Structural and Dynamical Properties of n-Alkane Molecules in Clathrate Phase of Syndiotactic Polystyrene

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Summary: Syndiotactic polystyrene (sPS) forms a clathrate phase with a variety of compounds. Not only rigid molecules but also flexible molecules can be stored in the cavities of the clathrate phase. To clarify the adjustment mechanism of a flexible guest molecule to the sPS clathrate system, the host and guest structures were investigated by means of solid-state ^{13}C NMR and Raman spectroscopy, and X-ray diffractometry for the sPS clathrates with a series of n-alkanes from n-hexane to n-decane. Although the 010 spacing of the host sPS lattice expanded slightly on going from n-hexane to n-heptane, it decreased markedly at n-octane and then increased gradually with the chain length of guest n-alkane. The conformational change of guest n-alkane molecules was involved in this anomalous change in the 010 spacing. Majority of the n-hexane and n-heptane molecules took extended chain structures in the clathrates, whereas all longer n-alkanes took bent chain structures. The mean-square displacement of hydrogen atoms in the clathrates was estimated by quasielastic neutron scattering experiments. It was confirmed that the host lattice contraction suppressed thermal motion of the clathrate system.

Keywords: conformational analysis; host guest system; neutron scattering; NMR; structure property relations

Introduction

Since the synthesis of syndiotactic polystyrene (sPS) was first reported,[1] a large number of studies have focused on the complex polymorphic behavior of this polymer. Its variety of crystalline states can be divided into two groups with respect to the main-chain conformation: α and β forms of planar Trans-Trans (TT) conformation,[2–7] and γ and δ forms of helical Trans-Trans-Gauche-Gauche (TTGG) conformation.[8–10] In addition to these crystalline phases, sPS forms a clathrate phase with a variety of small molecules such as chloroform, toluene and xylene. In the clathrate phase, guest molecules are found in cavities of the crystal lattice, each of which is surrounded by ten phenyl groups of sPS taking TTGG conformation.[11–13]

Existence of clathrate phase is one of the important characteristics of sPS. δ form is the first polymeric sieve obtained by extracting guest molecules from the clathrate phase.[8,14] In the δ form, the sPS framework of the clathrate phase is kept almost unchanged. This nanoporous structure is considered applicable to chemical separation and sensing devices, and many studies have been conducted on the structure and properties of this material.[15–21]

Recently, another potential of the clathrate phase has received attention. The sPS framework of the clathrate phase, which can be used as building blocks for func-

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tional composite materials. In order to add a new function to polymer materials, functional molecules are generally doped into the amorphous region; addition to the crystalline region is quite rare. However, the ability of sPS to hold various kinds of molecules as guests in the cavities can be used in making composite polymer materials with functional molecules. Such polymer crystalline region based composites would have the following advantages: regular arrangement of doped molecules, prevention (or retardation) of the doped molecules from dissipating from composite materials and aggregating in their surface or interiors, and the orientation control of doped molecules by controlling the arrangement of polymer crystalline region. Furthermore, by combining the characteristics of the host polymer materials and guest molecules, a new kind of functional materials can be developed. By using the guest exchange phenomenon,[10,22–24] the range of guest molecules for the sPS clathrate has been expanded. Some functional molecules have already been incorporated into the clathrate phase.[25–28]

Understanding the influence of the host–guest interaction on the structural and dynamical properties of guest molecules is important when producing the composite materials based on the sPS clathrate; but, so far, the influence has not been studied sufficiently. In this study, we examined the host–guest interaction in sPS clathrates with flexible guest molecules. Using a series of n-alkanes from n-hexane to n-decane, the chain-length dependence of structure and dynamical property was investigated. We showed that the clathrate lattice shrinks in n-octane on increasing the chain length of the guest n-alkane, which correlates the conformational change of the guest as well as the reduction of thermal motion in the clathrate system.

Experimental

Sample

Syndiotactic polystyrene (sPS) was supplied by Idemitsu Petrochemical Co., Ltd. The weight-average molecular weight (M_w) was 197, 000 g/mol and M_w/M_n was 1.98. Atactic polystyrene (aPS) was purchased from Aldrich Chemical Co. ($M_w = 280{,}000$) Chloroform and n-alkanes from n-hexane to n-decane were purchased from Nakalai Tesque and used without further purification.

