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Polymer−Solvent Interactions in Crystalline δ Form of Syndiotactic Polystyrene Viewed from the Solvent-Exchange Process in the δ Form and the Solvent Evaporation Phenomenon in the Thermally Induced $\delta-\gamma$ Phase Transition

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ABSTRACT: The δ form, one of various crystalline forms of syndiotactic polystyrene (sPS), is a complex between sPS and solvent molecules. This crystalline form shows a solvent exchange between the originally absorbed solvent B and the newly supplied solvent A when the δ form sample was exposed to the solvent A atmosphere. We have carried out the time-resolved infrared spectral measurement during this solvent-exchange process and found that the solvent-exchange rate was almost common to any pair of solvents where the solvents A and B were toluene, chloroform, or benzene. On the other hand, when the δ form sample was heated above 150 °C, it transferred to the γ form having no solvent molecules in the crystal lattice. The temperature, where most of solvent molecules were evaporated from the sample, was almost common to any kind of solvent originally absorbed in the δ form, as already pointed out by Gowd et al. [*Macromolecules* **2002**, *35*, 8509]. All these phenomena, i.e., the solvent-exchange phenomenon and the solvent evaporation phenomenon, were considered to come from the characteristic features of δ form crystal: the unique columnar structure and the relatively weak interactions between sPS chains and solvent molecules; the solvent molecules are trapped in the columns made by aggregated sPS chain stems. The solvent exchange was speculated to occur easily along the column axis. The evaporation of solvent in the δ-to-γ phase transition was considered to occur also along the column axis, and therefore almost no difference was observed for the different solvent system. When acetone was supplied to the δ form in the solvent-exchange experiment, the solvent originally trapped in the δ form was displaced by acetone molecules. But the original column structure was not affected by such a solvent exchange—different from the cases of other such solvent as toluene, benzene, or chloroform. The structure changed from δ to δ_e (empty δ) form for the first time when acetone evaporated from the sample at room temperature.

Introduction

Syndiotactic polystyrene (sPS) shows a complicated polymorphism depending on the crystallization conditions. The amorphous glass, prepared by quenching the molten sample, crystallizes into δ form[1,2] when it is exposed to the atmosphere of such organic solvent as benzene, toluene, etc., at room temperature. In the δ form sPS chains take the TTGG helical conformation and make a complex with solvent molecules. Rinsing the δ form in acetone or methanol gives the so-called empty δ_e form[16,17,26] where the TTGG chains are packed in a similar crystal lattice with that of the original δ form, but the solvent is taken away and the spaces having been occupied by solvent molecules are kept vacant. When the δ form sample is heated, the solvent molecules evaporate, and the γ form is obtained in which the TTGG chains are packed closely without remaining any vacancy due to evaporated solvent.[11,13,18−21,24,27−29] By further heating at higher temperature, the γ form transfers to the α form of all-trans zigzag conformation.[18,24,29]

In a series of papers,[22,23] we have studied the solvent-induced crystallization phenomenon of sPS glass into the δ form by carrying out the time-resolved measurements of the infrared and Raman spectra and the X-ray diffraction and clarified the structural evolution process from the microscopic point of view. When an organic solvent is supplied to the glass sample, the random coils experience a so-called micro-Brownian motion and are regularized into short helical segments, which grow to longer helices and gather together to form a crystal lattice with organic solvent molecules. The starting time of this crystallization phenomenon or the induction period and the growth rate of long helices are dependent on the kind of solvent: chloroform gives the highest crystallization rate, benzene the next, and then toluene.

As mentioned above, the δ form is a complex between sPS chains and organic solvent molecules. In the early days when the δ form was found out, it was said that the solvent molecules already existing in the δ form sample were exchanged when another kind of solvent was supplied to the sample.[13] But the details of this phenomenon were not clarified well enough. Recently, during the time-resolved measurement of the solvent-induced crystallization of the sPS sample, we have noticed that this solvent-exchange rate was quite high, and any pair of solvents could exhibit this exchange phenomenon at almost the same rate; for example, toluene and chloroform, benzene and toluene, and so on. Almost the common exchange rate for any pair of solvents suggests that it may come from the unique chain packing structure of the δ form. That is to say, by investigating the solvent-exchange phenomenon in detail, we may obtain some important information on the characteristic structural features and polymer−solvent interactions in the δ form crystal. The δ form is known to transfer to the γ form by heating[11,13,18−21,24,27−29] and to the δ_e form by rinsing in acetone or methanol.[16,17,26] These phenomena are speculated also to be related with the unique structure of the δ form.

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In the present paper we will report the details of the solvent-exchange phenomena in the δ form as well as the thermally induced δ-to-γ transition and the formation of δ_e form from the δ form. These phenomena were investigated by measuring the infrared spectra and X-ray diffraction as functions of temperature and time. On the basis of these experimental data, the essential features will be clarified about the unique packing structure and the polymer–solvent interactions of the δ form. The transition from the δ to γ form by heat treatment had been investigated.[11,13,18–21,24,27–29] But in-situ measurement in the heating process was reported only in ref 24 by X-ray measurement. We have carried out the in-situ infrared spectral measurement in order to clarify the details of the transition. Besides, we do not know of any paper in which the solvent-exchange phenomenon and the solvent evaporation phenomenon were discussed together from the common viewpoint of characteristic structural features of the δ form crystal.

