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Spectroscopic and Thermal Studies of Sulfonated Syndiotactic Polystyrene

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ABSTRACT: Sulfonation of highly stereoregular syndiotactic polystyrene has been accomplished in chloroform. The sulfonation can be well controlled and carried out to a higher degree than previously reported. The crystallization behavior of sulfonated syndiotactic polystyrene exhibits considerable differences in comparison to the neat sample. Both extended all-trans and *ttgg* helical chain conformations have been observed for the sulfonated samples. The melting temperatures observed range from 245 °C for the 6.3 mol % sample to 266 °C for the 1.4 mol % sample. The glass transition temperature is also perturbed by the sulfonation procedure. The irreversible transition from the helical to the all-trans chain conformation can be accomplished at 175 °C, much lower than observed for the neat sample. The temperature range for this transition is extremely broad, taking place from 160 to 190 °C.

Introduction

Generally speaking, most synthetic polymers contain significant structural defects in terms of molecular weight distribution or stereoregularity. The recent successful synthesis of highly stereoregular syndiotactic polystyrene has attracted much interest from the research community due to its completely ordered chain configuration and associated stable mechanical and chemical properties at elevated temperatures.[1-4] The structure of this polymer is, however, quite complex.[5-10] The crystallization rate, for example, is among the highest of all polymers considered in our laboratory. Depending on thermal history, the degree of crystallinity can also be extremely high, >74%.[6] Unlike other syndiotactic polymers, several polymorphic structures have been found.[5,7-10]

It is evident that the mechanical properties of these systems are dependent upon the mechanisms of deformation available to their structure, which, in turn, are related to morphological features such as degree of crystallinity, connectivity of crystals by amorphous chains, size (thickness and lateral dimension of lamellae), perfection of crystallites, and their participation in the superstructure. Therefore, the ability to control morphology formation governs the possibility of achieving improved mechanical performance of syndiotactic polystyrene. One widely used method for altering crystallization behavior is incorporation of additional functional groups into the chain to lower the degree of crystallinity. Crystallization kinetics can be reduced by introduction of a second component through chemical modification of the chain or by physical means such as cocrystallization.[11]

The principal objective of this study is to alter the crystallization behavior of syndiotactic polystyrene to obtain a morphology different from that of the homopolymer and thereby alter the mechanical properties. Specific attention has been focused on formation of ion-containing syndiotactic polystyrene. Due to the presence of long-range strong electrostatic interactions and larger size in comparison to nonpolar units, it is generally accepted that the pendant ionic groups interact or associate to form ion-rich regions in the nonpolar polymer matrix.[12] These systems have phase domains with submicroscopic dimensions (10 Å to 1 μm) intermediate between true solution and composite system dimensions. The controlled phase separation provides a new dimension in varying morphology and leads to enhancement of desirable properties, e.g., tensile strength and modulus. The ionic interactions and resultant polymer properties may depend on the ionic functionality, ionic moiety, degree of neutralization, and cation type.

Based on earlier studies, a sulfonation procedure has been reported by Moore et al.,[13] in which the solvent used was 1,2,4-trichlorobenzene. This aromatic solvent, although deactivated by the three chlorine substituents, can still be sulfonated by the sulfonating agent. Therefore the degree of sulfonation achieved is significantly less than expected from the reaction stoichiometry as reported.[13] In an extension of such a study using experimental syndiotactic polystyrenes supplied by Dow Chemical Co., we found alternate solvents for utilization in the sulfonation process and have thereby been able to control the degree of sulfonation to a higher degree. Structures of the resultant polymers are of great interest. Our thermal and spectroscopic results are reported here.

Experimental Section

Materials. The syndiotactic polystyrene used in these studies was obtained from Dow Chemical Co. ($M_w = 628000$). Methanol and 1,2-dichlorobenzene (ACS HPLC grade) were obtained from Aldrich. Other chemicals used were obtained from Fisher Scientific. With the exception of syndiotactic polystyrene and chloroform, all materials were used without further purification. Chloroform (200 mL) utilized as reaction solvent was washed with 200 mL of distilled water at least 6 times to remove the alcohol preservative. The chloroform was then dried overnight with 15 g of phosphorus pentoxide. The solvent was fractionally distilled in the presence of phosphorus pentoxide, and the component with a boiling point of 60.6-61.0 °C was collected.

