Highly Permeable and Selective Six-membered Ring Polyimide Membranes for Gas Separation Applications

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1. INTRODUCTION

Membrane-based gas separation technologies have attracted much attention in the past decades because they offerthe advantages of high efficiency, low energy consumption, low capital investment cost, simpleand easy to operate over traditional industrial separation processes. In the past decades aromatic polyimides have been extensively studied as membrane materials for gas separations because of their remarkable gas separation performances as well as excellentthermoxidative stability, high mechanical strength and modulus as compared with many other glassy polymers. However, up to date, almost all the polyimide membranes studied for gas separations are limited to five-membered ring polyimides (phthalimides). Quite few reports on the gas separation properties of six-membered ring polyimides (naphthalenic imides) are available. It has been identified thatsix-membered ring polyimides are much more stable to hydrolysis than five-membered ring polyimides making the former good candidates for producing highly durable membranes which are used under harsh conditions (e.g. high relative humidities and high temperatures). In this presentation, we report on the synthesis, characterization and gas separation performances of a series of organo-soluble six-membered ring polyimides. Their chemical structures are shown in **Fig. 1**.
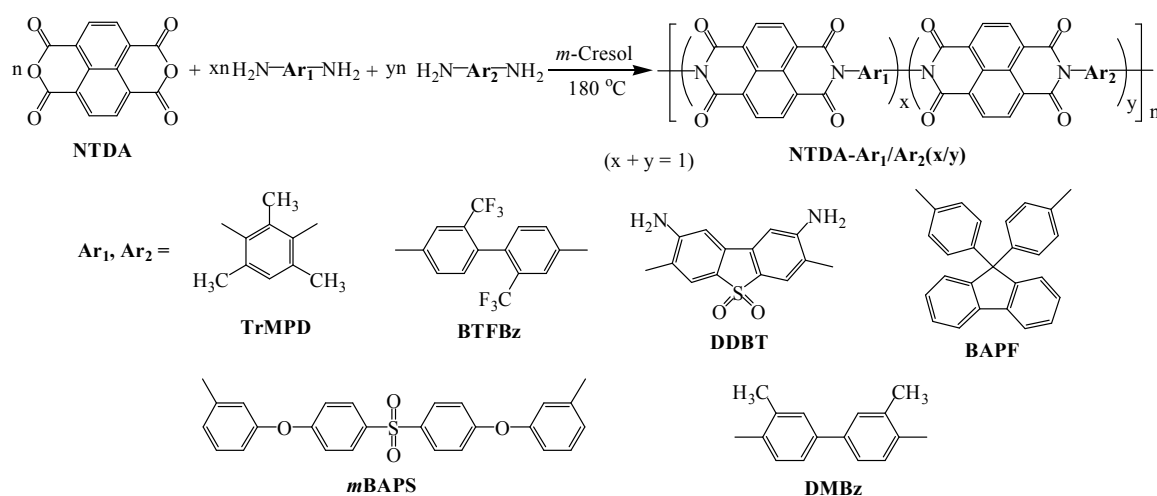
Fig. 1. Synthesis of the NTDA-Based polyimides.

1. EXPERIMENTAL

2.1 Polymer synthesis

A typical experimental procedure for the synthesis of the copolyimideNTDA-BTFBz/TrMPD(1/1, by mole) is described in the following as an example.

To a 100 mL completely dried three-neck flask were charged 0.9617g (3.0 mmol) of BTFBz, 0.4507g (3.0 mmol) of TrMPD and 20 mL of *m*-cresol. The reaction mixture was magnetically stirred at room temperature under nitrogenflow. After BTFBz and TrMPDwere completely dissolved, 1.6091g (6.0 mmol) of NTDA and 1.465g (12.0 mmol) of benzoic acid were added and the mixture was heated at 80°C for 4 h and 180°C for another 10 h. After cooling to room temperature, 1.55g (12mmol) of isoquinolinewas added in one portion and the reaction mixture was heated again at 180°C for 10 h. After cooling to ~120°C, the highly viscous dark-brown polyimide solution was diluted with 10 mL of *m*-cresol and subsequently poured into methanol. The resulting precipitate was collected by filtration, thoroughly washed with methanol and dried at 100 °C in vacuo for 10 h.

