Sorption and transport of carbon dioxide in a polyimide from 3,3′,4,4′-biphenyltetracarboxylic dianhydride and dimethyl-3,7-diaminodibenzothiophene-5,5′-dioxide

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Polyimide prepared from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and dimethyl-3,7-diaminodibenzothiophene-5,5′-dioxide (DDBT) displayed CO_2 plasticization effects on sorption and transport of CO_2, in spite of its very rigid polymer backbone. Slow components of solubility and permeability coefficients (S and P) were observed which were attributed to the relaxation of the polymer chain caused by dissolved CO_2 at a higher pressure. Increasing P with increasing feed pressure was represented by the extended dual-mode transport model taking into account the concentration dependence of the diffusion coefficient.

(Keywords: sorption; permeability; diffusion; CO_2 plasticization; polyimide; membrane)

INTRODUCTION

Aromatic polyimides with excellent physical and chemical stability have attracted much attention for their potential use in gas separation at high temperatures[1–9]. The polyimides based on 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) have the advantage of excellent processability in forming asymmetric membranes because of their good solubility in *p*-chlorophenol[3–5]. In a previous paper[6], we investigated the effect of molecular structure of BPDA-based polyimides on gas permeability and permselectivity, and found that a polyimide prepared from BPDA and dimethyl-3,7-diaminodibenzothiophene-5,5′-dioxide (DDBT), of which the molecular structure is shown in *Figure 1*, displayed excellent permeability to H_2 and CO_2 and excellent permselectivity to H_2 and CO_2 over CH_4.

In this study, sorption and transport of CO_2 in BPDA–DDBT polyimide are investigated at upstream pressures up to 28 atm* and temperatures of 35, 50 and 80°C. The effects of CO_2 conditioning and CO_2 plasticization of BPDA–DDBT polyimide films on the sorption and transport of CO_2 are investigated. The results are compared with those previously reported for other BPDA-based polyimides[7,8].

EXPERIMENTAL

BPDA–DDBT polyimide was prepared by condensation of BPDA with DDBT in a *p*-chlorophenol solution according to a procedure described elsewhere[7]. The DDBT sample used was a mixture of isomers having two methyl groups bonded at different positions of the aromatic ring, namely 63% at 2,8-, 33% at 2,6- and 4% at 4,6-positions. The films were cast from a *p*-chlorophenol solution of the polyimide onto glass plates. They were finally dried at 170°C for 20 h in a vacuum. Films 10–15 μm thick were used. CO_2 conditioning was carried out by exposing the as-cast films to CO_2 gas uniformly in a high pressure chamber at 25 or 35 atm and 80°C for 20 or 40 h and then degassing them at 80°C for 40 h.

The films were characterized by methods described

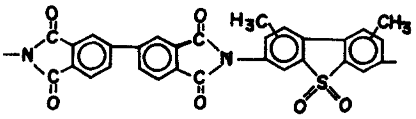

Figure 1 Chemical structure of BPDA–DDBT polyimide. Two methyl groups are bonded at different positions of the aromatic ring: 63% at 2,8-, 33% at 2,6- and 4% at 4,6-positions

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* 1 atm ≈ 0.1 MPa

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Table 1 Characterization of BPDA-based polyimide films[a]

Polyimide	T_g (°C)	d ($g\ cm^{-3}$)	δ^b ($(J\ cm^{-3})^{1/2}$)	V_f^c
BPDA-DDBT	>490	1.372	34.1	0.125
BPDA-DDS	350	1.410	32.7	0.118
BPDA-ODA	270	1.366	32.3	0.121

[a] For as-cast film
[b] Solubility parameter[10]
[c] Free-volume fraction[11]

