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Crystallization from the Bulk of Isotactic Polystyrene in the Extended Conformation

A Low Density Crystalline Form

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Summary

The extended conformation with non-staggered *tt* conformation of the skeletal bonds, has been crystallized from the bulk by exposure of isotactic polystyrene (iPS) films to solvent vapor at room temperature. Due to the predominant intramolecular interaction between the adjacent phenyls, solvent molecules are required to provide the stability required for crystallization. A unit cell with a = 21 A, b = 16.4 A and c = 30.6 A, with 4 chains and 8-16 solvent molecules has been proposed. It is shown that the extended conformation exists with significant perpetuation in the amorphous zones of semicrystalline films containing the threefold helical structure. It is suggested that the lower melting temperature of the extended form is due to the requirement of the presence of the solvent molecule and not due to intramolecular instability.

Introduction

The accessibility of the non-staggered *tt* conformation to the skeletal bonds in vinyl chains with planar substituents, has been shown by stereochemical calculations (SUNDARARAJAN, 1977, 1978, 1979, 1980; SUNDARARAJAN and FLORY, 1974; YOON et al, 1975). The X-ray diffraction obtained by ATKINS et al (1977) from the gels of isotactic polystyrene, prepared by quenching the solution in poor solvent, was different from that of the conventional threefold helical structure (NATTA and CORRADINI, 1960). It was first shown by SUNDARARAJAN (1979) that an extended helical conformation, such as shown in Figure 1, with non-staggered *tt* disposition of skeletal bonds would account for the diffraction pattern from the gels. Subsequent publications confirmed the possibility of such a chain conformation (ATKINS et al, 1980; LOVELL and WINDLE, 1980; CORRADINI et al, 1980).

The calculations showed (SUNDARARAJAN, 1979) that the energy of the extended conformation was lower than that of the threefold helical conformation by about 1 kcal/mol. In the former, as seen from Figure 1, the interaction between the adjacent phenyls predominates and as such, their interaction

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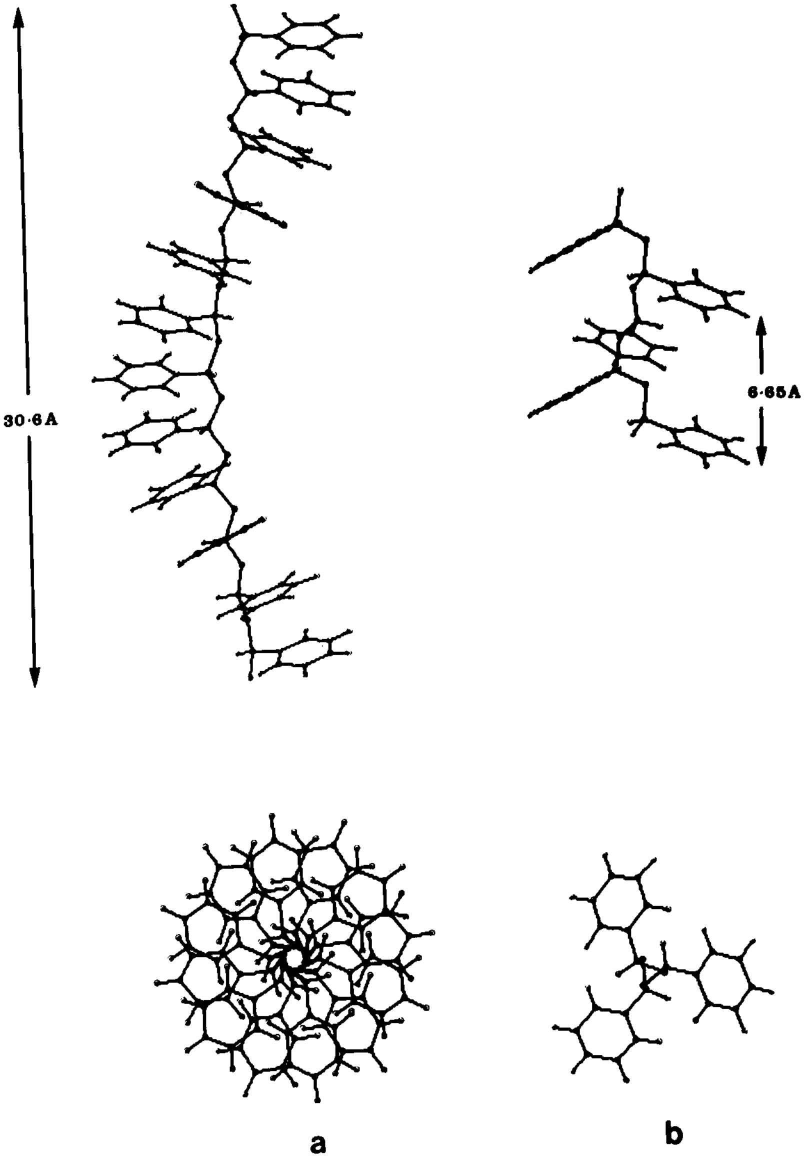


