



Guest exchange process in syndiotactic polystyrene thin films measured by ATR-FTIR spectroscopy

Yukihiro Uda, Fumitoshi Kaneko*, Tatsuya Kawaguchi

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received 17 October 2003; received in revised form 21 January 2004; accepted 4 February 2004

Abstract

Guest exchange and desorption processes in syndiotactic polystyrene(sPS)-solvent complex systems (δ form) were studied by means of ATR-FTIR spectroscopy. The intensities of the bands sensitive to the amount of guest molecules and the conformational order of sPS were followed to clarify the mechanism on the guest exchange. Rapid exchange of the guest molecules was observed on the exposure of the δ form sample to toluene and chloroform vapors. The desorption of guest molecules occurs in two stages, which correspond to the rapid desorption mainly from the amorphous region and the slow desorption mainly from the crystalline region, respectively. The diffusion coefficients of the desorbate molecules were evaluated. The time dependence of the intensities of the sPS bands showed that the conformational regularity of sPS changed during the guest exchange process, and the behavior depended on the combination of sorbate and desorbate.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Syndiotactic polystyrene; Complex; ATR-FTIR spectroscopy

1. Introduction

It is well known that some polymers interact with specific solvent molecules strongly and form characteristic aggregation states such as micelles, physical gels and inclusion complexes. These polymer–solvent superstructures present properties suitable for multiple technological applications [1,2].

Syndiotactic polystyrene(sPS)-solvent complex (δ form) has become of interest in recent years, where guest molecules are included in the cavities between sPS helices. It has been shown that the guest molecules are adsorbed in the cavities even when at low vapor activities [3–6]. Furthermore, it is suggested that the cavities memorize guest size and properties [3,4]. Some possible applications of this property of sPS such as chemical separations and water purification have been recently pointed out [7,8].

Syndiotactic polystyrene(sPS) has several crystalline phases: the α and β forms containing planar zigzag chains and the γ , δ and emptied δ forms containing helical chains of TTGG conformation. The δ form can be obtained by solvent casting or sorption of suitable compounds into

amorphous or semicrystalline sPS samples. The crystal structures of the δ form including toluene and iodine have been described by Chatani et al. [9,10]. Recently, De Rosa et al. have revealed the structure of the δ form containing 1,2-dichloroethane [11]. The δ form is stable at room temperature. By annealing the δ form above 120–130 °C, the guest molecules are evaporated, and the δ form is transformed to the γ form in which molecular conformation is still TTGG [9]. The γ form is transformed to the α form by rise of temperature. The emptied δ form in which guest molecules are removed from the cavities can be obtained by extraction of the δ form with boiling acetone [12,13]. By a novel stepwise extraction method with acetone and methanol, more perfect emptied δ form can be obtained [14].

The solvent-induced crystallization of the δ form has attracted attention [15–19]. When suitable solvent molecules are absorbed in the glassy samples of sPS, the crystallization of δ form is induced. Moreover, the crystalline phases, γ and empty δ absorb solvent molecules to transform into the δ form. Although there have been many studies on the sorption behavior of solvent molecules into the amorphous or crystalline phases of sPS, very few attempts have been carried out on the solvent sorption into the δ form. The peculiarity of the solvent sorption into the δ

* Corresponding author. Tel.: +81-656-054-53; fax: +81-656-052-88.
E-mail address: toshi@chem.sci.osaka-u.ac.jp (F. Kaneko).

form is that it is inevitably accompanied with the desorption of guest molecules initially present in the δ form. So it is important for a comprehensive understanding to investigate not only the sorption behavior of solvents but also the desorption of the guests.

Chatani et al. reported that the X-ray fibre pattern of the δ form was changed on exposure to a different kind of solvent [20]. They suggested that the guest was replaced with solvent molecules, but did not describe the details of this phenomenon. There are few studies about the replacements of the guest molecules in the δ form sample after their study and the mechanism of guest exchange has not been fully elucidated yet.

Our aim of this work is to confirm the replacement of guest molecules and to reveal the mechanism of the guest exchange process. It is useful for the analysis of a guest exchange process to follow the variations in the amounts of guest molecules and structural changes of sPS chains simultaneously. FTIR spectroscopy is a suitable technique for this purpose. Infrared spectra of the δ form contain not only the bands due to sPS but also the ones due to the guest molecules, and some of the former bands are sensitive to the conformational order of the sPS chains. By monitoring the intensities of these bands, we can grasp how the guest exchange proceeds in the δ form.

When applied to the guest exchange processes of polymer films, the ordinary IR transmission method has a problem; both solvent molecules in the vapor phase and those in the polymer film appear in IR spectrum and the extraction of the information about the latter from the spectrum is very difficult. The attenuated total reflection (ATR)-FTIR spectroscopy is a convenient method to avoid this obstacle. Since ATR-FTIR spectroscopy uses the evanescent waves generated in specimens, only the solvent molecules in the film actually contribute to IR spectra.

In this paper, we will describe the results of the desorption of guest molecules from the δ form and the guest exchange process in the δ form and discuss the difference of desorption behavior of guest molecules in two processes.

2. Background

2.1. Diffusion model

The equation for the analysis of Fickian diffusion of a penetrant through a thin film polymer sample using the ATR-FTIR method has been developed by Fieldson and Barbari and by Balik et al. [21–26]. When total reflection of a light beam occurs at the boundary between an ATR crystal and a polymer film, a standing electric field called an evanescent wave is generated in the film. The amplitude, E , decays exponentially with distance from the polymer

surface, z , as shown in Eq. (1),

$$E = E_0 \exp\left(-\frac{z}{d_p}\right) \quad (1)$$

where E_0 is the evanescent field amplitude at the polymer surface, and d_p is the penetration depth of the evanescent wave into the sample.

