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Extended-chain structure for isotactic polystyrene: additional X-ray diffraction and calorimetric results

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The recently discovered extended-chain structure in isotactic polystyrene gels opens new horizons on the stereochemistry of the polyolefins and molecular organization in polymeric gels. New X-ray fibre diffraction patterns obtained from stretched gels formed in different solvents support the contention that the structure is produced by intramolecular forces between contiguous units probably via adjacent aromatic appendages.

INTRODUCTION

The purpose of this paper is to make additions to recent reports on the newly emerging chain conformation in isotactic polystyrene (i-PS), to circumscribe more closely the experimental information presented previously and to make comparisons between quite recent structure proposals from other sources. In addition differential scanning calorimetric results show that this conformation exists within the gel junction zones which melt at a lower temperature than the usual crystalline phase of isotactic polystyrene.

X-ray diffraction and conformational analysis

Natta *et al.*¹ showed that in crystalline i-PS the molecular chains form three-fold helices with an axial advance (h) per styrene monomer of 0.222 nm, some 15% below the theoretical maximum extension of $h = 0.26 \text{ nm}^*$ for the styrene monomer in the all-*trans* (tt) fully-extended chain.

X-ray diffraction patterns of oriented gels of i-PS, obtained at high supercoolings in decalin, are quite different^{2,3} from the traditional Natta patterns¹. In particular a meridional reflection occurs at a spacing of 0.51 nm, together with successive orders, requiring an extended, or nearly extended, chain conformation^{2,3}. In addition to the 0.51 nm meridional reflection, layer lines are observed with six times this spacing at 3.06 nm which

equate with twelve styrene units³. The 0.51 nm meridional reflection indicates that the asymmetric unit correlates with a pair of styrene monomers rotating about an axis to generate a six-fold helix, the average advance (h) per styrene monomer being 0.255 nm, using bond angles from the crystal structure¹, which is only marginally below the fully-extended tt conformation.

Extended conformations for i-PS in the past were ruled out on stereochemical arguments^{4,5} and by computerized conformational analyses⁶⁻⁸. These latter three independent analyses calculated the potential energy for the meso dyad of i-PS as a function of the two backbone torsion angles ψ_1 and ψ_2 . (The all-*trans* tt conformation is defined by $\psi_1 = \psi_2 = 0^\circ$). Similar conclusions were obtained in all three conformational analyses: a pair of energy minima corresponding to right-handed and left-handed three-fold helices ($\psi_1 = 0^\circ, \psi_2 = \pm 120^\circ$ denoted by tg or $t\bar{g}$) and in addition an energy minimum close to the tt conformation. The steric hindrance arising from contiguous phenyl groups is relieved by rotations in the range $0^\circ - 20^\circ$ for ψ_1 and ψ_2 , but with rotations in opposite directions. Distortions of this kind generate a chain conformation which traces out an arc of a circle⁸ or a slowly spiralling helix of large diameter and small pitch⁹.

Helical conformations of polymers in which the asymmetric repeat correlates with two monomers is quite common in polysaccharides (see, for example, Atkins¹⁰) and results from perturbations of regular helices with a repeating unit equivalent to a single monomer, induced by factors such as: chain packing; solvent environment; non-stoichiometry of solvent molecules; or local influence of one monomer on its immediate neighbours. Thus it was considered simpler, in the first instance, to construct

* This distance may be varied somewhat by the particular values chosen for the C-C-C backbone angles

