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Neutron Diffraction and IR Spectroscopy Study on Crystalline Complexation of Syndiotactic Polystyrene with 15-Crown-5 and 18-Crown-6

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Neutron diffraction experiments were carried out in order to confirm that syndiotactic polystyrene (sPS) forms crystalline complexes with 15-crown-5 (15C5) and 18-crown-6 (18C6). A strong 010 reflection was observed in both sPS/15C5 and sPS/18C6 systems, which indicates a crystalline structure where crown ether molecules are sandwiched by polymer sheets consisting of sPS helices. It was also confirmed by IR spectroscopy that the orientation of host sPS lattice was preserved during the complexation using guest-exchange phenomenon.

Syndiotactic polystyrene (sPS) occupies a peculiar position in crystalline polymers. It exhibits polymorphism; a variety of crystalline states appear depending on crystallization conditions and thermal histry.[1] Besides, it forms crystalline complexes with many different kinds of chemical compounds.[2] In the crystalline complexes of sPS, the guest molecules are confined in small spaces between sPS helices. This unique feature of sPS has become of interest in recent years.

Many attempts have been made to exploit the ability of sPS to hold various kinds of molecules as guests in the crystalline region for developing a new kind of composite polymer materials. So far, many organic compounds have already been incorporated into sPS complexes such as dye,[3] fluorescent,[4–6] photoreactive,[6,7] and paramagnetic molecules.[8,9] According to the structural features, such as crystal symmetry and guest arrangement, the crystalline complexes of sPS can be at least classified into four groups, monoclinic δ-clathrate,[10] triclinic δ-clathrate,[11] δ-intercalate,[12] and ε-clathrate.[13] Irrespective of structural differences, sPS chains take $(T_2G_2)_2$ conformation in all the crystalline complexes.

It is probable that combining the characteristics of a host polymer lattice and a doped guest compound will develop a new kind of functional materials. Such crystalline polymer composites would provide the following advantages, the guest molecules are periodically arranged, the orientation of guest molecules is adjustable by controlling the orientation of host polymer crystallites, and the dissipation and/or aggregation of doped molecules are retarded.

Considering the possibility to build a molecular assembly in the cavities of the sPS crystalline region, we have tried to introduce crown ethers, which are renowned as the starting point of supramolecular chemistry and act as a host for various cations, into the sPS crystalline region as the first step. The three complexes, sPS/12C4, sPS/15C5, and sPS/18C6, were prepared by carrying out guest exchange[14] on films of sPS/$CHCl_3$ δ-clathrate complex. After confirming the complex formation of sPS with 12C4, the smallest crown ether of a 12-membered ring with four ethylene oxide units,[15] we pointed out the possibility that two larger crown ethers, 15C5 and 18C6 are also incorporated into the crystalline region of sPS mainly based on the results of IR spectroscopy and gravimetric measurements.[16] However, there remains a problem; more direct evidence for complexation by X-ray powder diffraction, i.e., the 010 reflection characteristic of sPS complexes, has not been obtained for 15C5 and 18C6 yet.

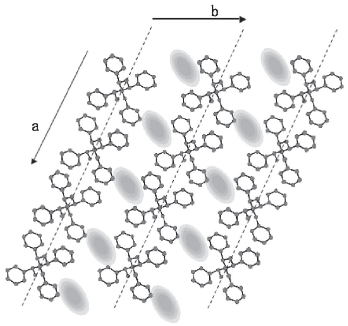

Figure 1. Crystal structure of sPS δ-clathrate. Guest molecules are stored in the cavities (shadowed in the figure) between polymer sheets.

The starting sPS/$CHCl_3$ δ-clathrate complex is schematically depicted in Figure 1, where sPS helices of $(T_2G_2)_2$ conformation are aligned side by side into polymer sheets; the guest molecules are confined in the space sandwiched by the polymer sheets. Concerning the complexation of with 12C4 by guest exchange, both the starting sPS/$CHCl_3$ and resultant sPS/12C4 complexes showed a distict 010 reflection corresponding to the intersheet distance between neighboring polymer sheets, as shown in Figure 2. The appearance of the 010 reflection in these complexes arises from the electron density contrast between the polymer sheet domain consisting of sPS helices and the guest domain. The reflection shifts from 8.2 to 7.4° on guest exchange, which corresponds to an expansion of the intersheet distance between neighboring polymer sheets from 1.08 to 1.19 nm. On the other hand, no clear 010 reflection was observed for sPS/15C5 and sPS/18C6, which might be because the electron density contrast between the host and guest domains decreases by the insertion of larger crown ether molecules.