The absorbance of a film of thickness L deposited on a ATR crystal can be given by:

$$A = \int_0^L N \varepsilon^* C E_0^2 \exp(-2\gamma z) dz \quad (2)$$

where ε^* is the effective extinction coefficient, N is the number of total reflections, C is the concentration of the penetrant and $\gamma = 1/d_p$.

For one-dimensional molecular desorption from a polymer film with a constant diffusion coefficient, the concentration profile is given by Eq. (3) with following assumptions, $C = C_0$ at $t = 0$ for $0 < z < L$, $C = 0$ at $t > 0$ for $z = L$ and $\partial C/\partial z = 0$ at $t > 0$ for $z = 0$.

$$\frac{C}{C_0} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right] \times \cos\left[\frac{(2n+1)\pi z}{2L}\right] \quad (3)$$

where C_0 is the initial concentration of the penetrant and D is the diffusion coefficient of the penetrant.

Substituting Eq. (3) into Eq. (2) and eliminating all terms in the series beyond the first, gives

$$\frac{A_t}{A_0} = \frac{8\gamma}{\pi[1 - \exp(-2\gamma L)]} \times \left[\frac{\exp\left(\frac{-D\pi^2 t}{4L^2}\right) \left(\frac{\pi}{2L} \exp(-2\gamma L) + (2\gamma)\right)}{\left(4\gamma^2 + \frac{\pi^2}{4L^2}\right)} \right] \quad (4)$$

where A_0 is the absorbance at starting point ($t = 0$ s).

If condition of Eq. (5) is fulfilled, Eq. (4) can be reduced to the expression in Eq. (6)

$$1 \gg \exp(-2\gamma L) \quad (5)$$

$$\ln\left(\frac{A_t}{A_0}\right) = \ln\left(\frac{64\gamma^2 L^2}{\pi(16\gamma^2 L^2 + \pi^2)}\right) - \frac{D\pi^2}{4L^2} t \quad (6)$$

In the plot of the logarithm of A_t/A_0 against time, the slope obtained by a linear least squares regression yields the diffusion coefficient, D according to Eq. (6). The diffusion coefficients, D obtained from this procedure agree well with values determined gravimetrically [22,24].

2.2. Critical sequence length

The infrared bands of crystalline polymers vary greatly

in the sensitivity to the conformational order of polymer chains. Kobayashi proposed the concept of the critical sequence length (CSL) which is defined as the shortest length of the sequence of a particular conformation necessary for the appearance of the band [27]. The values of CSL (represented by the number of monomeric residues m constituting the sequence) for various IR bands of sPS were evaluated through the intramolecular isotope dilution technique. In this study, the following two bands characteristic of TTGG sequences were used to monitor the conformational state of sPS chains, 571 cm^{-1} band with $m = 20\text{--}30$ and 548 cm^{-1} band with $m = 7\text{--}12$ [18].

3. Experimental

3.1. Preparation of polymer thin films

Syndiotactic polystyrene (sPS) was kindly supplied by Idemitsu Petrochemical Co., Ltd. The weight average molecular weight was $M_w = 197,000$ ($M_w/M_n = 1.98$).

Thin films of the δ form were prepared from chloroform or toluene solutions on an ATR crystal ($27.7 \times 10 \times 3\text{ mm}^3$) by spin coating at 1000 rpm. The thickness of the films was determined by comparing the absorbance of 1069 cm^{-1} band (ring mode of sPS) in transmission spectrum with that of the free-standing films of known thickness.

3.2. ATR-FTIR measurements

ATR-FTIR spectra were taken with a BIO-RAD FTS-60A FT-IR spectrometer equipped with a MCT detector at a resolution of 2 cm^{-1} . A prism of KRS-5 with a 60° bevel was used. The apparatus used is illustrated in Fig. 1. The inlet and outlet ports of the aluminum block are connected to Teflon tubing with Swagelok fittings. This system is composed of two pathways of solvent vapor, each of which

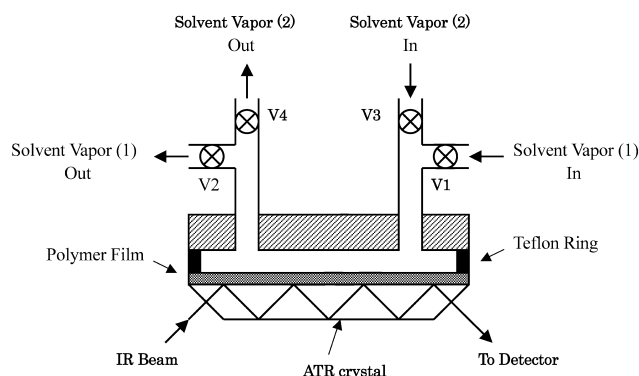


Fig. 1. Schematic of the apparatus for ATR-FTIR measurement. Solvent vapor (1) is the vapor of casting solvent (desorbate). Solvent vapor (2) is the vapor of solvent (sorbate) for the guest exchange measurement and air for the desorption measurement.

consists of a solvent reservoir and a circulating pump. In order to ensure that the circulating air is saturated with solvent vapor in the system, air is bubbled through the solvent in the reservoir at least for 5 min before the beginning of exposure of the sample. The sealing between the inner surface of the block and the ATR crystal is achieved by use of a Teflon ring.

The experimental procedure for guest exchange processes is as follows. Until the start of the exposure to a solvent vapor (sorbate), a specimen was kept in the vapor of casting solvent to prevent the desorption of solvent molecules (desorbate) from the specimen, by setting valves V1 and V2 open and V3 and V4 close. The exposure to the solvent (sorbate) in the reservoir was started by opening V3 and V4 and closing V1 and V2. ATR-FTIR spectra were measured at 1 s intervals. All the experiments were conducted at room temperature.

To separate a multicomponent band into individual peaks, curve fitting was done using mixed Gaussian and Lorentzian functions. The root mean square deviations of the spectra from the fitted curves were less than 0.002. The errors for the values A/A_0 of TTGG and amorphous bands were estimated to be less than 3 and 8%, respectively.

