Surface Adsorption of Hydrocarbon Gases on Polymeric Membranes

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We observed the surface adsorption layer of propane, propylene and propane/propylene (48.6 %/51.4 %) mixed gas on polyimide using X-ray and neutron reflectivity and determined the adsorption isotherm and the degree of swelling of the polyimide by each gas. The thickness of the adsorption layer of propane was much larger than that of propylene. This has been assigned to a higher affinity of propane to polyimide than propylene. The adsorption isotherm of the propane/propylene mixed gas was almost identical with that of propane, and the degree of swelling of polyimide by the mixed gas was the highest among propane, propylene and mixed gas. It was concluded that X-ray and neutron reflectivity methods are very useful for the examination of surface adsorption of gases on polymeric membranes and their swelling, because the adsorption layer thickness and the degree of swelling can be simultaneously determined.
Key words: X-ray Reflectivity, Surface Adsorption, Polyimide, Hydrocarbon Gas Permeation

1. INTRODUCTION

Dissolution and transport behavior of small molecules in polymeric materials is a topic in many fields of science and technology. Recently, the importance of such behavior has been recognized in the research field of separation membranes. Several polymeric membranes have an industrial success in many separation systems on the basis of the studies on the permeation phenomenon of small molecules in polymers. Separation membranes are of great interest from an industrial viewpoint. In addition to traditionally studied gas separation systems such as oxygen separation systems from air, recently hydrocarbon gas separation systems from gas elements of crude petroleum have been widely studied on the basis of the development of high performance engineering plastics such as polycarbonates, polysulfones and polyimides. Since it is very important to apply polymeric membranes in the petrochemical industries for both economical and ecological reasons, various glassy polymers with a higher mechanical stiffness and separation performance have been examined for these separation systems.

Polyimide is a promising membrane material in hydrocarbon gas separation systems because of its mechanical properties and thermostabillity in addition to its separation performance [1-4]. It was found that some polyimides with 2,2-bis (3,4-carboxyphenyl) hexafluoropropane dianhydride (6FDA) exhibit high separation performance for different gases, especially for the separation of olefin gases from paraffin gases [5-7]. Recently, we found that some of the 6FDA-based polyimides show much higher permeability of 1,3-butadiene than n-butane and of propylene than propane [8,9]. This means that these polyimides are applicable to the recovery systems of 1,3-butadiene from C4 gaseous elements of crude petroleum and of propylene from C3 gaseous elements. However, in the applications of polymeric membranes to hydrocarbon gas separation systems, swelling of the membranes by

the gases is one of the most important factors in determining the membrane performance. In practice, the swelling of the polyimides induced by hydrocarbon gases makes the prediction of the separation performance difficult. For example, the ideal separation factors for 1,3-butadiene versus n-butane in the 6FDA-based polyimides are 220 - 24000 at 298 K. However, the observed separation factors in the mixed gas system are 3 − 80, because the permeability coefficient of n-butane substantially increases for 1,3-butadiene. The swelling of the film induced by 1,3-butadiene is the origin of this increase [8]. Therefore, in the studies of hydrocarbon gas separation membranes, it is very important to elucidate the swelling behavior of the films by gases in addition to the separation performance.

A number of studies on the swelling of polymers by carbon dioxide have been performed with various experimental techniques [10-15]. In some studies, swelling effects were investigated through molecular dynamics by measuring the relaxation time of the segments using NMR [10-12]. In other studies, volume increases induced by gas were directly observed [14,15]. However, very few studies have been carried out on the swelling of polymers by hydrocarbon gases. Therefore, we investigated the swelling behavior of the 6FDA-based polyimides by hydrocarbon gases using X-ray and neutron reflectivity to observe thickness changes in thin polyimide films as a function of gas pressure [16-18]. In this study, the swelling behavior of the polymers in the surface regime is accurately elucidated because of the high sensitivity of the reflectivity methods to surfaces compared with other techniques. Moreover, reflectivity methods are expected to be sensitive to the surface adsorption of gases on polyimides, which is most likely to be formed near the saturated vapor pressure of gases. This behavior of the surface adsorption of gases and the swelling of polyimides by gases must play an important

role in the gas permeability and selectivity.