Experimental Section

Samples. sPS was kindly supplied by Idemitsu Petrochemical Co. Ltd. ($M_w = 203\,000$ g/mol, $M_w/M_n = 3.01$). The glassy samples were prepared by quenching the melt into an ice water bath. The amorphous content was checked by infrared spectra. The amorphous samples were exposed to the atmosphere of organic solvent at room temperature. The solvents used were toluene, benzene, chloroform, and acetone. The thickness of sample films was about 30 μm for the infrared spectral measurements and about 100 μm for the X-ray diffraction measurements. When the sample was exposed to solvent vapor, the sample was swollen more or less by absorbing solvent and the sample thickness changed. But this change was quite small as known from the actual measurement of the thickness before and after experiment and did not affect the infrared absorbance very seriously.

Time-Resolved Infrared Spectral Measurement. In the time-resolved measurement of infrared spectra in the atmosphere of solvent vapor, the homemade cell was used as already reported in a paper.[23] The infrared spectra were measured by a rapid-scanning-type Bio Rad FTS 60A/896 Fourier transform infrared spectrometer with an MCT (mercury–cadmium–telluride) detector at a resolving power 2 cm^{-1}. The measurement was started at the same time with the solvent injection, and the data were collected at a constant time interval of 16 s. The starting time (0 s) of the measurement was set equal to the solvent injection timing. Strictly speaking, we need to take into consideration the diffusion rate of solvent vapor; that is, the solvent vapor might take some time to reach the sample position and penetrate into the sample. But the solvent vapor was assumed in a good approximation to fill a small sample cell quite rapidly after the solvent injection.

Infrared Spectral Measurements during Heating. The δ form sample was prepared by dipping the sPS film into solvent directly. This sample was sandwiched between a pair of KBr plates and then set to a heating cell. The infrared spectral measurement was made at a resolving power 1 cm^{-1}.

X-ray Diffraction Measurements during Heating. The δ form sample was put into a glass capillary and set to a heating cell. The X-ray diffraction pattern was measured in the heating process by using a MAC Science DIP1000 system with an imaging plate as the 2-d detector. The graphite-monochromatized Cu Kα line ($\lambda = 1.5418$ Å) from a MAC Science SRA 18 KW X-ray generator was used as an incident beam.

Results and Discussion

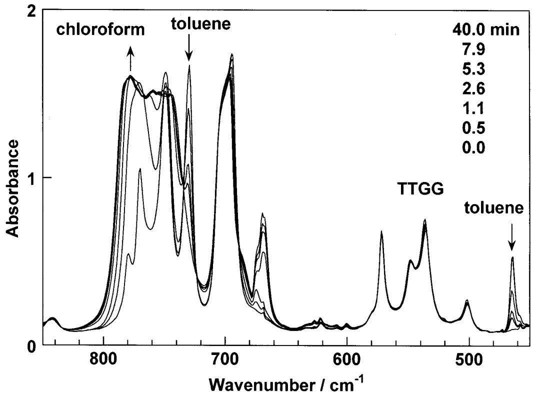

Figure 1. Time dependence of infrared spectra of the sPS δ(tol) form measured in the solvent-exchange process from toluene to chloroform.

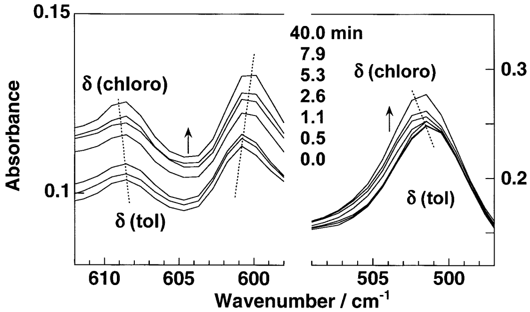

Figure 2. Time dependence of infrared spectra in the frequency region of 500–610 cm^{-1} measured for the sPS δ(tol) form in the solvent-exchange process from toluene to chloroform.

Solvent-Exchange Experiment. Figure 1 shows the time dependence of infrared spectra measured during the supply of chloroform to the δ form film containing toluene, where the amount of absorbed toluene in the starting sample was saturated well as being checked by the infrared spectral change. Immediately after the injection of chloroform, the infrared bands of toluene decreased in intensity steeply and the bands of chloroform increased instead. The bands characteristic of TTGG conformation were kept unchanged during this solvent-exchange process. The infrared bands in the frequency region of 500–600 cm^{-1} are sensitive to the difference in the crystalline state among the δ, δ_e, and γ forms, as already reported in a previous paper.[30] The band positions shifted when the solvent was gradually changed from toluene to chloroform as shown in Figure 2, indicating the structural transition from the δ form with toluene [δ(tol)] to the δ form with chloroform [δ(chloro)]. The structural change from δ(tol) to δ(chloro) could be checked also from the change in the X-ray diffraction pattern. For example, the X-ray diffraction profile was compared among the various samples before and after solvent exchange as shown in Figure 3. The basic X-ray diffraction profile was almost common and characteristic of the δ form, but the peak position and relative intensity of reflections were found to change depending on the type of exchanging solvents pair. It should be noted here that the X-ray diffraction profile taken for the sample which has experienced an exchange from chloroform to toluene [δ(chloro $\rightarrow$ tol)] is different from that of the original δ(tol) sample, although the solvent exchange was made almost perfectly as checked by the infrared spectral change. The similar observation is made also between the δ form prepared by solvent exchange from toluene to chloroform [δ(tol $\rightarrow$ chloro)] and the original δ(chloro).

