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FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDY OF CONFORMATION OF FREEZE-DRIED ISOTACTIC POLYSTYRENE

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Summary

Isotactic polystyrene samples were prepared by shock-cooling and subsequent freeze-drying from very dilute solutions in benzene. Fourier transform infrared spectroscopic studies on these samples indicated that there are conformational differences between them and a normal isotactic polystyrene. Comparison of the infrared spectra indicated that spectral changes occurred at the bands near 1261, 1085-1050, 982, 923-906, and 550 cm^{-1}. The changes in intensities of the crystalline bands show that the freeze-dried isotactic polystyrene from a very dilute solution exhibits a higher crystallinity than the annealed sample.

Introduction

Isotactic polystyrene (i-PS) has been considered as a slowly crystallizing polymer.[1] The half times for crystallization of i-PS from solution were a few hundred to ten thousand min dependent on the solvents used and the crystallization temperature.[1] Recently, the relation between gelation and crystallization of polystyrene has been studied by several authors.[2-5] X.-M. Xie et al. carried out Fourier transform infrared spectroscopic studies on the gelation and crystallization of polystyrene/carbon disulfide solutions[5] and found that the differences in crystallinity of the dried gels are dependent only on the polymer concentration in the wet gel state.

Recently, Xue has found that a considerable amount of crystalline phase is formed in a fraction of a second by shock-cooling a very dilute solution.[6] In this work, to elucidate the concentration dependence of the freeze-dried

PS, they were studied by FT-IR, and the spectra were compared with those of normal i-PS.

I-PS was kindly supplied by BASF Co. 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 1.8 10^4. The solvent benzene was distilled before use. I-PS was dissolved in the purified benzene to make a very dilute solution with concentration of 0.5 g/l 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 freeze-dried i-PS, was examined by means of a Fourier transform infrared spectrometer (Nicolet FT-IR 170 SX). PS samples were mixed with KBr powder to make transparent disks for IR measurement. Two hundred co- added interferograms at a resolution of 2 cm^{-1} were used to obtain each spectrum. Composition absorption peaks were separated into each component peak with a Lorentzian shape.

Results and Discussion

FT-IR spectra of freeze-dried i-PS were different from the spectrum of thermally annealed i-PS; this is illustrated in Figure 1 for an atactic PS, i-PS cooled from its melt and annealed at 180 °C for 90 min, and rapid-cooled and freeze-dried i-PS. Some bands of interest are indicated, for example, the 906 cm^{-1} band for atactic PS. In the case of annealed i-PS, this band tends to show a shoulder at the higher frequency side. For the freeze-dried i-PS, it splits into two bands at 921 and 902 cm^{-1}. The 921 cm^{-1} band is assigned to the out-of-plane C-H bending vibration related to crystallization.[5] The separation of 921 and 902 cm^{-1} bands has been assigned to associate with the crystal field splitting effect.

There is also a doublet at 1082 and 1052 cm^{-1} in the spectrum of the freeze-dried i-PS, which appears as a singlet at 1068 cm^{-1} in the atactic sample. The separation of 1082 and 1052 cm^{-1} bands was assigned to be associated with the difference in the sequence length of the conformation in the amorphous regions, which has a crystallization dependence.[6] The bands near 1261 and 982 cm^{-1} are typical crystallinity bands of polystyrene. Comparison of the intensities in 1261 and 982 cm^{-1} bands indicates that the freeze-dried i-PS exhibits a higher crystallinity than the annealed i-PS sample.

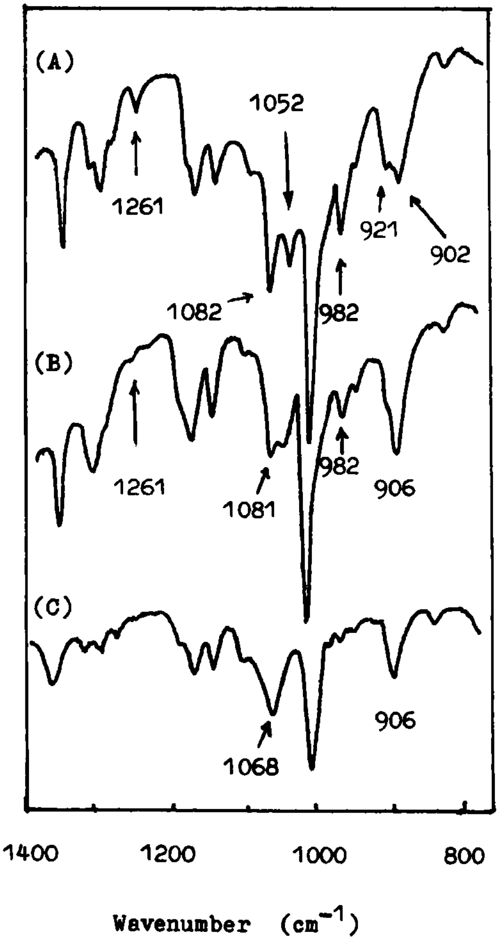

Fig.1 IR spectra of (A) freeze-dried i-PS from 0.5 g/l solution; (B) normal i-PS annealed at 180 °C for 90 min; (C) atactic PS

