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Control of Crystal Size and Orientation in Polymer Films by Host−Guest Interactions

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ABSTRACT: The unprecedented occurrence of two different kinds of uniplanar orientation by solution casting, observed for syndiotactic polystyrene (s-PS) films, has been rationalized in terms of host−guest interactions into molecular complex phases. Correlation lengths along different crystallographic directions (D_{hkl}), of molecular complex crystalline domains of s-PS with several different guest molecules, have been investigated by wide-angle X-ray diffraction. The chemical nature of the guest has a strong influence on the correlation length perpendicular to the *ac* plane (i.e., perpendicular to the layers of close-packed enantiomorphous helices) and a weak influence on the correlation lengths along *a* and *c* (chain) axes. Less and more favorable host−guest interactions lead to molecular complex domains with low and high degree of order perpendicular to the *ac* layers ($D_{010} < 6$ nm and $D_{010} > 7$ nm) and generate cast films with uniplanar (010) and (002) orientations, respectively.

Introduction

Solution-casting procedures generally lead to unoriented polymer films. However, it is well-known that solvent-casting of polymers can result in polymer chains lying preferentially parallel to the film plane.[1] Recently, it has been described that solution-casting of syndiotactic polystyrene (s-PS) can result in crystalline polymer chains lying preferentially parallel[2] or pependicular[3] to the film plane, depending on the solvent.

S-PS presents a complex polymorphic behavior which can be described in terms of two crystalline phases (α and β) presenting zigzag planar chains and two crystalline phases (γ and δ) presenting s(2/1)2 helices.[4,5] In particular, the δ form is nanoporous and has a density (0.98 g/cm^3)[5] definitely lower than amorphous s-PS (1.04 g/cm^3), which is close to that one of atactic polystyrene. The monoclinic structure of δ form of s-PS (space group $P2_1/a$; $a = 1.74$ nm; $b = 1.18$ nm; $c = 0.77$ nm; $\gamma = 117°$) has per unit cell two identical cavities centered on the center of symmetry and bounded by 10 phenyl rings (Figure 1A).[5] By sorption of suitable guest molecules into these cavities, as well as by different solution crystallization procedures, molecular complex (clathrate[6] and intercalate[7]) phases are easily achieved.

All known crystalline structures of s-PS clathrate and intercalate phases present several features common to the δ form. In fact, all are monoclinic with space group $P2_1/a$ and are characterized by the same *ac* layers of close-packed alternated enantiomorphous s(2/1)2 helices. Hence, all known s-PS molecular complexes present essentially the same *a* axis of the δ form (1.73 ± 0.25 nm) while their distance between the *ac* layers (d_{010}) can increase from 1.06 nm of the δ form at least up to 1.6 nm for some intercalate phases. For the sake of comparison with the δ form (Figure 1A), the along *c* projections of the clathrate phase with 1,2-dichloroethane ($a = 1.71$ nm; $b = 1.22$ nm; $c = 0.77$ nm; $\gamma = 120°$)[6d] and of the intercalate phase with norbornadiene ($a = 1.75$ nm; $b = 1.45$ nm; $c = 0.78$ nm; $\gamma = 108°$)[7a] are shown, just as examples, in parts B and C of Figure 1, respectively.

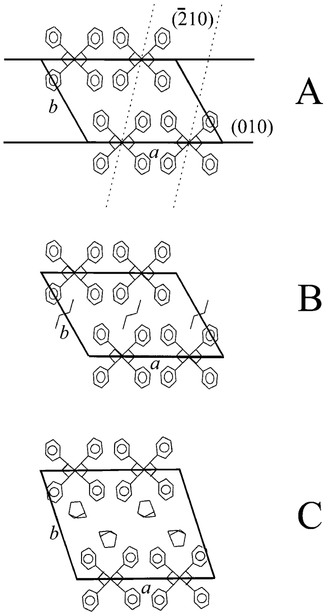

Figure 1. Along *c* projections of the monoclinic crystal structures (space group $P2_1/a$) of s-PS: (A) the empty δ phase; (B) a molecular complex clathrate phase (with 1,2-dichloroethane; host monomer unit/guest ratio 4/1); (C) a molecular complex intercalate phase (with norbornadiene; host monomer unit/guest ratio 2/1). Traces of (010) and $(\bar{2}10)$ planes are shown in (A).

