

# Characterization and Transport Properties of a Novel Aliphatic Polyamide with an Ethyl Branch

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**ABSTRACT:** The CO<sub>2</sub> gas and water vapor transport properties of a novel aliphatic polyamide with an ethyl branch were investigated. The polymer was characterized with density measurements, differential scanning calorimetry, thermogravimetric analysis, and wide-angle X-ray diffraction analyses, and the amorphous and glassy nature of the polymer at the ambient temperature were confirmed. The CO<sub>2</sub> sorption isotherm of the polymer appeared to obey the dual-mode sorption isotherm, which was characteristic of the glassy state. The water vapor sorption below a relative humidity of 0.4 or 0.5 was explained in terms of the Brunauer–Emmett–Teller sorption mechanism, whereas that

at a high relative humidity demonstrated a dissolution type of water vapor into the polyamide. The permeability coefficients of He, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> gases through the membrane were as follows:  $P(\text{He}) > P(\text{CO}_2) > P(\text{O}_2) > P(\text{N}_2)$ . The novel polyamide membrane was more permeable to CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> gases than nylon 6 and nylon 66 membranes, containing a crystalline and hydrogen-bonding nature. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1955–1960, 2005

**Key words:** amorphous; gas permeation; membranes; polyamides

## INTRODUCTION

Barrier polymers are gaining importance as materials for food packaging and gasoline tanks. The polyamides offer resistance to grease, oil, abrasion, and puncture; they are good gas, odor, and flavor barriers but poor barriers to water vapor.<sup>1–3</sup> Polyamides, because of their broad variety of physical and mechanical properties, are being used as important commercial fibers and plastics.

Crystallinity is an important factor because crystallites are generally impermeable and reduce the permeation rate.<sup>3</sup> Structurally regular polyamides exhibit extensive interchain hydrogen bonding and the ability to form an ordered (crystalline) structure, which incorporates the useful physical properties of these materials. The gas and water vapor transport properties of polyamide membranes are gaining significance. However, only a few reports are available.

Furthermore, a novel polyamide with an ethyl branch is estimated to inhibit regular hydrogen bonding (Scheme 1), has no crystalline and amorphous structure, and is expected to have new properties different from those of other crystalline polyamides.

Hence, an investigation of the gas and water vapor transport properties of an aliphatic polyamide with an ethyl branch was made. In this article, we describe the characterization and transport properties of the polyamide synthesized by the interfacial polycondensation of 2,4-diethyl glutaric acid and hexamethylenediamine.

## EXPERIMENTAL

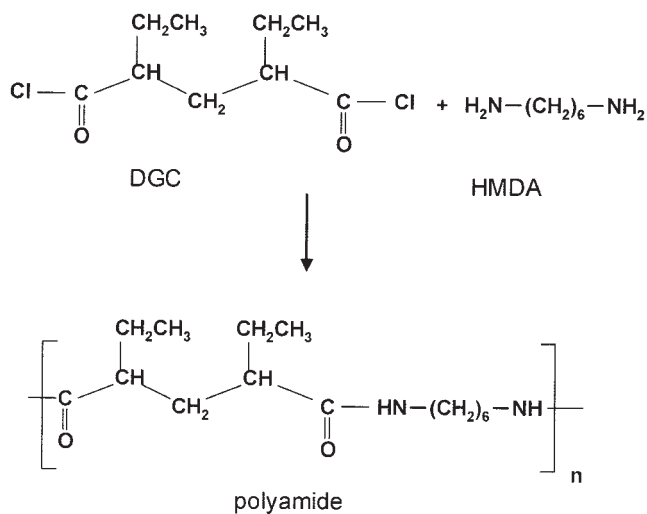
### Materials

The polyamide synthesized by the interfacial polycondensation of 2,4-diethyl glutaric acid and hexamethylenediamine was used in this study (Scheme 1). The polyamide films were prepared by the casting of a 15 wt % formic acid solution on a flat Teflon Petri dish at room temperature, and then the films were dried in a vacuum oven at room temperature for 48 h.

The CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and He gases used in the sorption and permeation experiments were greater than 99.9% pure and were used without further purification.

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### Synthesis of 2,4-diethyl glutaryl dichloride (DEGC)

Thionyl chloride (524 g, 4.40 mol) was placed in a three-necked flask fitted with a mechanical stirrer. A solution of 2,4-diethyl glutaric acid (DEGA) (188 g, 1.00 mol) and pyridine (158 g, 2.00 mmol) in chloroform (400 mL) was dropped slowly at 0°C. The mixture was further stirred for 1 h at 0°C and for 1.5 h at room temperature and was then filtered to remove pyridine hydrochloric acid salt. After residual chloroform, thionyl chloride, and pyridine were evaporated, the crude product was extracted with *n*-hexane and washed with water and aqueous Na<sub>2</sub>CO<sub>3</sub>. Distillation under a reduced pressure (110–115°C/17 mmHg) gave DEGC (156 g, 69.1%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz, δ, ppm): 2.81 (m, 2H), 2.35–1.71 (6H), 0.99 (m, 6H). Fourier transform infrared (FTIR; KBr, cm<sup>-1</sup>): 2971, 2938, 2880, 1792 (ν<sub>C=O</sub>), 1460, 1387, 1133, 971, 947, 910, 890, 785. ANAL. Calcd for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 48.02%; H, 6.27%. Found: C, 47.94%; H, 6.41%.

### Synthesis of the branched polyamide (typical procedure)

A solution of DEGC (36 g, 0.16 mol) in chloroform (170 mL) was placed in a round-bottom flask equipped with a mechanical stirrer. To the rapidly stirred solution was added a cooled solution of ethylenediamine (9.6 g, 0.16 mol) and sodium hydroxide (13 g, 0.32 mol) in water (170 mL) at 0°C, and the mixture was stirred for 2 h at 0°C, for 17 h at room temperature, and finally for 8 h at 40°C. The precipitated polymer (BPA25) was filtered, washed with water, and dried *in vacuo* at 60°C. The polyamide was further purified by precipitation in acetone from the formic acid solution, which was used for the characterization.

Yield: 94%. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 200 MHz, δ, ppm): 7.72 (2H), 3.13 (4H), 2.02 (2H), 1.56–1.31 (6H), 0.78 (6H). FTIR (KBr, cm<sup>-1</sup>): 3296, 2963, 2935, 2876, 1652 (ν<sub>C=O</sub>), 1555 (δ<sub>N-H</sub>), 1458, 1384, 1277, 1239. ANAL. Calcd for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 62.24%; H, 9.50%; N, 13.20% (C/N, 4.72). Found: C, 61.11%; H, 9.55%; N, 12.54% (C/N, 4.87).

### Methods

#### Thermal analysis

**Differential scanning calorimetry (DSC).** DSC was performed with a PerkinElmer Pyris Diamond DSC instrument (PerkinElmer, Inc., Wellesley, MA) at a heating rate of 10°C/min. A DSC thermogram was first obtained for the as-prepared sample, and the second thermogram was obtained for the cooled sample after the first scan; the midpoint of the heat capacity jump of the second scan was determined as the glass-transition temperature (*T*<sub>g</sub>).

**Thermogravimetric analysis (TGA).** TGA data in the temperature range of 30–500°C were obtained for the first heating process with a PerkinElmer Pyris 1 TGA instrument at a heating rate of 10°C/min under a nitrogen gas purge.

#### Density measurements

The density of the film was determined by a floatation method with a pycnometer at 25°C with a mixture of toluene and *n*-octyl bromide.

#### Wide-angle x-ray diffraction (WAXD)

The WAXD profile at room temperature was obtained with a RAD-RC (Rigaku Denki Co., Inc., Tokyo, Japan) with nickel-filtered Cu Kα radiation in the 2θ range of 2.5–30°.

