

GAS SORPTION, DIFFUSION AND PERMEATION OF ORDERED POLYMERIC MEMBRANES

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Abstract He, CO₂, O₂, N₂, CH₄, C₃H₈, and *t*-C₄H₁₀ gas permeability coefficients and diffusion coefficients of poly(4-methyl pentene-1) (PMP) with various degrees of crystallization were plotted against the degree of crystallization. The plot demonstrated a linear relationship. The gas permeability coefficient and diffusion coefficient of pure amorphous and pure crystalline PMPs were evaluated by a linear extrapolation to zero and 100% crystallinity, respectively. The relationship between the diffusion coefficient of crystalline parts of PMP and the kinetic diameter of penetrant gases was discussed. Syndiotactic polystyrene (SPS) could exist as δ form crystals complexed with organic solvents such as benzene, toluene, xylene, and ethylbenzene. The mesophase of SPS is prepared by annealing the δ form of crystalline complexes at a certain temperature for 1 h. The desorption of solvent during annealing almost does not result in changes of both the conformation of backbone chains and the crystal lattice. We could prepare the mesophase containing molecular cavities with the size and shape of the organic solvent molecules. The mesophase could sorb the same solvent after the manner of Langmuir sorption at low vapor pressure range while this would not be the case for solvents of different size and shape. This suggests a molecular recognition of organic solvent, and mesophase SPS might be useful for separation membrane and adsorptive material.

Keywords Gas sorption, Diffusion, Poly(4-methyl pentene-1), Molecular recognition

INTRODUCTION

There are many studies on amorphous polymeric membranes for separation of gases, ions, solutes, 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 requires a much more efficient polymeric membrane for separation uses^[1]. Conventional membranes are composed of amorphous glassy or rubbery polymeric substances so that there are micro voids or free volumes of broad size distribution. This causes a less perm-selective nature of conventional membranes. Although many polymeric membranes have been developed, they have similar size distributions. The separation performance of polymeric membranes is determined by the difference of permeability coefficients (permeability coefficient ratio), namely the difference in diffusion coefficient and solubility coefficient, respectively (diffusion coefficient ratio and solubility coefficient ratio). Separation is therefore controlled by the difference between the absolute values of the size of micro voids or free volumes in the membrane and the size of permeants used and also by the difference of solubility coefficients. So far there have been many trials to enhance the diffusion coefficient ratio and the solubility coefficient ratio. However the separation performance of membranes is still not very efficient. The essential problems for developing much more efficient separation membranes are related with the broad size distribution of micro voids or free volumes.

We have paid great attention to the studies of ordered (crystalline or mesophase) polymeric membranes, which are quite different from conventional amorphous glassy or rubbery polymeric membranes, with the aim of

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Received December 8, 1999

Invited lecture at the 6th Pacific Polymer Conference, December 7~11, Guangzhou, China

improving the present situation of membrane separation. If one could design the size of micro voids in an ordered region, a highly selective ordered polymeric membrane would be obtained. This may be used for the recognition of molecules such as enzymes. In the present article we studied first the diffusion and permeation of poly(4-methyl pentene-1) (PMP) which is well known to have a less densely packed crystal lattice compared to its amorphous state. The crystalline density is lower than the amorphous one for this polymer. We have a comprehensive understanding of the gas diffusion and permeation of the crystalline and amorphous states of crystalline polymeric membranes. Next we studied the preparation of the mesophase of syndiotactic polystyrene (SPS), which is considered to contain micro voids of almost the same size as the molecules of the solvent used for membrane preparation and also studied the vapor sorption of SPS mesophase membranes. Preliminary results of developing polymeric membranes with high selectivity for enzymes are introduced here.

DIFFUSION AND PERMEATION OF PMP

The degree of crystallinity of PMP was evaluated from the DSC thermogram. An endothermic peak appeared around 230°C, identifying the melting of PMP crystalline regions. One can evaluate the degree of crystallinity from the enthalpy of melting using the following Eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \quad (1)$$

where X_c is the degree of crystallinity, ΔH_m is the observed enthalpy of melting of PMP samples, ΔH_m^0 is the enthalpy of melting of PMP perfect crystals.

