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Time-resolved small-angle neutron scattering study on guest-exchange processes in co-crystals of syndiotactic polystyrene[1]

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Syndiotactic polystyrene (sPS) occupies a peculiar position among crystalline polymers: it forms co-crystals with many different kinds of chemical compounds, where the molecules are confined as guests in the regularly arranged cavities surrounded by the side phenyl groups. The guest molecules can be replaced smoothly by exposure to a vapour or a liquid of another compound, keeping the framework of the host polymer crystallites. It has been confirmed that the guest-exchange procedure is an effective way to incorporate a variety of chemical species into the crystalline region of syndiotactic polystyrene. In order to elucidate its characteristics, the guest-exchange process in co-crystals of syndiotactic polystyrene has been studied by *in situ* time-resolved small-angle neutron scattering measurements, exploiting the scattering length difference between fully protonated and deuterated isotopologues of guest compounds and employing fully deuterated syndiotactic polystyrene as the host matrix to avoid strong incoherent scattering. In this study, the guest-exchange process induced by exposure to the gas of small guest molecules was followed by monitoring of the reflections from crystalline lamellae. The lamellar reflections showed significant variations in intensity during the guest exchange, from which the diffusion coefficients of the guest molecules in the crystalline region could be evaluated.

1. Introduction

Syndiotactic polystyrene (sPS) occupies a unique position among crystalline polymers in that it exhibits polymorphism; a variety of crystalline states are generated depending on crystallization conditions and subsequent treatments (Sorrentino & Vittoria, 2009). Furthermore, it forms co-crystals with many different kinds of chemical compounds, where the low-mass molecules are included as guests into regularly arranged vacancies formed by host sPS chains of TTGG conformation (Guerra *et al.*, 2009). The co-crystals found so far are classified into four different types of groups, according to the crystal system and the shape of the spaces the guest molecules occupy: monoclinic δ clathrate (Chatani *et al.*, 1993; Tarallo *et al.*, 2010), monoclinic δ intercalate (Tarallo *et al.*, 2006; Petraccone *et al.*, 2005), triclinic δ clathrate (Tarallo, Petraccone *et al.*, 2010) and orthorhombic ε clathrate (Tarallo, Schiavone, Petraccone *et al.*, 2010). A significant aspect of sPS co-crystals is the diversity of guest molecules and the robustness of the host lattice (Guerra *et al.*, 2012). Many organic compounds have already been incorporated into sPS co-crystals, such as dye (Uda, Kaneko, Tanigaki & Kawaguchi, 2005), fluorescent (Itagaki *et al.*, 2008, Del Girolamo Del Mauro *et al.*, 2007), photo-reactive (Stegmaier *et al.*, 2005; D'Aniello *et al.*, 2007) and paramagnetic molecules (Albunia *et al.*, 2009; Kaneko *et al.*, 2006), which suggests the possibility that new functional materials, based on the polymer-crystalline region, could be created. On the other hand, when the guest molecules are removed by certain procedures such as supercritical carbon dioxide extraction (Reverchon *et al.*, 1999), the nanoporous crystalline region is left, which is considered to be promising as a material for chemical separation and sensing devices (Mensitieri *et al.*, 2003; Pilla *et al.*, 2009). Active research is now being carried out along these directions, that is, polymer/functional molecule crystalline composite materials and nanoporous crystalline materials.

Another important feature of sPS co-crystals is the guest-exchange phenomenon (Chatani *et al.*, 1992; Yoshioka & Tashiro, 2003; Uda *et al.*, 2004). A guest molecule is usually stable in an sPS lattice and stays there long, if sPS co-crystals are left without any treatment. However, some guest mol-

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[1] This article will form part of a virtual special issue of the journal, presenting some highlights of the 15th International Small-Angle Scattering Conference (SAS2012). This special issue will be available in early 2014.

ecules are smoothly replaced with another chemical on exposure to its vapour or liquid. The guest-exchange method has an advantage in that it enables sPS to form co-crystals even with chemical compounds that are difficult to incorporate directly into the crystalline region by the usual methods – solution-cast and solvent-induced crystallization methods. This simple method has opened the door for a wide range of molecules; many bulky molecules have been introduced into sPS co-crystals (Kaneko *et al.*, 2011; Kaneko & Sasaki, 2011).

So far wide-angle X-ray scattering (WAXS) and IR spectroscopy have been mainly employed to elucidate the characteristics of this useful guest-exchange phenomenon. Although WAXS provides useful structural information about the crystalline region, it is difficult to evaluate the variation of guest content from a small number of reflections in polymer samples. On the other hand, IR spectroscopy, which is sensitive to the quantity of old and new guests, cannot distinguish the molecules in the crystalline region from those in the amorphous region in most cases; the only exception is the case where the guest molecule exhibits clear frequency differences of the vibrational modes between crystalline and amorphous regions (Uda *et al.*, 2005). Accordingly, it is difficult to explore how the guest molecules in the crystalline region behave during the guest-exchange process only from WAXS and IR spectroscopy data. Experimental methods applicable to the guest-exchange process for a wide range of guest molecules are therefore required.