#### Gas sorption

A gas sorption experiment at 25°C was carried out with a gravimetric sorption apparatus with an electromicrobalance (type 2000, Cahn Instruments, Inc., Madison, WI). After sufficient drying of the films at about 10<sup>-5</sup> cmHg, the apparent amount of gas sorbed in the film at a fixed constant gas pressure was measured by the electromicrobalance and was corrected by the subtraction of a buoyancy contribution of the film to obtain a precise sorption amount.

#### Gas permeation

The film, mounted in a permeation cell, was degassed for 24 h at 10<sup>-5</sup> cmHg in a permeation apparatus. The downstream side of the film was evacuated for about

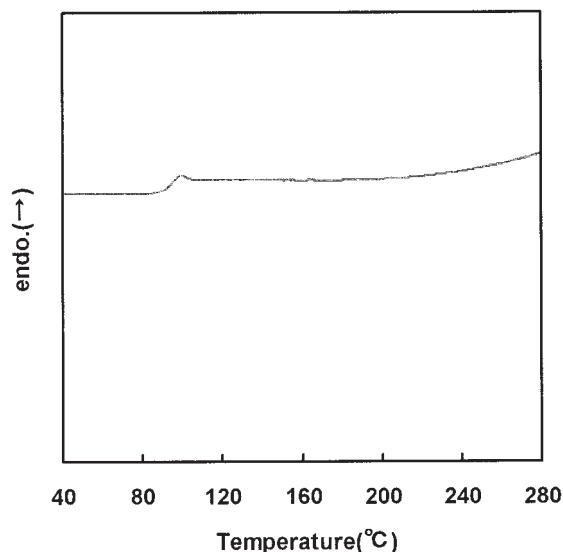


Figure 1 DSC thermogram of polyamide.

48 h under about  $10^{-5}$  cmHg. A large amount of the permeant gas was introduced into a reservoir in the upstream side, and the pressure of the permeant gas that permeated through the film to the downstream side was monitored with an MKS-Baratron pressure transducer (227AA). The permeability coefficient ( $P$ ) was evaluated from the steady-state gas permeation rate ( $dp_2/dt$ ):

$$P = \frac{273}{76} \left( \frac{V\ell}{ATp_1} \right) \left( \frac{dp_2}{dt} \right) \quad (1)$$

where  $V$  is the volume of the downstream side,  $\ell$  is the film thickness,  $A$  is the effective film area,  $p_1$  is the pressure of the gas in the upstream side,  $p_2$  is the pressure of the permeated gas in the downstream side, and  $T$  is the absolute temperature.

The diffusion coefficient ( $D$ ) of  $\text{CO}_2$  was deduced from the time lag ( $\theta$ )<sup>4</sup> provided by the linear extrapolation of the steady-state permeation line to the time axis:

$$D = \frac{\ell^2}{6\theta} \quad (2)$$

where  $\ell$  is the thickness of the film and  $\theta$  is the time lag.<sup>4</sup>

#### Water vapor sorption

Water vapor sorption isotherms at 25°C were obtained at each water vapor pressure by the quartz spring method, which consists of a quartz spring hanging down in a glassy tube. The spring constant of the quartz spring used, defining its elongation to weight,

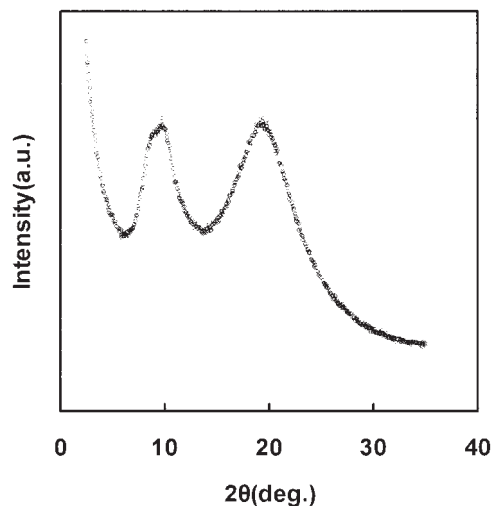


Figure 2 WAXD profile of polyamide.

was 0.855 m/g. The elongation, measured by a cathetometer with a precision of  $10^{-4}$  cm, could provide the water vapor sorption amount in the film.