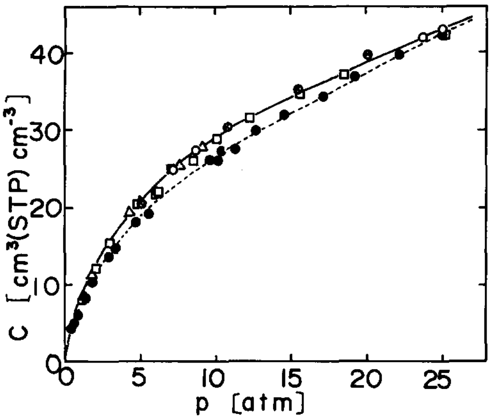

Figure 2 Effect of CO_2 conditioning on sorption isotherms of CO_2 in BPDA–DDBT polyimide films. Data were measured at equilibrium. As-cast films: ●. Films CO_2 conditioned at 25 atm and 80°C for 40 h: ○, first series; □, second series immediately after first series; △, third series after standing the samples in a vacuum at 80°C for 10 days after the second series; ⊗, fourth series after reconditioning at 35 atm of CO_2 and 80°C for 40 h after the third series

elsewhere[2]. The apparatus and procedures for CO_2 sorption and transport experiments have also been described elsewhere[2,9]. Unless otherwise noted, the permeation measurements were made over a period several times the diffusion time lag after introducing feed CO_2 and then the permeation cell with the sample film was evacuated for a period at least 20 times the diffusion time lag before the subsequent experiment. The sorption measurements were made until complete equilibrium was attained, and the sorption cell with the sample films was evacuated for a longer period than that required for attainment of sorption equilibrium before the subsequent experiment. The permeation and sorption experiments were carried out in order of increasing experimental pressure. In the cases noted later, permeation measurements were made over prolonged periods until completely steady-state permeation rates were attained.

RESULTS AND DISCUSSION

Characterization of BPDA-DDBT polyimide film

The properties of BPDA–DDBT polyimide are listed in *Table 1* together with those of BPDA–4,4′-oxydianiline (ODA) and BPDA–4,4′-diphenyldiaminosulphone (DDS) polyimides[7,8] for comparison. These polyimide films were amorphous. As can be expected from the molecular structure and the extremely high glass transition temperature (T_g), >490°C, BPDA–DDBT polyimide has the most rigid polymer backbone of these polyimides. This polymer is a kind of copolymer of three types of diamines differing in the substitution position of two methyl groups. Both the very rigid polymer backbone and bulky and irregularly bonded methyl side-groups may prevent efficient chain packing. The density of this polymer is lower than that of BPDA–DDS polyimide having a sulphonyl group per base unit of the polymer.

CO_2 conditioning effect on sorption and transport

Figure 2 shows the effect of CO_2 conditioning on sorption isotherms of CO_2 in BPDA–DDBT polyimide films at 80°C. CO_2 conditioning at 25 atm increased sorption by as much as 10% at 10 atm. Reconditioning at a higher pressure of CO_2 (35 atm) did not cause further appreciable increase in sorption. A tendency was observed that the sorption amounts would return to the original level after 6 months or more. The sorption data represented by open symbols are on the single sorption isotherm, indicating that the sorption isotherm for CO_2-conditioned films is reproducible within the experimental time scale.

Figure 3 shows the effect of CO_2 conditioning on the permeability coefficient P of CO_2 through a BPDA–DDBT polyimide film at 80°C. CO_2 conditioning at 35 atm and 80°C for 20 h increased the permeability coefficients by as much as 15% just after the CO_2 conditioning. Prolonging the CO_2 conditioning period from 20 to 40 h did not cause a further appreciable increase in permeability coefficient. *Figure 4* shows variations in the permeability coefficient and the effective diffusion coefficient $\bar{D}$, which was calculated as $\bar{D} = P/(C/10)$, at 80°C and 10 atm with the lapse of time after CO_2 conditioning. The permeability coefficient gradually decreased with time elapsed after CO_2 conditioning, finally levelled off at a value ≈20% smaller than the original value. The effective diffusion coefficient increased by about 5% just after CO_2 conditioning, then gradually decreased and finally levelled off at a value ≈25% smaller than the original.

