

Gas permeation properties of thianthrene-5,5,10,10-tetraoxide-containing polyimides

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Abstract

A series of thianthrene-5,5,10,10-tetraoxide-containing polyimides with great chain stiffness were prepared and their gas permeation properties were investigated. TADATO/DSDA(1/1)–DDBT copolyimide, which was prepared from thianthrene-2,3,7,8-tetracarboxylic dianhydride-5,5,10,10-tetraoxide (TADATO), 3,3',4,4'-diphenylsulfonyltetracarboxylic dianhydride (DSDA) and 3,7-diamino-2,8(6)-dimethylbenzothiophene sulfone (DDBT), displayed much higher CO₂ permeability coefficient (P_{CO_2}) than both DSDA–DDBT and TADATO–DDBT homopolyimides, but their ideal selectivity ($P_{\text{CO}_2}/P_{\text{N}_2}$) were similar. The higher CO₂ permeability coefficient of TADATO/DSDA(1/1)–DDBT was attributed to the higher diffusion coefficient as well as a little higher solubility coefficient. The separation performance of TADATO/DSDA(1/1)–DDBT toward CO₂/N₂ fell above the “upper bound” line, indicating the highest separation performance among the glassy polymer membranes developed so far. Furthermore, this polyimide showed a significantly higher selectivity of CO₂ over N₂ for mixed gas permeation than for single gas permeation (single gas: $P_{\text{CO}_2}/P_{\text{N}_2} = 35$, mixed gases: $P_{\text{CO}_2}/P_{\text{N}_2} = 49$, at 35°C and 2 atm). The “dual-mode” model was used to describe gas sorption and transport behaviors in the membrane. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Thianthrene-5,5,10,10-tetraoxide; Polyimide; Gas separation

1. Introduction

Polyimides, known for their excellent thermal and mechanical properties, have been extensively studied for gas separation applications in the past two decades [1–14]. Many studies have been devoted to the investigation of the relationship between chemical structure and gas permeation property of polyimides in order to develop membranes with both high permeability and high selectivity. It has been reported that polyimides having great chain stiffness, weak interchain interactions and loose chain packing tend to show high gas permeability due to large fractional free volume [1–5,7,9–11]. To achieve great chain stiffness both dianhydride and diamine residues of a polyimide are required to contain no flexible linkages. In addition, it is also very important to inhibit the rotation of imido rings around diamine residues (or C–N bond) and this can be achieved by introducing substituted groups such as methyl and isopropyl to the *ortho* positions of amino groups in diamine residues. Polymer chain packing is dependent on both chain stiffness and interchain interactions. Great chain

stiffness and weak interchain interactions result in loose packing of polymer chains. The interchain interaction is related to polar groups such as sulfonyl, carbonyl and hydroxyl in polymer structure besides the carbonyl groups of imido rings. Sulfonyl and carbonyl are electron-withdrawing groups. High density of these electron-withdrawing groups tends to yield strong interchain interactions due to dipole–dipole electrostatic attraction and inductive effect. In addition, the inter- and intra-segmental charge transfer (CT) between alternating dianhydride (electron acceptor) and diamine (electron donor) residues in planar polyimides are also responsible for the interchain interactions [15,16].

On the other hand, polyimides satisfying the above structural criteria (i.e. great chain stiffness, weak interchain interactions and loose chain packing) generally show rather poor selectivity. As shown in Table 1, polyimide derived from 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) and 2,4,6-trimethyl-1,3-phenylenediamine (TrMPD) shows an unusually high CO₂ permeation coefficient ($P_{\text{CO}_2} = 4.3 \times 10^{-8} \text{ cm}^3 \text{ (STP) cm}^{-1} \text{ s}^{-1} \text{ cmHg}^{-1}$) but a rather low ideal selectivity ($P_{\text{CO}_2}/P_{\text{CH}_4} = 16.6$) at 35°C and 10 atm [10]. The backbone chain of the polyimide is highly stiffened due to the bulky $-\text{C}(\text{CF}_3)_2-$ groups in 6FDA residues as well as the methyl groups in the *ortho*

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Table 1

A comparison of gas permeability coefficients and ideal selectivities of some polyimides (P is in barrer, 1 barrer = 10^{-10} cm³(STP) cm⁻¹ s⁻¹ cmHg⁻¹)

Polyimide	$[-SO_2-]^a$	P_{CO_2}	P_{CH_4}	P_{CO_2}/P_{CH_4}	Ref.
6FDA-TrMPD	0	431	26.0	16.6	[10]
BPDA-TrMPD	0	137	8.08	17.0	[10]
6FDA-DDBT	1	91	2.51	36	[9]
DSDA-DDBT	2	13.7	0.258	53	[9]

^a Number of sulfonyl groups per repeat unit.

positions of amino groups in diamine residues. Since the polyimide has no electron-withdrawing groups except carbonyl in imido rings and no CT complexes are formed due to the non-coplanar structure (the phenyl ring of TrMPD is almost perpendicular to the imido ring), the interchain interactions are very weak, leading to very loose interchain packing. Changing the diamine moiety from TrMPD to 3,7-diamino-2,8(6)-dimethyldibenzothiophene sulfone (DDBT) leads to an increase in interchain interactions due to the introduction of sulfonyl groups of DDBT to the polymer structure, but the highly stiffened backbone chain feature is almost remained. DDBT contains no flexible linkages, and the large mass decreases local mobility of polymer segments. Furthermore, sulfonyl in DDBT decreases the electron donating ability, and the CT interaction is thus weakened, leading to loose packing of polymer chains.