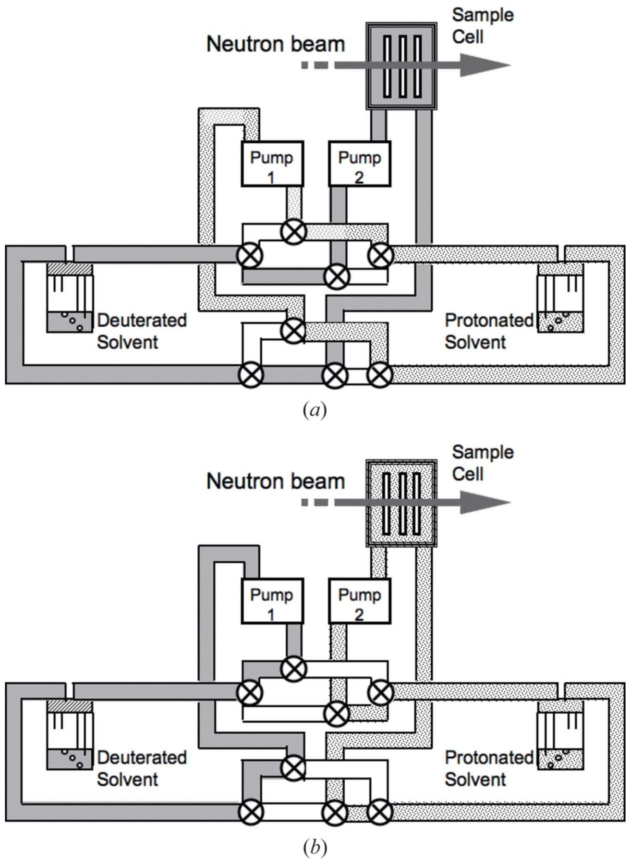
We supposed that small-angle scattering has potential as a tool for monitoring the behaviour of guest molecules in the crystalline region. The solid states of crystalline polymers can be approximated as one-dimensional stacks of crystalline and amorphous layers. As the guest exchange proceeds in the crystalline layers, the scattering length density (SLD) profile changes, which results in the intensity changes in the lamellar reflection. However, if the old and new guests are similar in terms of molecular size and atomic composition, the change in SLD caused by the guest exchange would be too small to give enough intensity changes for small-angle X-ray scattering analysis. Meanwhile, we began to conjecture that small-angle neutron scattering (SANS) experiments would provide valuable information about the guest-exchange process, even in the case of the same atomic composition, by exploiting the large difference in scattering length between a proton and a deuterium atom (Roe, 2000; Higgins & Benoit, 1994). For example, when the guest exchange from a fully deuterated guest to a fully protonated guest occurs in the crystalline region of deuterated sPS, a large depression of SLD in the crystalline lamellae would be brought about, which leads to a significant increase in intensity of the reflections due to the lamellar structure. The SANS method employing the two isotopologues seems to be promising, since it can be applied to any guest molecule as long as it includes H atoms, which is the notable advantage of this method over the IR spectroscopic method we employed in a previous study.

Recently, we have confirmed that such significant intensity changes actually happen in the lamellar reflections when the exposure gas is switched between protonated and deuterated isotopologues. Since the intensity reflects the contrast in SLD between the crystalline and the amorphous regions, the time dependence of the old and the new guest contents in the crystalline region could be evaluated from the intensity changes during the guest-exchange process. According to this expectation, we made an attempt in this study to estimate the diffusion coefficient of guest molecules in the crystalline region based on time-resolved SANS measurements and a simple diffusion model.

In this article, we will describe the results and analysis of the SANS experiments, which were carried out for the guest exchange of relatively small molecules. It will be shown that the diffusion coefficients of the guest molecules in the crystalline region are significantly smaller than those in the amorphous region and decrease as the size of the guest molecules increases.

2. Experimental

To avoid strong incoherent scattering, fully deuterated syndiotactic polystyrene (d-sPS, $\overline{M}_{\rm w}$ of 1.1×10^5 and $\overline{M}_{\rm w}/\overline{M}_{\rm n}$ of 1.9) was synthesized according to the coordination polymerization method developed by Ishihara *et al.* (1986), using fully deuterated styrene with a purity of more than 98%, purchased from Cambridge Isotope Laboratories. Chloro-



(*a*)

(*b*)

Figure 1
Schematic representation of the experimental setup for SANS experiments on the guest-exchange phenomenon of sPS: (*a*) under exposure to the deuterated isotopologue and (*b*) under exposure to the protonated isotopologue.

form, tetrahydrofuran (THF), benzene, toluene and their full deuterides (all purities were more than 98%) were purchased from Sigma–Aldrich and Armor Chemicals and used without further purification. Uniaxially oriented amorphous d-sPS samples about 50 µm thick were prepared as follows: amorphous film samples of d-sPS were obtained by quenching a melt of sPS in an ice-water bath, drawing the melt-quenched d-sPS film four times in an oil bath kept at 373 K and clipping well oriented portions from the drawn film. The oriented amorphous films were exposed to a vapour of chloroform to give oriented samples of sPS/chloroform co-crystal. Other chemicals were loaded as guests by exposing the sPS/chloroform co-crystal film to their vapours. The amorphous and crystalline states of these sPS samples were confirmed by powder X-ray diffraction. In order to increase the scattering intensity, an assembly of about three to five pieces of d-sPS film was subjected to SANS experiments.