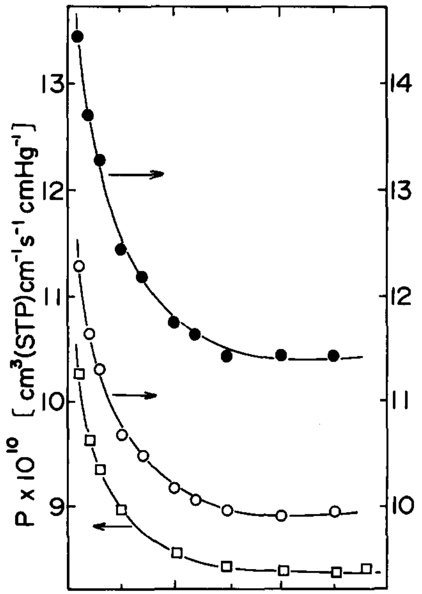

Figure 3 Effect of CO_2 conditioning on permeability coefficient of CO_2 through a BPDA–DDBT film at 80°C. ○, as-cast; ●, 7 days after CO_2 conditioning at 35 atm and 80°C for 20 h; □, 3 months after CO_2 conditioning

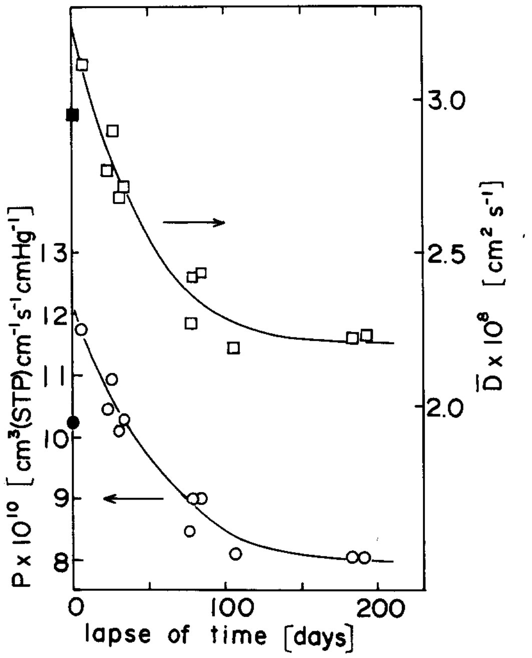

Figure 4 Variations in permeability and effective diffusion coefficients of CO_2 through a BPDA–DDBT polyimide film at 10 atm and 80°C with the lapse of time after CO_2 conditioning

The new stable state for the permeability and effective diffusion coefficients was attained after 3 months or more. Such gradual changes in P and $\bar{D}$ were not observed for the as-cast films which were kept in a desiccator without exposure to high pressure CO_2. Note that the CO_2 conditioning effects mentioned above are not observed for BPDA–ODA and BPDA–DDS polyimides[7,8].

It has been reported for polycarbonates based on bisphenol-A (PC)[12] and chloral bisphenol (BCPC)[13] that CO_2 conditioning increases both the solubility coefficients and the diffusion time-lags and decreases the permeability coefficients. On the other hand, it has been reported for poly(methyl methacrylate) (PMMA) and its related polymer that CO_2 conditioning decreases the diffusion time-lags and increases the permeability coefficients[13]. The present results are different from both cases. A response similar to the latter was observed just after CO_2 conditioning, whereas a response similar to the former was observed for the newly attained stable state. It is likely that sorbed CO_2 plasticized the polymer chain of BPDA–DDBT polyimide in a less efficient packing state to trigger off its rearrangement into a slightly denser structure for transport of CO_2.

The experimental results mentioned below were obtained for the newly attained stable state of films CO_2 conditioned at 25 atm and 80°C for 40 h for sorption or at 35 atm and 80°C for 20 h for permeation.

Effect of relaxation on sorption and transport

Figures 5 and *6* show variations in permeability coefficient and sorption amount, respectively, of CO_2 in BPDA–DDBT polyimide films with time t after CO_2 introduction. The equilibrium sorption and steady-state permeation should be achieved within 30 min, judging from the diffusion time-lag (<0.5 min for a film 13 μm thick at 80°C). However, this is the case only for pressures <3 atm. At higher pressures, the approach to equilibrium or steady state was extremely protracted, as shown in *Figures 5* and *6*. Sorption and permeation are considered to have two components. One is the normal, major, component achieved within several times the diffusion time-lag. The other is the slow, minor, component achieved over an extremely long time scale, the relative importance of which increases with increasing feed pressure. This behaviour was observed reproducibly, provided that the films stood in a vacuum as long as the time required to reach equilibrium or steady state before the subsequent measurement.

