Characterization of the Cavity in Poly(4-methyl-1-pentene) Crystal by Gas Permeation and ^{129}Xe NMR Measurements

Tomoyuki SUZUKI, Takaharu TANAKA, Megumi NAKAJIMA, Hiroaki YOSHIMIZU,[†] and Yoshiharu TSUJITA

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

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ABSTRACT: Characteristic cavity in a crystal part of poly(4-methyl-1-pentene) (PMP) has been investigated by gas permeation and ^{129}Xe NMR measurements for PMP membranes with various crystallinities. For the cavity, permeability coefficients of He, N₂, O₂, CH₄, and CO₂ have shown finite values, whereas those of C₃H₈ and *tert*-C₄H₁₀ have shown zero. From the analysis of ^{129}Xe NMR chemical shifts of ^{129}Xe sorbed in PMP membranes, it has been able to evaluate the size of the cavity in PMP crystal as about 4.5 Å. These findings have indicated that gas molecules less than about 4.5 Å can permeate the cavity in PMP crystal.

KEY WORDS Poly(4-methyl-1-pentene) / Gas Permeation / Xe Sorption / ^{129}Xe NMR Spectroscopy / ^{129}Xe NMR Chemical Shift /

For semi-crystalline polymers, gas and vapor transport phenomena, in general, do not take place in a crystal region because of tight packing of molecular chains.^{1–4} Poly(4-methyl-1-pentene) (PMP) is one of the semi-crystalline polymers, and is widely used in industries because of its good transparent, heat stable, and solvent-resistant properties. It is one of the significant properties of PMP that the density of crystal region is lower than that of amorphous region.^{5–7} Kusanagi *et al.* have investigated the crystal structure of PMP⁸ termed as “Form I”,⁹ which is characterized by molecular chains in 7/2 helical conformation packed in a tetragonal unit cell, and concluded that the lower density of crystal region is attributed to a coarse packing of the chains, as a result, the cylindrical cavity with a diameter of about 4 Å is formed in the crystal. This fact means that transport phenomena of gas and vapor molecules occur in not only amorphous but also crystal regions. Some groups have experimentally confirmed the transport phenomena of small molecules in the crystal region of PMP.^{10–13}

In recent years, ^{129}Xe NMR spectroscopy has become a powerful technique to characterize microstructures of various materials. Since Xe atom has a very large polarizability, induced ^{129}Xe NMR signal of ^{129}Xe in a medium is sensitively affected by surrounding microenvironments that disturb the electron density of Xe. In many cases of micro porous materials like zeolites, the NMR chemical shift of adsorbed ^{129}Xe , δ is explained by following equation;^{14–20}

$$\delta = \delta(\text{S}) + \delta(\text{Xe}) + \delta(\text{E}) + \delta(\text{SAS}) + \delta(\text{M}) \quad (1)$$

$\delta(\text{S})$ is the chemical shift due to the interaction between Xe atom and inner wall of hole. $\delta(\text{Xe})$ corresponds to the interaction between Xe atoms, and increases in proportion to the concentration of Xe. $\delta(\text{E})$, $\delta(\text{SAS})$, and $\delta(\text{M})$ are the terms explained by the contribution of the electric field created by multivalent cations, the interaction of Xe with strong adsorption sites, and the contribution of the magnetic field created by paramagnetic compensation cations, respectively. However, the contributions of $\delta(\text{E})$, $\delta(\text{SAS})$, and $\delta(\text{M})$ can be ignored for most of polymers because of absences of strong charge groups. Observed ^{129}Xe NMR chemical shifts, therefore, can be explained as sum of $\delta(\text{S})$ and $\delta(\text{Xe})$ for polymers. In many studies of zeolites,^{14–24} it has been reported that the $\delta(\text{S})$ value is strongly correlated with the size and nature of a hole in which Xe is sorbed. For polymer systems,^{25–39} in addition, some researches have also been reported about the relation between ^{129}Xe NMR chemical shift and size of hole that gives free volume or microvoids. Similarly it will be able to evaluate the size of the cavity in PMP crystal from $\delta(\text{S})$ value.

