Gas Transport Properties of Various Imidized Polyamic Acid Films

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ABSTRACT: The sorption and permeation of CO₂ in and through various imidized polyamic acid [PAA] films were investigated. Dual-mode sorption and partial immobilization models were applied to their phenomena and their behavior and structure are discussed. The amount of CO₂ sorption increased with imidization in PAA film up to the imide content of *ca.* 40%, and then decreased. This behavior can be attributed mainly to the variation of the Langmuir sorption capacity term (C_H'). In other words, it can be regarded that an unrelaxed volume and/or a microvoid fraction $[(V_g - V_l)/V_g]$ vary with imidization, which are functions of T_g and difference in the expansion coefficient between liquid and glassy states. C_H' was described by the product $(T_g - 25)$ and ΔC_p , difference of heat capacity between liquid and glassy states used instead of the expansion coefficient. On the other hand, the diffusion coefficient of Henry's law mode (D_D) is enhanced by the decrease of carboxyl group in PAA reducing the diffusion of penetrant with imidization up to *ca.* 40%, and then is depressed by restricted thermal mobility caused by considerably increased rigidity in the polymer chain with imidization. Variation in the diffusion coefficient of Langmuir mode behaved parallelly to D_D .

KEY WORDS Polyamic Acid / Imidization / Dual-Mode Sorption Model /
Partial Immobilization Model / CO₂ Gas Transport / Microvoid /

Glassy polymer films are effective as permselective films since their permeability is relatively high owing to the presence of an unrelaxed volume and/or a microvoid in spite of poor segmental mobility, and mechanical properties of glassy polymer are superior to those of rubbery polymer in mechanical strength and heat-stability, etc. It is important to clarify the transport mechanism of glassy polymer film in order to develop glassy permselective membranes. In particular, it is noteworthy that polyimide [PI] film, which has a higher T_g and more heat-stability, can be used in a gas separation system operated at high temperature.¹⁻⁵

It is known that the PI [poly(4,4'-oxydiphenyl pyromellitimide)] used in this study is synthesized through the condensation of pyromellitic acid dianhydride and 4,4'-diaminodiphenyl ether. The initial condensation product, a polyamic acid (polypyromellitic acid) [PAA] precursor is usually heated to complete the imidization reaction. Earlier studies have been reported on the properties and structure of PI.⁶ It has been also found that the physical properties, T_g , density, etc., of PAA vary by imidization. Various imidized PAA films are interesting and useful to elucidate their sorption and permeation mechanisms because their films have various structures with differ-

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ing T_g . It is expected that the effect of partial imidization might provide favorable transport properties.

In previous studies⁷⁻⁹ we reported the gas sorption and permeation in and through the glassy polymer films which have various thermal histories. The changes in the transport properties of these films can be attributed to the fact that the Langmuir sorption capacity term (C_H') and two diffusion coefficients according to both Henry's law and Langmuir modes depend on the thermal history.

In this study sorption and permeation measurements were performed at 25°C at pressure up to 1000 cmHg, and the influence of imidization in PAA films on CO₂ transport properties was examined by applying the dual-mode sorption^{10,11} and partial immobilization models¹²⁻¹⁴. The relationship between transport properties and imidization is discussed from the viewpoint of the variation of C_H' and primary structure of PAA.

EXPERIMENTAL

Materials

PAA film was supplied kindly by the Nissan Chemical Industries, Ltd. PAA film was cast from the *N*-methylpyrrolidone solution in which pyromellitic acid dianhydride and 4,4'-diaminodiphenyl ether were condensed, and was dried at 100°C for 1 h. It is known that PAA can be intramolecularly cyclized to PI by heating as follows:

PAA films were imidized at vacuum ($<10^{-3}$ mmHg) for various periods, 50, 100, 200, and 400 h, at 150°C after complete drying at vacuum ($<10^{-3}$ mmHg) at room temperature. The thickness of the obtained films ranged from 50 to 70 μm . PI film (the thickness is *ca.* 12.5 μm), which has an imide content of 100%, was supplied kindly by the Kanegafuchi Chemical Industry Co., Ltd. Imide content of various imidized PAA films was characterized by using an infrared spectroscopy (IR) [IR-700, Japan Spectroscopic Co., Ltd.] on the basis of ATR method [ATR-61].

Densities of various imidized PAA films were determined at 25°C by the floating method using a mixed solvent of *n*-hexane and carbon tetrachloride.