2.2 Film formation

For preparation ofsix-memberedcopolyimide membranes, 5 w/v% polymer solutionsin *m*-cresolwere cast onto glass plates and dried in an air oven at 110°C for 8 h. The as-cast membranes were peeled from the glass plates and subsequently soaked in hot methanol for 10 h to remove the residual solvent (*m*-cresol). The membranes were taken out and further dried at 120°C for 12 h in vacuo.

For preparation of the five-membered copolyimidemembrane PMDA-TrMPD/BTFBz(1/1),a 5 w/v% polymer solution in DMAc was cast onto a glass plate and dried in an air oven at 80 °C for 8 h. The as-cast membranes were peeled from the glass plates and further heat-treated successively at 150°C for 1 h, 250°C for1 h and 350°C for0.5 h.

2.3 Measurements

FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000PC spectrometer. Thermogravimetric analysis (TGA) was performed in nitrogen with a Pyris 1 TGA at a heating rate of 10°C min^{-1}. Dynamic thermomechanical analysis (DMA) was performed with a DMA 8000 at a heating rate of 5°C min^{-1}.Wide angle X-ray diffraction (WAXD) measurements were carried out on a D/max-2200/PC diffractometer with CuK$_\alpha$ radiation, λ = 1.54Å.

Tensile measurements were carried out with an Instron 4456 instrument under ambient atmosphere (room temperature, ~50% relative humidity) at a crosshead speed of 1 mm min^{-1}. For each kind of membrane, three sheets of samples were used for the measurements and the tensile stress (TS) and the elongation at break (EB) were estimated by the averaged values of the three samples.

2.4 Gas permeation test

Pure gas permeation tests were carried out on a GTR-1ADFE gas sorption coefficient and diffusion coefficient test machine (Japan) at35 °C at upstream pressure ranging from 0.1 to 0.5 MPa. The measurement was based on a vacuum time-lag method and the gas permeability coefficient (P) was determined from a steady state permeation flux in a period between 5 and 10 times the time lag (θ). The effective membrane area was 15.2 cm 2 . Apparent diffusion coefficient **D** was calculated from Eq. (1)

$$D = \frac{L^2}{6\kappa} \qquad (1)$$

where L is membrane thickness. Apparent solubility coefficient **S** was calculated from **P** and **D**:

$$S = \frac{P}{D} \qquad (2)$$

Ideal selectivity was calculated as the **P** ratio of pure gas pair **A** and **B**. It is equal to the product of the diffusivity selectivity and solubility selectivity.

$$\frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right)\left(\frac{S_A}{S_B}\right) \qquad (3)$$

3. RESULTS AND DISCUSSION

3.1. Polyimide synthesis and characterization

A series of NTDA-based six-membered ring polyimide copolymers were synthesized by one-step random condensation copolymerization process in *m*-cresol in the presence of isoquinoline and benzoic acid (catalysts) at 180 ℃ for 20 h. The aromatic diamines used for the polymerization are 2,4,6-trimethyl- 1,3-phenylenediamine (TrMPD), 2,2'-bis(trifluoromethyl)benzidine (BTFBz), 3,7-diamino-2,8-dimethyl dibenzothiophen sulfone (DDBT), 9,9-bis(4-aminophenyl)fluorene (BAPF),4,4'-bis (3-aminophenoxy)diphenyl sulfone (*m*BAPS) and 3,3'-dimethylbenzidine (DMBz).Thisone-step polymerization method has been employed for preparation of various sulfonated and *non*-sulfonated six-membered ring polyimides.The conventional two-step condensation polymerization method is not applicable to the synthesis of six-membered ring polyimides because as reported by Sek and coworkers [1,2] polyamic acid precursors are hardly formed during the process of condensation polymerization of 1,8-naphthalene-type dianhydrides (e.g. NTDA)and diamines. Moreover, high temperature is required to promote the polymerization reaction because NTDA does not react with the diamines at room temperature due to its low reactivity. Benzoic acid and isoquinoline are catalysts which are favorable for the formation of imido structure.
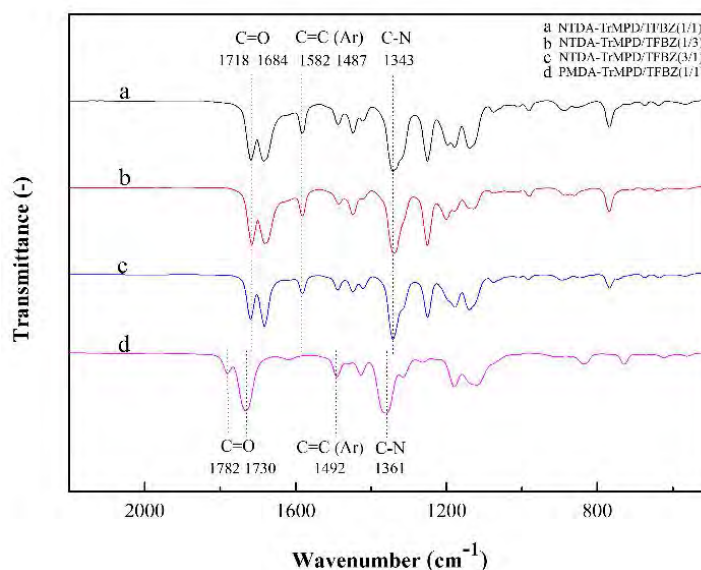