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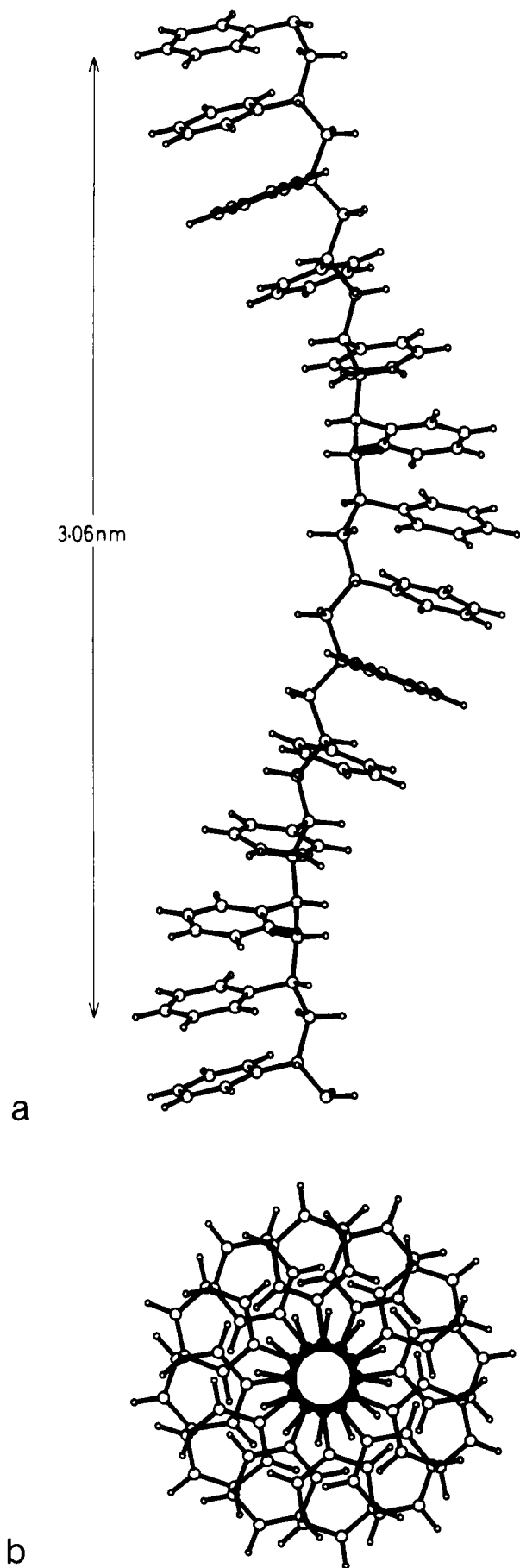


Figure 1 (a) Projection perpendicular to helix axis of the near all-*trans* i-PS, $\psi_1 = 23.1^\circ$ and $\psi_2 = 11.6^\circ$. The helix has twelve monomers in one turn with axial advance of 0.255 nm. (b) Projection down helix axis

regular twelve-fold helices with $h=0.255$ nm and later to consider modifications for alternating monomers, either by variation of the backbone torsional angles, or rotation of the phenyl groups, or both, to develop the six-fold character of the X-ray diffraction information.

Conformational analyses by Atkins *et al.*⁹ have shown that a highly extended twelve-fold helix is stereochemically feasible with low energy and with the necessary modifications of alternating torsion angle pairs to make the asymmetric unit a dimer would account for the layer line spacing and six-fold helical character observed in the X-ray diffraction pattern. The conformation is shown in Figure 1 and has torsion angles $\psi_1 = 23.1^\circ$ and $\psi_2 = 11.6^\circ$. Independent calculations by Sundarajan¹¹ and Corradini *et al.*¹² have confirmed the essential features of the structure. It is of interest to note that Stegan and Boyd¹³ have criticized previous conformational analyses as being too rigid; their own analysis has indicated greater conformational freedom than previously supposed. Lovell and Windle¹⁴ have proposed a model based on a sequence *ttts* where *s* represents a skew rotation of 40° – 60° from the *trans* position. No full-scale energy calculations have been undertaken and the stereochemical feasibility has been monitored only with space-filling models. Thus the proposed structure must await more rigorous testing before it can be decided if it is an acceptable alternative or modification to the models already discussed^{9,11,12}.

Support for an isotactic conformation different from the Natta conformation in polystyrene gels has come from an independent approach using Fourier transform infrared spectroscopy¹⁵. The spectra obtained from gel films were observed to be significantly different from those of amorphous and crystalline i-PS indicating that the gel form is in a different conformation than the Natta three-fold crystal structure. Computer-assisted subtraction procedures indicated that approximately 35% of the polystyrene chains participate in the gel component, effectively ruling out structural defects as the origin of the ordered gel component.