However, in comparison with 6FDA-TrMPD, 6FDA-DDBT should have larger interchain interactions due to dipole–dipole electrostatic attraction and inductive effect arising from sulfonyl groups. As a result, 6FDA-DDBT shows a reduced but still high P_{CO_2} (91×10^{-10} cm³(STP) cm⁻¹ s⁻¹ cmHg⁻¹) and a significantly increased selectivity ($P_{CO_2}/P_{CH_4} = 36$) at 35°C and 10 atm [9]. On the contrary, the polyimide derived from 3,3',4,4'-diphenylsulfonyl tetracarboxylic dianhydride (DSDA) and DDBT displays rather low P_{CO_2} (13.7×10^{-10} cm³(STP) cm⁻¹ s⁻¹ cmHg⁻¹) but very high selectivity ($P_{CO_2}/P_{CH_4} = 53$) at the same temperature and pressure [9]. The low permeability is due to the significantly reduced chain stiffness arising from the mobile $-SO_2-$ linkages in DSDA residues, while the high selectivity seems to be related to the high sulfonyl density. It is interesting to investigate the permeation properties of polyimides with great chain stiffness and strong interchain interactions. Good separation performance might be obtained if chain stiffness and interchain interactions could be well balanced.

We have previously reported an interesting dianhydride monomer, thianthrene-2,3,7,8-tetracarboxylic dianhydride-5,5,10,10-tetraoxide (TADATO), and the polyimide derived from this monomer and 4,4'-diaminophenyl ether (ODA) displayed high CO₂/N₂ and CO₂/CH₄ separation performance comparable to that of 6FDA-pODA polyimide [17]. TADATO has highly rigid non-coplanar structure and high density of sulfonyl groups. The use of this

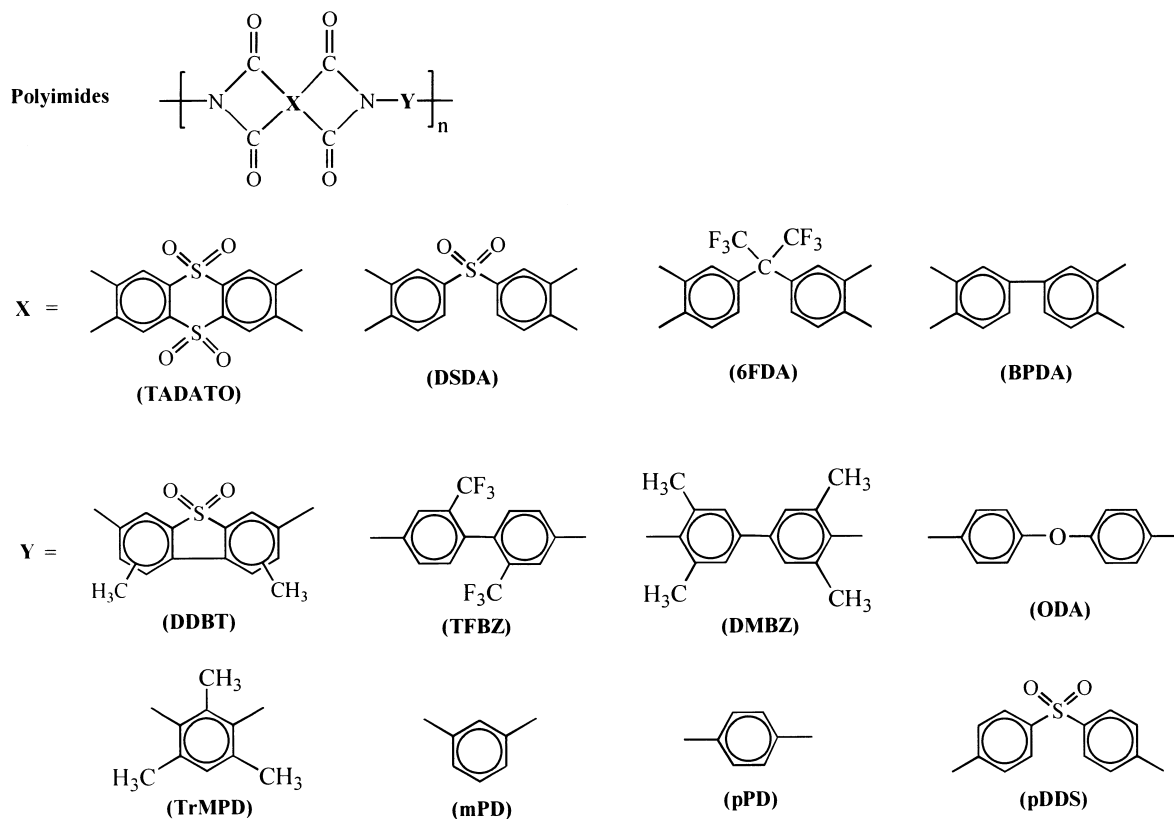


Fig. 1. Chemical structures of polyimides used in this study.

dianhydride as well as “rigid” diamine monomers may give useful information of gas permeation properties of polyimides with great chain stiffness and strong interchain interactions. In this paper, we report on our recent progress on the synthesis and gas permeation properties of a series of TADATO-based polyimides with great chain stiffness and different sulfonyl density. The chemical structures of polyimides used in this study are shown in Fig. 1.

2. Experimental

2.1. Materials

TADATO was prepared according to our previously reported method [17]. DSDA was purchased from Tokyo Kasei Organic Chemicals Co., Ltd., and purified by sublimation before use. 3,3',5,5'-Tetramethylbenzidine (TMBZ) and 2,2'-bis(trifluoromethyl)benzidine (TFBZ) were also purchased from Tokyo Kasei Organic Chemicals Co., Ltd., and used without further purification. DDBT is a mixture of isomers having its two methyl groups bonded at different positions of the aromatic rings, namely 63% at 2,8-, 33% at 2,6-, and 4% at 4,6-positions. It was supplied from Ube Industries Ltd. and was used as received. *N*-Methyl pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure and dehydrated with 4 Å molecular sieves.