Figure 1: Projections of the (a) extended helical conformation with nonstaggered tt state of the skeletal bonds and (b) threefold helical structure with the tg state of the skeletal bonds

with the adjacent chains or the solvent molecules can be expected to be insignificant. Hence, such a conformation can be expected to occur in profusion in poor solvent systems. Our recent studies (SUNDARARAJAN et al, 1982) on gelation of iPS from various solvents showed that although the gels can be prepared from a variety of solvents, the extended conformation occurred in bulky, cyclic hydrocarbon solvents, whereas a mixture of the extended and threefold helical structures or exclusively the latter resulted in substituted aromatic solvents.

Although the extended conformation was shown to be of lower energy than the threefold helix, such a conformation has never been reported in iPS crystallized from bulk. In the crystal structure studies of iPS, the bulk films are usually annealed at temperatures above 130°C. The extended conformation in the gels of iPS melts between 80 and 120°C, depending on the solvent used (WELLINGHOFF et al, 1979; SUNDARARAJAN et al, 1982). Hence, such a conformation has not been observed during bulk crystallization. Naturally, the question arises if it could be crystallized by annealing the films below its T_m, say, between 50 and 100°C. Our attempts showed that the extended conformation cannot be crystallized by annealing.

Since in the extended form, the intramolecular interaction predominates, the interchain interaction which is necessary for crystallization to occur is negligible. However, if such an interchain interaction is provided by an agent, such as the solvent molecule, crystallization can be expected to occur from the bulk. Hence, studies on the effect of exposing iPS films to solvent vapor were undertaken.

Experimental

Samples of iPS were obtained from Polysciences. These are the same as those used in the previous study (SUNDARARAJAN et al, 1982). Proton NMR analysis (G.K. Hamer, Personal Communication), using a Bruker WM-250 NMR spectrometer showed the isotactic dyad content of the samples to be 75-80%.