The initial experimental investigations were undertaken on polystyrene gels prepared from decalin (a mixture of *cis* and *trans* decalin with the latter predominating). It was naturally considered important to ascertain the relationship between the polymer chains and the solvents and to ensure that the structural features were emanating from the polymer rather than the possible organization in the solvent. Thus gels were obtained from both *trans*- and *cis*-decalin (and also from xylene) which have quite different molecular shapes. X-ray diffraction patterns from *trans*-decalin were similar to those published previously for technical decalin and a typical pattern is reproduced in Figure 2a. An X-ray diffraction pattern from polystyrene gels in *cis*-decalin is illustrated in Figure 2b for comparison.

The layer line periodicities are the same and again a meridional reflection occurs on the 6th layer line at spacing 0.51 nm yet there are a number of noticeable differences between the two X-ray diffraction patterns. The *cis*-decalin pattern has a pronounced first layer line whereas the *trans*-decalin pattern has weak 1st and 3rd layer lines. Indeed the weakness of diffracted intensity on odd order layer lines has prompted speculation regarding the possibility of two polystyrene chains intertwining to form a double helix¹¹ similar to the well-known concept in DNA. However, the weakness of odd order layer lines in the *trans*-decalin pattern should not form the basis for

support of a double helix until more rigorous testing is undertaken.

As stated in ref 9, all 'dried' gels contained appreciable amounts of solvent, although were completely dry to the touch. Even on most rigorous vacuum drying about 20% w/w solvent remained, somewhat below this value for