## RESULTS AND DISCUSSION

### Characterization

The solubilities of the prepared polyamide in different organic solvents such as formic acid, benzyl alcohol, phenol, and *m*-cresol were examined to prepare a cast film. The polyamide has good solubility in comparison with other polyamides such as nylon 66. In addition, this polyamide is almost soluble in alcohol solvents such as methanol and ethanol.

The DSC thermogram of polyamide shows no endothermic peak over a whole temperature range of 30–280°C (Fig. 1).  $T_g$  appears at 94°C from the heat capacity jump, as observed from the DSC thermogram of the second heating.

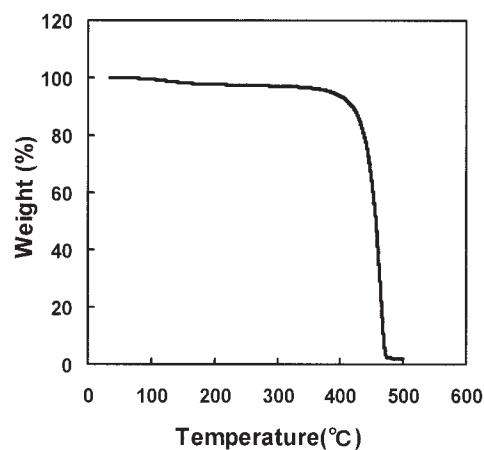
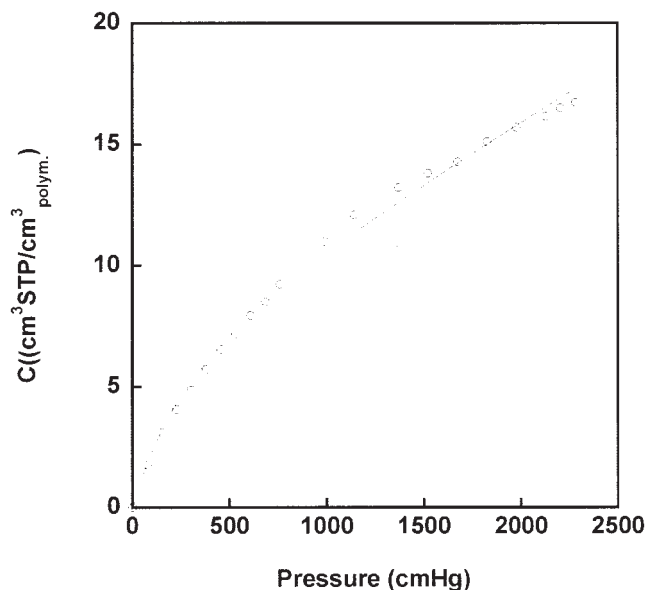


Figure 3 Thermogravimetric curve of polyamide.



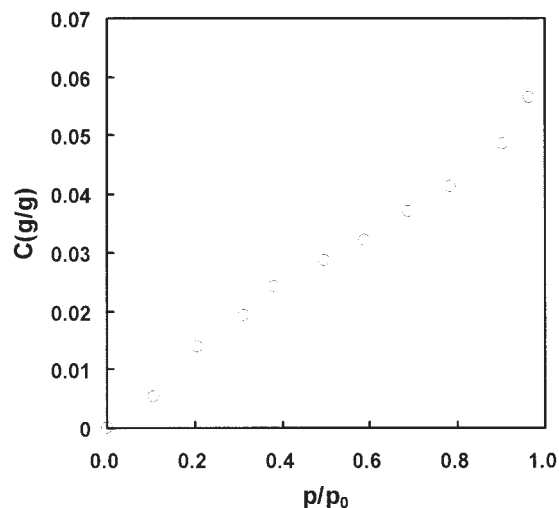
**Figure 4** CO<sub>2</sub> sorption isotherm of polyamide at 25°C: (○) observed and (—) curve-fitted by the dual-mode sorption model.