The permeability coefficients P of He, CO₂, O₂, N₂, CH₄, C₃H₈ and *t*-C₄H₁₀ measured at 25°C were plotted against the degree of crystallinity of PMP as shown in Fig. 1^[2]. It was found that P was proportional to the degree of crystallinity. The P values of the seven gases for the purely perfect crystalline and amorphous PMP membranes were evaluated from the linear extrapolation in Fig. 1 to 100% and 0% degree of crystallinity, respectively. It was found that the permeation coefficients of He, CO₂, O₂, N₂ and CH₄ for the crystalline PMP were not zero but characteristically finite values. The permeability coefficient of crystalline PMP is unexpectedly lower than that of amorphous PMP. This might conflict with the fact that the crystalline part of PMP has lower density than the amorphous one. Since the PMP membrane studied here is a non-orientated sample, the crystal axes of PMP crystals should be randomly orientated, and the crystalline permeability coefficient might apparently fall to the extrapolated value. This indicates the possibility of higher permeability coefficient for highly orientated PMP membranes. Such a probability should be pursued further.

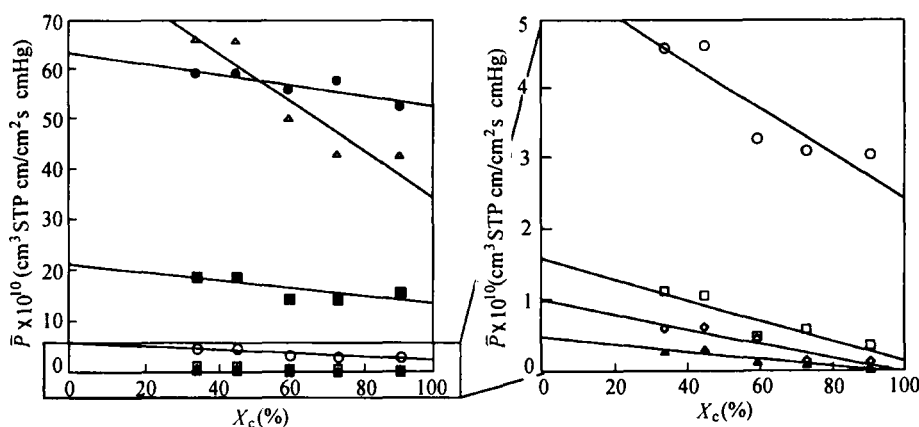


Fig. 1 Effect of degree of crystallinity on permeability coefficient of He, CO₂, O₂, N₂, CH₄, C₃H₈ and *t*-C₄H₁₀ for poly(4-methyl pentene-1)

● He; △ CO₂; ■ O₂; ○ N₂; □ CH₄; ◇ C₃H₈; ▲ *t*-C₄H₁₀

Similar examination was performed for the diffusion coefficient D of the seven different gases in PMP

membranes at 25°C (Fig. 2)^[2]. The D values in crystalline regions, D_{cryst} , and in amorphous regions, D_{amor} , were evaluated as in the case of P mentioned above. A similar result was observed, namely the crystalline diffusion coefficient was lower than the amorphous one, irrespective of the lower density, or the high free volume of crystalline PMP^[3-5].