To solve this problem, we planned to use neutron diffraction, which senses the scattering length density due to the nucleus potential, as a convenient tool for getting information from samples of low electron density contrast. Deuteration is a usual and convenient method to introduce a contrast of

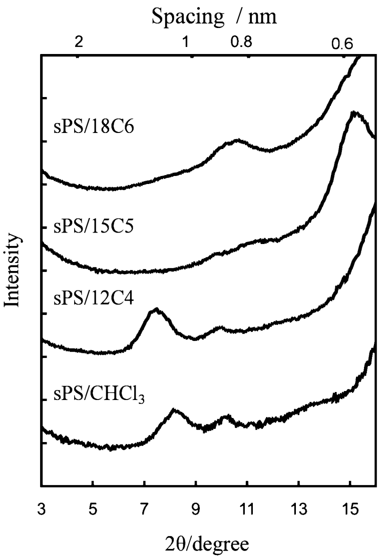

Figure 2. X-ray diffraction patterns obtained by an automatic powder diffractometer of sPS/$CHCl_3$, sPS/12C4, sPS/15C5, and sPS/18C6 complexes.

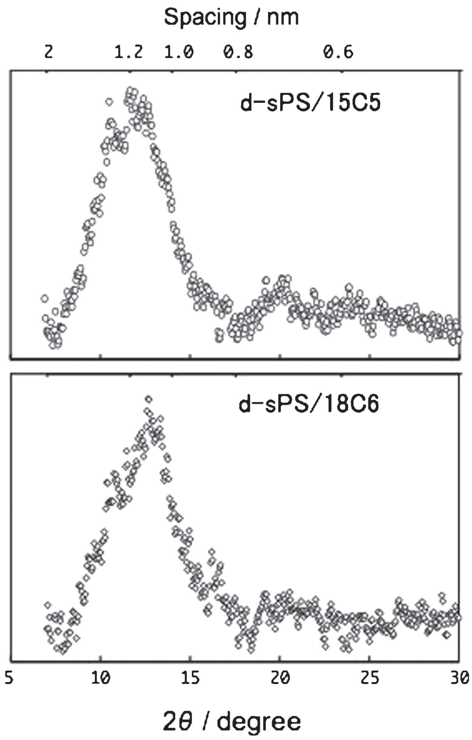

Figure 3. Neutron diffraction patterns of d-sPS/15C5 and d-sPS/18C6 complexes.

scattering length density in a sample without any large structural disturbance. We expected, therefore, that the 010 reflection would appear by employing the combination of deuterated sPS (d-sPS) and protonated crown ether to increase the scattering length contrast between the host and guest regions. Furthermore, we tried to confirm by using IR spectroscopy that the crystallites of sPS/crown ether complexes have a preferential orientaion.

sPS ($\bar{M}_w = 1.8 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 3.1$) was supplied by Idemitsu Kosan Co., Ltd., and d-sPS ($\bar{M}_w = 1.1 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 1.9$) was synthesized according to a method developed by Ishihara.[17] sPS/crown ether complex samples for IR experiments were made from cast films of sPS/$CHCl_3$ complex through guest exchange as described in the previous paper.[16] Uniaxially oriented samples of d-sPS/15C5 and d-sPS/18C6 were prepared by exposing four times drawn amorphous d-sPS film to toluene vapor at room temperature for 1 day and then subjecting it to guest exchange. Neutron diffraction measurements were performed using an Echidna diffractometer installed at OPAL reactor of ANSTO, Australia. The wavelength of the neutron beam was 0.2439 nm. The uniaxially oriented d-sPS/crown ether sample was loaded into a 9-mm diameter vanadium cell, in which the drawing direction of the sample was set perpendicular to the scattering plane. In this sample setting, the *hk*0 reflections would give the main features in the diffraction profile.