Fig. 2. FT-IR spectra of the copolyimides derived from NTDA, PMDA, TrMPD and BTFBz.

The FT-IR spectra of the copolyimide membranes derived from NTDA, TrMPD and BTFBz as well as the one derived from pyromellitic anhydride (PMDA) and the same diamines are shown in **Fig. 2**. For the NTDA-based copolyimides, the strong absorption bands around 1718 and 1684 cm^{-1} are assigned to the asymmetric and symmetric stretch vibration of carbonyl groups of the naphthalenicimido rings (six-membered rings). The band around 1343 cm^{-1} corresponds to the stretch vibrations of C-N bond of imido rings. The absorption bands around 1582 and 1487 cm^{-1}, respectively, are ascribed to the skeleton vibration of naphthalene and benzene rings. These FT-IR spectra confirmed the formation of the six-membered ring polyimides. For the PMDA-TrMPD/BTFBz(1/1) copolyimide, the characteristic absorption bands around 1782 and 1730 cm^{-1} are assigned to the asymmetric and symmetric stretch vibration of carbonyl groups of the five-membered imido rings. The peak at 1361 cm^{-1} corresponds to the stretch vibrations of C-N bond of imido rings. The band around 1492 cm^{-1}is assigned to benzene skeleton vibration.

3.2 Polymer solubility

The solubility behaviors of the synthesized polyimidehomopolymers and copolymersare shown in the **Table 1**. Except NTDA-*m*BAPS all the homopolymers displayed rather poor solubility in the test solvents. In contrast, almost all the copolyimides were well soluble in *m*-cresol, DMSO, NMP and DMAc at room temperature or upon heating indicating greatly improved solubility due to copolyerization. The greatly improved solubility of the copolyimides is likely attributed to the decreased structural regulation and symmetry due to copolymerization and such a phenomenon has also been observed with five-membered ring polyimides [3].

Table 1. Solubility, inherent viscosity and T_g of a series of NTDA-based and other related polyimides.

Polyimide	Solubility[a]					
	m-Cresol	DMSO	DMAc	NMP	CHCl$_3$	THF
NTDA-TrMPD	+-	-	-	-	-	-
NTDA-BTFBz	-	-	-	-	-	-
NTDA-BAPF	-	-	-	-	-	-
NTDA-DDBT	-	-	-	-	-	-
NTDA-DMBz	-	-	-	-	-	-
NTDA-*m*BAPS	++	++	+-	++	-	-
NTDA-TrMPD/BTFBz(3/1)	+ +	+ +	+ +	+ +	-	-
NTDA-TrMPD/BTFBz(1/1)	+ +	+ +	+ +	+ +	-	-
NTDA-TrMPD/BTFBz(1/2)	+ +	+	+	+ +	-	-
NTDA-TrMPD/BTFBz(1/3)	+ +	+-	+-	+ +	-	-
NTDA-TrMPD/BAPF(1/1)	+	++	++	++	+	-
NTDA-TrMPD/DDBT(1/1)	+	++	++	++	-	-
NTDA-DDBT/BTFBz(1/1)	+	++	++	++	-	-
NTDA-*m*BAPS/BTFBz(1/1)	+	++	++	++	-	-
NTDA-*m*BAPS/BAPF(1/1)	++	++	++	++	-	-
NTDA-*m*BAPS/DDBT(1/1)	+	++	++	++	-	-
PMDA-TrMPD/BTFBz(1/1)	+ +	+ +	+ +	+ +	-	-

[a]Solubility: '++': soluble at r.t.; '+': soluble on heating; '+-': partially soluble at heating; '−': insoluble

on heating.

