Study on δ-Form Complex in Syndiotactic Polystyrene-Organic Molecules System III.　Fine Structures of Complexes with Xylene Isomers by Means of High-Resolution Solid-State ^{13}C NMR Spectroscopy

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ABSTRACT:　Syndiotactic polystyrene (sPS) is known to form a clathrate compound with *p*-xylene and *m*-xylene, called δ-form complex. In this study, the structures of the sPS/*p*-xylene and sPS/*m*-xylene systems were investigated by high-resolution solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) and X-ray diffraction. From the Miller indices of the (0,1,0) reflection, it was confirmed that the distance between sPS helical chains in the *m*-xylene system was longer than that of the *p*-xylene system. It was concluded that the location of one methyl group of *m*-xylene in the sPS δ-form complex coincided with that of one methyl group of *p*-xylene, because the ^{13}C NMR chemical shift and spin-lattice relaxation time of the methyl carbon of *p*-xylene were similar to those of one methyl carbon of *m*-xylene in the sPS δ-form complex. The meta substituted another methyl group of *m*-xylene showed a low-field chemical shift, indicating it close to the two phenyl groups of sPS chains in the δ-form complex.

KEY WORDS　Syndiotactic Polystyrene / Xylene Isomer / High-Resolution Solid-State ^{13}C NMR Spectroscopy / Clathrate / Characterization /

The synthesis of highly stereo specific syndiotactic polystyrene (sPS), which forms clathrate with some organic molecules was reported.[1,2] The clathrate is a crystalline form in sPS polymorphism and is called δ-form complex.　In the δ-form complex, the organic molecule is placed in a molecular cavity formed by two adjacent sPS chains having the TTGG helical conformations. The distance of two adjacent sPS helical chains in the δ-form complex depends on the guest molecules.[3] Some clathrate complexes consisting of polymers and organic compounds have remarkably excellent properties as applicants in separation, purification, molecular-recognition, and so on. When molecular size and shape of an organic molecule are suitable for molecular cavity in the δ-form complex, the clathrate is expected to have high ability of the preferential complex formation with the organic molecule. Therefore the clathrate of the sPS can be applied to molecular level separation and/or molecular recognition.

So far, several authors reported the complexing behavior of sPS with organic molecules. Guerra *et al.* prepared the δ-form complex with 1,2-dichloroethane (DCE) and confirmed that DCE molecules in the δ-form complex take only the trans conformation by infrared (IR) analysis.[4—6] The conformation of 1,2-dichloropropane in the cavity exhibits similar behavior to DCE. These findings suggest that the van der Waals

interactions between the guest molecule and molecular cavity of the host in the δ-form complex play important roles for the stability of the δ-form complex. Vapor-sorption and complexing or decomplexing between sPS and aromatic hydrocarbons were investigated[7—17] and found to depend strongly on guest molecules. Preferential complexing of *p*-xylene was clearly revealed in sPS membrane prepared from a mixture of the *p*- and *m*-xylene isomers.[17—19] Sorption studies confirmed the preferential sorption by *p*-xylene.[18] These results indicate that the xylene isomers can be separated by sPS even though physical properties of the isomers are nearly identical.[20] The aim of this study is to clarify the fine structures and molecular mobility of the sPS/*p*-xylene and sPS/*m*-xylene systems, especially the effects of methyl groups of these isomers in the δ-form complex by high-resolution solid-state ^{13}C NMR spectroscopy.

EXPERIMENTAL

Materials

Syndiotactic polystyrene (sPS; $M_w = 200000$, $M_w/M_n = 2.00$, tacticity = 99.9% confirmed by ^{1}H NMR) was kindly supplied by Idemitsu Petrochemical Co. Ltd. and used without further purification. Atactic polystyrene (aPS; $M_w = 280000$) was purchased from Aldrich and *m*-xylene and *p*-xylene were purchased

from Nacalai Tesque Inc. and used without further purification. SPS was dissolved in p- or m-xylene at 130 °C and the solutions (10 wt%) were cast at room temperature. Specimens containing the δ-form complex were dried under vacuum at room temperature until weight loss was not observed. The aPS/m-xylene sample obtained by aPS/m-xylene solution was dried under vacuum until the content of m-xylene became equal to that the sPS/m-xylene system.

