

Studies on the δ -Form Complex in the Syndiotactic Polystyrene–Organic Molecule System. II. Structural Investigation of the δ -Form with *p*- and *m*-Xylene Isomers

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ABSTRACT: Syndiotactic polystyrene (sPS) membranes containing different mole fractions of *p*-xylene were prepared by a solution-casting procedure. Complex formation between sPS and xylene was studied by thermogravimetric analysis and Fourier transform infrared spectroscopy. The stability and desorption behavior of the sPS–guest solvent and phase transitions were studied by differential scanning calorimetry. The formation of the δ -form complex in the presence of different mole fractions of xylene isomers was

analyzed and confirmed. The mole fraction of *p*-xylene in the dried membrane was found to be higher than that of the corresponding mole fraction in the isomer solvent solution used for casting. This was attributed to the preferential complexing ability of *p*-xylene with sPS. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2882–2887, 2003

Key words: syndiotactic polystyrene; xylene isomers; TTGG; crystallization and inclusion chemistry

INTRODUCTION

Ever since the report of Ishihara et al. describing the synthesis of a highly stereo regular syndiotactic form of polystyrene,¹ several interesting reports^{2–6} discussing various properties of this polymer have been published. Syndiotactic polystyrene (sPS) exists in many polymorphic crystalline forms, viz., α , β , γ , and δ , that differ by the conformational order and the crystalline packing of chains having the same conformational order. Among the different polymorphic forms, the δ form has a clathrate structure that intercalates solvent molecules as guests. These sPS–solvent superstructures present a combination of structural characteristics and properties that makes them suitable for engineering and technological applications.^{7–11}

Syndiotactic polystyrene crystallizes in different forms depending on the crystallization condition and the nature of the solvents. There is experimental evidence^{12,13} pointing to the formation of polymer–solvent complexes that stabilize the ordered TTGG con-

formation of sPS in a gel and thin film. Syndiotactic polystyrene forms fibrillar clathrates owing to a TTGG helical strip (δ form) that is stabilized by different aromatic solvents such as benzene,¹⁴ toluene,¹⁵ ethylbenzene,¹⁶ *o*-xylene,¹⁷ and decalin.¹⁸ The formation and thermal stability of the TTGG helical conformation in sPS clathrate depends heavily on the type of organic solvent. Recently, we have reported the formation of a large amount of TTGG conformations in the sPS–toluene and *p*-xylene system with improved kinetics and thermal stability over the sPS–benzene, *m*-xylene, and mesitylene systems.¹⁹ It has been found that the sPS host is capable of selectively including some guest molecules by a noncovalent interaction in its hydrophobic cavity. Tsutsui et al.²⁰ have investigated the sorption behavior of sPS–, *p*-, and *m*-xylene systems individually. A brief report on the preferential complexing behavior of *p*-xylene with sPS from a mixture of xylene isomers has been recently reported by us.²¹ The complex formation between sPS and the xylene was studied, and the exact amount of solvent molecules present per styrene repeating unit was estimated. These results indicated that the preferential complexing ability of *p*-xylene was due to its favorable interaction with sPS. Herein we present the detailed studies of structural organization of the sPS δ -form complex with different mole fractions of xylene isomer solvents.

MATERIALS AND METHODS

Syndiotactic polystyrene (M_w : 2.11×10^5 , tacticity 99%, and a molecular dispersity of 2.8) was kindly

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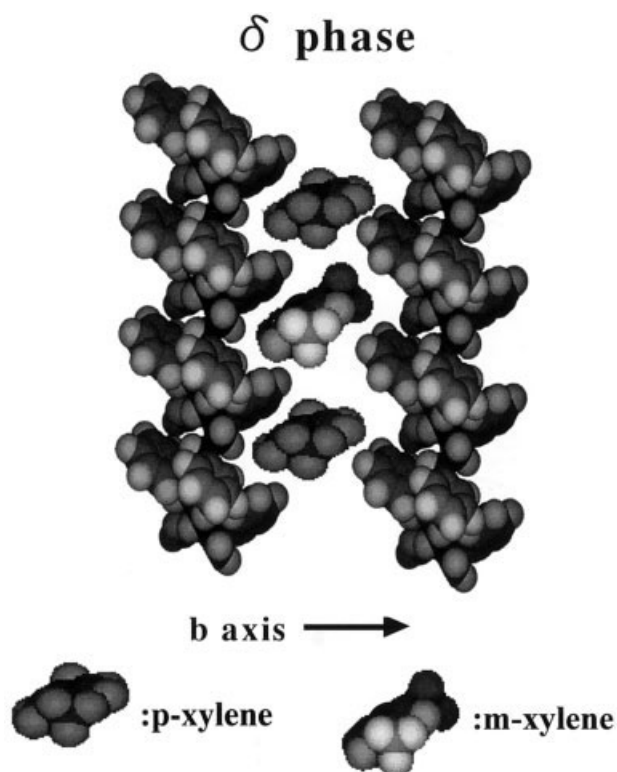