In this article, we demonstrate that reflectivity methods are powerful tools to detect surface adsorption of gases on polymers and the swelling of polymers induced by gases, simultaneously. As an example, a 6FDA-based polyimide in propane, propylene and propane/propylene mixed gas was examined.

2. EXPERIMENTAL

The diamines used were 2,2-bis (4-aminophenyl) hexafluoropropane (BAAF). The polyimide used was prepared by chemical imidization methods in this laboratory.   Refer to reference [8] for sample preparation.

Polyimide thin films for X-ray and neutron reflectivity measurements were prepared on Si(111) wafers by a spin-coating method.   The solution of 6FDA-BAAF in diethylene glycol dimethyl ether was filtered (2 µm pore size) and spun cast at 2000 rpm on cleaned silicon wafers.   The polymer concentrations were 2.5 and 5 wt%, giving film thickness of about 30 and 65 nm, respectively.   The former and the latter are termed 6FDA-BAAF (1) and 6FDA-BAAF (2), respectively. Each sample was baked at 423 K for 3 h after pre-annealing at 383 K for 1 h, and then at 463 K for 12 h to remove any residual solvent.   Hydrogenated propane,   propylene   and   propane/propylene (48.6 %/51.4 %) mixed gases were used for X-ray reflectivity measurements and deuterated propylene gas for neutron reflectivity measurements.

Regular thick dense films were prepared by casting polyimides solutions on clean glass plates with an applicator.   The films were dried in an oven at 383 - 463 K for 5 h under atmospheric pressure and then at 473 K for 72 h under vacuum.   Solutions were filtered through a 2 µm filter prior to casting in order to remove any large particles or impurities.   Films with 12 - 30 µm thickness were obtained.   These film densities were compared to the densities of thin films determined by X-ray reflectivity measurements [16].   The densities of the regular thick dense films were measured by floatation using zinc nitrate aqueous solutions.   We confirmed no residual solvent in the films used in this study using gas chromatography.

The X-ray reflectometer used in this study has a Johanson type quartz monochromator at the incident beam side, as schematically shown in Fig. 1 [17].   The measurements were performed in two modes using *CuKα* X-rays selected by reflection from the quartz monochromator.   One of them is the counter scan mode which is usually used.   All slits and the scintillation counter mounted on the 2θ axis are used as shown in Fig. 1.   Slit widths are 0.05 mm, 0.1 mm and 0.15 mm.   A θ-2θ scan is performed to measure the specular reflection signal after completely aligning the sample. Under this slit condition, the divergence angle of the incident beam, $\Delta\theta$, which decides the resolution, is 0.015 deg, and the direct beam intensity of 750,000 cps is obtained.

The other mode is used for the rapid characterization of the structural change of a thin film.   We call this mode the "RC mode".   None of the slits are used.   For this arrangement, all X-rays strike the sample surface at a glancing angle within $\Delta\theta$, which is equal to the
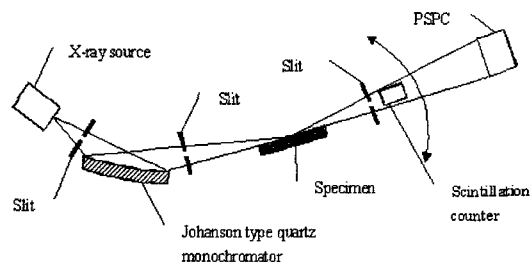

Fig. 1 Schematic drawing of the X-ray reflectometer used in this study.

focusing angle of the X-rays from the monochromator. In spite of the scintillation counter, a one dimensional position sensitive proportional counter (PSPC) located 1500 mm from the sample is used.   Without counter and sample scans, it simultaneously counts all X-rays reflected within $\Delta\theta$ from the sample surface, useful for *"in-situ"* measurements.