In this study, the characteristic cavity in PMP crystal is evaluated by gas permeation and ^{129}Xe NMR measurements for PMP membranes with various crystallinities. Paul *et al.* have shown that there is the cavity about 4 Å wide in PMP crystal from data on transport properties of several gases.^{10, 11} In their reports, however, there are no data relating to gas molecules over 4 Å. Therefore more detailed estimation of the cavity in PMP crystal is carried out. Additionally this study is performed to confirm the utility of ^{129}Xe NMR spec-

[†]To whom correspondence should be addressed (Phone and Fax: +81-52-735-5272, E-mail: yosimizu@mse.nitech.ac.jp).

Table I. Description and characteristics of PMP membranes

Sample	Solvent	Heat Treatment	ΔH_f (cal g ⁻¹)	X_C (%)
PMP34	—	—	5.1	34.3
PMP46	—	140 °C / 72 h	6.8	45.7
PMP60	Cyclohexane	25 °C / 24 h	8.9	60.1
PMP75	Xylene	70 °C / 24 h	11.1	74.8
PMP91	Cyclohexane	150 °C / 24 h	13.4	90.7
PMP96	Xylene	200 °C / 24 h	14.2	96.0

troscopy for dimensional evaluations of holes or cavities in polymers.

EXPERIMENTAL

Sample Preparations

Pellets and film of PMP were supplied from Mitsui Petrochemical Co., Ltd. The PMP is commercial one, and contains more than 95% of isotactic triads determined by ¹³C NMR spectroscopy. Six kinds of membranes with different crystallinities were prepared by appropriate treatments. From ¹³C NMR and X-Ray measurements, it was found that the crystal lattice structure contained in all membranes is Form I. Two lower-crystallinity membranes, PMP34 and PMP46, were prepared from a film of PMP; as-received, and treated at 140 °C / 72 h and cooled slowly *in vacuo*, respectively. The other higher-crystallinity membranes, PMP60, PMP75, PMP91, and PMP96, were prepared from pellets of PMP by solution casting method using cyclohexane or xylene as a solvent. Afterward they were treated at appropriate temperatures and then cooled slowly *in vacuo*. Detailed descriptions are stated in Table I. Heat of fusion of PMP crystal in the membrane, ΔH_f , was measured by differential scanning calorimeter (DSC-7, Perkin–Elmer Co.), and the values for each membrane are listed in Table I. From ΔH_f , crystallinity of the membrane (X_C) was determined by following equation;

$$X_C = \frac{\Delta H_f}{\Delta H_f^0} \quad (2)$$

where ΔH_f^0 is the heat of fusion for the 100% crystalline PMP ($\Delta H_f^0 = 14.8$ cal g⁻¹).^{10,40} Crystallinities of the membranes are summarized in Table I.

Gas Permeation Measurements

A Permeation apparatus prepared in our laboratory was used for gas permeation measurements.^{41,42} A membrane, which was held in the permeation cell sealed with O-rings, was degassed for 24 h or more at less than 10⁻⁵ cmHg in the permeation apparatus. Downstream side of the membrane was evacuated and remained about 10⁻⁵ cmHg. Permeant gas was introduced on the upstream side, and the pressure was

monitored using Baratron pressure transducer (Model 127AA; high-pressure type, MKS Instruments, Inc.). Permeability coefficient, $\bar{P}$, was evaluated from permeation rate that was monitored as the variation of pressure on the downstream side at steady state using another Baratron pressure transducer (Model 127AA; low-pressure type). Permeability coefficients of He, N₂, O₂, CH₄, CO₂, C₃H₈, and *tert*-C₄H₁₀ were measured at 76 cmHg and 25 °C.

Xe Sorption Measurements

Xe sorption measurement was carried out using a gravimetric sorption apparatus with an electric microbalance (CAHN 2000, Cahn Instruments, Inc.) at 25 °C. After sufficient evacuation of the membrane at about 10⁻⁵ cmHg, required pressure of Xe gas was introduced in the apparatus. Sorption amount of Xe for the membrane was corrected by subtracting the contribution of buoyancy under certain pressure.