A unique feature of s-PS crystallization is the achievement of high degrees of three different kinds of uniplanar orientations.[2,3,8] In particular, for solution crystallization by casting procedures it has been established that by using some solvents (benzene, chloroform, tetrahydrofuran) the (010) uniplanar orientation, for which the *ac* layers tend to be parallel to the film surface, is obtained.[2] This uniplanar orientation, also obtained by solvent induced crystallization in biaxially stretched s-PS films,[2b] presents the chain axes parallel to the film plane. However, casting procedures with different solvents (trichloroethylene, tetrachloroethylene, 1,2-dichloroethane) produce a preferential perpendicular orientation of the chain axes with respect to the film plane.[3] This perpendicular chain axis orientation, which according to a more general nomenclature, can be defined as (002) uniplanar orientation,[8b] is rather unusual

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and possibly unprecedented for high thickness films (up to 100−200 μm).

It is worth adding that these parallel and perpendicular orientations of polymer chains, which are achieved for molecular complex host−guest crystalline phases, can also be maintained, by suitable thermal or solvent treatments, after crystal phase transitions toward the helical γ and δ phases as well as toward the trans-planar α and β phases.[2,8]

In this paper, correlation lengths along different crystallographic directions of molecular complex crystalline domains of s-PS have been evaluated by X-ray diffraction, for films obtained by solution-casting procedures. The study is aimed to rationalize the unusual occurrence of two completely different uniplanar orientations and its guest dependence.

Experimental Section

The syndiotactic polystyrene used in this study was manufactured by Dow Chemicals under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. Mass average molar mass obtained by gel permeation chromotography (GPC) in trichlorobenzene at 135 °C was found to be $M_w = 3.2 \times 10^5$ g mol^{-1} with a polydispersity index $M_w/M_n = 3.9$. Solvents were purchased from Aldrich and used without further purification.

Oriented film samples presenting sPS molecular complex crystalline phases were obtained by casting procedure from 0.5 wt % solution at room temperature. Nonoriented powder samples were obtained milling cast films by hand with mortar and pestle.

X-ray diffraction patterns were obtained on a Bruker D8 automatic diffractometer operating with a nickel-filtered Cu Kα radiation.

Evaluation of the correlation length D_{hkl} of the crystalline domains (where an ordered disposition of the atoms is maintained) was effected by using the Scherrer formula

$$D_{hkl} = 0.9\lambda/\beta_{hkl} \cos \theta_{hkl}$$

where β_{hkl} is the full width at half-maximum expressed in radiant units, λ is the wavelength, and θ_{hkl} is the diffraction angle.

For $\beta < 1°$, the value of β was corrected from the experimental effects applying the procedure described in ref 9. In particular, a KBr powder sample having a width at half-maximum, under the same geometrical conditions, of 0.17° was used.

The degree of the different kinds of uniplanar orientations of the crystallites with respect to the film plane has been evaluated according to the method described in detail in ref 8b.

Results and Discussion

X-ray diffraction patterns collected by an automatic powder diffractometer of cast film obtained with benzene and tetrahydrofuran (THF) solutions (upper part of Figure 2A) show essentially only intense (010) reflections, thus indicating the presence of the corresponding uniplanar orientation.[2] On the other hand, X-ray diffraction patterns of cast films obtained with trichloroethylene (TCE) and 1,2-dichloroethane (DCE) (lower part of Figure 1A) show a prevailing (002) reflection, thus indicating the presence of the corresponding uniplanar orientation.[3]

Analogous X-ray diffraction patterns show that solution-casting or spin-coating procedures with s-PS produce films with (010) uniplanar orientation, when the solvent is chloroform, *m*-xylene, and norbornadiene, while they produce films with (002) uniplanar orientation (perpendicular chain axis orientation), when the solvent is in *p*-xylene and trichlorobenzene (third column of Table 1).

In most cases the degree of uniplanar orientation (f_{010} or f_{002}) is quite large and typically in the range 0.6−0.8. Moreover, for a given guest solvent, the kind and degree of uniplanar orientation obtained by casting procedures are generally poorly dependent on the casting temperature (at least for the range 20−70 °C) as well as on the polymer concentration (at least for the range from 0.2 up to 2 wt %). This suggests that the preference for a given uniplanar orientation in solution-casting of s-PS is driven by host−guest interactions into the molecular complex crystalline phases.

