

## CO<sub>2</sub> Permeation and Diffusion Properties of Semicrystalline Poly(4-methyl pentene-1) Membranes

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**ABSTRACT:** CO<sub>2</sub> permeation and diffusion behaviors of poly(4-methyl pentene-1) (PMP) with three different degrees of crystallinity were examined at –10 to 45°C. Permeation and diffusion coefficients in crystalline and amorphous parts of PMP were obtained by an extrapolation to 100 and 0% degrees of crystallinity, respectively. The inflection corresponding to the glass transition temperature of PMP was observed in Arrhenius plot of both the permeability and diffusion coefficients only for the amorphous part of PMP. The non zero values of permeation and diffusion coefficients of crystalline part of PMP indicated that the permeation and diffusion of CO<sub>2</sub> occurred even in the crystalline part of PMP. The permeation and diffusion of CO<sub>2</sub> for the crystalline part of PMP were Arrhenius type within experimental scatter.

**KEY WORDS** Poly(4-methyl pentene-1) / Gas Permeation / Gas Diffusion / Degree of Crystallinity /

The sorption, diffusion, and permeation of small molecules such as gas and vapor do not occur in and through a crystalline part of the crystalline polymers, in contrast to the amorphous part and amorphous polymers.<sup>1,2</sup> Therefore, the sorption, diffusion, and permeation of crystalline polymers are, in general, corrected by the degree of crystallinity using their quantities of purely amorphous phase.<sup>3–5</sup> We recently reported that change of CO<sub>2</sub> sorption for the polystyrene/polycarbonate blend membranes prepared by casting can be mainly explained from the amount of crystallite of the polycarbonate component, assuming that the crystallite cannot sorb CO<sub>2</sub>.<sup>6</sup>

Poly(4-methyl pentene-1) (PMP; Scheme 1) is used in chemical experiments, medical appliances, electronic microwave tableware, heat stable wire, etc. with good light, transparent, heat stable, and solvent resistant properties. It has higher density for an amorphous part and lower density for a crystalline part.<sup>7–9</sup> This indicates a negative volume change of melting at melting point. This polymer is also known to demonstrate characteristic thermodynamic properties of the pressure dependence of the melting temperature.<sup>10</sup> These facts suggest that a crystalline part of PMP is in a coarse packing of the PMP regular chain molecule compared with a random coiled amorphous part. Kusanagi *et al.* reported the crystal lattice structure of PMP, and concluded that the low density is due to the loose packing of the crystal.<sup>11</sup> There is coarse packing between PMP chains, *i.e.*, the molecular cavity or micro void of approximately 4 Å exists between the chain segments in this model. This is a probable merit for the gas separation membranes with both high permeability and high selectivity which are expected from the crystalline part of PMP.

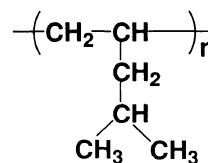
Paul *et al.* confirmed gas sorption and transport of a crystalline part of PMP.<sup>12</sup> They used the PMP with crystallinity levels ranging from 20 to 75%, including the crosslinking PMP to obtain low crystallinity, and reported that the solubilities for CO<sub>2</sub> and CH<sub>4</sub> in the

crystalline part of PMP are finite values from an extrapolation of the sorption results to 100% degree of crystallinity, assuming a two phase model. Further, regression analysis of the permeation data using a two-phase transport model<sup>13,14</sup> indicated that diffusion occurs at finite rates in the crystallite. However, they carried out sorption and permeation experiments at only 35°C, and did not directly estimate the diffusion coefficient. The gas diffusion coefficient in the crystalline part of PMP should be finite as well as the case of sorption and permeation.

In this study, CO<sub>2</sub> permeation and diffusion properties of semicrystalline PMP membranes with three different degrees of crystallinity were investigated at temperature range from –10 to 45°C, across the glass transition temperature ( $T_g$ ) of the PMP. Gas diffusion and permeability coefficients of purely crystalline and amorphous parts of PMP were evaluated by extrapolation of the observed values to 0 and 100% crystallinity, assuming this extrapolation gives almost the same results as the two-phase transport model. If this rough evaluation is adequate, the influence of  $T_g$  on gas diffusion and permeation will be observed only for the amorphous part of PMP.