Sanders has reported similar behaviour for CO_2 sorption kinetics in polyethersulphone and attributed the slow component to the CO_2-induced relaxation process[14]. It is likely that BPDA–DDBT polyimide was plasticized by dissolved CO_2 and relaxed to a new organizational state, in spite of the very rigid polymer backbone. This is strongly supported by the presence of the CO_2 conditioning effect mentioned above and of the concentration dependence of the diffusion coefficient to be mentioned below.

In the following sections, the sorption amount (C_{60}) and permeability coefficient ($P_{6\theta}$) measured at 60 min and several times the diffusion time-lag after CO_2 introduction, respectively, were used to investigate the sorption and transport properties in the unrelaxed state. The data (C_∞ and P_∞) measured at equilibrium or steady state were used to investigate the properties in the relaxed state.

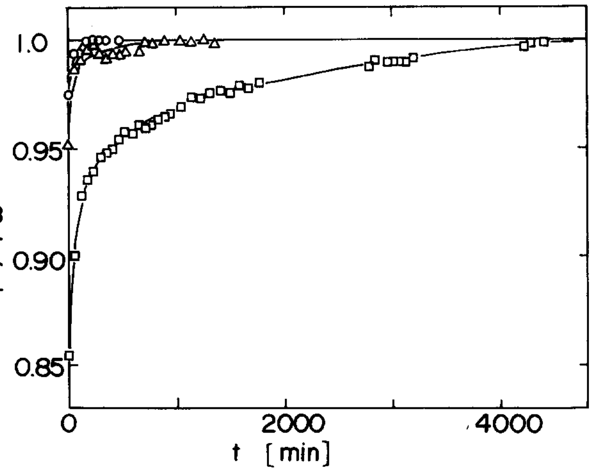

Figure 5 Variation in permeability coefficient of CO_2 through a BPDA–DDBT polyimide film with time elapsed after introduction of upstream CO_2 at 80°C: ○, 2.0 atm; △, 10.0 atm; □, 25.0 atm

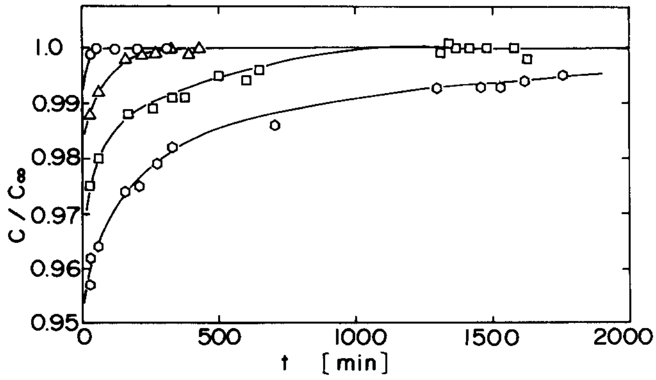

Figure 6 Variation in sorption amount of CO_2 in BPDA–DDBT polyimide films with time after introduction of CO_2 at 80°C: ○, 1.8 atm; △, 4.8 atm; □, 12.4 atm; ○, 25.0 atm

Sorption and transport properties in the unrelaxed state

Figures 7 and *8* show the sorption isotherms and the pressure dependence of the permeability coefficient of CO_2. Sorption and transport of gases in glassy polymers have been well described by the dual-mode sorption and mobility model[15]:

$$C = k_D p + C'_H bp/(1+bp) \qquad (1)$$

$$P = k_D D_D + C'_H b D_H/(1+bp) \qquad (2)$$

where k_D is Henry's law solubility constant, b is the Langmuir affinity constant, C'_H is the Langmuir capacity constant, D_D and D_H are the diffusion coefficients of the penetrant in Henry's law population and in Langmuir population, respectively, and p is the equilibrium pressure for equation (1) and the upstream pressure for equation (2). The sorption data shown in *Figure 7* were analysed by equation (1) using a nonlinear least-squares regression technique, and the sorption parameters thus obtained are listed in *Table 2*. The solid lines shown in *Figure 7* were calculated from equation (1) using the values of parameters given in *Table 2* and are in good agreement with the experimental data.