Figure 1 Schematic representation of xylene isomer clathrate in the δ form of sPS.

donated from the Idemitsu Petrochemical Co. Ltd., Tokyo, Japan. The isomer solvent containing *p*-xylene and *m*-xylene was procured as GR grade from Nacalai Tesque, Inc., Kyoto, Japan, and used without further purification. A solution casting procedure was used to prepare test membranes. A typical procedure involved the dissolution of sPS (1 wt %) in a mixture of *p*- and *m*-xylene isomers, with 0–1 mole fraction, at near its boiling point of 138°C. Membranes were prepared by casting from this homogeneous solution at room temperature. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Perkin Elmer DSC7 and a Seiko TG/DTA220, respectively, in the temperature range of 30–300°C at a heating rate of 5°C min⁻¹ under a nitrogen atmosphere. Fourier transform infrared (FTIR) spectra of the membranes were recorded using a Perkin Elmer FTIR spectrometer SPECTRUM 2000 between 4000 and 400 cm⁻¹ with a resolution of 1 cm⁻¹ at room temperature. The structural analysis was carried out using wide angle x-ray diffraction (WAXD) in a Rigaku RAD-RC instrument using CuK α radiation with a Ni filter in the 2θ range from 5°–30°.

RESULTS AND DISCUSSION

Structural representation of δ -phase formation in the sPS–xylene system (*p*- and *m*-xylene) is shown in Fig-

ure 1. Guest molecules are hosted in the cavities formed by sPS chains of the crystalline δ form. No bonding between the guest (solvent molecules) and the host (sPS) was observed in the system during the complex formation except van der Waals forces that might be essential to the stability of the structure. Further, the stability also depends on the volume, shape, and size of the guest molecules. Generally, the interaction between host–guests is greater in aromatic compounds compared to aliphatic compounds. C···H bonding is also very important in a wide variety of aromatic compounds and to a lesser extent, in aliphatic compounds.²² Based on this information, we expected the formation of the δ form in the sPS–xylene system with both *p*- and *m*-isomeric solvents due to their similar physical properties.²⁰ This could stabilize the helical form by incorporating *p*- and *m*-xylene molecules in between the phenyl groups of the sPS main chain.

In a previous article²¹ we demonstrated that *p*-xylene shows a preferential complexing behavior with sPS. We estimated the exact amount of solvent content in the sPS–xylene membrane by comparing the results of TGA and FTIR studies of the dried sPS membrane and the isomer solution composition. This is plotted in Figure 2. It can be seen from the figure that the amount of xylene isomer in the membrane increases linearly with the amount of the respective xylene isomers in the mixed solution. Further, the mole fraction of *p*-xylene is stabilized around 0.5 when the corresponding mole fraction in the membrane is less than 0.8. Moreover, when the mole fraction in solution is increased from 0.8 to 1, the mole fraction of *p*-xylene in the membrane is similar to the solution composition.