For *in situ* time-resolved SANS measurements during the guest-exchange processes, an experimental setup composed of a sample cell and a dual gas-circulating system (see Fig. 1) which was based on our setup for previous Fourier transform IR measurements was employed (Uda *et al.*, 2004). The sample cell designed for transmission measurements was equipped with two quartz windows and thermostated with circulating water. This setup made it possible to change the gas environment in the sample cell in a moment with eight remote-controlled valves driven by compressed air. Until the start of the exposure to the new guest vapour, the specimen in the cell was kept in the original guest vapour to prevent its desorption from the specimen. Time-resolved SANS measurement was started by a trigger signal from the valve controller at the moment the vapour circulating into the cell was switched from an old guest vapour to a new guest vapour. In the following sections of this article, the results of SANS measurements are shown as a function of time from the input of the trigger signal. The gas atmosphere in the cell was completely switched within a second.

All SANS experiments were carried out on uniaxially drawn samples using the KWS-1 instrument of the Jülich Centre for Neutron Science outstation at Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) in Garching, Germany (Radulescu *et al.*, 2012). Scattering data were obtained using a two-dimensional detector with an active area of 60 × 60 cm and 128 × 128 channels. A wavelength λ of 0.7 nm (Δλ/λ = 10%) and a sample-to-detector distance of 4 m were chosen. The typical measured sample area was about 4 × 6 mm. The one-dimensional intensity function $I_1(q)$ was obtained from the two-dimensional data corrected for detector sensitivity, instrumental noise and scattering from the empty cell by reading pixel values and merging them with an appropriate width along the central meridian, and then subtracting the scattering data of amorphous sPS as the background correction. During the measurements, the sample cell and the reservoirs of guest molecules were kept at 303 and 293 K, respectively.

3. Results and discussion

3.1. Changes in SANS images during the guest-exchange process

Fig. 2 shows SANS images of the changes on exposure of an sPS co-crystal with deuterated benzene (d-benzene) to a vapour of protonated benzene (h-benzene) and on its reverse process. Owing to the deuterated sPS matrix, clear intensity changes were observed with low background. In the beginning, the sPS/d-benzene co-crystal exhibited no striking features. Just after the exposure to the h-benzene vapour, two first-order reflections due to the periodic structure of the crystalline lamellae started to appear clearly in the meridian direction and the two reflections increased in intensity with time. When the circulating vapour was switched from h-benzene to d-benzene, the two reflections decreased in intensity with time and finally disappeared.

Fig. 3 shows the time dependence of one-dimensional scattering intensity $I_1(q)$ obtained from two-dimensional SANS data during the guest exchange from d-benzene to h-benzene and its reverse process. In both cases, remarkable intensity changes were observed. In the exchange from d-benzene to h-benzene, the lamellar reflection with a peak around $q = 0.06$ Å^{-1} increased smoothly in intensity with time; immediately after the inception of exposure to the h-benzene vapour, the rapid intensity increase started and then obviously slowed down after about 100 s.

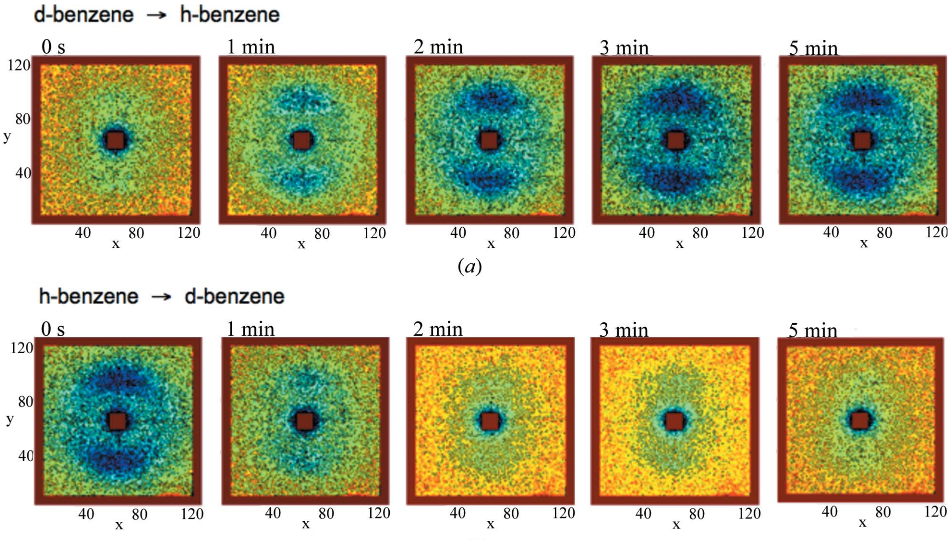


Figure 2
Changes in the SANS profile on the guest exchange between h- and d-benzene: (*a*) from d-benzene to h-benzene and (*b*) from h-benzene to d-benzene.

