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Surface adsorption of propane, propylene and propane/propylene mixed gas on polyimide observed with X-ray and neutron reflectivity

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Abstract

We observed the surface adsorption layer of propylene, propane and propane/propylene mixed gas on a polyimide film as a function of pressure using X-ray (XR) and neutron (NR) reflectivity. It was initially confirmed by NR that the surface layer is an adsorption layer of propylene using deuterated gas. We have determined by XR the adsorption isotherms of these gases and found that the thickness of the surface adsorption layer of propane and propane/propylene mixed gas is much larger than that of propylene and the isotherm of propane/propylene mixed gas is similar to that of propane. The former and the latter findings predict that the affinity of propane to the polyimide is greater than propylene and the content of propane is much higher than that of propylene in the adsorption layer. We also evaluated the permeability coefficients of these gases as a function of the applied pressure, and found that the permeability coefficients begin to increase at a pressure corresponding to the onset of the adsorption layer. This suggests that the surface adsorption layer of the gas plays an important role in the hydrocarbon gas permeation mechanism in a polymer membrane, while a swelling of the polyimide film is the basis for the increase in the permeability with pressure.

Keywords: X-ray reflectivity; Polyimide; Gas adsorption

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1. Introduction

Many studies have been performed on the adsorption of a gas on a solid surface under saturated vapor pressure [1–10]. The adsorption isotherm has been explained using the Lifshitz theory that is based on a van der Waals interaction between the vapor and solid through an adsorbed liquid layer. Similar adsorption of a gas could be observed on a polymer surface. The adsorption layer is thought to play an important role in the absorption and diffusion of small molecules into a polymer, and hence, affect the gas permeability of a polymer.

Recently, we observed a surface low density layer of propylene on polyimide synthesized from 2,2-bis (3,4-carboxyphenyl)hexafluoropropane dianhydride (6FDA) with X-ray reflectivity (XR) measurements [11]. The 6FDA-based polyimides have been reported to be a promising membrane material for some gas separations because they exhibit a high separation performance for different gases [12–17]. In a previous paper [11], it was found that this surface layer thickness increases with the relative vapor pressure (P/P_0), where (P_0) is the saturated pressure at a given temperature. At $P/P_0 > 0.9$, the thickness is about 6 nm. It was also found that the thickness of the surface layer decreases with increasing temperature, and the layer immediately disappears when the sample chamber is evacuated again. Therefore, it was concluded that propylene is adsorbed on the polyimide surface. We also observed a substantial increase in the permeability with propylene adsorption, suggesting that the adsorption layer plays an important role in the high propylene permeability in 6FDA-based polyimide at high pressure.

In this study, we first performed neutron reflectivity (NR) measurements on the polyimide in propylene in order to directly confirm if the surface layer is an adsorbed layer or not. In a previous study, we found that the surface layer has a lower electron density than that of the polyimide. On the

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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 NR, than that of the polyimide, because the scattering length of deuterium is much larger than that of hydrogen [18].

Second, we investigated the adsorption of propane and propane/propylene mixed gas on the polyimide using XR as a function of the gas pressure, and discussed the adsorption behavior of these gases compared with that of propylene [11] and the relation to the permeability in the polyimide.

2. Experimental section

2.1. Sample preparation

The chemical structure of the polyimide used in this study is shown in Ref. [11]. The diamine was 2,2-bis (4-aminophenyl)hexafluoropropane (BAAF). The polyimide was prepared by chemical imidization methods in this laboratory. The weight-average molecular weight, M_w, is 27,600, and the molecular weight distribution in terms of M_w/M_n is 1.83. Refer to Ref. [16] for preparation of the polymer.

Using the 6FDA-BAAF cast film with a 20 μm thickness, the permeability coefficients of propane, propylene and the propane/propylene mixed gas were measured by a pressure transform method with an applied pressure. For details, refer to Ref. [16].

Polyimide thin films for XR and NR 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 mixed gases were used for XR measurements and deuterated propylene gas for NR measurements.

