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Selective Sorption Behaviors of Organic Solvent to Syndiotactic Polystyrene Mesophase Membranes with Molecular Cavity

Yoshiharu Tsujita, Saeko Mouri, Deveraj Amutharani, Muthusamy Sivakumar, Yusuke Yamamoto, Atsushi Saito, Shunsuke Suzuki, and Hiroaki Yoshimizu

Polymeric Materials Course, Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555 Japan

INTRODUCTION

There are many studies on amorphous polymeric membranes for separation of gas, ion, solute, water, and so on. Although the separation membrane has been successful in a certain sense and has been utilized in a wide field of chemical engineering, membrane technology expects a much more efficient separation polymeric membrane.(1-3) Conventional membranes are composed of amorphous glassy or rubbery polymeric substances so that there are in a broad distribution of micro void size or free volume. Membrane with a narrow distribution of micro void size or free volume.

We have an attention to ordered polymeric membrane with a limited size of micro void or free volume, i.e., molecular cavity different from conventional amorphous glassy or rubbery polymeric membranes to break through a present membrane separation.(4) If one could design the size of micro void in an ordered region, one can prepare a highly selective ordered polymeric membrane. This may direct a molecular recognition such as enzyme. In the present article we studied the preparation of mesophase of syndiotactic polystyrene(sPS), containing almost the same size of molecular cavity as solvent used for membrane preparation and gas and vapor sorption to the sPS mesophase membrane. Preliminary results to develop highly selective polymeric membranes are presented here.

EXPERIMENTAL

sPS was kindly provided by Idemitsu Petroleum Co. Ltd. Molecular weight and dispersity of sPS were informed to be $M_w=200,000$, and $M_w/M_n=2.0$. sPS pellets was not dissolved in good solvent at room temperature but dissolved at higher temperature and crystalline δ form complex was obtained by either cooling or solution cast. Cast film thus obtained was then after annealed at 100 to 170°C for a certain period or extracted stepwisely by poor or non-solvent and finally by methanol to get sPS mesophase with controlled molecular cavity. Annealing temperature is dependent upon complexed solvent used. The better solvent to sPS, the higher annealing temperature.

RESULT AND DISCUSSION

Mesophase of sPS was prepared by annealing or extraction by poor or non solvent of δ form complex(toluene) with crystal lattice of $a=17.48\text{\AA}$, $b=13.27\text{\AA}$, $c=7.71\text{\AA}$, and $\gamma=122^\circ$ (5-7). Various δ forms are prepared by using good solvent. Especially the crystal lattice of b axis increases with the increase in the size of complexed solvent. The crystal lattice of c axis is almost unchanged. Therefore one might control the size of molecular cavity of sPS mesophase

membrane. Mesophase is formed by a desorption of complexed solvent remaining almost no structural change of both conformation of backbone chain sPS(TTGG) and crystal lattice(Fig.1). Mesophase contains the molecular cavity with the size and shape of solvent desorbed. Various types of sPS mesophase have been prepared depending upon solvent used such as toluene, p-xylene, m-xylene, ethyl benzene, chlorobenzene, chloroform, and so on. This means the formation of sPS mesophase with the molecular cavity reminiscent of the size and shape of these solvents, which is available to membranes and adsorptive materials.

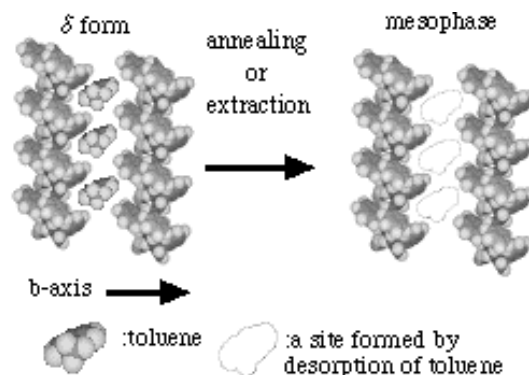


Figure 1. Schematic representation of δ form and mesophase of sPS

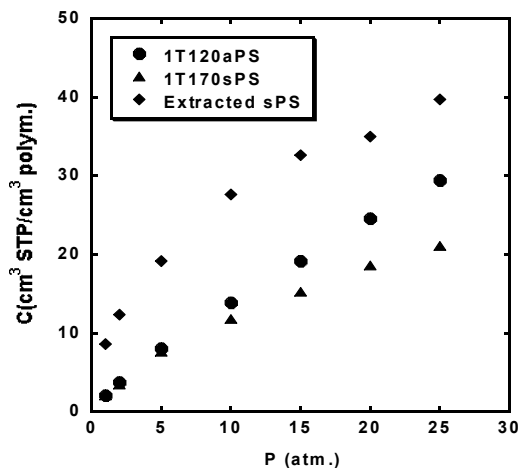


Figure 2. CO₂ sorption isotherm of sPS mesophase membranes; \bullet : 1T170sPS(annealed), \blacklozenge : sPS extracted, and \bullet : 1T120aPS(amorphous)

CO₂ sorption isotherm of sPS mesophase membranes at 25°C is shown in Fig.2. It was found that CO₂ sorption amount of sPS mesophase obtained by extraction method is 2 to 3 times higher than that by annealing method. This shows the production of higher content of mesophase or molecular cavity by extraction method than by annealing method. The isotherm demonstrates a concave against pressure axis at low pressure range and linear region at high pressure range and suggests a dual mode type sorption mechanism. Dual mode sorption is described by the sum of sorption amount of Henry sorption(C_D)and Langmuir sorption(C_H).

$$C = C_D + C_H$$

$$= k_D p + \frac{C_H' b p}{1 + b p}$$

where p is pressure, k_D is the Henry's solubility coefficient, C_H' is Langmuir saturation constant, and b is Langmuir affinity constant. The dual mode sorption parameters are evaluated by a curve fitting method(Tab. 1).