4. Results

4.1. Desorption of guest molecules from the δ form

Fig. 2 shows the ATR-FTIR spectral change of the δ form film containing chloroform ($\delta(\text{chloroform})$) on exposure to air. Just after the initiation of the exposure, the chloroform band at 1219 cm^{-1} decreased in intensity remarkably. The intensity was reduced within the first 5 s to one-half of the initial value (A_0 : the intensity at $t = 0$), and then decreased slowly as shown in Fig. 3.

The bands due to sPS showed a change in intensity (Fig. 2(b)). The region from 520 to 560 cm^{-1} can be decomposed into three bands as shown in Fig. 4, a broad band due to amorphous components around 541 cm^{-1} and two bands due to TTGG sequences at 535 and 548 cm^{-1} [28–32]. Fig. 3 shows the time dependence of the intensities of the TTGG bands at 571 and 548 cm^{-1} and the amorphous band at 541 cm^{-1} . As the chloroform band became weak, these TTGG bands decreased in intensity, while the amorphous band increased in intensity. The extent of the intensity decrease of the TTGG bands depended on the critical sequence length. The band at 548 cm^{-1} with $m = 7\text{--}12$ started to decrease in intensity soon after the beginning of the exposure, while the band at 571 cm^{-1} with $m = 20\text{--}30$ exhibited a long term intensity depression.

These results indicate that chloroform molecules are desorbed gradually from the δ form film on exposure to air, and the TTGG conformation stabilized by chloroform

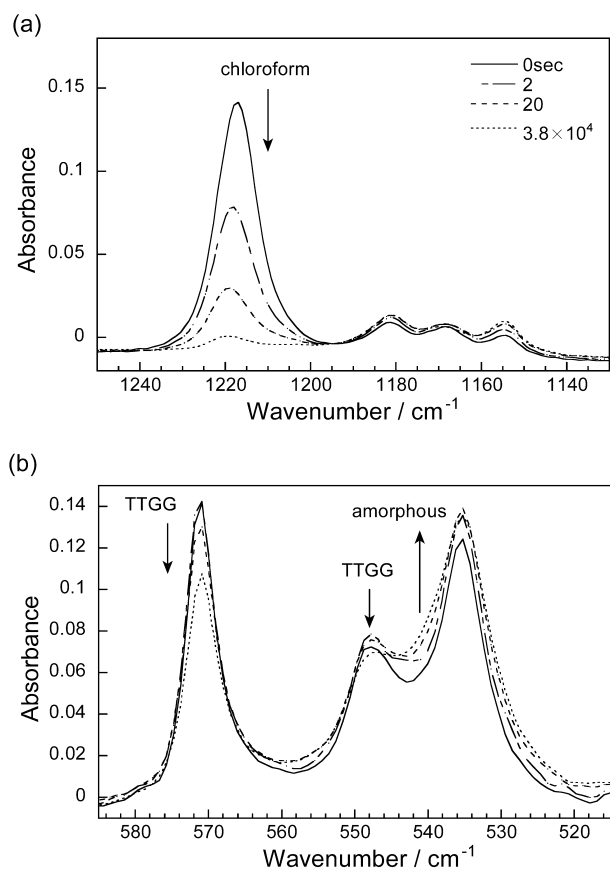


Fig. 2. ATR-FTIR spectral change of the δ form (complex with chloroform) exposed to air: (a) $1130\text{--}1250\text{ cm}^{-1}$ region (b) $515\text{--}585\text{ cm}^{-1}$ region.

molecules becomes partly disordered, especially in short TTGG sequences.

Similar spectral changes were observed in the δ (toluene) system as shown in Fig. 5, though the desorption of toluene molecules took a longer time than that of chloroform.

4.2. Guest exchange process in the δ form

4.2.1. δ (Chloroform)/toluene system

Fig. 6 shows the ATR-FTIR spectral change of the δ (chloroform) film on exposure to toluene vapor. The time dependence of the intensities of the bands due to toluene, chloroform, TTGG sequences and amorphous of sPS is shown in Fig. 7. The intensity of toluene is normalized with its value at the final stage. The intensity of the toluene band started to increase immediately after the initiation of the exposure, and that of the chloroform band started to decrease. The desorption rate of chloroform was much faster on exposure to toluene than on exposure to air. Although it took about 2000 s before the intensity of the chloroform band reduced to 20% of its initial value when the film was exposed to air, it took only 3 s in this case. This result indicates that the penetration of toluene molecules into the film promotes desorption of chloroform molecules from the film. On the other hand, a rise in intensity took

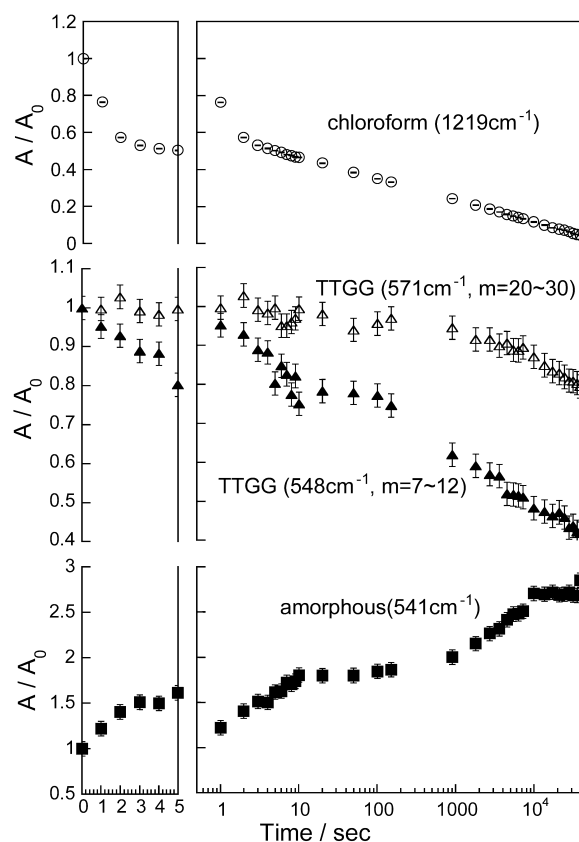


Fig. 3. Time dependence of the intensity of the bands of chloroform, TTGG sequences and amorphous when the δ form (complex with chloroform) was exposed to air. The intensities were normalized with the intensities at starting point ($t = 0$ s).