### EXPERIMENTAL

Pellet and film like PMP were supplied by the Mitsui Petrochemical Co., Ltd. The polymer is a pure homopolymer which contains more than 95% of isotactic dyads by means of <sup>13</sup>C NMR spectroscopy, for a commercial PMP which is almost same sample as one used here.<sup>15</sup> The PMP pellet was compression molded



Scheme 1.

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**Table I.** Degree of crystallinity ( $X_c$ ), heat of fusion ( $\Delta H_f$ ), and melting temperature ( $T_m$ ) of PMP

Sample	$X_c$	$\Delta H_f/\text{cal g}^{-1}$	$T_m/^\circ\text{C}$
As received	0.293	4.35	226.5
Quenched	0.514	7.60	231.7
Slowly cooled	0.775	10.26	235.6

at 280°C for 10 min to form a membrane (the thickness is *ca.* 100  $\mu\text{m}$ ) and this membrane was quenched to 0°C or slowly cooled to room temperature at 1.5°C min<sup>-1</sup> and at different degrees of crystallinity. The film with thickness of 95  $\mu\text{m}$  was used as a membrane without further treatment.

The crystallinity of these membranes was evaluated using the heat of melting for PMP purely perfect crystal of 14.8 cal g<sup>-1</sup><sup>16</sup> and an endothermic quantity of the fusion of the PMP crystal measured by differential scanning calorimetry (DSC) manufactured by Perkin-Elmer Co. Approximately 5 mg PMP were placed in a DSC pan and the thermogram was obtained from 25 to 280°C at a scanning rate of 20°C min<sup>-1</sup>. CO<sub>2</sub> with a purity of more than 99% was utilized without further purification.

The permeability coefficients of CO<sub>2</sub> for PMP membranes were obtained from -10 to 45°C. The details of permeation measurement were described elsewhere.<sup>17</sup> The diffusion coefficients of PMP membranes were determined by the time lag method.<sup>18</sup>

## RESULTS AND DISCUSSION

### Degree of Crystallinity

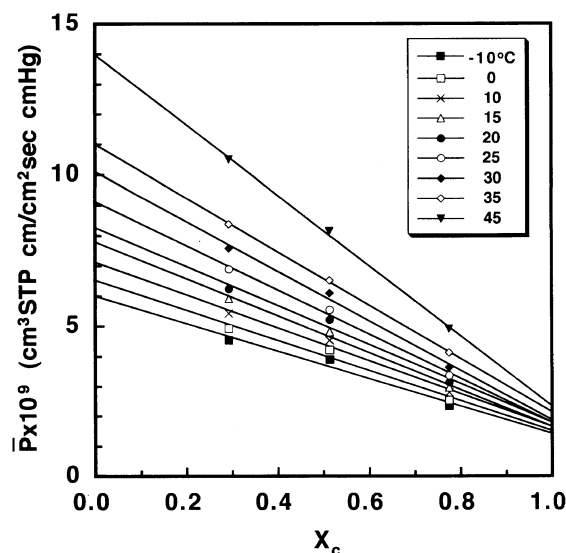
There are many methods to analyze degree of crystallinity such as wide-angle X-ray scattering, infrared absorption, solid state NMR, and thermal analyses. We evaluated the degree of crystallinity of PMP from the DSC thermogram in here, because a good linear relationship between the heats of fusion determined by DSC and the crystallinity from X-ray diffraction had been reported.<sup>12</sup> An endothermic peak appeared around 230°C, identifying the melting of the PMP crystalline part. One can evaluate the degree of crystallinity from the heat of fusion corresponding to an endothermic peak area as,

