers by Pauling,[2] Huggins and others the helix structure is the only one possible in polyamides containing asymmetric all *d*- or all *l*-carbon atoms. It satisfies the equivalence postulate because (*a*) owing to the presence of asymmetric carbon atoms, successive structural units must be isomorphous; (*b*) owing to the presence of the polar amide bonds, successive structural units must be isoclined.

(*2*) Another way of obtaining a succession of equivalent structural units corresponds to the case in which adjacent structural units are isomorphous anticlined. The repetition of adjacent units occurs through the operation of a binary axis perpendicular to the chain axis. Pairs of adjacent anticlined units repeat themselves along the chain axis through the operation of a helicoidal translation. In fact, the presence of binary axes perpendicular to the chain axis does not hinder a helicoidal repetition.

(*3*) Another case is that in which adjacent structural units are enantiomorphous isoclined. The repetition of adjacent structural units occurs in this case through the operation of a glide plane with translation parallel

* Presently: Istituto di Chimica Generale, Università, Naples.

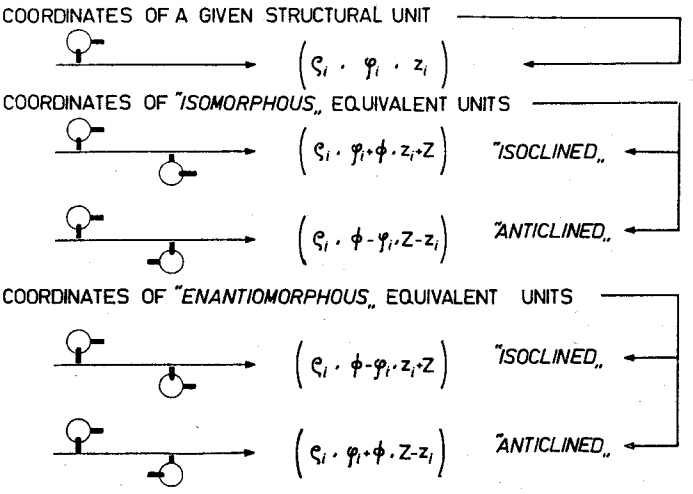


Fig. 1. Coordinates of various structural units.

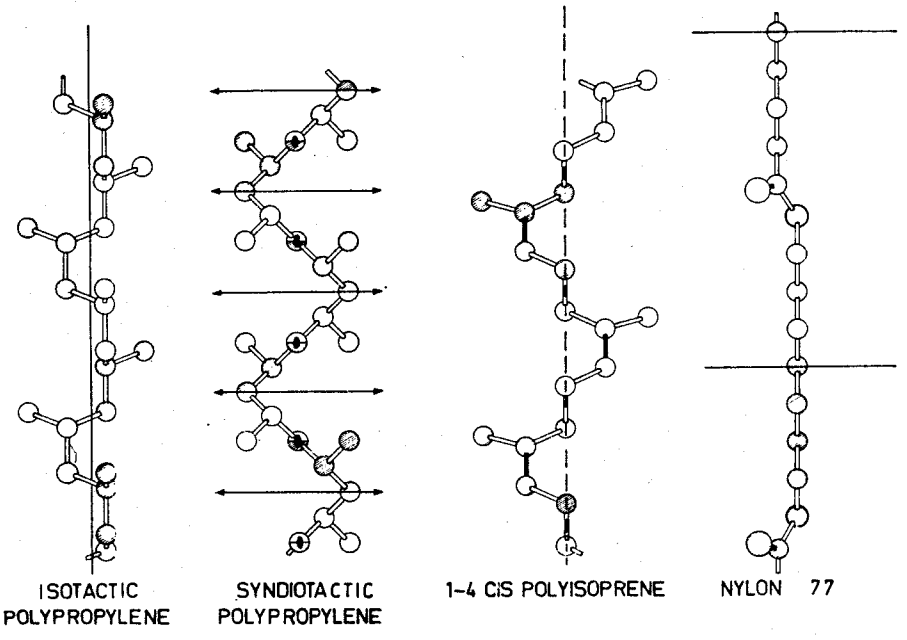


Fig. 2. Examples of different types of chain conformation.

to the chain axis. A glide plane is not compatible with a helicoidal repetition of pairs of adjacent structural units.