The syndiotactic polymer used in this study is an experimental material slightly different in purity from experimental samples used in previous studies. To improve the solubility of the syndiotactic polystyrene in the sulfonation reaction and remove residual catalyst, the following procedure was undertaken. Syndiotactic polystyrene (10 g) was stirred in 150 mL of a 2 wt % methanol solution of HCl for 2 h to remove residual metal catalyst. The polymer was then filtered and dried under vacuum at 70 °C for 2 h after which the polymer was extracted with MEK overnight to remove the atactic component. Five grams of this syndiotactic polystyrene was mixed with 150 mL of 1,2-dichlorobenzene in a 250-mL round-bottom flask and heated under reflux (ca. 180 °C) for 0.5 h to dissolve all syndiotactic polystyrene.

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Table 1. Degree of Sulfonation (mol %) of Sulfonated Syndiotactic Polystyrene Samples Prepared: (a) Expected from the Reaction Stoichiometry Compared with (b) That Determined from Elemental Analysis

	sample		
	SsPS-1	SsPS-2	SsPS-3
(a)	10	7	5
(b)	6.3	4.4	3.4

The solution was then cooled to 130 °C and precipitated in 3000 mL of cold methanol. The precipitate was filtered and dried at 70 °C under vacuum overnight. This step appeared to be critical in the preparation of the solubilized sample. To remove the residual 1,2-dichlorobenzene, 2 g of this syndiotactic polystyrene was dissolved in 100 mL of chloroform under reflux (ca. 60 °C). The solution was then again precipitated in 2000 mL of cold methanol. The precipitate was filtered and dried under vacuum at 50 °C for 2 days for further studies.

Sulfonation Procedure. One gram of the syndiotactic polystyrene obtained with the above procedure was mixed with 50 mL of purified chloroform in a 100-mL three-neck round-bottom flask and heated to the boiling point (ca. 60 °C) under nitrogen purge until all the polymer was dissolved. The solution was then cooled to 50 °C, and acetyl sulfate in chloroform was slowly added.[14] The amount of acetyl sulfate was determined by the desired degree of sulfonation. The solution was kept at 50 °C for 2 h for the reaction to proceed and then precipitated in 1000 mL of boiling distilled water. The precipitate was then washed with distilled water, filtered, and dried under vacuum at 90 °C for 2 days. The degree of sulfonation was determined by elemental analysis. Two parallel analyses were performed for each sample.

Characterization Methods. A DuPont 2910 differential scanning calorimeter equipped with a nitrogen purge was used to study the thermal properties of the syndiotactic polystyrene and sulfonated syndiotactic polystyrene. The heating rate was maintained at 20 °C/min. Crystallization and melting temperatures were defined as the peak maximum or minimum of the exothermic or endothermic transitions, respectively. The glass transition temperatures were taken as the inflection of the curves of the step transition in the heat flow. To investigate the crystallization behavior of the various samples prepared, melt-quenched samples were obtained by heating the samples in the DSC to 300 °C followed by quenching the cell with liquid nitrogen at a cooling rate of 150 °C/min. The amorphous samples were prepared by heating the samples to 300 °C under a nitrogen atmosphere followed by quenching into liquid nitrogen.

Infrared spectra were obtained with an IBM-38 Fourier transform infrared spectrometer, with 256 scans collected for each spectrum. The band resolution was maintained at 2 cm^{-1} for all measurements. Sample films were cast in aluminum pans from a 1.0 wt % solution in ethylbenzene and dried under vacuum at 110 °C, which is sufficiently high for removal of residual solvent.[6] Samples were annealed in DSC under nitrogen purge at 150, 160, 170, 180, 190, and 200 °C.

Results and Discussion

As mentioned previously, in an earlier study sulfonation of the aromatic solvents used occurred along with polystyrene.[13] As such a possibility does not exist in the procedure presented here, a higher degree of sulfonation can be achieved. The degree of sulfonation of the sulfonated syndiotactic polystyrene samples obtained from the elemental analysis is compared with that calculated from the amount of sulfonating agent used in the reaction. Conversions of the sulfonation are found to be above 60%. Results are summarized in Table 1.