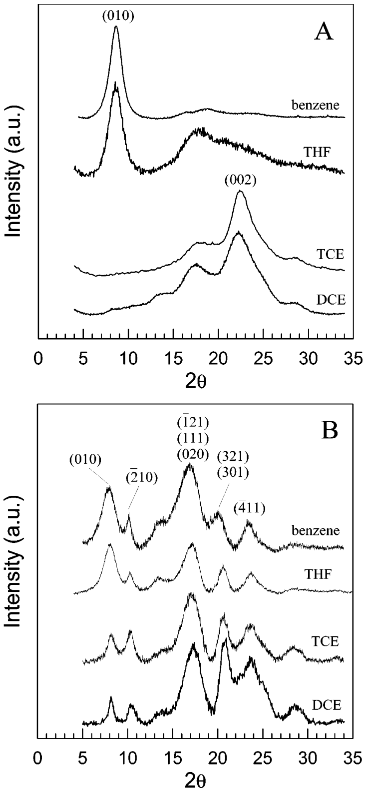

Figure 2. X-ray diffraction patterns of (A) s-PS films, cast from solutions in different solvents, and (B) cast films of (A) after milling to fine powders and amorphous halo subtraction. Miller indexes of relevant reflections are indicated.

Because of the high degree of both (010) and (002) uniplanar orientations, only the correlation length perpendicular to (010) and (002) planes, listed in fourth and fifth columns of Table 1, respectively, can be obtained by X-ray diffraction patterns like those of Figure 2A.

Information relative to the structural order along different crystallographic directions can be more easily obtained by X-ray diffraction patterns of powders. For instance, X-ray diffraction patterns of powders obtained by milling of the cast films of Figure 2A are shown in Figure 2B, after subtraction of the amorphous halo. On the basis of X-ray diffraction patterns analogous to those of Figure 2B, the correlation lengths D_{hkl} along directions perpendicular to the crystalline planes have been calculated for the rather isolated (010), $(\bar{2}10)$, and $(\bar{4}11)$ diffraction peaks (columns 6−8 of Table 1, respectively).

It is worth noting that D_{010} values of cast films with (010) orientation (fourth column) and D_{010} values of the corresponding milled films (sixth column) are similar. This suggests that milling of cast films into powder has no or little effect on the correlation distances of the crystalline domains.

For all the considered molecular complexes, low $D_{\bar{4}11}$ values (in the range 5−7 nm; eighth column of Table 1) are observed, thus confirming low correlation lengths along the *c* axis (not larger than 3 nm; fifth column of Table 1). This poor guest dependence of the correlation length along the *c* axis can be

Table 1. Correlation Lengths along Directions Perpendicular to the (010), (002), $(\bar{2}10)$, and $(\bar{4}11)$ Crystalline Planes of Molecular Complex Phases with Different Guests in s-PS Cast Films

		cast films			milled cast films		
guest	d_{010} (nm)	orientation	D_{010} (nm)	D_{002} (nm)	D_{010} (nm)	$D_{\bar{2}10}$ (nm)	$D_{\bar{4}11}$ (nm)
benzene	1.13	010	5.2		4.2	12.0	5.5
tetrahydrofuran	1.10	010	4.4		4.9	9.9	5.5
chloroform	1.09	010	5.0		5.3	11.4	6.2
m-xylene	1.16	010	5.2		5.9	9.7	5.5
norbornadiene	1.34	010	5.9		5.9	11.0	5.6
trichloroethylene	1.04	002		2.9	7.2	7.8	4.8
p-xylene	1.12	002		2.3	7.7	9.6	7.4
1,2-dichloroethane	1.04	002		2.5	14.0	8.1	
trichlorobenzene	1.13	002		2.6	14.4	13.4	

easily rationalized by the prevalence of intramolecular interactions along the polymer chain axis.

Moreover, for all the considered molecular complexes, large correlation lengths are observed along the direction perpendicular to the $(\bar{2}10)$ planes (in the range 8−13 nm, seventh column of Table 1), i.e., along a direction forming a small angle (less than 20°) with the *a* axis (Figure 1). Hence, these results indicate high correlation lengths along the *a* axis, independently of chemical nature of the guest molecule. The high correlation length along the *a* axis and its poor guest dependence can be easily rationalized by the energy efficient close-packing of s-PS enantiomorphous helices along this direction (Figure 1).

Larger guest dependence is instead observed for the correlation length perpendicular to the *ac* layers (D_{010} in the range 4−14 nm, sixth column of Table 1).

By a comparison of the data of Table 1, no correlation occurs between D_{010} (sixth column) and Bragg distances d_{010} values (second column), while a clear correlation exists between D_{010} and the kind of uniplanar orientation obtained by solution casting (third column). In particular, D_{010} is in the range 4−6 nm for molecular complex phases with (010) orientation while it is in the range 7−15 nm for molecular complex phases with (002) orientation.