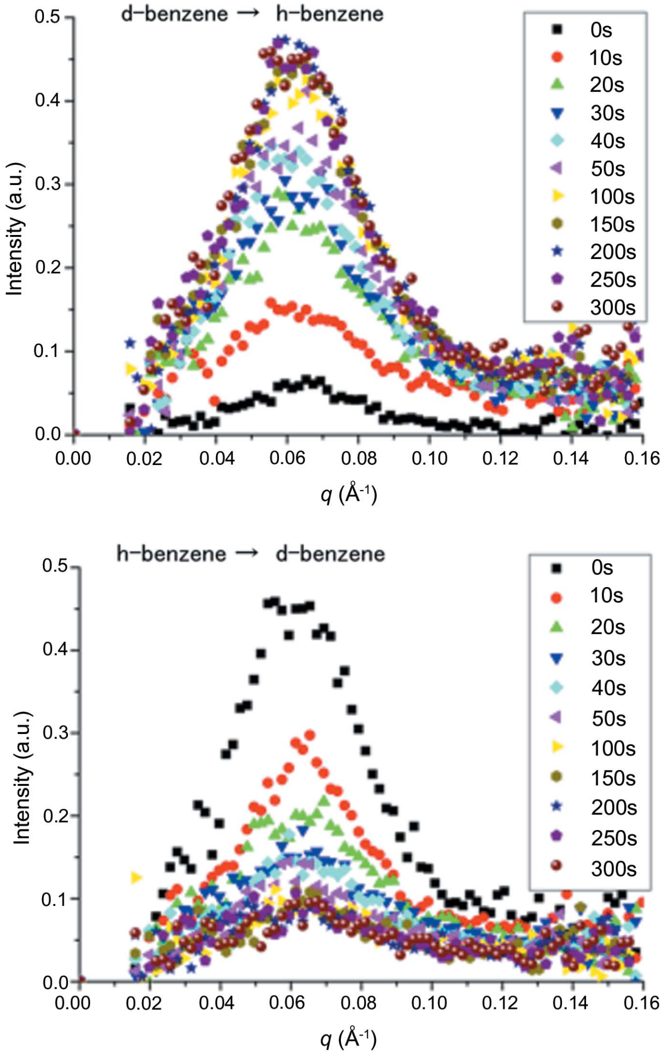


Figure 3

Time-dependent changes in lamellar reflection intensity during the guest exchange between deuterated and protonated benzene.

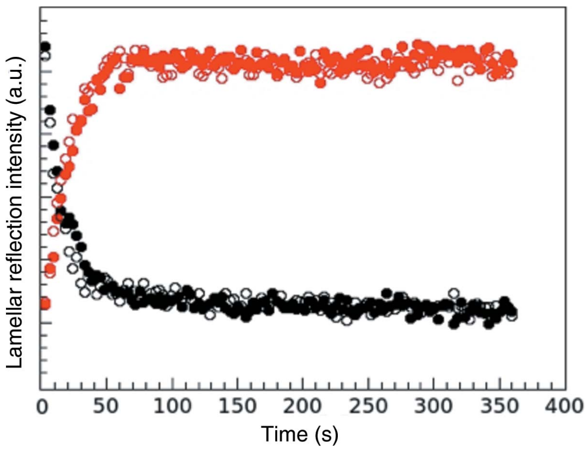


Figure 4

Time dependence of the integrated lamellar reflection intensity measured in two sets of SANS experiments on the guest-exchange processes from deuterated to protonated chloroform (red open and closed circles) and from protonated to deuterated chloroform (black open and closed circles). The integration was made in the region of $q = 0.02–0.14$ Å^{-1}.

Such clear intensity changes were observed for all of the combinations of protonated and deuterated isotopologues employed in this study. The intensity changes induced by the switch of circulating vapour were reversible and reproducible in all cases. An example obtained on the switch between h-chloroform and d-chloroform is shown in Fig. 4. The intensity changes of the lamellar reflections in the two sets of experiments are in good agreement with each other in both the d to h and h to d exchanges. It is found that the rate of intensity change varies with the type of circulating molecules, as shown in Fig. 5.

Although the sample exposed to the circulating vapour swelled somewhat, the influence on the higher-order structure seemed to be very small; the lamellar repeat distance hardly changed on the exposure. Since the guest exchange between isotopologues has no significant effect on the sample thickness, the influence of the swelling has not been taken into account in the data analysis.