(*4*) Finally, suppose that adjacent structural units are enantiomorphous anticlined. The repetition of adjacent structural units may occur through the operation of a center or through the operation of a plane of symmetry perpendicular to the chain axis.

Like the glide plane in case (*3*), neither a center nor a symmetry plane is compatible with a helicoidal repetition of pairs of adjacent structural units.

Figure 2 shows some typical examples of actual chain conformations satisfying the principles stated above. (*a*) Isotactic polypropylene is an example of a succession of isomorphous isoclined units along a ternary

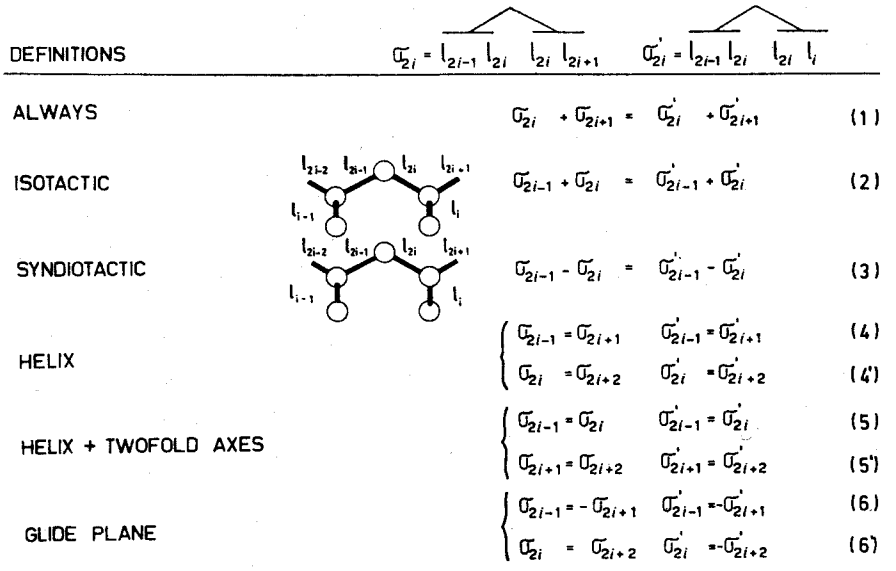


Figure 3.

helix.[3] (*b*) Syndiotactic polypropylene gives an example of a succession of alternately isomorphous anticlined units, symmetry-related in pairs by binary axes perpendicular to the chain axis. Note that successive pairs of adjacent units repeat themselves along a binary helix.[4] (*c*) 1-4-Polyisoprene is an example of a succession of alternately enantiomorphous isoclined units, which repeat themselves through the operation of a glide plane. (*d*) Nylon 77 is an example of a succession of alternately enantiomorphous anticlined units, related by a plane of symmetry. Note that in this case the structural unit is one half the monomeric unit.

Now let us discuss in detail the implications of the equivalence postulate in the case of a vinyl polymer having a regular structure (isotactic or syndiotactic). Let us consider segments of chains of vinyl polymers such as those of Figure 3. Although the chain atoms are placed on a plane for sake of simplicity no assumptions shall be made here about the actual values of internal rotation angles along the chain.