2.2. Polymerization

2.2.1. TADATO–DDBT homopolyimide

The polyimide was prepared according to our previously reported method [18]. The acid form of TADATO, thianthrene-2,3,7,8-tetracarboxylic acid-5,5,10,10-tetraoxide (TADATO-4A) and DDBT were polymerized in NMP in the presence of triphenyl phosphite and pyridine to give a polyamic acid precursor followed by chemical imidization to form the final polyimide.

2.2.2. TADATO/DSDA(1/1)–DDBT copolyimide

To a completely dried 100 ml 4-neck flask equipped with a mechanical stirring device were charged 0.709 g (2.58 mmol) DDBT and 7 ml anhydrous NMP under N₂ flow. After DDBT was completely dissolved, 0.500 g (1.19 mmol) TADATO was added in one portion and the reaction mixture was stirred for 2 h to give an amine end-capped oligomer. Then 0.500 g (1.39 mmol) DSDA was added in several portions over 4 h to fulfill the polymerization. The resulting polyamic acid solution was diluted with additional 5 ml NMP followed by thermal imidization in the presence of xylene at 180°C for 5 h. After cooling to room temperature, the solution mixture was poured into methanol, the resulting precipitate was filtered off and dried in vacuo.

2.2.3. TADATO–TMBZ and TADATO–DDBT/TFBZ(1/1) polyimides

TMBZ (0.571 g (2.38 mmol)) was dissolved in 5 ml NMP in a completely dried 100-ml 4-neck flask with magnetic stirring under N₂ flow. 1.020 g (2.42 mmol) TADATO was added portion-wise to the diamine solutions (total solid concentration: ~24 wt%). The solution mixture was stirred at room temperature for 8 h, and then diluted with additional 20 ml NMP. After that, excessive acetic anhydride and triethylamine were added and the reaction mixture was stirred at room temperature for over 20 h. The resulting viscous solution mixture was precipitated from methanol, and the precipitate was filtered off and dried in vacuo.

The above procedure was followed for the preparation of TADATO–DDBT/TFBZ(1/1) polyimide except that DDBT and TFBZ co-monomer were used instead of TMBZ.

2.3. Film formation and characterization

Films were prepared by casting 2–5 wt% of polyimides in DMAc onto glass dishes and dried at 80°C for 6 h. The as-cast films were further dried at 200°C for 20 h in vacuo except for TADATO–DDBT films, which were immersed in benzene (room temperature, one day) and subsequently dried at 130°C for 20 h in vacuo.

Wide angle X-ray diffraction (WAXD) measurements were performed on a Shimadzu XD-D1 diffractometer with CuK_α radiation, $\lambda = 1.54 \text{ \AA}$. Permeability coefficient P was measured by means of the vacuum time-lag method and the ideal selectivity is calculated from the permeability ratio of the gas pair. In the case of mixed gases, separation factor α defined by Eq. (1) is used instead of the ideal selectivity

$$\alpha = [y(1-x)]/[x(1-y)] \quad (1)$$

where x and y are molar fractions of CO₂ in feed and permeate determined by gas chromatography, respectively. Sorption isotherms for CO₂, N₂, and CH₄ were determined up to 30 atm at 35°C using a dual-volume sorption cell equipped with a micro-balance.

3. Results and discussion

3.1. Synthesis and characterization of the polyimides

We have previously reported that the conventional two-step method could not give high molecular weight TADATO–DDBT polyimide, and the cast films were too brittle to be used for gas permeation measurement [17]. In contrast, the Yamazaki–Higashi phosphorylation method was very effective for preparing this polyimide [18], and therefore this method was employed in this study. For other TADATO-based polyimides such as TADATO–DSDA(1/1)–DDBT, TADATO–DDBT/TFBZ(1/1) and TADATO–TMBZ, the conventional 2-step synthetic method was found still effective probably due to the

Table 2
Physical properties of a series of TADATO-based and other related polyimides

Polymer	Density (g/cm ³)	<i>d</i> -Spacing (Å)	<i>V_F</i> (-)	Solubility ^a			Ref.
				DMAc	NMP	CH ₂ Cl ₂	
TADATO–DDBT	1.409	4.7	0.175	+	+	–	^b
TADATO/DSDA(1/1)–DDBT	1.418	4.9	0.152	+	+	–	^b
TADATO–DDBT/TFBZ(1/1)	1.453		0.178	+	+	–	^b
TADATO–TMBZ	1.316		0.168	+	+	–	^b
TADATO–TFBZ	1.521	5.2	0.167	+	+	–	[17]
TADATO–ODA	1.462	4.7	0.147	–	–	–	[17]
DSDA–DDBT	1.401	5.2	0.141	+	+	–	[9]
BPDA–DDBT	1.372		0.125	–	–	–	[9]
6FDA–DDBT	1.421	6.3	0.169	+	+	–	[9]
6FDA–mPD	1.474		0.160	+	+	–	[10]
BPDA–TrMPD	1.241		0.155	–	–	+	[10]
BPDA–ODA	1.366	5.1	0.126	–	–	–	[17]
PMDA–ODA	1.395	4.5	0.135	–	–	–	[17]

^a “+” = soluble; “–” = insoluble.

^b This study.

relatively higher monomer reactivity (DSDA > TADATO; TFBZ and TMBZ > DDBT), and all of these films were tough enough for gas permeation measurements. Since TADATO–DDBT polyimide showed poor thermal stability [18], the as-cast films could not be dried at high temperature (200°C) as performed with other TADATO-based polyimides, instead they were primarily immersed in benzene for one day and then dried at 130°C in vacuo to remove the residual solvents.