Methods

Wide-angle X-ray diffraction patterns were recorded with nickel-filtered Cu Kα radiation (3.2 kW) by a Rigaku RAD-RC type X-ray diffractmeter at scanning rate of 1° min^{-1} and accumulation number 5. Amount of the guest molecule in the complex was determined by TGA. The high-resolution solid-state ^{13}C NMR spectra were obtained by a Varian UNITY 400 plus NMR spectrometer at 100.57 MHz under magic angle spinning (MAS; spinning rate of MAS was *ca.* 6 kHz) and high-power ^{1}H dipolar-decoupling (DD; strength of DD was about 60 kHz). High-resolution solid-state ^{13}C NMR spectra observed with cross polarization (CP; contact time in CP was 2 ms) and without CP were denoted as CP/MAS and DD/MAS, respectively. Repetition times were 5 s (with CP) and 10 s (without CP). Numbers of scans were 3000 (with CP) and 12000 (without CP). Approximately 300 mg sample was packed into a 7 mm o.d. zirconia rotor. ^{13}C NMR chemical shift of the methyne carbon of a solid adamantane (29.5 ppm relative to TMS) was used as an external reference standard. Spin-lattice relaxation times of ^{13}C nuclei, (T_1^C), were measured by Torchia's pulse sequence.[21]

RESULTS AND DISCUSSION

Estimation of crystallinity of the δ-form complex is very difficult and only a few papers[17,22] have been reported the crystallinity. In the present study, we calculated approximate crystallinity of the δ-form complex (χ_c^δ) as,

$$\chi_c^\delta = \Delta W \times \frac{4M_{styrene} + M_{xylene}}{M_{xylene}} \quad (1)$$

where ΔW is weight loss measured by TGA, and $M_{styrene}$ and M_{xylene} are molecular weights of styrene monomer and xylene, respectively. In this equation, one guest molecule was assumed present in the cavity formed by the four sPS monomer units in the δ-form complex, as also in previous reports on sPS/toluene system.[23,24] p- And m-xylene isomers in these systems were considered completely incorporated into the δ-
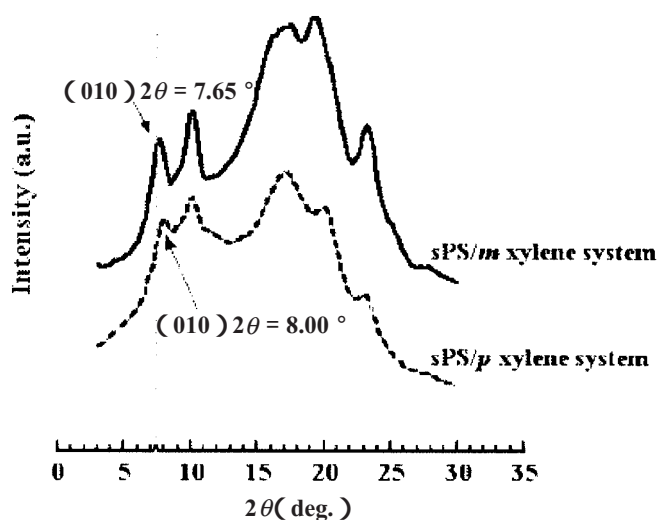


Figure 1. X-ray profiles of sPS/p-xylene and sPS/m-xylene systems at room temperature.

form complex. χ_c^δ were 70 and 65% for sPS/p-xylene and sPS/m-xylene systems, respectively, approximately agreeing with previous reports.[17,19]