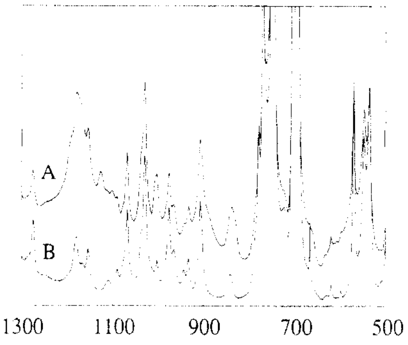

Figure 1. Infrared spectra obtained for (A) 4.4 mol % sulfonated PS and (B) neat sPS.

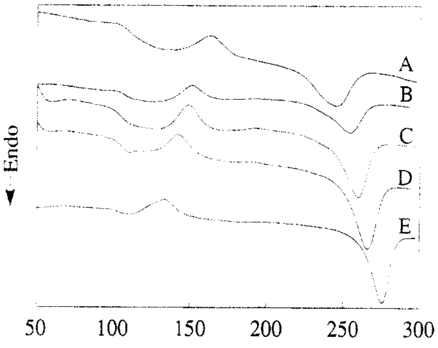

Figure 2. DSC scans of solvent-precipitated sulfonated sPS: (A) 6.3 mol %; (B) 4.4 mol %; (C) 3.4 mol %; (D) 1.4 mol %; (E) 0 mol %.

It is expected that substitution should take place predominantly at the *para* position. The position of the sulfo group on the benzene ring of the styrene unit has been confirmed by infrared spectroscopy. The infrared spectra of the solvent-cast film of syndiotactic polystyrene and the 4.4 mol % sulfonated syndiotactic polystyrene are shown in Figure 1. Variations in sample thickness were normalized by measuring the integrated intensities of structurally insensitive bands at 1600 and 1582 cm^{-1}. These two extremely localized bands are assigned to the benzene ring stretching vibrations and are insensitive to structural changes associated with sulfonation along the chain.[15] The intensity of the band at about 840 cm^{-1}, assignable to CH out-of-plane vibrations for *para*-disubstituted benzene, was extremely sensitive to the degree of sulfonation,[15] suggesting that the sulfo group must be predominantly at the *para* position. Since the neighboring benzene units were separated by two backbone carbon atoms, substitution of one ring would not affect the sulfonation of neighboring rings. Therefore, the lightly sulfonated samples can be considered as random copolymers.

Figure 2 presents DSC scans for solvent-precipiated samples with sulfonation at 1.4, 3.4, 4.4, and 6.3 mol % as well as one obtained for neat syndiotactic polystyrene. A crystallization exotherm is observed for each sample. The crystallization temperature increases with increasing sulfonation, starting at 134 °C for syndiotactic polystyrene, reaching 164 °C for the 6.3 mol % sulfonated syndiotactic polystyrene. This implies that the crystallization rates can be reduced by incorporation of the sulfonated component for a given crystallization temperature. There is a melting endotherm in the 240–280 °C range for each sample. For samples with a high degree of sulfonation, the enthalpic change at melting is small, implying a lower degree of crystallinity.

Generally, the degree of crystallinity of crystallizable polymer materials can be estimated by measuring the enthalpic change at melt. The melting enthalpy of highly crystalline syndiotactic polystyrene has been reported to be 28 J/g.[5] Using this value, all of the solvent-precipitated samples were found to possess a substantial amount of

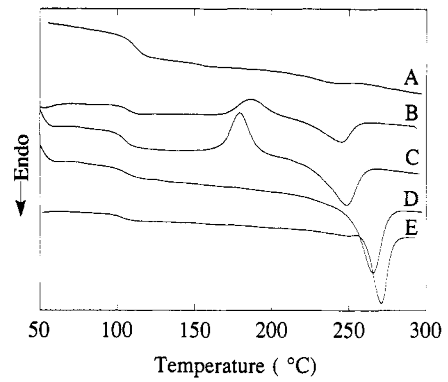

Figure 3. DSC scans of melt-quenched sulfonated sPS: (A) 6.3 mol %; (B) 4.4 mol %; (C) 3.4 mol %; (D) 1.4 mol %; (E) 0 mol %.