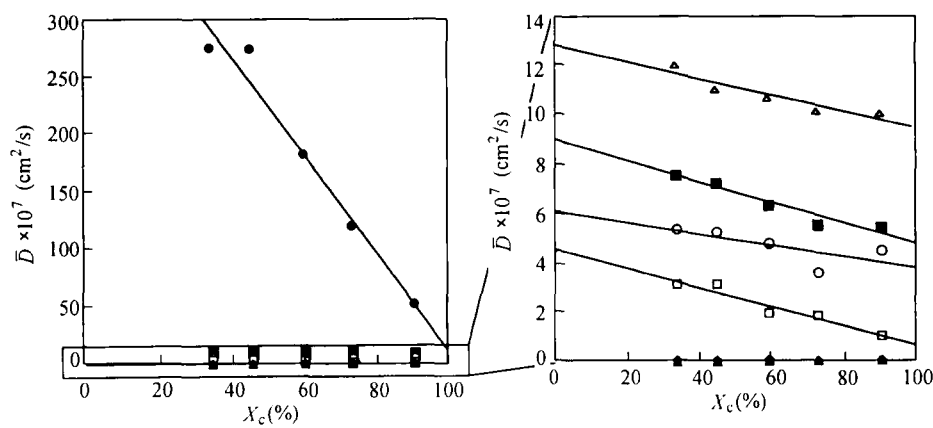


Fig. 2 Effect of degree of crystallinity on diffusion coefficient of He, CO₂, O₂, N₂, CH₄, C₃H₈ and *t*-C₄H₁₀ for poly(4-methyl pentene-1)
● He; △ CO₂; ■ O₂; ○ N₂; □ CH₄; ◇ C₃H₈; ▲ *t*-C₄H₁₀

The temperature dependence of permeability coefficient and diffusion coefficient was examined not only for interpreting the gas transport mechanism but also for membrane applications. The temperature dependences of P_{cryst} , P_{amor} and D_{cryst} , D_{amor} of CO₂ for the crystalline and amorphous parts of PMP are shown in Figs. 3 and 4, respectively^[6]. A linear relationship between P_{cryst} and D_{cryst} and the reciprocal of temperature was obtained within experimental error, indicating the Arrhenius type of gas permeation and diffusion in the crystalline phase, irrespective of the presence of glass transition in the amorphous phase. One can estimate the activation energy of diffusion from the slope of an Arrhenius type linear temperature dependence. The glass transition temperature of PMP is reported to be 20~30°C^[3, 7]. One can see an inflection point around 10°C in the Arrhenius plot of the diffusion coefficient in amorphous phase. This inflection is a general behavior of amorphous polymers during glass transition. It is clear that the activation energy of diffusion in the liquid state is larger than that in the glassy state.

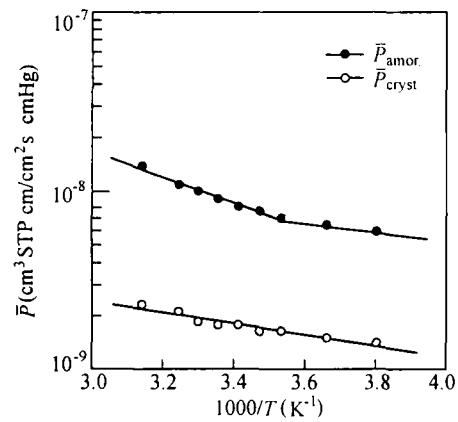


Fig. 3 The temperature dependence of CO₂ permeability coefficient of crystalline (○) and amorphous (●) parts of poly(4-methyl pentene-1) (P_{cryst} , P_{amor})

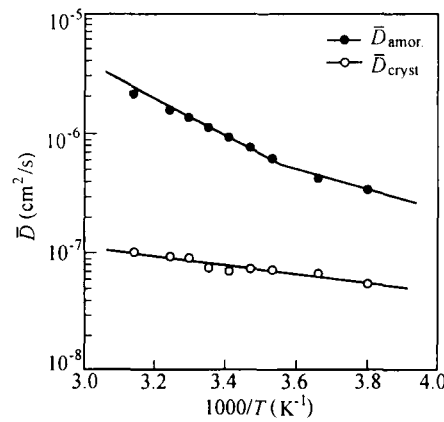


Fig. 4 The temperature dependence of CO₂ diffusion coefficient of crystalline (○) and amorphous (●) parts of poly(4-methylpentene-1) (D_{cryst} , D_{amor})

It is interesting to examine the correlation between the crystalline diffusion coefficient and the size of diffusant gases. The crystalline diffusion coefficient at 25°C was plotted against the kinetic diameter^[8] of seven diffusant gases in Fig. 5^[2]. The crystalline diffusion coefficient is decreasing and is roughly proportional to the diameter of the diffusant gases, although there is a certain scattering. One can see a zero crystalline diffusion coefficient at approximately 0.4 nm diameter of diffusant gas. This means that there is no diffusion of the diffusant gas molecules larger than approximately 0.4 nm in the crystalline part of PMP. X-ray diffraction studies indicated a coarse packing of PMP chains with molecular cavities or micro voids of approximately 0.4 nm detected from a projection of the a-b plane of the crystal lattice structure of PMP^[9].

