Infrared Bands Sensitive to the Chain Packing Mode in the Crystalline δ, δ_e, and γ Forms of Syndiotactic Polystyrene

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Received December 26, 2002
Revised Manuscript Received February 19, 2003

Introduction. Syndiotactic polystyrene (sPS) shows a complicated polymorph depending on the crystallization conditions. The glassy sample prepared by quenching the melt crystallizes to the δ form in the atmosphere of organic solvent vapor.[1−24] This δ form changes into the empty δ form (δ_e) by washing the δ form in boiling acetone.[16,23] By rinsing this sample in methanol, the more perfect δ_e form is prepared.[25] In the δ_e form the sPS chains with the TTGG helical conformation are packed, and all the solvent molecules are taken away but with keeping the empty spaces originally occupied by the solvents.[16] When the δ form is heated above 150 °C, it transforms to the γ form,[2,4,17−20,23,24] in which the organic solvent molecules are purged away and only the sPS chains are closely packed in the crystal lattice. The sPS film cast from the acetone solution also gives the γ form.[26]

Identification of the crystalline forms of δ, δ_e, and γ is important in the structural study of the transition behavior among them. The X-ray diffraction method may be useful as a tool to identify these crystalline forms.[1−8,11−20,23−26] It is difficult, however, to distinguish concretely the positional relation between sPS chains and solvent molecules in the crystal lattice without the detailed structure analysis.[3,4,11,15] Rather, vibrational spectroscopy gives us more concrete information on the local packing structure and the polymer−polymer and/or polymer−solvent interactions. It has been said for a long time that the infrared spectra of sPS are sensitive to the chain conformation[27−31] but are not very sensitive to the difference in chain packing mode. Moyses and Spell pointed out the spectral pattern difference between the α and γ forms in the 920−960 cm^{-1} region.[17] Recently, we have found that several infrared bands, in particular the bands in the region of 500−800 cm^{-1}, are different in their profiles between the δ, δ_e, and γ forms, as will be described in the present paper. These characteristic bands are weak in intensity and seem to have been overlooked by many researchers for a long time. Since these three crystalline forms have essentially the same chain conformation, the difference in infrared spectra is considered to reflect a difference in chain packing mode or the difference in intermolecular interactions between polymer chains and/or between polymer chains and organic solvents. This spectral information is expected to be quite useful in the study of the structural changes occurring in the phase transitions between δ, δ_e, and γ forms.

Experimental Section. a. Samples. sPS samples (M_w 203 000, M_w/M_n 3.01) were supplied by Idemitsu Petrochemical Co. Ltd., Japan. Glassy samples were prepared by quenching the melt into ice−water. The δ form was prepared by immersing the glassy sample directly into solvent. As the solvent, chloroform, toluene, benzene, and acetone were used in the present study. The δ_e form could be prepared by rinsing the δ form in acetone[16] and then washing it in methanol. We found that the δ_e form could be made also by rinsing the δ form directly in methanol without pretreatment in acetone. The γ form was prepared by dipping the glassy sample into acetone[26] or by heating the δ form above 150 °C and cooling to room temperature.[2,4,17−20,23,24]

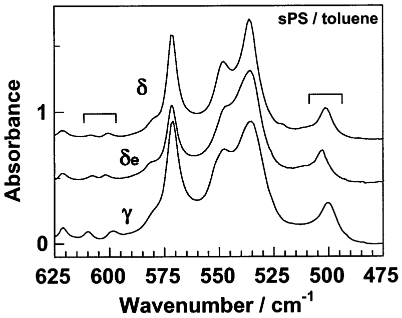

Figure 1. Infrared spectra of the δ, δ_e, and γ forms of the sPS/toluene system measured at room temperature.

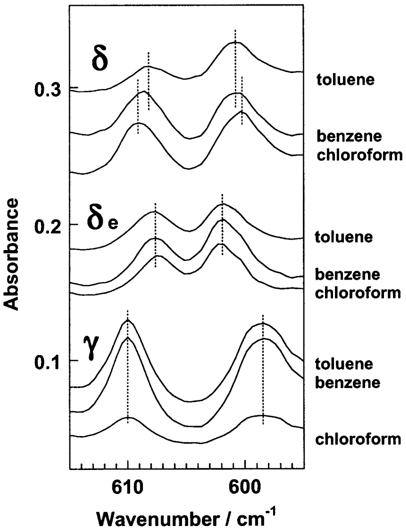

Figure 2. Infrared spectra in the region of 595−615 cm^{-1} measured at room temperature for the various samples of the sPS/solvent system.

b. Measurements. Identification of the thus-prepared three crystalline forms was made by measuring the X-ray diffraction profiles with a Rigaku RAD-ROC X-ray diffractometer. The graphite-monochromatized Cu Kα line (λ = 1.541 78 Å) was used at the power of X-ray generator 40 kV and 200 mA. The infrared spectra were measured at a resolving power 1 cm^{-1} with a Bio Rad FTS60A/896 FT-IR spectrometer.