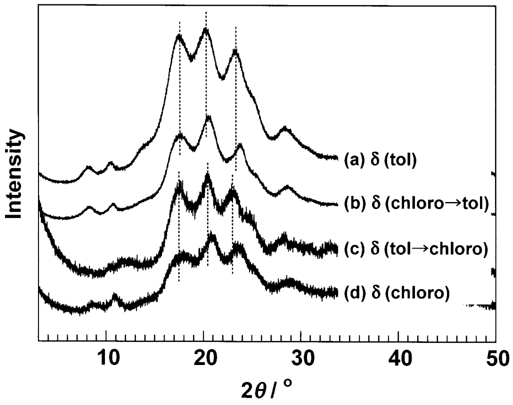

Figure 3. Comparison of X-ray diffraction profile between the δ form samples containing toluene or chloroform. (a) The sample containing toluene as an original solvent [δ(tol)], (b) the sample containing toluene after the solvent exchange from chloroform to toluene [δ(chloro→tol)], (c) the sample containing chloroform after the solvent exchange from toluene to chloroform [δ(tol→chloro)], and (d) the sample containing chloroform as an original solvent [δ(chloro)].

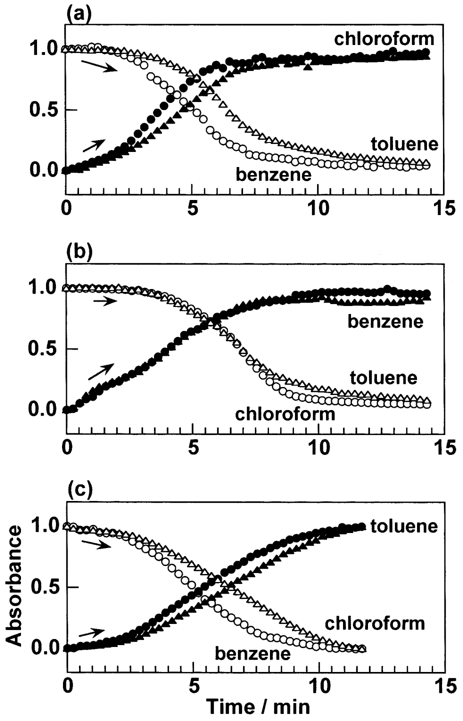

Figure 4. Time dependence of the normalized infrared absorbance estimated for sPS δ form samples in the solvent-exchange process: (a) from benzene or toluene to chloroform, (b) toluene or chloroform to benzene, and (c) chloroform or benzene to toluene.

Figure 4 shows the time dependence of infrared absorbance estimated for the solvent bands, where the relatively well isolated solvent bands were used (465 cm^{-1} for toluene, 670 cm^{-1} for benzene, and 1220 cm^{-1} for chloroform), and the evaluation of integrated intensity was made after the curve separation. The solvent exchange was observed to start immediately after the injection of a new solvent and completed around 10 min. Similar plots are given for the various pairs of solvents between toluene, benzene, and chloroform. For all the pairs of solvents the exchange time was almost the same within the experimental error as long as the films of the same thickness were used in the experiments. It is easily speculated that the solvent-exchange rate depends on the sample morphology. For example, the smaller crystallites may experience a solvent exchange at higher rate, and the sample containing lower amount of absorbed solvent may show easier solvent exchange. Besides, the different kind of solvent may give the different morphology at the final stage of crystallization, reflecting on the difference in solvent-exchange rate. But, Figure 4 shows that the solvent exchange occurs at almost the same rate as long as the sample thickness was adjusted to the same value, and the sample was saturated with enough solvent before the solvent-exchange experiment. This implies that the solvent exchange occurs too fast to show detectable difference in the exchange rate. Of course, a slight difference was observed in Figure 4 depending on the pair of the solvents, but this difference seems to give a minor effect to this exchange phenomenon. An important point is to notice that the solvent exchange occurs at quite high rate and at very similar rate irrespective of the different pair of solvents.

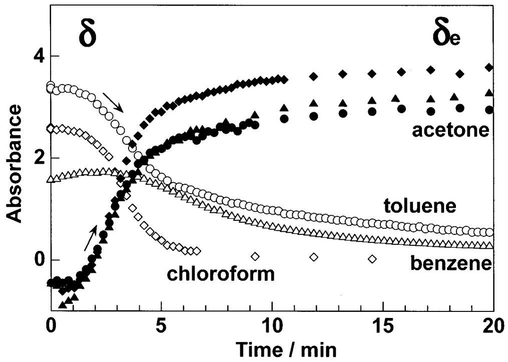

Figure 5. Time dependence of infrared absorbance estimated for sPS δ form samples in the solvent-exchange process from benzene, toluene or chloroform to acetone.

Figure 5 shows the solvent-exchange experiment between acetone and other three kinds of solvent used in Figure 4. The infrared band intensity intrinsic of chloroform (667 cm^{-1}), benzene (670 cm^{-1}), or toluene (465 cm^{-1}) decreased gradually, and the intensity of the acetone band at 1730 cm^{-1} increased instead, indicating that the initially included solvent was purged away and acetone molecules penetrated into the sample. When this acetone-containing sample was left for a while at room temperature, the acetone evaporated and the δ_e form was formed finally, in which the acetone molecules were not included anymore, but the vacancies were remained in the spaces occupied originally by the solvent molecules. The change in X-ray diffraction profile confirmed the formation of the δ_e form. It is noticed in Figure 5 that, different from the above-mentioned experiment shown in Figure 4, the acetone-exchange rate was different depending on the type of the solvent initially contained in the δ form. The exchange rate was in the order of chloroform > benzene > toluene. As reported already,[30] the infrared bands in the 500−600 cm^{-1} region are sensitive to the difference in the crystalline form (δ, δ_e, and γ). Figure 6 shows the time dependence of infrared spectra measured in the course of solvent exchange from toluene to acetone. The peak positions of the δ(tol) bands were not shifted but kept the same positions during the solvent-exchange process (see Figure 5). The band positions changed to those intrinsic of the δ_e form for the first time when acetone evaporated almost perfectly from the wet sample

