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Carbon-13 Nuclear Magnetic Resonance Study of Chain Conformation in the Solid Polymorphs of Syndiotactic Polystyrene

Ishihara et al.[1] have recently reported the synthesis of highly stereoregular, crystalline, syndiotactic polystyrene (s-PS), which was quickly confirmed and expanded upon by Zambelli et al.[2] X-ray[1,3] and electron[4] diffraction patterns obtained from oriented fibers and films yielded a chain axis repeat distance of 5.1 Å, which is consistent with a planar zigzag, all-trans conformation for the s-PS chains. These form I crystals melt at ca. 270 °C.

When s-PS is cast from dilute solution[5,6] in solvents such as chloroform or 1,2-dichlorobenzene or when melt-quenched, amorphous films or fibers are swollen[3,7] in chloroform, dichloromethane, 1,2-dibromo- or dichloroethane, or cyclohexane, a different crystalline polymorph is obtained. X-ray diffraction patterns observed[3] for the oriented, swollen form II fibers yielded a fiber repeat of 7.5 Å, which is consistent with a ...ttggttgg... chain conformation observed[8] previously for syndiotactic polypropylene (s-PP).

DSC[3,7] and IR[5,6] observations indicate that a solid–solid phase transition to form II crystals occurs at T = 190–200 °C. Once the thermal conversion of form II to form I s-PS is complete, it has not been possible to recover form II s-PS without melting or dissolving the form I crystals and reexposing them to the swelling solvents. X-ray diffraction patterns observed[7] on the swollen form II fibers suggest the formation of crystalline molecular compounds between the s-PS chains and the swelling solvent molecules, which was confirmed[3] by thermal gravimetric analysis (TGA).

In this paper we describe our initial efforts to study the conformations of s-PS chains in their form I and form II polymorphs. Our principal experimental probe is high-resolution, solid-state ^{13}C NMR spectroscopy, with emphasis placed on the chemical shift positions of the ^{13}C resonances observed in both polymorphs. Our motivation for this approach derives from the demonstrated[9] sensitivity of ^{13}C chemical shifts observed in solid-state polymer ^{13}C NMR spectra to their solid-state conformations.

s-PS was kindly provided by A. Zambelli. The sample was observed by ^{13}C NMR in solution to be highly syndiotactic (rr > 95%). Forms I and II of s-PS were obtained by bulk crystallization from the melt at room temperature or by annealing melt-quenched films at 200 °C and by exposing melt-quenched films to the vapors of chloroform or dichloromethane.

^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer at a static magnetic field of 4.7 T (50.3 MHz for ^{13}C). Magic-angle sample spinning (MAS) at speeds of ca. 3 kHz were achieved with a Doty Scientific probe, which utilizes a double air-bearing design. An 80-kHz radio frequency field strength was used for ^{1}H dipolar decoupling (DD), with a decoupling period of 200 ms. A 3-ms cross-polarization (CP) time was found to be optimum at room temperature where all spectra were recorded.

All s-PS samples were packed in aluminum oxide rotors with Kel-F [poly(chlorotrifluoroethylene)] end caps. The spectra were referenced to the resonance of poly(oxymethylene) (POM) at 89.1 ppm[10] from TMS recorded immediately prior to and after each s-PS spectrum.

All samples were also observed by DSC, TGA, and X-ray diffraction for the purpose of characterizing and monitoring their structures. These observations together with additional NMR results will be reported[11] upon their completion.

The CPMAS/DD ^{13}C NMR spectra of forms I and II of s-PS are presented in Figure 1. The aromatic C_1 carbons resonate at 146.1 (I) and 147.2 (II) ppm, while the remaining aromatic resonances appear at 129.8 (II) and 127.4 (II) ppm and at 128.3 (I) ppm. The methine carbons are observed to resonate at 41.3 (II) and 43.4 (I) ppm, where the shoulder at 41.4 ppm in the form I spectrum is produced by the amorphous methine carbons, as indicated by comparison to the CPMAS/DD spectrum (not shown) of a melt-quenched, amorphous sample of s-PS. A single CH_2 carbon resonance at 48.4 ppm is observed in the form I spectrum, while two CH_2 resonances at 49.1 and 38.1 ppm are seen in the form II spectrum. These resonance assignments are consistent with the spectrum of s-PS recorded in solution.[1,11]

The solid-state ^{13}C NMR spectra observed for forms I and II s-PS are consistent with those expected from γ-gauche shielding effects[12] if the chains adopt the planar zigzag, ...tttt... and 2_1 helical, ...ttggttgg... conformations, respectively. In the ...ttggttgg... conformation half of the CH_2 carbons are gauche to two γ substituents (CH's), while the remaining half are trans to both γ-CH substituents. We expect, as was observed[13] in the CPMAS/DD ^{13}C NMR spectrum of s-PP, to see two CH_2 resonances separated by two γ effects, or ca. (2)(5 ppm) = 10 ppm. The actual observed separation is 11 ppm. In the ...tttt... conformation of form I s-PS, all methylene carbons are in the trans arrangement with their γ substituents (CH's). We therefore expect to see and do observe a single CH_2 resonance in form I s-PS at nearly the same chemical shift position as the most downfield of the two CH_2 resonances observed for the form II polymorph.