All the TADATO-based polyimides except TADATO–ODA were found soluble in dipolar aprotic solvents such as NMP and DMAc indicating good solubility properties of these polyimides. The WAXD curves showed that all the TADATO-based polyimides were amorphous. From the scattering angles (2θ) in the centers of the broad peaks, the *d*-spacing values in these films were calculated in terms of Bragg's equation, $n\lambda = 2d \sin \theta$, and the results are listed in Table 2. TADATO–DDBT showed the same *d*-spacing value as TADATO–ODA despite the fact that the former had much greater chain stiffness than the latter. For TADATO–DDBT, TADATO–DSDA(1/1)–DDBT and DSDA–DDBT, the *d*-spacing values slightly increased in

that order, which was reverse to the order of chain stiffness and sulfonyl density. Furthermore, all the TADATO-based polyimides showed much smaller *d*-spacing values than 6FDA–DDBT. This is likely due to the strong intersegmental interactions in TADATO-based polyimides. Fractional free volume *V_F* was calculated from Eq. (2):

$$V_F = (V_T - V_0)/V_T \quad (2)$$

where *V_T* is the molar volume per repeating unit of polymer at temperature *T*, and *V₀* is the hypothetical volume occupied by the molecules at 0 K per mole of the repeating unit. *V_T* is determined from the polymer film density, and *V₀* is estimated to be 1.3 times the van der Waals volume calculated by Bondi's group contribution method [19,20]. TADATO–DDBT displayed the largest *V_F* due to the highest chain stiffness. The incorporation of relatively less rigid units such as DSDA led to a decrease in *V_F*. The relatively flexible polyimides such as TADATO–ODA and DSDA–DDBT showed much smaller *V_F* values. Therefore, it is easy to understand that the *V_F* values of TADATO–DDBT, TADATO/DSDA(1/1)–DDBT and DSDA–DDBT decreased in that order. However, the *d*-spacing values of

Table 3

Gas permeation properties of TADATO-based polyimides at 2 atm and 35°C (*P* is in barrer, 1 barrer = 10⁻¹⁰ cm³(STP) cm⁻¹ s⁻¹ cmHg⁻¹)

Polyimide	<i>P_{CO₂}</i>	<i>P_{N₂}</i>	<i>P_{CH₄}</i>	<i>P_{H₂}</i>	<i>P_{O₂}</i>	<i>P_{CO₂}/P_{N₂}</i>	<i>P_{CO₂}/P_{CH₄}</i>	<i>P_{O₂}/P_{N₂}</i>	Ref.
TADATO–DDBT	24	0.70	0.59			34	41		^a
TADATO/DSDA(1/1)–DDBT	45	1.27	0.75	86	7.7	35	60	6.1	^a
TADATO–DDBT/TFBZ(1/1)	19	0.69	0.47			29	40		^a
TADATO–TMBZ	39	1.33	1.21	58	6.6	29	32	5.0	^a
TADATO–ODA	9.6	0.27	0.18	19	1.60	36	53	5.9	[17]
DSDA–DDBT ^b	14.5	0.37	0.23		3.29	39	63	6.6	^a
6FDA–DDBT	91	3.71	1.98	156	18.8	24.6	46	5.1	[9]
BPDA–TrMPD	182	7.5	8.0	210	32	24.2	22.8	4.3	[10]

^a This study.

^b 1 atm.

Table 4
Solubility coefficient, diffusion coefficient; solubility selectivity, and diffusivity selectivity of three kinds of polyimides at 35°C and 1 atm

Polyimide	P_{CO_2}	S_{CO_2}	D_{CO_2}	$P_{\text{CO}_2}/P_{\text{N}_2}$	$S_{\text{CO}_2}/S_{\text{N}_2}$	$D_{\text{CO}_2}/D_{\text{N}_2}$	$P_{\text{CO}_2}/P_{\text{CH}_4}$	$S_{\text{CO}_2}/S_{\text{CH}_4}$	$D_{\text{CO}_2}/D_{\text{CH}_4}$
TADATO–DDBT	26	25	1.04	36	21	1.72	43	5.7	7.5
TADATO/DSDA(1/1)–DDBT	50	32	1.60	37	23	1.57	62	6.2	10.0
DSDA–DDBT	14.5	28	0.52	39	22	1.80	–	–	–

these three kinds of polyimides are just in a reverse order as mentioned above although the difference is rather small. This is inconsistent with the fact that polymers having larger d -spacing generally tend to have larger V_F , and it is difficult to give a proper explanation at present. Nevertheless, such a phenomenon has also been observed with some other polyimides. PMDA–ODA, for example, has a small d -spacing but a larger V_F than BPDA–ODA as shown in Table 2. Further studies are needed to clearly elucidate the effects of chemical structure on d -spacing and V_F of these polyimides.

3.2. Gas permeation properties of TADATO-based polyimides

3.2.1. Single gas permeation

Table 3 lists the gas permeation data of a series of

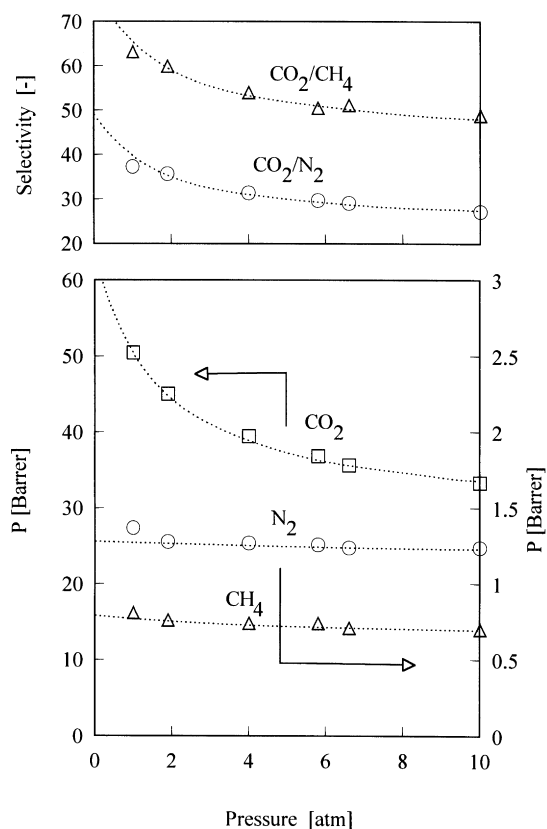


Fig. 2. Gas permeation coefficient and ideal selectivity of TADATO/DSDA(1/1)–DDBT polyimide membrane as a function of upstream pressure at 35°C. The plots are experimental data, and the dotted lines refer to the calculated data from the dual-mode model.

