Structural, Conformational, and Motional Studies of the Crystalline Polymorphs of Syndiotactic Polystyrene

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ABSTRACT: High-resolution ^{13}C NMR, X-ray diffraction, and calorimetric (DSC and TGA) techniques were employed to study the crystalline polymorphs of syndiotactic polystyrene (s-PS). Even though several different X-ray diffractograms were observed for s-PS samples crystallized from the melt during slow cooling to room temperature, from annealing melt-quenched, amorphous films above 200 °C, from casting films from high-boiling solvents, or from immersion of melt-quenched films into liquids such as dichloromethane or chloroform, only two different crystalline chain conformations were indicated by the solid-state CPMAS/DD ^{13}C NMR spectra recorded for these samples. Spin–lattice relaxation times, $T_1(^{13}C)$, observed for the carbons in those s-PS polymorphs whose crystalline chains adopt the extended, all-trans, planar zigzag conformation were 2–10 times longer than the corresponding $T_1(^{13}C)$'s observed for the s-PS polymorphs whose chains crystallize into the 2_1-helical, ...ttggttgg... conformation. The role played by the solvent molecules, which induce and then are incorporated into the 2_1-helical, ...ttggttgg... polymorphs, is discussed in light of these observations.

Introduction

Five years ago Ishihara et al.[1] described the first synthesis of highly stereoregular syndiotactic polystyrene (s-PS). They found s-PS to be semicrystalline, with a melting temperature of ca. 270 °C, and the crystalline chains in their samples adopted the extended, all-trans, planar zigzag conformation, leading to an observed X-ray fiber repeat of 5.1 Å. Shortly thereafter, Immirzi et al.,[2] Vittoria et al.,[3] Nyquist,[4] and Reynolds et al.[5] found that when s-PS is cast from either dilute solutions in solvents, such as chloroform or 1,2-dichlorobenzene, or melt-quenched, amorphous fibers or films are swollen in liquids, such as chloroform, dichloromethane, 1,2-dibromo- or dichloroethane, or cyclohexane, different crystalline polymorphs of s-PS may be obtained. X-ray diffraction patterns obtained on the oriented, swollen s-PS fibers yielded a fiber repeat of ca. 7.5 Å, which is consistent with the ...ttggttgg... crystalline chain conformation observed[6] previously for syndiotactic polypropylene (s-PP).

DSC[2,3] and IR[4,5] observations indicated that an irreversible solid–solid phase transition from the ...ttggttgg... polymorphs to the ...tttttttt... polymorph occurs at 190–200 °C. It was not found possible to recover the ...ttggttgg... polymorphs without melting or dissolving the ...tttttttt... crystals and reexposing them to the swelling solvents.

Grassi et al.[7] and the present authors[8] utilized high-resolution, solid-state ^{13}C NMR to confirm the chain conformations (...tttttttt... and ...ttggttgg...) suggested for the s-PS polymorphs. This was achieved by a comparison of methylene carbon resonances. Two resonances separated by 10–11 ppm were observed for the ...ttggttgg... s-PS polymorphs, very similar to the methylene doublet observed[9] for s-PP, with 2_1-helical, ...ttggttgg... crystalline chains, while a single methylene resonance was observed for the all-trans polymorph very near the most downfield resonance of the ...ttggttgg... s-PS methylene doublet.

Most recently, Guerra et al.[10,11] have reported X-ray and IR observations of many s-PS polymorphs obtained both by melt crystallization and exposure to solvents. Their X-ray diffractograms and IR spectra were sensitive to structural details of the polymorphs beyond those of whether or not the crystalline chains adopt either the ...tttttttt... or ...ttggttgg... conformations. It was the purpose of the present study to apply high-resolution, solid-state ^{13}C NMR to learn about the structures, conformations, and mobilities of s-PS polymorphs that were simultaneously characterized by X-ray diffraction and calorimetric methods, including DSC and TGA observations.