Figure 3 shows the neutron diffraction diagrams of d-sPS/18C6 and d-sPS/15C5 complexes, which gave an intense reflection due to the 010 lattice plane. The fact that the 010 reflection overwhelms other *hk*0 reflections strongly supports the structure model where hydrogenated crown ether molecules are inserted between the polymer sheets.

In the previous study,[15] it was observed that the intersheet distance expanded from 1.08 to 1.19 nm during the guest exchange from sPS/$CHCl_3$ to sPS/12C4. From the 2θ value at the peak top, the intersheet distance was roughly estimated to be 1.2 nm for sPS/15C5 and 1.1 nm for sPS/18C6, which means that nearly the same magnitude of intersheet expansion took place during the complexation with 15C5 while the intersheet distance remained unchanged during the complexation with 18C6. It could be said at least that the 15C5 and 18C6 induce no significant intersheet expansion compared with 12C4, which appears to contradict the molecular sizes of guest crown ethers. According to previous research on the conformational states of these crown ethers, the flexibility increases with the repeating C_2H_4O group.[18–20] Therefore, 18C6 would be able to adjust better the space between polymer sheets than 15C5 and 12C4, which would be the main cause for the fact that no clear expansion took place in the complexation of sPS/18C6.

The crystallites in sPS complex films often exhibit preferential orientation on the substate plate.[21,22] As for the cast film of sPS/$CHCl_3$ complex, the *ac* plane is parallel to the substate plane. The preferential orientation of crystallites was confirmed to be kept during the guest-exchange procedure with 12C4 by using 010 reflection. However, because of the absense of 010 reflection in X-ray diffractogram, the preservation of the preferential orientation was not able to be verified for 15C5 and 18C6. Due to the shortage of neutron beam time, we tried to investigate the orientation of crystallites by using IR spectroscopy. Figure 4 shows the transmission IR spectra of a starting sPS/$CHCl_3$ and resultant sPS/12C4, sPS/15C5, and sPS/18C6 films after being subjected to guest exchange, together with the IR spectrum of unoriented complex film for comparison. The band at 609 cm^{-1} is polarized perpendicular to the *ac* plane, and the band at 600 cm^{-1} is polarized parallel to the *a* axis.[23] In ordinary IR transmission measurement on a polymer film, the electric field of the incident radiation is parallel to the film surface, so that vibrational modes parallel to the surface are emphasized in the spectrum. Comparing with the unoriented sPS/THF complex

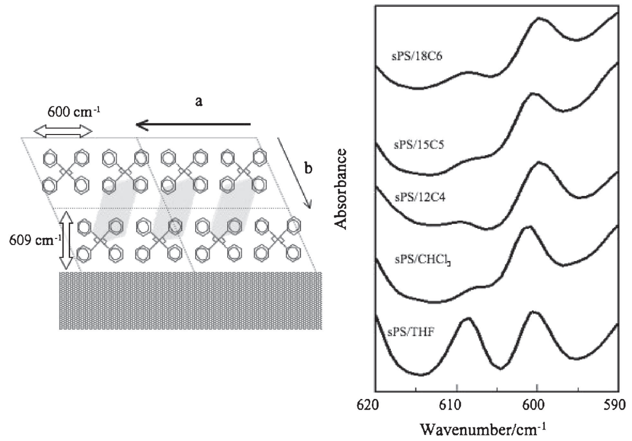

Figure 4. Infrared spectra of sPS complex films. The films of sPS complexes with 12C4, 15C5, and 18C6 were prepared from cast sPS/$CHCl_3$ films. The sPS/THF film was an unoriented film obtained from a glass sample.

film, all the starting and resultant films showed a marked intensity decrease in the 609 cm^{-1} band, which indicates that the preferential orientation in the starting complex was kept in all the sPS/crown ether complexes.