TADATO-based polyimides at 2 atm and 35°C. For comparison purpose, the data of DSDA–DDBT, 6FDA–DDBT and BPDA–TrMPD polyimides are also listed in this table. Gas permeability coefficients of these polyimides are in the order: TADATO–ODA < DSDA–DDBT < TADATO–DDBT/TFBZ(1/1) < TADATO–DDBT < TADATO–TMBZ < TADATO/DSDA(1/1)–DDBT < 6FDA–DDBT < BPDA–TrMPD. According to the differences in chain stiffness and V_F , these polyimides can be classified into two categories. TADATO–ODA and DSDA–DDBT have relatively flexible backbone chains and rather small V_F due to the presence of flexible linkages in backbone chains (–O– in ODA and –SO₂– in DSDA residues), whereas the other polyimides have fairly high chain stiffness and large V_F . Therefore, the former two polyimides showed lower permeability coefficients than the latter six ones. TADATO–TMBZ has similar highly stiffened backbone chains but not so strong interchain interactions as TADATO–DDBT due to the relatively lower sulfonyl density, resulting in higher gas permeability coefficients. The backbone chains of 6FDA–DDBT is also highly stiffened but the interchain interactions are considered to be even weaker than those in TADATO–TMBZ due to the lower sulfonyl density, and therefore it exhibited much higher permeability coefficients than both TADATO–DDBT and TADATO–TMBZ. BPDA–TrMPD has no electron-withdrawing groups except carbonyl in imido rings and thus displayed the highest gas permeability coefficients.

On the other hand, the permselectivity showed roughly an opposite dependence on polymer structure. The highly permeable BPDA–TrMPD displayed the poorest selectivity, while the least permeable TADATO–ODA exhibited fairly high selectivity. This is the well-known trade-off phenomenon as discovered by Robeson [21]. However, a comparison of the gas permeation data of TADATO–ODA and TADATO–DDBT revealed that although the latter had much higher CO₂ permeability coefficient, their CO₂/N₂ selectivities were almost the same. TADATO–DDBT also showed a roughly similar CO₂/N₂ selectivity but higher CO₂ permeability than DSDA–DDBT. It should be noted that the CO₂/CH₄ selectivity of TADATO–DDBT was much smaller than that of TADATO–ODA and DSDA–DDBT. The introduction of TFBZ to the structure of TADATO–DDBT yielded similar V_F , but the separation performance turned even poorer, that is, TADATO–DDBT/TFBZ(1/1) copolyimide showed both lower permeability and lower selectivity than TADATO–DDBT. On the contrary, the incorporation of DSDA to the structure of

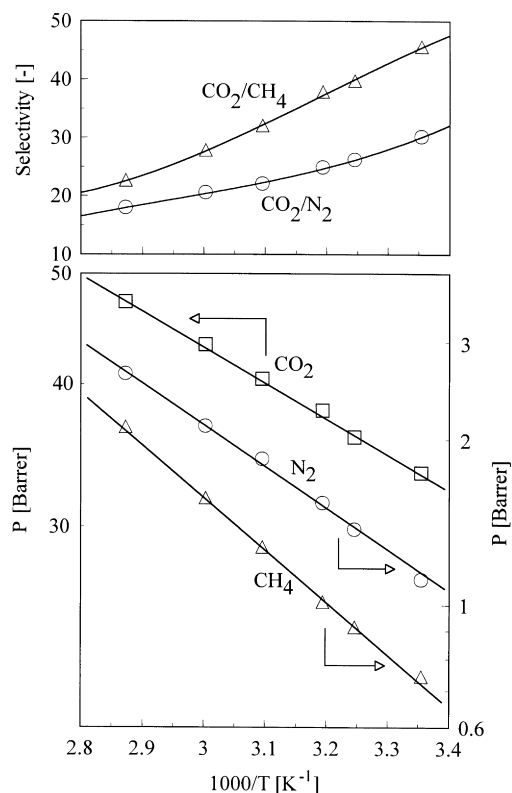


Fig. 3. Gas permeation coefficient and ideal selectivity of TADATO/DSDA(1/1)-DDBT polyimide as a function of temperature at 10 atm.

TADATO-DDBT was found very effective for improving gas separation performance. TADATO/DSDA(1/1)-DDBT copolyimide showed a selectivity similar (CO_2/N_2) or even larger (CO_2/CH_4) but much higher CO_2 permeability coefficient than both TADATO-DDBT and DSDA-DDBT. In fact, it displayed the highest separation performance among the TADATO-based polyimides. This is probably because the chain stiffness and the interchain interactions for this copolyimide were well balanced.

