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Morphological Study of Phase Transition Behavior in Syndiotactic Polystyrene

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ABSTRACT: Highly ordered helical syndiotactic polystyrene (sPS) crystal mats have been grown from dilute ethylbenzene solution. The morphology of the as-grown mats consists of ribbonlike structures, with the sPS chains oriented perpendicular to the mat surface. The as-grown crystals are complexed structures with an estimated ratio of one ethylbenzene molecule for approximately six sPS chemical repeat units. Upon annealing at 106 °C for 5 h, the solvent is driven from the crystal lattice. While chain orientation and conformation are retained, the ribbonlike morphology is irreversibly disrupted with a shrinking of the *b*-axis spacing, which is indicative of intermolecular disordering caused by solvent expulsion. Upon annealing at 202 °C, the chain conformation changes irreversibly from TTGG to all-trans. A completely new lamellar morphology is formed with the chain orientation parallel to the mat surface. A complete molecular reordering at the segmental and morphological levels thus occurs during this phase transition which cannot be accounted for by cooperative bond rotation or any other equilibrium mechanism. This observation is consistent with the irreversible nature of the transition and further emphasizes the critical role of solvent in formation of the less favored helical crystal phases associated with syndiotactic polystyrene.

Introduction

Recently highly stereoregular syndiotactic polystyrene has attracted great interest in this material.[1–4] Depending on thermal history, syndiotactic polystyrene (sPS) exhibits several polymorphic crystalline structures. Helical crystals are formed in the presence of most solvents, whereas the more favorable all-trans phase crystallizes from the melt, drawn, or crystallites annealed at elevated temperatures.[5–12] Studies of the detailed microstructure of this crystalline form have been undertaken.[13–16] Only limited structural and morphological information is available for the helical crystalline phases, including sPS–solvent complexes.[6,9,10,17]

Two phase transitions are associated with unannealed solution-grown helical crystals, or the δ form,[10] of syndiotactic polystyrene. The first occurs at ~100 °C and is due to expulsion of solvent molecules from the crystal lattice. It has been suggested that the solvent molecules stabilize the TTGG conformation and that decomplexation leads to slight disordering of the crystalline structure.[18] A helical chain conformation is retained at this transition and labeled as the γ phase.[10] The segmental conformation (TTGG) of this "dry" helical phase has been suggested to be identical to the δ phase.[19] The second phase transition occurs from drawing the material or annealing near 200 °C and involves formation of an all-trans chain conformation. This phase transition is irreversible and cannot be treated as a true thermodynamic phase transition. An X-ray diffraction study of this transition induced by straining the material has indicated that the γ-phase crystallites display plastic behavior upon deformation, i.e. they do not orient in the strain direction as small brittle crystalline units prior to the conformational change.[20] An entropy-driven, two-step mechanism for this transition, in which the chain conformation changes first from TGGT to TTGT and then to TTTT has been proposed on the basis of molecular simulation data.[21] However, no detailed mechanism as a function of annealing based on experimental results has been proposed for this transition to date.

Two goals are pursued in this study: (1) a detailed morphological characterization of the δ-phase sPS crystals grown from dilute ethylbenzene solution, and (2) more importantly, examination of the evolution of the morphology through each of the two phase transitions. Observed morphological changes provide information concerning the mechanism of each transition. Results are interpreted by comparing these observations to changes in both chain orientation and chain conformation as a function of identical thermal history. Our results are presented herein.

Experimental Section

Syndiotactic polystyrene (M_w = 600 000, M_n = 200 000) used in these studies was provided by the Dow Chemical Co. The steric purity was determined by MEK extraction to be greater than 99%. Syndiotactic polystyrene crystals were isothermally grown from 0.05 wt % ethylbenzene solution at 50 °C and filtered at the same temperature onto 25-mm Tefsep laminated PTFE membranes with a pore size of 0.20 μm. As-grown crystals were dried for more than 1 week under vacuum below 50 °C. The highly oriented sPS thin film was prepared by drawing cast films from a 0.5 % 1,2,4-trichlorobenzene solution at 200 °C by the method of Petermann and Gohil.[22]

Differential scanning calorimetry (DSC) scans were performed in a DuPont 2000 calorimeter at a heating rate of 20 °C/min under a nitrogen gas purge. Thermogravimetric analysis (TGA) data were obtained with a DuPont 2950 thermogravimetric analyzer at a scan rate of 5 °C/min. Wide-angle X-ray diffraction patterns were obtained with nickel-filtered Cu Kα radiation utilizing a Statton flat photographic camera. The WAXD photographs were taken at room temperature with a pinhole collimator and camera distance of 54 mm. Diffraction patterns were obtained with the crystal mat perpendicular to and tilted approximately 45° with respect to the incident X-ray beam.

Samples for electron microscopy were prepared by putting a drop of sPS–ethylbenzene suspension onto vapor-deposited carbon-coated copper grids. The morphological studies were performed with a JEOL 100CX transmission electron microscope at 100 kV. Electron diffraction (ED) has been carried out at 100 kV on an area of 0.5 μm. The camera length was calibrated with an internal Au standard.