Table 1. Dual-mode sorption parameters of various annealed and extracted sPS films

sample	C_H'	$k_D \times 10^2$	$b \times 10^3$
1T120(aPS)	5.86	1.29	3.10
1T170	13.55	0.57	1.71
5T120	13.9	0.58	1.71
Extracted sPS	26.28	0.85	0.47

C_H' :Langmuir sorption capacity ; $\text{cm}^3(\text{STP})/\text{cm}^3(\text{polym.})$
 k_D :Henry's law solubility coefficient; $\text{cm}^3(\text{STP})/\text{cm}^3(\text{polym.})\text{cmHg}$.
 b :affinity constant of Langmuir site ; cmHg^{-1} .

Langmuir saturation constant C_H' of sPS mesophase obtained by extraction method, which is understandable in terms of the amount of molecular cavity is about 2 times higher. Extraction method is much more effective to produce sPS mesophase with higher amount of molecular cavity.

Toluene or chloroform vapor sorption isotherms at 25°C of sPS mesophase annealed at 170°C and for 1 hour(1T170sPS) and extracted from acetone-methanol exhibit Langmuir type at the lower relative vapor pressure range and do dissolved type at higher relative vapor pressure(Fig. 3). It is interpreted in terms of sorption of the solvent to the sorption site of the molecular cavity, which is characterized by Langmuir sorption mechanism.

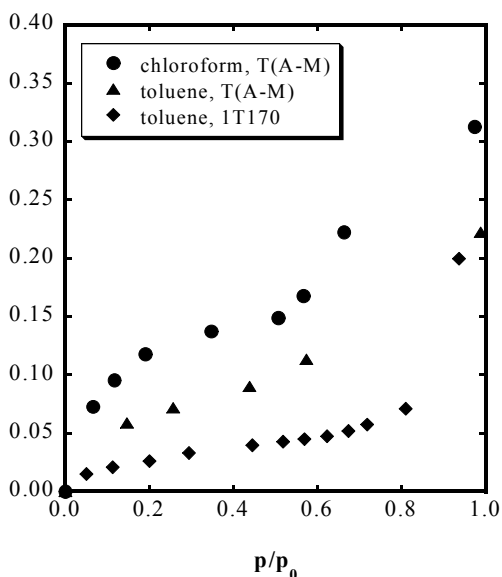


Figure 3. Toluene or chloroform vapor sorption isotherms at 25°C of sPS mesophase annealed(1T170sPS) or extracted

Vapor sorption isotherms vary with interaction parameter of sPS-solvent system, that is, benzene vapor sorption isotherm exhibits a narrow Langmuir type sorption range up to relative vapor pressure of about 0.3 and on the other hand ethyl benzene does up to 0.8. It was found that solvent molecules could be first sorbed in a manner of Langmuir type into the molecular cavity of toluene and then after full saturation into molecular cavity dissolved type sorption mechanism could occur with the increase of vapor pressure depending upon the interaction parameter of sPS-solvent system.

sPS mesophase with the molecular cavity of toluene or p-xylene could sorp much more p-xylene than m-xylene in the

low relative vapor pressure range of the p-xylene sorption isotherm.

Toluene and benzene sorption isotherms at 25°C of 1T170sPS from toluene/benzene(1:1) methanol solution are shown in Fig. 4. In addition sorption isotherm of pure component of toluene or benzene methanol solution is also shown in the figure. It is noted that sorption amount of pure toluene and toluene mixture into the molecular cavity of mesophase is almost the same and on the other hand sorption amount of benzene from the mixture is considerably small compared to the sorption amount of pure benzene. The toluene sorption amount from the toluene/benzene (1:1) mixed solution was about 5 times higher than the benzene one. It was found that selective toluene sorption from mixed solution of toluene/benzene is remarkable. This suggests mesophase sPS might provide molecular recognition and might be useful for separation membrane and adsorptive material.

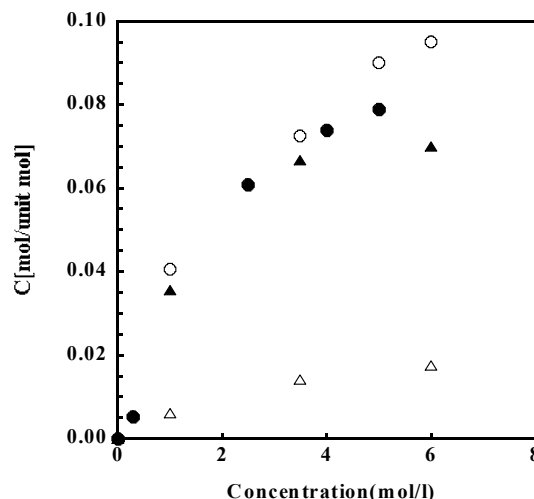


Figure 4. Toluene and benzene solvent sorption isotherms at 25°C of sPS mesophase (1T170sPS) when sorbed from methanol solution of mixed toluene/benzene(1:1) and pure component of toluene or benzene: toluene(•) and benzene(•) when sorbed from mixed solution and toluene(○) and benzene(○) when sorbed from pure component solution

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