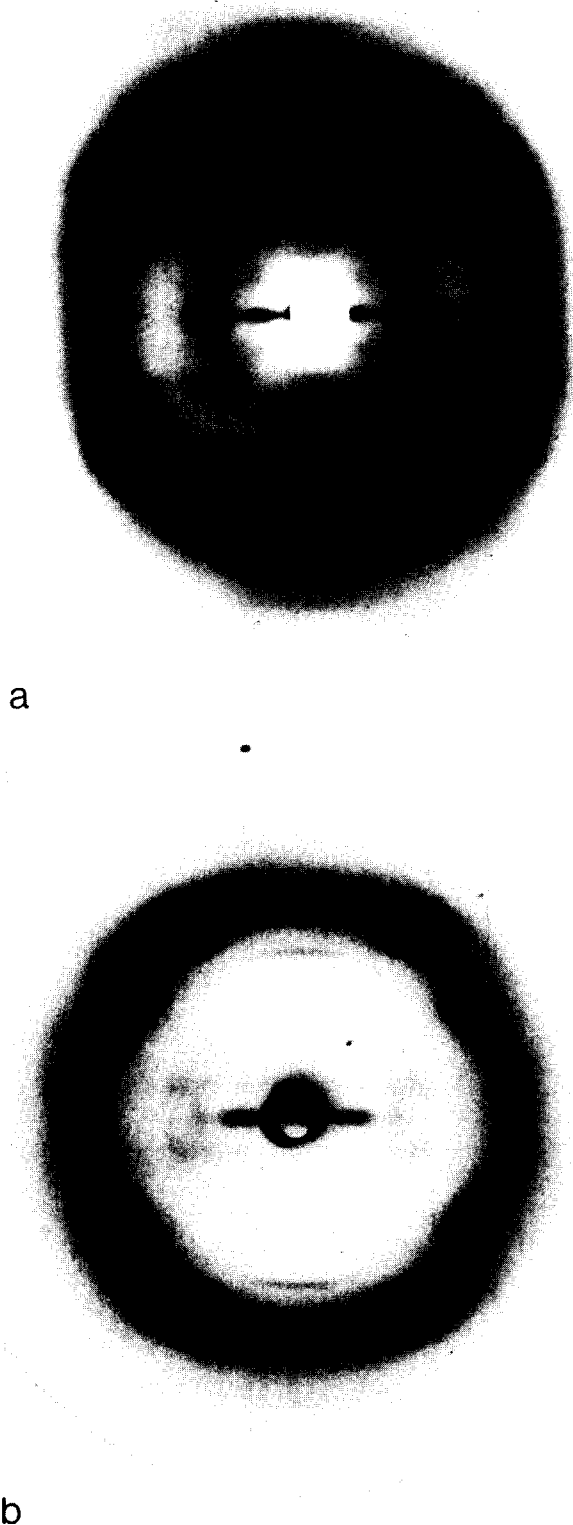


Figure 2 X-ray fibre diffraction patterns of i-PS gels: (a) i-PS in *trans*-decalin showing rather weak odd order layer lines at spacing 3.06 nm; (b) i-PS in *cis*-decalin showing strong first order layer line, again with spacing 3.06 nm

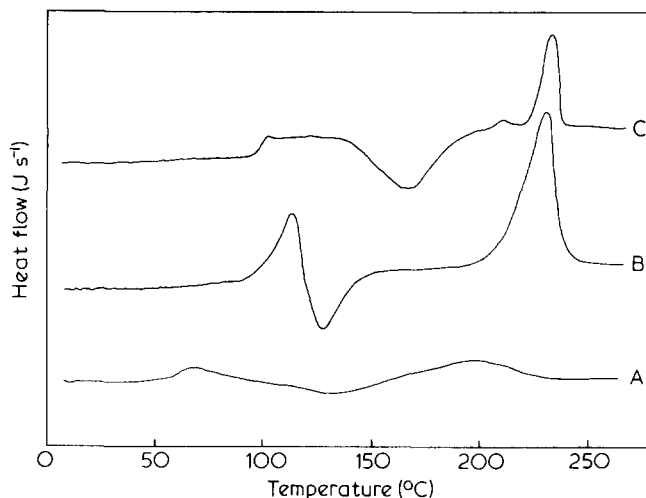


Figure 3 D.s.c. curves of i-PS gels: (a) as-formed polystyrene (*trans*-decalin gel, 10% w/w of polymer); (b) solvent-extracted gel; (c) i-PS (rescan of b), heating rate 10°C min⁻¹. For comparison **Figure 3c** shows the thermogram which results on rescanning the sample in **Figure 3b** after melting and quenching to 0°C. This trace is typical of initially amorphous i-PS where the transition around 100°C is due to T_g . (Note that the T_g transition is absent – or hardly recognizable in gel processed samples.)

trans- and somewhat above for *cis*-decalin preparations as determined by weighing before and after melting *in vacuo*, the total removal in the latter case having been ascertained by infra-red spectroscopy. The complete removal of solvent from the gel state without melting, however, could be achieved by exchanging the solvent with other miscible, though more volatile liquid, such as acetone and diethyl ether. As a result of this procedure the completely solvent-free, initially observed *cis*-decalin gel pattern disappeared and the Natta pattern took its place (whether the former transformed into the latter or whether it merely disappeared and the Natta structure formed separately we cannot say).

However, the completely solvent-free *trans*-decalin sample retained the corresponding gel pattern (i.e. with comparatively pronounced layer lines at 1.5 nm and 0.75 nm). Consequently, we can say that the occurrence of the layer lines which are characteristic of the near extended *tt* backbone do not rely on the presence of solvent for their existence. However, the solvent may well influence the relative intensity of the layer lines and the maxima along them. Thus, while the new backbone geometry proposed appears firm, details relying on the intensities (such as side group orientation, interchain relations, etc.) could well depend on additional extraneous factors, such as bound solvent. Conversely, it can be said that the detailed intensities do not merit in depth analysis until the external variables which influence it are fully appreciated and controlled. Even so in the light of the above, the *trans*-decalin gel pattern is more likely to reflect the intrinsic structure of polystyrene.