Results and Discussion. Figure 1 shows the infrared spectra of the δ, δ_e, and γ forms obtained for the sPS/toluene system as an example. The infrared spectra are almost common to these three forms except some frequency regions. Figure 2 shows the expanded 600 cm^{-1} spectral region, where the band positions are significantly different among these three crystalline forms. A pair of bands at 608.2 and 600.8 cm^{-1} is unique to the δ form, a pair at 607.6 and 601.9 cm^{-1} for the δ_e form, and a pair at 610.0 and 598.5 cm^{-1} for the γ form. (In the present experiment the resolving power of

10.1021/ma026005t CCC: $25.00

Table 1. Infrared Bands (in cm^{-1}) Characteristic of δ, δ_e, and γ

δ(toluene)	δ(benzene)	δ(chloroform)	δ_e	γ
779.2	779.2		780.0	778.0
769.5	769.5		770.0	768.0
608.2	608.5	609.1	607.6	610.0
600.8	600.8	600.3	601.9	598.5
571.0	571.0	572.0	571.0	572.0
501.4	501.8	501.8	502.8	500.3

infrared spectra was 1 cm^{-1}. The peak positions of these bands were estimated by carrying out the curve fittings.) By changing the kind of solvent, these infrared bands of the δ form shifted slightly but significantly: (608.2, 600.8 cm^{-1}) for toluene, (608.5, 600.8 cm^{-1}) for benzene, and (609.1, 600.3 cm^{-1}) for chloroform. In the cases of the δ_e and δ forms, the band position is almost the same among the different solvent systems. The 500 cm^{-1} region is also sensitive to the crystalline form. The infrared band of the δ form with toluene is at 501.4 cm^{-1}, different from that of the δ_e form at 502.8 cm^{-1} and that of the γ form at 500.3 cm^{-1}. By changing toluene to benzene or chloroform, the band of δ form shifted to 501.8 cm^{-1}. The δ_e and γ show the bands at almost the same positions irrespective of the kind of solvent. The infrared bands in the 770 cm^{-1} region are also in the same situation. The band frequencies observed differently for the three crystalline forms are listed in Table 1. As already mentioned, in the crystal lattice of the δ_e form, vacant spaces are kept which were originally occupied by the solvent molecules. But, as seen in Figure 2, the infrared band positions are not mostly dependent on the solvent type. This suggests that the infrared band positions of the δ_e form are determined in an approximation by intramolecular interaction of chains separated by the empty spaces of solvent molecules and are modified only slightly by weak interactions between the distant chains. By introducing solvent molecules into the vacant spaces of the δ_e form, that is, in the δ form the polymer−solvent interactions are generated and the band positions are shifted more or less depending on the solvent type. The similar situation can be seen also for the γ form. By erasing the vacant space, the direct polymer−polymer interactions become stronger, and the infrared bands are shifted furthermore in the γ form. These situations can be checked by the observation that the gap between the two bands shown in Figure 2 is the smallest in the δ_e form and increases in the δ form and is the largest in the γ form. Roughly speaking, the polymer chains are affected by the surrounding molecules through the following interactions: in the δ form the interactions between chain−solvent−chain, in the δ_e form between chain−(vacancy)−chain, and in the γ form between chain−chain−chain. Of course, to check these assumptions, we need to perform the energy calculation, for example, about the crystal structures of these crystalline forms.