Let us call l_{2i-1} and l_{2i} two bonds adjacent to the same CH_2 group, and l_{2i} and l_{2i+1} two bonds of the chain adjacent to the same CHR group. With every bond l_j two internal rotation angles σ_j and σ'_j may be associated; σ_j is related to the conformation of three consecutive bonds along the chain, whereas σ'_j is related to the conformation of three consecutive bonds, comprising a C-R and the l_j bonds. For instance, σ_{2i} is the angle between the $l_{2i-1}l_{2i}$ and $l_{2i}l_{2i+1}$ planes whereas σ'_{2i} is the angle between the $l_{2i-1}l_{2i}$ and $l_{2i}l_i$ planes. The internal rotation angles relative to bonds adjacent to the same CHR group are always connected by relation (1); the internal rotation angles relative to bonds adjacent to the same CH_2 groups are connected by different mathematical relations whether the polymer is isotactic or syndiotactic. If the polymer is isotactic, relation (2) holds; if the polymer is syndiotactic, $\sigma_{2i-1} - \sigma_{2i}$ is always, per se, equal to $\sigma'_{2i-1} - \sigma'_{2i}$. Rela-

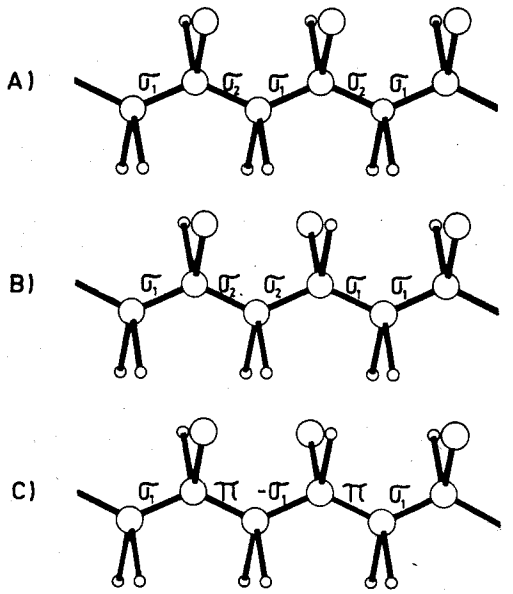


Fig. 4. Succession of internal rotation angles for (*A*) an isotactic polymer; (*B*) a syndiotactic polymer having a helicoidal conformation associated with binary axes; (*C*) a syndiotactic polymer having a glide plane conformation.

tions (2) and (3) are necessary and sufficient conditions in order for a vinyl polymer to be isotactic or syndiotactic.

Simply, it is possible to establish from relations (1), (2), and (3) the possible symmetry operators in the repetition of equivalent monomeric units along the chain axis of a regular vinyl polymer, taking into account the four modes above discussed of repetition of equivalent structural units.

(*1*) Suppose that two adjacent structural units are repeated through the operation of a screw axis. Then clearly, relations (4) and (4′) hold. Substitution of eq. (4) in eq. (1) gives relation (2), that is, a helix structure is possible only for an isotactic polymer.

(*2*) Suppose that two adjacent structural units are repeated through the operation of a binary axis, perpendicular to the chain axis and necessarily passing through the carbon atom of the CH_2 group. Then, clearly relations (5) and (5′) hold. Whatever value we give to σ_{2i} and σ_{2i+1} relation (3) is satisfied, whereas relation (2) is not; that is, a syndiotactic polymer only may have a helix with a binary axis structure.

(*3*) If two adjacent monomeric units are repeated through the operation of a glide plane, clearly relations (6) and (6′) hold. Substituting eq. (6) in eq. (1) we obtain relation (3); that is a glide plane structure is compatible only with a syndiotactic configuration of the chain. Repetition occurs every two monomeric units; if tetrahedral angles along thec hain are assumed, then one of the two internal rotation angles, σ_{2i} or σ_{2i+1}, must be equal to 180°.

