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Rapid Crystallization of Isotactic Polystyrene by Shock-Cooling and Subsequent Freeze-Drying of Its Very Dilute Solution

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Isotactic polystyrene (i-PS) has been considered as a slowly crystallizing polymer.[1] Several papers deal with the crystalline growth rate of i-PS as a function of temperature both in the bulk and in solution.[2] The half-times for crystallization of i-PS from solutions were a few hundred to ten thousand minutes depending upon the solvent used and the crystallization temperature.[1]

We have found that a considerable amount of crystalline phase was formed in a fraction of a second by shock-cooling a very dilute solution (0.04% by weight) of i-PS by injection into liquid nitrogen, followed by freeze-drying the frozen solution under vacuum. Annealing the shock-cooled and freeze-dried i-PS could further crystallize it, resulting in a much higher crystallinity than annealing an ordinary i-PS.

i-PS was kindly supplied by Department of Polymer Chemistry, Kyoto University, Kyoto, Japan. It was freed from atactic polystyrene by dissolving the polymer in methylene chloride (1 g/L) and dropping the solution into excess methyl ketone. After evaporation of methylene chloride, i-PS precipitated quantitatively from the ketone, leaving atactic polystyrene in solution. ^{13}C NMR spectra showed that the i-PS sample contained 90% isotactic triads. The number-average molecular weight of this highly stereoregular i-PS was 18×10^4. The solvent benzene was distilled before use. i-PS was dissolved in the purified benzene to make a very dilute solution with a concentration of 0.04% by weight at 50 °C. The warm solution was injected directly into liquid nitrogen so that it was frozen in a fraction of a second. The frozen solvent was then sublimed in vacuum. The resulting PS powder, designated as the shock-cooled i-PS, was examined by means of a wide-angle X-ray diffractometer (Rigaku D/Max-Ra) and a Fourier transform infrared spectrometer (Nicolet FT-IR 170 SX).

The wide-angle X-ray diffraction (WAXD) pattern recorded from a shock-cooled i-PS from a very dilute solution (0.04% in concentration by weight) shows several crystalline peaks which could be indexed according to ref 2.

$$300 \quad 220 \quad 211 \quad \left\{\begin{matrix}410\\311\end{matrix}\right. \quad \left\{\begin{matrix}330\\321\end{matrix}\right. \quad \left\{\begin{matrix}222\\421\end{matrix}\right.$$

The diffractogram of Figure 1B was recorded from a freeze-dried i-PS from a shock-cooled semidilute solution in benzene with a concentration of 0.5% by weight. Figure 1C was recorded from an amorphous i-PS sample quenched from its melt. Both diffraction patterns of Figure 1B,C exhibit broad and intensive bands, with the center at $2\theta = 18.4°$. Figure 1 indicates clearly that the i-PS prepared by shock-cooling and subsequent freeze-drying from the very dilute solution (0.04% by weight) is partially crystalline, while the i-PS prepared from the semidilute solution (0.5% by weight) is mainly in an amorphous phase.

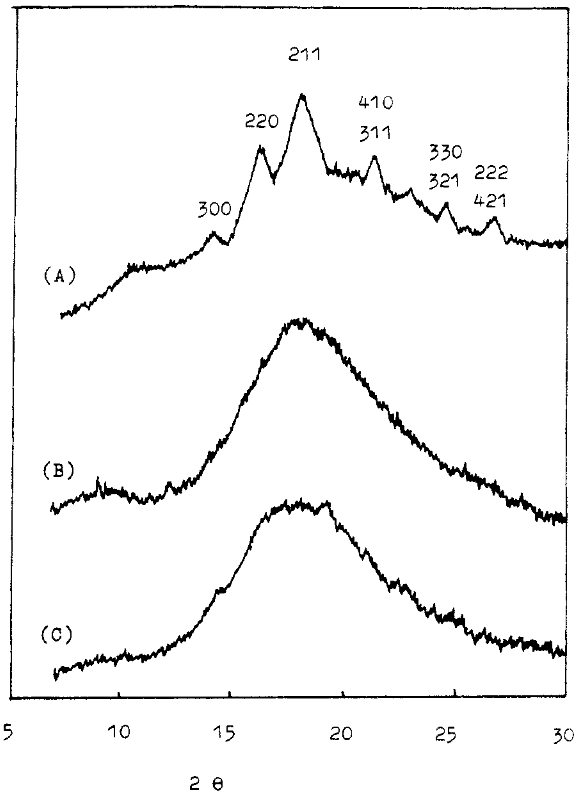

Figure 1. Wide-angle X-ray diffraction curves recorded from (A) a shock-cooled and freeze-dried i-PS from a 0.04% solution, (B) a shock-cooled and freeze-dried i-PS from a 0.5% solution, and (C) a quenched normal i-PS sample.

It was reported that i-PS could crystallize by slowly cooling the melt to room temperature or by annealing the polymer at 180 °C.[1,3] Figure 2 shows the comparison of WAXD patterns recorded from an annealed shock-cooled i-PS and from two annealed normal i-PS samples. The "normal" i-PS means a sample identical to the shock-cooled ones in every respect but the shock-cooling and subsequent freeze-drying. Figure 2A recorded from the i-PS which had been freeze-drying treated and then annealed at 180 °C for 13 min exhibits sharp peaks in the range of 2θ = 5–30° of the diffractogram, indicating that the sample was highly crystallized. Diffractograms of Figure 2B,C were recorded from normal i-PS samples which were crystallized based on the methods described in the literature.[1-3] The sample for Figure 2B was first cooled rapidly from its melt to 20 °C by pouring it into water and then annealed at 180 °C for 13 min, and that for Figure 2C was cooled slowly (0.5 °C/min) from its melt to room temperature. Comparison of the intensity and the sharpness of crystalline peaks of the diffractograms in Figure 2 indicates that the annealing of the shock-cooled i-PS could result in much higher crystallinity than annealing the normal samples.