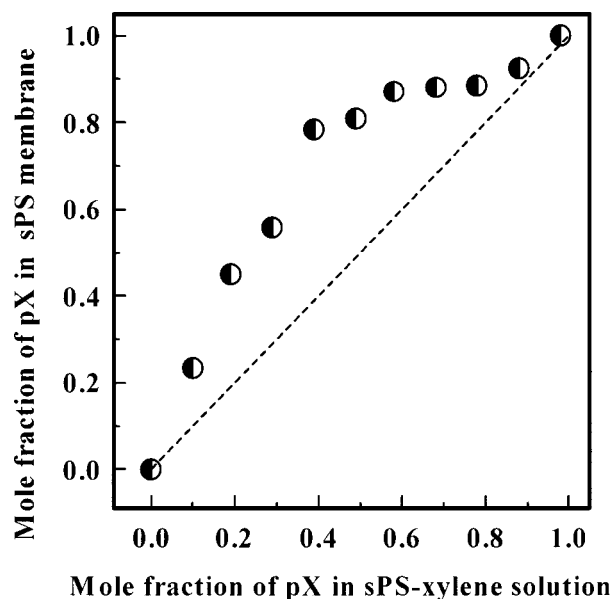


Figure 2 The mole fraction of *p*-xylene in sPS–xylene isomer solution vs dried sPS membrane.²¹

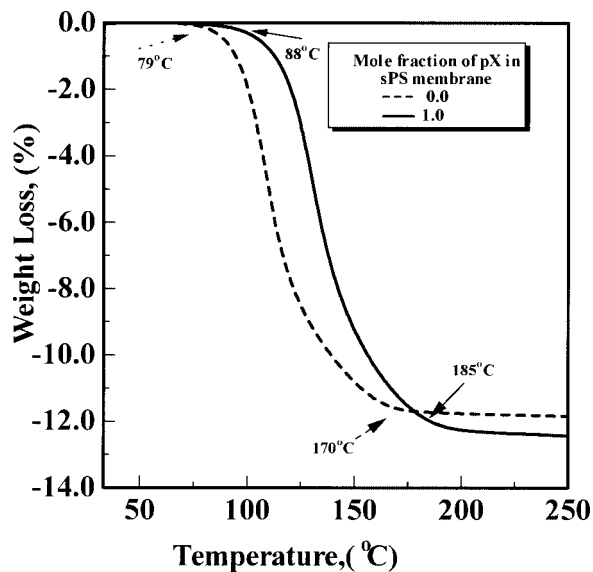


Figure 3 TGA thermograms of weight loss of guest solvents in different mole fractions of *p*-xylene in sPS membrane.

When the mole fraction of *p*-xylene in solution is less than 0.5, its corresponding mole fraction in the membrane is higher than the solution composition. These observations suggest a preferential intake of *P*-xylene from solution to membrane. This preferential intake of *para* isomer can be attributed to the increased van der Waals interaction between the *para* isomer and sPS helices.

Desorption peak temperature and stability of the sPS-*p*-xylene isomer complexes

Figure 3 depicts the TG of the sPS membrane containing 0 and 1 mole fraction of *p*-xylene. All the membranes show a weight loss around 79–185°C. Weight loss starts at 79 and 88°C in membranes containing 0 and 1 mole fraction of *p*-xylene. Estimated weight loss was also found to show a marginal difference, i.e., 12.2 and 13.4 wt %, for 0 and 1 mole fraction of *p*-xylene, respectively. These results indicate that the thermal stability of the δ -form complex in sPS-*p*-xylene (1.0 mole fraction of *p*-xylene) membrane is more than that of the sPS-*m*-xylene (0.0 mole fraction of *p*-xylene) membrane. This could be attributed to the ability of the *para* isomer to fit more tightly into the cavities than the corresponding *meta* isomer. DSC thermograms of sPS membranes with different mole fractions are presented in Figure 4. The endothermic peaks observed at 103°C [Figure 4(a)], 117°C [Fig. 4(b)], and 123°C [Fig. 4(c)] are associated with the desorption of xylene isomer solvents from the sPS-*p*-xylene membranes containing 0, 0.8, and 1 mole fraction of *p*-xylene. This suggests that the thermal stability of the δ phase increases with increasing quantity of *p*-isomer in the solvent.