3.2. Model for data analysis

In this study, all time-resolved SANS measurements were carried out on exposure to a vapour saturated at 293 K, which means that the vapour pressure was in the range of ~20 mm Hg (toluene) to 160 mm Hg (chloroform) (1 mm Hg = 133 Pa). Irrespective of the difference in vapour pressure, all chemicals employed exhibited nearly the same time-dependent changes in the SANS profile. In comparison with the exchange procedure of contact to a liquid, the vapour exposure procedure in these conditions did not make the sPS film samples swell so much. Actually, the observed lamellar repeat period of around 10 nm was nearly the same as that in a

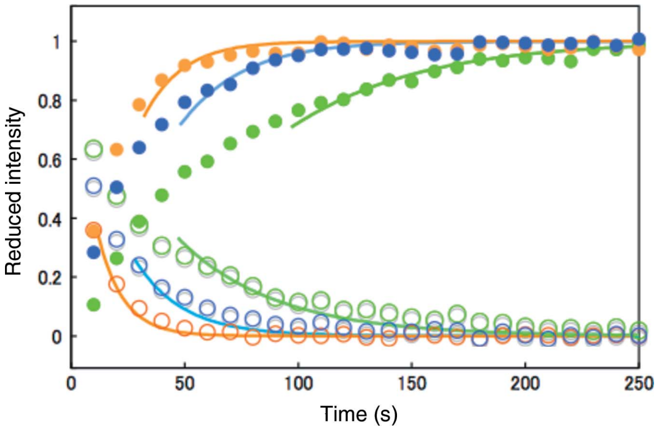


Figure 5

Time dependence of the integrated lamellar reflection intensity during the guest-exchange processes from deuterated to protonated isotopologue (closed circles) and from protonated to deuterated isotopologue (open circles) and for toluene (green), benzene (blue) and THF (orange). The integration was made in the region of $q = 0.02–0.14$ Å^{-1}. The intensity data are reduced by setting the maximum intensity to 1.0 and setting the minimum intensity to 0.0, corresponding to the states completely occupied by protonated and deuterated isotopologues, respectively. The lines represent the results of the fitting with equations (11*a*) and (12*a*). For the fitting, the data points in the initial stage were not included, considering the approximation used for these equations.

well dried sPS co-crystal film and was clearly smaller than that in an sPS co-crystal film soaked in a liquid (Kaneko *et al.*, 2013*b*). According to the previous studies, sPS forms a clathrate structure with all of the employed chemicals, where one guest molecule is included for every four styrene units (Rizzo *et al.*, 2005; Tarallo *et al.*, 2006). Consequently, full inclusion of protonated guest molecules leads to a significant decrease in the SLD of the crystalline region. From these observations, it can be considered that the content of the protonated isotopologue in the crystalline region chiefly determines the SANS profile as follows. In the beginning, the deuterated molecules are fully stored in crystalline lamellae, in which condition the difference in SLD between the crystalline and amorphous regions $|\Delta\rho(x)|$ is very low, actually resulting in faint lamellar reflections. After the inception of exposure to the protonated isotopologue, $|\Delta\rho(x)|$ increases and the reflection intensity becomes strong, as the guest exchange from deuterated to protonated molecules proceeds in the crystalline region.

According to the view given above about the SANS profile changes, here we try to build a simple model to evaluate the diffusibility of guest molecules in the crystalline region during the guest-exchange process. At first, the guest-exchange process induced by the switch of circulating gas is simplified as follows. (1) The solid states of sPS co-crystals can be approximated as one-dimensional stacks of crystalline and amorphous layers. (2) The crystalline layers have a uniform and constant thickness. (3) The diffusion coefficient of the guest in the crystalline region dominates the overall guest-exchange rate, since the diffusion of a guest molecule is very much slower in the crystalline region than in the amorphous region; at least a difference of several orders of magnitude is predicted from a previous IR study (Uda *et al.*, 2005). (4) The time lag in the onset of guest exchange between crystalline layers is ignored; in other words, the guest-exchange process proceeds concurrently for all crystalline layers. (5) The guest molecules in the crystalline region obey Fick's law of diffusion.

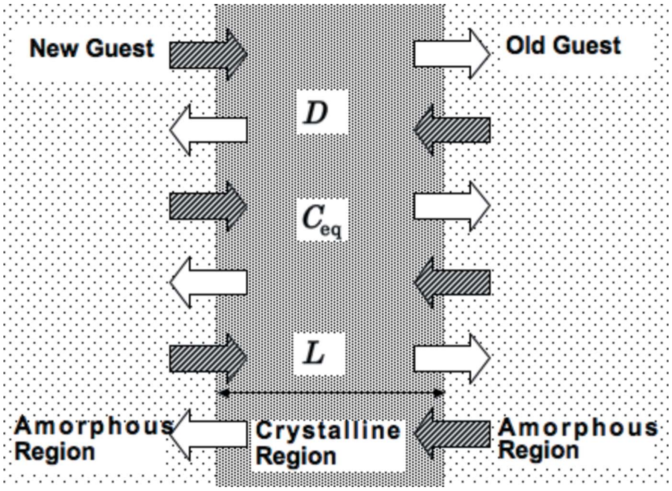


Figure 6
Model for the analysis of guest diffusibility. The crystalline region is a plate with thickness L, guest diffusion coefficient D and guest concentration C_{eq}.