Figure 1 shows X-ray diffraction profiles of the sPS/p-xylene and sPS/m-xylene systems. There are mainly five diffraction peaks typical of the δ-form complex of sPS.[23,24] The diffraction peak around 2θ = 8° was assigned to the (0,1,0) plane. This corresponds to the distance between two adjacent sPS helical chains along the b-axis of the unit cell of the δ-form complex. Other diffraction peaks observed at wider angle were observed at almost the same angle. Thus, structural differences of these δ-form complexes can be discussed by the (0,1,0) plane. In the sPS/p-xylene system, the peak appears at almost the same angle as in the sPS/toluene system.[23,24] This supports the previous findings that either methyl group of p-xylene exists at the same site in the cavity as that of the methyl group of toluene in the sPS/toluene system. In the sPS/m-xylene system, however, the reflection was observed at smaller 2θ angle, indicating that the distance of the helical sPS chains in the sPS/m-xylene system is longer than that of the sPS/p-xylene system. Assuming γ (= 121.2°) the same as that of sPS/toluene system,[23,24] the lattice constant along the b-axis can be calculated from the 2θ angles of (1,0,0) plane for the sPS/p-xylene and sPS/m-xylene systems to be 13.2 and 13.6 Å, respectively. The structure of δ-form complex depends on the guest molecular size and shape.
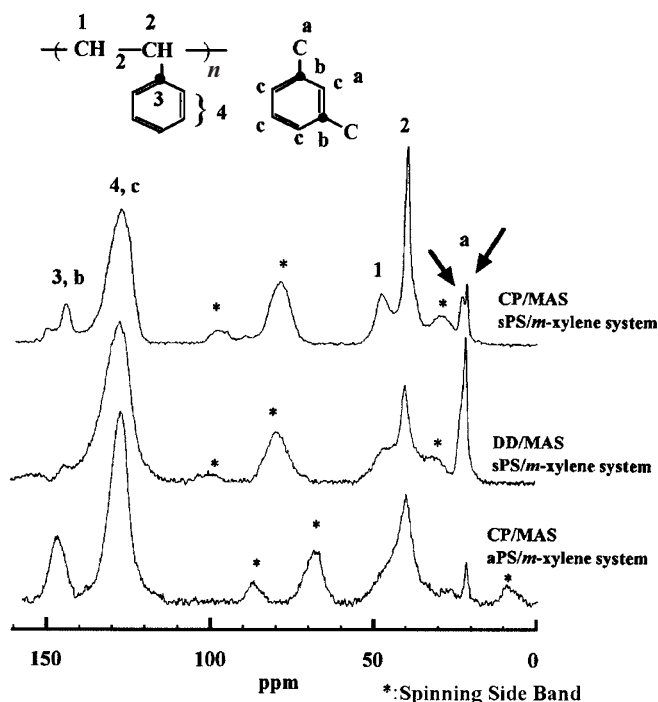
The effect of the methyl group substituted at the *para-* or *meta-* position of the phenyl ring on fine structure and local molecular motion was investigated by high-resolution solid-state ^{13}C NMR spectroscopy. ^{13}C NMR spectra of amorphous sPS and sPS/p-xylene system are shown in Figure 2. Assignments of the peaks
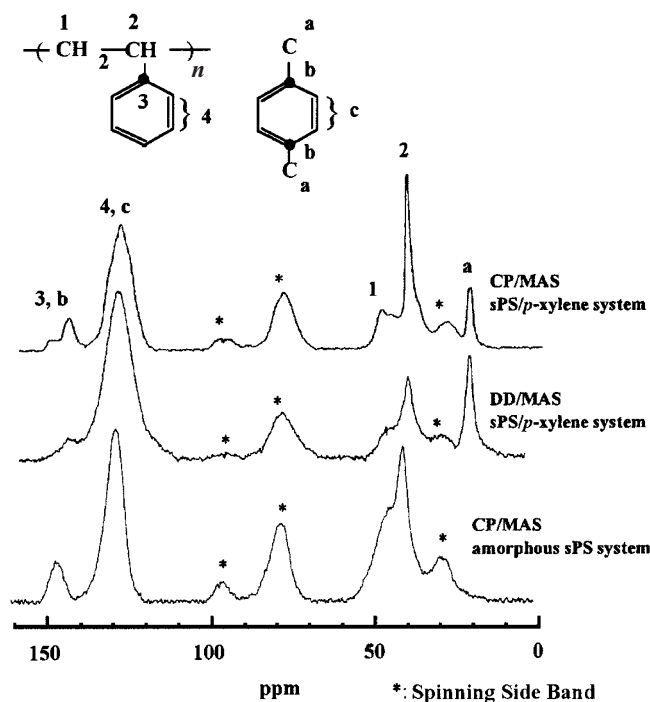
Figure 2. The high-resolution solid-state ^{13}C NMR spectra of sPS/p-xylene system and amorphous sPS at room temperature.