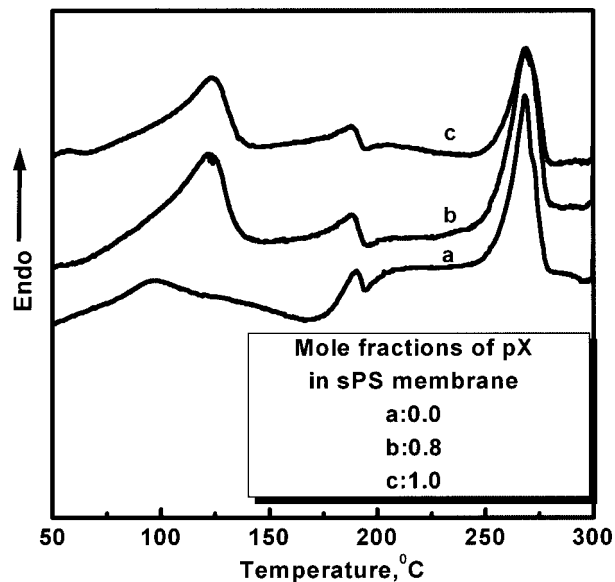


Figure 4 DSC thermograms of different mole fraction of *p*-xylene in sPS membrane.

The glass transition temperature of the sPS membranes overlaps with the broad endothermic solvent desorption peak. The fact that the desorption peak temperature of *p*-xylene (1.0 mole fraction of *p*-xylene) is higher than that of the *m*-xylene (0.0 mole fraction of *p*-xylene) is consistent with our previous findings.²¹ It is remarkable that the difference in the desorption temperature of sPS-*p*- and *m*-xylene membranes was over by 20°C, considering the similar boiling points of the isomer solvents (boiling point of *p*- and *m*-xylenes are 138 and 139°C, respectively). One would expect the formation of clathrates with different sizes, when

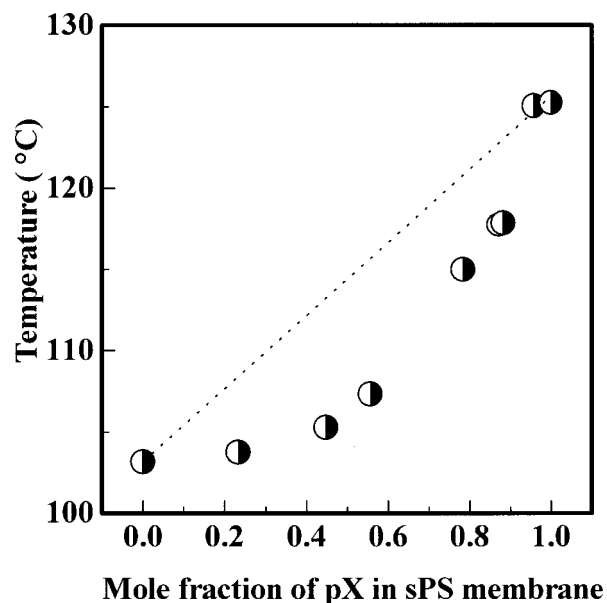


Figure 5 The desorption temperature vs mole fraction of *p*-xylene in sPS membrane.