The WAXD profile shows two broad amorphous peaks at about  $2\theta = 10^\circ$  and  $2\theta = 20^\circ$  (Fig. 2). A similar profile has been reported for amorphous poly(1-butene), which also has an ethyl branch in a repeating unit.<sup>5</sup> Therefore, the peak at  $2\theta = 10^\circ$  may correspond to the average interchain distance for polymers having an ethyl branch in an amorphous state, and the peak at  $2\theta = 20^\circ$ , which is normally observed for amorphous polymers, corresponds to the average interatomic distance. These two amorphous peaks did not change remarkably up to 200°C. This fact confirms the presence of an amorphous structure in the polyamide over the whole temperature range studied. The polarized microscopy observation also establishes the amorphous structure of the polyamide film. The amorphous structure in the polyamide is the result of a disordered chain conformation caused by the ethyl branch. A double ethyl branch in a repeating unit, as shown in Scheme 1, might disturb the densely ordered polymer chain alignment and lead to the amorphous structure.

The density of the amorphous polyamide was found to be 1.0519 g/cm<sup>3</sup> at 25°C by a floatation

**TABLE I**  
Dual-Mode Sorption Parameters of the CO<sub>2</sub>  
Gas of Polyamide

$C_H'$ [ $\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ polymer}}$ ]	$k_D \times 10^3$ [ $\frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ polymer cmHg}}$ ]	$b \times 10^3$ (cmHg <sup>-1</sup> )
7.84	4.58	3.13



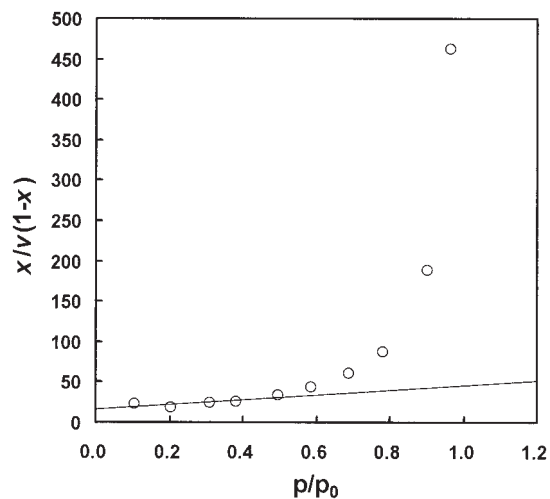
**Figure 5** Water vapor sorption isotherm of polyamide at 25°C.

method, and it has a lower density than other crystalline polyamides, such as nylon 6, nylon 66, and nylon 11.

The TGA profile of this polyamide shows that it has nearly the same thermal stability as nylon 66 up to about 439°C (10% weight loss), beyond which the decomposition of the polyamide begins (Fig. 3).

### Sorption properties

The sorption isotherm of CO<sub>2</sub> at 25°C of the polyamide film is shown in Figure 4. The isotherm is concave against the pressure axis in the low-pressure range and linear in the high-pressure range. This could be described adequately with the dual-mode sorption



**Figure 6** BET plot of the polyamide-water vapor system at 25°C.

TABLE II  
Permeability ( $P$ ), Diffusion ( $D$ ), and Solubility ( $S$ ) Coefficients of Polyamide at 25°C and 76 cmHg

Polymer	Gas	$P \times 10^{10}$	$D \times 10^9$	$S \times 10^2$	$D_D \times 10^8$	$D_H \times 10^8$	$F$
		$\left[ \frac{\text{cm}^3 (\text{STP})\text{cm}}{\text{cm}^2 \text{ s cmHg}} \right]$	$\left( \frac{\text{cm}^2}{\text{s}} \right)$	$\left( \frac{\text{cm}^3 \text{STP}}{\text{cm}^3_{\text{polymer}} \text{ cmHg}} \right)$	$(\text{cm}^2 \text{ s})$	$(\text{cm}^2 \text{ s})$	
Novel polyamide	CO <sub>2</sub>	1.18	5.10	2.325	3.694	0.371	0.1
	O <sub>2</sub>	0.356	—	—	—	—	—
	N <sub>2</sub>	0.0903	—	—	—	—	—
	He	7.65	—	—	—	—	—
Nylon 6	CO <sub>2</sub>	0.114 <sup>a</sup>	—	—	—	—	—
	O <sub>2</sub>	0.04935 <sup>a</sup>	—	—	—	—	—
	N <sub>2</sub>	0.01233 <sup>a</sup>	—	—	—	—	—
Nylon 66	CO <sub>2</sub>	0.1095 <sup>b</sup>	0.819 <sup>b</sup>	1.337 <sup>b</sup>	—	—	—

