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Solvent-Induced Cocrystallization of the α (Threefold Helical) and β (Extended) Structures of Isotactic Polystyrene: Determination of X-ray Crystallinity and Disorder Parameter

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ABSTRACT: The threefold helical ($n = 3$ and $p = 6.6$ Å) and the extended ($n = 12$ and $p = 30.6$ Å) conformations of isotactic polystyrene (iPS), denoted here by α and β structures respectively, have been cocrystallized in the same film by vapor exposure of amorphous films to hexahydroindan and cyclooctane. The crystallinity and disorder parameters, attributable to each of the structures, have been determined for films exposed to the solvent vapor, at several temperatures close to the ambient. Until close to the melting of the β structure, its crystallinity was found to be higher than or close to that of the α form, and the film has a total crystallinity of ~0.7 (by dry weight). Following the melting of the β form, even prolonged annealing does not increase the crystallinity of the film, now containing only the α form, beyond ~0.3. Highly crystalline iPS films have never before been obtained because conventional annealing methods crystallize only the α form. These results show that contrary to what has been believed until now, the population of the near-tt conformation is comparable to that of the tg and its perpetuation is also significant. The morphology of the β structure crystallized with hexahydroindan vapor is spherulitic and that obtained with cyclooctane is ringed-spherulitic. The various results are rationalized in terms of the known interpretations of the phenomenon of solvent-induced crystallization (SINC) of polymers.

Introduction

It has been shown[1] recently that the extended conformation of isotactic polystyrene (iPS), with 12 monomers in a repeat distance of 30.6 Å, illustrated in Figure 1, can be crystallized from the bulk, by exposure of amorphous iPS films to suitable solvent vapor, at ambient temperature. This supports the theoretical conclusion[2] that the nonstaggered trans–trans conformation of contiguous skeletal bonds is accessible to the iPS chain and shows that the perpetuation of such a conformation is also significant. From the X-ray diffraction data, an orthorhombic unit cell with $a = 21.0$ Å, $b = 16.4$ Å, and $c = 30.6$ Å was proposed.[1] So far, it has been possible to crystallize the extended conformation by either solvent exposure[1] or by gelation,[3,4] using specific solvents, but not by annealing. It was suggested[1,4] that in order for the extended conformation to crystallize, the specific solvent molecules are necessary to provide the interchain bridge interaction. On the basis of (i) the unit cell dimensions and density criterion, (ii) variation of the intensities of the X-ray reflections with the solvent used for crystallization, and (iii) variation of the melting temperature of this structure with the type of solvent, it was concluded that the solvent molecules are occluded in the lattice. Additional support for this conclusion stems from the variation of the spacings[4] of the equatorial reflections with the type of solvent used, in the case of gels of iPS containing the extended conformation in the crystalline domains.

For convenience of expression, let us henceforth denote the crystal structure containing the threefold helical conformation[5] by α and that corresponding to the extended conformation, by β. This notation conforms to the general practice of describing helical and extended conformations by these symbols.

The phenomenon of solvent-induced crystallization (SINC) of polymers has been discussed by several authors,[6–13] and theoretical interpretations of the events related to crystallization have been put forth. The reader is referred to the literature cited above for detailed discussion of the phenomenon. Briefly, the driving force for the SINC is considered to be the plasticizing effect of the solvent on the amorphous phase, leading to a depression of the T_g. The increased segmental mobility afforded by the "lubricating" effect of the solvent enables the rearrangement of the chain segments into the thermodynamically favorable state. The depression of the T_g must be to a temperature well below the crystallization temperature, T_c (the experimental temperature). This depends on the amount of solvent absorbed, which in turn is a function of the degree of polymer–solvent interaction. Since the solvent exercises a much greater influence on the T_g than on the T_m, the crystallization regime is effectively expanded, its extent depending upon the polymer–solvent pair. The widening of the crystallization regime has a pronounced effect on the crystallization rate. This is seen in the rapid crystallization of polycarbonate upon exposure to solvent vapor.[12,13] It is known that this polymer evades such expeditious crystallization by thermal means. Makarewicz and Wilkes[9] have shown that by widening the T_m–T_g interval by 50%, for poly(ethylene terephthalate), a 10-fold increase in crystallization rate results. In the process of the development of associative interaction between the chain segments leading to crystallization, the solvent molecules are excluded from between the chains and are expelled into the amorphous zones.

In the case of the crystallization of the β structure of iPS, the solvent plays a dual role. In addition to contributing to the depression of T_g, the solvent is also occluded in the lattice. Because of this additional requirement, the shape and size of the solvent molecule, and its interaction with the segments of the chain in the near-tt conformation, become important. Thus, a given solvent which crystallizes the α structure might not induce the crystallization of the β structure. For example, although the α structure crystallizes readily upon exposure to ethylbenzene or methylene chloride vapor, it has not been possible so far to crystallize the β structure using these solvents. The converse, however, would be possible: a solvent which crystallizes the β structure could crystallize the α, since the latter requires only the depression of the T_g.

During the SINC of the α and β structures, each would possess its own mechanism and rate of nucleation and growth. It is possible that for a given solvent, the growth curves for the two structures overlap in some temperature range, in which cocrystallization of the two structures would be possible. Depending on the temperature of crystallization, each structure would exhibit different degrees of crystallinity, crystallite size, and disorder. Al-