2.2. X-ray reflectivity

XR measurements were performed using our home-built X-ray reflectometer. Refer to Ref. [11] for our instrument and the data analysis method used in this study. The sample films were placed in a chamber with two beryllium windows under vacuum or with various gases. The window thickness was 2 mm. The chamber was placed on the θ axis of the goniometer. The temperature was controlled at 298 ± 0.5 K during the measurements. The gases used in this study were hydrogenated propane, propylene and a propane/propylene (48.6%/51.4%) mixed gas. The measurements were performed under the counter scan mode in which a θ–2θ scan was taken to measure the specular reflection signal after completely aligning the sample.

2.3. Neutron reflectivity

NR measurements were performed on the MINE reflectometer installed at the cold neutron guide C3-1-2 in JRR-3M reactor, Tokai. Performance of the reflectometer has been described in detail elsewhere [19]. For the measurements under pressure, we constructed a pressure cell, which is schematically shown in Fig. 1. Deuterated propylene (C_3D_6) gas was condensed in the gas condensation tube shown in Fig. 1. This pressure system allows a polyimide film to be pressurized with C_3D_6 gas up to the saturated vapor pressure at room temperature (298 K). The two windows of the cell were made of sapphire with the thickness of 4 mm. Neutron transmittance of the two sapphire windows 8 mm total thickness was about 91%.

The data analysis methods for NR are similar to that for XR except for the refractive index of neutrons, which is given by the following equations.

$$n = 1 - \frac{\lambda^2}{2\pi}\rho \qquad (1)$$

$$\rho = \sum_{i=1}^{n} n_i b_i \qquad (2)$$

Here, λ is the neutron wavelength, n_i the number density of the ith atom in a molecule, and b_i the scattering length of the ith atom in a molecule.

3. Results and discussion

3.1. NR study on propylene adsorption

The observed reflectivity profile is shown in Fig. 2(a) for 6FDA-BAAF (1) in deuterated propylene at 11.8 atm. As previously reported [11], we observed a low density surface layer on the polyimide using XR. In order to confirm if this surface layer is an adsorption layer of propylene, the

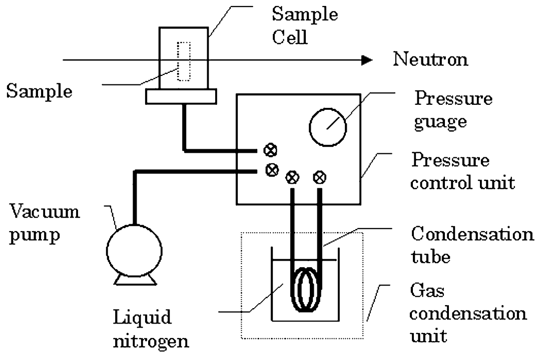

Fig. 1. Schematic diagram of the experimental system for neutron reflectivity measurements of polyimide thin films in deuterated propylene.