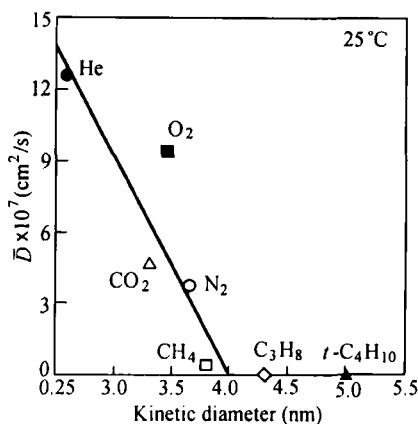


Fig. 5 The plot of crystalline diffusion coefficient ($\bar{D}_{\text{cryst}}$) of poly(4-methyl pentene-1) at 25°C against kinetic diameter of seven diffusant gases of He, CO₂, O₂, N₂, CH₄, C₃H₈ and *t*-C₄H₁₀

PREPARATION OF SPS MESOPHASE

SPS can be dissolved at high temperatures in organic solvents such as benzene, toluene and xylene. When the solution is cooled down to room temperature an SPS gel is formed. The gel is composed of δ form crystal complexed with the organic solvent. The crystal lattice has parameters $a = 1.748$ nm, $b = 1.327$ nm, $c = 0.771$ nm and $\gamma = 122^\circ$ and TTGG conformation of 2₁ helix. The mesophase SPS is prepared by annealing of δ form crystalline complex. The desorption of solvent during annealing almost does not result in changes of both the conformation of backbone chain and the crystal lattice^[10-12]. A typical SPS mesophase is demonstrated in Fig. 6. The mesophase contains molecular cavities with the size and shape of the desorbed solvent molecules. Various types of SPS mesophase have been prepared depending upon the solvents used. Up to now SPS mesophases have been prepared with solvents such as toluene, *p*-xylene, ethyl benzene and chlorobenzene. It means that SPS mesophases with molecular cavities reminiscent of the size and shape of the solvent molecules are available as membranes and adsorptive materials.

VAPOR SORPTION ONTO SPS MESOPHASE

SPS mesophase with molecular cavity similar to toluene was prepared by the annealing method mentioned above. The toluene vapor sorption isotherm at 25°C for the SPS mesophase prepared by annealing at 170°C for 1 h (1T170SPS) is shown in Fig. 7^[12]. For comparison the isotherm for atactic PS is also shown in Fig. 7. The latter demonstrates the so-called dissolving type sorption isotherm, indicating the good solvent nature of toluene for atactic PS. On the other hand 1T170SPS exhibits a Langmuir type sorption isotherm in the low relative vapor pressure range and a change to a dissolving type isotherm at high relative pressures. It is interpreted in terms of sorption of the solvent at the sorption site of the molecular cavity, which is characterized by Langmuir sorption mechanism. A similar *p*-xylene vapor sorption isotherm was obtained for 1PX140SPS prepared from *p*-xylene as

shown in Fig. 8^[11]. 1PX140SPS was prepared by annealing of the δ form of the SPS-*p*-xylene crystalline complex at 140°C for 1 h. It was found that the proper annealing condition is different for SPS-toluene and SPS-*p*-xylene, indicating differences in complex formation by the two solvent systems.