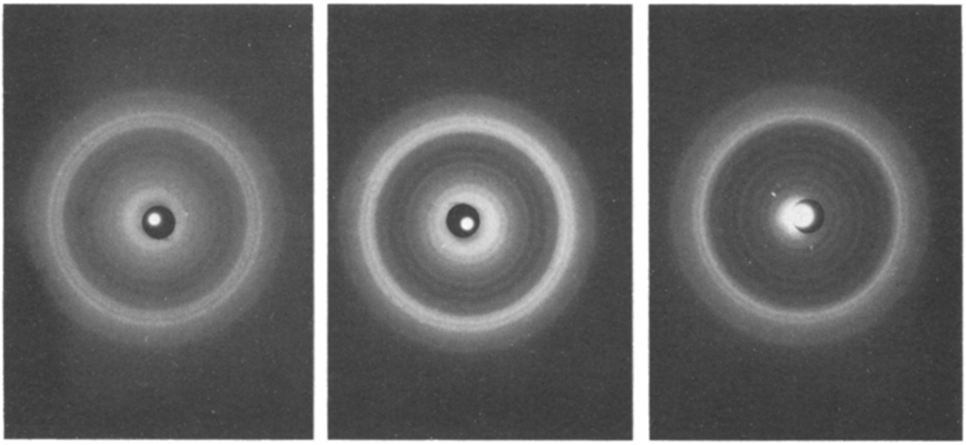
Amorphous films for vapor exposure were obtained in two ways: (i) the samples were sandwiched between a pair of glass slides and a melt-quenched film was prepared. No external pressure was applied; (ii) a 15% (W/V) solution of the sample in toluene (ACS grade) was poured on a glass plate and a film was prepared under ambient conditions. The resulting films in both cases were amorphous, as determined by wide-angle X-ray diffraction.

As in the previous study (SUNDARARAJAN et al, 1982), hexahydroindan (b.p. 167°C), cyclooctane (b.p. 151°C), ethylbenzene (b.p. 136°C), and nitrobenzene (b.p. 210°C) were used for vapor exposure. All the solvents were of spectroscopic grade, with the exception of nitrobenzene, which was AR grade. The films were exposed to the solvent vapor by placing them over the mouth of a small bottle containing the solvent, and both were enclosed in a glass chamber. The time of exposure varied from 24 hrs to 18 days, depending on the sample and the solvent. The setup is admittedly primitive. However, the aim of this study is to identify the conformation rather than measure the diffusion rates, etc. The vapor exposed films were dried under ambient conditions for 24 hrs before analysis.

The films were characterized by X-ray diffraction and scanning electron microscopy. The X-ray patterns, in the wide-angle region, were recorded using a box-type flat film camera (W. Warhus & Co., Wilmington, DE). Copper K_α radiation ($\lambda = 1.5418$ A) was used. Micrographs were recorded using an ISI Super II scanning electron microscope. Densities of the films were determined by flotation in concentrated NaCℓ solution at 25°C via appropriate dilution. The solution densities were measured using a Westphal balance.

Results and Discussion

The X-ray diffraction patterns of the films exposed to any of the four solvent vapors showed that crystallization has occurred. Figure 2 shows the patterns obtained by exposing the toluene-cast iPS film to hexahydroindan, nitrobenzene and cyclooctane. The patterns were similar in the case of the melt-quenched amorphous films exposed to the above solvents. It is seen that as many as 14 reflections are present in Figure 2. The reflections with spacings of 20.5 and 5.1 A, characteristic of the extended conformation are present. None of the other reflections correspond to the threefold helical form but the extended form. This was confirmed by the loss of these reflections upon annealing the films at 125°C. The patterns also show that the extended form has been exclusively crystallized from the bulk. Although there is a reflection of spacing at 4.8 A, similar to that in the crystal structure of the threefold form (NATTA and CORRADINI, 1960), the absence of any other strong reflection corresponding to the latter leads to the conclusion that this reflection occurs also in the crystal structure of the extended form. The measured *d* spacings are given in Table 1.



a b c

Figure 2: X-ray diffraction patterns from the toluene-cast iPS films exposed to (a) hexahydroindan (3 days), (b) nitrobenzene (5 days), and (c) cyclooctane (24 hrs)

