FT-IR Study of Concentration Dependence for Crystallization of Isotactic Polystyrene Arising from Freeze-Drying Dilute Solutions

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Some recent measurements have focused on the consequences of rapidly taking polymers from the dilute-solution regime to a concentrated state. An attempt was made to characterize the extent of polymer chain overlap in solutions of varying concentrations by characterizing the freeze-dried polymers.[1] For this purpose solutions containing a mixture of polystyrene labeled with donor and acceptor fluorophores was rapidly frozen by immersing the rotating flask in liquid nitrogen, followed by vacuum sublimation of the solvent at −5 to 0 °C. The resulting freeze-dried powder was pressed into a pellet, and its reflectance fluorescence was recorded. The emission spectra showed a strong increase of nonradiative energy transfer with an increasing concentration of the solution from which the sample was prepared. This was interpreted as an indication that during the rapid freezing the extent of chain interpenetration which had existed in solution had been preserved. In particular, it was concluded that, in PS freeze-dried from a solution which was 4 times more dilute than the critical overlap concentration, C^*, very little chain entanglement existed.[1–3] However, a solid state ^{13}C NMR dipolar dephasing experiment for a freeze-dried sample consisting of a mixture of hydrogenated and deuterated PS indicated that highly interpenetrated chains existed.[4,5] It seems that further experimentation is desirable to reconcile the curious contradictions between the NMR and fluorescence experiments.

We have found that a considerable amount of a crystalline phase was formed by shock-cooling a very dilute solution of isotactic polystyrene (i-PS) (0.05 wt %) followed by sublimation of the solvent.[6] Wide-angle X-ray diffraction patterns recorded from the shock-cooled and freeze-dried i-PS and from a normal i-PS cooled from the melt and then annealed at 180 °C for 13 min indicated that freeze-dried i-PS has higher crystallizability.[6]

We assume that crystallization of freeze-dried i-PS is related to the extent of chain entanglement in the solution from which the sample was prepared. Recently, our FT-IR study indicated that there is no significant difference between the freeze-dried i-PS sample prepared from 0.83 g/dL ($C^*/C = 4$) and the bulk material precipitated from a concentrated solution (5 wt %). This result is in agreement with a ^{13}C NMR study.[4,5] Of particular interest here is the observation of crystallization on freeze-drying from very dilute solution ($C^*/C > 30$).

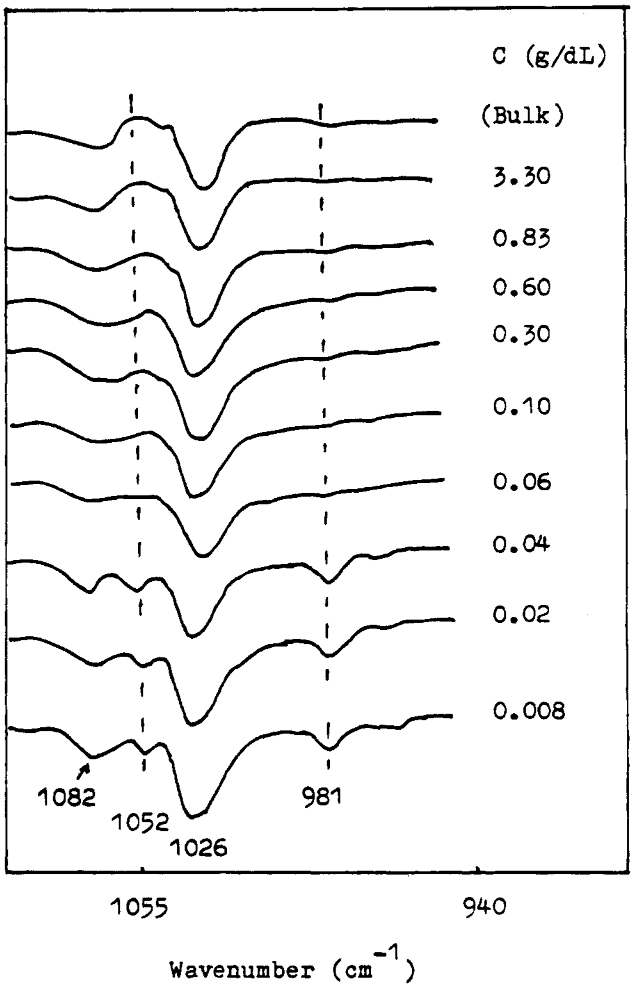

Figure 1. FT-IR spectra of freeze-dried i-PS from varying concentration solutions.

i-PS with molecular weight $M_n = 10^5$ was kindly supplied by BASF Co. The solvent benzene was distilled before use. i-PS was dissolved in the purified benzene and refluxed for 6 h to make solutions with concentrations from 3.3 g/dL (C^*) to 0.008 g/dL. Warm solutions (50 °C) were injected directly into liquid nitrogen so that they were frozen in a fraction of a second. The frozen solvent was then sublimed in vacuum at −5 to 0 °C. The resulting freeze-dried PS glass was examined by Fourier transform infrared spectrometry (Nicolet FT-IR 170 SX).