Under these assumptions, the time dependence of the lamellar reflection intensity can be analyzed by examining the changes in the old and the new guest contents in one crystalline layer embedded in the amorphous region with the one-dimensional diffusion model shown in Fig. 6. The crystalline layer is treated as a plate with thickness L. In the beginning, the crystalline layer and the surrounding amorphous layers are filled with the old guest and the concentration in the crystalline region is C_{eq}. On exposure to the vapour of a new guest, the old guest in the amorphous region is quickly replaced with the new guest. Then, a guest exchange in the crystalline layer proceeds through an outward flow of the old guest and an inward flow of the new guest with diffusion coefficient D. Supposing a sudden discontinuous switch from the old to the new guest in the amorphous region at time $t = 0$, the average concentration of the old guest over the crystalline layer, $\overline{C}_{old}(t)$, varies continuously from C_{eq} to 0 according to equation (1) (Shewmon, 1963):

$$\overline{C}_{\rm old}(t) = C_{\rm eq}\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left[-\frac{D(2n+1)^2\pi^2 t}{L^2}\right]. \qquad (1)$$

Except in the early stage of the process, equation (1*a*) can be substituted for equation (1):

$$\overline{C}_{\rm old}(t) = \overline{C}_{\rm eq}\frac{8}{\pi^2}\exp\left(-\frac{D\pi^2 t}{L^2}\right), \qquad (1a)$$

since the terms with $n \geq 1$ in the summation converge faster to 0. The average concentration of the new guest, $\overline{C}_{new}(t)$, varies from 0 to C_{eq} according to equation (2),

$$\overline{C}_{\rm new}(t) = C_{\rm eq}\left\{1 - \frac{8}{(2n+1)^2\pi^2}\sum_{n=0}^{\infty}\exp\left[-\frac{D(2n+1)^2\pi^2 t}{L^2}\right]\right\}, \qquad (2)$$

under the assumption that the total concentration for the old and the new guests in the crystalline region is constant, *i.e.* $\overline{C}_{old}(t) + \overline{C}_{new}(t) = C_{eq}$. Equation (2) can be approximated by equation (2*a*):

$$\overline{C}_{\rm new}(t) = C_{\rm eq}\left[1 - \frac{8}{\pi^2}\exp\left(-\frac{D\pi^2 t}{L^2}\right)\right]. \qquad (2a)$$

The average SLD of the crystal layer, $\overline{\rho}_{cry}(t)$, is given by

$$\overline{\rho}_{\rm cry}(t) = b_{\rm old}\overline{C}_{\rm old}(t) + b_{\rm new}\overline{C}_{\rm new}(t) + \rho_{\rm cry,sPS}, \qquad (3)$$

where b_{old} and b_{new} are the molecular scattering lengths of the old and new guests and $\rho_{cry,sPS}$ is the contribution of the deuterated sPS component in the crystal layer. Similarly, the average SLD of the surrounding amorphous region is given by

$$\overline{\rho}_{\rm am,\,old} = b_{\rm old}\overline{C}_{\rm am,\,old} + \rho_{\rm am,sPS} \quad t < 0 \qquad (4)$$

until just before the inception of exposure to the new guest vapour and by

$$\overline{\rho}_{\rm am,\,new} = b_{\rm new}\overline{C}_{\rm am,\,new} + \rho_{\rm am,sPS} \quad t \geq 0 \qquad (5)$$

after the inception of exposure to the new guest vapour, where $\overline{C}_{am,old}$ and $\overline{C}_{am,new}$ are the average concentrations of the old and the new guests in the amorphous region, which are assumed to be time independent, and $\rho_{\rm am,sPS}$ is the contribution of the sPS component in the amorphous region. Here, it is supposed that the vapour exposure does not change the sPS concentration in the amorphous region markedly, and therefore, $\rho_{\rm am,sPS}$ is set to be constant.

Since the intensity of the lamellar reflection is proportional to the square of the difference in SLD between the amorphous and the crystalline regions, the time dependence of the intensity $I(t)$ is written as

$$\begin{aligned} I(t) &= k\left[\overline{\rho}_{\rm cry}(t) - \overline{\rho}_{\rm am,\,new}\right]^2 \\ &= k\big\{b_{\rm old}\overline{C}_{\rm old}(t) + b_{\rm new}[\overline{C}_{\rm new}(t) - \overline{C}_{\rm am,\,new}] \\ &\quad + (\rho_{\rm cry,sPS} - \rho_{\rm am,sPS})\big\}^2, \end{aligned} \tag{6}$$

where k is a constant. Using the approximation of equations (1a) and (2a), $I(t)$ can be described with the following relation:

$$I(t) = k\left[A\exp\left(-2\frac{D\pi^2}{L^2}t\right) + B\exp\left(-\frac{D\pi^2}{L^2}t\right) + C\right], \tag{7}$$

where

$$A = \left[\frac{8C_{\rm eq}(b_{\rm old} - b_{\rm new})}{\pi^2}\right]^2, \tag{8}$$

$$\begin{aligned} B = 2&\left[\frac{8C_{\rm eq}(b_{\rm old} - b_{\rm new})}{\pi^2}\right] \\ &\times\left[(C_{\rm eq} - \overline{C}_{\rm am,new})b_{\rm new} + (\rho_{\rm cry,sPS} - \rho_{\rm am,sPS})\right] \end{aligned} \tag{9}$$

and

$$C = \left[\left(C_{\rm eq} - \overline{C}_{\rm am,new}\right)b_{\rm new} + \left(\rho_{\rm cry,sPS} - \rho_{\rm am,sPS}\right)\right]^2. \tag{10}$$

It is shown from equation (7) that the intensity converges to kC as $t \to +\infty$.