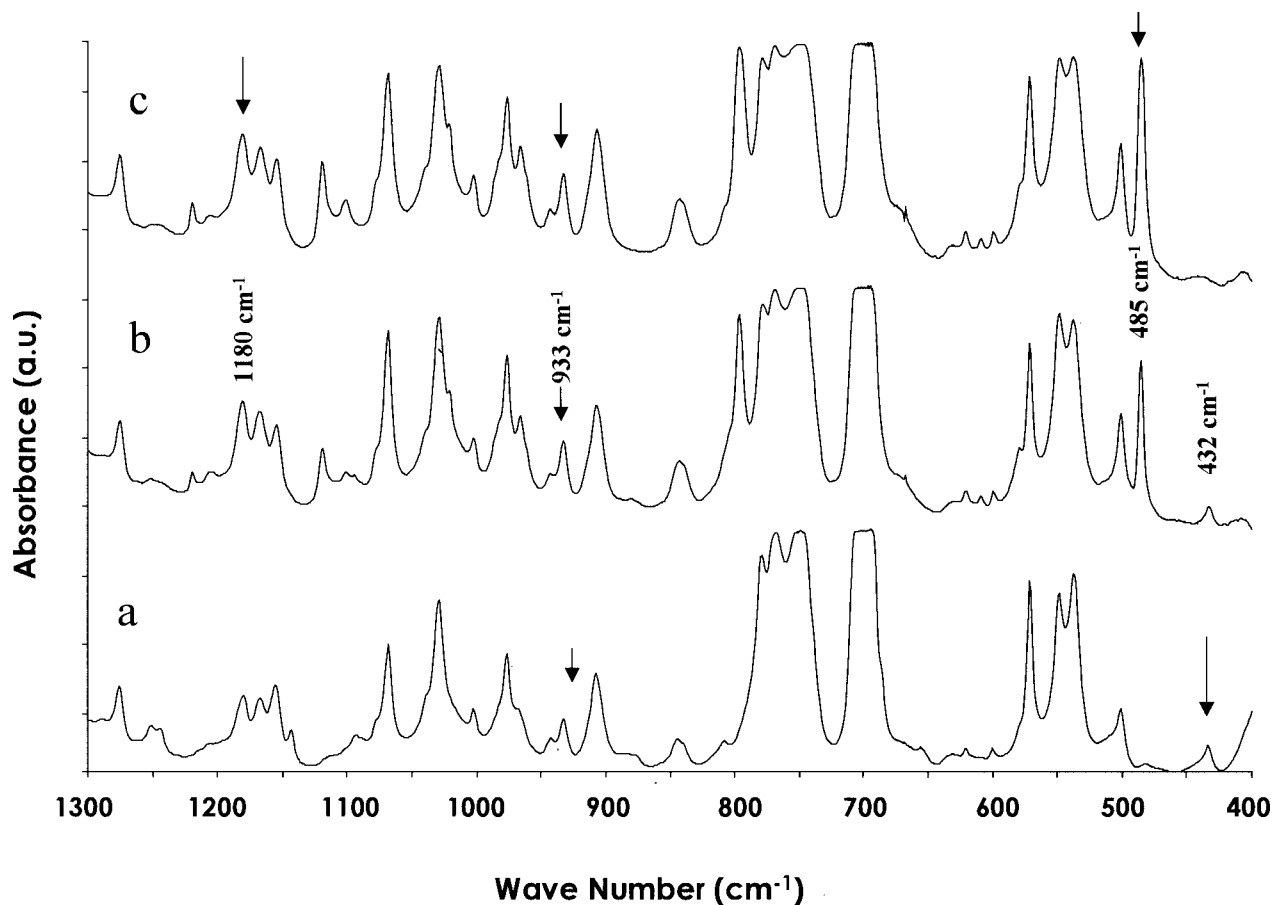


Figure 6 FTIR spectrums of as cast sPS membranes with different mole fraction of *p*-xylene; (a) 0.0, (b) 0.8, and (c) 0.1 mole fraction of *p*-xylene.

they are cast from mixtures of xylene isomer solvents (Fig. 1). However, the broad endothermic peak at 117°C for the sPS-xylene membrane containing 0.8 mole fraction of *p*-xylene indicates the presence of predominantly *p*-xylene with traces of *meta* isomer. Similar results were obtained for other compositions.

The desorption temperature (T_d) of the sPS-xylene membrane was plotted against the mole fraction of *p*-xylene in the membrane and is presented in Figure 5. The desorption temperature increases from 103 to 123°C when the mole fraction of *p*-xylene in the sPS membrane is increased from 0 to 1. However, this increase in desorption temperature has two linear ranges with different slopes. The initial rise is gradual until about a 0.5 mole fraction. Between 0.5 to 1 mole fraction, a steep rise in the desorption temperature is noticed.

These results are also substantiated by the quantitative analysis of mole fraction of *p*-xylene in dried sPS films²¹ as a function of solution composition (cf. Fig. 2). Enthalpy of the desorption estimated from the endothermic peak is found to be 14.56 and 19.92 Jg⁻¹ for the mole fraction of *p*-xylene 0 and 1, respectively. This indicates an increased crystallinity of the sPS membrane with increasing *p*-xylene isomer content.

Content of TTGG helical conformation

In this section, the amount of TTGG helical conformation in the sPS membrane containing both *p*- and *m*-xylenes is estimated from the FTIR spectra of the membranes. Several studies^{15,23–25} have dealt with the characterization of sPS-organic solvent systems by FTIR. The selective FTIR fingerprints of the sPS-xylene system are shown in Figure 6, which illustrate the presence of *p*-xylene (485 cm⁻¹), *m*-xylene (432 cm⁻¹), and TTGG helical conformation (933 cm⁻¹). The spectrum is essentially identical to membranes cast from other aromatic hydrocarbons^{26,27} except for the respective solvent peaks. The significant spectral changes are noticed for the peak at 933 cm⁻¹ (corresponding to the TTGG conformation) in the sPS membrane containing increasing mole fractions of *p*-xylene. The content of TTGG conformation in the sPS-xylene membrane can be monitored from the intensity of absorbance at 933 cm⁻¹. The intensity of the peak at 933 cm⁻¹ is normalized with respect to the intensity of the peak at 1180 cm⁻¹ to correct for the thickness of the membrane.^{28,29} The higher amount of TTGG helix is observed in the solution cast sPS membrane when compared to the solvent-induced crystallization