Because of severe steric interactions in the $\bar{g}$ conformation illustrated in Figure 2, only the t and g bond con-

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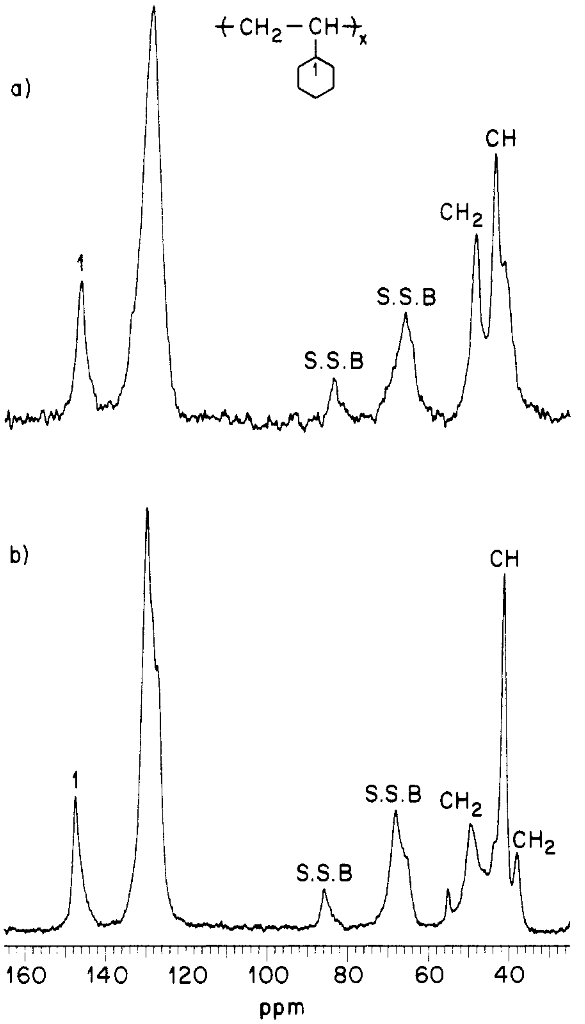

Figure 1. CPMAS/DD ^{13}C NMR spectra of form I (a) and form II (b) s-PS. The form II sample of (b) was obtained by absorption of dichloromethane into an amorphous, melt-quenched film of s-PS.

formations are permitted in polystyrene.[14] As a result, in the t conformation the methine carbon is γ-gauche to the aromatic C_1, while in the g conformation it is γ-gauche to the methylene CH_2 carbon. If $\gamma_{CH,C_1} \approx \gamma_{CH,CH_2}$, then we would expect the chemical shifts of the CH resonances in forms I and II of s-PS to be nearly coincident. In fact they are separated by 2 ppm, which may be a consequence of $\gamma_{CH,C_1} \neq \gamma_{CH,CH_2}$ or possibly due to different packing environments[9] in the two polymorphs.

In the ...ttggttgg... conformation of form II s-PS all C_1 aromatic carbons are gauche to one γ-CH substituent and trans to the other (see Figure 2). On the other hand, in the ...tttt... conformation of form I s-PS all C_1 aromatic carbons are gauche to both of their γ-CH substituents. We therefore expect to see C_1 (I) resonate one $\gamma_{C_1,CH}$ upfield from C (II). On the basis of the shielding at aromatic carbons produced by γ-gauche aliphatic carbons, as observed[15] in alkylbenzenes, we would expect C_1 (I) to come ca. 2.5 ppm upfield from C_1 (II). The observed C_1 resonance of form I does come upfield from C_1 (II), but by only 1.1 ppm not 2.5 ppm. This discrepancy may be accounted[9] for by the different packing arrangements in the two polymorphs but is outside the effects[17] produced by the ring currents of neighboring phenyl rings.

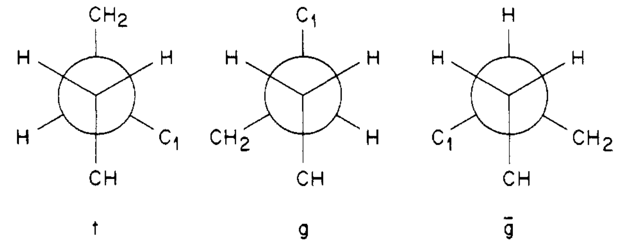

Figure 2. Newman projections along the CH_2–CH bond in s-PS.

Even though form II s-PS samples obtained by different techniques may exhibit[7,11] different X-ray diffraction patterns, with each, however, giving[7] a 7.5-Å fiber repeat, the CPMAS/DD ^{13}C NMR spectrum shown for the form II sample in Figure 1 is characteristic for all form II samples we have observed to date. This suggests that the ..., ttggttgg..., 2_1 helical conformation is adopted by s-PS in all of its crystalline form II polymorphs, irrespective of the swelling solvent employed.

The small resonance observed at 55 ppm in the spectrum of form II s-PS belongs to the dichloromethane that was used in the crystallization of this sample. Because we observe the CH_2Cl_2 signal in a CPMAS/DD spectrum, this indicates a limited mobility for the solvent molecules used to induce form II crystallization in melt-quenched, amorphous films. The suggestion[3,7] that crystalline molecular compounds are formed between the swelling solvent molecules and the 2_1 helical s-PS chains is confirmed by our observation of the CH_2Cl_2 signal by CPMAS/DD ^{13}C NMR.

After submission of this paper, a paper by Grassi et al.[18] also reported the CPMAS/DD ^{13}C NMR spectra of forms I and II of s-PS. Their spectra are in agreement with those presented here in Figure 1.

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