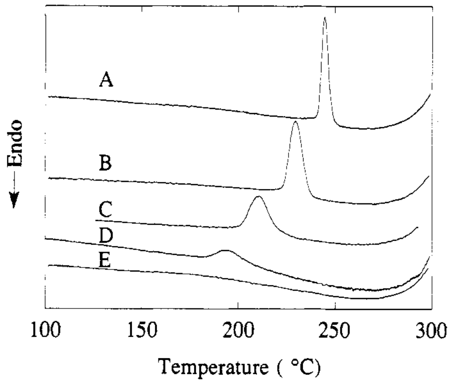

Figure 4. DSC cooling curves of sulfonated sPS with sulfonation of (A) 0 mol %, (B) 1.4 mol %, (C) 3.4 mol %, (D) 4.4 mol %, and (E) 6.3 mol % from the melt at a cooling rate of 2 °C/min.

crystalline structure. Even for materials sulfonated up to 6.3 mol %, the melting enthalpy was observed to be 13.7 J/g, which suggests that its degree of crystallinity is still about half that of highly crystalline syndiotactic polystyrene.

For the melt-quenched samples, the crystallization exotherm for the 3.4 mol % sulfonated syndiotactic polystyrene shifted from 149 to 180 °C, while that for the 4.4 mol % sample shifted from 152 to 188 °C. For the 1.4 and 6.3 mol % sulfonated syndiotactic polystyrene samples, the crystallization exotherm completely disappeared. The DSC curves are shown in Figure 3. With the presence of the melting endotherm for 1.4 mol % sulfonated syndiotactic polystyrene and the near absence for the 6.3 mol % sample, it can be concluded that the 1.4 mol % sulfonated syndiotactic polystyrene crystallized sufficiently fast, forming crystallites either in the quenching process or during reheating. The 6.3 mol % sample crystallized sufficiently slowly upon quenching and reheating to form crystallites. DSC measurements for all samples cooled from the melt at 300 °C with a cooling rate of 2 °C/min are presented in Figure 4. Upon increase in sulfonation, it can be seen that the crystallization peak becomes broader, the onset point shifts to a lower temperature, and the 6.3 mol % sample nearly did not crystallize.

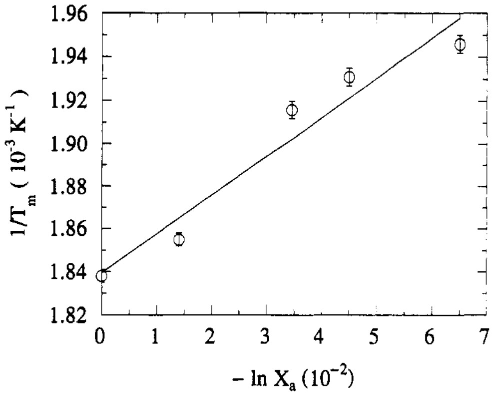

Figure 5. Melting point depression of the sulfonated sPS.

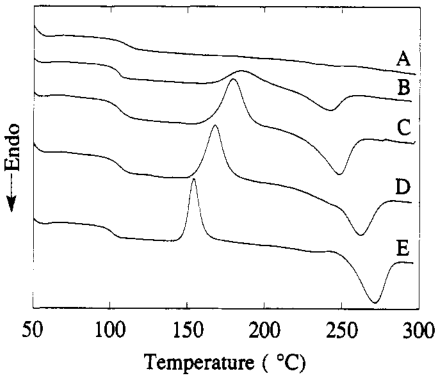

Figure 6. DSC scans of amorphous sulfonated sPS: (A) 6.3 mol %; (B) 4.4 mol %; (C) 3.4 mol %; (D) 1.4 mol %; (E) 0 mol %.

DSC data, as expected, exhibit a systematic trend of melting temperature depression with increasing sulfonation. The T_m of neat syndiotactic polystyrene is around 270 °C, similar to the value previously obtained.[1,5,16] For the 6.3 mol % sulfonated syndiotactic polystyrene sample, the T_m decreases to ~241 °C. It may reasonably be assumed that in sulfonated syndiotactic polystyrene, due to the large size of the substituent group, the sulfonated styrene unit could not be accommodated in the syndiotactic polystyrene crystalline lattice and exists only in the amorphous region. These lightly sulfonated syndiotactic polystyrenes are treated as random copolymers with a crystallizable component of stereoregular syndiotactic styrene units and noncrystallizable sulfonated styrene units. The noncrystallizable sulfonated units interrupt or terminate crystal growth along the molecular chain direction, limiting the size of the crystallites achievable and resulting in a systematic depression of the melting point. The theory of this kind of model has been developed by Flory.[17] The dependence of the melting point on the concentration of crystallizable units in a random copolymer is given by