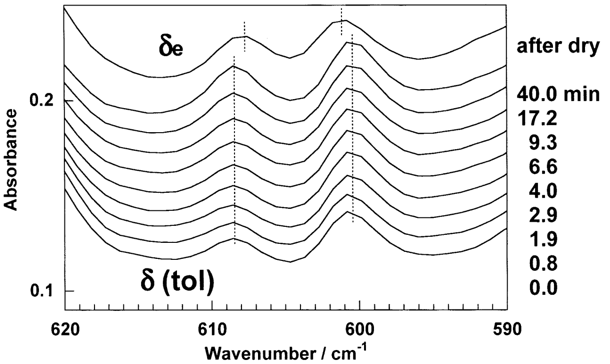

Figure 6. Time dependence of infrared spectra in the frequency region of 590−620 cm^{-1} measured for the sPS δ(tol) sample in the solvent-exchange process from toluene to acetone.

by drying up at room temperature. The details of this behavior will be discussed in a later section.

As mentioned in the introductory section, when the amorphous sPS sample was subjected to a solvent atmosphere, the induction period of crystallization and the crystallization rate were dependent on the type of the solvent. But, once the crystal structure of the δ form was formed, the guest solvent was replaced quite easily with other type of solvent at almost the same rate. This suggests that the interactions between sPS chains and solvent molecules are not strong, and the high pressure due to newly added solvent vapor purges the original solvent molecules easily. Another point is a size effect of solvent molecules. The effective volume of the solvent used here is 86 Å^3 for toluene, 73 Å^3 for benzene, 61 Å^3 for chloroform, and 54 Å^3 for acetone. In this way the effective volume is largely different from each other, but the solvent exchange occurs quite smoothly and almost commonly for any pair of the used solvents.

Such smooth and rapid solvent exchange might originate from the morphological effect intrinsic of polymer material. For example, when the crystallite size or the lamellar thickness is very thin and the chain packing in the crystal lattice is not perfect, the solvent exchange might occur relatively easily. The degree of crystallinity might affect the solvent-exchange rate. The solvent may penetrate and diffuse relatively easily into the sample with low degree of crystallinity and with imperfect crystallites. If such morphology of the δ form is different depending on the solvent used, the solvent-exchange rate or the solvent-exchange timing might be different more or less. The slight difference of exchange rate detected in Figure 4 among the pairs of solvents (for example, toluene−chloroform and benzene−chloroform) might come from such a morphological effect. At the same time, however, we need to notice that the pair of toluene−chloroform and that of chloroform−toluene, for example, gave essentially the same exchange rate as seen in Figure 4a,c. The same thing can be said also to the set of benzene−chloroform and the set of benzene−toluene. This means that, even when the morphology or crystallinity of the starting δ sample might be different depending on the kind of absorbed solvent, there may exist some characteristic feature which should be the rate-determining stage of this solvent-exchange phenomenon. We speculate that this might be a characteristic feature of the crystal structure of the δ form. As shown in Figure 7, the δ form consists of the columnar structure of sPS chain stems, and the solvent molecules are trapped in these columns. As a possibility we may speculate, as illustrated in Figure 8, that an outer solvent A (for example, toluene) approaches the surface of δ form crystallite, and then the distance between the neighboring T_2G_2 chain stems is slightly increased due to a swelling effect, resulting in a slight expansion of the column radius, just like an opening of gate. Then the solvent A can migrate into the tunnel and pushes out the solvent B (chloroform). After that the complex between original polymer stems and new solvent A is stabilized and the gate is closed again, where the columnar size is different from the original size because the kind of solvent is changed anymore. Another possible way of opening the gate is a cooperative movement of phenylene side groups of the sPS chain stems, which may make the column radius wider at a moment and allow the solvent molecules A to enter the columns smoothly. We cannot judge which model is better for the explanation of solvent-exchange phenomenon. Other different types of model might be there, of course. We have to perform any experiment to check these models, for example, the time-resolved X-ray diffraction measurement during the solvent-exchange process. Anyway, an easy exchange of solvents at almost common rate (Figure 4) is considered to come from such a unique columnar structure of the δ form.

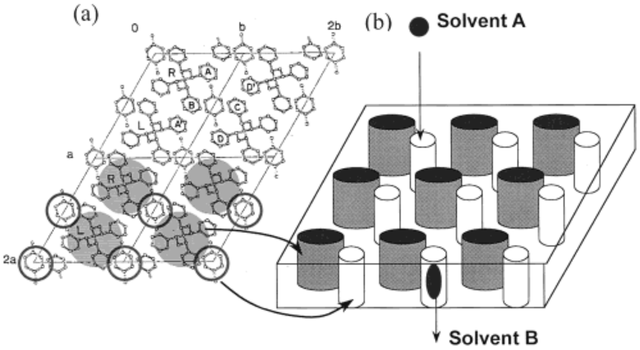

Figure 7. Schematic illustration of crystal structure of sPS δ(tol) form.[11] (a) The sPS chains create empty columns into which organic solvent molecules are trapped to form a complex. (b) Solvent molecule A is approaching the crystallite of δ(tol), and solvent molecule B is purged away. Dark-color poles are chain stems, and white poles are columns of solvents.