Film samples of the sPS clathrate containing n-alkanes were prepared as follows: initially, films of sPS/chloroform clathrate (thickness: 40–50 μm) were prepared by casting an sPS/chloroform solution on a glass plate. The films were then soaked in liquid n-alkane for at least 3 days. Each sample was maintained under vacuum for 24 h before measurements were taken. The weight fractions of n-alkanes were about 8%.

Film samples of aPS containing n-alkanes were prepared by soaking in each liquid n-alkane for 1 h: n-hexane and n-heptane at room temperature, and n-octane, n-nonane, and n-decane at 50 °C.

Measurements

Powder X-ray diffraction diagrams were measured using a Rigaku RINT-2000 diffractometer with Cu Kα radiation. The data were collected at a rate of 0.5°/min with a step size of 0.05°.

Polarized IR spectra were taken using a JASCO FT/IR 510 spectrometer and a wire-grid polarizer at a resolution of 2 cm^{-1}. The number of accumulation cycles was 128. Raman spectra were taken using a BIORAD FT-Raman spectrometer with a YAG Nd near-IR laser as an exciting source. The 180° backscattering light was collected at a resolution of 2 cm^{-1} with 1K–4K scans. An Oxford flow-type cryostat was used to prevent samples from getting heated by irradiation of the laser beam.

^{13}C CP/MAS spectra were measured at room temperature with a Chemomagnetics CMX-300 spectrometer (JEOL) at 75.5 MHz and a CP/MAS accessory. The sample was contained in a 5-mm bullet type rotor made of zirconium. The magic angle spinning (MAS) rate was set to 5 kHz to avoid the overlap of spinning side bands.

The FIDs were apodized by an exponential window function, and the number of scans, spectral width, and data points were 1K–2K, 15 kHz and 8K, respectively.

Quasielastic neutron scattering (QNS) measurements were carried out with a direct geometry chopper-type spectrometer AGNES (in the Institute for Solid State Physics, The University of Tokyo), which is installed at the cold neutron guide (C3-1) of JRR-3M (Tokai, Japan). The energy resolution was 0.12 meV and the scattering vector was $Q\,(=4\pi\sin\theta/\lambda)$. range was 0.23–2.70 Å^{-1}.

Lattice Contraction for Clathrates with Increase in n-Alkane Chain Length

Figure 1 shows the variation in lattice spacing measured by powder X-ray diffraction, accompanying the increase in n-alkane chain length. The TTGG helical polymer chains are aligned side by side along the *a* axis into polymer sheets, which are stacked upon each other in layers. The guest molecules are sandwiched between the polymer sheets. The 010 spacing corresponds to the distance between neighboring polymer sheets that hold guest n-alkane molecules. Although the 010 spacing expands slightly from n-hexane through n-heptane, it decreases markedly between n-heptane and n-octane and then increases gradually with length. However, even in n-decane the 010 spacing does not recover to the level in n-hexane. Conversely, the $\bar{2}10$ spacing shows no clear chain-length dependence. The $\bar{2}10$ spacing corresponds to the distance between neighboring TTGG helices within a polymer sheet. This result suggests that the chain length of n-alkanes has no large influence on the array of TTGG helices in a polymer sheet.

Conformational Changes of n-Alkanes

Figure 2 shows the solid-state NMR spectra of sPS/n-alkane clathrates together with those of aPS/n-alkane mixtures. For the sPS clathrates, the signals due to the n-alkane component exhibit a marked dependence on chain length. In particular, the profile of these signals change remarkably between n-heptane and n-octane. The sPS/n-hexane and sPS/n-heptane clathrates exhibit the relatively narrow signals due to C_1, C_2, C_3, and C_4 (only in sPS/n-heptane) carbon atoms. However, these signals become significantly broadened in the clathrates with n-octane, n-nonane, and n-decane. In