From the above experimental results obtained by neutron diffractometry and IR spectroscopy, it has been clarified that sPS forms with all the three crown ethers, 12C4, 15C5, and 18C6, essentially the same crystalline complex structure where guest molecules are incorporated between polymer sheets, keeping the preferential orietation of crystallographic axes during guest exchange procedure, though neither sPS/15C5 and sPS/18C6 exhibit clear evidence in X-ray diffraction. This study also demonstrated that neutron diffraction experiments employing the combination between deuterated polymer matrix and hydrogenated guest (and vice versa) would provide valuable crystallographic information about polymer crystalline complexes.

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References

1 A. Sorrentino, V. Vittoria, in *Syndiotactic Polystyrene: Synthesis, Characterization, Processing, and Applications*, ed. by J. Schellenberg, Wiley, Hoboken, **2009**, pp. 157–192.
2 G. Guerra, A. R. Albunia, C. D'Aniello, in *Syndiotactic Polystyrene: Synthesis, Characterization, Processing, and Applications*, ed. by J. Schellenberg, Wiley, Hoboken, **2009**, pp. 194–236.
3 Y. Uda, F. Kaneko, N. Tanigaki, T. Kawaguchi, *Adv. Mater.* **2005**, *17*, 1846.
4 H. Itagaki, T. Sago, M. Uematsu, G. Yoshioka, A. Correa, V. Venditto, G. Guerra, *Macromolecules* **2008**, *41*, 9156.
5 A. D. G. Del Mauro, M. Carotenuto, V. Venditto, V. Petraccone, M. Scoponi, G. Guerra, *Chem. Mater.* **2007**, *19*, 6041.
6 C. D'Aniello, P. Musto, V. Venditto, G. Guerra, *J. Mater. Chem.* **2007**, *17*, 531.
7 P. Stegmaier, A. D. G. Del Mauro, V. Venditto, G. Guerra, *Adv. Mater.* **2005**, *17*, 1166.
8 F. Kaneko, Y. Uda, A. Kajiwara, N. Tanigaki, *Macromol. Rapid Commun.* **2006**, *27*, 1643.
9 A. R. Albunia, C. D'Aniello, G. Guerra, D. Gatteschi, M. Mannini, L. Sorace, *Chem. Mater.* **2009**, *21*, 4750.
10 Y. Chatani, Y. Shimane, T. Inagaki, T. Ijitsu, T. Yukinari, H. Shikuma, *Polymer* **1993**, *34*, 1620.
11 O. Tarallo, V. Petraccone, A. R. Albunia, C. Daniel, G. Guerra, *Macromolecules* **2010**, *43*, 8549.
12 V. Petraccone, O. Tarallo, V. Venditto, G. Guerra, *Macromolecules* **2005**, *38*, 6965.
13 O. Tarallo, M. M. Schiavone, V. Petraccone, C. Daniel, P. Rizzo, G. Guerra, *Macromolecules* **2010**, *43*, 1455.
14 Y. Uda, F. Kaneko, T. Kawaguchi, *Macromol. Rapid Commun.* **2004**, *25*, 1900.
15 F. Kaneko, N. Kashihara, T. Tsuchida, K. Okuyama, *Macromol. Rapid Commun.* **2010**, *31*, 554.
16 F. Kaneko, K. Sasaki, N. Kashihara, K. Okuyama, *Soft Mater.* **2011**, *9*, 107.
17 N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* **1986**, *19*, 2464.
18 G. Wipff, P. Weiner, P. Kollman, *J. Am. Chem. Soc.* **1982**, *104*, 3249.
19 A. A. El-Azhary, A. A. Al-Kahtani, *Spectrochim. Acta, Part A* **2000**, *56*, 2783.
20 M. D. Paulsen, J. R. Rustad, B. P. Hay, *J. Mol. Struct.: THEOCHEM* **1997**, *397*, 1.
21 P. Rizzo, M. Lamberti, A. R. Albunia, O. R. de Ballesteros, G. Guerra, *Macromolecules* **2002**, *35*, 5854.
22 P. Rizzo, A. Spatola, A. D. G. Del Mauro, G. Guerra, *Macromolecules* **2005**, *38*, 10089.
23 F. J. Torres, B. Civalleri, A. Meyer, P. Musto, A. R. Albunia, P. Rizzo, G. Guerra, *J. Phys. Chem. B* **2009**, *113*, 5059.