The information on the infrared bands assigned to the different crystalline forms of δ, δ_e, and γ is important and seems useful for tracing the structural changes occurring in the phase transition from the δ form to δ_e or γ form. The transition behavior from the δ to γ form was investigated by Gowd et al. by carrying out the in-situ X-ray diffraction measurement during the heating process.[32] We checked their X-ray result from the viewpoint of infrared spectroscopy. That is to say, we measured the infrared spectra during the heating process starting from the δ form. Figure 3a shows the temperature dependence of the infrared bands in the 600−610 cm^{-1} region measured for the δ form with chloroform at the resolving power 1 cm^{-1}, where the sample film used in this experiment had a thickness of ca. 100 μm in order to increase the signal-to-noise ratio enough for the quantitative analysis of the band profile. As the temperature was increased, the 600.3 and 609.1 cm^{-1} bands of the δ form decreased in intensity and the 610.0 and 598.5 cm^{-1} bands of the γ form appeared and increased in intensity. The spectral profiles were deconvoluted at first into three pairs of the bands intrinsic to the δ, δ_e, and γ forms (Table 1), but the contribution of the δ_e bands was always zero even when the various deconvolution methods were tried. If the δ form transfers to the δ_e form once and then to the γ form, the gap of the two bands should be *narrower at first and then wider in the γ region*. The actual spectral profile and the deconvolution result did not support this possibility at all. Figure 3b shows the linear relation between the integrated intensities of the δ and γ bands which were estimated after curve separations. As well-known, this type of plot should show the linear relation when the system contains only the two phases and the transition occurs between only these two phases without any contribution from the third phase.[33] Figure 3b supports this concept clearly: the 609 cm^{-1} δ band increased the intensity in proportion to the intensity increment of another δ band at 600 cm^{-1}, and the 599 cm^{-1} γ band decreased in intensity oppositely. An observation of a clear isosbestic point, or a common crossing point at a constant vibrational frequency for a series of overlapped infrared spectra, supports this conclusion although the spectra shown in Figure 3a are shifted manually along the intensity axis for clear view.

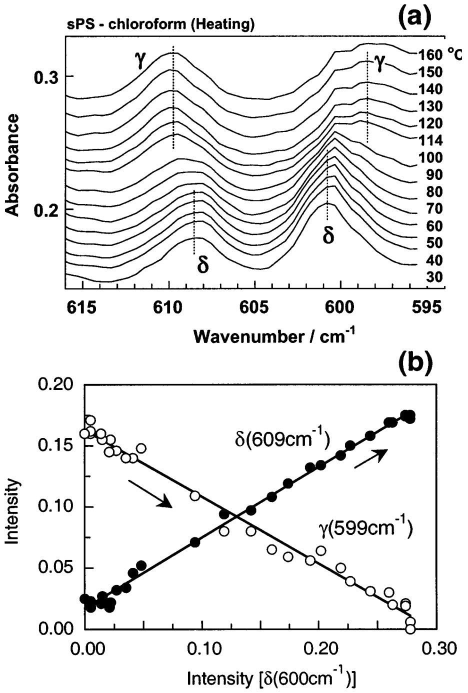

Figure 3. (a) Temperature dependence of infrared spectra measured during the heating process of the δ form prepared from the sPS/chloroform system and (b) the integrated intensities of the δ (609 cm^{-1}) and γ (599 cm^{-1}) bands plotted against the intensity of the 600 cm^{-1} band of the δ form.

In this way, as long as we observe the phase transition from the eye of infrared spectroscopy, we may say that the δ form transfers directly to the γ form without passing through the δ_e form as an intermediate form when the sample is heated. People might say that the transition from the δ to γ form was already known by the X-ray diffraction studies.[2,4,17−20,23,24] But, these studies measured the X-ray diffraction profiles at room temperature for the samples annealed at high temperatures. To clarify the phase transition behavior itself, we need to carry out the in-situ measurement during the heating process. Gowd et al. reported this type of measurement for the X-ray diffraction and pointed out the direct transition from the δ to γ forms.[32] But the X-ray diffraction pattern is too complicated to conclude it definitely. Rather, the present infrared spectral measurement seems to give us a clearer result. Of course, when we imagine the structural change from the δ form to the γ form from the microscopic point of view, the structure similar to the δ_e form should be generated even transiently on the way from δ to γ form. But, this δ_e-like structure might be only temporary and cannot be detected in the infrared spectral experiment. To catch this structure, we will need to carry out the rapidly time-resolved measurement during the temperature jump from the δ to γ form.

In this way the infrared bands detected for the three different crystalline forms are expected to give us many useful information necessary for the structural study of the phase transition in sPS sample. The detailed discussion will be reported in a separate paper.

Acknowledgment. The authors thank Idemitsu Petrochemicals Co. Ltd., Japan, for supplying the sPS sample.

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MA026005T