As can be seen in *Figure 8*, with increasing upstream pressure, the permeability coefficient of CO_2 decreased at lower pressures and levelled off or increased at higher pressures. The dotted lines were calculated from equation (2) using the values of sorption parameters in *Table 2* with appropriate values of D_D and D_H. The permeability coefficient at higher pressures deviated from the dotted lines more at lower temperatures. This behaviour is probably due to CO_2 plasticization of the polymer chain. Stern *et al.* extended the dual-mode mobility model to the case where the diffusion coefficient is given by an exponential function of concentration[16]. According to this model, the pressure dependence of the permeability coefficient is given by the following equation:

$$P = \{D(0)/(\beta p)\}\langle \exp[\beta k_D p\{1 + FK/(1+bp)\}] - 1\rangle \qquad (3)$$

where $D(0)$ is the diffusion coefficient at zero concentration in the matrix, F is the fraction of Langmuir sorption species having a finite mobility, β is an empirical parameter representing the extent of the concentration dependence of the diffusion coefficient, and $K = C'_H b/k_D$. The data shown in *Figure 8* were analysed by equation (3) using a nonlinear least-squares regression technique with the values of sorption parameters in *Table 2*. The transport parameters thus obtained are listed in *Table 3*. The solid lines shown in *Figure 8* were calculated from equation (3) and are in good agreement with the experimental data, indicating that the pressure dependence of the permeability coefficient was satisfactorily described by the extended dual-mode mobility model. Note that an increase in permeability coefficient with increasing feed pressure is not observed for BPDA–DDS and BPDA–ODA polyimides[7,8].

Increasing permeability of CO_2 with increasing feed

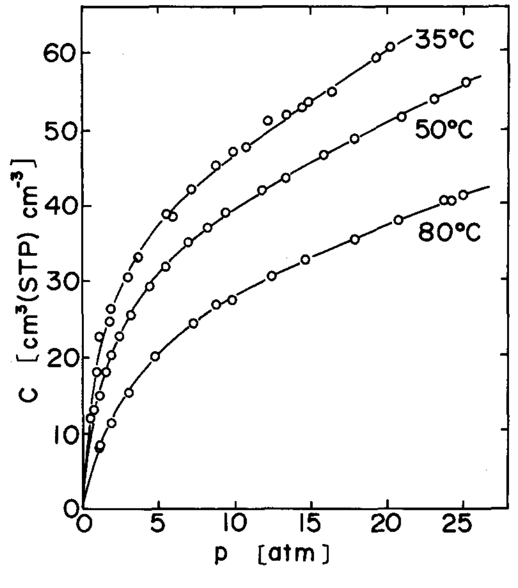

Figure 7 Sorption isotherms of CO_2 (C_{60}) in BPDA–DDBT polyimide films. The solid lines were calculated from equation (1)

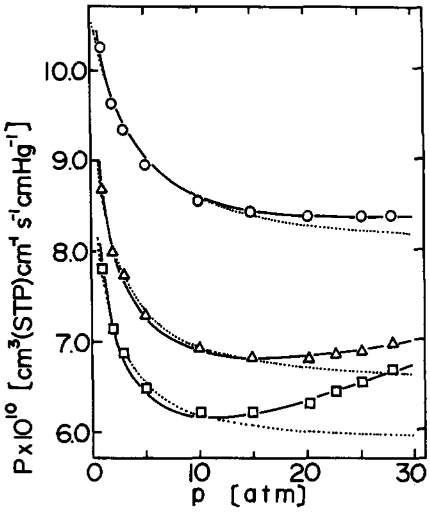

Figure 8 Pressure dependence of permeability coefficient of CO_2 ($P_{6\theta}$) through a BPDA–DDBT polyimide film. The dotted and solid lines were calculated from equations (2) and (3), respectively

Table 2 Sorption parameters of CO_2 in BPDA–DDBT polyimide film[a]

Temp. (°C)		C^b (cm³ (s.t.p.) cm⁻³)	k_D (cm³ (s.t.p.) cm⁻³ atm⁻¹)	C'_H (cm³ (s.t.p.) cm⁻³)	b (atm⁻¹)	$C'_H b/k_D$
80	C_{60}	37.5	0.646	28.5	0.311	13.7
	C_∞	38.7	0.673	29.6	0.288	12.7
50	C_{60}	50.9	0.906	35.6	0.585	23.0
	C_∞	52.3	0.993	35.1	0.603	21.3
35	C_{60}	60.2	1.17	39.0	0.847	28.2
	C_∞	62.5	1.30	38.8	0.807	24.2