The sample environment was maintained in a chamber with beryllium windows under a vacuum or under various gas pressures up to 100 atm.   The chamber was placed on the θ axis of the goniometer.   All measurements were performed at 298 $\pm$ 0.5 K.

Neutron reflectivity measurements were performed on the MINE reflectometer installed at the cold neutron guide C3-1-2 in JRR-3M reactor, Tokai.   The performance of the reflectometer has been described in detail elsewhere [19].   For the measurements under pressure, we have constructed a pressure cell [18]. Deuterated propylene gas was condensed in a gas condensation tube.   This pressure system allows a polyimide film to be pressurized with deuterated propylene gas up to the saturated vapor pressure at room temperature (298 K).   Two windows of the cell were made of sapphire with the thickness of 4 mm.   The neutron transmittance of the two sapphire windows 8 mm thick in total was about 91 %.

3. DATA ANALYTICAL METHOD

The index of refraction at X-ray energies is slightly less than one and is written as $n = 1 - \delta - i\beta$, where

$$\delta = \frac{r_e\lambda^2}{2\pi}\frac{\rho}{M}N_0\sum_{i=1}^{n}x_if_{1i} \qquad (1)$$

$$\beta = \frac{r_e\lambda^2}{2\pi}\frac{\rho}{M}N_0\sum_{i=1}^{n}x_if_{2i} \qquad (2)$$

Here, r_e is the classical electron radius, λ is the X-ray wavelength, M is the molecular weight, ρ is the mass density, N_0 is Avogadro's number, x_i is the molar fraction of the i'th atom of the atomic scattering factor f_i of real and imaginary components, f_{1i} and f_{2i}, and n is the number of atoms in a molecule.   The reflection of X-rays from a layered medium was discussed by Parratt [20] who derived a recursion formula to calculate the reflected intensity from successive interfaces.   The theory was modified to include the effects of interface roughness [21].

The calculated model spectra using the recursion formula are converted to the X-ray reflectivity data by

the nonlinear least squares method. Each layer is described by four parameters: δ, β in the Equations (1) and (2), thickness and roughness. One additional parameter is a scale factor that is shifted for the overall data. Another parameter is an offset angle that is needed to convert the experimental θ into absolute θ. The calculated reflectivity data is convoluted with a Gaussian function representing the instrumental resolution function. Good fits to the data could be obtained in the cases of the as-deposited films under vacuum using a model with only a single polyimide film on the silicon.

For neutrons, the refractive index is modified in the following form.

$$n = 1 - \delta$$

$$\delta = \frac{\lambda^2}{2\pi} \sum_{i=1}^{n} n_i b_i$$

Here, λ is the neutron wavelength, n_i the number density of the i-th atom in a molecule, b_i the scattering length of the i-th atom in a molecule.

4. RESULTS AND DISCUSSION

Prior to this study, the density values of four kinds of 6FDA-based polyimide thin films including 6FDA-BAAF polyimide were determined by X-ray reflectivity measurements under vacuum. The diamines of these polyimides were α-α'-bis (4-aminophenyl)-1,4-diisopropylbenzene, 2,4,6-trimethyl-1,3-phenylenediamine and 3,3'-diaminobenzophenon. The density values obtained with X-ray reflectivity agreed with the values of their regular thick dense films determined by floating methods, indicating that an X-ray reflectivity measurement provides an accurate density of a 6FDA-based polyimide thin film in addition to an accurate thickness determination and that a single layer model used in the fitting analysis is appropriate [16].

4.1 X-ray reflectivity of 6FDA-BAAF in propylene

Fig. 2 shows the X-ray reflectivity data for the as-deposited 6FDA-BAAF (2) film under vacuum and in propylene at the relative vapor pressure shown in the figure. The most obvious effect of the exposure to gas is an increase in the oscillation frequency corresponding to an increase in film thickness. Good fits to the data could be obtained in the cases of the as-deposited films under vacuum using a single layer model. However, over $P/P_0 > 0.25$ (P_0: the saturated vapor pressure of propylene at room temperature, about 12 atm), the fits to the data became very poor using the same model. The observed data could be reproduced by the addition of a surface low density layer of $0.7 - 0.9$ g/cm^3 to the model. Hereafter, this model is termed the double layer model. However, the best fits could not be obtained below P/P_0 $= 0.5$. This was most likely due to the thinness of the surface layer. It is thought that wider range measurements are required for the analysis of the surface layer with a thickness below 3 nm.