place for the 548 cm^{-1} band. The increment of intensity was greater in the 548 cm^{-1} band with small m -value than the 571 cm^{-1} band with large m -value. An intensity decrease was observed for the amorphous band. These spectral changes suggest that amorphous segments transform to a certain extent into the complex containing toluene molecules as chloroform molecules are replaced with toluene molecules in the film.

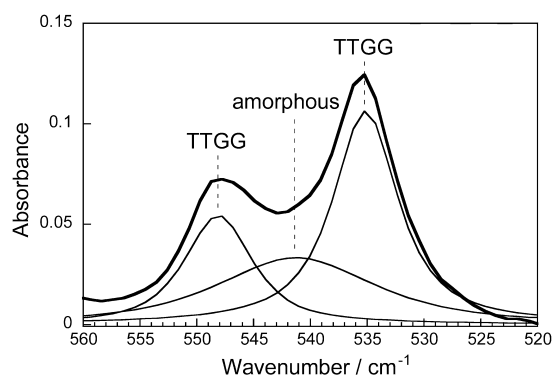


Fig. 4. An example of curve-fitting of the ATR-FTIR spectra of the δ form sample in the frequency range $520\text{--}560\text{ cm}^{-1}$.

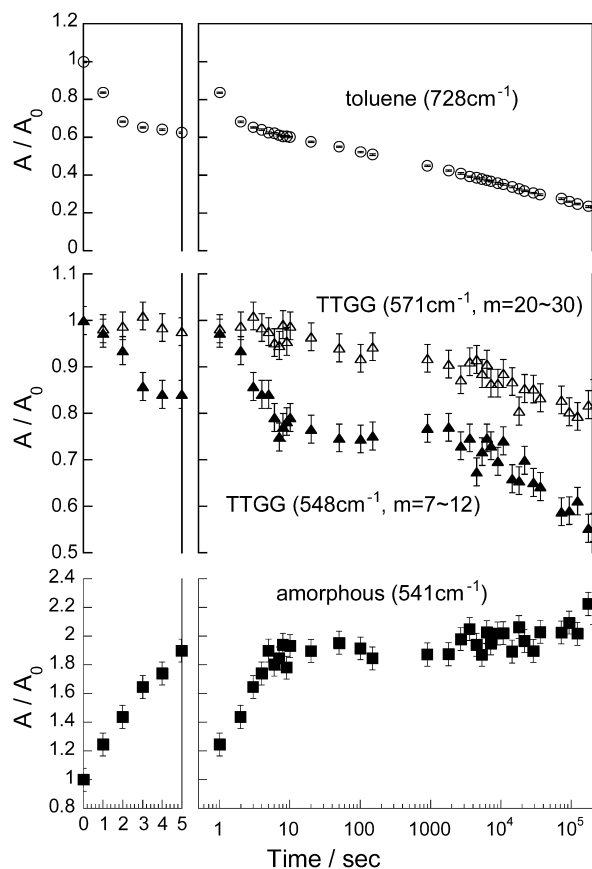


Fig. 5. Time dependence of the intensity of the bands of toluene, TTGG sequences and amorphous when the δ form (complex with toluene) was exposed to air.

4.2.2. δ (Toluene)/chloroform system

On exposure to chloroform vapor, the δ (toluene) film showed the intensity changes of the bands due to TTGG segments, amorphous and solvents as shown in Fig. 8. Although the sorption and desorption behaviors of δ (toluene)/chloroform system were similar to those of the δ (chloroform)/toluene one, the desorption rate of toluene in the initial stage was lower than that of chloroform as shown in Fig. 9. Furthermore, δ (toluene)/chloroform system exhibited characteristic intensity variations of the sPS bands. The TTGG band at 548 cm^{-1} with $m = 7\text{--}12$ decreased in intensity up to 5 s and then increased in intensity gradually, while the TTGG band at 571 cm^{-1} with $m = 20\text{--}30$ remained almost unchanged throughout the whole process. On the other hand, the intensity of the amorphous band increased immediately after the start of exposure, and then decreased soon.

From these spectral changes, we infer the following structural changes. Short helical segments are partly destroyed when chloroform molecules penetrate into the film, and then begin to re-form with chloroform molecules. On the other hand, the conformational regularity of the longer helical segment is kept during the guest exchange process.

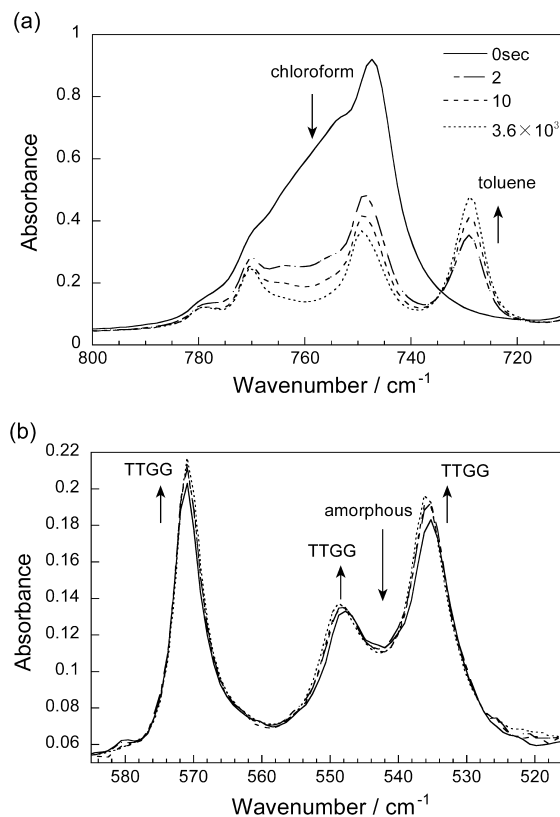


Fig. 6. ATR-FTIR spectral change of the δ form (complex with chloroform) exposed to toluene.