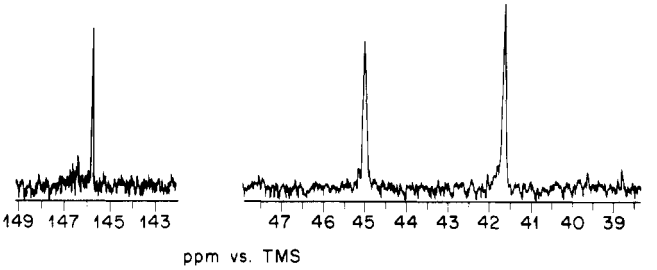

Figure 1. ^{13}C NMR spectrum of s-PS recorded at 130 °C in a 5 wt % solution of trichlorobenzene. Protonated phenyl carbon region of the spectrum is not shown because of the extensive overlap of s-SP and the more abundant solvent resonances.

Experimental Section

s-PS Polymorph Samples. The s-PS employed here was kindly provided by Professor A. Zambelli. The as-received sample (S_0) was melted by heating to 300 °C and followed by quenching into a dry ice–acetone slurry to produce an amorphous sample (S_a). Two samples of the α-polymorph[10] were obtained by melting the as-received sample at 300 °C followed by crystallizing at room temperature (S_{α_1}) or by quenching into a dry ice–acetone slurry and then annealing at 200 °C for 3 h (S_{α_2}). Sample S_β was obtained by casting a film from 1,2-dichlorobenzene at 170 °C. Samples S_{δ_1} and S_{δ_2} were obtained by immersion of an amorphous film of s-PS (S_a) into dichloromethane for several days at room temperature or by evaporation of solvent from a chloroform solution/suspension, respectively. Samples S_{γ_1} and S_{γ_2} were obtained from S_{δ_1} and S_{δ_2} by drying them under vacuum at 100–120 °C for 12 h.

NMR Measurements. ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer operating at a static magnetic field strength of 4.7 T (^{13}C resonance of 50.3 MHz). Magic angle spinning (MAS) of the samples at speeds of ca. 3 kHz was achieved with a Doty Scientific probe, which uses a double air bearing design. s-PS samples were packed in aluminum oxide rotors

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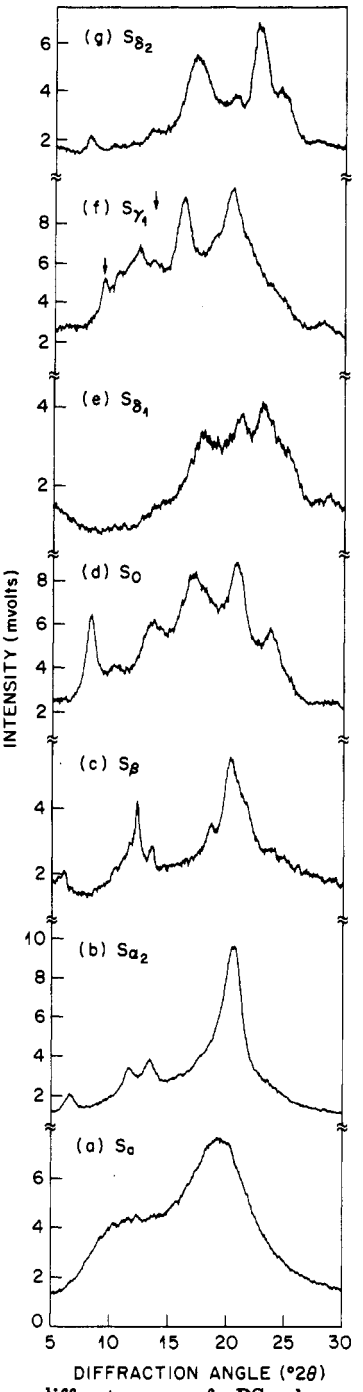

Figure 2. X-ray diffractograms of s-PS polymorphs: (a) S_α, (b) S_{α_2}, (c) S_β, (d) S_o, (e) S_{δ_1}, (f) S_{γ_1}, and (g) S_{δ_2}.