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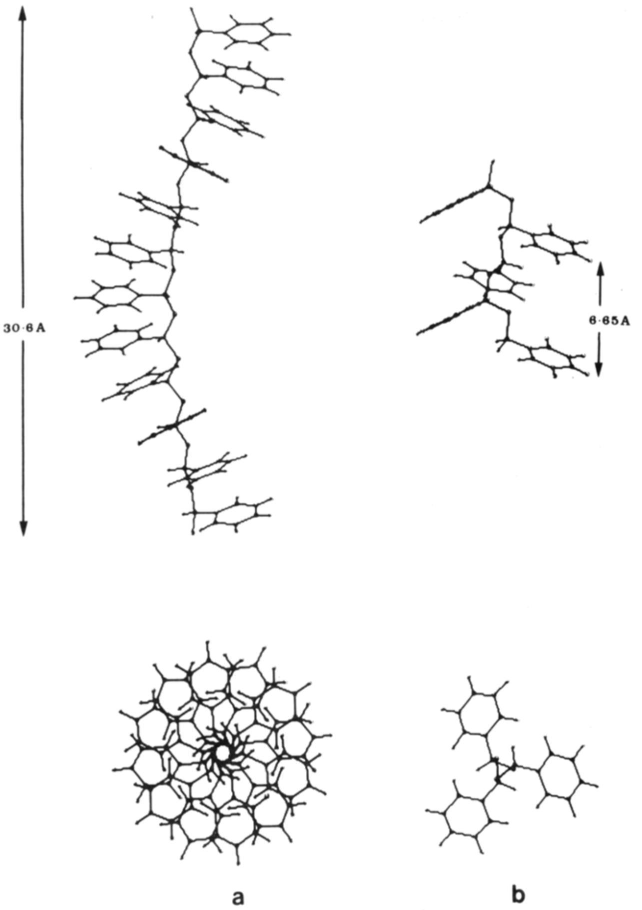

Figure 1. Projections of (a) extended and (b) threefold helical conformations of isotactic polystyrene.

though compound growth curves of this nature are not readily available for iPS, such cocrystallization has been achieved in our recent experiments, by exposing iPS films to hexahydroindan and cyclooctane vapor, at several temperatures close to the ambient. The results are interpreted in terms of the known concepts of SINC. The crystallization of iPS described here is an interesting example in two respects: (i) the solvent molecules, during SINC, are occluded in the lattice of the β structure. Similar solvent occlusion in the lattice has been reported in the studies on the SINC of syndiotactic poly(methyl methacrylate),[14] and the crystallization of certain biopolymers upon exposure to high humidity conditions. This has not been the case with other synthetic polymers such as PET and polycarbonate, the SINC of which has been dealt with extensively in the literature; (ii) in all the cases studied so far, only one crystal structure results upon SINC. In the present case, with the solvents mentioned above, cocrystallization of both α and β structures occurs.

X-ray diffraction has been used to measure the equilibrium crystallinity, and disorder parameter corresponding to the α and β structures in the cocrystallized iPS films. The disorder parameter[15] calculated here gives an indication of the combined effects of the thermal vibrations and lattice imperfections (both first and second kind) on the coherent scattering. In addition to the defects normally arising in crystalline polymer films due to interruption in the perpetuation of the crystalline conformation, the lack of perfect order in the packing of the lattice-occluded solvent molecules, as in the case of the β structure, reflect on the disorder parameter k. It thus enables comparison of the structural features of the two cocrystallized polymorphs. Discussion in this paper is confined to the above equilibrium parameters, and the morphological aspects are treated in the forthcoming paper.[16] The kinetics of diffusion and growth are not considered here, although these are important in understanding the process of SINC in iPS.

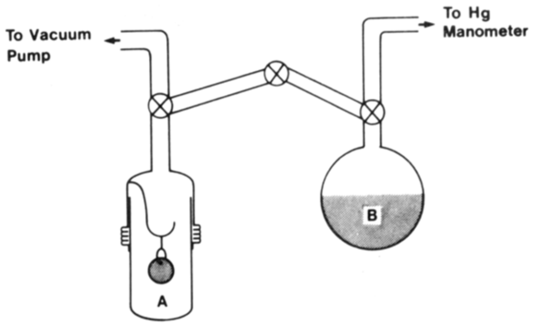

Figure 2. Schematic of the apparatus used for solvent vapor exposure (see text).

Experimental Procedure and Methods

The sample of iPS (M_w = 149 552, M_n = 19 772) used in the present studies was obtained from Pressure Chemical Co. It was crystalline as received. The isotactic triad content was estimated to be 97%, by proton NMR analysis using a Bruker WM250 spectrometer (courtesy of Dr. G. K. Hamer of this laboratory). All the solvents used were of spectroscopic grade.

Unoriented, amorphous, melt-quenched films of uniform dimensions and free of air bubbles were prepared using a hot die press. Films of uniform thickness of 0.2 mm were made by melting a prepressed powdered pellet at 245 °C in a simple piston-type cylindrical die for several hours under vacuum. The die press was then quenched in cold water. The unoriented, amorphous nature of the resultant films was verified by wide-angle X-ray diffraction.

The apparatus used for organic vapor exposure experiments is shown in Figure 2. The solvent was introduced into the solvent chamber, B. To remove air from the system, a freeze–pump–thaw technique was repeatedly applied several times. This technique involves freezing the solvent in liquid nitrogen, followed by thawing it to ambient temperature while applying constant vacuum. After degassing the solvent chamber, the polymer film was suspended by a copper wire in the absorption chamber, A. Vacuum was again applied, first to the absorption chamber and then to the solvent chamber. The entire apparatus was placed in a thermostated bath at the desired temperature. The vapor pressure of the solvent could be monitored with a mercury manometer.

Following the vapor exposure, the film was dried for 1 day under vacuum at ambient temperature. It was then weighed to determine the equilibrium mass uptake, and the thickness was measured, using a micrometer, to estimate the extent of swelling. X-ray data were then collected. In order to ensure that equilibrium crystallinity had been achieved, the sample was reexposed to the vapor under identical conditions for several more days and the measurements repeated. Although the time taken for reaching equilibrium varied from one sample to the other depending on the temperature of exposure, it was roughly of the order of 7 days.

Some of the samples were also analyzed with a Perkin-Elmer DSC-2C differential scanning calorimeter (DSC). The DSC traces were recorded with approximately 5–8 mg of the sample, in a nitrogen atmosphere, at a heating rate of 20 °C/min. Transmission electron micrographs were recorded for select samples with a Philips EM400 microscope, operating at 120 kV.