Results and Discussion

Syndiotactic polystyrene (sPS) grown from dilute ethylbenzene solution exhibits much higher order than

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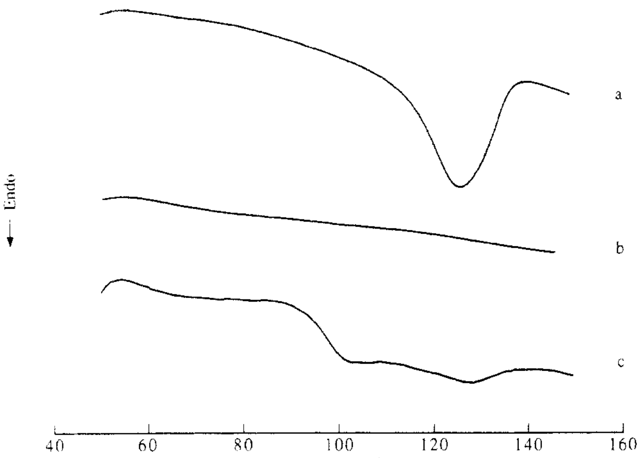

Figure 1. DSC traces of the first heating of (a) solution-grown sPS crystals unannealed, (b) solution crystals annealed at 106 °C for 10 h, and (c) sPS crystallized by slowly cooling from the melt and annealed at 106 °C for 10 h.

samples previously studied in this laboratory. This feature is important to minimize the contribution of amorphous regions and more confidently understand the crystalline state from experimental data. The degree of crystallinity (X_c) for the as-crystallized syndiotactic polystyrene cannot be determined from the heat of fusion with the conventional calorimetric technique. The enthalpy of fusion is measured to be independent of initial sample crystallinity due to extremely fast recrystallization upon heating in the DSC apparatus.[23] For semicrystalline polymers, the degree of crystallinity has been estimated by measuring the change in heat capacity at the glass transition in comparison to a quenched, amorphous sample.[24] This method has been applied to melt-crystallized syndiotactic polystyrene.[25] In that study, a degree of crystallinity of 74% was obtained in approximate agreement with a value obtained from solvent adsorption experiments for similarly prepared samples.[23]

First-run thermograms of (a) an as-grown crystal mat of syndiotactic polystyrene, (b) a mat annealed at 106 °C for 10 h, and (c) a melt-crystallized sample annealed under identical conditions are shown in Figure 1. The observed endotherm in Figure 1a, with onset at ~100 °C, is due to decomplexation of the material, as affirmed below. For solution-grown crystals prior to annealing, there is no measurable glass transition, observed at 85–100 °C for other semicrystalline sPS samples.[25] Even after the mat is annealed at 106 °C for 10 h, when thermal contact with the DSC pan is better and the endotherm has been eliminated, T_g still was not observed. The amorphous content of this sample is therefore too low to measure, indicating a degree of crystallinity appreciably higher than observed for the melt-crystallized sample. Furthermore, since annealing was conducted slightly above T_g, it is assumed that a negligible increase in order or crystallization occurred upon annealing and that the high degree of crystallinity is indicative of the initial polymer–solvent complex. As a control experiment, the change in heat capacity for the annealed melt-crystallized sample is 0.22 J/(g °C), very close to that of 0.16 J/(g °C) obtained earlier,[25] therfore providing a standard for comparison. A glass transition is always measured in films cast from solution or from melt-crystallized samples (Figure 1c). The nearly immeasurably small change in heat capacity at T_g for the solution-grown crystals must be associated with a high degree of crystallinity, certainly higher than 74%.

Wide-angle X-ray diffraction (WAXD) is used to examine chain conformation and orientation for filtered crystal mats. Figure 2 shows the WAXD photographs for unannealed solution-grown sPS crystal mats. The diffraction pattern shown in Figure 2a was obtained by setting the crystal mat surface perpendicular to the incident X-ray beam; the pattern shown in Figure 2b was obtained by tilting the specimen surface ~45° with respect to the incident beam. The measured sample *d* spacings are listed in Table I, utilizing the notation of Guerra et al.[10] In Figure 2a,b, the innermost two diffraction rings are indexed as the (010) and (200) reflections.[26] The assignment of (010) and (200) reflections are consistent with the data presented earlier, in that the *b* axis shrinks upon decomplexation while the *a* axis remains unchanged. The entire set of diffraction data associated with δ and γ forms listed in Table I is consistent with a helical chain conformation for the as-grown crystal mats.[9] The observed reflections are not indexed because we disagree with the exact structural parameters provided in the earlier study.[17] Detailed analyses have been carried out for highly oriented samples. A separate publication is being prepared. Infrared spectra of these syndiotactic polystyrene samples also conclusively show that the chain conformation is helical. Bands at 502, 548, 572, 934, and 943 cm^{-1}, indicative of gauche linkages in the sPS chains, are observed.[26] Both the (010) and (200) reflections are observed along the meridian direction for the solution-grown crystal mats tilted with respect to the incident X-ray beam (Figure 2b). This observation indicates that chain orientation exists in the crystal mats and, as is the case with many filtered solution crystals, the crystal *c* axis (chain direction) is nearly normal to the mat surface.

Bright field electron micrographs of helical sPS crystal mats are shown in Figure 3. Generally lamellar, dendritic, or spherulitic morphologies exist for crystalline polymer systems. In fact, lamellar crystals have been observed for syndiotactic polystyrene crystallized from the melt.[14] An interesting unique ribbonlike morphology is observed for crystals grown from solution (Figure 3a). The ribbons range from 300 to 1000 Å in width; the length is approximately several microns. Due to the small ribbon size, single crystals cannot be isolated to be studied by electron diffraction. We therefore cannot at this time indicate whether each ribbon is indeed a single crystal. These ribbons aggregate after the solvent is removed. This ribbon morphology is specific to, and therefore most probably a result of, inclusion of solvent molecules in the unit cell.

The first phase transition of syndiotactic polystyrene is clearly shown in Figure 1a. Thermal gravimetric analysis (TGA) and X-ray diffraction indicate that this transition is associated with decomplexation. TGA thermograms for the as-grown sPS crystals dried under vacuum at 55 °C are shown in Figure 4. Approximately a 5% weight loss difference is observed between the sample dried for 10 days under vacuum and the as-filtered crystal mat, possibly due to elimination of residual-free solvent in the amorphous region or part of the complexed solvent in the crystalline region if the interaction between the solvent molecules and the sPS chains in the complex is weak. This intermolecular interaction was suggested by Shimane to be a relatively weak van der Waals type for an sPS/toluene complex.[17] The similarity in structure between toluene and ethylbenzene suggests that the weight loss difference attributed to decomplexation is reasonable. By growing crystals from dilute solution, we attempt to obtain an accurate picture of the structure by minimizing or eliminating the contribution of solvent in the amorphous regions to the observed weight loss in the TGA experiment.