At the same time we need to take the weak interaction between polymer and solvent into consideration in such a discussion. As known from the observation that the infrared bands of solvent appear at slightly different frequency positions from those of pure liquid solvent, the interaction between polymer chains and solvent molecules cannot be ignored perfectly. But this shift is only several wavenumbers, and the spectral pattern of the trapped solvent is similar in the whole frequency region to that of the pure liquid, suggesting that the solvent molecules in the complex may behave like in the liquid state, although the half-width of the infrared band, which reflects the mobility of the molecules, is slightly narrower for the complex due to the limited thermal motion in the crystal lattice of the complex. Guerra et al. performed the molecular dynamics (MD) calculation about the diffusion of such small molecules as helium or carbon dioxide in the δ form lattice.[25] They found that carbon dioxide molecules penetrated into the crystal lattice along the columnar axis. Effective volume, molecular shape, and interaction with sPS chains might be different between carbon dioxide and organic solvents used in our experiment, but their MD calculation is quite suggestive for the interpretation of the solvent-

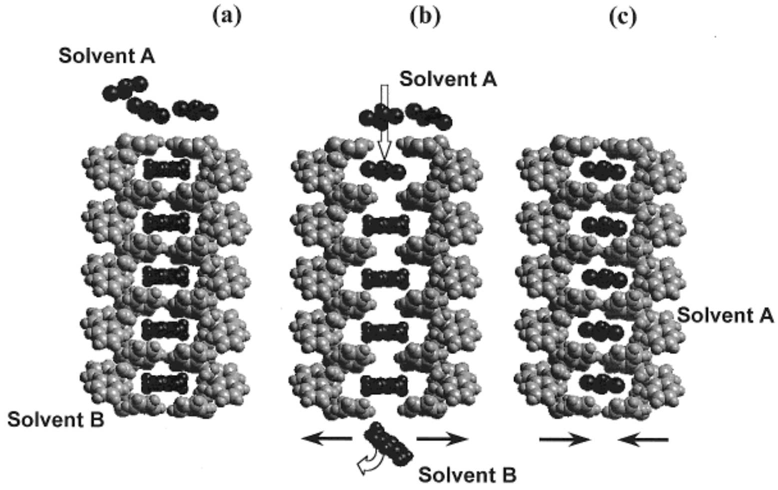

Figure 8. Illustration of solvent-exchange mechanism in sPS−solvent complex system. (a) New solvent (A) comes to the surface of the crystallite of the δ form containing solvent B. (b) The column created by sPS chain stems is expanded, and the originally existing solvent B is purged out. The new solvent A diffuses into the column. (c) The column is closed again, and the sPS−solvent A system is stabilized. The picture was drawn using Cerius^2 (Accelrys Inc.).

exchange phenomenon described in the present paper. We are now carrying out the molecular dynamics calculation for the sPS−organic solvent system to check our mechanism concretely.

In the previous section we pointed out the different observations in the solvent-exchange experiments between a pair of toluene and chloroform, for example, and a pair of toluene and acetone. In the former case the infrared bands in the 600 cm^{-1} region changed their positions apparently continuously between toluene and chloroform (see Figure 2). But, when toluene molecules were displaced by acetone, the infrared bands did not show any significant position shift as long as the sample was exposed in an acetone atmosphere (see Figure 6). The bands shifted to the positions characteristic of the δ_e form for the first time when the acetone evaporated away from the sample in the ambient atmosphere and the δ form transferred to the δ_e form. The toluene molecule has a larger volume (73 Å^3) than that of the acetone molecule (54 Å^3), and the interaction between sPS chain and acetone is much weaker than between sPS and toluene, as known from the lower solubility of sPS into acetone. Therefore, the column structure is speculated to be unchanged even when acetone molecules occupy the toluene spaces. When the acetone molecules evaporate from the sample, the crystal lattice changes immediately to the energetically stable δ_e form.

In the previous section we pointed out the slight but significant difference in X-ray diffraction profiles between δ(tol) and δ(chloro→tol), between δ(chloro) and δ(tol→chloro), and so on (see Figure 3). That is to say, the crystal lattice is not necessarily the same even after the solvent exchange occurs perfectly. According to the X-ray structure analysis,[5,11−13] the δ form is considered to have essentially the isomorphic structure with stoichiometric content of sPS monomeric units and solvent molecules (i.e., two chains and two organic molecules in the unit cell) for any kind of solvent used in the present paper, but the cell parameters are varied depending on the kind of solvent. Therefore, the δ(tol) and the δ(chloro→tol) should show the same X-ray diffraction profile as long as the solvent is fully absorbed into the crystalline region. (The perfectness of solvent exchange was checked by the infrared spectral measurement.) The actually observed slight different in X-ray diffraction profile may come from the difference in the morphology of the starting sample, as discussed in the previous section. For example, the crystal lattice parameters of orthorhombic polyethylene are known to be affected quite sensitively by a slight difference in sample preparation condition.[31−33] The similar situation might occur in the sPS−solvent system. Anyway, this problem is important for understanding the characteristic morphological feature of polymer material.

Thermally Induced δ-to-γ Phase Transition. As stated in the introductory section, the δ form transfers to the γ form by heating above 150 °C. Figure 9 shows the temperature dependence of infrared spectra starting from the δ form [δ(tol)]. As the temperature increased, the bands characteristic of the δ form decreased in intensity and the bands of toluene molecules decreased in parallel. As the toluene band intensity decreased to some extent, the bands of the γ form increased instead (see Figure 9a). It should be emphasized here that some infrared bands intrinsic of the γ from could be distinguished from those of the δ and δ_e forms, although most of the bands are common to these three forms.[18,30] Around 120 °C the bands of the δ form and toluene molecules disappeared almost perfectly, and the γ bands were mainly observed. As the temperature increased furthermore, the bands of the γ form decreased steeply in a narrow temperature range of 190 °C and those of the α form increased instead (see Figure 9b). The integrated intensity was evaluated for several bands characteristic of each form through the spectral deconvolution method[23] and was plotted against temperature as shown in Figure 10. The α bands disappeared above 250 °C due to the melting of the sample. As seen from Figure 10, the transition from δ to γ form occurs in a wide temperature region, different from the sharp transition from γ to α form.