3.3 Mechanical properties

Table 2 shows the tensile stress (TS), elongation at break (EB) and Young's modulus (YM) of the copolyimides derived from NTDA, PMDA, TrMPD and DDBT. NTDA-TrMPD/BTFBz(3/1) displays a moderate tensile stress at break (42 MPa) and a low elongation at break (6.0%) due to its moderate molecular weight. Nevertheless, it could form tough membranes via solution cast method. NTDA-TrMPD/BTFBz(1/3) exhibit much higher tensile stress at break (98 MPa) and larger elongation at break (11 %) indicating that high molecular weight of this polyimide. From this table, it can also be seen that NTDA-based polyimide membranes showed much higher Yong's moduli than the PMDA-based one. The measurements of the mechanical properties of other polyimide membranes are in progress.

Table 2. Mechanical properties of a series of NTDA-based and other related polyimides

Polyimide	Mechanical properties[a]		
	TS[b] (MPa)	EB[c] (%)	YM[d](GPa)
NTDA-TrMPD/BTFBz(3/1)	42	6.0	7.1
NTDA-TrMPD/BTFBz(1/1)	69	19	5.9
NTDA-TrMPD/BTFBz(1/3)	98	11	5.7
PMDA-TrMPD/BTFBz(1/1)	85	9.0	1.5

[a]Mechanical properties: Measured at room temperature 28 ºC, humidity level 66%, the rate of stretching 6mm/min.
TS[b]: Tensile strength at break; EB[c]: Elongation at break; YM[d]: Young's modulus.

3.4 Thermal stability

The thermal stabilities of the prepared copolyimide membraneswere determined by TGA (**Fig.3**). The decomposition temperatures at one percent weight loss (T_d^1) and five percent weight (T_d^5) are estimated from the TGA curves and the data are summarized in **Table 3**. All the NTDA-based copolyimides exhibit higher $T_d^1$and T_d^5 than the PMDA-based copolyimide indicating better thermal stability of the former. This is attributed to the higher thermal resistance of the naphthalimide than that of phthalimide.
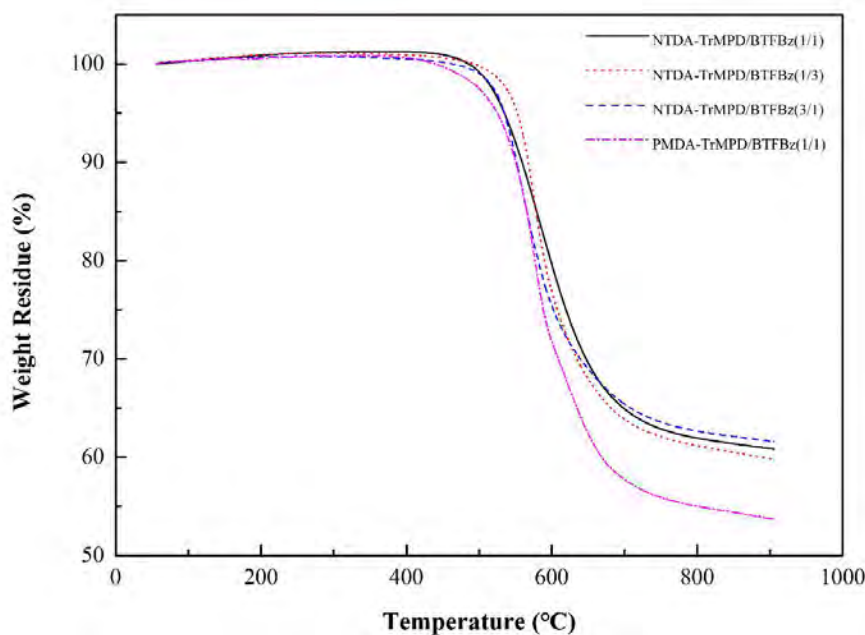
Fig. 3. TGA curves of the copolyimide films in nitrogen atmosphere at a heating rate of 10 ºC min^{-1}.