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{R}{\Delta H_f}\ln X_a \tag{1}$$

where T_m° is the melting point of the crystalline homopolymer, T_m is that of the copolymer, ΔH_f is the heat of fusion per mole of homopolymer unit, and X_a is the mole fraction of crystallizable units. While the melting temperatures we have measured are by no means ultimate or equilibrium values, they serve as a valid yardstick for comparing a series of samples with the same thermal history. The results of this approach for the melt-quenched samples are shown in Figure 5. The slope of this straight line gives a ΔH_f of 44 J/g for 100% crystalline syndiotactic polystyrene, which is in good agreement with the value obtained previously, which is 28 J/g for the ~70% crystalline sample. The success of this approximation implies that our assumption is reasonable that the acid units are not crystallizable and reside in the amorphous region of the copolymer.

The amorphous samples are compared in Figure 6. As the degree of sulfonation increases, T_g increases from 102 °C for neat syndiotactic polystyrene to 110 °C for the 6.3 mol % sulfonated sample. For partially sulfonated atactic polystyrene, it has been shown that T_g (measured by a

Table 2. Thermal Properties of the Sulfonated Syndiotactic Polystyrene Samples with Different Thermal Histories: (a) Solvent-Precipitated, (b) Melt-Quenched, and (c) Amorphous

	T_g (°C)	ΔC_p (J/(gK))	T_x (°C)	ΔH_x (J/g)	T_m (°C)	ΔH_m (J/g)
		Syndiotactic Polystyrene				
(a)	104	0.15	134	9.3	276	29.0
(b)	103	0.19		0	271	19.3
(c)	102	0.35	154	15.5	271	22.0
		1.4% Sulfonated				
(a)	107	0.26	143	5.5	266	20.6
(b)	106	0.20		0	266	19.2
(c)	105	0.32	168	13.4	262	14.4
		3.4% Sulfonated				
(a)	105	0.38	149	6.9	260	19.5
(b)	105	0.34	180	11.2	249	14.8
(c)	106	0.39	180	14.0	248	14.3
		4.4% Sulfonated				
(a)	107	0.34	152	6.9	255	19.0
(b)	107	0.27	188	9.7	245	11.8
(c)	106	0.42	185	10.6	242	10.2
		6.3% Sulfonated				
(a)	110	0.45	164	5.7	245	13.7
(b)	112	0.35		0	241	1.0
(c)	110	0.34		0		

dilatometric technique) increases linearly up to a styrenesulfonic acid weight fraction of 0.15.[18] The T_g values at specific chemical compositions reported are higher than the ones we measured for syndiotactic polystyrenes. For example, in that earlier study, for 4.4 and 6.6 mol % samples, the T_g's found were 115 and 124 °C, respectively. It was mentioned that the increase in T_g in the earlier study may also be attributed to the presence of cross-links. Our findings for syndiotactic polystyrenes are different from those reported by Orler and Moore.[13] In their study, for materials containing up to 3.4 mol % sulfonation, the T_g changes little with increasing acid content. As discussed previously, the melting temperature decreases from 271 °C for the neat syndiotactic polystyrene to 242 °C for 4.4 mol % sulfonated syndiotactic polystyrene. As proposed above, in sulfonated syndiotactic polystyrenes the sulfonated styrene units should remain in the amorphous region. Thus compared with syndiotactic polystyrene, due to strong interactions between the sulfo groups, e.g., hydrogen bonding, the mobility of the polymer chains was reduced, raising T_g in the sulfonated samples. DSC data are summarized in Table 2.

Syndiotactic polystyrene has been reported to possess several crystalline structures depending on the specific crystallization conditions.[5,9,10,16,19-24] It has also been previously reported that the stable all-trans phase crystallizes from the melt, while samples cast from dilute solution generally form a *ttgg* helical structure.[5,9] This helical chain transforms irreversibly to the all-trans conformation upon drawing or on heating near 190 °C.[5,25] Infrared spectroscopy has been applied in characterization of the crystalline structures as well as characterization of the phase transition of syndiotactic polystyrene.[5,22-25] Several infrared bands have been assigned for characterization of different chain conformations. The 548- and 571-cm^{-1} bands and the 934/943-cm^{-1} doublet are indicative of the presence of a helical crystalline phase, while the 1222-cm^{-1} band is associated with a long trans sequence.[1,5,21,22] These band assignments were used for characterization of the structure of sulfonated syndiotactic polystyrenes.