Heat capacity and T_g of various imidized PAA films were obtained by using a differential scanning calorimetry (DSC) [SSC 560, Seiko Electronics Co., Ltd.]. Glass transition temperature (T_g) of unimidized PAA and PI films were *ca.* 155°C and 410°C, respectively.

Method

The films sealed with a teflon ring was degassed for 24 h at 10^{-4} mmHg in a permeation apparatus. The permeation measurement is as follows: evacuation of a downstream side of the film up to about 10^{-4} mmHg, introduction of permeant gas to an up-stream side and the monitoring permeated gas pressure in the down-stream side using a MKS-Baratron pressure transducer (227AA). The permeability coefficient was evaluated by a steady gas permeation rate.

Sorption measurement was carried out by using a gravimetric sorption apparatus with electromicrobalance the Cahn-2000 (Cahn Instruments, Inc.). After sufficiently drying the films at about 10^{-4} mmHg, the amount of CO₂ gas sorbed in a film under a certain fixed pressure was corrected by subtracting a buoyancy contribution.

The magnitude of purity of CO₂ used in the

sorption and permeation measurements was of a greater purity than 99.9% and was used without further purification.

RESULTS AND DISCUSSION

Imidization

PAA films were imidized under vacuum for various periods at 150°C. The IR spectrum of PAA film imidized for 200 h at 150°C is illustrated in Figure 1 in contrast to those of unimidized PAA and PI films. The absorbance in the vicinity of 880 cm⁻¹ is assigned to the deformation vibration of isolated C-H attached to a phenyl ring, which is independent of imide content and is regarded as an internal

Figure 1. Infrared absorption spectra of unimidized PAA film (a), PAA film imidized for 200 h at 150°C (b), and PI film (c).

standard to determine imide content. The absorbance in the vicinity of 725 cm⁻¹ was assigned to an out-of-plane carbonyl bending vibration¹⁵ and its intensity increased with imidization of PAA film. A similar spectrum variation was observed for another PAA film. The change in intensity at 725 cm⁻¹ can be used to determine imide content using an internal standard at 880 cm⁻¹. The imide content obtained is shown in Figure 2 as a function of imidization periods at 150°C. The density of various imidized PAA films is also shown in Figure 2.

Sorption Properties

Figure 3 shows the CO₂ sorption isotherms at 25°C of various imidized PAA films. The dashed line in Figure 3 shows the data of as received PI reported previously by us.⁹ The amount of CO₂ sorption increased with imidization up to ca. 40% over the entire pressure range. However, the decrease in CO₂ sorption amount was observed when imide content exceeded ca. 40%. This sorption behavior can be explained by applying the dual-mode sorption model represented by the following equation,^{10,11}

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

where C is the total penetrant concentration, C_D is the penetrant concentration due to

Figure 2. Imide content and density of various imidized PAA films against imidization period at 150°C.

Figure 3. CO₂ sorption isotherms at 25°C of PAA films imidized for various periods at 150°C: a, 0 h; b, 50 h; c, 100 h; d, 200 h; e, 400 h; f, PI film.⁹ The closed circles are experimental data and the solid line corresponds to the calculated curve based on the dual-mode sorption model (eq 1).

Figure 4. Imide content dependence of dual-mode sorption parameter, k_D , b , and C_H' for CO₂ of various imidized PAA and PI⁹ films.

Henry's law contribution, C_H is the concentration of penetrant held in "microvoid" or Langmuir sorption site, k_D is the Henry's law constant, p is the pressure of penetrant at equilibrium, b is the affinity constant of pene-

trant to the Langmuir site, and C_H' is the hole saturation constant in the Langmuir sorption mode. It might be assumed that this sorption behavior is attributed mainly to the variation of Langmuir-mode sorption process. One can evaluate dual-mode sorption parameters in eq 1 by the non-linear least square method using isotherm data. The parameters obtained are shown in Figure 4 as a function of imide content. k_D and b increased slightly with imidization, indicating a slight change in primary structure and affinity to the microvoid of various imidized PAA films. The C_H' increased with imidization up to *ca.* 40%, and then decreased obviously.