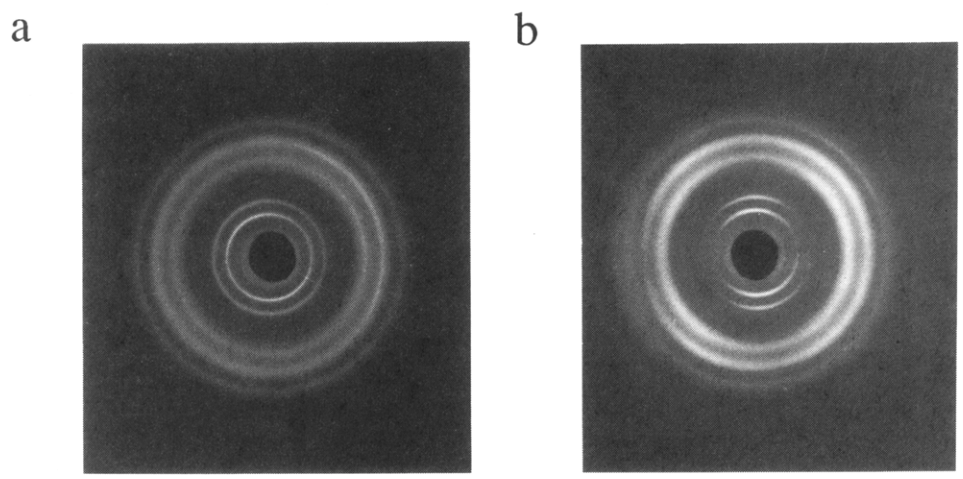

Figure 2. Wide-angle X-ray diffraction patterns of unannealed sPS solution-grown crystals with the mat surface oriented (a) perpendicular to the incident X-ray beam and (b) ~45° with respect to the incident X-ray beam (tilted).

Table I
Wide-Angle X-ray Diffraction Data Obtained for Solution-Grown sPS Crystalline Mats

unannealed			annealed 106 °C, 1 h			annealed 106 °C, 5 h		annealed 142 °C, 5 h			annealed 202 °C, 5 h		
d (Å)	I	(*hkl*)	*d* (Å)	I		*d* (Å)	I	*d* (Å)	I	(*hkl*)[14]	*d* (Å)	I	(*hkl*)[14]
											13.12	s	110
11.34	s	010	11.34	s	δ								
			9.59	m	γ	9.65	s	9.59	s	010			
8.77	s	200	8.89	s	$\delta + \gamma$	8.62	m	8.62	s	200			
											8.59	vw	210
			7.62	vw	γ	7.49	vw	7.31	vw		7.54	s	300
6.64	w		6.44	vs	$\delta + \gamma$	6.37	w	6.40	w		6.57	s	220
			5.75	m	γ	5.67	vs	5.66	vs				
5.16	vs		5.22	s	δ						4.99	w	410
4.39	vs		4.45	vs	$\delta + \gamma$	4.62	s	4.50	s		4.35	vs	211
3.84	m		3.88	m	δ	3.80	m	4.00	m				
			3.62	vw	γ			3.61	w		3.75	w	600
3.24	vw		3.27	vw	$\delta + \gamma$			3.22	w		2.56	m	$10\bar{2}$[16]
δ form			$\delta + \gamma$ forms			γ form		γ form			α form		

That is, if the polymer/solvent interaction is very weak, as has been suggested, it may be impossible to completely separate decomplexation and solvent expulsion effects from the amorphous regions during heat drying. It may therefore also be impossible to obtain an exact ratio of solvent to sPS chemical repeat unit in the δ phase without the preparation of single crystals. TGA of solution-grown sPS crystals annealed at 101 °C show that weight loss increases as a function of annealing time (Figure 5), indicative of the decomplexation process. The TGA scans of samples annealed at 101 °C for 32 h and 142 °C for 5 h exhibit no weight loss, indicating completion of decomplexation.

Previous studies of sPS-solvent complexes have not provided detailed structures or morphologies of these states. In their study of the sPS/CH_2Cl_2 complex, Immirzi et al determined that the mole ratio of CH_2Cl_2 to sPS chemical repeat unit in the crystalline phase is "certainly less than 1:25".[6] Gomez and Tonelli report the number of CH_2Cl_2 molecules per monomer repeat to be less than 1:13 for the same complex.[19] The difference in ratios presented by the two groups is undoubtedly due to the difference in amorphous content in each since the samples studied were prepared by solvent crystallization of amorphous films and not under conditions which control the degree of crystallinity. Therefore both studies presented an upper limit for the polymer:solvent ratio and not an absolute number. It is possible, however, that residual solvent in the amorphous state can give an artificially large number of solvent molecules per sPS monomer unit. In another study in which the degree of crystallinity was known, a value of one CH_2Cl_2 molecule per seven or eight sPS chemical repeats in the crystalline phase has been measured, a significantly lower value than presented in the above studies.[27] Shimane et al proposed a 1:4 molar ratio for the toluene–sPS complex, even though the measured weight loss (ca. 14.2%) was less than the 18% expected from the proposed unit cell in which the polymer chains are in direct contact along the *a* axis and the solvent molecules are positioned between the polymer chains along the *b* axis.[17] The observed smaller weight loss may arise from the fact that solvent in the amorphous region can be easily eliminated. Even elimination of some solvent molecules in the crystalline region may occur, as previously mentioned.[17] For the solution grown sPS–ethylbenzene complex, we observe the weight loss to be approximately 15%, similar to that observed by Shimane for complexes of sPS and solvents containing a phenyl ring.