Since the i-PS chain in the crystalline phase is a 3_1 helix,[4] conformational changes might play an important role during crystallization from solutions. Helms and Challa showed that during crystallization from dilute solutions of i-PS in a mixture of toluene and ether, helices are formed which aggregate to crystals afterward.[5] The conformation of i-PS in dilute solution in various solvents has been investigated by different authors.[6,7] The general conclusion has been that i-PS molecules contain helical segments in solutions, with the number and length depending on temperature and solvent.[7] Recently, Qian *et al.* have put forward a concept of the concentration boundary of the solutions from very dilute to semidilute.[8] The critical concentration value could be identified clearly, designated

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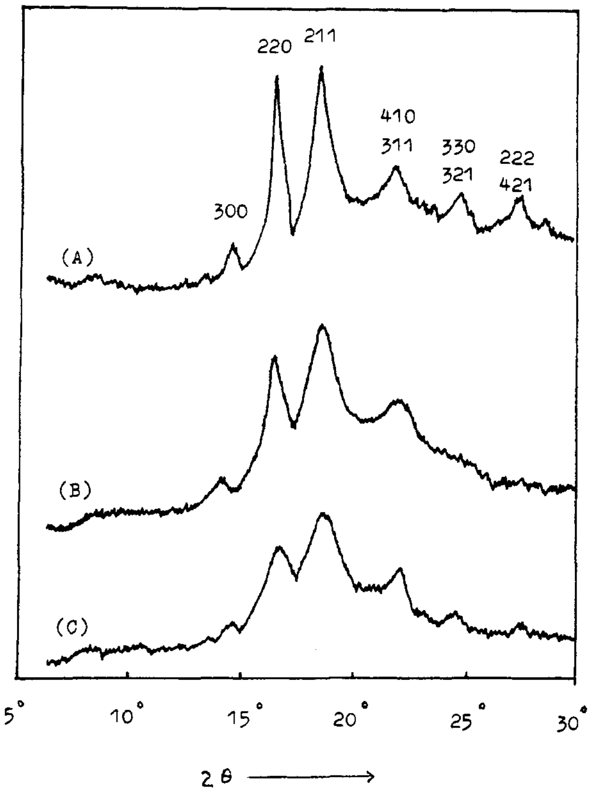

Figure 2. Wide-angle X-ray diffraction curves recorded from (A) a shock-cooled i-PS annealed at 180 °C for 13 min, (B) a normal i-PS cooled from the melt to 20 °C and then annealed at 180 °C for 13 min, (C) a normal i-PS cooled from the melt slowly (0.5 °C/min) to room temperature.

as C_s. At and beyond C_s the effect of interchain interactions begins to the felt by the chains in solution. On further increase of concentration the coils will overlap each other. The C_s value of polystyrene with a weight-average molecular weight of 30×10^4 in a dichloroethane solution was measured to be 0.05% by use of excimer fluorescence.[8] On the basis of this concept, we propose that the coils of i-PS in a very dilute solution contain a considerable amount of 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 and crystals, as evidenced by the WAXD spectrum in Figure 1A. Since the coils of the freeze-dried i-PS contain few chain entanglements, the amorphous part seems more easily able to move cross the crystalline boundary upon annealing. So annealing the freeze-dried i-PS could yield much higher crystallinity than annealing the normal i-PS. However, the shock-cooled i-PS prepared from a semidilute solution with a concentration above C_s is mainly in an amorphous phase as shown in Figure 1B.

Figure 3 illustrates IR spectra recorded from an annealed freeze-dried i-PS (Figure 3A) and from an annealed normal i-PS (Figure 3B). In Figure 3A, the band at 1261 cm^{-1} and the doublets at 1081–1051, 920–902, and 563–550 cm^{-1} are the characteristic IR bands of a crystalline i-PS.[9] Figure 3B shows a spectrum recorded from less crystalline i-PS. IR studies confirmed that the crystallinity of the annealed freezes-dried i-PS is much higher than that of the annealed normal i-PS.

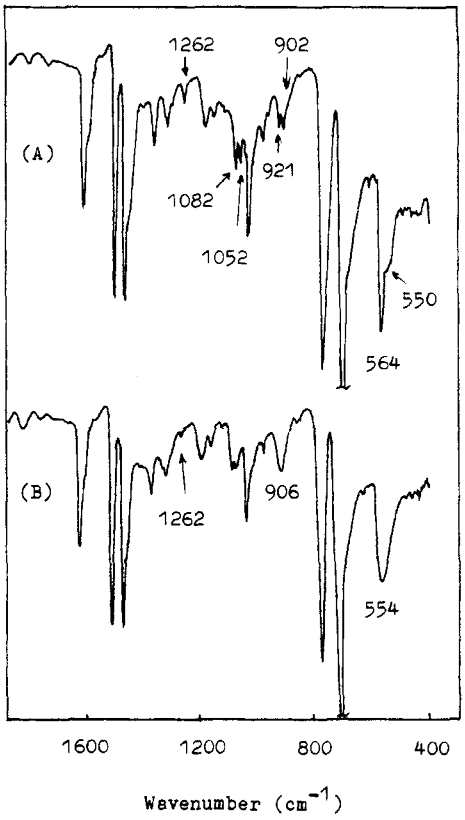

Figure 3. IR spectra recorded from a shock-cooled i-PS (A) and a normal i-PS (B) after they had been annealed at 180 °C.

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