X-ray diffraction data were collected with a Philips automated powder diffractometer Model PW 1050/80 fitted with a proportional counter, pulse-height analyzer, and a graphite crystal monochromator placed in the diffracted beam. Nickel-filtered Cu Kα radiation (λ = 1.5418 Å) was used. Alignment of the diffractometer was checked before all measurements by a silicon wafer provided with the instrument for this purpose. All intensity measurements were corrected for background scattering from air by subtracting the intensity measured over the given angular range without a sample in the X-ray beam.

Table I
Comparison of Crystallinity and Disorder Parameters for the α Form, Crystallized by Annealing and Solvent Exposure

treatment	$X_c(\alpha)$	$k(\alpha)$
annealed: 200 °C	0.29	1
SINC: 23 °C, ethylbenzene	0.20	4

Crystallinity and disorder parameters were determined by using the method developed by Ruland,[15] as modified by Vonk.[17] In Ruland's method the crystalline fraction of a two-phase system, X_c, is calculated using the equation

$$X_c = \frac{\int_0^\infty s^2 I_{cr}\,ds \int_0^\infty s^2 \overline{f^2}\,ds}{\int_0^\infty s^2 I\,ds \int_0^\infty s^2 \overline{f^2} D\,ds} \tag{1}$$

where $\overline{f^2} = \sum N_i f_i^2 / \sum N_i$, f_i is the scattering factor of an atom of type i, N_i is the number of atoms of type i, $s = (2 \sin \theta)/\lambda$, I is the total scattered intensity, I_{cr} is the scattered intensity under crystalline peaks, and D is the "disorder" function. To a first approximation, D is taken as $\exp(-ks^2)$, where k includes both thermal motions and lattice imperfections.

Vonk[17] has devised a method for deriving the value of k graphically. In this method, a value of $R(s_p)$ is first determined from the following equation:

$$R(s_p) = \frac{\int_0^{s_p} I s^2\,ds}{\int_0^{s_p} I_{cr} s^2\,ds} \tag{2}$$

The value of s_p are the upper limits of s and must be chosen such that each interval, 0 to s_p, contains several crystalline diffraction peaks. Plots of $R(s_p)$ on the ordinate vs. s_p^2 on the abscissa are then made. The intercept of these plots with the ordinate then equals $1/X_c$, with the slope being equal to $k/2X_c$. The parameter k takes into account the loss of coherent scattered intensity due to deviations of the atoms from their ideal positions caused by (i) thermal motions, (ii) lattice imperfections of the first kind (in which long-range order is conserved), and (iii) lattice imperfections of the second kind (in which long-range order is destroyed). For a more complete discussion of this method, see ref 17.

In this study, scattered intensity data were recorded for all samples out to $s = 0.40$ Å^{-1}. The values for s^2I and s^2I_{cr} were determined by measuring the area under the curve on plots of s^2I vs. s in each of four intervals limited by $s_p = 0.20$, 0.24, 0.30, and 0.40. Separation of amorphous scattering from crystalline peaks was accomplished manually. Due to the presence of a crystal monochromator in the diffracted beam, corrections for incoherent scattering were not considered.

Results and Discussion

1. Crystallinity of the α Structure (Threefold Helical Structure). The X-ray crystallinity X_c and disorder parameter, k, for two films of iPS, in which the α form has been crystallized, are given in Table I. One of the films was crystallized by annealing at 200 °C in vacuo for 94 h, and the other, by exposure to ethylbenzene vapor at 23 °C, for 4 days. The crystallinity corresponding to the former is 0.29, which is in excellent agreement with what has been reported previously[18] for iPS. Although Natta et al.[5] reported a maximum crystallinity of ~0.5 for the samples, with $M_w > 10^6$, annealed at various temperatures, later work by Challa et al.[18] estimates the crystallinity to be about 0.30, for samples annealed at temperatures similar to the present work. Overbergh et al.[11] also arrived at a maximum crystallinity of 0.33 for samples annealed for several hours following solvent-induced crystallization. Thus, a crystallinity of ~0.3 seems to be typical for annealed iPS films. The disorder parameter for the annealed film was deduced (Table I) to be $k = 1$, which indicates a high degree of crystallite perfection.

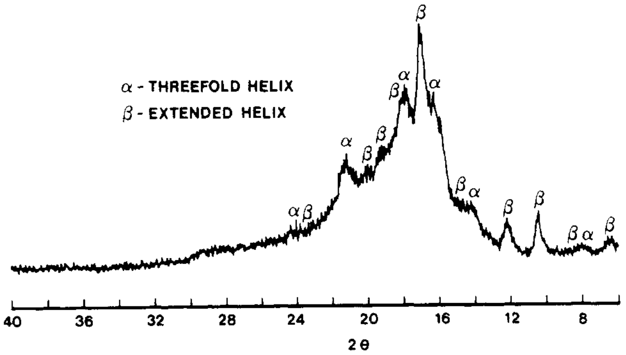

Figure 3. X-ray diffractometer trace from a cocrystallized iPS film. The peaks due to the α and β forms are marked.

On the other hand, the film exposed to ethylbenzene vapor shows a crystallinity of 0.20 and $k = 4$. The increase in k, compared to the case of the annealed film, reflects poorer crystallite perfection. As the SINC of the α form proceeds, solvent molecules are excluded from between the chains as the segments aggregate and crystallize. The depression of T_g, resulting from solvent exposure, shifts the maximum growth rate to lower temperatures, and the crystallization regime broadens as the volume fraction of the polymer in the mixture decreases up to a certain composition ratio.[10] Thus the increased growth rate caused by the addition of the diluent contributes to an increase in k.

The lower crystallinity of 0.2 obtained for the solvent-exposed film can be rationalized by considering several factors. The type of solvent and the experimental temperature would certainly influence the crystallinity. Overbergh et al.[11] reported $X_c = 0.23$ and 0.27 for iPS films exposed to dichloromethane and acetone, respectively. The extent of depression of T_g and the accompanying effects outlined above influence the ultimate value of X_c. The correction to the measured X_c discussed in the next section, based on the amount of solvent in the amorphous areas, does not affect the value of crystallinity of 0.2 mentioned above, since in this case the weight fraction of the absorbed solvent is very low (0.08). In any case, the crystallinity of the α form, achieved via either annealing or solvent exposure does not exceed ~0.3.