$$X_c = \Delta H_f / \Delta H_f^0 \quad (1)$$

where  $X_c$ ,  $\Delta H_f$ , and  $\Delta H_f^0$  are the degree of crystallinity, the observed heat of fusion of PMP, and the heat of fusion of PMP assumed perfect crystal, respectively. The thermal properties of PMP are listed in Table I. Paul *et al.*, used the crosslinked PMP to obtain the low  $X_c$  materials, and permeation data of the crosslinked PMP were deleted for estimation of the permeability coefficient in the crystalline part of PMP because the crosslinking strongly influences for permeability coefficient.<sup>12</sup> Fortunately, we obtained the PMP film with  $X_c=0.29$  which was not crosslinking. We use only three PMP, but the range of  $X_c$  was relatively wider than that of Paul.

### Permeation

The permeability coefficients ( $\bar{P}$ ) of CO<sub>2</sub> measured

**Figure 1.** Plots of permeability coefficient ( $\bar{P}$ ) of CO<sub>2</sub> for PMP membranes from -10 to 45°C against the degree of crystallinity ( $X_c$ ).

from -10 to 45°C are plotted against the degree of crystallinity of PMP in Figure 1.  $\bar{P}$  of CO<sub>2</sub> for all the PMP membranes increased with temperature and observed  $\bar{P}$  at each temperature was almost proportional to the degree of crystallinity. Paul *et al.*, reported the  $\bar{P}$  of CO<sub>2</sub> for the PMP with crystallinity range of about 50–75%, and permeation data analyzed by the two-phase transport model. They emphasized that  $\bar{P}$  in the crystalline part of PMP are non-zero. Their analyzed curves of  $\bar{P}$  vs. crystallinity (Figure 13 in ref 12) almost equal the linear relationship considering the scatter of the data.  $\bar{P}$  of the PMP with  $X_c=0.29$  is very close to the expected value from Paul, although absolute  $\bar{P}$  obtained here were slightly lower.  $\bar{P}$  of CO<sub>2</sub> for the purely perfect crystalline ( $\bar{P}_{\text{cryst.}}$ ) and amorphous ( $\bar{P}_{\text{amor.}}$ ) PMP membrane were evaluated from the linear extrapolation to 1 and 0 of the  $X_c$ , respectively, as shown in Figure 1. This procedure is rough because of using only three points of  $X_c$ , and all data have relatively large scatter from the calculated line by the at-least squares method. The scatter became large at lower temperature.

However, it was found that the  $\bar{P}_{\text{cryst.}}$  of CO<sub>2</sub> at all temperatures were not zero but characteristically finite value. That is, the permeation of CO<sub>2</sub> occurs in not only amorphous but also crystalline part of PMP. The crystal of PMP gives the space in size of about 4 Å, sufficiently large for the CO<sub>2</sub> molecule.

The ratio of  $\bar{P}_{\text{cryst.}}$  to  $\bar{P}_{\text{amor.}}$  at 35°C is almost 1/5 which agrees with Paul. The fact that  $\bar{P}_{\text{cryst.}}$  is lower than  $\bar{P}_{\text{amor.}}$  at temperature is near and above  $T_g$ , is understandable from viewpoint of the molecular motion of PMP. Although the density of crystalline part of PMP was smaller than that of amorphous one, this relationship was kept at under  $T_g$ . This suggests that the  $\bar{P}_{\text{cryst.}}$  is probably anisotropy on crystal axes of PMP, and  $\bar{P}_{\text{cryst.}}$  apparently reduces to the extrapolated value, since the PMP membranes studied here are a non-orientated sample, namely the crystalline part should be randomly orientated. In addition, since the crystallites act as physical crosslinks in the semicrystalline polymers,<sup>19</sup> actual  $\bar{P}_{\text{amor.}}$  decreases with  $X_c$ , and the actual  $\bar{P}_{\text{cryst.}}$  may