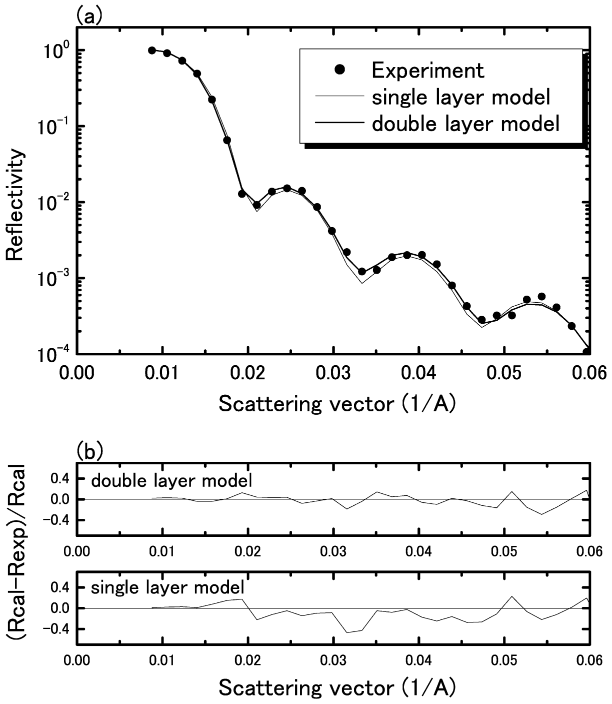

Fig. 2. (a) Neutron reflectivity of 6FDA-BAAF (1) film in C_3D_6 at 11.8 atm, Experiment: closed circle. Calculation: solid bold line, a double layer model is used for the fitting procedure. The model is composed of a Si substrate, a polyimide film and a surface layer. Calculation: solid line, a single layer model is used for the fitting procedure, which is composed of a Si substrate, and a polyimide film. (b) deviation plots for both models.

observed NR data was fitted to both the theoretical reflectivity calculated from the single layer model and that of the double layer model, which are schematically illustrated in Fig. 3. The results of the fittings are shown in Fig. 2(a) with the deviation plots for both models (Fig. 2(b)). The fitness of the double layer model is very good and no systematic errors are observed as seen in Fig. 2(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 NR data. Furthermore, the value of χ^2 for the single layer model is two times larger than that for the double layer model. Therefore, it is 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 previous X-ray study of 5.8 nm at 10.4 atm [11]. Furthermore, the scattering length density of the surface layer of $4.1 \pm 0.4 \times 10^{-4}\ \text{nm}^{-2}$ is also very close to that of the liquid C_3D_6 layer, $4.46 \times 10^{-4}\ \text{nm}^{-2}$, which was calculated under the assumption that the density of the liquid C_3D_6 is the same as that of the liquid C_3H_6 at 293 K. The polyimide layer thickness at 0 and 11.8 atm was 31.5 and 34.4 nm, respectively. The thickness increase in the polyimide layer by gas-induced swelling was about 10%, which also agrees with the previous study. The scattering length density of the polyimide layer at 0 and 11.8 atm was $3.2 \pm 0.3 \times 10^{-4}\ \text{nm}^{-2}$ and $3.6 \pm 0.3 \times 10^{-4}\ \text{nm}^{-2}$, respectively. These values are in good agreement with the value calculated from the bulk density of this polyimide, $3.39 \times 10^{-4}\ \text{nm}^{-2}$. 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 the 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 due to the thinness of the polyimide layer.

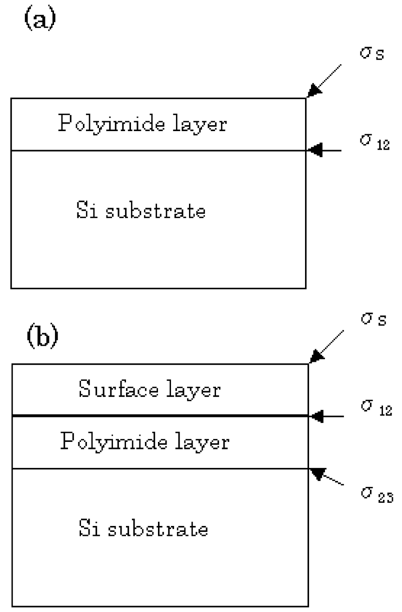

Fig. 3. Fitting models for neutron reflectivity data. (a) single layer model; polyimide layer and Si substrate with interface roughness on each interface. (b) double layer model; a surface layer, polyimide layer and Si substrate with interface roughness on each interface.

Unfortunately, it was impossible to characterize a thinner surface adsorption layer on the polyimide below 11.8 atm because the large scattering and absorbance of neutrons by the gas made the dynamic range very narrow in the NR measurements.