2. Exposure to Hexahydroindan Vapor at Several Temperatures. X-ray analysis of the films exposed to hexahydroindan vapor at temperatures above ambient (but less than the T_m of the β form) showed that both the α and β forms have cocrystallized. Such a cocrystallization was rationalized above in terms of overlap of the growth curves for the two conformers. A typical diffractometer trace is shown in Figure 3, with the peaks due to the α and β forms identified. The crystallinity and disorder parameter corresponding to each of the structures are listed in Table II, along with the overall crystallinity, swelling, and absorption data, for various temperatures of solvent exposure, from 30 to 45 °C. This temperature range is below the T_m of the β form crystallized using hexahydroindan (~60 °C). Plots of the variation of the degree of absorption and crystallinity with temperature are shown in Figure 4. All the parameters given in Table II and Figure 4 are equilibrium values.

Depending on the temperature of vapor exposure, the overall crystallinity achieved, using this solvent, upon cocrystallization of the α and β forms varies from 0.45 to 0.54. Bear in mind that these values are derived for films which include the solvent. For illustrative comparison with thermally annealed films, the overall crystallinity can be corrected for the absorbed solvent in the amorphous re-

Table II
Parameters Derived for the Cocrystallized Film of iPS by Exposure to Hexahydroindan Vapor

T, °C	$X_c(O)^a$	$k(O)^a$	$X_c(\beta)^b$	$k(\beta)^b$	$X_c(\alpha)^c$	$k(\alpha)^c$	$C \times 10^2$, g of solvent/g of dry polymer	swelling, mm	$X_c(O)^{cor}$
30	0.54	22	0.36	35	0.19	8	48	0.17	0.71
35	0.48	11	0.30	29	0.22	5	36	0.14	0.59
40	0.46	13	0.24	30	0.25	4	32	0.12	0.56
45	0.45	13	0.14	18	0.31	12	30	0.13	0.56

[a] $X_c(O)$ and $k(O)$ correspond to the overall values. [b] $X_c(\beta)$ and $k(\beta)$ correspond to the β form. [c] $X_c(\alpha)$ and $k(\alpha)$ correspond to the α form.

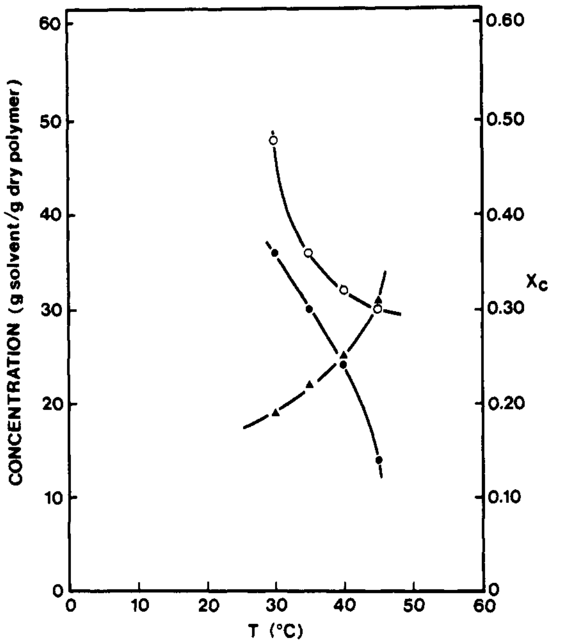

Figure 4. Variation of the crystallinities (X_c, right ordinate) of the β (●) and the α (▲) structures are shown as a function of temperature of vapor exposure to hexahydroindan. The (%) concentration (○) of the absorbed solvent at each temperature is also given (left ordinate).

gions, so that the crystallinities can be compared on a dry basis. The corrected crystallinity is given by

$$X_c(\text{cor}) = X_c(\text{measd})/(1 - \omega_s) \qquad (3)$$

where ω_s is the weight fraction of the solvent in the amorphous regions. This equation is similar to that used in diffractometry of mixtures of components. We proceed to determine ω_s as follows: It was proposed[1] that the β structure contains 4 chains and 8–16 solvent molecules in the unit cell. With hexahydroindan and cyclooctane, the weight ratio of the occluded solvent and the polymer would be between 1/6 and 1/3. Let us approximate it to 1/4. Then, the weight fraction of the lattice-occluded solvent, ω_l is given by

$$\omega_l = X_c(\beta)/4 \qquad (4)$$

The weight fraction of the total amount of solvent in the film is

$$\omega_t = (W_p - W_d)/W_p \qquad (5)$$

where W_p is the weight of the plasticized film and W_d, that of the initial dry film. The weight fraction of the solvent in the amorphous region is then

$$\omega_s = \omega_t - \omega_l \qquad (6)$$

Using eq 3–6 and the solvent concentration data in Table II, X_c(cor) were calculated and are given in the last column of Table II. It is seen that the corrected overall crystallinity varies from 0.71 at 30 °C to 0.56 at 45 °C. It is interesting to note that these values are comparable to the crystallinities derived[17,19] for other highly crystalline polymers such as poly(1-butene) and poly(4-methyl-1-pentene). As noted above, the solvent-corrected X_c values are illustrative and depend on the value used for the number of solvent molecules in the unit cell of the β structure. Nevertheless, compared to the annealed films, in which the α structure alone is crystallized, the contribution of the β structure to the total X_c in the cocrystallized films, can be readily appreciated. The value of $X_c(\beta) = 0.36$ at 30 °C, attributable to the β structure, is comparable to the crystallinity of ~0.3 reported so far for annealed films with the α form. This shows that the population of the crystallizable portions of the chains in the near-tt conformation is comparable to that of the segments of the chain in the tg conformation. The theoretical calculations showed[2] that the extended conformation is in fact lower in energy by 1 kcal mol^{-1} than the threefold helix. It is also interesting to note that Painter et al.,[20] using FTIR methods, estimated that 35% of the chains in the β form comprise the crystalline component in the dried gels of iPS prepared using decalin.