In general, Langmuir-mode sorption is interpreted by the sorption of CO₂ gas with a liquid-like volume into an unrelaxed volume and/or a microvoid of glassy polymers. Namely, C_H' is represented by the following equation,¹⁶⁻¹⁸

$$C_H' = 22400 \left(\frac{V_g - V_l}{V_g} \right) \frac{1}{V_{CO_2}} \quad (2)$$

where $(V_g - V_l)/V_g$ is the unrelaxed volume

fraction, the difference between the observed specific volume at the glassy state (V_g) and the volume at super cooled equilibrium liquid state (V_l) to the V_g , and V_{CO_2} is the molar volume of liquid-like CO_2 in the Langmuir sorption site. The unrelaxed volume fraction can be also related to T_g by the following expression,

$$\begin{aligned} (V_g - V_l)/V_g \\ = (\alpha_l - \alpha_g)(T_g - T)/\{1 - \alpha_g(T_g - T)\} \\ \approx (\alpha_l - \alpha_g)(T_g - T) \end{aligned} \quad (3)$$

where α_l and α_g are the thermal expansion coefficients for liquid and glassy states, respectively.

A specific volume of polymer can be discussed parallelly with enthalpy. A difference between heat capacities at liquid and glassy states at T_g ($\Delta C_p = C_{pl} - C_{pg}$) is used instead of $(\alpha_l - \alpha_g)$ as the measure of variation in C_H' . Therefore, the enthalpy difference between glassy and liquid states at T_g ($H_g - H_l$) can be expressed by the following equation corresponding to eq 3,

$$H_g - H_l = \Delta C_p(T_g - T) \quad (4)$$

C_H' of CO_2 gas is related to the T_g of polymer through eq 3 or 4. When the difference in $(\alpha_l - \alpha_g)$ or ΔC_p is assumed to be constant, the larger the difference between T_g and observation temperature, the higher is C_H' according to eq 3 and 4. It has been reported that C_H' of commonly used glassy polymer is approximately proportional to $(T_g - T)$.¹⁶⁻¹⁹ T_g of PAA film studied here increased from *ca.* 155°C of unimidized PAA to *ca.* 410°C of PI with imidization. However C_H' did not increase proportionally, but decrease clearly in spite of the increase of T_g when imide content exceeds *ca.* 40%. This behavior suggests that $(\alpha_l - \alpha_g)$ and/or ΔC_p decrease with imidization, reflecting the rigidity of the polymer chain. It can be considered that the variation in C_H' of various imidized PAA films is caused by both raising of T_g and decrease of $(\alpha_l - \alpha_g)$ and/or ΔC_p .

Heat capacities of PAA of various imide content were measured carefully by DSC on the basis of the heat capacity of sapphire as a standard sample, because the $(\alpha_l - \alpha_g)$ cannot be obtained precisely. The temperature dependence of the heat capacities of PAA films is shown in Figure 5. T_g of each PAA film was observed at the bar point in Figure 5. In the C_p curves of PAA films imidized for 0 and 50 h, an endothermic peak which might be caused by imidization during DSC measurement in the vicinity of T_g was observed. Although ΔC_p has to be determined as the difference of C_p between liquid and glassy states at T_g , ΔC_p of PAA films imidized for 0 and 50 h could not be obtained due to the endothermic peak. ΔC_p of PAA films imidized at 150°C for 100, 200, and 400 h is listed in Table I with their T_g . The

Figure 5. Heat capacity (C_p) of PAA films imidized for various periods: a, 0 h; b, 50 h; c, 100 h; d, 200 h; e, 400 h at 150°C.

Table I. T_g , C_H , ΔC_p of various imidized PAA films

Sample	Imidization period at 150°C h	T_g	C_H	ΔC_p	$\Delta C_p(T_g - 25)$
		°C	cm ³ cm ⁻³	J g ⁻¹ deg ⁻¹	J g ⁻¹
PAA	100	227.1	26.9	0.463	93.6
	200	234.1	24.5	0.408	85.3
	400	244.6	23.5	0.365	80.1

Figure 6. Relationship between C_H and $(T_g - 25)$ (a) and $\Delta C_p(T_g - 25)$ (b) of PAA films imidized for various periods: c, 100 h; d, 200 h; e, 400 h.

values decreased with increase of T_g . Figures 6(a) and (b) show the variation in C_H of three PAA films listed in Table I as a function of $(T_g - 25)$ and $\Delta C_p(T_g - 25)$, respectively. The linear relationship between C_H and $(T_g - 25)$ which is attained for usual glassy polymers could not be obtained, but C_H was proportional to $\Delta C_p(T_g - 25)$. This result supports the prediction mentioned above and suggests that the variation in C_H must depend on both ΔC_p or $(\alpha_1 - \alpha_g)$ and $(T_g - T)$.