3.2. XR study on propane and propane/propylene adsorption

Fig. 4 shows the XR data for 6FDA-BAAF (1) under vacuum and in propane at various pressures. As the gas pressure increases, the oscillation frequency corresponding to the film thickness increases. The reflectivity calculated from the single layer model was fitted to the observed reflectivity from the film under vacuum, and had a good agreement. However, in propane, the fit of the single layer model to the data becomes worse with the increasing pressure although they are not shown here. The reflectivity

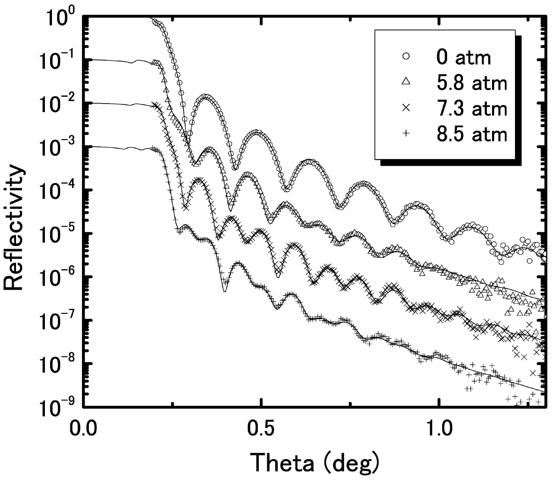

Fig. 4. X-ray reflectivities of 6FDA-BAAF (1) film in propane at 0 atm (○), at 5.8 atm (△), at 7.3 atm (×) and at 8.5 atm (+). The solid lines are the best fitting results except at 0 atm using the double layer model. The result at 0 atm is the best fitting calculation with a single layer model.

calculated from the double layer model was then fitted to the observed data as done for propylene [11]. As shown by the solid lines in the figure, the fitness is very good. The XR data also indicate that the double layer model is appropriate to describe the reflectivity from the polyimide film in propane. Similar fitting were obtained for 6FDA-BAAF (1) in propane/propylene mixed gas and 6FDA-BAAF (2) in propane and the mixed gas. The fitting parameters thus obtained are summarized in Table 1. The densities of all the as-deposited films evaluated in the fittings agree with that of the 20 μm 6FDA-BAAF cast films thick determined using a floating method (1.47 g/cm^3), thus supporting the validity of the fittings.

The thickness of the surface adsorption layer on the polyimide is plotted as a function of the pressure (adsorption isotherm) in Fig. 5, where the previous XR results (Ref. [11]) and the NR result (in this article) on the propylene adsorption layer are also included. It is noted that the present NR result is consistent with the previous XR results, showing again the validity of the double layer model. 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 as 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 the propane adsorption layer is much larger than that of propylene. This suggests that the affinity of propane to the polyimide is higher than 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 propane content in the adsorption layer is much larger than the gas so that the isotherm would be apparently similar to that of propane. This idea is also supported by the pressure dependence of the permeability coefficient as will be discussed later. As shown in our previous paper [11] the formation of the surface adsorption layer of propylene seems to begin at about 6 atm. For propane and propane/propylene mixed gas,

Table 1
Best fitting calculation parameters of 6FDA-BAAF in propane and propane/propylene using double layer model. Double layer model: with a surface layer on 6FDA-BAAF film