(*4*) Repetition of two adjacent units in an enantiomorphous anticlined way cannot be obtained clearly through the operation of a center of symmetry; it could be obtained through the operation of a plane of symmetry

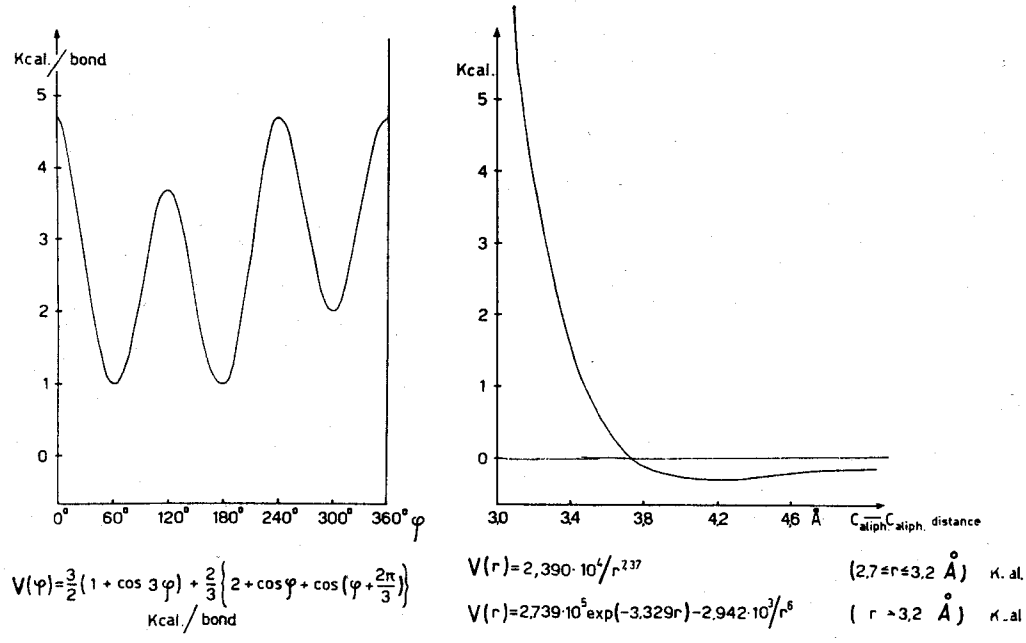


Fig. 5. Graphical representation of the interaction potential function for aliphatic carbon atoms separated by three and four bonds.

perpendicular to the chain axis. This leads to a completely planar conformation of the main chain. Such a conformation is a degenerate case of all the three structures considered above.

Concluding, with reference to Figure 4 we have seen from the equivalence postulate that: (*1*) an isotactic polymer must have a helicoidal chain conformation, characterized by a succession of internal rotation angles along the chain σ_1, σ_2, σ_1, σ_2 ...; (*2*) a syndiotactic polymer can have either a helicoidal chain conformation associated with binary axes, characterized by a succession of internal rotation angles along the chain σ_1, σ_1, σ_2, σ_2, ... or a glide plane chain conformation characterized by a succession of internal rotation angles along the chain σ_1, π, $-\sigma_1$, π....

In this way, the equivalence postulate strongly limits the possible chain models of isotactic and syndiotactic polymers. Now, another useful postulate can be introduced, that is, the conformation actually assumed by the chain in the crystal state is such that the internal energy of the chain, considered as not subjected to crystal-field forces, is the lowest, or very near to the lowest.

An approximate calculation of the internal energy of an isolated chain, as a function of the internal rotation angles allowed by the equivalence postulate, has been carried out by us for polypropylene with criteria given for the first time by Liquori.[5] We must first consider the barriers opposing free rotation around carbon—carbon bonds along the chain. As a first approximation, we have assumed the barriers to be of the same type as those postulated for low molecular weight compounds such as 1,1′-dimethylpropane (Fig. 5).[6] In this way we take into account, as a rough