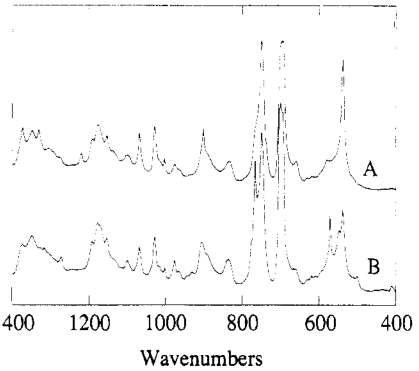

Figure 7. Infrared spectra obtained for the 4.4 mol % sulfonated sPS sample: (A) annealed at 190 °C for 12 h; (B) annealed at 160 °C for 16 h.

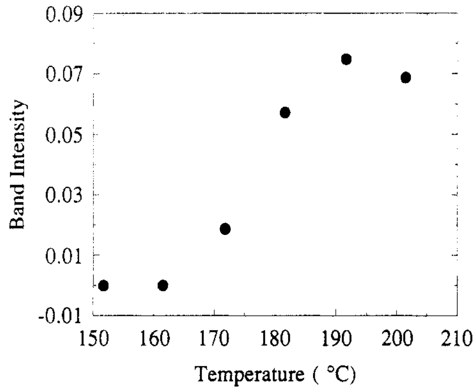

Figure 8. Normalized integrated intensity of the 1222-cm^{-1} band measured for samples annealed at long times at various temperatures.

Infrared spectra of the solution-cast 4.4 mol % sulfonated syndiotactic polystyrene film after annealing at 160 and 190 °C are shown in Figure 7. The 934/943-cm^{-1} doublet and the 571- and 548-cm^{-1} bands are observed for the film annealed at 160 °C. For the sample annealed at 190 °C, these features disappear; only the 1222-cm^{-1} band is present. Thus the sulfonated syndiotactic polystyrene can also possess the helical and all-trans crystalline structures, and the phase transition still exists between these two structures. The integrated intensity of the trans band at 1222 cm^{-1} and the 571-cm^{-1} band assigned to the helical conformation are monitored to follow this transition from the helical to the all-trans structure. Again all data (Figure 8) are normalized with respect to the bands at 1600 and 1582 cm^{-1}. The transition for the neat syndiotactic polystyrene around 192 °C is extremely sharp and involves a high degree of cooperativity of molecular motion.[25] For the 4.4 mol % sulfonated syndiotactic polystyrene, the temperature range of this transition is much broader, in the range from 160 to 190 °C. The broadened transition temperature range has been observed for all sulfonated samples. This implies that the molecular motion is less cooperative and the energy barrier for this transition is lower than that of syndiotactic polystyrene, consistent with the idea proposed above that the crystal dimension along the polymer chain direction is smaller for sulfonated syndiotactic polystyrene.

Conclusions

In this study, we have demonstrated the possibility of sulfonating highly stereoregular syndiotactic polystyrene. Sample solubility is a most important experimental parameter. By reducing the degree of crystallinity of the as-prepared sample, we found it possible to dissolve syndiotactic polystyrene in a common solvent such as chloroform. Using such a solvent, the sulfonation can be controlled and conducted to a higher level than previously reported. In this study, we have also found that the crystallization behavior of syndiotactic polystyrene can be altered significantly by polymer sulfonation. Similar to the neat sample, both the all-trans and helical chain conformations were observed for the semicrystalline sample. The degree of crystallinity and the melting temperature are significantly lowered by the presence of the sulfo groups. The glass transitions are increased as well. Crystallization rate is much slower in comparison to the neat sample. The mechanical properties of this highly ordered polymer are dependent upon the mechanisms of deformation available to their structure, which, in turn, are related to morphological features such as degree of crystallinity, connectivity of crystals by amorphous chains, size (thickness and lateral dimension of lamellae), perfection of crystallites, and their participation in the superstructure. Therefore, the ability to control morphology formation governs the possibility of achieving improved mechanical performance of syndiotactic polystyrene.

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