Two special cases are given consideration here. (i) There is no contrast in SLD between the crystalline and the amorphous region in the beginning, *i.e.* $\rho_{\rm cry}(0) = \rho_{\rm am,new}$, which corresponds to $b_{\rm old}(C_{\rm eq} - \overline{C}_{\rm am,new}) = \rho_{\rm am,sPS} - \rho_{\rm cry,sPS}$, giving equation (11):

$$\begin{aligned} I(t) = k(C_{\rm eq} - \overline{C}_{\rm am,new})^2(b_{\rm old} - b_{\rm new})^2 &\left\{\left[\frac{8C_{\rm eq}}{\pi^2(C_{\rm eq} - \overline{C}_{\rm am,new})}\right]^2\right. \\ \times\exp\left(-2\frac{D\pi^2}{L^2}t\right) - 2&\left[\frac{8C_{\rm eq}}{\pi^2(C_{\rm eq} - \overline{C}_{\rm am,new})}\right] \\ \times\exp\left(-\frac{D\pi^2}{L^2}t\right) + 1&\left.\vphantom{\frac{1}{1}}\right\}. \end{aligned} \tag{11}$$

(ii) There is no contrast in SLD in the final stage, *i.e.* $\rho_{\rm cry}(+\infty) = \rho_{\rm am,old}$, which corresponds to $b_{\rm new}(C_{\rm eq} - \overline{C}_{\rm am,new}) = \rho_{\rm am,sPS} - \rho_{\rm cry,sPS}$, giving equation (12):

$$I(t) = k\left[\frac{8C_{\rm eq}(b_{\rm old} - b_{\rm new})}{\pi^2}\right]^2\exp\left(-2\frac{D\pi^2}{L^2}t\right). \tag{12}$$

Assuming that the guest concentration in the crystalline region is much higher than that in the amorphous region, the following rough approximation $C_{\rm eq} - \overline{C}_{\rm am,new} \simeq C_{\rm eq}$ is applied, and $8/\pi^2$ is also approximated by 1, leading to equations (11a) and (12a):

$$\begin{aligned} I(t) = &\,kC_{\rm eq}^2(b_{\rm old} - b_{\rm new})^2 \\ &\times\left[\exp\left(-2\frac{D\pi^2}{L^2}t\right) - 2\exp\left(-\frac{D\pi^2}{L^2}t\right) + 1\right], \end{aligned} \tag{11a}$$

and

$$I(t) = kC_{\rm eq}^2(b_{\rm old} - b_{\rm new})^2\exp\left(-2\frac{D\pi^2}{L^2}t\right). \tag{12a}$$

The time dependence of the intensity given by equations (11a) and (12a) is depicted in Fig. 7. Equation (11a) for case (i) can be regarded as a rough sketch of the intensity changes on the guest exchange from d-guest to h-guest in the deuterated sPS matrix, and equation (12a) for case (ii) roughly illustrates the intensity changes on the reverse process. Since the intensity is proportional not to the SLD difference between the crystalline and the amorphous region but to the square of the SLD difference, the effect of a unit change in the SLD difference on the intensity depends on the value of the SLD difference. The larger the SLD difference, the larger the effect on the intensity. Therefore, it is expected that the intensity change rate in the initial stage will be larger in the h to d process than in the d to h process, as shown in Fig. 7; the intensity change on the h to d process converges faster than that on the d to h process, which gives a characteristic that a point of intersection for the two lines is found much lower than the middle of the two extremes of the reduced intensity. Actually, this tendency can be seen also in Fig. 5; the point of intersection is located below 0.4 for all three cases, suggesting the faster convergence in the h to d process for these chemicals. However, the observed asymmetry between the d to h process and the h to d process in Fig. 5 is not so obvious as the graph of equations (11a) and (12a) shows, which suggests the oversimplification of these equations. We speculate that the other factors ignored in the present model, such as the disregard for lamellar thickness distribution and the diffusion process in the amorphous region, also can contribute to the less obvious tendency in the experimental data. A more realistic model including such

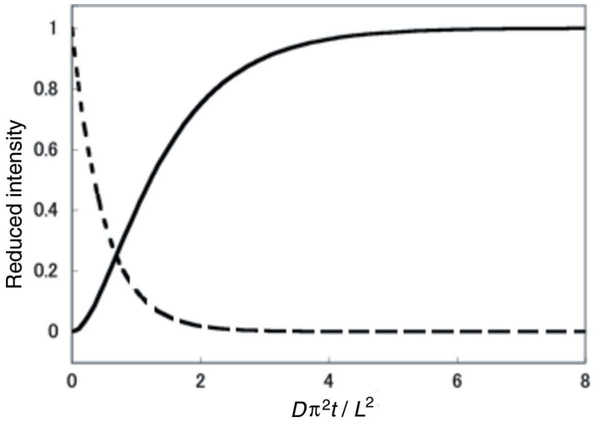


Figure 7
Intensity-time relation given by equations 11(a) (solid line) and 12(a) (broken line).

factors would be required for a wide range of applications on the guest-exchange phenomenon.