Figure 3. The high-resolution solid-state ^{13}C NMR spectra of sPS/m-xylene and aPS/m-xylene systems at room temperature.

were made according to literatures.[26–29] In the ^{13}C CP/MAS NMR spectrum of amorphous sPS, peaks assigned at methyne and methylene carbons of sPS were relatively broad, indicating the absence of ordered conformation. Relatively sharp peaks were seen for the δ-form complex which indicating highly-ordered conformation of sPS. ^{13}C CP/MAS NMR spectra of sPS/m-xylene and aPS/m-xylene systems are shown in Figure 3. The ^{13}C CP/MAS NMR spectrum of the sPS/m-xylene system showed similar features to that of sPS/p-xylene system, and hence it has an ordered conformation.

Peaks observed at 20 ppm can be easily assigned to the methyl carbons of the p- and m-xylene isomers by comparing them with the spectrum of amorphous sPS (see Figures 2 and 3). Two peaks were observed for the sPS/m-xylene system at 21.8 and 23.2 ppm whose intensities were almost the same. Only one peak was observed at 21.5 and 22.0 ppm for the sPS/p-xylene and aPS/m-xylene systems, respectively. ^{13}C NMR chemical shift of one methyl carbon of m-xylene in the δ-form complex was lower field by about 1 ppm comparing with that of another methyl carbon of m-xylene. One of possibilities ring-currents[30] in phenyl groups of sPS might have resulted this low-field shift. These results can be explained as follows: 1. One methyl carbon of m-xylene in the δ-form complex is located where the effective magnetic field differs from that of other methyl carbon. For aPS/m-xylene and sPS/p-xylene systems, environments of methyl carbons of m-xylene and p-

xylene are equivalent in chemical shifts. 2. The motion of m-xylene in the δ-form complex is much less compared with the frequency corresponding to difference in chemical shift (= $2\pi \times \Delta\delta \times 100.57$ Hz, i.e., about 8.8×10^2 Hz). The m-xylene molecules are thus fixed in the cavity of the δ-form complex.

CP enhances the intensity of rigid carbons. Further, ^{13}C DD/MAS NMR spectra with short repetition time (10 s),[31,32] the intensity of the relatively mobile carbons was highly enhanced. The local mobility of the methyl carbons of p- and m-xylene isomers can be determined by comparing the intensities of the peak for ^{13}C DD/MAS and ^{13}C CP/MAS NMR spectra. Therefore, peak intensity of methyl carbon appears relatively higher than that of other carbons such as methylene(around 50 ppm) and methyne(around 40 ppm) carbons of sPS in the DD/MAS spectra. Peak intensity of the methyl carbon at 21.8 ppm was obviously larger than that of the methyl carbon at 23.2 ppm in the DD/MAS spectrum of sPS/m-xylene system. One methyl carbon appearing at 23.2 ppm was relatively restricted in local motion, in comparison with the other appeared at 21.8 ppm for m-xylene in δ-form complex. Trezza and Grassi reported the rotation of the methyl group of toluene-d_8 in the sPS δ-form complex to be very fast by solid-state ^{2}H NMR spectroscopy.[33] The local motion of methyl groups of xylene isomers in the sPS δ-form complexes may rotate very fast as toluene-d_8.

Spin-lattice relaxation times of ^{13}C ($T_1{}^C$) were mea-

Table I. ^{13}C spin-lattice relaxation time, T_1^C for methyl carbons of *p*- and *m*-xylene isomers, in the sPS δ-form complex

	Carbons	T_1^C (sec.)
sPS/*p*-xylene system	CH$_3$ of *p*-xylene (21.5 ppm)	8.6
sPS/*m*-xylene system	CH$_3$ of *m*-xylene (21.8 ppm)	8.5
	CH$_3$ of *m*-xylene (23.1 ppm)	6.9
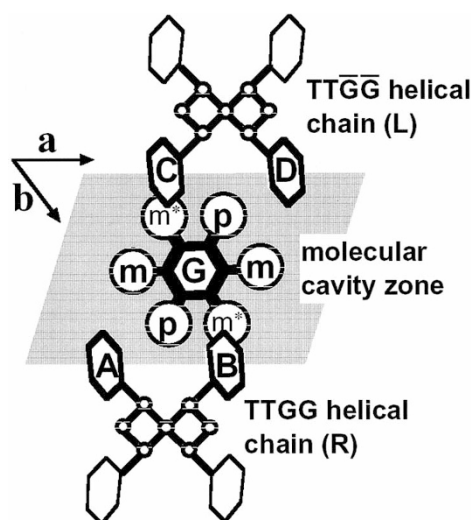
Figure 4. Schematically represented model of the δ-form complex of sPS/xylene system viewed along the sPS TTGG helical chain axis. The guest molecule (*p*- or *m*-xylene; marked as "G") is surrounded by the phenyl groups of sPS (marked as "A", "B", "C", and "D"). The methyl groups of the guest are drawn by six lettered circles (The details are described in the text.).