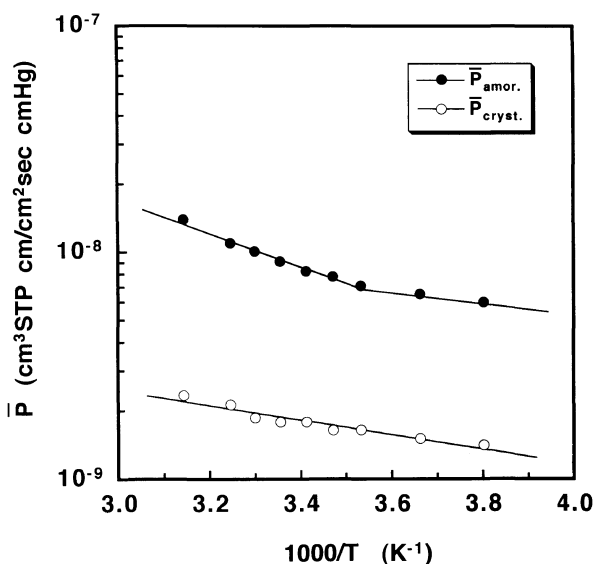


Figure 2. Arrhenius plots of permeability coefficients of CO<sub>2</sub> for the crystalline ( $\bar{P}_{\text{cryst.}}$ ) and amorphous ( $\bar{P}_{\text{amor.}}$ ) parts of PMP.

be even higher than  $\bar{P}_{\text{cryst.}}$  obtained here.

Arrhenius plots of  $\bar{P}_{\text{cryst.}}$  and  $\bar{P}_{\text{amor.}}$  for CO<sub>2</sub> are shown in Figure 2. The inflection at about 10°C corresponding to  $T_g$  was observed only for  $\bar{P}_{\text{amor.}}$ . This is general behavior on glass transition of amorphous polymers. The activation energy of permeation in liquid state is larger than that in glassy state. The inflection point of PMP is not the same as the  $T_g$  reported to be about 20–30°C.<sup>7,12</sup> For the semicrystalline polymers, the segmental motion of the amorphous part is more restricted due to the presence of crystallites in PMP. In here,  $\bar{P}_{\text{amor.}}$  were estimated under the assumption of perfect amorphous ( $X_c=0$ ). Therefore, it can be said that  $T_g$  determined by the  $\bar{P}_{\text{amor.}}$  should be lower than that determined using the semicrystalline PMP samples. These findings show that it is possible to estimate  $\bar{P}_{\text{cryst.}}$  and  $\bar{P}_{\text{amor.}}$  by linear extrapolation.

The linear relationship between  $\bar{P}_{\text{cryst.}}$  and reciprocal of temperature was obtained within experimental scatter, indicating Arrhenius type gas permeation in the crystalline part of PMP, irrespective of the presence of glass transition in amorphous part of one. The activation energy of CO<sub>2</sub> permeation for the crystallite of PMP was almost the same as that for the amorphous part of PMP in the glassy state.

#### Diffusion

The diffusion coefficients ( $\bar{D}$ ) of PMP were determined by the time lag method, since Paul *et al.* reported that the sorption isotherm at 35°C for the PMP with various crystallinity follows a linear relationship, or Henry's law, as expected for polymers close to or above their  $T_g$ , although crystallinity was about 75%. We previously reported that the some polypeptides in the ordered structure ( $\alpha$ -helix) with various side chains which were mainly made of hydrocarbons exhibit the rubbery-type gas sorption isotherms,<sup>19,20</sup> because the diffusion and permeation occur in the side chain region whose mobility is much higher than that of the main chain. The secondary dispersions ( $\beta$ -dispersions) associated with thermal motion of the side chains in the amorphous and