In propylene, there are "nodes" in the oscillation as shown by Fig. 2. The position of the "node" is about θ $= 0.6$ deg at $P/P_0 = 0.64$ and $\theta = 0.4$ deg at $P/P_0 = 0.96$. This is due to the surface low density layer. The higher

the relative vapor pressure, the lower the position of the "node", indicating an increase in the surface layer thickness with the relative vapor pressure. At $P/P_0 >$ 0.9, the thickness was about 6 nm. This surface layer may be induced by the swelling or by the X-ray radiation. However, the measurements were repeated at the same relative vapor pressure, and good reproducibility was obtained. Moreover, the surface layer immediately disappeared when the sample chamber was placed under vacuum again.
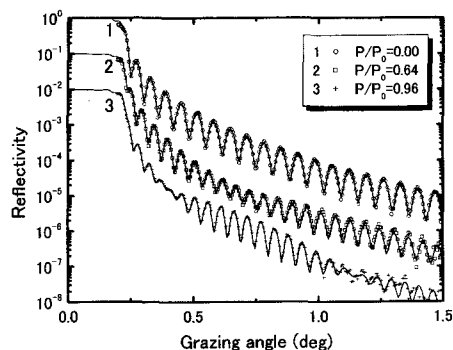

Fig. 2   X-ray reflectivities of as-deposited 6FDA -BAAF (2) film in a vacuum ($\bigcirc$), in propylene at $P/P_0 =$ 0.64 ($\square$) and at $P/P_0 = 0.96$ (+). The solid lines are the best fitting calculation results. The single layer and double layer models are used for $P/P_0 = 0.00$ and for $P/P_0 = 0.64$ and 0.96, respectively. The initial film thickness is 66.8 nm in vacuum.

This disappearance of the surface layer is also rapidly induced by a temperature change. Fig. 3 shows the raw reflectivity data for 6FDA-BAAF (1) thin film at each temperature indicated in the figure for the RC mode. The channel number can be identified by the reflective angle. The measurement of each data took 3 minutes and the change in temperature took 1 minute. The "node" located at the channel number of 280 at 299 K is rapidly shifted to a larger number by the temperature increase, implying that a rapid thinning of the surface layer occurs with temperature increase. One possible explanation for the observed phenomenon is that the surface layer consists of highly condensed propylene.

4.2 Neutron reflectivity of 6FDA-BAAF in propylene

As described above, we found that the surface layer has a lower electron density than that of the polyimide. On the contrary, if the surface layer is an adsorbed propylene layer, the adsorption layer of deuterated propylene is expected to have a higher scattering length density, which is proved by neutron reflectivity, than that of the polyimide, because the scattering length of deuterium is much larger than that of hydrogen [22]. Consequently, we can confirm if the surface layer is an adsorbed one or not by neutron reflectivity.

The observed neutron reflectivity profile is shown in Fig. 4 (a) for 6FDA-BAAF in deuterated propylene at 11.8 atm. The observed neutron reflectivity data was fitted to both theoretical reflectivity calculated from the single layer model and that of the double layer model. The results of fits are shown in Fig. 4 (a) with the deviation plots for both the models (Fig. 4(b)). The
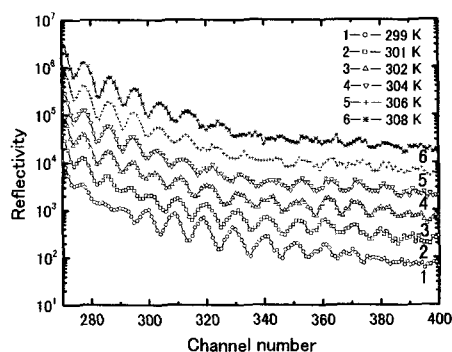
Fig. 3 X-ray reflectivities of 6FDA-BAAF (1) film in propylene ($P/P_0 = 0.99$) at 299 K (○), at 301 K (□), at 302 K (△), at 304 K (▽), at 306 K (+) and at 308 K (✳). The initial film thickness is 30.7 nm in vacuum.