This correlation between D_{010} and the kind of uniplanar orientation can be understood by considering the shape and size of crystalline domains for cast films with (010) and (002) uniplanar orientations, as suggested by the data of Table 1 and schematically shown in parts A and B of Figure 3, respectively. In fact, the direction of close-packing of enantiomorphous s-PS helices (*a* axis), which is always characterized by high correlation length, remains parallel to the film plane, for all considered cast films. For low correlation length along the direction perpendicular to the *ac* layers ($D_{010} < 6$ nm), the chain axis *c* tends to be parallel to the film plane (Figure 3A), as generally observed for uniplanar orientations of semicrystalline polymers.[10] On the other hand, for high correlation length along the direction perpendicular to the *ac* layers ($D_{010} > 7$ nm), the chain axis *c*, being characterized by a much lower correlation length, remains perpendicular to the film plane (Figure 3B).

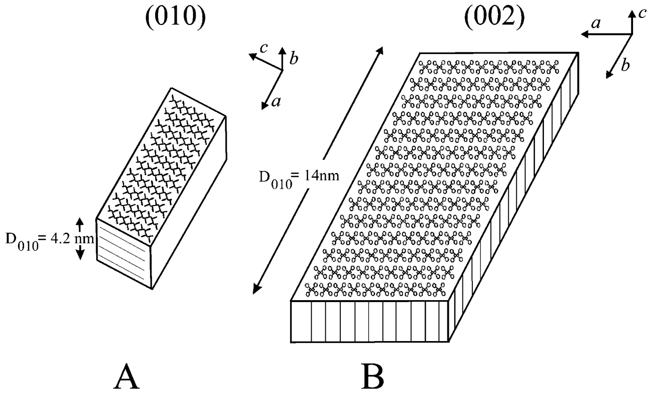

Figure 3. Schematic view of crystalline domains of s-PS molecular complex phases obtained with benzene (A) and DCE (B) that respectively lead to the (010) and (002) uniplanar orientations. These two kinds of uniplanar orientations are generated by poor and good host−guest interactions, leading to correlation length perpendicular to the *ac* plane, being low ($D_{010} \leq 6$ nm) and high ($D_{010} \geq 7$ nm), respectively.

Because of the guest location into the monoclinic unit cells of Figure 1, it is reasonable to expect that high and low values of D_{010}, observed for different s-PS molecular complex phases, would be due to more or less efficient host−guest interactions. An at least qualitative correlation between D_{010} values of Table 1 and stability of s-PS molecular complex crystalline phases is confirmed by one presently available experimental knowledge. For instance, D_{010}(*p*-xylene) > D_{010}(*m*-xylene) from Table 1 well accounts for the well-known preferential complexing ability of *p*-xylene with respect to *m*-xylene.[11]

Conclusions

Correlation lengths (i.e., the range of structural order) along different crystal directions, for molecular complex phases of s-PS solution-cast films, have been evaluated on the basis of width at half-maximum of wide-angle X-ray diffraction peaks.

The reported results indicate that the chemical nature of the guest has a scarce influence on correlation length along the chain axis *c*, being always low (roughly 3 nm) as well as on correlation length along the *a* axis, i.e., the direction of energy-efficient close-packing of enantiomorphous helices, being rather high (possibly always larger than 10 nm). Larger is the guest influence on the correlation length perpendicular to the *ac* polymer layers, which can change depending on the guest from 4 up to 14 nm. These results have been rationalized on the basis of the known crystalline structures of s-PS molecular complexes (Figure 1).

The analysis has also shown that guest molecules leading to molecular complex domains with low and high degree of order perpendicular to the *ac* layers ($D_{010} < 6$ nm and $D_{010} > 7$ nm) generate cast films with (010) and (002) uniplanar orientations, respectively.

These results have been rationalized on the basis of the shape of structurally ordered domains. For poor host−guest interactions, leading to low D_{010} values, *ac* layers tend to be parallel to the film plane (Figure 3A). On the other hand, for good host−guest interactions, leading to high D_{010} values, chain axes, being characterized by a much lower correlation length, remain perpendicular to the film plane (Figure 3B).

The occurrence of an at least qualitative correlation between D_{010} values measured for solution-cast films and stability of s-PS molecular complex crystalline phases is suggested by one presently available literature data. Of course, additional experiments are required to support the possible occurrence of a quantitative correlation.

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