[a] C_{60} is at 60 min and C_∞ is in the equilibrium state
[b] At 20 atm

pressure has been reported for some glassy polymers such as PMMA, its related polymers[13] and cellulose acetate (CA)[17]. Sanders has reported that polyethersulphone is highly plasticized by dissolved CO_2 but that the permeability coefficient of the polymer to CO_2 decreases with increasing feed pressure[14]. Plasticization of the polymer matrix alone is not a sufficient condition for the permeability to increase with feed pressure. Sanders has proposed the necessity of large sidegroups on the polymer backbone controlling the diffusivity of penetrants. Plasticization of the polymer by CO_2 is likely to facilitate the motion of large sidegroups, resulting in large concentration dependence of the diffusion coefficient in comparison with the straight-chain polymers. For the polymers mentioned above, the motions of methyl ester and acetyl groups at temperatures of −45 and 51°C, respectively, are considered to be responsible for the plasticization of permeation properties. In the present case, motion of methyl groups on the rigid polymer backbone is considered to be responsible. This is different from the case of poly(2,6-dimethylphenylene oxide) (PPO), where methyl groups are considered to be too small to cause the permeability to increase with increasing pressure. This difference may arise from a difference in the rigidity of the polymer backbone between those two polymers.

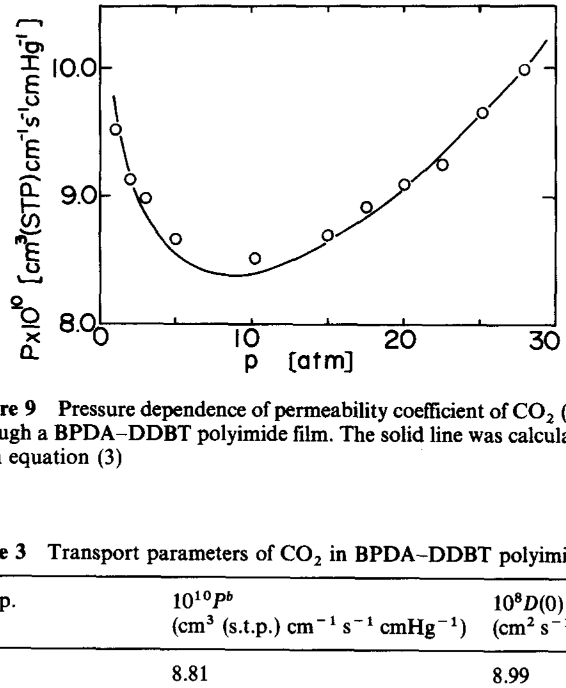

Figure 9 Pressure dependence of permeability coefficient of CO_2 (P_∞) through a BPDA–DDBT polyimide film. The solid line was calculated from equation (3)

Sorption and transport properties in the relaxed state

The sorption isotherms at equilibrium are well described by equation (1) in a similar manner to those at unrelaxed state. The sorption parameters at equilibrium are listed in *Table 2*. As can be seen from *Table 2*, the increase in sorption accompanying the CO_2-induced relaxation process was primarily due to the increase in k_D. The relaxation to a new organizational state hardly changed the amount of microvoids.

Figure 9 shows the pressure dependence of the permeability coefficient in the relaxed state and at 80°C. With increasing feed pressure, the permeability coefficient decreased and then increased at pressures >10 atm. The data shown in *Figure 9* were analysed by equation (3) using a nonlinear least-squares regression technique with the values of sorption parameters at equilibrium given in *Table 2*. The transport parameters were determined as $D(0)=6.6\times10^{-8}\,cm^2\,s^{-1}$, $F=0.063$, $\beta=0.041\,cm^3\,cm^{-3}$ (s.t.p.) at 80°C. The solid line shown in *Figure 9* was calculated from equation (3) and is in good agreement with the experimental data.

The β value is eight times the corresponding β value for the unrelaxed state and is of the same order as that reported for permeation of acetone vapour through CA[18]. This indicates that relaxation caused rearrangement of the local packing of the polymer to an extent that allowed easier passage of penetrants.