¹²⁹Xe NMR Measurements

Cut membrane was packed about 1 g into a 10 mmϕ Pyrex NMR sample tube with thick wall (Type 513-7 JYH-7, Wilmad), and degassed. Required amount of Xe (with natural abundance of ¹²⁹Xe) was introduced into the NMR tube with the aid of liquid nitrogen, after which the tube was sealed with Teflon[®] valve. Internal pressure was determined from sorption amount of Xe for the membrane and weight variation of the NMR tube. ¹²⁹Xe NMR spectrum was recorded on JEOL GX400 NMR spectrometer at 110 MHz and 25 °C. All of ¹²⁹Xe NMR chemical shifts were referenced to an external standard of gaseous ¹²⁹Xe at zero-pressure as 0 ppm.

RESULTS AND DISCUSSION

Gas Permeation Properties of PMP Membranes

Figure 1 shows the plots of gas permeability coefficients, $\bar{P}$ s, against crystallinity of the membranes. It appears that $\bar{P}$ decreases with increasing crystallinity. This finding is probably attributed to an increase in tortuous diffusion path.^{10,13} In the cylindrical cavity formed in PMP crystal, a gas molecule diffuses restrict-

Figure 1. Permeability coefficients of several gases for PMP membranes with various crystallinities at 76 cmHg and 25 °C. (b) shows the expansion of the low-permeability region of (a).

Figure 2. Permeability coefficients of several gases for the cavity in PMP crystal ($\bar{P}_c$) plotted against van der Waals diameter of gas molecule.

edly along molecular chains of PMP. Because the PMP crystal in the membranes studied here should orientate randomly, tortuous diffusion path of a gas molecule increases with increasing crystallinity. For He, N₂, O₂, CH₄, and CO₂, however, $\bar{P}_s$ extrapolated to $X_c = 1$, *i.e.*, permeability coefficients for the cavity, $\bar{P}_c$ s, show finite values, whereas those for C₃H₈, and tert-C₄H₁₀ are zero. These results indicate that the cavity in PMP crystal possesses selective permeation based on the size of a gas molecule. The $\bar{P}_c$ s are plotted against corresponding van der Waals diameter of a gas molecule⁴³ in Figure 2. It is recognized that the $\bar{P}_c$ decreases as

Figure 3. Xe sorption isotherms for PMP membranes with various crystallinities at 25 °C.

the diameter of a gas molecule increases, and eventually leads to zero. This result suggests the width of the cavity in PMP crystal lies between 4.1 Å that is the diameter of CO₂ and CH₄ and 5.2 Å that is that of C₃H₈. This estimation is fundamentally consistent with the results obtained from X-Ray analysis by Kusanagi *et al.* and gas transport measurements by Paul *et al.*^{8,10,11}

Xe Sorption and ^{129}Xe NMR Measurements

Figure 3 shows Xe sorption isotherms of PMP membranes at 25 °C. It appears that sorption amount of Xe increases in proportion to applied pressure. These isotherms can be described by the Henry's mode sorp-

Figure 4. Crystallinity dependence of Henry's law coefficient of Xe for PMP at 25 °C.

Figure 5. ^{129}Xe NMR spectrum for PMP60 at 760 cmHg and 25 °C.

tion as typically expected for rubbery polymers;^{42, 44}

$$C = k_D p \quad (3)$$

where C is the sorption amount of Xe, p is the pressure, and k_D is the Henry's law coefficient. The k_D was estimated by least-square method, and plotted against crystallinity in Figure 4. It can be seen that the k_D decreases linearly with increasing crystallinity. However, in Figure 4, the k_D extrapolated to $X_C = 1$, *i.e.*, Henry's law coefficient for the cavity shows a finite value. This finding indicates that Xe atom is soluble in the cavity on the basis of the Henry's law. At the present stage, it can be said the width of the cavity lies between 4.4 Å that is the diameter of Xe and 5.2 Å that is that of C_3H_8 .

Figure 5 shows the ^{129}Xe NMR spectrum obtained for PMP60 at 760 cmHg, where higher- and lower-field peaks are derived from gaseous ^{129}Xe and ^{129}Xe sorbed in PMP60 membrane, respectively. It appears that the spectrum of ^{129}Xe sorbed in PMP60 reveals only one peak although amorphous and crystal regions exist as sorption sites, and similar spectra were obtained for the others. Koons *et al.* have reported that the peak changes from single peak to two peaks by cooling because diffusion rate of Xe between amorphous and crystal regions decreases as temperature is lowered.⁴⁵ Consequently, it can be deduced that Xe atoms dissolved in

Figure 6. ^{129}Xe NMR spectra of ^{129}Xe sorbed in PMP60 at various pressures.