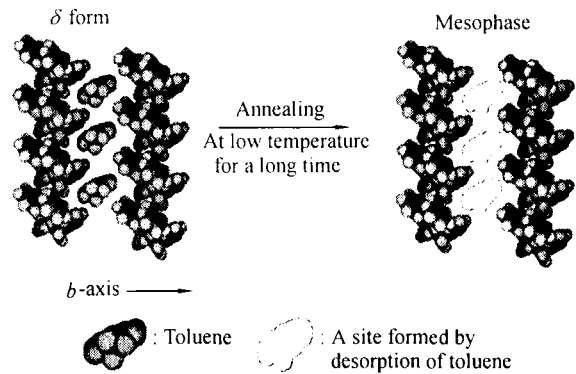


Fig. 6 Schematic representation of δ form and mesophase of SPS

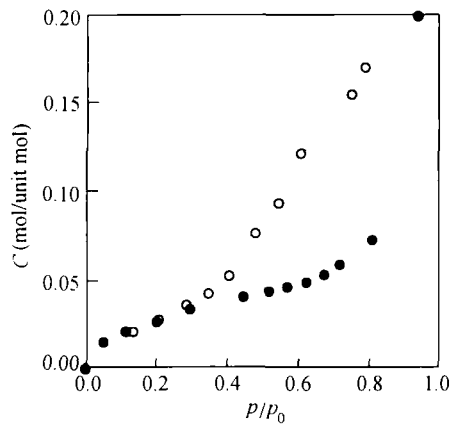


Fig. 7 Toluene vapor sorption isotherm of SPS mesophase (1T170SPS) (●) and atactic polystyrene (1T140APS) (○) at 25°C

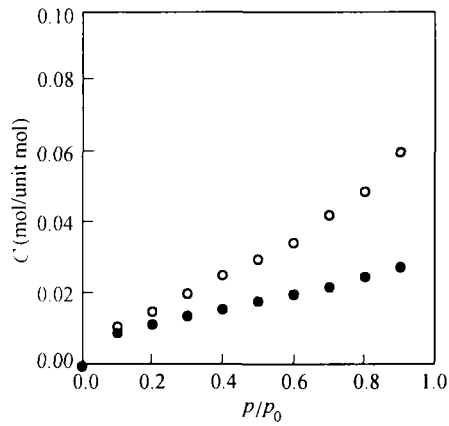


Fig. 8 *p*-Xylene vapor sorption isotherm of SPS mesophase (1PX140SPS) (●) and atactic polystyrene (1PX140APS) (○) at 25°C

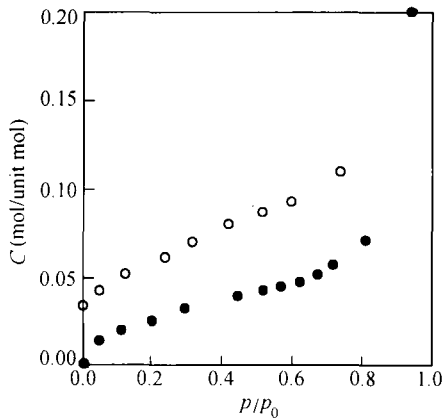


Fig. 9 Toluene vapor sorption isotherm of SPS mesophase (1T170SPS) at 25°C
● First run; ○ Second run

The first and second runs of toluene vapor sorption isotherms of 1T170SPS are shown in Fig. 9 (the first run is the same as the previous figure)^[12]. The sorption experiment of the first run was performed from the low relative vapor pressure side to a high relative vapor pressure value of about 0.95. Thereafter the sample was dried thoroughly at room temperature until there is no weight change of the sample. However the sorption amount does not reach zero but approaches a value of 0.35 mol/unit mol. From thermogravimetric analysis and the infrared absorption spectrum of the dried sample after the first run it was found that SPS can sorb toluene into the molecular cavity vacated by toluene, in other words, SPS can complex again with toluene at the molecular cavity. Then second run was carried out by a manner similar to that of the first run. In this case one could see no Langmuir type sorption mechanism because the molecular cavity is full of toluene and there is no remaining molecular cavity.

Benzene, *p*-xylene, *m*-xylene, and ethylbenzene vapor sorption isotherms of 1T170SPS at 25°C are shown in Figs. 10, 11 and 12, respectively^[11]. Some of them are compared with the previous isotherm of toluene (Fig. 7). The isotherms vary with the interaction parameter of SPS-solvent systems, that is, the benzene vapor sorption

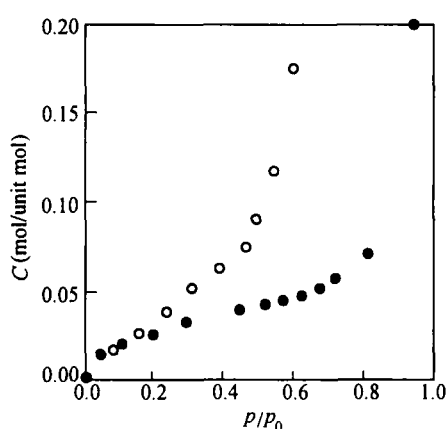


Fig. 10 Toluene and benzene vapor sorption isotherms of SPS mesophase (1T170SPS) at 25°C