3.3. Diffusion coefficients in the crystalline region

According to the model described above, the value of $D\pi^2/L^2$ in the exponential functions can be evaluated by fitting the time dependence of the lamellar reflection intensity $I(t)$ for the h to d process to equation (11*a*) and that for the d to h process to equation (12*a*). The value of the thickness, L, is obtained using the method of Strobl from a one-dimensional correlation function (Strobl *et al.*, 1980), $\Gamma_1(x)$, calculated by Fourier transformation of the one-dimensional scattering intensity $I_1(q)$; in the present study, L is estimated to be about 35 Å by using the results of a previous SANS study (Kaneko *et al.*, 2013*a*). By combining the values of $D\pi^2/L^2$ and L, the diffusion coefficient D is obtained for each guest molecule. The D values obtained for both the h to d and the d to h processes are listed in Table 1.

Table 1
Diffusion coefficients of some guest molecules in the crystalline region, estimated from the time dependence of lamellar reflection intensity.

	Diffusion coefficient (cm^2 s^{-1})		
Guest	H to D process	D to H process	Molecular volume (Å^3)
Chloroform	6.6×10^{-16}	9.9×10^{-16}	70.1
Tetrahydrofuran	5.6×10^{-16}	7.7×10^{-16}	78.0
Benzene	3.0×10^{-16}	4.8×10^{-16}	84.0
Toluene	1.5×10^{-16}	2.4×10^{-16}	100.6

The diffusion coefficients in the crystalline region during the guest exchange are in the range of 1.0×10^{-15}–1.0×10^{-16} cm^2 s^{-1} and are therefore quite small in comparison with the diffusion coefficients of around the order of 10^{-8} cm^2 s^{-1} measured for some compounds in the amorphous region (Uda *et al.*, 2005, Kaneko & Tsuchida, 2013). As equations (1*a*) and (2*a*) show, the rates of concentration change of the old and the new guests significantly slow down with the increase in lamellar thickness L. Therefore, it is considered that the thinness of the crystalline layer is a quite crucial factor for a smooth guest exchange of the molecules as focused on here.

There is a fourfold difference in the diffusion coefficient between chloroform and toluene. Generally, the diffusion coefficient of a low-mass molecule in a matrix depends on its molecular volume and flexibility (Van Krevelen & Hoftyzer, 1976; Arnould & Laurence, 1992; Kovarski, 1997). In this study, the compounds used are all rigid molecules and, therefore, the difference in diffusion coefficient would be attributable to their molecular volumes. As can be seen from Table 1, a clear tendency can be recognized; the diffusion coefficient decreases as the molecular volume increases. A similar relationship between bulk diffusion coefficient and molecular volume has been observed on the guest exchange from chloroform to *n*-alkanes (Kaneko & Tsuchida, 2013).

Although it can be expected that there would be no essential difference in the diffusion mechanism between the h to d and the d to h processes and therefore the two processes would proceed with the same diffusion coefficient, there is a systematic difference in diffusion coefficient between the two processes as shown in Table 1. The diffusion coefficient for the d to h process is 40–60% larger than that for the h to d process, though the diffusion coefficient varies in the same way with guest size in both of the two processes. We conjecture that the following factors arising from the present model would be the causes for the systematic differences in the diffusion coefficients obtained. In the course of model construction, some bold assumptions were made for simplicity and easy handling; the distribution of lamellar thickness and starting time were ignored, and it was supposed that all crystalline lamellae have the same thickness and that guest exchange starts in all crystalline lamellae at the same time. Furthermore, in order to obtain the final results as simple functions shown in equations (11*a*) and (12*a*), several approximations are introduced, for example, the higher terms in equations (1) and (2) relating to faster convergence are not included in the ensuing derivation, and a sudden change of SLD in the amorphous region at the inception of the guest-exchange process is assumed.

Although the present model can be regarded as giving the order of a diffusion coefficient for the guest-exchange process of sPS, a more sophisticated model, including the above factors or a simulation method, is required to obtain a more accurate evaluation, which is an issue for future work.

4. Conclusion

In situ time-resolved SANS measurements were applied to a study on the guest-exchange process in co-crystals of sPS, which was induced by exposure to a vapour of a new guest. The guest-exchange process in the crystalline region could be followed by observing the significant intensity changes of the lamellar reflections, which were caused by the alternation between protonated and deuterated isotopologues of the guest molecules in the crystalline region. By using a simple one-dimensional Fickian diffusion model for a finite plate, an equation describing the relationship between the time dependence of the lamellar reflection and the diffusion coefficient of guest molecules was obtained. The diffusion coefficient in the crystalline region during the guest-exchange process was evaluated for chloroform, THF, benzene and toluene, and the results showed that the guest exchange in the crystalline lamellae proceeds with a diffusion coefficient of the order of 10^{-16} cm^2 s^{-1}, being several order of magnitude smaller than those in the amorphous region. It was also shown that the diffusion coefficient decreases with the increase of molecular volume.

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