TABLE 1

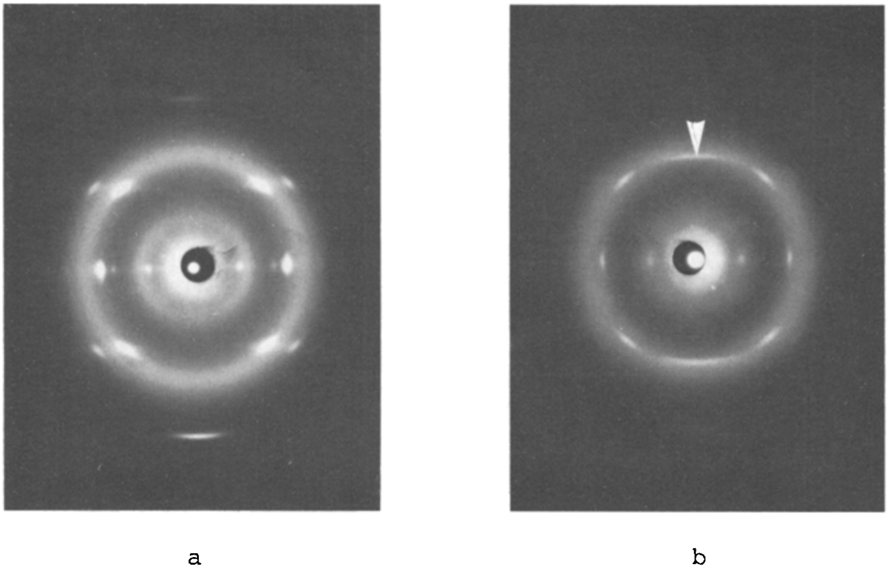
Interplanar spacings (A) and Miller Indices for the extended conformation of iPS

No.	d(obs)	d(calc)	(hkl)
1	21.0	21.0	100
2	16.4	16.4	010
3	13.04	12.92	110
4	10.43	10.50	200
5	8.12	8.20	020
6	7.02	7.00	300
		6.93	014
7	6.02	5.93	312
		5.95	222
		6.11	123
8	5.25	5.32	320
		5.29	130
		5.25	400
		5.24	321
9	5.04	5.10	006
10	4.79	4.85	230
		4.79	231
		4.75	412
		4.82	033
		4.72	323
		4.78	125
11	4.46	4.42	420
		4.49	413
		4.45	034
		4.44	315
		4.44	225
		4.42	216
12	3.58	3.54	340
		3.63	522
		3.51	523
		3.55	433
		3.58	243
		3.61	044
		3.59	514
		3.56	144
		3.58	425
		3.52	335
		3.57	416
		3.66	406
13	3.07	3.13	250
		3.11	251
		3.07	252
		3.08	443
		3.01	054
		3.05	534
		3.06	345
		3.06	246
		3.04	436
14	2.95	2.93	540
		2.97	350
		2.96	351
		2.92	541
		2.92	352
		2.99	253
		2.98	444
		2.98	154
		2.90	254
		2.92	535
		2.91	346

The number of reflections in Figure 2 is greater than that reported so far for this structure. The quality of the pattern is also superior due to the virtual absence of diffuse scattering arising from the excess solvent in the case of gels. By trial and error, a unit cell with a = 21.0 A, b = 16.4 A, and c = 30.6 A has been arrived at. The indices of the reflections, using this unit cell are also given in Table 1. The measured density of the solvent-exposed films varied from 1.028 to 1.034 g.cm^{-3}. With the above unit cell, and 4 chains per cell, the calculated density would be 0.943 and 1.099 g.cm^{-3}, with 8 and 16 solvent molecules, respectively. Thus, the extended form can be called the low density crystal structure form of iPS.

The amorphous film of iPS, exposed to ethylbenzene showed the crystallization of only the threefold helical form. Thus, either the extended conformation or the threefold helical form can be crystallized from the bulk, by an appropriate choice of the solvent vapor. While the threefold form can be crystallized by either annealing or solvent exposure, the extended form can be crystallized only by solvent vapor exposure.

Since the intramolecular energy of the extended conformation is more favourable than the threefold helical form, it is likely that the former exists in significant proportions in the amorphous parts of the semicrystalline film containing the threefold helical structure in the crystalline domains. In such a case, it should be possible to crystallize the extended form by solvent exposure of semicrystalline films.