Atm	σ_s (nm)	First layer			Second layer		
		Density (g/cm^3)	Thickness (nm)	σ_{12} (nm)	Density (g/cm^3)	Thickness (nm)	σ_{23} (nm)
6FDA-BAAF (1) in propane							
0.0	0.8 ± 0.1	–	–	–	1.47 ± 0.06	28.5 ± 0.2	1.2 ± 0.2
5.8	1.8 ± 0.3	0.93 ± 0.13	10.5 ± 0.5	1.6 ± 0.5	1.31 ± 0.12	29.9 ± 0.6	0.6 ± 0.2
7.3	1.6 ± 0.2	0.87 ± 0.12	15.6 ± 0.4	1.7 ± 0.4	1.34 ± 0.09	30.5 ± 0.4	0.6 ± 0.2
8.5	2.0 ± 0.5	0.67 ± 0.22	23.1 ± 0.5	2.0 ± 0.4	1.33 ± 0.10	31.0 ± 0.6	0.7 ± 0.2
6FDA-BAAF (2) in propane							
0.0	0.5 ± 0.1	–	–	–	1.48 ± 0.03	64.1 ± 0.2	0.5 ± 0.1
5.4	0.5 ± 0.3	0.79 ± 0.13	3.8 ± 0.5	2.1 ± 0.5	1.46 ± 0.12	69.0 ± 0.6	0.5 ± 0.2
7.8	1.5 ± 0.2	0.97 ± 0.12	15.6 ± 0.4	1.2 ± 0.4	1.38 ± 0.08	70.5 ± 0.4	0.4 ± 0.2
8.5	1.8 ± 0.3	1.01 ± 0.13	33.3 ± 0.5	0.9 ± 0.8	1.39 ± 0.09	71.4 ± 0.5	0.4 ± 0.2
6FDA-BAAF (1) in propane/propylene							
0.0	0.9 ± 0.1	–	–	–	1.44 ± 0.04	28.7 ± 0.1	1.0 ± 0.1
5.3	1.1 ± 0.2	0.68 ± 0.12	5.0 ± 0.4	2.3 ± 0.5	1.42 ± 0.06	30.7 ± 0.4	0.3 ± 0.2
7.7	1.7 ± 0.3	1.01 ± 0.12	15.0 ± 0.5	1.4 ± 0.5	1.30 ± 0.08	31.8 ± 0.4	0.3 ± 0.3
9.3	2.0 ± 0.5	0.88 ± 0.12	30.5 ± 0.6	1.6 ± 0.5	1.27 ± 0.10	32.7 ± 0.5	0.4 ± 0.2
6FDA-BAAF (2) in propane/propylene							
0.0	0.7 ± 0.2	–	–	–	1.50 ± 0.04	66.0 ± 0.2	1.2 ± 0.2
5.3	1.3 ± 0.2	0.67 ± 0.12	6.3 ± 0.4	2.8 ± 0.8	1.40 ± 0.06	69.5 ± 0.4	0.1 ± 0.2
6.8	1.4 ± 0.3	1.01 ± 0.12	9.9 ± 0.5	1.2 ± 0.5	1.40 ± 0.08	71.4 ± 0.4	0.1 ± 0.3
8.4	1.1 ± 0.5	0.89 ± 0.12	18.1 ± 0.6	1.2 ± 0.5	1.37 ± 0.10	74.1 ± 0.5	0.3 ± 0.2

Roughness σ_s: surface, σ_{12}: first layer/second layer, σ_{23}: second layer/substrate.

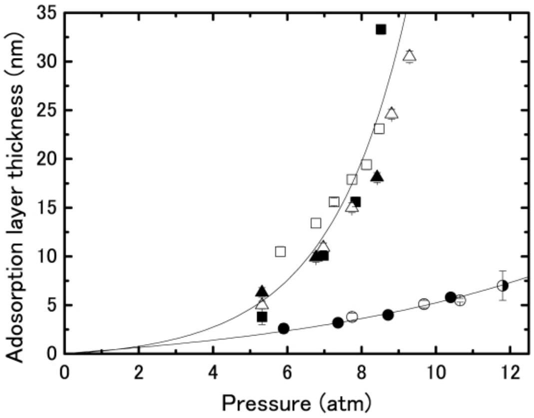

Fig. 5. Thickness of the surface adsorption layer on polyimide by X-ray reflectivity. Open circle; on 6FDA-BAAF (1) in propylene, closed circle; on 6FDA-BAAF (2) in propylene, open square; on 6FDA-BAAF (1) in propane, closed square; on 6FDA-BAAF (2) in propane, open triangle; on 6FDA-BAAF (1) in propane/propylene 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.