Figure 1 illustrates the expanded IR spectra in the region of 1100−940 cm^{-1}. In spectra for the i-PS glass freeze-dried from very dilute solutions for which $C <$ 0.04 g/dL, the band at 981 cm^{-1} and the doublets at 1082−1052 cm^{-1} are the characteristic IR bands of crystalline i-PS.[7] However, the IR spectra for the samples prepared from solutions $C >$ 0.10 g/dL show much weaker bands in this region, indicating that no crystalline PS exists in these samples. There is little difference in the IR spectra between the i-PS freeze-dried from 0.83 g/dL solution and the bulk material precipitated from a concentrated solution (5 wt %) which is supposed to be amorphous since crystal growth of i-PS from dilute solution in good solvents (benzene is one of the best) is very slow.[9]

Figures 2 and 3 illustrate IR spectra recorded from the freeze-dried i-PS after annealing at 180 °C for 3 and 5 min, respectively. Little change could be observed

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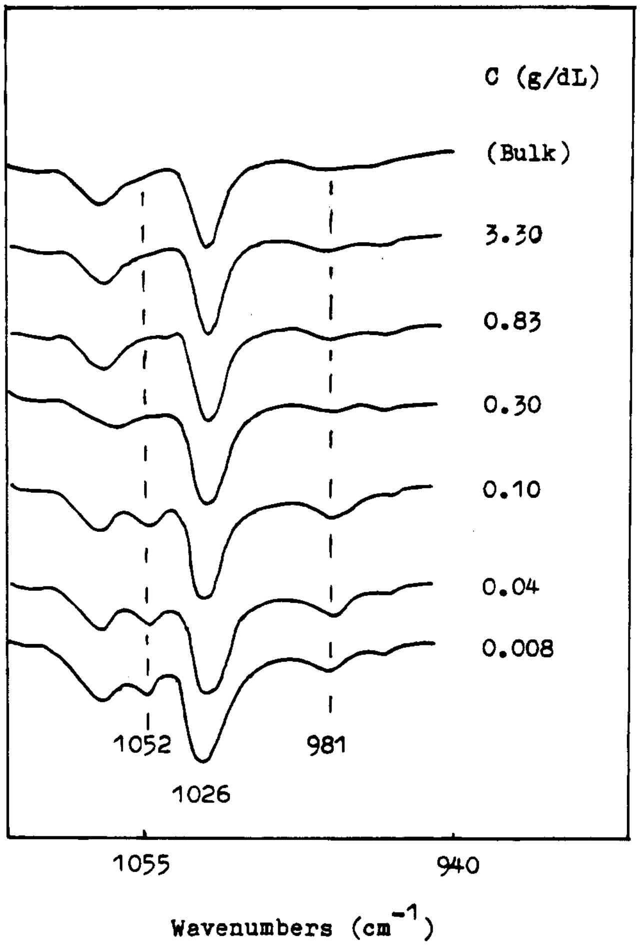

Figure 2. FT-IR of freeze-dried i-PS after annealing at 180 °C for 3 min.

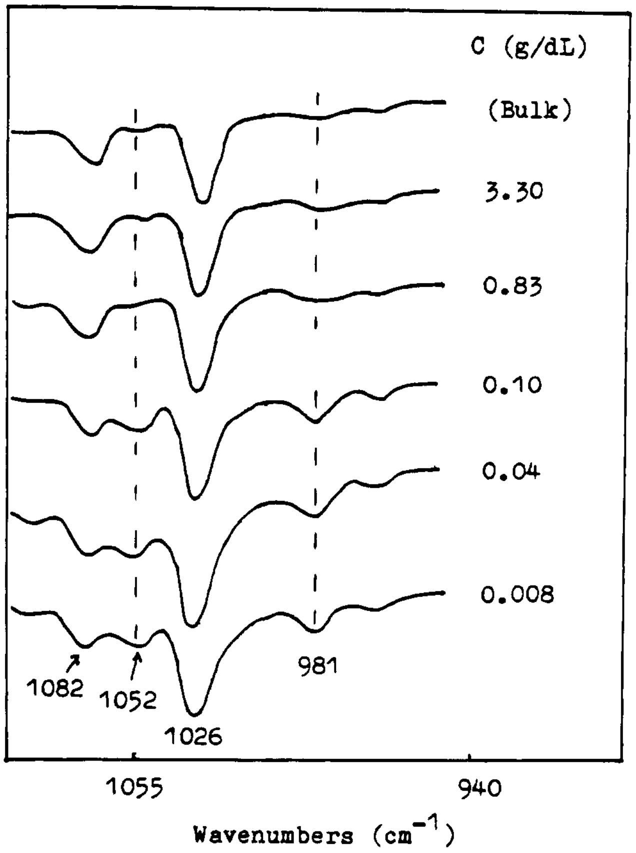

Figure 3. FT-IR spectra of freeze-dried i-PS after annealing at 180 °C for 5 min. (The concentration of the original solutions is indicated on the right of each spectrum.)