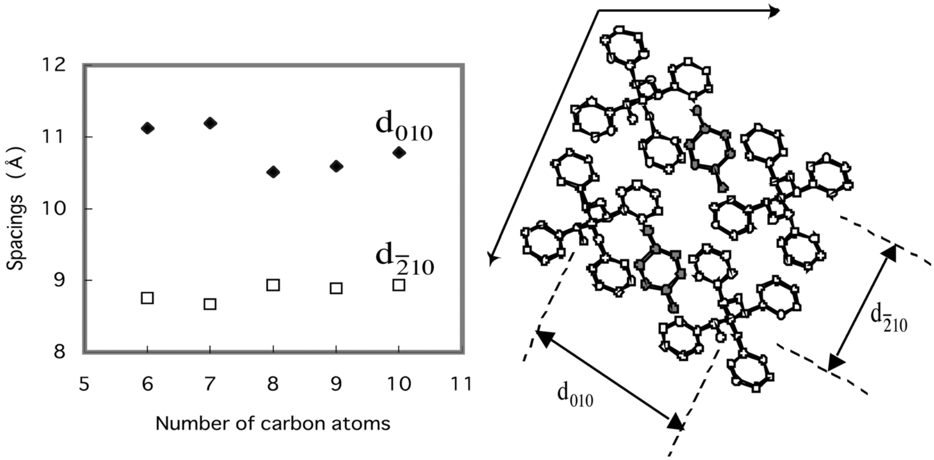

Figure 1.
Change in the lattice spacing of sPS/n-alkane clathrates. Left: Variation of 010 and $\bar{2}10$ lattice spacing depending on the chain length of n-alkane. Right: Crystal structure of the sPS clathrate with toluene (after Chatani [11]).

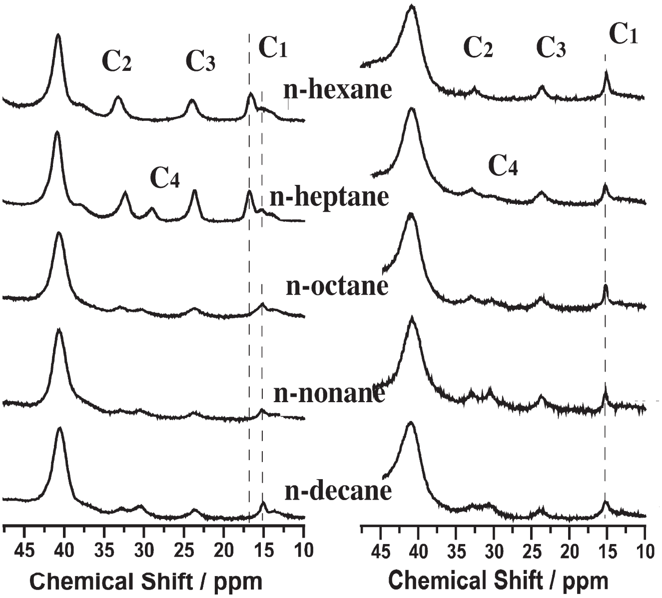

Figure 2.
Solid-state NMR spectra of sPS/n-alkane clathrates and aPS/n-alkane mixtures.

particular, the signal of the C_1 (methyl) atom shows characteristic behavior. In the sPS/n-hexane and sPS/n-heptane clathrate, the C_1 signal consists of two components: the sharp component at 16.3 ppm and the broadened component in upfield (low ppm). The sharp component corresponds to methyl terminals of extended hydrocarbon chains, and disappears in the clathrates with longer n-alkanes; only the upfield component with a small peak at 15.2 ppm is observed. When disordered, hydrocarbon chains show the upfield shifts for carbon signals due to the γ-gauche and vicinal gauche effect.[29,30] Therefore, the change in the C_1 signal suggests that all-trans conformation is possible only for n-hexane and n-heptane, and longer n-alkanes take only bent conformations in the cavities of the clathrate phase.

The signals due to C_1, C_2, C_3, and C_4 carbons in aPS/n-alkane mixtures have similar characteristics as those in the clathrates with longer n-alkanes (Figure 2). Since aPS is a typical amorphous polymer (T_g: approximately 100 °C), mixed n-alkane molecules are thought to be conformationally disordered. The spectral similarity strongly suggests the bent conformation of n-alkane in the cavities of sPS/n-octane, sPS/n-nonane, and sPS/n-octane clathrates. The C_1 atom in the aPS matrix exhibits only the upfield component with a sharp signal at 15.2 ppm. Although the motion of n-alkane is more or less constrained in the glassy aPS matrix, despite a reduction in T_g to some extent, the methyl terminal must be more mobile than the other carbons, which is believed to lead to the sharper C_1 signal.