5. Discussion

5.1. Influence of film thickness

According to the previous studies, it follows that the guest desorption from the δ form is not detectable in several hours, though they can be easily removed by heating or soaking into suitable solvent [12–14,33–36]. However, we observed a smooth desorption from the δ form on exposure to air in this study. The discrepancy can be attributed to a large difference in film thickness; we used films of $2\text{ }\mu\text{m}$ in this study, in contrast to several tens to hundreds μm in thickness in the previous studies. Assuming that desorption exhibits Fickian behavior, the desorption rate becomes 100 times faster when sample thickness becomes one-tenth. For this reason, the desorption of guest molecules was speedy enough to be detectable in this study.

Another possible factor that might promote the desorption of guest molecules is the influence of the free surface and interface between sPS and KRS-5 substrate on the structure of the thin films of the δ form. If the crystallinity is lowered, the diffusion of small molecules in thin films is accelerated, which results in the increase in the desorption rate. However, the influence of the surface and the substrate seem to be small as to the $2\text{ }\mu\text{m}$ -thick films used in the present study. There is no essential spectral difference between the transmission FTIR spectra of a free-standing

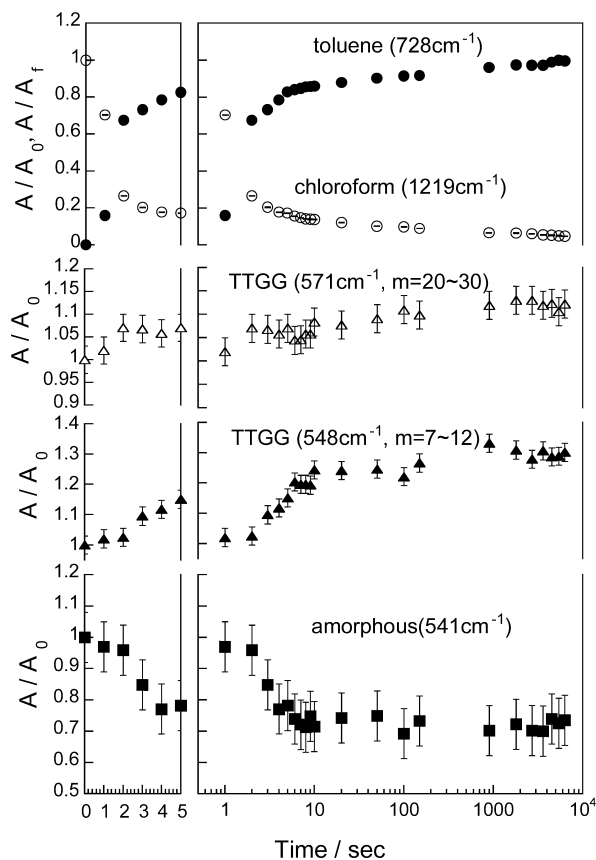


Fig. 7. Time dependence of the intensity of the bands of chloroform, toluene, TTGG sequences and amorphous when the δ form (complex with chloroform) was exposed to toluene. The intensities of chloroform, TTGG and amorphous were normalized with A_0 . The intensity of toluene was normalized with the intensity at the final stage (A_f).

20 μm -thick δ (chloroform) film and a 2 μm -thick δ (chloroform) film supported on KRS-5 prism. Generally, the effect of film thickness on the polymer structure appears for the films less than 100 nm thick [37,38]. Furthermore, no particular interaction such as hydrogen bonding and charge transfer is expected between sPS and KRS-5 substrate. Therefore, the effect of surface and substrate on the complex structure is thought to be negligible in 2 μm -thick films.

As described above, the great difference in desorption behavior between the present study and the previous studies can be attributed to the large difference in film thickness and explained by an usual desorption mechanism. In addition, it seems that there is no essential structural peculiarity in the 2 μm -thick films studied by ATR method. Therefore, we think that the results in this study are not specific to the thin films of sPS complex system but represent one of its characteristics of the sPS complex system.

5.2. Mechanism of guest desorption

The desorption rate of chloroform was much faster than that of toluene, which can be ascribed to the greater stability of toluene molecules in the cavities between sPS helices. It