● Toluene; ○ Benzene

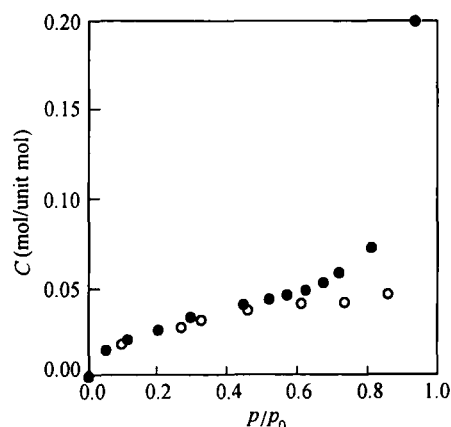


Fig. 11 Toluene and *p*-xylene vapor sorption isotherms of SPS mesophase (1T170SPS) at 25°C

● Toluene; ○ *p*-Xylene

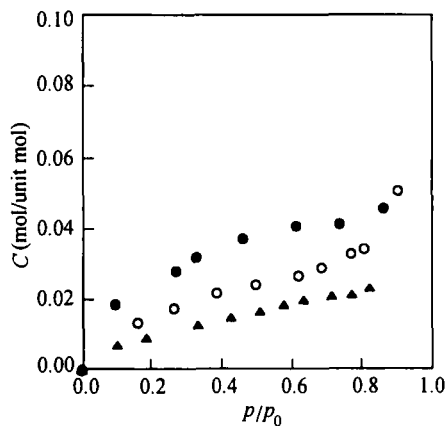


Fig. 12 *p*-Xylene, *m*-xylene and ethylbenzene vapor sorption isotherms of SPS mesophase (1T170SPS) at 25°C

● *p*-Xylene; ○ *m*-Xylene; ▲ Ethyl benzene

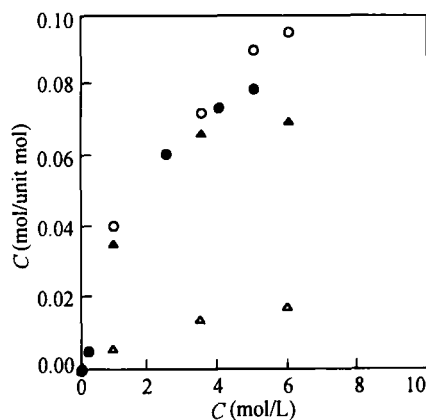


Fig. 13 Toluene and benzene solvent sorption isotherms of SPS mesophase (1T170SPS) at 25°C in methanol solution of mixed toluene/benzene (1:1) and pure component of toluene or benzene

▲ Toluene; △ Benzene sorbed in toluene/benzene methanol solution; ● Toluene; ○ Benzene sorbed in single component methanol solutions

isotherm exhibits a narrow Langmuir type sorption in the range up to a relative vapor pressure of about 0.3; for ethylbenzene the range extends up to 0.8. In contrast, the benzene vapor sorption isotherm demonstrates dissolving type sorption in a lower relative vapor pressure range than that of ethylbenzene. It was found that solvent molecules such as benzene, *p*-xylene, *m*-xylene and ethylbenzene could be sorbed in a Langmuir type manner into the molecular cavity caused by toluene and the dissolving type sorption mechanism could occur in a lower vapor pressure range depending upon the interaction parameter of SPS-solvent systems.

Toluene and benzene sorption isotherms at 25 °C for 1T170SPS from toluene/benzene (1:1) methanol solution are shown in Fig. 13^[13]. In addition sorption isotherms of pure component of toluene or benzene are also shown in Fig. 13. It is noted that the toluene amount sorbed from solutions of toluene and toluene/benzene mixtures in the molecular cavity of SPS mesophases is almost the same, and on the other hand the sorption amount of benzene from the mixture solution is considerably smaller compared to that from the single component solution. It was found that the toluene selective sorption into the molecular cavity from mixture solution of toluene/ benzene is remarkable. This suggests that mesophase SPS might provide molecular recognition and might be useful as separation membranes and adsorptive materials.

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