fitness of the double layer model is very good and no systematic errors are observed as seen in Fig. 4 (b). On the other hand, the single layer model shows some systematic errors at around Q = 0.03 and 0.045 $Å^{-1}$, suggesting that the double layer model is much more appropriate to describe the neutron reflectivity data. Furthermore, the value of χ^2 for the single layer model is twice larger than that for the double layer model. It is therefore concluded that there is an adsorption layer of propylene on the polyimide surface. The thickness of the surface layer evaluated in the double layer model is 7 ± 1.5 nm, which agrees with that obtained in the X-ray work: 5.8 nm at 10.4 atm. Furthermore, the scattering length density of the surface layer 4.1 ± 0.4 × 10^{-4} nm^{-2} is also very close to that of the liquid deuterated propylene layer, 4.46 × 10^{-4} nm^{-2}, which was calculated under an assumption that the density of liquid deuterated propylene is the same as that of liquid hydrogenated propylene at 293 K. The scattering length density of the polyimide layer at 0 atm and 11.8 atm was 3.2 ± 0.3 × 10^{-4} nm^{-2} and 3.6 ± 0.3 × 10^{-4} nm^{-2}, respectively. These values agree well with the value calculated from the bulk density of this polyimide, 3.39 × 10^{-4} nm^{-2}. All the results confirm that the surface layer on the polyimide is an adsorption layer. In particular, the surface layer has a high scattering length density compared with the polyimide layer. This clearly indicates a condensation of deuterated gas on the polyimide. Actually, the scattering length density in the polyimide layer may gradually change in accordance with the distance from the interface between the surface layer and the polyimide layer. We think that the double layer model could well explain the reflectivity profile owing to a thinness of the polyimide layer.

4.3 X-ray reflectivity of 6FDA-BAAF in propane and propane/propylene mixed gas

The thickness of the adsorption layer of propane is much larger than that of propylene. In Fig. 5, X-ray reflectivity data is shown for 6FDA-BAAF in propane at various gas pressures. X-ray reflectivity profiles are largely modified with a large adsorption amount on the film compared with that under a vacuum. The reflectivity calculated from the double layer model was fitted to the observed data as done for propylene. As
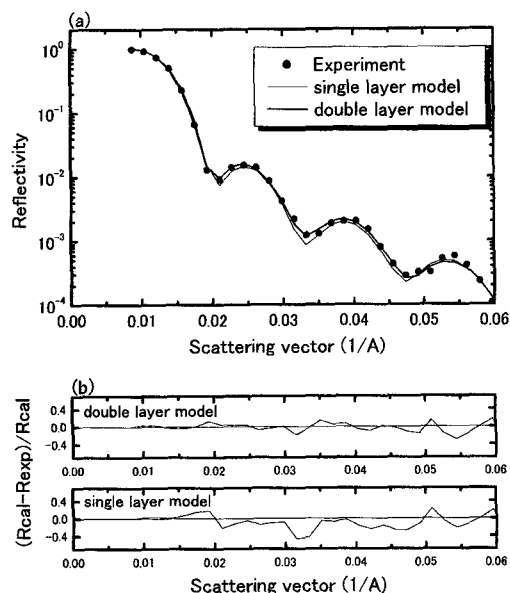