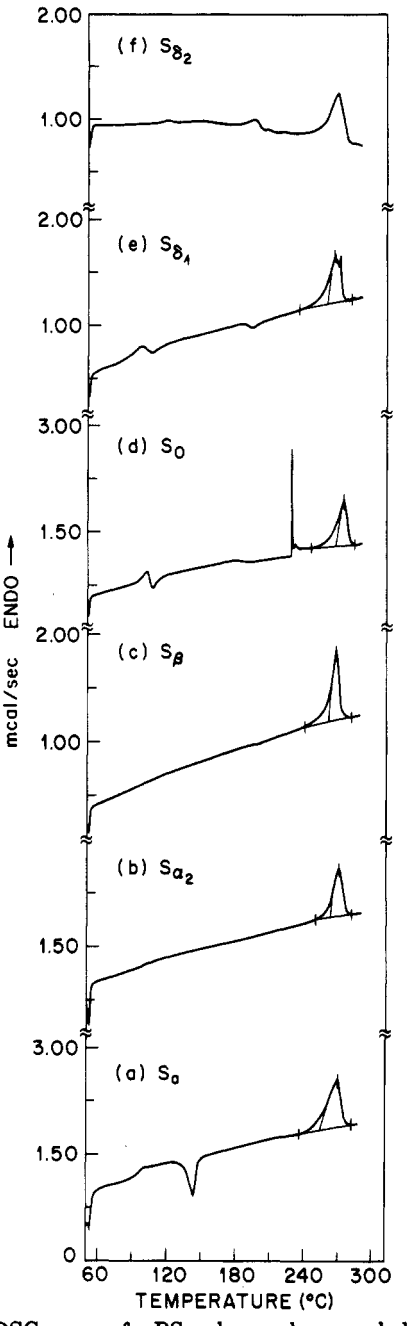

Figure 3. DSC scans of s-PS polymorphs recorded with a 10 °C/min heating rate: (a) S_α, (b) S_{α_2}, (c) S_β, (d) S_o, (e) S_{δ_1}, and (f) S_{δ_2}.

with end caps made of Kel-F [poly(chlorotrifluoroethylene)]. A 45-kHz radio-frequency field strength was used for dipolar decoupling (DD) of the ^1H spins, with a decoupling period of 200 ms. The optimal cross-polarization (CP) time was found to be 2 ms. Spectra were recorded with CP (CPMAS/DD) and without CP (MAS/DD), where the delay between decoupling pulses in the MAS/DD spectra was 5 s. All spectra were recorded at 25 °C and referenced[12] to the resonance of poly(oxymethylene) (89.1 ppm from TMS) that was recorded externally.

Spin–lattice relaxation times, $T_1(^{13}C)$, were measured under the CP condition by application of the pulse sequence developed by Torchia.[13] The $T_1(^{13}C)$ data were analyzed by a nonlinear, least-squares method.

A solution ^{13}C NMR spectrum of our s-PS sample was recorded at 130 °C for a 5% by weight polymer solution in trichlorobenzene using the Varian XL-200 spectrometer with a Zens probe. Spectra were proton-decoupled and recorded with full nuclear Overhauser enhancement. The time between pulses was 2 s, DMSO-d_6 provided the signal lock, and HMDS was used as an internal reference (2.0 ppm from TMS).

X-ray Diffraction Measurements. X-ray diffractograms were recorded in the reflection geometry at 1° (2θ/min) under Ni-filtered Cu Kα radiation. A Rigaku diffractometer was employed.

Calorimetric Measurements. Differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) traces were made with Perkin-Elmer Series DSC-4 and 7 thermal analysis systems, respectively. DSC samples were 5–10 mg, while for the TGA observations 3–5-mg samples were employed. A heating rate of 10 °C/min was used in all the DSC and TGA measurements.