PERTINENT THERMAL MEASUREMENTS

The existence of the different crystal phases is also reflected by the thermal behaviour. Out of a more extensive study correlating differential scanning calorimetry (d.s.c.) with X-ray diffraction (the latter including diffraction recorded at the elevated temperatures) a few d.s.c. traces will be quoted to reinforce what has been stated above.

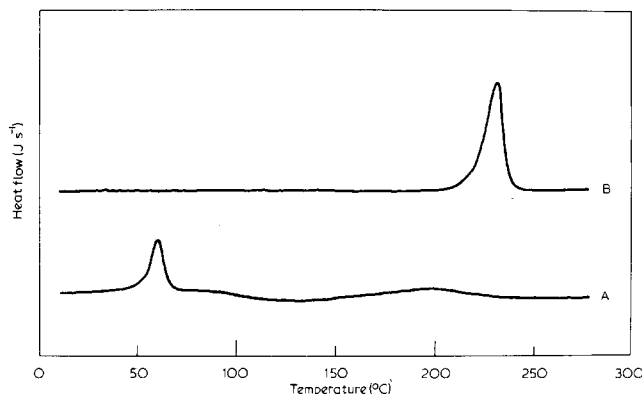


Figure 4 D.s.c. curves of i-PS gels: (a) As-formed polystyrene *cis*-decalin gel, 10% w/w of polymer; (b) solvent-extracted gel, heating rate $10^{\circ}\text{C min}^{-1}$

Figure 3a shows a typical thermogram of an as-formed *trans*-decalin gel obtained in the original unoriented comparatively dilute (10% w/w) gel state (hence the weak features). The most noticeable feature is an endotherm at $60^{\circ}\text{--}70^{\circ}\text{C}$ (of about $1\text{--}2\text{ J g}^{-1}$ gel) which we know to be the gel melting point. The shallow exotherm–endotherm following corresponds to crystallization into the Natta structure and to the subsequent melting of the latter. Stretched wet gels display similar behaviour. The $\sim 60^{\circ}\text{C}$ endotherm associated with the wet gel melting was still recognizable in the d.s.c. traces of nominally dried gels, which nevertheless still contained 15–20% solvent, but with additional features at higher temperatures. These consist of a sharp endotherm–exotherm pair at 110° and 130°C , respectively, which by parallel X-ray evidence, corresponds to the melting of dried gel crystals and to the formation of the Natta structure respectively, together with a further endotherm at $\sim 200^{\circ}\text{C}$ and above, corresponding to the melting of the Natta crystals. These latter features are prominently displayed by the thermogram of Figure 3b which corresponds to a gel totally dried via the solvent extraction procedure (not the 60°C endotherm which in the total absence of solvent has disappeared altogether).

Figures 4a and 4b give the patterns analogous to Figures 3a and 3b for polystyrene gel formed from *cis*-decalin. We again see the gel melting peak at $\sim 60^{\circ}\text{C}$, in this case more prominent. This peak, however, disappears completely on solvent extraction, an effect which is also apparent from the X-ray pattern, which in such samples reveals only the Natta pattern. The endotherm above

200°C then corresponds, just as in Figure 3b, to the melting of these latter crystals.

It follows that all the phases and their mutual transformations and/or melting are displayed also by the thermal behaviour. In particular, the d.s.c. information supports the particular X-ray evidence that the *trans*-decalin gel crystals can exist without solvent while the *cis*-decalin gel crystals rely on the presence of solvent for their existence. This reinforces the X-ray work that it is the *trans*-decalin pattern which is likely to be intrinsic to the polymer and consequently ought to remain the focus of attention. This, however, should not remove the need for an awareness of the fact that certain solvents can have intimate association with the gel crystals to the extent of modifying the X-ray intensities.

CONCLUSIONS

While no firm conclusion emerges the existence of the near-extended *tt* chain conformation of i-PS has gained further support. In particular, new variants have been found and conditions under which the new conformation type arises have been more closely circumscribed which should aid the eventual full unravelling of the new structure. This, we feel, opens a new discussion on the issue of chain conformations in polyolefins.

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