Table 3. Decomposition temperatures at one percent weight loss (T_d^1) and five percent weight loss (T_d^5) of the synthesized copolyimides

Polyimide	T_d^1 (ºC)	T_d^5 (ºC)
NTDA-TrMPD/BTFBz(3/1)	500	533
NTDA-TrMPD/BTFBz(1/1)	504	535
NTDA-TrMPD/BTFBz(1/3)	520	553
PMDA-TrMPD/BTFBz(1/1)	472	525

3.5 XRD patterns

Fig. 4 shows the XRD patterns of the copolyimide membranes. For all the samples no sharp but very broad diffraction peaks are observed indicating completely amorphous morphologies of these samples. From the scattering angles (2θ) in the centers of the broad peaks, the *d*-spacing values in these copolyimide films are calculated in terms of Bragg's equation, $n\lambda = 2d \sin \theta$. The d-spacing values are 6.7 for NTDA-TrMPD/BTFBz(3/1), 6.5 for NTDA-TrMPD/BTFBz(1/1), 6.2 for NTDA-TrMPD/BTFBz(1/2), 6.1 for NTDA-TrMPD/BTFBz(1/3), and 5.8 for PMDA-TrMPD/BTFBz(1/1), respectively. Among the NTDA-based copolyimides, the d-spacing values decrease with decreasing the molar fraction of TrMPD moiety in the copolyimides. This is because the methyl groups adjacent to the amino groups of TrMPD moiety restrict the rotation of the imido rings along the C-N axis making it more rigid than BTFBz. In addition, all the NTDA-based copolyimides showed larger *d*-spacing values than PMDA-TrMPD/BTFBz(1/1). Even though NTDA-TrMPD/BTFBz(1/3) and NTDA-TrMPD/BTFBz(1/2) have lower content of TrMPD moiety than PMDA-TrMPD/BTFBz(1/1), the former shows larger *d*-spacing values than the latter. This should be ascribed to the structural difference in the dianhydride moieties (NTDA and PMDA). Computer simulation results suggest that 1,8-Naphthalimido rings show more twist structure than phthalimide

rings making the former have fairly loose chain packing.
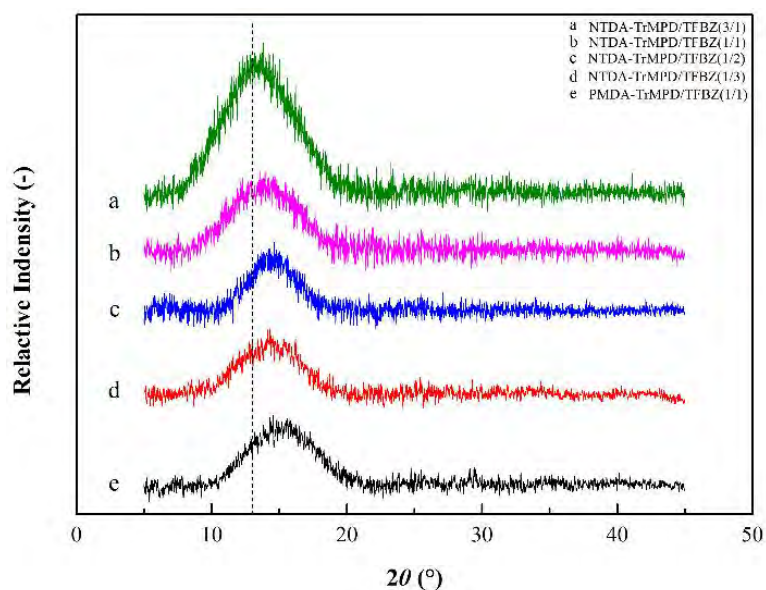
Fig. 4. X-ray diffraction patterns of the copolyimides films prepared from NTDA, PMDA, TrMPD and BTFBz.

3.6 Gas permeability study

Gas permeability coefficient and selectivity are two key parameters for evaluation of gas separation performance of a dense polymeric membrane. **Table 4** lists the pure gas permeation data ofthe prepared copolyimides membranesat 2 atm and 35ºC. For the copolyimides derived from NTDA, PMDA, TrMPD and BTFBz, the permeability coefficients of all the tested gases are in the order: PMDA-TrMPD/BTFBz(1/1) < NTDA-TrMPD/BTFBz(1/3) < NTDA-TrMPD/BTFBz(1/2) < NTDA-TrMPD/BTFBz(1/1) <NTDA-TrMPD/ BTFBz(3/1), which is just consistent with the order of their *d*-spacing values. The permeability coefficient is closely dependent on the molar content of TrMPD moiety in the copolyimidestructures. Raising the TrMPD/BTFBz molar ratio from 1:3 to 1:1 led to more than four-fold increases in permeability coefficient of each kind of gas.However, further raising the TrMPD/BTFBz molar ratio from 1:1 to 3:1 resulted in only minor increases in gas permeability coefficients. On the other hand, the copolyimide composition shows very weak impact on ideal selectivity, i.e., the selectivity values of these copolyimide membranes are roughly close to each other with only a few exceptions (for NTDA-TrMPD/BTFBz(3/1) its selectivity values to CO_2/CH_4 and $O_2/N_2$are relatively lower).NTDA-TrMPD/BTFBz(1/1)exhibits approximately one order of magnitude higher gas permeability coefficients but roughly similar selectivity values to that of PMDA-TrMPD/BTFBz(1/1) despite their exactly the same diamine composition indicating much better separation performance of the former.