Table 4 lists gas sorption and permeation data of TADATO-DDBT, TADATO/DSDA(1/1)-DDBT and DSDA-DDBT for CO_2/N_2 and CO_2/CH_4 systems at 35°C and 1 atm. The solubility coefficient S was obtained by sorption measurements and the diffusion coefficient D was

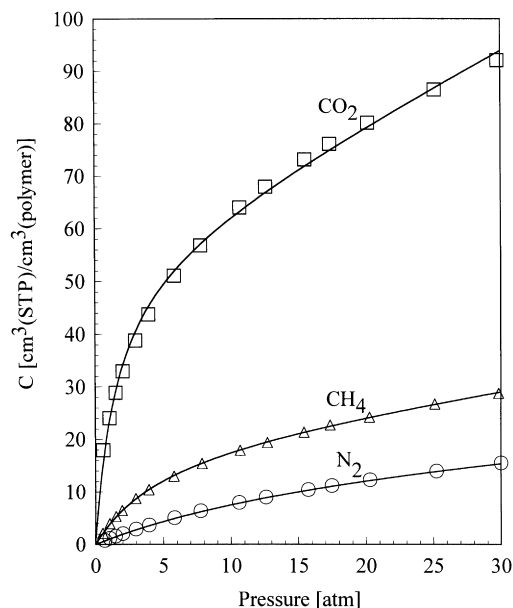


Fig. 4. Sorption isomers of CO_2 , N_2 and CH_4 in TADATO/DSDA(1/1)-DDBT polyimide membrane at 35°C .

calculated from the ratio of P to S ; i.e. $D = P/S$. It can be seen that for TADATO/DSDA(1/1)-DDBT the higher P_{CO_2} is attributed to the larger D_{CO_2} as well as a little larger S_{CO_2} than those of TADATO-DDBT and DSDA-DDBT, while the similar $P_{\text{CO}_2}/P_{\text{N}_2}$ is due to the similar $S_{\text{CO}_2}/S_{\text{N}_2}$ and $D_{\text{CO}_2}/D_{\text{N}_2}$. For TADATO-DDBT, the poor CO_2/CH_4 selectivity is due to the rather low $D_{\text{CO}_2}/D_{\text{CH}_4}$ and $S_{\text{CO}_2}/S_{\text{CH}_4}$.

Gas permeability coefficients and ideal selectivity for TADATO/DSDA(1/1)-DDBT as a function of the upstream pressure and temperature are shown in Figs. 2 and 3, respectively. The CO_2 permeability coefficient initially decreased with an increase in upstream pressure and then the tendency turned less significant, while the permeability coefficients for N_2 and CH_4 were weakly dependent on upstream pressure. As a result, the ideal selectivity of CO_2 over N_2 and CH_4 initially decreased with an increase in upstream pressure and then turned almost constant. On the other hand, with an increase in temperature, N_2 and CH_4 permeability coefficients increased faster than that of CO_2 leading to a

Table 5

Activation energies for permeation and diffusion and enthalpies of sorption for penetrants in some polyimide membranes at 10 atm (E_p , E_D and ΔH_S are in kJ mol^{-1})

Polyimide	E_p			E_D			ΔH_S			Ref.
	CO_2	CH_4	N_2	CO_2	CH_4	N_2	CO_2	CH_4	N_2	
TADATO-DDBT(1/1)-DDBT	6.0	18	15	23	34	34	-17	-15	-19	^a
6FDA-pPD	6.4	22	-	19	35	-	-13	-13	-	[10]
6FAD-TrMPD	-1.7	7.8	-	12	20	-	-14	-13	-	[10]
BPDA-DDBT	6.7	20	-	23	34	-	-16	-14	-	^a
BPDA-pDDS	12	29	-	29	46	-	-17	-17	-	[12]

^a This study.

Table 6

Gas sorption and transport parameters of CO₂, CH₄ and N₂ in polyimide membranes at 35°C (the units of k_D , C'_H , and b are in cm³(STP) cm⁻³ atm⁻¹, cm³(STP) cm⁻³, atm⁻¹, respectively. The units of D_D and D_H are in 10⁻⁸ cm² s⁻¹)

Polyimide	Gas	k_D	C'_H	b	D_D	D_H
TADATO/DSDA(1/1)-DDBT	CO ₂	1.36	55.8	0.635	16.1	0.76
DSDA-DDBT		1.27	50.5	0.643	–	–
BPDA-DDBT		1.17	39.0	0.847	3.4	0.11
TADATO-ODA		1.09	42.3	0.635	–	–
TADATO/DSDA(1/1)-DDBT	CH ₄	0.385	20.3	0.200	1.27	0.0283
DSDA-DDBT		0.331	18.4	0.201	–	–
TADATO/DSDA(1/1)-DDBT	N ₂	0.155	17.8	0.050	5.51	0.132
DSDA-DDBT		0.283	7.8	0.105	–	–

decrease in ideal selectivity. This is a normal behavior as observed with most glassy polymeric membranes.

From the temperature dependence of P , D and S , activation energies for permeation (E_p) and diffusion (E_D), and heat of sorption (ΔH_S) were calculated. Table 5 lists the results at 10 atm for TADATO/DSDA(1/1)-DDBT. Since no data for DSDA-DDBT and 6FDA-DDBT can be found from literature, the data of other polyimides such as 6FDA-pPD, 6FDA-TrMPD, BPDA-DDBT and BPDA-pDDS were used for comparison [10,12]. The values of E_p were in the reverse order of permeability; i.e. 6FDA-TrMPD < TADATO/DSDA(1/1)-DDBT < 6FDA-pPD < BPDA-DDBT < BPDA-pDDS. TADATO/DSDA(1/1)-DDBT showed a little larger E_D and a little more negative ΔH_S than 6FDA-TrMPD and 6FDA-pPD (non-sulfonyl containing polyimides).