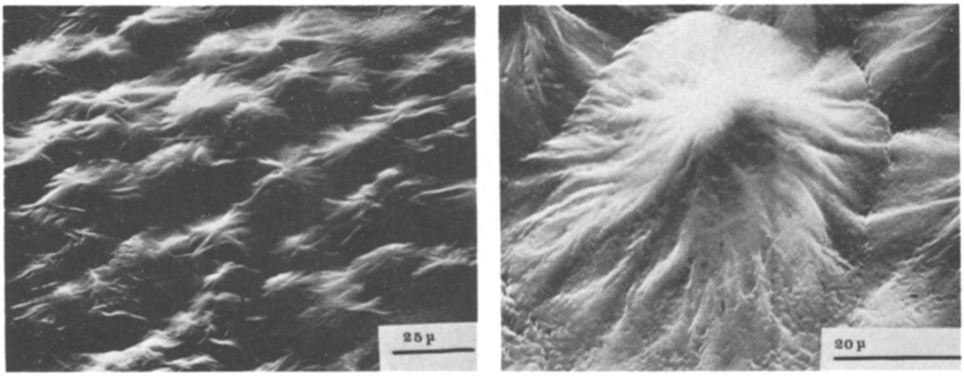


a b

Figure 3: X-ray diffraction patterns (a) from iPS films annealed at 200°C for 1 hr, showing the threefold helical structure, and (b) after exposure to hexahydroindan vapor for three days. The reflections due to the extended form and threefold helical form are seen in (b)

An amorphous, melt-cast film of iPS was annealed at 200°C, for 1 hr. The X-ray pattern from it, shown in Figure 3(a), exhibits the threefold helical structure. This semicrystalline film was then exposed to hexahydroindan for 3 days, at room temperature. The X-ray pattern recorded after vapor exposure is shown in Figure 3(b). It is clearly seen that the crystallization of the extended form has occurred, as shown by the presence of the 5.1 A reflection. Thus, the crystallization of the extended conformation in semicrystalline iPS films already containing the threefold helical form shows that the former is indeed present in significant proportions and perpetuation in the amorphous parts of the film, and that the solvent molecule induces the crystallization to occur.

Scanning electron micrographs of a melt-quenched iPS film, after exposure to hexahydroindan vapor for 3 days, are shown in Figure 4. It is seen that dendritic structures, of the order of 20-30μ in diameter, are found in profusion. The enlarged view in Figure 4(b) shows the line of discontinuity between two dendrites. The spherulitic nature was confirmed by observing these structures, using a polarizing optical microscope. Thin lamellar structures, of the order of 0.3-0.6μ are seen in Figure 4(b), radiating from the centre. The dendrite structures are identified as due to the crystalline extended conformation, since these are lost upon annealing the film at 120°C. Similar morphologies, with differences in size and texture of the dendrites were observed with films exposed to various solvents used here, and these will be published elsewhere.



a

b

Figure 4: Scanning electron micrographs of melt-quenched iPS films, after exposure to hexahydroindan vapor for 3 days. (b) is an enlarged view of one of the dendrites seen in (a)

Conclusions

The extended conformation has been crystallized from the bulk by exposing amorphous iPS films to solvent vapor at room temperature. Due to the predominant intramolecular interaction present in such a conformation, solvent molecules are necessary to provide the intermolecular interaction required for crystallization. Further, the fact that the crystallization can be achieved at room temperature by vapor exposure, shows that the extended conformation is not an unstable conformation in the intramolecular sense. Hence, its lower melting temperature compared to the threefold helical structure can be attributed to the collapse of the intermolecular interaction, upon removel of the solvent molecule.

The preference for the non-staggered tt state has been hitherto neglected in the interpretation of the solution properties of iPS. The profusion and perpetuation of such a conformation, exhibited here shows the inclusion of intramolecular short-range interactions of this type, in addition to the long-range segmental interaction becomes important in understanding the behavior of iPS in solution and in the amorphous state.

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