The extended conformation of guest n-hexane and n-heptane in the clathrates are confirmed with longitudinal acoustic modes (LAM) observed in low-frequency Raman spectra. The most in-phase LAM, LAM-1, is an accordion-like motion. Ordered hydrocarbon chains show a LAM-1 band at frequencies that are nearly inversely proportional to their chain length.[31–33] The LAM-1 band is expected to appear at 373 cm^{-1} for n-hexane and at 311 cm^{-1} for n-heptane. The sPS/n-hexane and sPS/n-heptane clathrates exhibit Raman bands at these frequencies (Figure 3).

Thermal Motion of Hydrogen Atom

Dynamic scattering laws $S(Q,\omega)$ obtained by QNS experiments consist of two components, a sharp intense peak due to the elastic scattering and a broadened quasielastic peak, both of which are centered at $\omega = 0$. The quasielastic peak of the sPS clathrates was so weak that only the elastic component was traceable during the study. This was because T_g of the main component sPS was approximately 100 °C and all its diffusive motions were frozen in the amorphous region as well as the crystalline region (crystallinity: ca. 40%). The elastic scattering intensity $I_{el}(Q)$ decreases with an increase in the Q value, which relates to the thermal motion of atoms. The mean-square displacement $\langle U^2\rangle$ can be evaluated using the following Debye-Waller formula,

$$\ln(I_{el}(Q)/I_{el}(0)) = -(1/3)\langle U^2\rangle Q^2$$

where $I_{el}(0)$ is $I_{el}(Q)$ at $Q = 0$.[34] The results obtained are summarized in Figure 4. There is a clear difference in $\langle U^2\rangle$ between the sPS/n-heptane and sPS/n-octane clathrates. The $\langle U^2\rangle$ value drops about 8% at sPS/n-octane, the same position where the 010 spacing becomes narrow, in spite of the large contribution of the amorphous region to QNS.

The $\langle U^2\rangle$ value can be regarded as a measure for the motion of hydrogen atoms in the clathrate system, since hydrogen has an overwhelmingly large incoherent cross section. Therefore, the drop of $\langle U^2\rangle$ suggests that the thermal motion of the sPS clathrate is decreased in the clathrates with n-octane and longer n-alkanes in connection with the lattice contraction.

Discussion

As described above, the sPS/n-alkane clathrates show a unique dependence of the 010 spacing on the chain length of guest n-alkanes. In spite of an increase by one methylene group, the 010 spacing of the host sPS lattice becomes narrow on going from n-heptane to n-octane. The results of solid-state ^{13}C NMR experiments show that the conformational change of guest n-alkanes relate to this host lattice contraction; a high ratio of n-hexane and n-heptane molecules take the extended conformation, whereas only the bent conformation is found for n-octane, n-nonane, and n-decane. The appearance of the LAM-1 band supports this extended conformation of n-hexane and n-heptane. A similar preferential conformation in the sPS clathrate was reported in 1,2-dichloro-

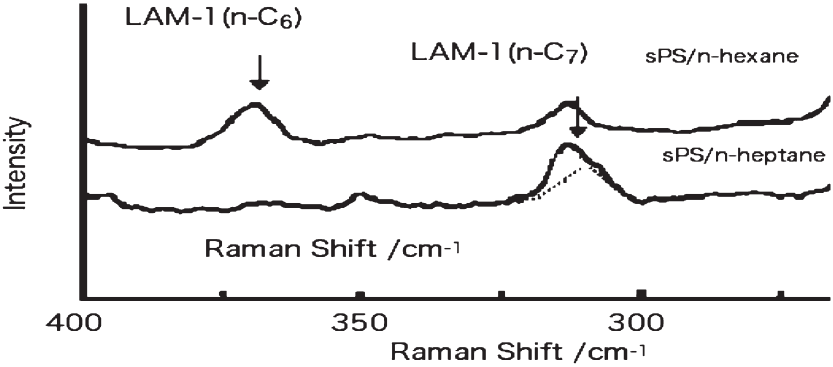

Figure 3.