As mentioned already, bands in the 500−600 cm^{-1} region are sensitive to the crystalline forms. As shown in Figure 11a, these bands were found to change only between the δ and γ forms in the transition region of 80−120 °C. No bands intrinsic of the δ_e form appeared on the way of transition from δ to γ form, even when the infrared spectra were measured at a resolving power of 1 cm^{-1}. When the infrared absorbance of the γ form is plotted against that of the δ form, this plot gives a

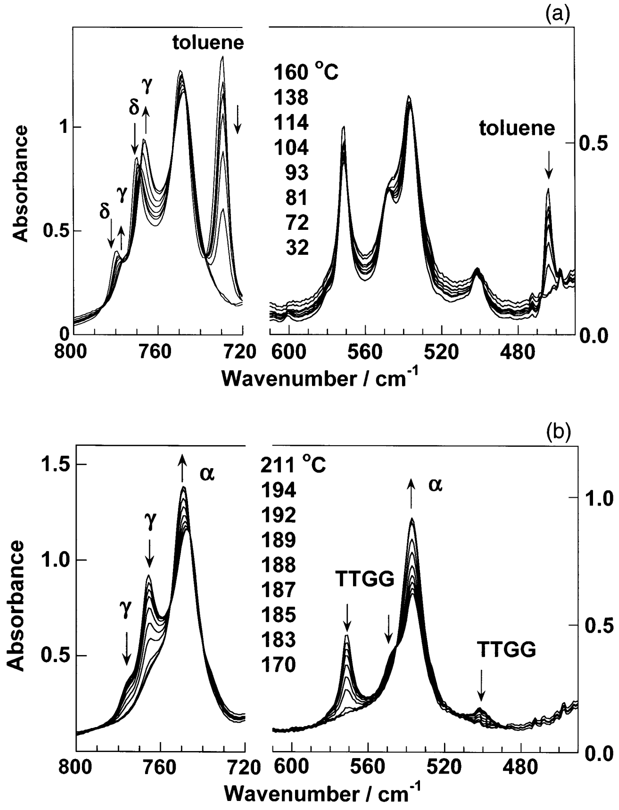

Figure 9. Temperature dependence of infrared spectra of δ(tol) form measured in the heating process: (a) 32−160 °C and (b) 170−211 °C.

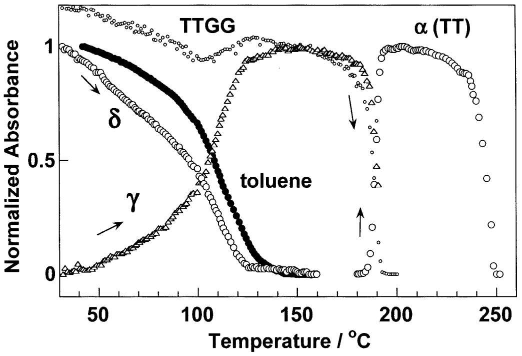

Figure 10. Temperature dependence of infrared absorbance estimated for the bands characteristic of δ, γ, and α forms and toluene.

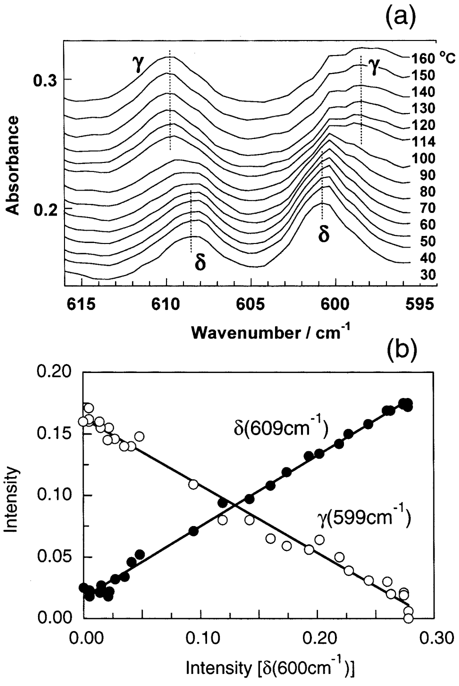

Figure 11. (a) Temperature dependence of infrared spectra measured in the phase transition from δ(chloro) to γ form caused by heating. (b) Integrated intensities of the 609 cm^{-1} δ band and 599 cm^{-1} γ band plotted against the intensity of the 600 cm^{-1} band of the δ form.