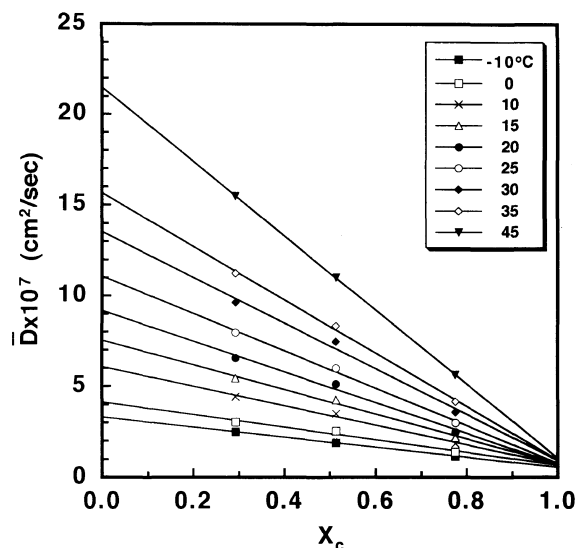


Figure 3. Plots of diffusion coefficient ( $\bar{D}$ ) of CO<sub>2</sub> for PMP membranes from –10 to 45°C against the degree of crystallinity ( $X_c$ ).

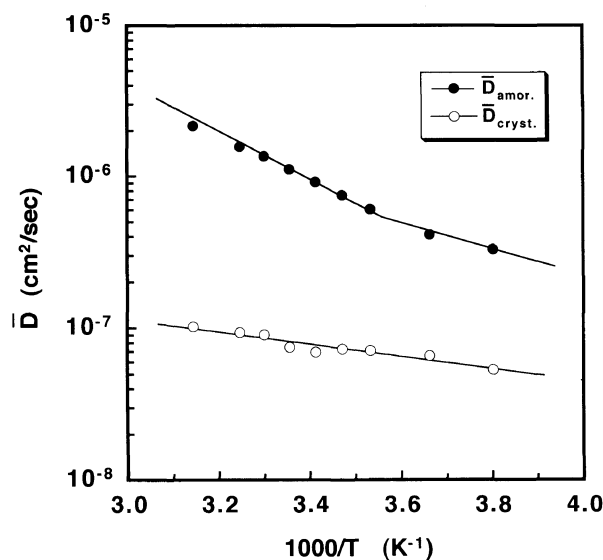


Figure 4. Arrhenius plots of diffusion coefficients of CO<sub>2</sub> for the crystalline ( $\bar{D}_{\text{cryst.}}$ ) and amorphous ( $\bar{D}_{\text{amor.}}$ ) parts of PMP.

crystalline parts of PMP were observed at about –150 to –160°C (at 110 Hz).<sup>21</sup> The mobility of side chain is thus much higher than that of main chain in the amorphous and crystalline parts of PMP at –10 to 45°C. Estimation of  $\bar{D}$  by time lag method may thus be suitable not only for rubbery amorphous but also glassy amorphous and crystalline parts of PMP.

Similar results were obtained for  $\bar{D}$  as shown in Figure 3. Therefore,  $\bar{D}$  for the crystalline ( $\bar{D}_{\text{cryst.}}$ ) and amorphous ( $\bar{D}_{\text{amor.}}$ ) parts of PMP were evaluated as well as the case of permeation. A similar tendency of CO<sub>2</sub> diffusion of PMP was observed:  $\bar{D}_{\text{cryst.}}$  was lower than  $\bar{D}_{\text{amor.}}$ , irrespective of smaller density for crystalline part of PMP.  $\bar{D}_{\text{amor.}}$  almost agreed with the reported values by Paul *et al.*, from the relation of  $\bar{P} = \bar{D} \bar{S}$  where  $\bar{S}$  is the observed solubility coefficient at 35°C.

Figure 4 shows Arrhenius plots of  $\bar{D}_{\text{cryst.}}$  and  $\bar{D}_{\text{amor.}}$  for CO<sub>2</sub>. The inflection at 10°C was observed only for  $\bar{D}_{\text{amor.}}$ , indicating that the linear extrapolation to examine

the  $\bar{D}_{\text{cryst.}}$  and  $\bar{D}_{\text{amor.}}$  is substantially reasonable. These results for diffusion can be interpreted as well as the permeation mentioned above. The possibility of gas permeation and diffusion for the crystalline part of PMP was confirmed from measurement of not only permeability but also diffusion coefficients using the PMP membranes with  $X_c = 0.29\text{--}0.78$ .

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