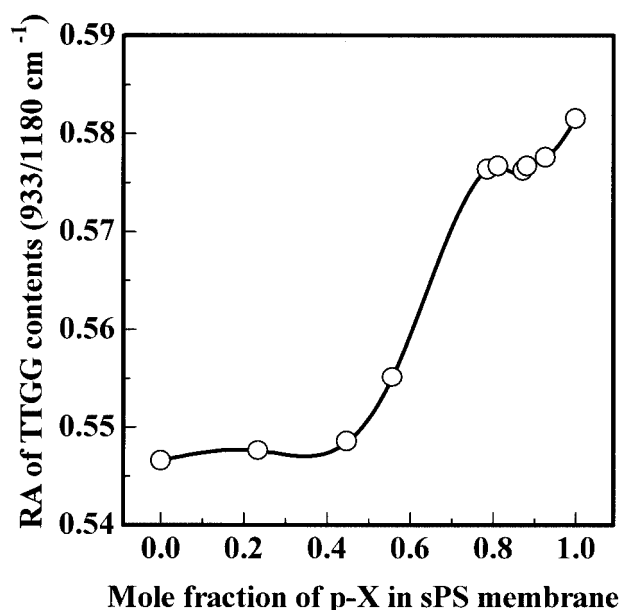


Figure 7 The relative absorbance of TTGG helices with different mole fraction of *p*-xylene in sPS membrane.

method. Figure 7 shows the plot of relative intensities at 933 cm^{-1} (RA_{933}) against the mole fraction of *p*-xylene in the sPS membrane. The relative intensity (RA_{933}) gradually increases until the mole fraction of *p*-xylene is 0.4. Between 0.4 and 0.8 mole fraction, a large increase is noticed, which remains constant with further increase in the mole fraction of *p*-xylene. This increase in the helical conformations in *p*-xylene-clathrate can be related to an increased crystallinity of the sPS membrane. This finding is in agreement with Tsutsui et al.,²⁰ who observed higher TTGG conformation and faster gelation rates in the sPS-*p*-xylene system.

X-ray diffraction study of sPS-xylene isomer system

In the sPS-organic solvent complexes, the guest molecules are hosted in the cavities generated by two adjacent phenyl groups. The guest molecules are located inside the cavities formed by two adjacent TTGG helices and the interdistance between the helices is strongly dependent on the guest molecule's volume, size, and shape.³⁰ The interdistance of helices in the sPS-*p*-xylene complex is smaller than that of the sPS-*m*-xylene due to different molecular size and shape of the guest solvents.²¹ Figure 8 shows the WAXD profiles of as-cast sPS-xylene membranes (mole fraction of *p*-xylene = 0.0, 0.8, and 1.0). As seen from this figure, the membranes with different mole fractions of *p*-xylene in the isomer mixture give remarkably different X-ray profiles, indicating the participation of solvents in the complex formation. The characteristic diffraction peaks at a 2θ of about 7.6° , 10.0° , 16.5° , 17.4° , 19.4° , and 23.4° , are attributed to the δ -form

conformation. The precise location and relative intensities of the peaks change with the type of solvent. The WAXD patterns and FTIR spectra clearly indicate the presence of xylene isomer clathrates in the sPS. One of the diffraction peaks at $2\theta = 7.6^\circ$ corresponds to the interdistance³⁰ between two adjacent TTGG helical sPS chains, i.e., the *b*-axis of the δ form of sPS. The calculated³¹ *b*-axis spacing of sPS-*m*-xylene is larger than that of the sPS-*p*-xylene. Hence, the presence of *m*-xylene solvent is likely to hinder the well-ordered intermolecular association along the *b*-axis. This increased *b* spacing in the case of *m*-xylene is due to the *meta* position substitution. The unit cell of the δ form of sPS is believed to be monoclinic from the crystal structural analysis of the helical form of sPS as reported by Chatani et al.³¹