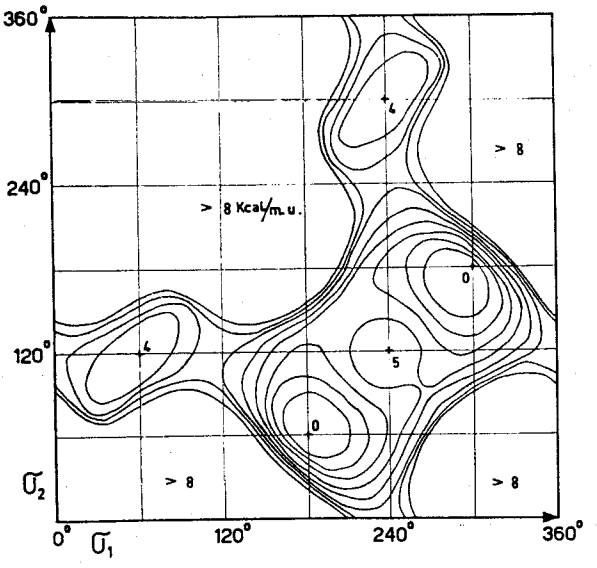


Fig. 6. Internal energy of an isotactic polypropylene chain for different helicoidal conformations.

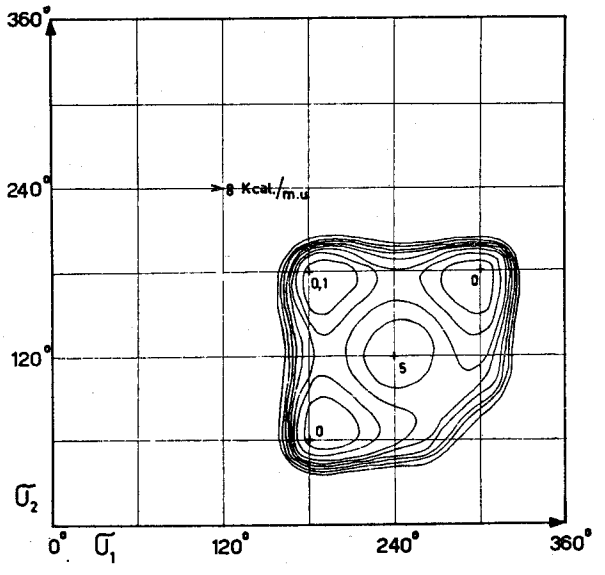


Fig. 7. Internal energy of a syndiotactic polypropylene chain for different helicoidal conformations.

approximation, the interaction between carbon atoms separated by three bonds.

The energy (in kcal./mμ) due to van der Waals interaction contacts between carbon atoms (and between the hydrogen atoms belonging to them) separated by four bonds has been assumed in the simplified form (according to Mason and Kreevoy[7] and as a function of the carbon–carbon distance) and is given in Figure 5.

Contacts between atoms separated by more than four C—C bonds have not been taken into consideration (though important for some values of σ_1

and σ_2), because they are negligible in the regions of minimum energies found.

The C—C—C angles (112°) and the C—C distances (1.54 A.) have been furthermore assumed constant. In the case of the chain conformation of isotactic crystalline polypropylene only two energy minima are allowed, corresponding respectively to a ternary right- or left-handed helix, as it has been experimentally found (Fig. 6).[3] In the case of the conformation of the chain of syndiotactic polypropylene, three equal minima of energy exist, corresponding respectively to: $\sigma_1 = 180°$, $\sigma_2 = 60°$; $\sigma_1 = 300°$, $\sigma_2 = 180°$; $\sigma_1 = 180°$, $\sigma_2 = 180°$. The analysis of Figure 7 refers to

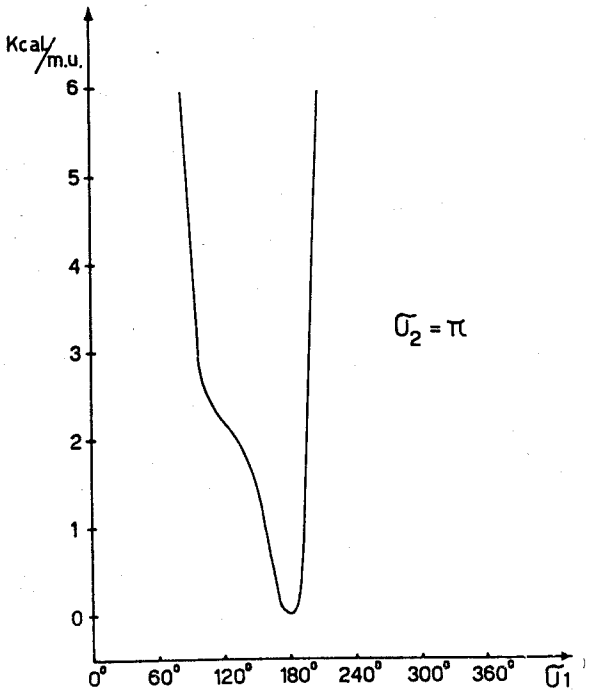


Fig. 8. Internal energy of a syndiotactic polypropylene chain for different glide plane conformations.