<sup>a</sup> Corrected value of nylon 6 (estimated with 23% crystallinity).<sup>8</sup>

<sup>b</sup> Corrected value of nylon 66 (37% crystallinity).<sup>9</sup>

model, which is represented by the following equation:<sup>6,7</sup>

$$C = C_D + C_H = k_D p + \frac{C_H' b p}{1 + b p} \quad (3)$$

where  $C$  is the total CO<sub>2</sub> concentration,  $C_D$  is the concentration of CO<sub>2</sub> due to the contribution of Henry's law,  $C_H$  is the concentration of CO<sub>2</sub> held in Langmuir sorption sites or microvoids,  $k_D$  is the solubility coefficient of Henry's law,  $p$  is the pressure of penetrant CO<sub>2</sub>,  $b$  is the affinity constant to the Langmuir sorption site, and  $C_H'$  is the hole saturation constant in the Langmuir sorption mode. The dual-mode sorption parameters have been obtained by the nonlinear least-square curve fitting of eq. (3) with the experimental data (Table I), and they show that the polyamide studied here has an amorphous, glassy structure.

The water vapor sorption isotherm at 25°C of the polyamide is well represented by the sigmoid type (Fig. 5). This fact is explained in terms of the Brunauer–Emmett–Teller (BET) sorption mechanism<sup>8</sup> at a low relative humidity and in terms of a dissolution-type sorption mechanism at a high relative humidity. The amount of water sorbed into a unit mole of the polyamide is determined from the BET equation as follows:

$$\frac{x}{v(1-x)} = \frac{1}{v_m c} + \frac{(c-1)x}{v_m c} \quad (4)$$

where  $v$  is the sorption amount of water vapor,  $x$  is the relative humidity,  $v_m$  is the volume of water vapor when the total surface area is covered by monolayer sorption, and  $c$  is the constant relating to the energy of sorption.

The BET plot has been applied to the observed water vapor sorption data (Fig. 6). The plot provides linearity below 0.4 or 0.5 relative humidity. The BET sorption mechanism to the polyamide can be realized

below 0.4 or 0.5 relative humidity. The slope and intercept of the straight line on the BET plot, corresponding to the values of  $v_m$  and  $c$  in eq. (4), respectively, have been obtained, as shown in Figure 6.  $v_m$  is  $0.026 \pm 0.0045$  (g/g), and  $c$  is  $2.47 \pm 0.69$ . This indicates that with a molecular weight of 268 per repeating unit of the polyamide,  $0.38 \pm 0.07$  water molecules are sorbed into the repeating unit mole of the polyamide in a manner of BET sorption.

### Permeation properties

The permeability coefficients at 25°C of CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and He were obtained from permeation experiments (Table II). The gas permeability coefficient of this novel polyamide is roughly 10 times higher than that of nylon 6 and nylon 66. This fact also suggests that the polyamide is not crystalline but amorphous. The permeability coefficients in the amorphous phase of nylon 6 and nylon 66 were corrected on the basis of the