Results and Discussion

Stereoregularity of s-PS. The ^{13}C NMR solution spectrum of our s-PS sample recorded in trichlorobenzene at 130 °C is presented in Figure 1. That region of the spectrum containing the protonated phenyl ring carbon

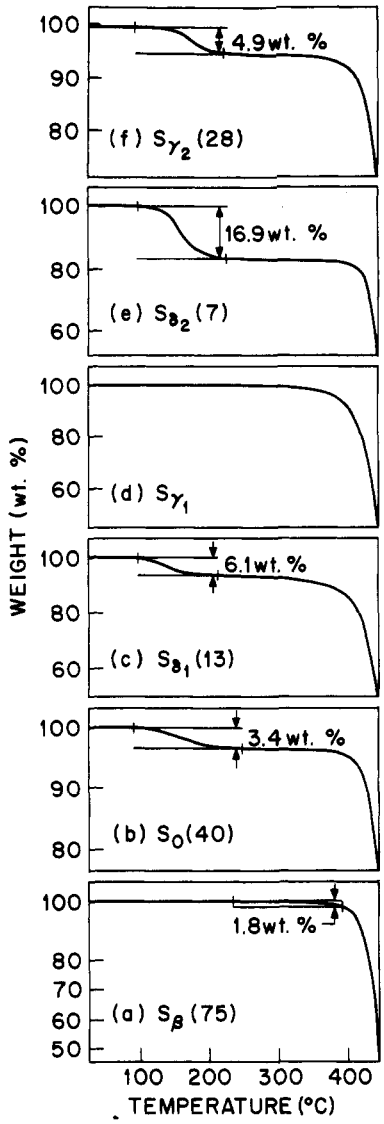

Figure 4. TGA scans of s-PS polymorphs recorded with a 10 °C/min heating rate: (a) S_β, (b) S_o, (c) S_{δ_1}, (d) S_{γ_1}, (e) S_{δ_2}, and (f) S_{γ_2}. Numbers in parentheses correspond to the ratios of s-PS repeat units to solvent molecules.

resonances is not shown because of extensive overlap with the more abundant solvent resonances. However, it is apparent from the remaining spectral regions, particularly the methylene carbon region known[14,15] to be highly sensitive to the PS stereosequence, that only single resonances are observed for the CH (41.6 ppm), CH_2 (45.0 ppm), and C_1 (145.7 ppm) carbons, which correspond[14,15] to the syndiotactic stereosequence.

X-ray Diffractograms and Thermal Traces. A compilation of the X-ray diffractograms recorded for our s-PS samples is presented in Figure 2, while shown in Figures 3 and 4 are the DSC and TGA scans recorded for many of the same polymorphic s-PS samples. Despite the seeming variety of X-ray diffractograms exhibited by the s-PS polymorphs in Figure 2 (also see the X-ray diffractograms presented by Vittoria et al.,[3] Guerra et al.,[10] and Vittoria[16]), their X-ray fiber diagrams[1,2] yield only two identity periods. Samples like S_{α_1}, S_{α_2}, and S_β exhibit a fiber repeat of 5.1 Å (...ttttttt...), while samples like S_o, S_{γ_1}, S_{γ_2}, S_{δ_1}, and S_{δ_2} have an ca. 7.5-Å fiber repeat (...ttggttgg...) (see Figure 5).

Irrespective of whether or not solvent is present in the sample (see Figure 4), only two crystalline conformations are observed for the s-PS polymorphs; the all-trans, planar

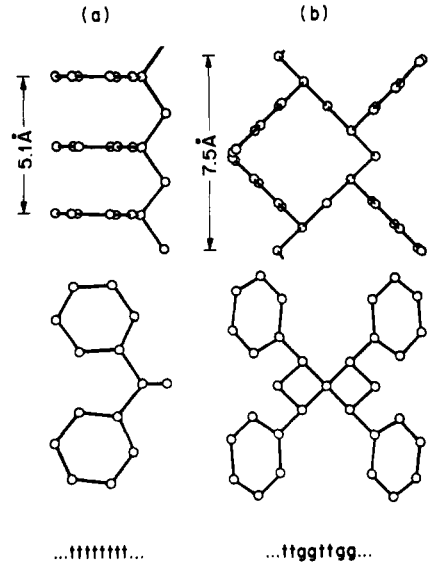

Figure 5. Views perpendicular to (upper) and along (lower) the backbone of s-PS in the (a) ...ttttttt... and (b) ...ttggttgg... conformations.