Permeation Properties

Figure 7(a) shows the pressure dependence of the CO₂ permeability coefficient at 25°C through various imidized PAA films. The dashed line in Figure 7(a) shows the data of as received PI film previously reported by us.⁹ The decreasing trend of permeability coefficient with pressure, which is characteristic of

gas permeation through glassy polymers, was observed for each PAA film. The permeability coefficient at a fixed pressure increased with imidization up to ca. 40%, and then decreased. The pressure dependence of permeability coefficient can be analyzed by applying the partial immobilization model represented by the following equation,¹²⁻¹⁴

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

which was derived by assuming the individual diffusion coefficient for Henry's law mode and Langmuir mode, D_D and D_H , respectively. Figure 7(b) demonstrates the plots of the permeability coefficient of various imidized PAA films as a function of $(1 + b p)^{-1}$. The agreement between the calculated line according to eq 5 and experimental data is excellent as seen for other glassy polymers which obey the partial immobilization model. The intercepts of these lines on the high- and low-pressure sides ($p = \infty$ and $p = 0$) correspond to the values of $k_D D_D$ and $k_D D_D + D_H C_H' b$ in eq 5, respectively. Once one knows the dual-mode sorption parameters, the two diffusion coefficients, D_D and D_H , can be determined from the slope and the intercept in the high pressure range in Figure 7(b) by the non-linear least square method.

D_D and D_H are shown in Figure 8 as a function of imide content. D_D increased gradually up to an imide content of ca. 40%, and then decreased. It might be considered that carboxyl groups in PAA may hinder the diffusion of CO₂ molecules.²⁰ The increase in D_D

Figure 7. (a) Pressure dependence of permeability coefficients at 25°C, and (b) permeability coefficients plotted in accordance with the partial immobilization model (eq 5) for CO_2 of PAA films imidized for various periods at 150°C: a, 0 h; b, 50 h; c, 100 h; d, 200 h; e, 400 h; f, PI film.⁹

Figure 8. Imide content dependence of diffusion coefficients of Henry- and Langmuir-modes and its ratio $F (=D_H/D_D)$ for CO_2 of various imidized PAA and PI⁹ films.

can be attributed to the fact that the reduction of the number of carboxyl groups during imidization accelerated the CO_2 diffusivity, overcoming the depression of CO_2 diffusivity due to enhanced rigidity subject to initial imidization. It is assumed that D_D decreased

by an overwhelming depression of CO_2 diffusivity in spite of much reduction of carboxyl groups when the imide content exceeded *ca.* 40%. On the other hand, D_H also behaved in a similar manner to D_D . It can be assumed that the diffusivity of CO_2 molecules sorbed by the Langmuir mode might be accelerated by increase in C_H' up to an imide content of *ca.* 40%, and then might decrease reflecting reduction of C_H' . This means that CO_2 molecules diffuse more easily with increase in C_H' which indicates increase in the size and/or number of microvoids. The decrease in D_H above *ca.* 40% was more marked. This might be attributed to the fact the rigidity of the polymer chain caused by imidization also depressed the diffusivity of CO_2 molecules sorbed by Langmuir mode. As a result, the two diffusion coefficients of PAA film having imide content of *ca.* 40% might be higher.

The ratio between two diffusion coefficients [$F = D_H/D_D$] is also shown in Figure 8. The decrease in F with imidization suggests that the CO_2 molecules sorbed by Langmuir mode are

immobilized considerably by enhancement of the rigidity in the polymer chain.

In conclusion, the amount of CO₂ sorption and CO₂ permeability coefficient increased with imidization in PAA films up to an imide content of *ca.* 40%, and then decreased. This behavior can be attributed mainly to variation in C_H' . The variation in C_H' was represented adequately by a function of $\Delta C_p (T_g - 25)$.

On the other hand, D_D is accelerated by decrease in carboxyl groups in PAA with imidization up to *ca.* 40%, and then decreases by depressed molecular motion caused by the increase in the rigidity in the main chain with imidization in spite of the decrease in carboxyl groups. The variation in D_H is related to change in C_H' and rigidity of the segment. Further studies on the gas separation using various imidized PAA films with different microvoids will be carried out.

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