structural models of the helix and twofold axis type. A minimum for the completely planar chain structure is found also in the analysis of models of the glide plane type (Fig. 8).

The first and second conformations of Figure 7 correspond to those found for the right- and left-handed helix of syndiotactic polypropylene.[3] 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]

Detailed calculations have been made also for the crystalline polymers of alkenyl ethers and have contributed to the establishment of their configuration.

References

1. Natta, G., and P. Corradini, *Nuovo Cimento Suppl.*, **15**, 9 (1960); G. Natta and P. Corradini, *J. Polymer Sci.*, **39**, 29 (1959); P. Corradini, *Accad. naz. Lincei, Roma*, **38**, 7 (1960).

2. Pauling, L., R. B. Corey, and H. R. Branson, *Proc. Nat. Acad. Sci. U.S.*, **37**, 205 (1951).

3. Natta, G., and P. Corradini, *Nuovo Cimento Suppl.*, **15**, 40 (1960).

4. Natta, G., I. Pasquon, P. Corradini, M. Peraldo, M. Pegoraro, and A. Zambelli, *Atti. accad. Nazl. Lincei, Rend.*, **28**, 539 (1960).

5. Liquori, A. M., *IV Corso Estivo*, Varenna, 1961, p. 311; G. Natta, P. Corradini, P. Ganis, *Makromol. Chem.*, **39**, 238 (1960).

6. Mizushima S., and I. Shimanochi, *J. Am. Chem. Soc.*, **71**, 1320 (1949).

7. Mason, E. A., and M. M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 5808 (1955).

8. Natta, G., and P. Corradini, *J. Polymer Sci.*, **20**, 251 (1956).

9. Natta, G., P. Corradini, and I. W. Bassi, *Makromol. Chem.*, **33**, 247 (1959); P. Corradini and P. Ganis, *Nuovo Cimento Suppl.*, **15**, 96 (1960); P. Corradini and P. Ganis, *J. Polymer Sci.*, **43**, 311 (1960).

Synopsis

The postulate of geometric equivalence of the monomeric units of a tactic chain with regard to an axis (I) and the postulate that the conformation is such that the internal energy of the chain, considered as not subjected to external forces, is the lowest (II), can be applied to the prediction of the conformation in the crystalline state of chains of unknown configuration, as demonstrated by the application of these postulates to known structures. Postulate (I) leads easily to the prediction of the possible linear chain repetition groups for a succession of monomeric units of given absolute configuration. In the case of polypropylene, for instance, it can be easily shown that isotactic polypropylene should have a helicoidal chain conformation, whereas syndiotactic polypropylene should have a glide plane or a helix (associated with two-fold axes perpendicular to the chain axis) chain conformation. The angles of internal rotation defining the actual conformation of tactic polypropylene chains can be predicted on the basis of postulate (II) through semiquantitative methods of minimization of the internal energy content.