FT-Raman spectra of sPS/n-hexane and sPS/n-heptane clathrates. The arrowed band of sPS/n-heptane clathrate consists of two components, a band due to sPS and a LAM-1 band due to n-heptane. The LAM-1 (n-C_7) component is designated by the dotted line.

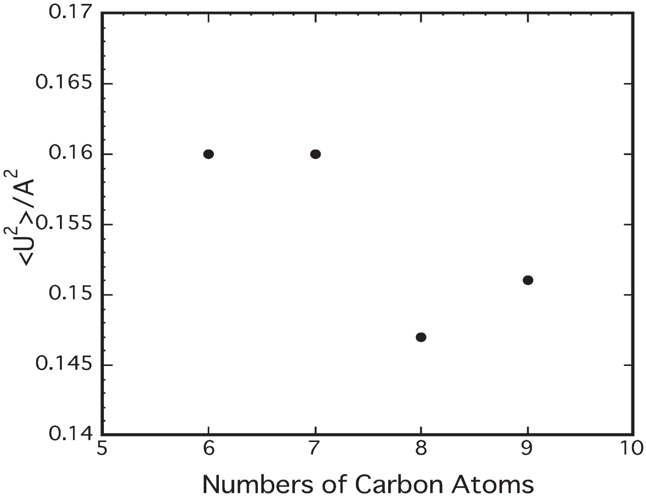

Figure 4.
Dependence of $\langle U^2 \rangle$ on the chain length of guest n-alkanes at 300 K.

ethane (DCE); the Cl-C-C-Cl portion adopts trans conformation for the majority of DCE molecules.[13]

In the sPS clathrates, the TTGG helical polymer chains align along the *a* axis of polymer sheets, between which the guest molecules are sandwiched. Planar guest molecules such as benzene, toluene, and xylene are stored in the cavities with their molecular plane perpendicular to the sPS helices. It can be inferred that the molecular axes of n-hexane and n-heptane are also nearly perpendicular to the sPS TTGG helices. In the clathrate with 1,2-DCE, two chloride terminals are intruded into the polymer walls on opposite sides. The situation is the same with the methyl terminals of p-xylene.[35] We suggest that the methyl terminals of n-hexane and n-heptane contacts with the walls on the opposite sides. In this case, the increase in the chain length of n-alkane would lead to the expansion of the 010 spacing. The lattice expansion decreases density of the middle zone and the interaction between polymer sheets becomes weak, regardless of whether it is a direct interaction or guest-mediated interaction. Accordingly, the stability of the system deteriorates.

We infer that the lattice contraction accompanying the guest conformational change occurs to prevent the decrease in stability. The bent conformation is energetically higher than the extended one, but it makes the polymer sheets move closer to one another and the middle zone becomes dense. The balance between the two factors, bent n-alkane conformation and lattice expansion, must determine the point at which the conformational change takes place. The length of n-heptane, ca. 7.6 Å, should be the criterion. Recently, we have found a similar phenomenon in the sPS clathrates with carboxylic acid dimers;[36] acetic acid forms a planar dimeric structure with cyclic hydrogen bonds, whereas propionic acid exhibits an anomaly in dimeric hydrogen bonds due to the distortion of dimeric units. The inter-terminal distance of a planar dimer is slightly less than 7.6 Å for acetic acid and clearly exceeds this value for propionic acid.

The increase in the density of the middle zone by the lattice contraction may have a significant effect on the dynamical properties of the clathrate system. It can be inferred that the increased host–guest interactions depress the thermal motion of the guest and its surrounding, for example the phenyl groups of sPS, which agrees with the results obtained by QNS experiments (Figure 4). In this study, we used conventional hydrogenated samples for both host sPS and guest n-alkanes and the $\langle U^2 \rangle$ value obtained reflects the dynamic properties of the whole region of the clathrate samples. In spite of such an adverse condition that about half of the QNS intensity is due to the amorphous part, the mean-square displacement $\langle U^2 \rangle$ of hydrogen atoms exhibits a clear decrease at the same position, n-octane; the influence of the lattice contraction on thermal motion could therefore be significant. In order to obtain further information about thermal motion in each region and analyze the guest motion in more detail, we are now preparing QNS experiments using fully and partially deuterated sPS samples.

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