As mentioned previously, TGA data obtained for these samples suggest that the first phase transition is due to the decomplexation process. Wide-angle X-ray diffraction data also indicate that the solvent is expelled directly from the crystalline regions of the polymer. Wide-angle X-ray diffraction patterns of sPS crystal mats annealed above the first phase transition temperature are shown in Figure 6. Upon comparison of Figure 6b,c to data presented in Figure 2b, it can be seen that, after annealing at 106 or 142 °C for 5 h, both the chain conformation and orientation in the crystals are retained, and while the crystalline *a*

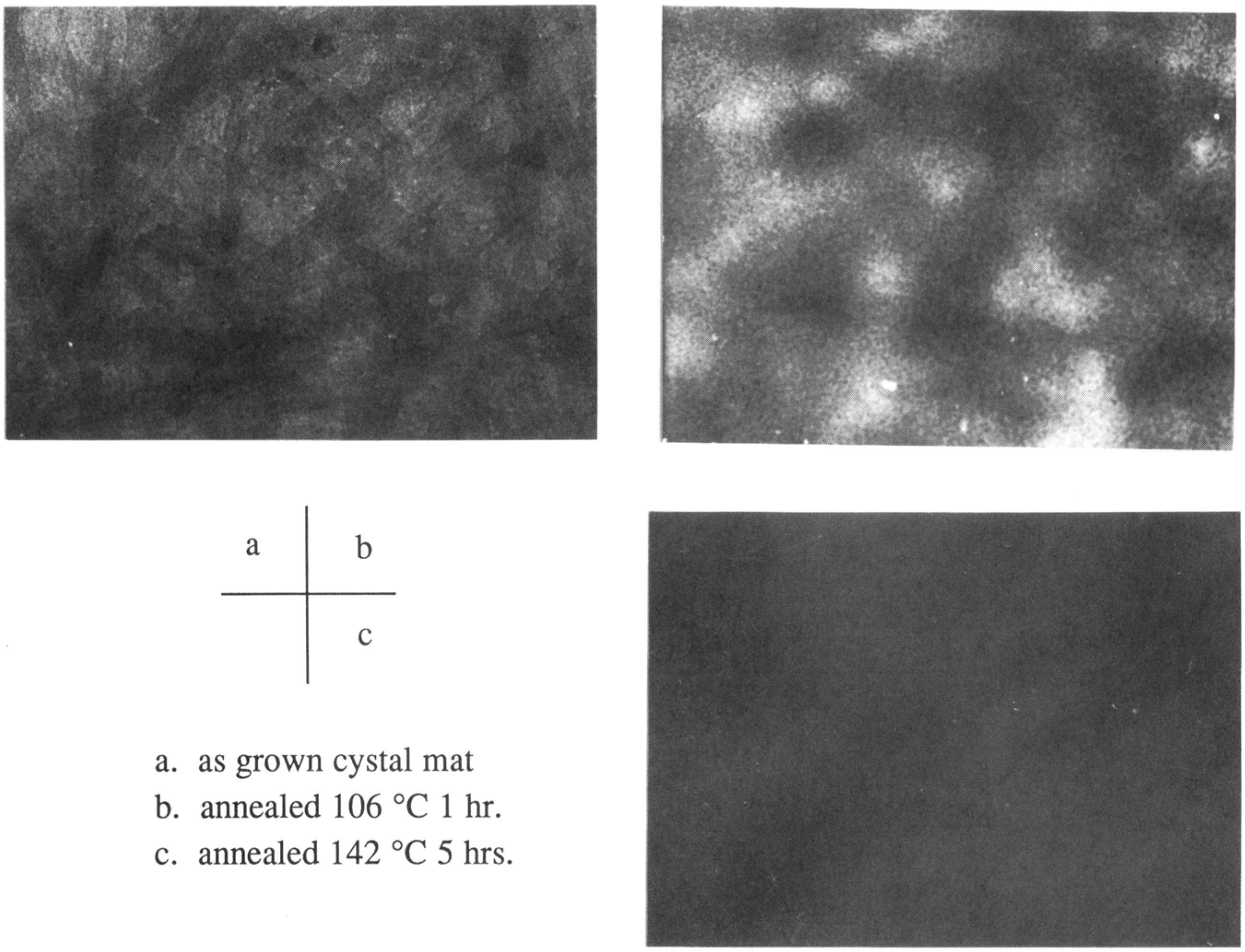

Figure 3. Bright field electron micrographs of helical solution-grown sPS crystals: (a) unannealed, (b) annealed at 106 °C for 1 h, and (c) annealed at 142 °C for 5 h.

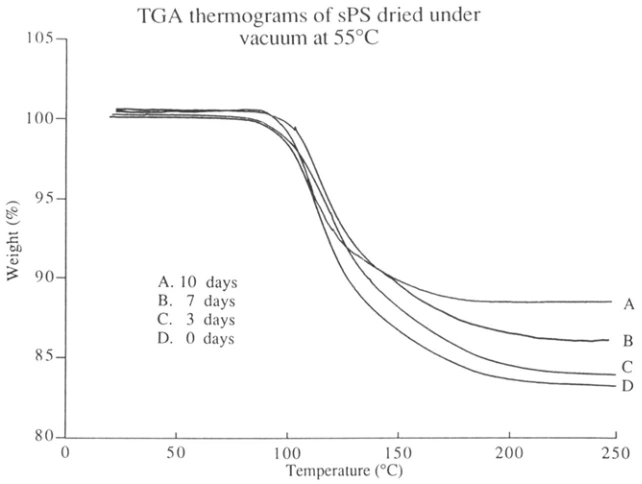

Figure 4. TGA thermograms of as-grown sPS crystals dried at different times under vacuum at 55 °C as labeled.