Table II shows that the disorder parameter k for the β structure is large compared to the α form. Up to 40 °C, k for the β structure is about 4–8 times larger than for the α. This can be attributed to a large extent, to the inefficient packing in the former. It was proposed[1] that the β structure crystallizes in an orthorhombic unit cell with 4 chains and 8–16 solvent molecules in the cell. If the ordering of the occluded solvent is irregular, the lattice packing and hence the degree of crystallite perfection would be affected. On the basis of measured and calculated densities, the β structure was described before[1,21] as a low-density crystalline form of iPS. It is reflected here in the high values of k. Although these results pertain to bulk-crystallized films, supportive conclusions can be recalled from the DSC work of Wellinghoff et al.[22] on the gels of iPS. They attributed the lower melting temperature and the absolute heat of melting of 3–5 cal/g of the β structure, in contrast to the higher melting α form with a heat of melting of 20 cal/g, to the differences in the interchain packing of the two conformers.

As the temperature of vapor exposure is increased, the crystallinity of the β structure declines moderately up to 40 °C and drastically at 45 °C. The value of $k(\beta)$ shows the same trend. The concentration of the absorbed solvent also decreases with increase in temperature of exposure. The values of $X_c(\alpha)$ and $k(\alpha)$ show a significant increase between 40 and 45 °C. It is possible that this behavior is due to the experimental conditions approaching the maximum in nucleation and growth rate for this form. Graphical illustrations presented in Figure 4 show these variations.

It is seen that as the melting temperature of the β form is approached (~60 °C with this solvent), the fraction of crystallites in this form drops. Granting that hexahydroindan is occluded in the lattice of the β form, it can be considered an "interactive" penetrant as far as the chain segments in the near-tt conformation are concerned. The

Table III
Parameters Derived for the Cocrystallized Film of iPS by Exposure to Cyclooctane Vapor[a]

T, °C	X_c(O)	k(O)	$X_c(\beta)$	$k(\beta)$	$X_c(\alpha)$	$k(\alpha)$	$C \times 10^2$, g of solvent/g of dry polymer	swelling, mm	$X_c(\mathrm{O})^{\mathrm{cor}}$
25	0.48	26	0.37	48	0.13	8	54	0.18	0.65
30	0.46	18	0.35	38	0.15	6	47	0.16	0.60
35	0.48	19	0.32	34	0.16	8	38	0.16	0.60
45	0.48	15	0.33	31	0.17	6	39	0.16	0.60
55	0.43	16	0.14	24	0.29	13	30	0.13	0.53

[a] See footnote to Table II.

addition of such an interactive penetrant enlarges the crystallization temperature regime, increases the growth rate, and the temperature corresponding to the maximum of the growth rate is lowered.[7,10] This is readily seen in the results presented in Table II. At 30 °C, where the supercooling is high, a large number of poorly developed crystallites result, due to the enhanced nucleation and growth rate. However, near the T_m of the β form, a decrease in nucleation density and growth rate result in a smaller fraction of more perfect crystallites.

It is seen from Figure 4 that the concentration of the absorbed solvent decreases significantly from 30 to 35 °C and moderately thereafter. The crystallinity of the β form decreases while that of the α structure increases. The decrease in the amount of the solvent absorbed can be rationalized in terms of a combination of the following factors: (i) as the crystallization temperature T_c is increased, the critical concentration of the solvent necessary to depress the T_g below T_c would decrease; (ii) since the $X_c(\beta)$ is reduced, the number of solvent molecules required for occlusion in the lattice decreases; and (iii) the increase in the crystallinity of the α form retards the absorption of the solvent beyond a certain amount.

3. Exposure to Cyclooctane Vapor at Several Temperatures. Cyclooctane is another solvent which is known to promote the crystallization of the β structure, as has been shown previously.[1] It has been found in the present study that cocrystallization of both structures has been achieved using this solvent as well. The values of X_c and k, corresponding to the two conformers, and the overall value of X_c and k, the amounts of absorbed solvent and swelling, are given in Table III. Some of these data are shown as a function of temperature in Figure 5. Again, these results correspond to equilibrium conditions.

Table III and Figure 5 show that the values of $X_c(\alpha)$, $X_c(\beta)$, and the overall X_c do not change significantly in the temperature range of 25 to 45 °C. This suggests that the growth curves for the two conformers overlap to the same extent in this temperature range. Beyond 45 °C, the crossover occurs, the $X_c(\beta)$ decreases drastically, and $X_c(\alpha)$ increases significantly. It is seen that, generally, over the temperature range up to 45 °C, the value of $X_c(\alpha)$ is lower than that measured for the case of hexahydroindan vapor (cf. Table II). Similar to the latter, as the T_m of the β form is approached (~80 °C using cyclooctane), the decreased supercooling results in diminished nucleation and growth rates. The disorder parameters follow the same trend as in Table II. The overall X_c, corrected for the solvent absorbed varies as before, from 0.53 and 0.65, when the contributions from both α and β structures are included.

The equilibrium concentration of the absorbed solvent decreases with increase in temperature. Since the crystallinities of the two conformers remain almost constant in the range of 25 to 45 °C, it can be concluded that the equilibrium mass uptake is not influenced by crystallinity, but by the reduced amount of solvent required to depress the T_g below T_c as the latter is increased. It is interesting to note that the equilibrium mass uptake in the case of hexahydroindan and cyclooctane shows a striking similarity at high supercoolings. Swelling is quite significant in both cases and follows the same trend as the solvent absorption.

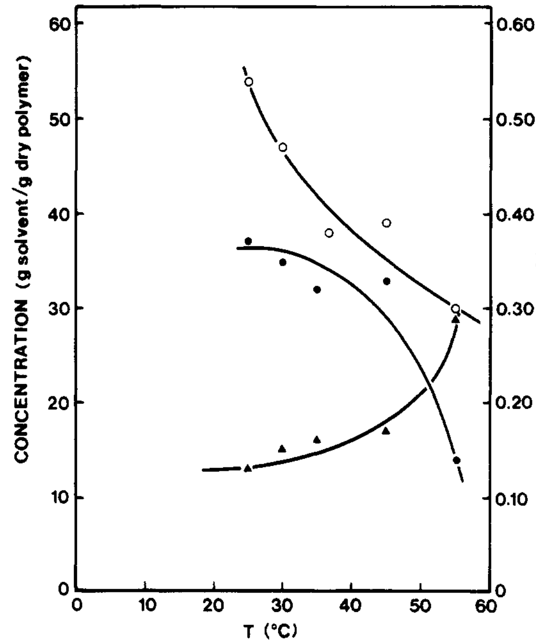

Figure 5. Same as Figure 4, but for the case of cyclooctane vapor.