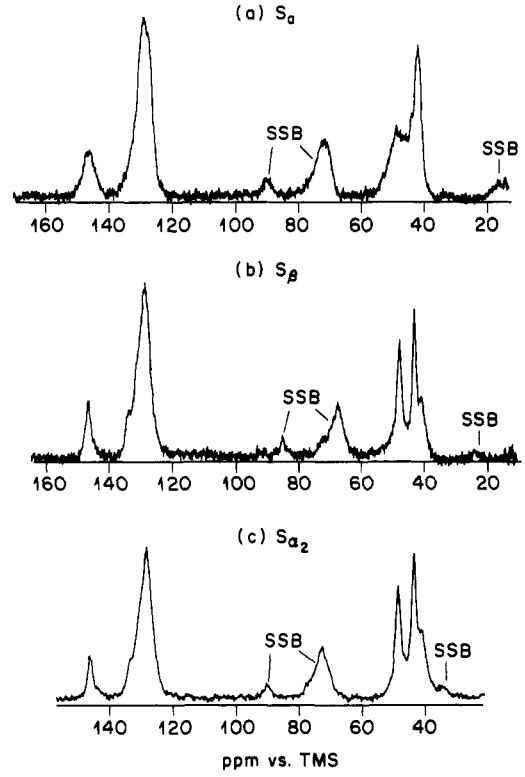

Figure 6. CPMAS/DD ^{13}C NMR spectra of (a) S_α, (b) S_β, and (c) S_{α_2} samples of s-PS recorded at room temperature. SSB = spinning side band.

zigzag (α and β) and the 2_1-helical, ...ttggttgg... (γ and δ) conformations. Apparently differences in the packing of s-PS chains in these two crystalline conformations result in the variety of crystalline polymorphs observed for s-PS. This conclusion receives corroboration from the CPMAS/DD ^{13}C NMR spectra reported for the s-PS polymorphs in Figures 6 and 7, where only two distinct spectra are observed; one for those polymorphs with the ...ttttttt... crystalline chain conformation (Figure 6) and the other for the ...ttggttgg... crystalline chain conformation containing polymorphs (Figure 7).

Only minor differences exist between the CPMAS/DD spectra of those s-PS polymorphs adopting the all-trans, planar zigzag conformation despite the differences between

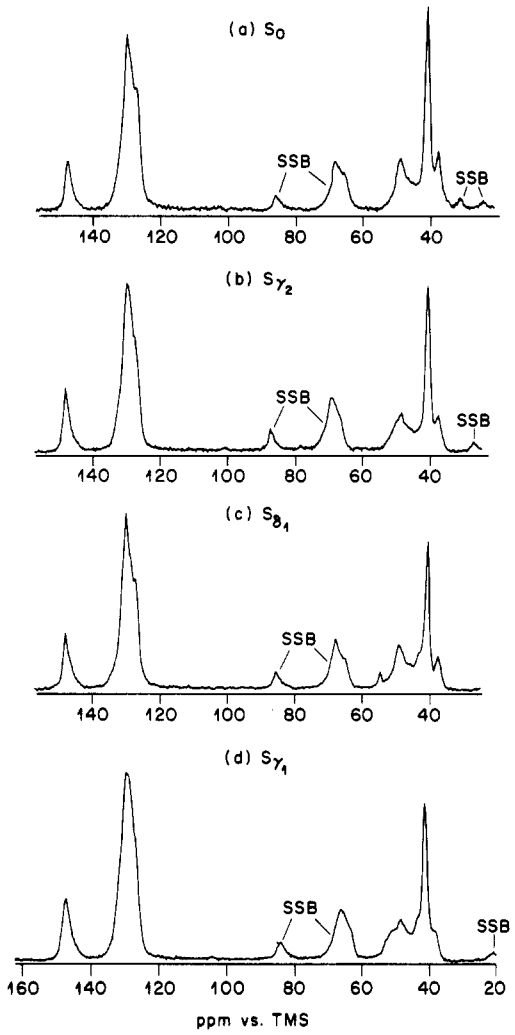

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Figure 7. CPMAS/DD ^{13}C NMR spectra of (a) S_o, (b) S_{δ_2}, (c) S_{γ_2}, and (d) S_{δ_1} samples of s-PS recorded at room temperature. SSB = spinning side band.