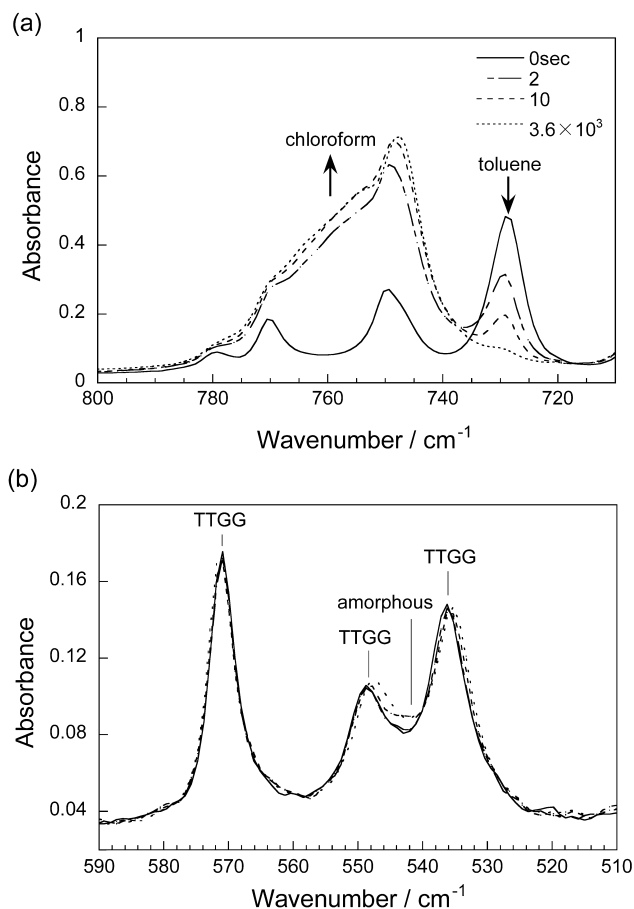


Fig. 8. ATR-FTIR spectral change of the δ form (complex with toluene) exposed to chloroform.

has been suggested that there exist strong interactions between sPS and molecules possessing an aromatic ring, such as benzene, toluene and xylene. For example, a small amount of addition of benzene to an sPS/chloroform solution accelerates the formation of TTGG sequences and subsequent gelation [39].

As shown in Figs. 3 and 5, the conformational order of sPS chains decreased as a result of guest desorption. However, when the intensity of the chloroform band decreased to 5% of its initial value, the TTGG band with $m = 20-30$ decreased only by 20% of its initial value, which indicates that a greater part of long TTGG helices are preserved on the desorption of guest molecules. The intensity depression of the band with small CSL ($m = 7-12$) was rather larger than that of the band with large CSL ($m = 20-30$). It seems that short TTGG helices in small crystallites or the intermediate region becomes disordered with the desorption of guest molecules, while long TTGG helices in relatively large crystallites keep their conformational regularity.

The intensity decrease of the solvent band in the first 2 s was much greater than that of the TTGG band with $m = 7-12$, which suggests that the intensity depression observed in the first 2 s is mainly due to the desorption from the

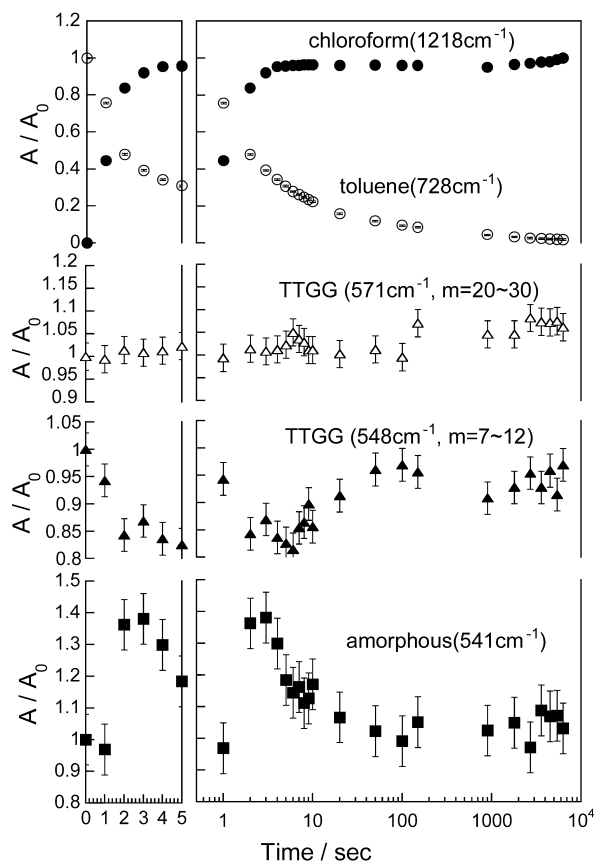


Fig. 9. Time dependence of the intensity of the bands of chloroform, toluene, TTGG sequences and amorphous when the δ form (complex with toluene) was exposed to chloroform.

amorphous region, but due to the desorption from a complex in the subsequent period.

5.3. Mechanism of guest exchange

5.3.1. Acceleration of desorption

Diffusion of small molecules in polymer matrixes becomes significantly slow below glass transition temperature (T_g) where the segmental motions of polymer chain are frozen. Since sPS has a T_g of about 100 °C, the rate of diffusion of small molecules seems to be low in sPS amorphous at room temperature. However, if a plasticizer is added to a polymer matrix, the diffusibility of polymer matrix is kept high even below original T_g . Solvent molecules usually act as a plasticizer for polymers.

As shown in Fig. 10, the guest molecules were desorbed much faster on exposure to a solvent vapor than on exposure to air. We consider that one of the reason for this difference is the diffusibility of molecules in the amorphous region of sPS samples. As the desorption in air proceeds, the concentration of guest molecules in sPS amorphous is lowered, and therefore, the guest molecules become more difficult to diffuse in the film. On the other hand, such a decrease of diffusibility would not occur on the desorption

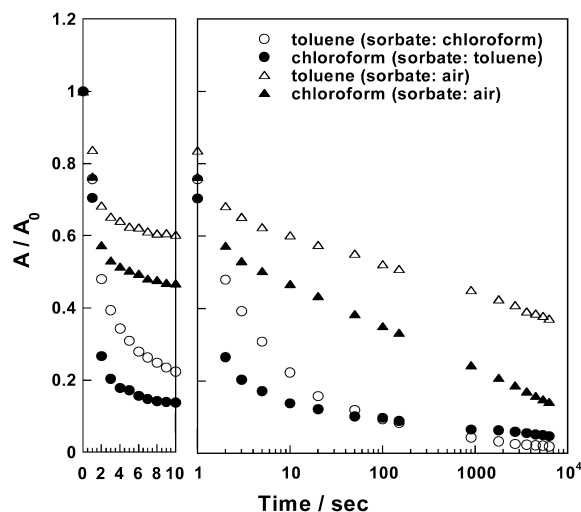


Fig. 10. Desorption behavior of the guest molecules initially included in the δ form samples on exposure to solvent vapor or air.

induced by the sorption of another kind of molecules, since the sorbate molecules act as a plasticizer.