Comparison of sorption and transport properties between BPDA–DDBT and other BPDA-based polyimides

To investigate the influence of molecular structure on CO_2 sorption and transport properties, the properties of BPDA–DDBT polyimide are compared with those previously reported for other BPDA-based polyimides[7,8] in *Tables 4* and *5*. For BPDA–DDBT polyimide, transport parameters obtained from equation (2) are used for comparison in *Table 5* in order to neglect the CO_2 plasticization effect on the diffusion coefficient.

Comparison between BPDA–ODA and BPDA–DDS indicates that introduction of a sulphonyl group with

Table 3 Transport parameters of CO_2 in BPDA–DDBT polyimide film[a]

Temp. (°C)	$10^{10}P^b$ (cm^3 (s.t.p.) cm^{-1} s^{-1} cmHg^{-1})	$10^8D(0)$ (cm^2 s^{-1})	F	$10^3\beta$ (cm^3 cm^{-3} (s.t.p.))
80	8.81	8.99	0.031	4.9
50	6.81	5.03	0.031	7.8
35	6.28	3.39	0.033	11.5

[a] The values of the parameters are for unrelaxed state
[b] At 20 atm

Table 4 Sorption parameters and enthalpies of CO_2 in polyimide films[a]

Polyimide	C^b (cm^3 (s.t.p.) cm^{-3})	k_D (cm^3 (s.t.p.) cm^{-3} atm^{-1})	C'_H (cm^3 (s.t.p.) cm^{-3})	b (atm^{-1})	C'_Hb/k_D	ΔH_D (kJ mol^{-1})	ΔH_b (kJ mol^{-1})	$\Delta H_{C=O}{}^c$ (kJ mol^{-1})
BPDA–DDBT	37.5	0.646	28.5	0.311	13.7	−11.9	−20	−26
BPDA–DDS	29.7	0.647	19.8	0.279	8.5	−15.3	−22	−30
BPDA–ODA	17.7	0.449	10.6	0.236	5.6	−10.7	−18	−30

[a] The parameters are at 80°C. The parameters for BPDA–DDBT polyimide are for C_{60}
[b] At 20 atm
[c] Determined van't Hoff plots of $k(=C'_Hb+k_D)$

Table 5 Transport parameters and activation energies of CO_2 through polyimide films[a]

Polyimide	$10^{10}P^b$ (cm^3 (s.t.p.) cm^{-1} s^{-1} cmHg^{-1})	$10^9\bar{D}^b$ (cm^2 s^{-1})	$10^9 D_D$ (cm^2 s^{-1})	$10^9 D_H$ (cm^2 s^{-1})	D_H/D_D	ΔE_P (kJ mol^{-1})	$\Delta E_{\bar{D}}$ (kJ mol^{-1})	ΔE_{D_D} (kJ mol^{-1})	ΔE_{D_H} (kJ mol^{-1})
BPDA–DDBT	8.81	35.7	89.8	2.81	0.031	6.9	16.5	19.5	19
BPDA–DDS	4.51	23.1	45.9#	3.0#	0.065#	12.7	26.7	27.4#	30#
BPDA–DDS	1.22	10.5	17.8#	1.7#	0.096#	18.5	33.4	29.8#	26#

[a] The parameters are at 80°C
[b] At 20 atm
Fugacity-based quantities

greater affinity to CO_2 and stiffer than the ether group resulted in increases in k_D, b and C'_H. Changing the diamine from DDS to DDBT resulted in 1.3, 1.5 and 2.0 fold increases in C, $\bar{D}$ and P, respectively. The increase in C was mainly attributed to the increase in C'_H owing to extremely high T_g. Both k_D and b hardly changed. The ratio of Langmuir component to Henry's law component in the sorption increased considerably. BPDA–DDBT polyimide seems to have a more open structure for diffusion of CO_2 molecules than BPDA–DDS polyimide, judging from both the higher diffusion coefficient and the lower activation energy for diffusion. The presence of bulky methyl side-groups irregularly bonded to the highly rigid polymer backbone is considered to be the origin of less efficient packing of the polymer chain in BPDA–DDBT polyimide. This is also considered to be responsible for the effects of CO_2 conditioning and CO_2 plasticization on the sorption and permeation properties.

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