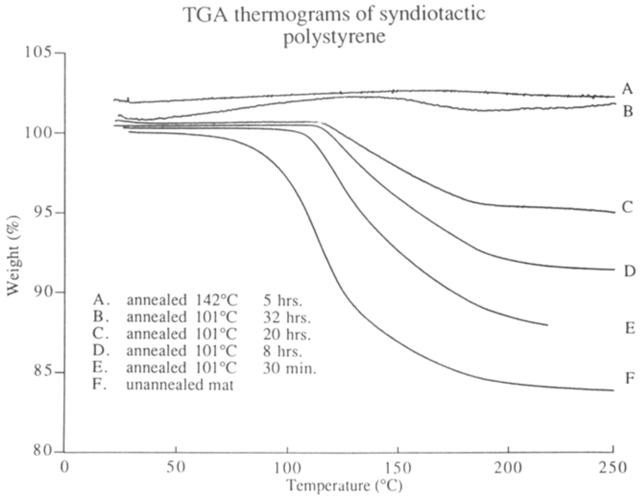

Figure 5. TGA thermograms of sPS crystals unannealed, annealed at 101 °C at different times, and annealed at 142 °C for 5 h, as labeled.

spacing corresponding to the (200) reflection changes only slightly, the *b* spacing corresponding to the (010) reflection shrinks markedly. The crystal packing changes from δ to spacings expected for the γ crystal form.[10,17] We have calculated this *b*-axis shrinkage to be about 1.7 Å (see Table I), similar to the 1.85 Å observed by Shimane for a sPS–toluene complex annealed at 130 °C for 1 h.[17] Figure 6a shows that two (010) reflections are observed corresponding to two distinct *b* spacings. Therefore the δ and γ crystalline forms coexist in the crystals annealed at 106 °C for 1 h, indicating that decomplexation occurs at this point.

Nakaoki has suggested that the TTGG conformation of a complex of syndiotactic polystyrene and chloroform is stabilized by solvent and that structural disordering occurs during decomplexation as solvent is expelled from the crystal lattice.[18] The formation of more ordered TTGG sequences then occurs as the annealing temperature is raised above 100 °C.[18,25] Interestingly, definite correlations

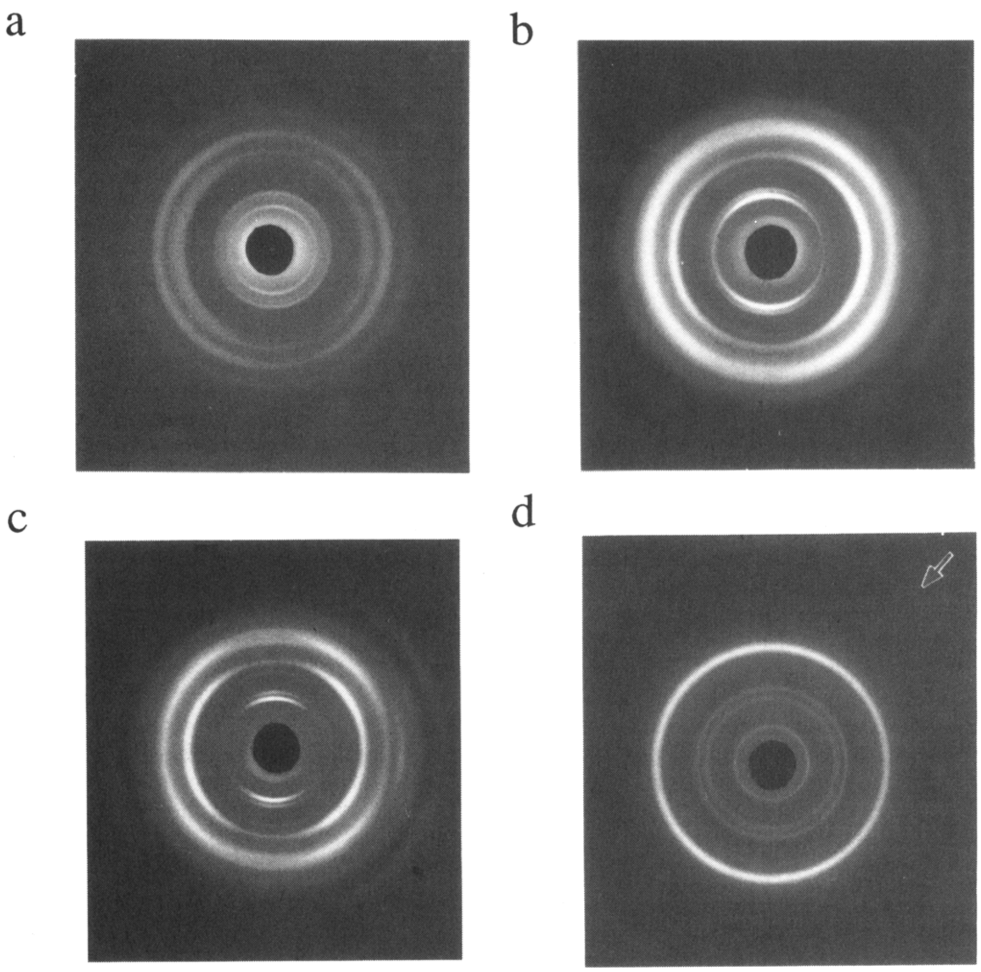

Figure 6. Wide-angle X-ray diffraction patterns of sPS solution-grown crystals with the following thermal histories: (a) annealed at 106 °C for 1 h (tilted); (b) annealed at 106 °C for 5 h (tilted); (c) annealed at 142 °C for 5 h (tilted); (d) annealed at 202 °C for 5 h.