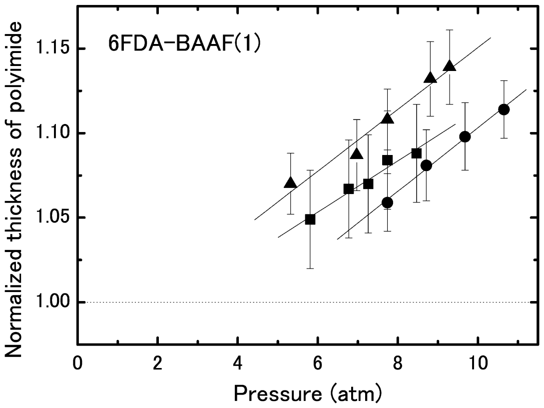

Fig. 6. Polyimide thickness normalized by the as-deposited film thickness for 6FDA-BAAF (1). Circle; in propylene, square; in propane, triangle; in propane/propylene mixed gas.

the onset pressure of adsorption would be about 4 atm, if we assume that the thickness of the adsorption layer is the same as propylene at the onset pressure. This assumption is physically identical with the idea that there is a critical thickness to stabilize an adsorption layer on the polyimide.

Fig. 6 shows the pressure dependence of the second layer for 6FDA-BAAF (1), 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 propylene, and hence the higher degree of swelling by propane than propylene is expected. On the other hand, the highest degree of swelling by the mixed gas cannot be easily understood. This may be due to some interactions between propane and propylene in the polyimide. At this moment, we have no direct proof to support this idea, but if there are no interactions between them, the degree of swelling should not be more than that of propane.

Extrapolating the normalized thickness to the value under vacuum ($=1$), the pressure does not become zero, meaning that there is a threshold pressure for swelling although it is hard to say how large the threshold is, and it must be related to the onset of the formation of the adsorption layer on the polyimide. If we assume that the swelling is triggered by the formation of the adsorption layer, the threshold pressure must be 6 and 4 atm for propylene and for propane and propane/propylene mixed gas, respectively.

3.3. Permeability coefficients and selectivity

The propane and propylene permeability coefficients are shown in Fig. 7 as a function of the applied pressure in the single gas systems. The permeability coefficients of both gases are almost independent of the applied pressure below 4 and 6 atm, respectively, while they begin to increase at pressures above these threshold pressures. The increments are of one order of magnitude around the corresponding saturated pressure. This is very important information for application of the 6FDA-BAAF polyimide as a gas permeation membrane, because one tenth of the membrane area is enough for the same amount of gas permeation at a high applied pressure. The threshold pressure almost corresponds to the onset of the formation of the adsorption layer for each gas as described above. It is expected that the adsorption layer supplies more propylene or propane to the polyimide than the gas phase, and hence the permeability coefficient begins to increase above the threshold pressure. If the increase in the gas permeability coefficient is caused only by the adsorption, the permeability coefficient might level off with the increasing layer thickness. However, the experimental result shows the continuous increase in the permeability coefficient with pressure. In order to explain this, we have to take into account the continuous swelling of the polyimide (see Fig. 6). The swelling makes voids or free volume in the polyimide larger and the molecular motions

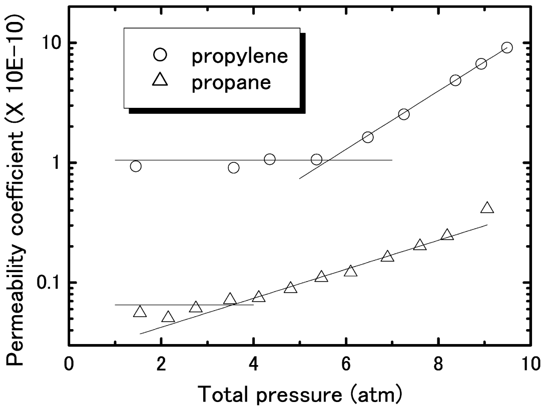

Fig. 7. Permeability coefficient (cm^3 (STP)cm/cm^2 s cmHg) of propane (triangle) and propylene (circle) in the single gas system.