PMP diffuse fast, and then exchange rapidly between amorphous and crystal regions in the NMR time scale at measured temperature (25 °C). Figure 6 shows ^{129}Xe NMR spectra of ^{129}Xe sorbed in PMP60 obtained at various pressures. It is recognized that the peak shifts to low magnetic field with increasing pressure, or sorption amount of Xe, and similar behaviors were observed for the others. These downfield shifts are caused by an increase in the interaction among Xe atoms, that is, the contribution of the term $\delta(\text{Xe})$ in eq 1. The ^{129}Xe NMR chemical shifts plotted against sorption amount of Xe are shown in Figure 7. It appears that the NMR chemical shifts show linear low-field shifts with increasing sorption amount of Xe. It can be said that the NMR chemical shift extrapolated to $C = 0$ is identical with $\delta(\text{S})$ which reflects the mean size of the hole gives free volume or cavity in PMP. It can be seen from Figure 7 that the $\delta(\text{S})$ value becomes larger as crystallinity is increased. This fact suggests that a sorption site of Xe in PMP is confined as crystallinity is increased.

When ^{129}Xe NMR chemical shift of ^{129}Xe in a zeolite is determined only by the interaction between Xe atom and inner wall of hole, and contributions of paramagnetic species or electric fields ($\delta(\text{E})$, $\delta(\text{SAS})$, or $\delta(\text{M})$ in eq 1) are absent or negligible, a mean free path of Xe, λ , is linked to $\delta(\text{S})$. Hence the mean size of the hole gives free volume or cavity in PMP can be esti-

Figure 7. ^{129}Xe NMR chemical shifts plotted against sorption amount of Xe.

Table II. $\delta(\text{S})$, D_{S} , and D_{C} values for PMP membranes

Sample	$\delta(\text{S})$ (ppm)	D_{S} (Å)	D_{C} (Å)
PMP34	217.0	4.89	4.65
PMP60	217.2	4.88	4.64
PMP75	220.0	4.83	4.61
PMP96	228.1	4.67	4.53

mated by following relation.^{14, 15}

$$\delta(\text{S}) = 243 \times \frac{2.054}{2.054 + \lambda} \quad (4)$$

When the shape of the hole is assumed to be spherical, following relation is derived.

$$\lambda = \frac{(D_{\text{S}} - D_{\text{Xe}})}{2} \quad (5)$$

On the other hand, λ is described by following equation for cylindrical hole.

$$\lambda = D_{\text{C}} - D_{\text{Xe}} \quad (6)$$

D_{S} is the diameter of the spherical hole, D_{C} is that of the cylindrical hole, and D_{Xe} is the van der Waals diameter of Xe = 4.4 Å. D_{S} and D_{C} values for each membrane are summarized in Table II. It should be noted that D_{S} and D_{C} values decrease with increasing crystallinity and, in particular, the D_{C} value approaches to 4.5 Å at $X_{\text{C}} = 1$. This value is consistent with the results of gas permeation and Xe sorption measurements mentioned above. From the present study, it is concluded that the width of the cylindrical cavity in PMP crystal is about 4.5 Å.

CONCLUSIONS

In this study, we have evaluated the cavity in PMP crystal by gas permeation and ^{129}Xe NMR measurements. For the cavity, permeability coefficients of He,

N_2 , O_2 , CH_4 , and CO_2 show finite values, whereas those of C_3H_8 and *tert*- C_4H_{10} show zero. Analyzing NMR chemical shifts of ^{129}Xe sorbed in PMP membranes, it is able to evaluate the size of the cylindrical cavity as about 4.5 Å. It is concluded that gas molecules less than about 4.5 Å can permeate the cylindrical cavity in PMP crystal and, in addition, ^{129}Xe NMR spectroscopy is a powerful technique to characterize microstructures in polymers.

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