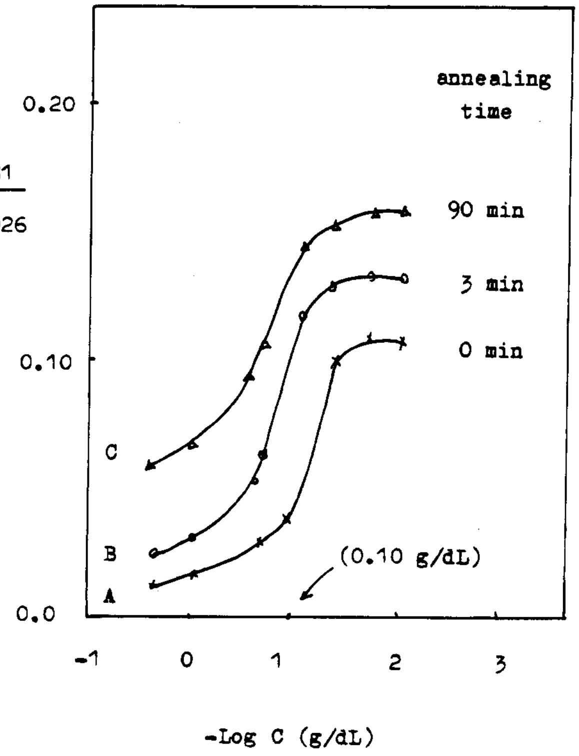

Figure 4. Plots of the relative intensities ($I_{981\ \mathrm{cm}^{-1}}/I_{1026\ \mathrm{cm}^{-1}}$) versus concentration for freeze-dried i-PS after annealing at 180 °C.

in the spectra of Figures 2 and 3 for i-PS glasses freeze-dried from $C > 0.30$ g/dL solutions and the bulk material after annealing. However, the bands at 1052 and 981 cm^{-1} in the spectrum recorded from 0.10 g/dL i-PS solution increased significantly in intensity, indicating that annealing this sample yielded a considerable amount of crystalline material.

The 1026 cm^{-1} band in IR spectra is less sensitive to annealing, which can be used as an internal standard for comparison of crystallinity. Semilogarithmic plots of the relative intensity, $I_{981\ \mathrm{cm}^{-1}}/I_{1026\ \mathrm{cm}^{-1}}$, versus concentration (Figure 4A) can be used to measure the concentration dependence of crystallization.[7] Of particular interest here is the observation of a concentration boundary near 0.04 g/dL ($-\log C = 1.4$) for the freeze-dried i-PS. At and below 0.04 g/dL, a considerable amount of crystalline material formed on rapid-cooling and freeze-drying the very dilute solutions. When the concentration was increased, much less crystalline material formed during the same process. Figure 4C and 4B for the annealed samples show another boundary at 0.10 g/dL ($-\log C = 1$), indicating that a considerable amount of crystalline material formed on annealing this sample.

The i-PS chain in the crystalline phase is a 3/1 helix.[8] The conformation of i-PS in dilute solution in various solvents has been investigated by different authors.[9,10] The general conclusion has been that i-PS molecules contain helical segments in solution with the number and length depending on temperature, concentration, and solvent.[10] Recently, Qian et al. and Chen et al. have proposed a concept of a concentration boundary C_s of solutions well below C^* ($C^*/C_s > 40$) based on studies of excimer fluorescence and size-exclusion chromatography.[11] Beyond C_s the effect of interchain interactions begins to be felt by the macromolecular chains. On a further increase of concentration the coils will overlap. Our studies of the concentration dependence for the crystallization arising from freeze-drying dilute solutions of i-PS show agreement with Qian's theory. We propose that the coils of i-PS in very dilute solution ($C < 0.04$ g/dL)) contain many helical segments with few chain entanglements. As the solution was frozen rapidly, the helical segments aggregated to crystals, resulting in a freeze-dried i-PS with a considerable amount of nuclei crystallizing in a fraction of a second. Beyond this boundary, fewer helical segments exist in the solutions so that little crystalline material was detected in the i-PS freeze-dried from solutions for which $C > 0.04$ g/dL. It is hard to prove rigorously that no change in the interpenetration of flexible molecular coils occurred during the rapid freezing process of polymer solutions used in this study. Yet, the internal consistency of the data leaves little doubt that this assumption, on which all interpretations are based, is valid.

Another important concentration boundary was found in 0.10 g/dL solution. On one hand the chain coils in 0.10 g/dL solution contain few 3/1 helix segments so that there is little crystalline fraction in the initial freeze-dried sample; but on the other hand, the coils of the freeze-dried glass derived from this solution are in an expanded state with fewer entanglements which could crystallize upon annealing at a much higher rate than the i-PS glass prepared from more concentrated solutions. The freeze-dried i-PS coils derived from a 0.83 g/dL solution are highly interpenetrated so that they crystallized slowly upon annealing. As a matter of fact, Figures 1–3 show little difference in crystallinity between the freeze-dried i-PS derived from 0.83 g/dL and from 3.3 g/dL solutions or the bulk i-PS quenched from the melt, indicating that these i-PS samples contain the same extent of chain entanglements. This conclusion is in good agreement with a ^{13}C NMR study.[4]

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