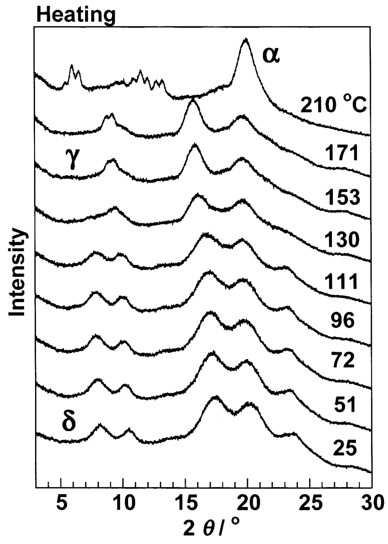

Figure 12. Temperature dependence of X-ray diffraction profile in the heating process from δ(tol) to γ form and to α form.

straight line as shown in Figure 11b, indicating that the transition occurs between only the two crystalline phases without appearance of any such intermediate phase as δ_e form.[34,35] The similar phenomenon could be found also in the X-ray diffraction measurement. Figure 12 shows the temperature dependence of the X-ray diffraction profile in the heating process from the δ form [δ(tol)]. The pattern changed from δ to γ form in the temperature region of 80−120 °C. The intensities evaluated for infrared bands and X-ray diffractions are plotted against temperature in Figure 13. The infrared and X-ray data are quite consistent with each other, and a clear phase transition was observed between the δ and γ forms. A similar observation was made by Gowd et al., who analyzed the temperature-dependent X-ray diffraction profiles in the δ-to-γ transition process.[24] In this way, the crystallite of the δ form transfers to that of the γ form immediately once the solvent molecules are evaporated. But the crystallite size (or even the domain size in the crystallite) has a broad distribution, and so the evaporation temperature of solvent may be different depending on the crystallite (or domain) size, resulting in the transition in a wide temperature range (Figure 10).

The intensity of the solvent band is plotted against temperature for the various types of δ form as shown in Figure 14. The intensity decreased with increasing temperature. The decreasing rate is different among the various solvents possibly due to the difference in molecular size of solvent, interaction strength between sPS and solvent, and/or the sample morphology, but the temperature region where these bands almost perfectly disappeared was found to be common to all the samples,

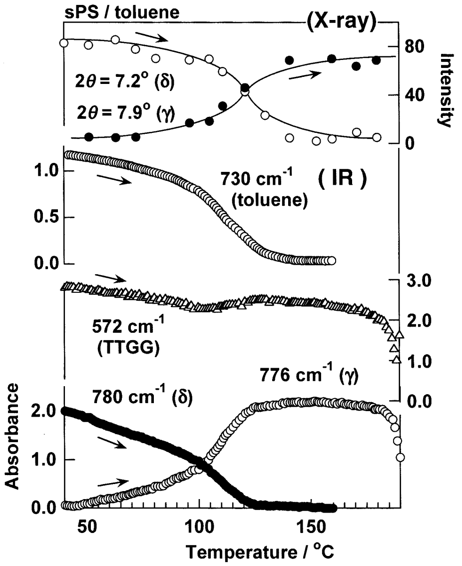

Figure 13. Temperature dependence of X-ray diffraction intensity and infrared band absorbances estimated for the δ and γ forms in the heating process from 40 to 200 °C.

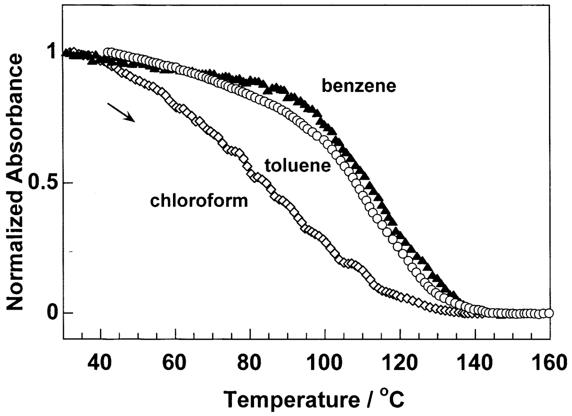

Figure 14. Comparison of the temperature dependence of infrared band intensity estimated for the sPS δ form samples containing benzene, toluene, and chloroform (refer to Figure 10).

about 130−140 °C. This observation suggests that the evaporation of solvent molecules from the δ form occurs in almost the same temperature region irrespective of the type of the used solvent molecules, as already pointed out by Gowd et al.[24] In the section of solvent-exchange experiment we found that the exchange rate was almost common to the various kinds of solvent. In the solvent evaporation phenomenon discussed here also the evaporation behavior was similar to all the samples. Therefore, as one possibility, we might speculate that the columnar model proposed for the solvent-exchange phenomenon could be reasonably applied here also (Figure 7). By increasing temperature, the radius of column is expanded to some extent, and the thermally activated solvent molecules escape easily along the columnar axis because the polymer−solvent interactions are weak. As a result, the crystal lattice of the δ form may change *transiently* to that of the δ_e form, but the latter transfers immediately to more stable γ form. Therefore, the δ_e form could not be caught in the infrared and X-ray diffraction measurements.

In this way the unique columnar structure of the δ form and the weak intermolecular interactions between polymer and solvent allow us to make a reasonable interpretation about the transition phenomena common to the various types of solvent: the solvent-exchange phenomena and the thermally induced δ-to-γ transition.

Conclusions

In the present paper we measured the time and/or temperature dependence of infrared spectra and X-ray diffraction to investigate the solvent-exchange phenomenon of the sPS δ form and the thermally induced phase transition between the δ and γ forms. The solvent exchange between the original solvent and newly added solvent was found to occur quite easily at room temperature. This could be observed for *any pair of solvents used here*. The solvent molecules also escaped from the δ form by heating to give the γ form. This phenomenon was observed *in almost the same temperature region* irrespective of the kind of solvent absorbed in the original δ form. These two phenomena were speculated to come from the unique crystal structure of the δ form. The aggregation of sPS chains of TTGG conformation forms a columnar structure, and the solvent molecules are trapped in these columns. By heating or by supplying new solvent, the original solvent molecules are purged away easily along the columnar axis because of the relatively weak intermolecular interactions between sPS chains and solvent molecules. In the process of solvent exchange from toluene to acetone, the columnar structure of δ(tol) form is not modified very much even when acetone molecules invade the columns, but the δ(tol) changes to δ_e form for the first time when acetone is evaporated from the sample. To check the mechanism of solvent evaporation from the columnar structure, we are now carrying out a molecular dynamics calculation. Of course, we must not forget the morphological effect on the phenomena observed here. The slight differences in the solvent-exchange curves (Figure 4) and in the X-ray diffraction profile (Figure 3) between the different pairs of solvents might come from such a morphological effect. A detailed study is needed anyway.