Fig. 4 shows the sorption isotherms of CO₂, N₂ and CH₄ for TADATO/DSDA(1/1)-DDBT. Sorption amounts are in the order: CO₂ ≫ CH₄ > N₂, which is consistent with the results of gas permeation measurements. The sorption of gases in glassy polymers is usually described in terms of the “dual mode” sorption model written as:

$$C = k_D p + b C'_H p / (1 + b p) \quad (3)$$

where k_D , C'_H and b are the Henry's law coefficient, Langmuir capacity constant and an affinity parameter, respectively, and p is the applied pressure. The values of k_D , C'_H and b can be calculated by a non-linear least-squares fit of sorption data to Eq. (3) and the results are listed in Table 6. For purposes of comparison, the data of these parameters for

Table 7

A comparison of permeation properties for pure and mixed CO₂/N₂ at 2 atm and 35°C (P is in barrer, 1 barrer = 10⁻¹⁰ cm³(STP) cm⁻¹ s⁻¹ cmHg⁻¹)

Polyimide	Gas	P_{CO_2}	P_{N_2}	α_{CO_2/N_2}
TADATO/DSDA(1/1)-DDBT	Pure	45	1.27	35
	Mixed (CO ₂ :20 mol%)	45	0.91	49
DSDA-DDBT	Pure	14.5	0.37	39
	Mixed (CO ₂ : 20 mol%)	12.5	0.246	51

DSDA-DDBT and TADATO-ODA are also listed in this table. TADATO/DSDA(1/1)-DDBT displayed very similar b but larger k_D and C'_H to CO₂ than DSDA-DDBT and TADATO-ODA, and this is the reason for its higher CO₂ solubility coefficient.

For pure gas permeation, the permeability coefficient P can be given by Eq. (4) according to the “dual-mode” transport model [22,23]:

$$P = k_D D_D + C'_H b D_H / (1 + b p) \quad (4)$$

where D_D and D_H are the diffusion coefficients of the penetrant in the Henry's law population and the Langmuir population, respectively. A plot of P versus $(1 + b p)^{-1}$ gave a straight line and the parameters D_D and D_H were thus calculated by a linear least-squares analysis. The results for TADATO/DSDA(1/1)-DDBT at 35°C are also listed in Table 6 together with the sorption data. Using these parameters and Eq. 4, the permeability coefficients at different pressure can also be calculated as shown in Fig. 2 (dotted lines). It is obvious that pure gas transport in the membrane fits the dual-mode model well.

3.2.2. Separation for CO₂/N₂ mixture

Table 7 shows the permeability and separation factor of TADATO/DSDA(1/1)-DDBT for the CO₂/N₂ mixture containing 20% CO₂ at 35°C and 2 atm (total pressure). The value of P_{CO_2} is the same for single and mixed gas permeation (or smaller for mixed gases in view of the partial pressure of CO₂), whereas the value of P_{N_2} is significantly smaller for mixed gas permeation than for single gas permeation. As a result, the mixed gas selectivity (separation factor) is much higher than the ideal selectivity. This is likely related to the high density of sulfonyl groups in the polymer structure, leading to high affinity of the membrane to CO₂ through electronic induction effect. The high affinity to CO₂ resulted in strongly preferential sorption of CO₂ in the membrane, and thus the permeation of N₂ was significantly hindered leading to much higher separation factor for CO₂/N₂ mixture. This phenomenon was also observed with some other polyimides with high density of sulfonyl groups such as DSDA-DDBT (see Table 7).

Gas permeability coefficient and separation factor as a

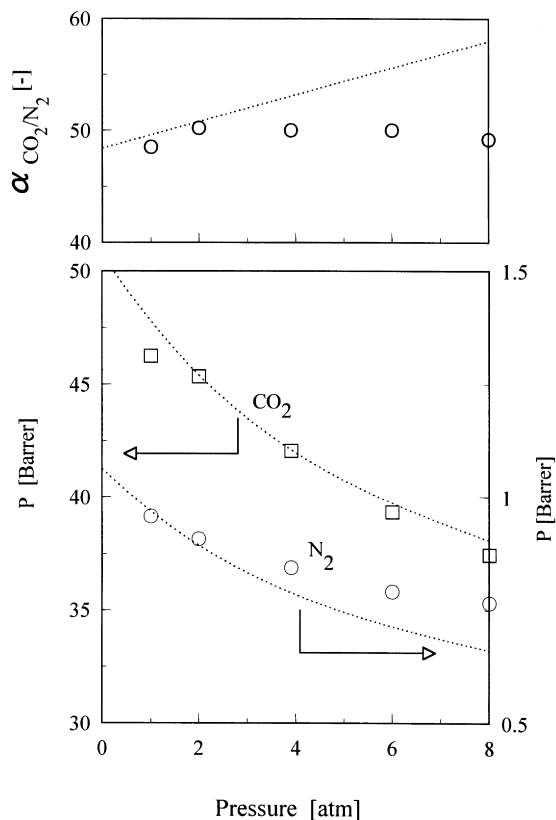


Fig. 5. Gas permeation coefficient and separation factor of TADATO/DSDA(1/1)-DDBT polyimide for CO₂/N₂ mixture (CO₂: 20 mol%) as a function of total upstream pressure at 35°C. The plots are experimental data, and the dotted lines refer to the calculated data from the dual-mode model.

function of the overall upstream pressure and temperature are shown in Figs. 5 and 6, respectively. Unlike the case of pure gas permeation, CO₂ and N₂ permeability coefficients decreased by a similar factor with an increase in upstream pressure, and therefore the separation factor remained almost unchanged. On the other hand, with an increase in temperature, the permeability coefficient for N₂ increased by a factor of about 2.5 from 28 to 75°C, whereas that for CO₂ remained almost unchanged. Therefore, the separation factor decreased significantly with increasing temperature. When the temperature was raised to 75°C, the separation performance for mixed and pure gases turned almost identical.