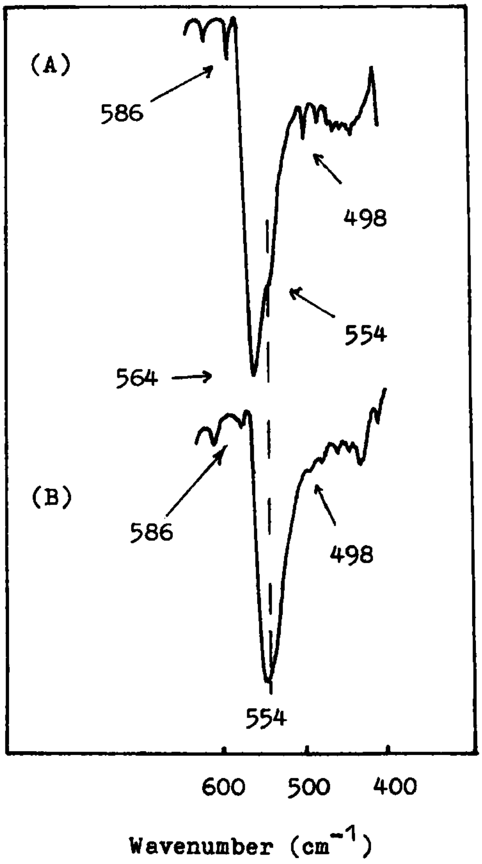

Figure 2. IR spectra (600-400 cm^{-1}) of freeze-dried i- PS: (A) from a 0.5 g/l solution; (B) from a 5 g/l solution.

In order to investigate the conformational changes in i-PS, the 600-450 cm^{-1} region, which is sensitive to conformation, was analyzed, as shown in Figure 2.

In this region, the spectrum of freeze-dried 0.5 g/l i-PS shows a strong and sharp band at 564 cm^{-1}, while the freeze-dried 5 g/l sample exhibits a broad band at 554 cm^{-1} which is related to the amorphous phase. On the other hand, the 586 and 498 cm^{-1} bands of the freeze-dried 0.5 g/l were assigned as crystallinity (regularity) bands by Painter and Koenig,[6] whereas only weak band appear at 586 cm^{-1} in the spectrum of freeze-dried 5 g/l i-PS.

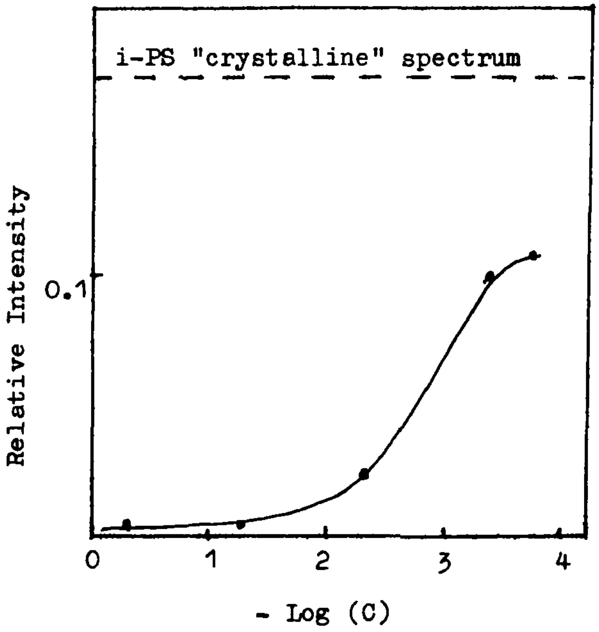

Figure 3. Plot of the relative intensities of 1261 cm^{-1}/1451 cm^{-1} for freeze-dried i-PS against the concentration of the original solutions.

The relative intensity of 1261 cm^{-1} to 1451 cm^{-1} band for freeze-dried i-PS is plotted against the polymer concentration of the original solutions in Figure 3.

The intensity of a pure "crystalline" spectrum, which was obtained by subtracting the amorphous spectrum of a quenched sample from that for the annealed sample, is used as the upper limit of crystallinity for i-PS.[7] The crystallinity of freeze-dried i-PS decreases with increasing polymer concentration of original solutions.

Since the i-PS chain in the crystalline phase is a 3_1-helix,[4] conformational changes might play an important rôle during rapid cooling of solutions. The conformation of i-PS in dilute solutions has been investigated by different authors.[8,9] The general conclusion has been that i-PS molecules contain helical segments in solutions with the number and length depending on temperature and solvent.[9] Recently, Qian et al. have put forward a concept of a concentration boundary of the solutions from very dilute to semi-dilute.[10,11] The critical concentration value could be identified clearly, designated as C_s. At and beyond C_s the effect of inter-chain interactions begin to be felt by the chains in solution. On further increase of concentration the coils will overlap each other. Based on this concept, we propose that the coils of i-PS in a very dilute solution contain 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 considerable amount of nuclei and crystalline. 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 2B.

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