sured to confirm the local mobility of methyl carbons in sPS/*p*-xylene and sPS/*m*-xylene systems. T_1^C were determined at room temperature by Torchia's method, and are given in Table I. T_1^C of methyl carbons in sPS/*p*-xylene and sPS/*m*-xylene systems become longer at higher temperature and thus are in an extremely narrow region of the BPP theory.[34] Shorter T_1^C was found to indicate relatively immobile carbon at room temperature. T_1^C for the peak at 23.2 ppm was shorter than that at 21.8 ppm in the sPS/*m*-xylene complex, indicating that the mobility of the carbon corresponding to the peak at 23.2 ppm is restricted. The mobility of the methyl carbon at 21.5 ppm was very similar to that of the methyl carbon of the *p*-xylene in the sPS/*p*-xylene system.

A structural model of the δ-form complex for the sPS/*p*-xylene and sPS/*m*-xylene systems is proposed on the basis of the present data and results of several authors.[23, 24, 35—37] Figure 4 indicates a schematic representation of the δ-form complex model in which the two adjacent right-handed (–TTGG–)$_2$, left-handed (–$\overline{TT}$GG–)$_2$ helical sPS chains accommodated one symbolized guest molecule.

For the crystal structure of sPS/toluene system, Chatani *et al.*[23, 24] maintain that guest molecules oc-

cupy isolated holes (molecular cavities) between sPS chains. In the case of *p*-xylene, the positions of two methyl groups are almost the same as for the methyl group of toluene of the sPS/toluene system, and cannot be distinguished because of symmetric location ("p" in Figure 4). One methyl group of *m*-xylene ("p") is at the same site as that of *p*-xylene from the fact that the ^{13}C NMR chemical shift and T_1^C of one methyl carbon of *m*-xylene are almost the same as those of the methyl carbon of *p*-xylene. The other methyl group of *m*-xylene must thus exist at the site marked "m" and "m*" in the cavity (Figure 4). However, the methyl group as "m*" overlaps the phenyl group of sPS if the b-axis is kept at 13.6 Å. Hence, the one methyl group of *m*-xylene is located at the "m" position in Figure 4.

The methyl group "m" is located close to the nearest phenyl ring of sPS and probably is subjected to a stronger field due to the ring-current of phenyl groups compared to other methyl carbons "p". Thus, the two methyl carbon peaks at 21.8 and 23.2 ppm in the ^{13}C NMR spectra of the sPS/*m*-xylene system can be assigned to methyl carbons "p" and "m", respectively. The local mobility of the methyl group "m" is restricted by steric hindrance with phenyl groups of sPS. The wide distance between sPS chains in the sPS/*m*-xylene system can be explained by repulsive interactions between the methyl group(m*) of *m*-xylene and phenyl groups of sPS.

CONCLUSIONS

To clarify fine structures of the δ-form complexes in sPS/*p*-xylene and sPS/*m*-xylene systems were investigated by X-ray diffraction and high-resolution solid-state ^{13}C NMR. From Miller indices (1,0,0) reflection, the distance between sPS helical chains in sPS/*m*-xylene system was longer than in the sPS/*p*-xylene system. Methyl carbon peaks in ^{13}C NMR spectra for sPS/*p*-xylene and sPS/*m*-xylene systems were observed as singlet and doublet, respectively. The location of one methyl group in *m*-xylene in the δ-form complex coincided with that of the one of methyl groups of *p*-xylene. Another methyl group of *m*-xylene was located close to the phenyl groups of sPS from the ^{13}C NMR chemical shift and spin lattice relaxation time. This study clarifies different of complex formation between sPS with *p*-xylene and *m*-xylene. In a subsequent paper, complex formation in sPS with aromatic hydrocarbons systems will be discussed.

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