The transport of mixed gases can also be described in terms of the dual-mode model; i.e. for the gas mixture of A and B, the permeability coefficient can be predicted by the following equation [22,23]:

$$P_A = k_D D_D [1 + F_A K_A / (1 + b_A p_A + b_B p_B)] \quad (6)$$

where $F_A = D_{HA}/D_{DA}$ and $K_A = C'_H b_A/k_{DA}$. For purposes of comparison, the calculated data (dotted lines) are also shown in Fig. 5. The correlation for P_{CO_2} between the calculated and experimental data was fairly good. However, small deviations were observed for P_{N_2} at pressure over 4 atm. Since P_{N_2} is rather small and a little difference in

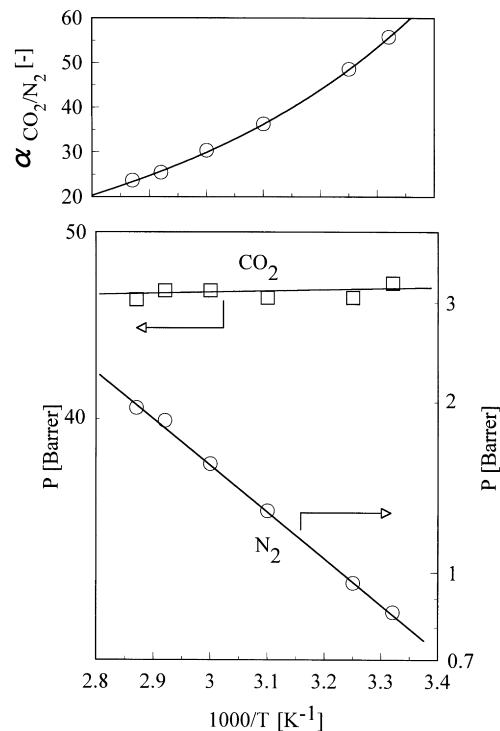


Fig. 6. Gas permeation coefficient and separation factor of TADATO/DSDA(1/1)-DDBT polyimide for CO₂/N₂ mixture (CO₂: 20 mol%) as a function of temperature at a total upstream pressure of 1 atm.

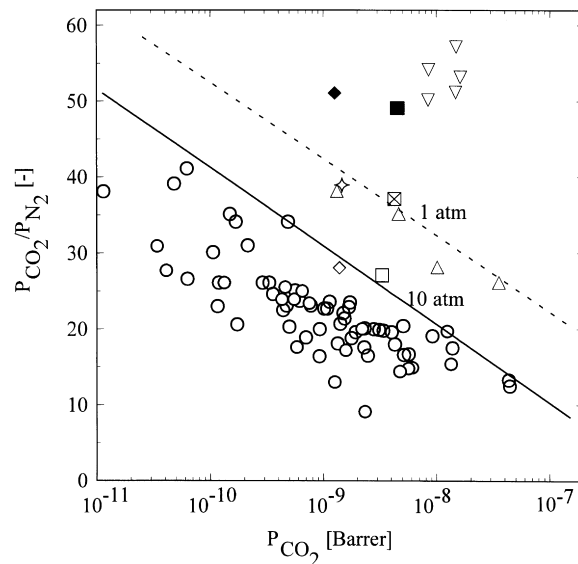


Fig. 7. Comparison of CO₂/N₂ separation performance for various glassy polymers: (□, ⊠, ■) TADATO/DSDA(1/1)-DDBT; (◇, ◆, ♦) DSDA-DDBT; (△) CARDO-type polyimides; (▽) poly(ether imide) segmented polymers; (○) other glassy polymers. The symbols □, ◇ and ○ are at 10 atm and 35°C; ⊠ and ◆ are at 1 atm and 35°C; △ is at 1 atm and 25°C; ▽ is at 2 atm and 35°C. Open keys and closed ones refer to single gas and mixed gases (CO₂: 20 mol%) permeation, respectively.

P_{N_2} can cause fairly large difference in separation factor. Thus, some deviations were observed for the separation factors. Nevertheless, the correlation is still fairly good indicating that gas transport in the membrane fits the dual-mode model well.

A comparison of CO_2/N_2 separation performance for TADATO/DSDA(1/1)–DDBT copolyimide with other glassy polymers at 10 atm and 35°C is shown in Fig. 7. The solid line in this figure is the trade-off line of the CO_2/N_2 separation performance observed for various glassy linear polymeric membranes at 10 atm and 35°C. The plot of TADATO/DSDA(1/1)–DDBT fell above the “upper bound” line indicating the highest separation performance among the glassy polymer membranes developed so far. The CO_2/N_2 separation performance of glassy polymers significantly depends on measuring pressure and temperature. CARDO-type polyimides have been reported to have high CO_2/N_2 separation performance at low feed pressure (1 atm) and 25°C [14]. As can be seen, TADATO/DSDA(1/1)–DDBT polyimide showed even a little better performance than these CARDO-type ones. Furthermore, TADATO/DSDA(1/1)–DDBT exhibited much better separation performance for mixed gases than for pure gas. However, the separation performance is still somewhat poorer than that of the rubbery poly(ether imide) segmented copolymers, which have been reported to have very high CO_2/N_2 separation performance [8].

4. Conclusions

1. Polyimides with great chain stiffness and high density of sulfonyl groups tended to show lower gas permeability but higher selectivity than those with similar chain stiffness but low density of sulfonyl groups.
2. TADATO/DSDA(1/1)–DDBT copolyimide displayed much higher CO_2 permeability coefficient but similar ideal selectivity of CO_2 over N_2 to TADATO–DDBT and DSDA–DDBT homopolyimides. The higher CO_2 permeability coefficient of TADATO/DSDA(1/1)–DDBT is attributed to the higher diffusion coefficient as well as a little higher solubility coefficient, while the similar selectivity is due to the similar solubility selectivity and diffusivity selectivity.
3. TADATO/DSDA(1/1)–DDBT copolyimide displayed much larger selectivity for mixed CO_2/N_2 permeation than for pure gas permeation at relatively low temperature, but the difference tended to decrease with increasing temperature.
4. In comparison with many other glassy polymers, TADATO/DSDA(1/1)–DDBT copolyimide showed high CO_2/N_2 separation performance.
5. Gas sorption and transport in TADATO/DSDA(1/1)–DDBT membrane can be described in terms of the dual-mode model.

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