Comparing the values of $X_c(\beta)$ and $k(\beta)$ in Tables II and III, two features are obvious: (i) the drastic reduction in $X_c(\beta)$ occurs between 40 and 45 °C with hexahydroindan and between 45 and 55 °C in the case of cyclooctane exposure. Before this "crossover", the $X_c(\beta)$ is the same at a given temperature, with both solvents; (ii) the values of $k(\beta)$ are slightly higher for the case of cyclooctane vapor exposure. These differences are understandable considering that the specific solvent–polymer segment interactions, at the short-range level, would differ in the two cases and so would the packing of the lattice-occluded solvent.

The resultant morphology was also found to be solvent dependent. Two films, exposed at 30 °C to hexahydroindan and cyclooctane, were ultramicrotomed and examined with the polarizing optical and transmission electron microscopes. Spherulitic morphology was observed in both cases, and the positively birefringent spherulites were of the same size, with an average diameter of ~10 μm. However, only the film crystallized with cyclooctane vapor contained *ringed* spherulites, with a regular periodicity of ~3 μm, as shown in Figure 6. Preliminary electron diffraction results suggest that the spherulites are due to the β structure. Thus, the nature of the solvent and SINC conditions influence the morphology, and can be expected to affect, e.g., the rheological properties. The morphological aspects of the cocrystallized films will be treated further elsewhere.[16]

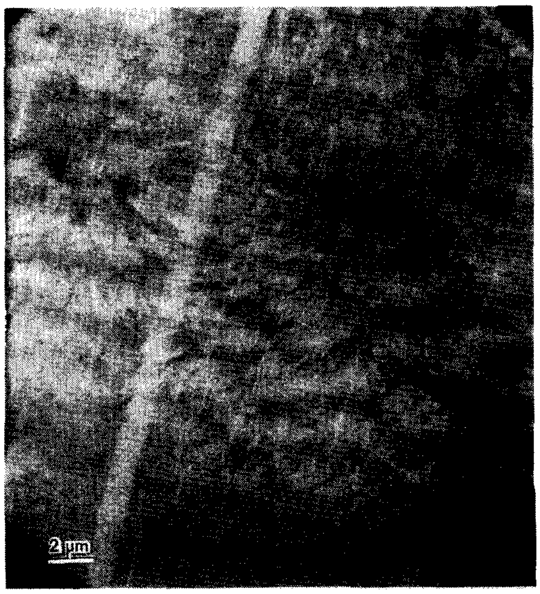

Figure 6. Transmission electron micrograph of the iPS film exposed to cyclooctane vapor at 30 °C, showing ringed spherulitic morphology.

Table IV
Crystallinity and Disorder Parameters Derived for iPS Film Following the Sequence of Treatments Indicated[a]

treatment	$X_c(\mathrm{O})$	$k(\mathrm{O})$	$X_c(\beta)$	$k(\beta)$	$X_c(\alpha)$	$k(\alpha)$
hexahydroindan, 30 °C	0.55	13	0.35	34	0.23	7
ethylbenzene, 23 °C					0.26	5
reexposed to ethylbenzene, 23 °C					0.20	2
annealed at 190 °C, 16 h					0.27	2

[a] See text.

4. Solvent Annealing. Analogous to thermal annealing, the effect of "annealing" a cocrystallized film by vapor exposure to a solvent which is known to crystallize the α structure was investigated. A cocrystallized film was prepared by exposure to hexahydroindan vapor at 30 °C. This film was then exposed to ethylbenzene vapor, at ambient conditions, for 24 h. The values of X_c and k, before and after the exposure to ethylbenzene, are given in Table IV. It is evident that the absorption of ethylbenzene vapor caused the melting of the β structure. The concentration of the absorbed solvent dropped from 37% to 6%, implying that solvent exchange has occurred. Atkins et al.[23] observed that a gel prepared from *cis*-decalin, when solvent exchanged with a more volatile solvent such as acetone or diethyl ether, showed the presence of only the α structure. It was suggested[23] that this effect was attributable to the melting of the β form and/or mutual conformational tranformation. The results in Table IV show that the solvent exchange causes only the melting of the β structure. Further exposure to ethylbenzene vapor resulted in a decrease in $X_c(\alpha)$, and an improved k, suggesting that the crystallites reorganize into a more stable phase. Subsequently, the film was annealed at 190 °C, for 16 h. The crystallinity increased to 0.27, but not higher. This rules out the possibility of transformation of the extended conformation to the threefold helical form and supports the previous conclusion[1] that the melting of the β structure and the crystallization of the α form are independent events.

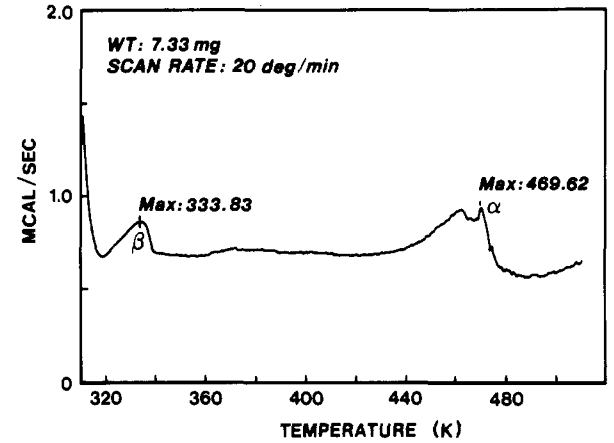

Figure 7. DSC trace of the cocrystallized iPS film.