Résumé

Le postulat de l'équivalence géométrique des unités monomériques d'une chaîne tactique par rapport à une axe (I) ainsi que le postulat d'une conformation associée à une valeur minimale de l'énergie interne de la chaîne, considérée comme n'étant pas soumises à des forces extérieures (II), peuvent être utilisés pour la prédiction de la configuration à l'état cristallin des chaînes dont la configuration est inconnue. Ceci a été démontré par l'application de ces postulats à des structures connues. Le postulat (I) conduit aisément à la prédiction de la répitition possible des groupes d'une chaîne linéaire pour une succession d'unités monomériques ayant une configuration absolue déterminée. Dans le cas du polypropylène par exemple, on a pu aisément montrer que la conformation du polymère isotactique devait être celle d'une chaîne hélicoidale tandis que celle du polymère syndiotactique devait être celle d'un plan horizontal ou d'une hélice (associée à deux axes perpendiculaires à l'axe de la chaîne). Les angles de rotation interne définissant la conformation réelle des chaînes tactiques de polypropylène peuvent être prédits sur la base du postulat (II) grâce à des méthodes semiquantitatives de calcul de la valeur minimale de l'énergie interne.

Zusammenfassung

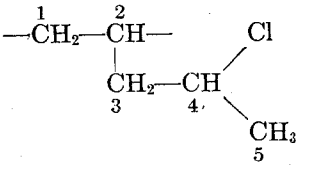
Das Postulat der geometrischen Äquivalenz der Monomereinheiten einer taktischen Kette in bezug auf eine Achse (I) und das Postulat, dass die Kette eine solche Konformation annimmt, dass ihre innere Energie ohne Einwirkung äusserer Kräfte den kleinsten Wert hat (II), können zur Vorhersage der Konformation von Ketten mit unbekannter Konfiguration im kristallinen Zustand verwendet werden, wie durch Anwendung dieser Postulate auf bekannte Strukturen gezeigt wird. Postulat (I) führt für eine Folge monomerer Einheiten mit gegebener absoluter Konfiguration leicht zur Vorhersage der möglichen, wiederkehrenden Gruppen einer linearen Kette. Im Falle des Polypropylens kann z.B. leicht gezeigt werden, dass isotaktisches Polypropylen eine Helixkettenkonformation besitzen sollte, während syndiotaktisches Polypropylen eine Gleitebenen- oder Helix- (verbunden mit zweifachen Achsen senkrecht zur Kettenachse)-kettenkonformation haben sollte. Die inneren Rotationswinkel, welche die tatsachliche Konformation taktischer Polypropylenketten festlegen, können auf Grund von Postulat (II) durch halbquantitative Methoden der Minimumsbildung der inneren Energie vorhergesagt werden.

Discussion

R. W. Lenz (*Eastern Research Lab., Dow Chemical Co., Framingham, Mass.*): For a polymer capable of existing in a helical conformation, what structural requirements must be met in order to have a conformation of only one screw sense?

Will you get it if the center of asymmetry is located *only* in the pendant group?

G. Natta: We expect a difference in stability of left- and right-handed helices also if the center of asymmetry is located in the pendant group. Eventually this difference may be low. Consider, for example, the hypothetical case of poly-4-chloro-1-pentene:



The internal rotation angle 1-2-3-4 tends to be *trans*, whereas Cl-2-3-4 tends to be *gauche*. As C_2 is asymmetric, that sense of screw will be stabilized, which corresponds to the possibility of giving the internal rotation angle 1-2-3-4 a *trans* conformation.

R. Stein (*University of Massachusetts, Amherst, Mass.*): Would a comparison of your calculated energy of an isolated chain with the free energy of a random chain indicate that helices should be stable in the amorphous state?

G. Natta: In the paper we have given, we have attempted a calculation of internal energy content of regular chains as a function of internal rotation angles. Minimization of free energy requires consideration of possible inversions of the screw sense along the chain. Detailed calculations are being made by Corradini and Allegra. In the case of polypropylene, the helical conformations are expected also in the amorphous state; thus:

(1) Isotactic: ...(TG)(TG)(TT)(*G*T)(*G*T)(G′G″)(TG)(TG)...
(2) Syndiotactic: ...(TT)(GG)(TT)(TT)(TT)(GG)(TT)(GG)(TT)(TT)(*GG*)...

where *G* and G are enantiomorphous *gauche* bonds, T are *trans* bonds, and G′ and G″ are *gauche* bonds with $\sigma \neq \pm 60°$.