Kurzmitteilung

On the Conformation and Stereoregularity
of Isotactic Vinyl Polymer Chains

by

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The recent papers of Flory and coworkers[1,2] on the stereoregularity of vinyl polymer chains have prompted us to make a few comments.

The view that syndiotactic units of the type $(\ldots d\,d\,d\,\bar{d}\,\bar{l}\,l\,l\,l\ldots)$ could be incorporated in the crystal lattice of isotactic polymers as formulated by Flory cannot be accepted because this implies that senses of rotation of neighbouring chains in the crystal lattice must be random. This is equivalent to stating that all the structural determinations on isotactic polymers[3] performed up to now — in particular the assignment of space group and symmetry elements — are wrong.

To mention but one argument against this view: in the case of poly-α-butene, the fact that each right-handed helix is surrounded by left-handed helices and *vice versa* is demonstrated by the observation that 6 chains are contained in each hexagonal unit cell with $a = 17.7$ Å, $c = 6.5$ Å, whereas all possible X-ray reflections with $-h + k + l \neq 3n$ are absent[4].

On the other hand, Natta et al.[5] found that isomorphous substitution of monomeric units is possible in the lattice of the crystalline polymer provided that the substitution does not interfere strongly with the conformation and the shape of the chain backbone. Perhaps this principle may be applied to the inclusion of syndiotactic units of the type $(\ldots d\,d\,\bar{d}\,\bar{l}\,\bar{d}\,d\,d\ldots)$ which would leave the helical sense unchanged. However, the crystal strain implied in such a sequence would severely limit the number of such units which could be incorporated in the crystal.

The statement that characteristic ratios $\langle r_0^2 \rangle / nl^2$ calculated for a perfect isotactic chain are much greater than observed by experiment (ca. 9 to 10) does not apply if reasonable values of the energy required for a helical sense inversion in a sequence $\ldots G{-}T\ (G'_{-}G''_{+})\ TG_{+}\ldots$ are assumed[6].

A value $\geqslant 5$ kcal·mole^{-1}, as suggested by FLORY, does not agree with all calculated values from the conformational analyses performed so far for vinyl polymers and other model compounds[7-9] *).

However, we agree that it is difficult to escape from the conclusion that present theories predict a negative coefficient of the unperturbed end-to-end distance with temperature in isotactic polymers.

According to solution measurements by MORAGLIO[11], the temperature coefficient of the unperturbed dimensions of isotactic polypentene is indeed negative. Derivation of this temperature coefficient from stress-temperature measurements on the bulk polymer may be questioned at least in some cases. For instance, the temperature coefficient of the unperturbed dimensions in 1.4-*cis*-polybutadiene derived from solution studies is opposite in sign to that derived from measurements in the bulk polymer[12]. Furthermore, the view is widely accepted that chain segments show some preference to become parallel among themselves in the amorphous state or in the melt.

NMR measurements[13] are strongly indicative of a degree of steric purity much higher than 90 % in isotactic polypropylene, contrary to the suggestions of FLORY. In the spectra of deuterated polypropylene, the presence of syndiotactic units in an amount higher than 2—3 % would have been detected, at least as a peak slightly displaced from the usual one[14].

The fairly good symmetry of the observed quartet does not allow a percentage of syndiotactic units higher than 5 % in the samples investigated, even in the very unfortunate instance, recently suggested by FLORY and BALDESCHWIELER[15], that the syndiotactic peak is shifted, so as to be obscured by one of the peaks of the isotactic quartet.

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*) It seems also to disagree with the energy of steric repulsion between neighbouring groups in polyisobutylene, which is estimated by various methods to be 6.5 kcal/m.u.[10]. It is impossible to build a chain of polyisobutylene avoiding 2 or 3 very short contact distances ($\leqslant 3.0$ Å) per monomeric unit between carbon atoms separated by 4 bonds; moreover, reasonable models can be built only by considerably displacing the internal rotation angles about single bonds from the staggered conformations. At the inversion $G'G''$ between two different senses of spiralization of polypropylene there are no contact distances between carbon atoms shorter than 3.0 Å. It may be inferred that values of $E_{G'-G''+}$ as low as, and perhaps lower than 2.7 kcal·mole^{-1} for polypropylene are quite reasonable[6]. When such values are assumed for $E_{G'-G''+}$ it can be shown that calculated $\langle r_0^2 \rangle/nl^2$ values are well within the observed values. This is also in agreement with the results reported in Fig. 4 of the quoted paper by FLORY et al.[2], which point out that values of $E_{G'-G''+}$ ($= -RT\ln\omega$ in the symbolism of the authors) between 1.8 and 3.1 kcal/m.u. correspond to calculated values of $\langle r_0^2 \rangle/nl^2$ between 9 and 10 at room temperature.

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