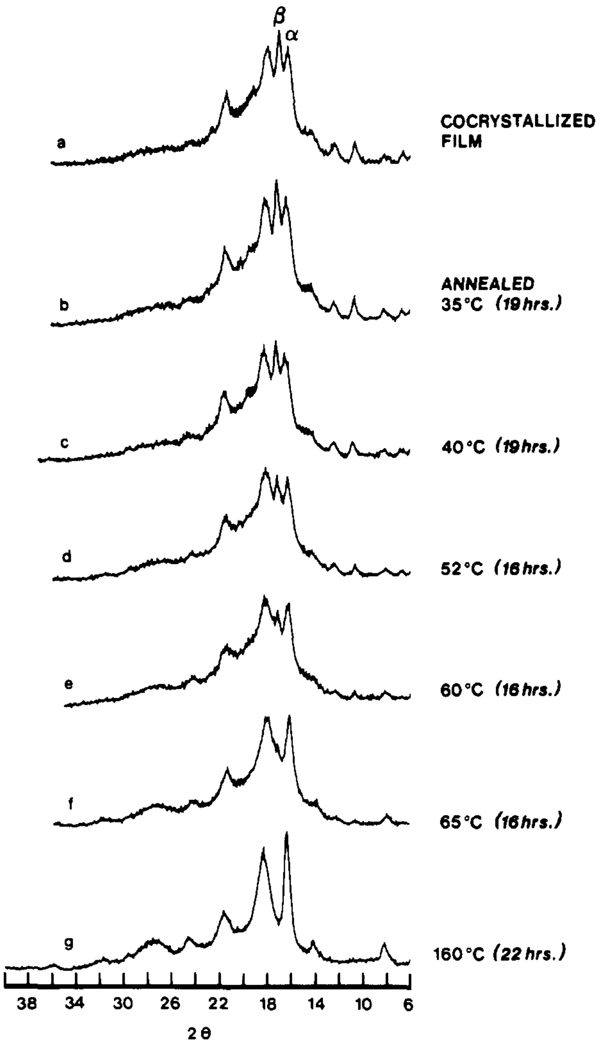

Figure 8. X-ray diffractometer traces recorded for the cocrystallized iPS film, following annealing at various temperatures indicated. The principal peaks due to the α and β forms are marked in trace a.

5. Thermal Annealing of a Cocrystallized Film. The results discussed above pertain to exposure of iPS films to solvent vapor, at various temperatures. In this section, the results of annealing a cocrystallized film (obtained using hexahydroindan vapor) at various temperatures, below, at, and above the T_m of the β form, are presented. A typical DSC trace of the cocrystallized film is shown in Figure 7. A series of X-ray diffractometer traces, recorded after annealing the same film successively at temperatures indicated, is shown in Figure 8. The overall values of X_c and k as well as those corresponding to the two polymorphs are given in Table V.

Table V
Variation of Crystallinity and Disorder Parameters for Cocrystallized iPS Film Following Annealing at Temperatures Indicated[a]

T, °C	$X_c(\text{O})$	$k(\text{O})$	$X_c(\beta)$	$k(\beta)$	$X_c(\alpha)$	$k(\alpha)$
	0.48	11	0.30	29	0.22	5
35	0.44	12	0.25	29	0.22	10
40	0.47	14	0.25	28	0.23	8
52	0.45	14	0.23	24	0.23	8
60	0.39	11	0.16	22	0.24	8
65	0.34	6	0.09	16	0.25	4
160	0.29	2			0.29	2

[a] See footnote to Table II.

Below the T_m of the β form, in the range from 35 to 52 °C, the values of X_c and k show no significant change. It is seen from parts b and c of Figure 8 that the diffraction maxima associated with the two structures remain fairly constant. This shows that the crystallites in the β structure are stable below their melting temperature. A slight decrease in the intensity of the peaks due to this structure is noted in Figure 8d, after annealing at 52 °C, and a decrease in $X_c(\beta)$ and an improvement in $k(\beta)$ are noted in Table V. From the DSC trace, it is seen that the melting endotherm of the β structure is fairly broad. Since this temperature is close to the onset of the melting of the β form, the decrease in $X_c(\beta)$ can be attributed to the melting of the smaller, less perfect, crystallites. When the film is annealed at 60 °C, midway in the melting endotherm of the β form, the value of $X_c(\beta)$ drops further. The $X_c(\alpha)$ and $k(\alpha)$ remain constant, however, through this temperature range, confirming that the melting of the β form has no influence on the crystallinity of the α structure. The decrease in $X_c(\beta)$ continues through the melting endotherm and after annealing at 65 °C, the diffraction maxima, corresponding to the β form are hardly noticeable in Figure 8f. Finally, at 160 °C, well above the T_m of the β form, $X_c(\alpha)$ improves to a value comparable to that deduced for a film annealed directly (cf. Table I). Note that once the β form melts, the contribution to the overall X_c is derived only from the α form and even prolonged annealing does not increase X_c to the value recorded for the initial cocrystallized film.

Conclusions

Cocrystallization of both the α and β structures of iPS has been achieved, by exposure of amorphous iPS films to hexahydroindan and cyclooctane vapor. The crystallinities corresponding to the two conformers have been determined. It is shown that upon melting of the β structure, the chain segments which participated in this structure exercise no influence on the crystallinity of the α form.

The overall crystallinity obtained with the cocrystallized films exceeds 0.50. Previous estimates of the crystallinity of the iPS films, in which the α form alone had been crystallized, have been of the order of 0.3. The significant additional contribution of the β structure to the overall crystallinity has now been demonstrated here quantitatively. The large values of the disorder parameter obtained here for the β form shows that the lattice-occluded solvent molecules are disordered and thus, this low-melting polymorph is a low-density crystalline form of iPS.

The various parameters determined here correspond to equilibrium values following solvent exposure. The question arises as to whether, during the cocrystallization process, the α or the β form crystallizes first or whether both of them do simultaneously. The morphological features[16] indicate that the crystallites in the β form can act as effective nucleating sites for the crystallization of the α structure. Wellinghoff et al.[22] concluded similarly, based on their calorimetric studies. Whether the same mechanism applies to the experimental conditions used here can be determined only by systematic kinetic studies.