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References and Notes

(1) Daniel, C.; Guerra, G.; Musto, P. *Macromolecules* **2002**, *35*, 2243.
(2) van Hooy-Corstjens, C. S. J.; Magusin, P. C. M. M.; Rastogi, S.; Lemstra, P. J. *Macromolecules* **2002**, *35*, 6630.
(3) Musto, P.; Manzari, M.; Guerra, G. *Macromolecules* **2000**, *33*, 143.
(4) Goossens, H.; Rastogi, S.; Lemstra, P. *Macromol. Symp.* **1999**, *138*, 99.
(5) De Rosa, C.; Rizzo, P.; de Ballesteros, O. R.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103.
(6) Tsutsui, K.; Katsumata, T.; Fukatsu, H.; Yoshimizu, H.; Kinoshita, T.; Tsujita, Y. *Polym. J.* **1999**, *31*, 268.
(7) Tsutsui, K.; Katsumata, T.; Yamamoto, Y.; Fukatsu, H.; Yoshimizu, H.; Kinoshita, T.; Tsujita, Y. *Polymer* **1999**, *40*, 3815.
(8) Guerra, G.; Manfredi, C.; Musto, P.; Tavone, S. *Macromolecules* **1998**, *31*, 1329.
(9) Moyses, S.; Sonntag, P.; Spells, S. J.; Laveix, O. *Polymer* **1998**, *39*, 3537.
(10) Rastogi, S.; Goossens, J. G. P.; Lemstra, P. J. *Macromolecules* **1998**, *31*, 2983.
(11) Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620.
(12) Chatani, Y.; Inagaki, T.; Shimane, Y.; Shikuma, H. *Polymer* **1993**, *34*, 4841.
(13) Chatani, Y.; Shimane, Y.; Inoue, Y.; Inahaki, T.; Ishioka, T. *Polymer* **1992**, *33*, 488.

(14) Vittoria, V.; Russo, R.; de Candia, F. *Polymer* **1991**, *32*, 3371.
(15) Vittoria, V.; Filho, A. R.; de Candia, F. *Polym. Bull.* **1991**, *26*, 445.
(16) Guadagno, L.; Baldi, P.; Vittoria, V.; Guerra, G. *Macromol. Chem. Phys.* **1998**, *199*, 2671.
(17) De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. *Macromolecules* **1997**, *30*, 4147.
(18) Moyses, S.; Spells, S. J. *Macromolecules* **1999**, *32*, 2684.
(19) Tsutsui, K.; Tsujita, Y.; Yoshimizu, H.; Kinoshita, T. *Polymer* **1998**, *39*, 5177.
(20) De Candia, F.; Cartenuto, M.; Guadagno, L.; Vittoria, V. *J. Macromol. Sci., Phys.* **1996**, *B35*, 265.
(21) Wang, Y. K.; Savage, J. D.; Yang, D.; Hsu, S. L. *Macromolecules* **1992**, *25*, 3659.
(22) Tashiro, K.; Yoshioka, A. *Macromolecules* **2002**, *35*, 410.
(23) Tashiro, K.; Ueno, Y.; Yoshioka, A.; Kobayashi, M. *Macromolecules* **2001**, *34*, 310.
(24) Gowd, E. B.; Nair, S. S.; Ramesh, C. *Macromolecules* **2002**, *35*, 8509.
(25) Milano, G.; Guerra, G.; M.-Plathe, F. *Chem. Mater.* **2002**, *14*, 2977.
(26) Mori, S.; Amutharani, D.; Yamamoto, Y.; Tsujita, Y.; Yoshimizu, H. *Polym. Prepr. Jpn.* **2002**, *51*, 2592.
(27) Manfredi, C.; de Rosa, C.; Buerra, G.; Rapacciuolo, M.; Auriemma, F.; Corradini, P. *Makromol. Chem. Phys.* **1995**, *196*, 2795.
(28) De Candia, F.; Guadagno, L.; Vittoria, V. *J. Macromol. Sci., Phys.* **1995**, *B34*, 95.
(29) Naddeo, C.; Guadagno, L.; Aciemo, D. *Macromol. Symp.* **1999**, *138*, 209.
(30) Yoshioka, A.; Tashiro, K. *Macromolecules*, in press.
(31) Chatani, Y.; Ueda, Y.; Tadokoro, H. *Rep. Prog. Polym. Phys. Jpn.* **1977**, *20*, 179.
(32) Tadokoto, H. In *Fiber Diffraction Methods*; French, A. D., Gardner, K. H., Eds.; ACS Symposium Series 141; American Chemical Society: Washington, DC, 1980; p 43.
(33) Tashiro, K.; Ishino, K.; Ohta, T. *Polymer* **1999**, *40*, 3469.
(34) Tashiro, K.; Nakai, Y.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1980**, *13*, 137.
(35) Tashiro, K.; Kamae, T.; Kobayashi, M.; Matsumoto, A. *Macromolecules* **1999**, *32*, 2449.

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