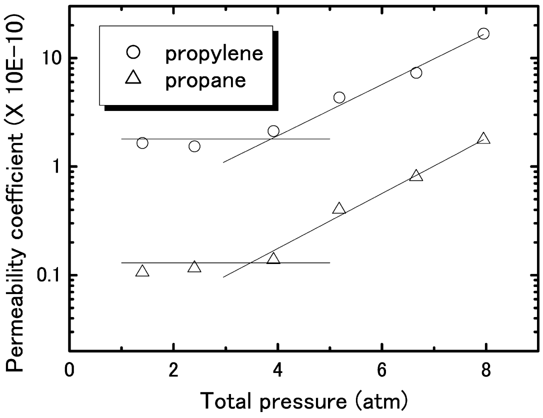

Fig. 8. Permeability coefficient (cm^3 (STP)cm/cm^2 s cmHg) of propane (triangle) and propylene (circle) in the mixed gas system.

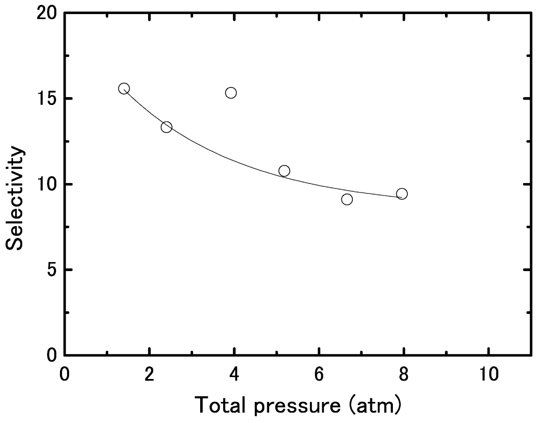

Fig. 9. Selectivity of propylene from propane/propylene mixed gas. Line is a guideline.

more active, which must accelerate the gas permeation in the polyimide. The former was observed with positronium annihilation life time spectroscopy [20] and the latter with quasi-elastic neutron scattering [21].

Fig. 8 shows the pressure dependence of the permeability coefficients of propane and propylene in the mixed gas. The threshold pressure of propylene is around 4 atm, being 2 atm lower than in the single gas system and the same as that of propane. This must be because the propylene content in the layer is lower than that in the gas state, which may also be due to a higher affinity of propane to polyimide than that of propylene as expected from the adsorption isotherm of the mixed gas. In principle, this speculation could be confirmed using a NR technique, which will be done in the future. The pressure dependence of the permeability coefficient becomes stronger for propane and weaker for propylene in the mixed gas than in the single gas. As a result, both dependences are almost identical in the mixed gas.

As shown in Fig. 9, the selectivity of propylene from propane/propylene mixed gas in the propane/propylene mixed gas system is 10–15, and not strongly dependent on the pressure. On the other hand, in the 1,3-butadinene/butane mixed gas system, the selectivity is strongly dependent on the applied pressure. The selectivity of 1,3-butadiene from 1,3-butadiene/*n*-butane mixed gas is 10–15 at a relatively low pressure, but becomes 3 or less at a higher pressure [16]. The pressure independent nature in the propane/propylene mixed gas system has been explained by some interactions between propane and propylene in the polyimide. In other words, each gas does not move independently as expected from the adsorption isotherm of the mixed gas (see Fig. 5).

4. Conclusion

In this study, we observed the surface adsorption layer of propane, propylene and propane/propylene mixed gas on polyimide using NR and XR, 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 the 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. The former was explained in terms of the propane-rich content in the mixed gas, which may also be due to the higher affinity of propane to the polyimide than propylene and the latter by some interactions between propane and propylene in the polyimide.

The permeability coefficients of propane, propylene and propane/propylene mixed gas began to increase at the onset of the formation of the surface adsorption layer and continued to increase with pressure. These observations indicate that the surface adsorption layer plays an important role in the gas permeability while the gas-induced swelling is the basis for the gas permeation. In the mixed gas, the permeability coefficients for both gases are not strongly dependent on the pressure. It also may be due to the propane-rich content in the mixed gas adsorption layer that originated from the higher affinity of propane to polyimide and some interactions between propane and propylene in the polyimide.

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