The 2θ values of the diffraction peak corresponding to the *b*-axis value of the sPS-xylene membranes were plotted against the mole fraction of *p*-xylene in the membrane and shown in Figure 9. It can be seen from the figure that the interdistance of helices in sPS decreases with increasing mole fraction of *p*-xylene. The change is gradual in the mole fraction range between 0 and 0.5. Further increase in *p*-xylene mole fraction does not markedly change the interdistance. This trend is similar to the trend observed for the varying TTGG content shown in Figure 7. In other words, the interdistance increases with decreasing mole fraction of *p*-xylene in the membrane.

CONCLUSIONS

Characterization of the sPS-xylene complex prepared with mixtures of *p*- and *m*-xylene isomers has shown

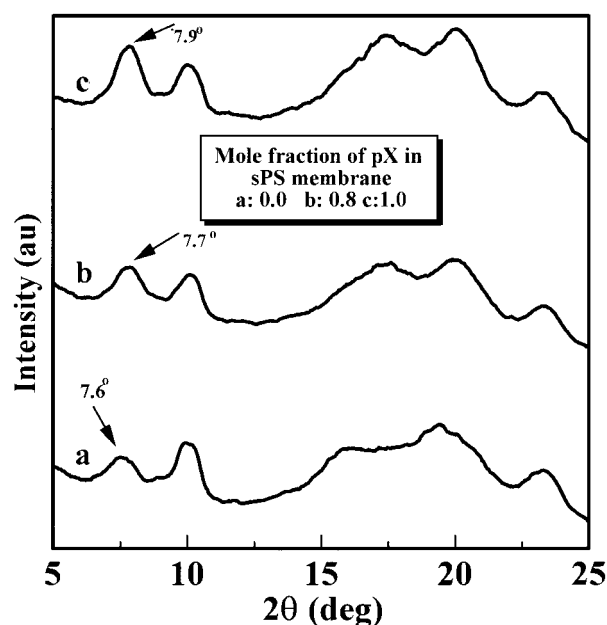


Figure 8 WAXD profiles of different mole fraction of *p*-xylene in sPS membrane.

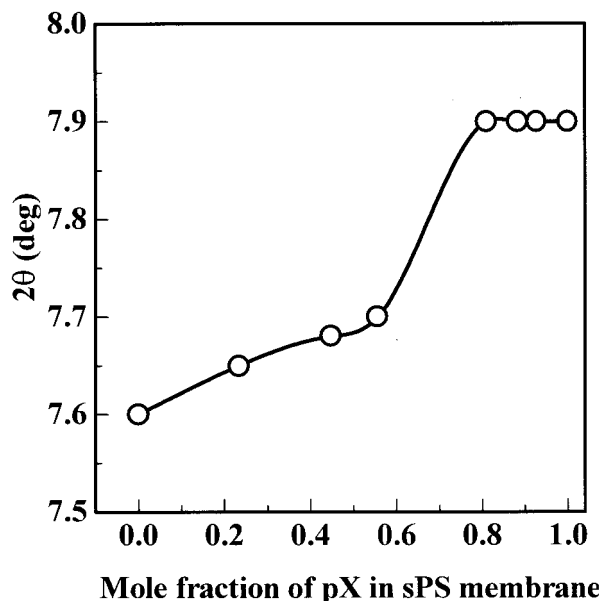


Figure 9 The 2θ values of WAXD profiles in sPS membranes with different mole fractions of *p*-xylene.

preferential complexing of *p*-xylene. FTIR and WAXD patterns confirm the presence of a large amount of TTGG conformation in the sPS-*p*-xylene membranes. In the sPS-*xylene* molecular compounds, the interaction between the polymer and guest molecules occurs through van der Waals interactions. The thermal stability of the sPS-*p*-xylene system is greater than that of the sPS-*m*-xylene system. More of the TTGG helical conformation was observed with the *p*-xylene system than with the *m*-xylene system. Furthermore, the *b*-axis distance in the sPS-*p*-xylene system is shorter than that in the sPS-*m*-xylene system, leading to increased van der Waals interaction in the sPS-*p*-xylene system.

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