Another reason for the rapid desorption would be the destruction of the complex by the sorbed molecules. The intensity reduction of the TTGG bands in the first several seconds in the δ (toluene)/chloroform system (Fig. 9) suggests that the complex of short TTGG helices are partly destroyed in the early period of the desorption. Therefore, we infer that the remarkable decrease of desorbate in the first several seconds on exposure to a solvent vapor results from the desorption not only from the amorphous region but also from the complex of short TTGG helices.

5.3.2. Influence of solvent molecules

As described in the section for the desorption in air, solvent molecules differ from each other in the strength of ability to form TTGG helices of sPS, and the ability of toluene is stronger than that of chloroform. This difference has a large influence on the structural changes of sPS helices on exposure to solvent vapor.

When a film of the δ (chloroform) was exposed to toluene vapor, the amount of the complex increased as chloroform molecules were replaced with toluene molecules; 30% of amorphous sPS transforms to TTGG sequences. The fact that the band with small CSL increased in intensity markedly compared with the band with large CSL (Fig. 7) suggests that the increase of a complex is not due to the thickening of crystal lamella but due to the formation of new short TTGG helices.

Another type structural changes of sPS took place on the guest exchange from toluene to chloroform, as shown in Fig. 9. Once the intensity of the amorphous band increased, but it gradually decreased to the initial value. The reverse intensity changes were observed for the TTGG band with small CSL, while no clear intensity changes were observed for the TTGG band with large CSL. From these spectral changes, the following processes can be deduced. The short

helices of the δ (toluene) complex collapse rapidly when more solvable chloroform molecules penetrate into a film, and then the sPS chains re-form complexes with surrounding chloroform molecules.

We infer that the difference between the above two cases can be attributed to the weak ability of chloroform to form complexes. It seems that the destruction and re-formation of the complex take place in both δ (toluene)/chloroform and δ (chloroform)/toluene systems. However, the weak complex formability of chloroform would retard the complex re-formation in the δ (toluene)/chloroform system, which results in an intensity increase of the amorphous band.

5.3.3. Diffusion behavior of guest molecules

We infer that the desorption consists of two different processes, the fast desorption and the slow desorption. The former process mainly contributes to the first stage, and the latter to the second stage. For each stage, the region which the guest molecules are desorbed from is different between the desorption in air and the guest exchange. In the desorption process on the exposure to air, the first stage is the desorption from the amorphous region and the second stage is from the complex. In the guest exchange process, the first stage is the desorption from the amorphous region and the complex of short TTGG helices and the second stage is from the complex of long TTGG helices. The diffusion coefficient of the slow process was evaluated by the method described below.

Assuming that the measured absorption intensity A_t at time t can be separated into two components due to the fast and slow processes, A_{ft} and A_{st} , we obtain the following relation.

$$\frac{A_t}{A_0} = \frac{A_{ft} + A_{st}}{A_{f0} + A_{s0}} \quad (7)$$

Here A_0 , A_{f0} and A_{s0} are intensities at $t = 0$. We also assume that the fast and slow processes follow Fick's second law and their diffusion coefficients, D_f and D_s satisfy the condition $D_f \gg D_s$. If A_{ft} becomes negligible compared with A_{st} , which is satisfied for $t > 100$ s in Fig. 10, Eq. (7) can be reduced to:

$$\frac{A_t}{A_0} = \frac{A_{st}}{A_0} \quad (8)$$

from Eq. (6) we obtain:

$$A_{st} = A_{s0} \frac{64\gamma^2 L^2}{\pi(16\gamma^2 L^2 + \pi^2)} \exp\left(-\frac{D_s \pi^2}{4L^2} t\right) \quad (9)$$

substituting Eq. (9) into Eq. (8) gives

$$\ln\left(\frac{A_t}{A_0}\right) = \ln\left(\frac{64\gamma^2 L^2}{\pi(16\gamma^2 L^2 + \pi^2)}\right) + \ln\left(\frac{A_{s0}}{A_0}\right) - \frac{D_s \pi^2}{4L^2} t \quad (10)$$

therefore, the value of D_s can be determined by plotting the

value of $\ln(A_t/A_0)$ as a function of time. The results are given in Table 1.

In the first stage, the desorption rate for the guest exchange process was larger than that for the desorption process in air and chloroform was desorbed faster than toluene as shown in Fig. 10. For the guest exchange process, the desorption of chloroform slowed down significantly; the D_s value of chloroform is smaller than that of toluene. It seems that the slow-down in the second stage is caused by the strong complex formability of the sorbate, toluene. On exposure of the δ (sPS/chloroform) film to toluene, the total amount of the complex helices increases by about 30% as chloroform is replaced with toluene. This leads to the increase of the crystallinity, and therefore, the diffusion coefficient D_s becomes smaller.

6. Conclusion

The desorption process of the guest molecules in the sPS-solvent complex (δ form) on exposure to air and also to a solvent vapor was studied with a film specimen of several microns in thickness through ATR-FTIR spectroscopy. Not only the variations of the amount of guest molecules but also the conformational state of sPS was followed with the bands sensitive to TTGG sequences in order to clarify the structural changes accompanying desorption and guest exchange.

On the exposure of a thin film of the δ form to air, a gradual desorption of the guest molecules was observed at room temperature. The TTGG sequences of sPS, in particular the short sequence, collapsed to some extent, as the desorption proceeded.

The exchange of the guest molecules started immediately after the inception of the exposure of a thin film to a solvent vapor. Most molecules in the amorphous and short TTGG helices had been replaced in the first several seconds, while the replacement of the molecules stored in long TTGG helices proceeded slowly. Contrary to the desorption process in air, no significant destruction of the TTGG helices was not observed.