Fig. 4 (a) Neutron reflectivity of 6FDA-BAAF (1) film in deuterated propylene gas at 11.8 atm, Closed circles are the experimental data. Solid bold line is the result of the fit with a double layer model which is composed of a Si substrate, a polyimide film and a surface layer. Solid line is the result of the fit with a single layer model which is composed of a Si substrate and a polyimide film. (b) Deviation plots for both models. The initial film thickness is 31.5 nm in vacuum.
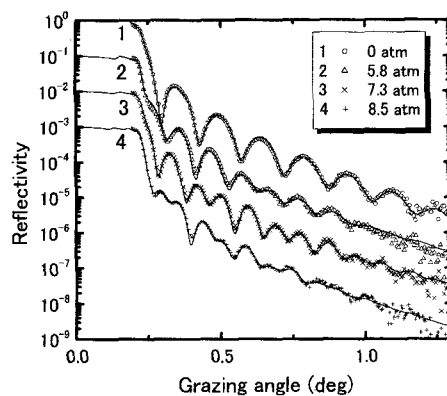

Fig. 5 X-ray reflectivities of 6FDA-BAAF (1) film in propane at 0 atm (○), at 5.8 atm (△), at 7.3 atm (×) and at 8.5 atm (+). The solid lines are the results of the best fits. The single layer and double layer models were used in the fits for 0 atm and for 5.8, 7.3 and 8.5 atm, respectively. The initial film thickness is 28.5 nm in vacuum.

shown by solid lines in the figure, the fitness is very good, indicating that the double layer model is appropriate to describe the reflectivity from the polyimide film in propane. Similar good agreements of fits and a large adsorption on polyimide were observed for 6FDA-BAAF in the propane/propylene mixed gas.

The thickness of the surface adsorption layer on polyimide is plotted as a function of the pressure (adsorption isotherm) in Fig. 6. It is noted that the
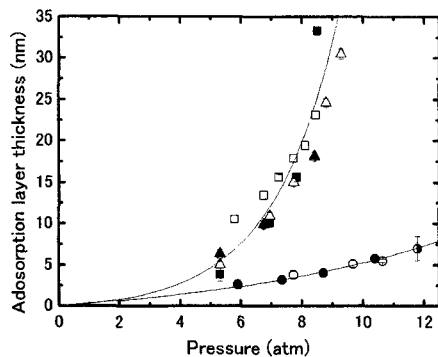
Fig. 6 Thickness of the surface adsorption layer on polyimide by X-ray reflectivity. Open circle; on 6FDA-BAAF (1) in propylene, closed circle; on 6FDA-BAAF (2) in propylene, open square; on 6FDA-BAAF (1) in propane, closed square; on 6FDA-BAAF (2) in propane, open triangle; on 6FDA-BAAF (1) in propane/propylene mixed gas, closed triangle; on 6FDA-BAAF (2) in propane/propylene mixed gas and open/closed circle; on 6FDA-BAAF (1) in deuterated propylene by neutron reflectivity. 6FDA-BAAF (1) and 6FDA-BAAF (2) have a thickness of about 30 nm and 65 nm in vacuum, respectively.

neutron reflectivity results are consistent with the X-ray reflectivity results, showing again the validity of the double layer model in the analysis of the neutron reflectivity data. The thickness of the adsorption layer is almost independent of the polyimide thickness for each gas. This fact also supports the assignment of the first layer to an adsorption layer. In the case of propylene, the thickness of the adsorption layer is about 7 nm near the saturated vapor pressure. On the other hand, the thickness of propane adsorption layer is much larger than that of propylene. This suggests that the affinity of propane to the polyimide is higher than that of propylene.

It is interesting to point out that the adsorption isotherms of propane/propylene mixed gas are very similar to that of propane. One of the possible reasons is that the content of propane in the adsorption layer is much larger than the gas so that the isotherm would be apparently similar to that of propane. This idea will be confirmed by neutron reflectivity measurements.