As mentioned above, the cocrystallization of α and β forms by SINC, adds a new dimension to the phenomenon itself. Both α and β forms crystallizing upon solvent exposure and the β form occluding the solvent molecules in the lattice offer another example for modeling the process of SINC. In essence, Figures 4 and 5 represent part of the phase diagram of the crystalline polymorphs of iPS, upon exposure to solvent vapor. Under the conditions of these experiments, it can be speculated that the maximum crystallinity of the β form occurs at about 25 °C, and that of the α, between 50 and 60 °C. Growth rates for the two structures should follow a similar trend, based on the pattern of variation of k with temperature. It was not possible to extend the curves in Figures 4 and 5 to temperatures lower than 25 °C, due to experimental difficulties.

The success in the crystallization of the β structure in the bulk clearly supports the theoretical conclusions[2] on the accessibility of the nonstaggered tt conformation of contiguous skeletal bonds in iPS, and the perpetuation which is necessary for crystallization would indicate that the tt conformation is not just an occasional defect which serves to disrupt the tg sequence. It has been shown in a series of papers[24,25] that for isotactic vinyl chains with planar substituents, including disubstituted chains such as PMMA, the near-tt conformation is accessible. The recent thoughts[26,27] on the crystalline structure of isotactic PMMA confirm this conclusion. The lack of incidence of such β structures from other vinyl chains of this type is not due to the absence of these conformations but rather due to the insufficient understanding of the conditions which would lead to their crystallization.

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Registry No. *i*PS, 25086-18-4; hexahydroindan, 496-10-6; cyclooctane, 292-64-8; ethylbenzene, 100-41-4.

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Solution Properties and Chain Dimensions of Poly(*n*-alkyl methacrylates)

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ABSTRACT: The influence of *n*-alkyl side-chain length on the unperturbed chain dimensions of poly(*n*-alkyl methacrylates) has been examined. For the cases where the side-chain groups were decyl (C_{10}), tridecyl (C_{13}), stearyl (C_{18}), and docosyl (C_{22}), the unperturbed dimensions expressed in terms of the characteristic ratio were found to be, respectively, 13.0, 14.7, 20.4, and 23.6. This trend demonstrates that a change in the identity of the *n*-alkyl group is reflected in the unperturbed posture of the chain backbone.

Introduction

The influence of side groups on the unperturbed dimensions of substituted polyethylene chains is well documented.[2] In the case of the polymethacrylates, interest has focused on the changes induced by altering the length of the *n*-alkyl ester group (methyl to dodecyl)[3-8] or the identity of the ester linkage, e.g., as in poly(cyclohexyl methacrylate) and poly(*S*-cyclohexyl thiomethacrylate).[9,10]

An understanding of the properties of such poly(*n*-alkyl methacrylates) is at least particularly dependent on the ability to relate their equilibrium configuration-dependent behavior to their structure. The application of matrix methods[11,12] in the form of the rotational isomeric state (RIS) model has been used to calculate configurational properties, e.g., Flory's characteristic ratio (C_∞), for various polymers. The general approach involves a consideration of bond lengths and angles as well as the short-range contributions to potentials affecting rotation about the main-chain bonds.

The RIS model, though, has not been used to evaluate the influence of the chain length of the *n*-alkyl ester group on the unperturbed chain dimensions of the poly(*n*-alkyl methacrylates). This paper presents our experimental findings pertaining to C_∞ for poly(*n*-alkyl methacrylates) where the *n*-alkyl group was decyl (PDMA), tridecyl (PTDMA), stearyl (PSMA), or docosyl (PDCMA).

Experimental Section

The decyl, tridecyl, and stearyl methacrylate monomers were obtained from Polysciences, Inc. The docosyl methacrylate monomer was synthesized in toluene as follows:

$$CH_2{=}C(CH_3)\text{-}CO\text{-}OCH_3 + n\text{-}C_{22}H_{45}OH \rightarrow CH_2{=}C(CH_3)\text{-}CO\text{-}OC_{22}H_{45} + CH_3OH$$

with *p*-toluenesulfonic acid as the catalyst. The methanol was distilled off during the reaction. The solid docosyl methacrylate was then purified by recrystallization from hexane solution at ca. -30 °C. The monomer was then vacuum-dried. Both ^{1}H NMR and IR were used to check monomer purity. The results indicated that all the monomers used in this work were virtually free of impurities.

Table I
Refractive Index Differences for Poly(*n*-alkyl methacrylates)

sample	solvent	temp, °C	d*n*/d*c*
PDMA	cyclohexane	30	0.0544[a]
	ethyl acetate	25	0.1146[b]
PTDMA	tetrahydrofuran	30	0.0828[a]
	ethyl acetate	27	0.1209[b]
PSMA	cyclohexane	20	0.0539[a]
	n-propyl acetate	36	0.1070[b]
PDCMA	cyclohexane	30	0.0545[a]
	amyl acetate	31	0.0903[b]

[a] 633 nm. [b] 436 nm.

The solution polymerizations were done under vacuum at 50 °C using purified AIBN as the initiator and benzene as the solvent. Two polymerizations were done for each monomer. The samples were fractionated using dilute (~1% (w/v)) toluene solutions with methanol as the nonsolvent. All of the solvents used in this work were dried and distilled prior to use. GC analysis of these solvents did not reveal any impurities.

Polymer molecular weight characterization was done using a combination of light scattering, membrane osmometry, and size exclusion chromatography (SEC). The Chromatix KMX-6 low-angle laser photometer (λ = 633 nm) was used for the light scattering molecular weight measurements while the Sofica PGD (λ = 436 nm) was used for the Θ temperature determinations. The d*n*/d*c* values were determined with the Chromatix KMX-16 refractometer (λ = 633 nm) and the Brice-Phoenix refractometer (λ = 436 nm). These results are shown in Table I.

The respective Θ temperatures were determined in the usual fashion by plotting the light scattering second virial coefficient