The desorption and exchange behaviors depended markedly on desorbates and/or sorbates, which was interpreted with the difference in the strength of sPS-guest interactions.

Table 1
Diffusion coefficients for the desorbate molecules

Solvent (desorbate)	D_s (cm ² /s)
Chloroform (air)	2.83×10^{-12}
Toluene (air)	8.92×10^{-13}
Chloroform (exchange)	2.26×10^{-12}
Toluene (exchange)	2.85×10^{-12}

Acknowledgements

The authors thank Idemitsu Petrochemical Co., Ltd for supplying the sPS samples. They also thank Mr Masayoshi Nishiyama (Central Workshop, Osaka University) for his help in the ATR-FTIR measurement.

References

- [1] Dusek K. *Adv Polym Sci* 1993;109.
- [2] Dusek K. *Adv Polym Sci* 1993;110.
- [3] Tsutsui K, Tsujita Y, Yoshimizu H, Kinoshita T. *Polymer* 1998;39: 5177.
- [4] Tsutsui K, Katsumata T, Yamamoto Y, Fukatsu H, Yoshimizu H, Kinoshita T, Tsujita Y. *Polymer* 1999;40:3815.
- [5] Manfredi C, Del Nobile MA, Mensitieri G, Guerra G, Rapacciuolo M. *J Polym Sci, Part B: Polym Phys* 1997;35:133.
- [6] Guerra G, Manfredi C, Musto P, Tavone S. *Macromolecules* 1998;31: 1329.
- [7] Guerra G, Milano G, Venditto V, Lofferredo F, Ruiz de Ballesteros O, Cavallo L, De Rosa C. *Macromol Symp* 1999;138:131.
- [8] Tamai Y, Fukuda M. *Polymer* 2003;44:3279.
- [9] Chatani Y, Shimane Y, Inagaki T, Ijitsu T, Yukinari T, Shikuma H. *Polymer* 1993;34:1620.
- [10] Chatani Y, Shimane Y, Inagaki T, Shikuma H. *Polymer* 1993;34: 4841.
- [11] De Rosa C, Rizzo P, De Ballesteros OR, Petraccone V, Guerra G. *Polymer* 1999;40:2103.
- [12] De Rosa C, Guerra G, Petraccone V, Pirozzi B. *Macromolecules* 1997;30:4147.
- [13] Manfredi C, De Rosa C, Guerra G, Rapacciuolo M, Auriemma F, Corradini P. *Macromol Chem Phys* 1995;196:2795.
- [14] Amutha Rani D, Yamamoto Y, Mori S, Sivakumar Y, Tsujita Y, Yoshimizu H. *J Polym Sci, Part B: Polym Phys* 2003;41:269.
- [15] Vittoria V, Russo R, Candia F. *Polymer* 1991;32:3371.
- [16] Tashiro K, Ueno Y, Yoshioka A, Kaneko F, Kobayashi M. *Macromol Symp* 1999;33:141.
- [17] Tashiro K, Sasaki S, Ueno Y, Yoshioka A, Kobayashi M. *Korea Polym J* 2000;8:103.
- [18] Tashiro K, Ueno Y, Yoshioka A, Kobayashi M. *Macromolecules* 2001;34:310.
- [19] Tashiro K, Yoshioka A. *Macromolecules* 2002;35:410.
- [20] Chatani Y, Shimane Y, Inoue Y, Inagaki T, Ishioka T, Ijitsu T, Yukinari T. *Polymer* 1992;33:488.
- [21] Schlotter NE, Furlan PY. *Vib Spectrosc* 1992;3:147.
- [22] Balik CM, Simendinger WH. *Polymer* 1998;39:4723.
- [23] Fieldson GT, Barbari TA. *Polymer* 1993;34:1146.
- [24] Hong SU, Barbari TA, Sloan JM. *J Polym Sci, Part B: Polym Phys* 1997;35:1261.
- [25] Hong SU, Barbari TA, Sloan JM. *J Polym Sci, Part B: Polym Phys* 1998;36:337.
- [26] Hong SU, Barbari TA. *J Polym Sci, Part B: Polym Phys* 2001;39:908.
- [27] Kobayashi M, Akita K, Tadokoro H. *Macromol Chem* 1968;118:324.
- [28] Reynolds NM, Savage JD, Hsu SL. *Macromolecules* 1989;22:2867.
- [29] Kobayashi M, Nakaoki T, Ishihara N. *Macromolecules* 1989;22:4377.
- [30] Kobayashi M, Nakaoki T, Ishihara N. *Macromolecules* 1990;23:78.
- [31] Nyquist RA, Putzig CL, Leugers MA, McLachlan RD, Thill B. *Appl Spectrosc* 1992;46:981.
- [32] Kobayashi M, Yoshioka T, Imai M, Itoh Y. *Macromolecules* 1995;28: 7376.
- [33] Nakaoki T, Kobayashi M. *J Mol Struct* 1991;242:315.
- [34] Guadagno L, Baldi P, Vittoria V, Guerra G. *Macromol Chem Phys* 1998;199:2671.
- [35] Musto P, Manzari M, Guerra G. *Macromolecules* 1999;32:2770.
- [36] Amutha Rani D, Yamamoto Y, Saito A, Sivakumar Y, Tsujita Y, Yoshimizu H, Kinoshita T. *J Polym Sci, Part B: Polym Phys* 2002;40: 530.
- [37] Jones RAL, Richards RW. *Polymer at surfaces and interfaces*. London: Cambridge University Press; 1999.
- [38] Garbassi F, Morra M, Occhiello E. *Polymer surfaces from physics to technology*. Chichester: Wiley; 1994.
- [39] Kobayashi M. *Macromol Symp* 1997;114:1.