Fig. 7 shows the pressure dependence of the second layer (polyimide layer) thickness for 6FDA-BAAF, which is normalized to the value under vacuum. The increase in the thickness must be caused by the gas-induced swelling of the polyimide. The degree of swelling by the gases is in the order of propane/propylene mixed gas, propane and propylene at a given pressure. As mentioned above, the affinity of propane may be higher than that of propylene, and hence the higher degree of swelling of propane than propylene is expected. On the other hand, the highest degree of swelling of the mixed gas cannot be easily understood. This may be due to some interactions between the propane and propylene in the polyimide. This behavior of gas adsorption on the polyimide and the swelling of the polyimide by the gases are discussed in relation to
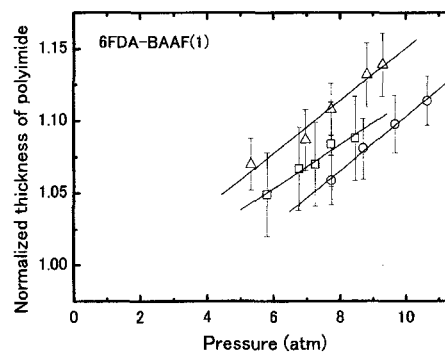

Fig. 7 Polyimide thickness normalized to the as-deposited film thickness for 6FDA-BAAF (1) with a thickness of about 30 nm in vacuum. Circle; in propylene, square; in propane, triangle; in propane/propylene mixed gas.
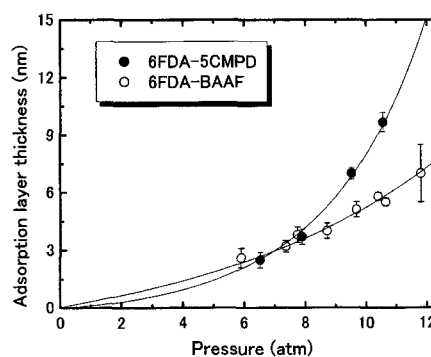

Fig. 8 Thickness of the surface adsorption layer on 6FDA-5CMPD and 6FDA-BAAF in propylene.
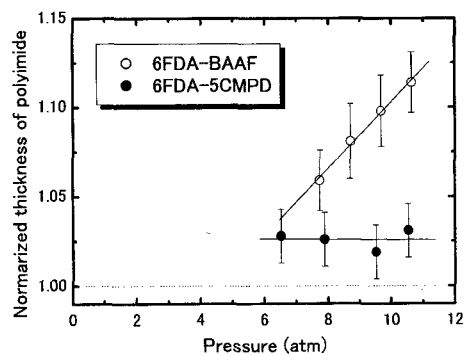

Fig. 9 Polyimide thickness normalized to the as-deposited film thickness for 6FDA-BAAF and 6FDA-5CMPD in propylene.

the gas permeability of the polyimide [19].

For 6FDA-5CMPD polyimide, Figs. 8 and 9 show thickness change of the surface adsorption layer and thickness increase of polyimide in propylene compared with 6FDA-BAAF, respectively. This polyimide is not expected to be swollen by propylene on the basis of the propylene permeation performance. The adsorption isotherm of propylene in 6FDA-5CMPD is equilibrated to that in 6FDA-BAAF (Fig. 8). However, the degree

of swelling of 6FDA-5CMPD is much lower than that of 6FDA-BAAF (Fig. 9). This typically indicates that reflectivity methods can simultaneously detect the surface adsorption of gases and the swelling of polymers induced by gases, implying that these methods are very useful for the examination of the surface adsorption of gases on polymeric membranes and their swelling induced by gases.

5. CONCLUSION

We observed the surface adsorption layer of propane, propylene and propane/propylene mixed gas on polyimide using X-ray and neutron reflectivity and determined the adsorption isotherm and the degree of swelling of polyimide by each gas. The thickness of the adsorption layer of propane was much larger than that of propylene. This has been assigned to a higher affinity of propane to polyimide than propylene. The adsorption isotherm of the propane/propylene mixed gas was almost identical with that of propane, and the degree of swelling of the polyimide by the mixed gas was the highest among propane, propylene and mixed gas.

It was concluded that X-ray and neutron reflectivity methods are very useful for the examination of surface adsorption of gases on polymeric membranes and their swelling.

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