Table II
Electron Diffraction Data Obtained for Solution-Grown sPS Crystals

unannealed			unannealed; high vacuum			annealed 142 °C, 5 h			annealed 202 °C, 15 h			annealed 220 °C, 5 h		
d (Å)	I	(*hkl*)	*d* (Å)	I	(*hkl*)	*d* (Å)	I	(*hkl*)	*d* (Å)	I	(*hkl*)[14]	*d* (Å)	I	(*hkl*)[14]
									13.22	vs	110	13.22	vs	110
11.42	vs	010	10.77	vs	010	9.69	vs	010						
8.77	s	200	8.77	s	200	8.77	s	200						
									7.52	m	300	7.52	m	300
						6.45	w		6.51	m	220	6.51	m	220
						5.62	m					5.62	vw	400
5.24	m		5.24	m								5.09	vw	320
4.44	m		4.44	m		4.44	m		4.32	vs	211	4.32	vs	211
3.81	m		3.81	w					2.56	m	$10\bar{2}$[16]	2.56	m	$10\bar{2}$[16]
												2.40	vw	212
									1.67	m		1.67	m	
												1.26	m	$10\bar{4}$

can be drawn between changes in the overall morphology with changes in chain conformation and chain orientation of sPS crystals. Examination of the electron micrographs of the mats shown in Figure 3 indicates that decomplexation involves disordering via disruption of the ribbonlike morphology initially observed. It is apparent that solvent plays a large role in the interchain order yielding the ribbonlike structure. After annealing at 106 °C for 1 h when δ and γ crystallites are present, the ribbon morphology becomes diffuse (Figure 3b), indicating that decomplexation has begun. For the mat annealed at 142 °C for 5 h, the ribbonlike morphology is completely destroyed. However, electron diffraction (see Table II), along with WAXD and infrared data, indicates no change in both molecular conformation and chain orientation during decomplexation. Therefore any increased perfection of the TTGG sequences due to annealing of the dry or decomplexed state is not reflected in the morphology. Effects of decomplexation and annealing on the morphology of syndiotactic polystyrene crystal mats can then be separated. The interpretation of the change in mat morphology upon decomplexation being interchain in nature is in agreement with the shrinkage of the *b*-axis spacing observed with WAXD.

Table II shows d_{hkl} spacings obtained from electron diffraction patterns of crystal mats as a function of annealing. WAXD data in Table I for samples of identical thermal history show the *a* and *b* spacings from the (200)

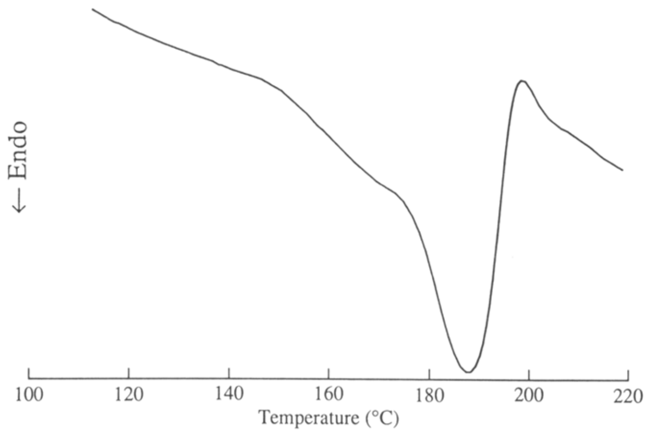

Figure 7. DSC thermogram of the first heating of solution-grown sPS crystals annealed at 142 °C for 5 h.

and (010) reflections to be very similar to those obtained with electron diffraction. For the as-grown mat placed in the high vacuum (>10^{-5} mm Hg) of the electron microscope sample chamber for 24 h prior to the diffraction measurement, the *b* spacing from the (010) reflection obtained is much shorter (10.77 Å) than that of the initial state (11.42 Å). This difference is due to the existence of a weak interaction between solvent molecules and polymer chains in the complex. In this case, decomplexation occurs readily for the extremely thin sample during the morphological and electron diffraction measurements due to the high-vacuum and high-energy electron-beam bombing in the electron microscope.

The high degree of order exhibited for the solution-grown crystals in the dry γ phase is reflected by the observed increase in the magnitude of the helix to trans endotherm for the solution-grown crystals as opposed to cast films. DSC is utilized in this manner to examine the relative degree of crystallinity of the decomplexed material. It has been shown that in semicrystalline cast films the magnitude of the endotherm associated with the helix to all-trans phase transition at ~190 °C is dependent on the initial amount of helical crystalline content in the sample.[25] For a semicrystalline cast film a tiny, nearly quantitatively immeasurable exotherm attributed to amorphous chains crystallizing to all-trans crystals has been observed.[9] No endotherm is observed in this sample. In another study, a nearly immeasurable endotherm has been observed at the same temperature for a film annealed at 150 °C. In this study, a semicrystalline sample annealed at 170 °C yielded a measurable endotherm of 4.1 J/g. It was concluded that the magnitude of this endotherm increases with increasing initial helical crystalline content as the sample is annealed just below the phase transition temperature. Figure 7 shows the DSC thermogram of the first heating of a solution-grown crystal sample annealed at 142 °C. This sample exhibits no weight loss in the TGA (see Figure 5, curve a) and therefore contains no complexed molecules. The rate of heating is 20 °C/min. The magnitude of the endotherm seen at ~190 °C is 7.9 J/g. The solution grown crystalline sample was annealed at 142 °C, even less than the 150 °C annealing temperature for the cast film in our previous study where a miniscule endotherm was observed. The enthalpy was nearly double