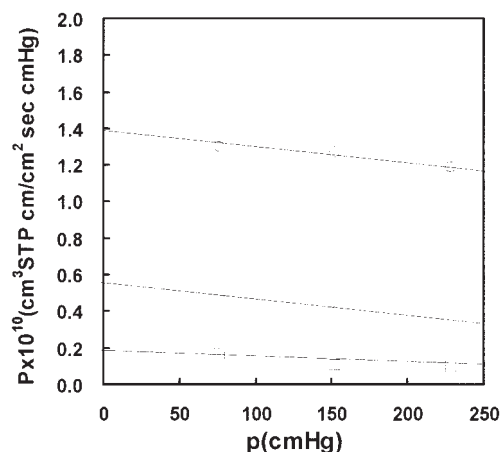
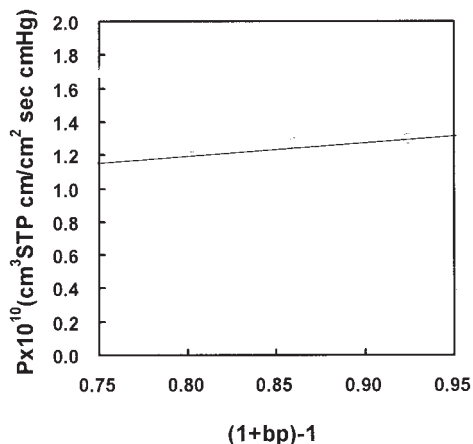


Figure 7 Pressure dependence of the permeability coefficient ( $P$ ) of polyamide for (○) CO<sub>2</sub>, (◇) O<sub>2</sub>, and (□) N<sub>2</sub> at 25°C.



**Figure 8**  $\text{CO}_2$  permeability coefficient ( $P$ ) plotted in accordance with the partial immobilization model.

degree of crystallinity.<sup>9,10</sup> Table II indicates that the novel polyamide is more permeable to  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$  than nylon 6 and nylon 66 amorphous films. Furthermore, the permeability coefficient of  $\text{CO}_2$  of the novel polyamide is 10 times higher than the corrected values of nylon 6 and nylon 66, whereas the permeability coefficients of  $\text{O}_2$  and  $\text{N}_2$  are seven times higher than the corrected values of nylon 6. This fact might correspond to a larger diffusion coefficient of the novel polyamide. However, the permselectivity of  $\text{O}_2$  to  $\text{N}_2$  ( $\sim 4.0$ ) is almost the same as that of nylon 6.

Permeation is analyzed by the partial immobilization model, which is usually applied to the glassy state. To elucidate in detail, two types of diffusion coefficients, Henry mode and Langmuir mode, have been determined from the pressure dependence of the permeability coefficient with the following equation:<sup>11</sup>

$$P = k_D D_D + \frac{D_H C_H' b}{1 + bp} \quad (5)$$

where  $D_D$  and  $D_H$  are the diffusion coefficients of Henry's law mode and the Langmuir mode, respectively. Figure 7 shows the pressure dependence of the permeability coefficient of the novel polyamide, and Figure 8 shows plots of the permeability coefficient through the film as a function of  $(1+bp)^{-1}$ , corresponding to eq. (5). The slope and intercept of the straight line corresponding to the values of  $D_H C_H' b$

and  $k_D D_D$  in eq. (5), respectively, have been determined with a linear least-square method. The obtained  $D_D$  and  $D_H$  values are tabulated in Table II with their ratio  $F$  (i.e.,  $D_H/D_D$ ).  $D_H$  is almost one-tenth of  $D_D$ , as usually observed.

The development of a novel polyamide with a different amine moiety and an investigation of the gas transport properties are being considered for future studies.

## CONCLUSIONS

A novel membrane of a polyamide with an ethyl branch was synthesized and found to be amorphous because of the presence of the ethyl branch by analyses of WAXD, DSC, and so forth. The water vapor sorption was interpreted in terms of BET sorption. At a low humidity below 0.4 or 0.5, the  $\text{CO}_2$  sorption isotherm demonstrated the dual-mode sorption mechanism, reflecting the glassy state in the amorphous phase of the novel polyamide. This polyamide has higher gas permeability than nylon 66 and nylon 6, probably because of the amorphous, glassy state. The permeation mechanism of the polyamide is well described by the partial immobilization model characteristic of its glassy state.

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