Table I
Spin-Lattice Relaxation Times, $T_1(^{13}C)$ (s), for the Crystalline Carbons in s-PS Polymorphs

sample	C_1	C_{2-6}	CH_2 (~49 ppm)	CH	CH_2 (~38 ppm)
S_a	78	60	83	65	
S_{α_1}	400	120	400	200	
S_{α_2}	140	134		280	
S_o	74	54	58	59	55
S_{δ_1}	32	24	30	28	30

their modes of chain packing[10] made apparent by their X-ray diffractograms. In a like manner the disparate X-ray diffractograms seen for the ...ttggttgg... polymorphs are not reflected in their CPMAS/DD spectra, which are very similar.

Table I presents the spin-lattice relaxation times, $T_1(^{13}C)$, recorded under CP[13] at room temperature for amorphous s-PS (S_a) and two s-PS samples each of the ...tttttttt... (S_{α_1}, S_{α_2}) and ...ttggttgg... (S_o and S_{δ_1}) crystalline polymorphs. Clearly the mobility of the s-PS chains in the ...tttttttt... polymorphs is restricted compared to their mobility in the ...ttggttgg... polymorphs based on the much shorter $T_1(^{13}C)$'s observed for the latter. $T_1(^{13}C)$'s for the ...tttttttt... polymorphs are 2–10 times longer than those observed for the ...ttggttgg... polymorphs.

On the surface this behavior may not seem surprising, because the ...ttggttgg... polymorphs can only be obtained by solvent-induced crystallization with concomitant incorporation of solvent molecules. Note that in Figure 7c there is a small solvent resonance (CH_2Cl_2) observed at 55 ppm. Because the solvent resonance is observed under the CP condition, we suggest that the solvent is relatively rigid and probably resides at least in part in the crystalline portions of sample S_{δ_1}. When the MAS/DD spectrum (not shown) of sample S_{δ_1} was recorded, a solvent peak was observed, but the methylene resonances at ca. 49 and 38 ppm were nearly absent. This permits us to conclude that the MAS/DD spectrum only detects amorphous s-PS carbons and that solvent molecules reside in both the crystalline and amorphous portions of the ...ttggttgg... sample S_{δ_1}.

From Figure 4c we know that sample S_{δ_1} contains 1 CH_2Cl_2 solvent molecule for every 13 s-PS repeat units. Apparently at this level of solvent incorporation, i.e., less than 1 solvent molecule per 13 s-PS repeat units [also see sample S_o in Figures 4b and 7a and Table I], the included solvent serves to loosen the crystalline interchain packing enough to produce the dramatic reductions observed in the $T_1(^{13}C)$'s of the ...ttggttgg... polymorphs compared to those measured for the solvent-free, melt-crystallized ...tttttttt... polymorphs.

Even the $T_1(^{13}C)$'s measured for the completely amorphous sample S_a equal or exceed those of the solvent-induced ...ttggttgg... polymorphs S_o and S_{δ_1}. Considering the level of solvent inclusion (well below 1 solvent molecule for every 13–40 s-PS repeat units), it may be useful to consider the sites of solvent incorporation as defects in the s-PS crystal. It would appear that s-SP chains in the ...ttggttgg..., crystalline polymorphs are at least as mobile as those in the completely disordered, glassy portions of these samples.

^2H NMR studies of the ...ttggttgg... polymorphs of s-PS formed by immersion in CD_2Cl_2 might reveal the motional restrictions placed on the included CD_2Cl_2 solvent molecules by the s-PS crystalline lattice.

References and Notes

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