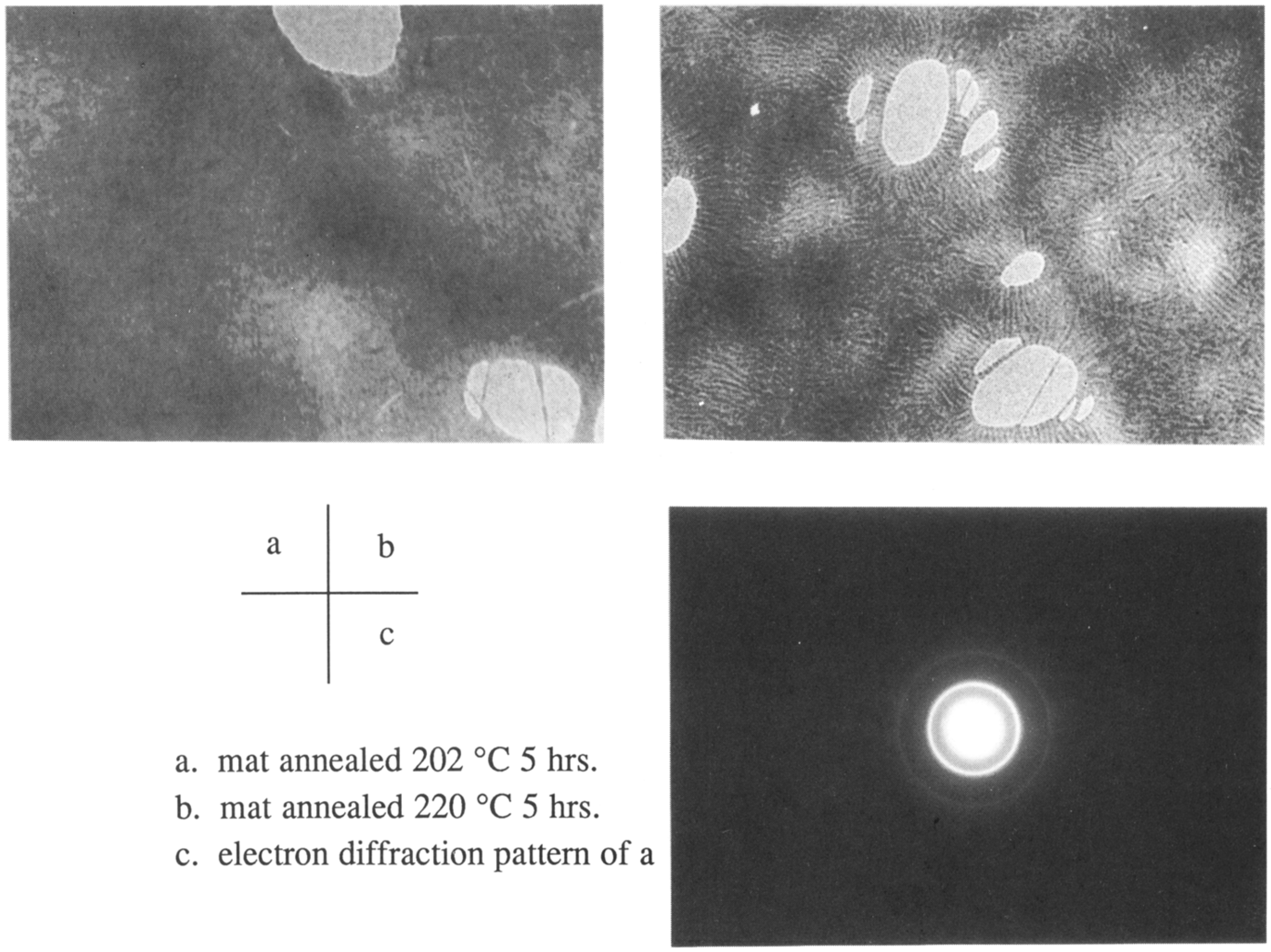

Figure 8. Bright field electron micrographs of solution-grown sPS crystals: (a) annealed at 202 °C for 5 h; (b) annealed at 220 °C for 5 h; (c) the electron diffraction pattern of (a).

that of the cast film annealed at 170 °C.[25] The helical crystalline content, and therefore the degree of crystallinity, is greater for the solution-grown sPS crystals in the γ or decomplexed crystalline phase than for the cast films previously studied. A similar endotherm, approximately one-fifth the magnitude of the melting transition (5–6 J/g) has been observed for γ-phase crystals, but the detailed thermal history of this sample was not presented.[10] This interpretation of a highly ordered state is consistent with the lack of change in heat capacity at the glass transition discussed earlier.

A higher temperature helix to all-trans phase transition occurs for syndiotactic polystyrene at ~190 °C, shown in Figure 7. The associated conformational change and kinetics of this phase transition for semicrystalline solution cast films have been studied.[8,9,25] This transition is irreversible and nonequilibrious in nature. Therefore a traditional helix/coil or other equilibrium model cannot be applied in order to understand the transition mechanism. The chain conformation, orientation, and overall morphology of solution crystal mats before and after this transition provide information on the scale and magnitude of the structural change.

For the crystal mat annealed at 202 °C for 5 h, the WAXD patterns for the specimens perpendicular and tilted 45° with respect to the incident beam are identical (shown in Figure 6d). The spacings obtained (see Table I) are consistent with those previously reported for the all-trans α crystalline phase.[14,16] Therefore the crystal chain conformation changes from the helical γ form to the all-trans α form upon annealing above the second phase transition temperature. Recently, it has been shown that in the α phase the planar zigzag chains are packed in the hexagonal unit cell, but with different orientation and relative height of the phenyl groups.[16] It was suggested that the α form of sPS has two modifications: ordered (α''), with the space group $P3c1$ (instead of $P\bar{6}2c$ as proposed in ref 14), and disordered (α') with the space group $R\bar{3}c$.[16] In this study, the wide-angle X-ray diffraction data for the solution-grown crystal mat annealed at 202 °C for 5 h is close to that of the disordered α' modification. However, the very weak (210) diffraction which belongs to the ordered α'' modification is also observed. No difference was found between the WAXD patterns of the samples perpendicular to and tilted with respect to the incident beam, indicating that a specific orientation normal to the mat surfact does not exist. However, the appearance of the $(10\bar{2})$[16] reflection, as indicated by the arrow in Figure 6d, shows that the c-axis (chain direction) orientation changes from normal to parallel to the mat surface after annealing at 202 °C for 5 h.

Annealing above the second phase transition temperature results in the formation and development of lamellar morphology, as shown in Figure 8a,b. The lamellar crystals are seen "edge-on". From the d_{hkl} spacing values (Table II) and the appearance of the $(10\bar{2})$ and $(10\bar{4})$ reflections on the electron diffraction pattern of an untilted mat (indicated by the arrows in Figure 8c), it is concluded that only all-trans crystals exist and that the c-axis orientation (chain direction) is in the plane of the crystal mat. The lamellar thickness increases with increasing annealing temperature. The thickness is approximately 100 Å for the crystals annealed at 202 °C for 5 h and at least double that for the mat annealed at 220 °C for 5 h. The electron diffraction data for the crystal mat annealed at 202 °C for 5 h is consistent with that of the disordered α' form of sPS, while the sample annealed at 220 °C for 5 h exhibits reflections close to that of the ordered α'' modification.[10,16]

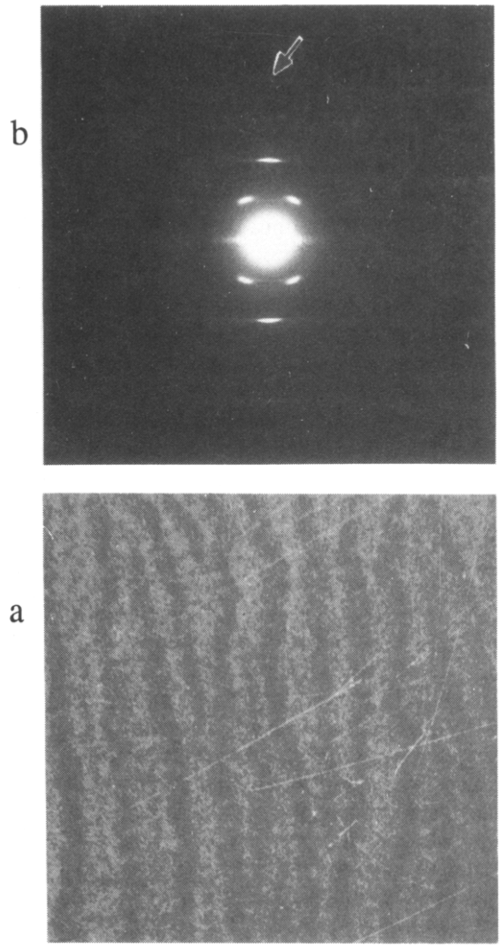

Figure 9. Bright field electron micrograph (a) and electron diffraction pattern (b) of an extremely highly oriented sPS film.

The lamellar morphology and molecular chain orientation can be compared with that of an extremely highly oriented thin film prepared by the method of Petermann and Gohil,[22] shown in Figure 9. In this sample, lamellar crystals are packed parallel and normal to the draw direction (Figure 9a). As shown by the electron diffraction pattern (Figure 9b), the molecular chains are parallel to the film surface and oriented in the draw direction. The morphology and electron diffraction pattern of this thin film are similar to those observed in the dilute solution-grown crystal mats annealed above 200 °C except that one-dimensional orientation and packing are found in the highly oriented thin film.

The change, at the segmental level, in chain conformation through this transition is therefore associated with larger scale molecular reordering. The fact that an entirely new morphology develops, along with a complete change in chain orientation, shows that complete molecular reordering occurs, not simply the cooperative rotation of bonds. This observation, consistent with the irreversibility of the transition and the lower energy state being the all-trans chain conformation, emphasizes the critical role of solvent in formation of the higher energy helical crystalline phase, as the resultant structure differs from the most energetically favored all-trans state at the segmental and morphological levels.

Conclusions

Syndiotactic polystyrene (sPS) of extremely high crystallinity was prepared by growth from dilute ethylbenzene solution. This method of sample preparation is vital to minimize contributions of the amorphous regions to the TGA data and also to the observed vibrational spectra. The as-grown crystal mats, a complexed structure of solvent molecules and sPS chains, exhibit a ribbonlike morphology in which the polymer chains possess a helical TTGG chain conformation and are preferentially oriented perpendicular to the mat surface. Upon decomplexation at approximately 100 °C, solvent is expelled from the crystal lattice and the ribbonlike morphology is damaged, while the initial chain orientation and conformation are retained. This initial disordering, which causes the disruption of the ribbonlike morphology, is indicative of the large role of solvent in the interchain order leading to the ribbon and aggregated ribbon structures in the initial complexed state. The *b*-axis spacing of the crystals is observed to shrink upon decomplexation, in agreement with the change in interchain order observed in the TEM experiment. This observation also supports the contention that sPS exhibits a single helical chain conformation, even though changes in diffraction occur with decomplexation. Upon further annealing of the decomplexed or dry helical phase, the morphology remains completely disrupted. Therefore any increased perfection of the TTGG sequences due to annealing the dry state is not reflected in the morphology and the effects of decomplexation and annealing on the morphology of syndiotactic polystyrene crystal mats can be separated. Annealing above the helix to all-trans phase transition temperatures changes the morphology and orientation. Lamellar crystals form and increase in thickness upon further annealing. The chains orient parallel to the mat surface. Therefore changes in chain conformation occur in conjunction with major morphological changes, indicating that this transition involves complete molecular reordering and not simply the cooperative rotation of bonds along the chains. This observation is consistent with the nonequilibrium, irreversible nature of this transition and further emphasizes the vital role of solvent in formation of the helical crystal phase, which is structurally completely different from the energetically favored all-trans, lamellar structure.

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