Table 4. Gas Permeabilities and Permselectivities for the six-memberedand the five-membered polyimides membranes at 35 °C and 2atm.

Polyimide	Permeability[a](barrer)				Permselectivity		
	N_2	O_2	CO_2	CH_4	O_2/N_2	CO_2/N_2	CO_2/CH_4
NTDA-TrMPD/BTFBz(3/1)	51.2	172	987	68.3	3.37	19.3	14.5
NTDA-TrMPD/BTFBz(1/1)	45.5	164	930	43.0	3.60	20.4	21.6
NTDA-TrMPD/BTFBz(1/2)	19.4	68.8	405	18.0	3.55	21.0	22.5
NTDA-TrMPD/BTFBz(1/3)	9.98	39.9	222	9.41	4.00	22.2	23.6
PMDA-TrMPD/BTFBz(1/1)	10.3	41.8	216	8.71	3.84	21.0	24.8
NTDA-TrMPD/DDBT(1/1)	75.7	297	1660	82.9	3.92	21.9	20.0

NTDA-DDBT/BTFBz(1/1)	40.2	142	839	36.8	3.53	20.9	22.8
NTDA-BAPF/DDBT(1/1)	28.4	95.9	713	35.6	3.38	25.1	20.0
NTDA-*m*BAPS/DDBT(1/1)	1.82	6.64	37	1.46	3.65	20.3	25.3

[a]1Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}.

As shown in this table, among the copolyimide membranes synthesized in this study NTDA-TrMPD/DDBT(1/1) displayed the highest gas permeability coefficient which is almost double of that of the foregoing mentioned highly permeable NTDA-TrMPD/BTFBz(1/1) for each gas. Moreover, the difference in selectivity (O_2/N_2, CO_2/N_2, CO_2/CH_4) between these two membranes (NTDA-TrMPD/BTFBz(1/1) and NTDA-TrMPD/DDBT(1/1)) is quite small indicating better separation performance of the NTDA-TrMPD/DDBT(1/1). The higher gas permeability coefficients of the NTDA-TrMPD/DDBT(1/1) is because DDBT is more rigid than BTFBz, while the strong polar sulfonyl groups of DDBT ensures the membrane maintaining high selectivities.

BAPF is a bulky diamine, and the relevant copolyimideNTDA-DDBT/BAPF(1/1)is also highly permeable. Its permeability coefficient of a given gas is close to that ofNTDA-TrMPD/BTFBz(1/1). It shows slightly lower selectivities for $O_2/N_2$and CO_2/CH_4 but high selectivity for CO_2/N_2 than NTDA-TrMPD/BTFBz(1/1).

NTDA-*m*BAPS/DDBT(1/1) displayed the lowest gas permeability coefficients among the copolyimides of this study. For a given gas, NTDA-*m*BAPS/DDBT(1/1) exhibited about two orders of magnitude lower permeability coefficient than NTDA-TrMPD/DDBT(1/1). This is because *m*BAPS is a highly flexible diamine leading to very dense packing of the polymer chains.

Gas permeation through a polymeric membrane is usually elucidated in terms of sorption-diffusion mode. The permeability coefficient (P) is the product of solubility coefficient (S) and diffusivity coefficient (D), while the permselectivity is the product of solubility selectivity (S_A/S_B, A and B refer to a pair of gases) and diffusivity selectivity (D_A/D_B). **Table 5** summarized the gas solubility coefficient and diffusion coefficient values of the copolyimide membranesprepared from PMDA, NTDA, TrMPD and BTFBz. It can be seen that for each individual gas the diffusion coefficients are in the order: PMDA-TrMPD/BTFBz(1/1) < NTDA-TrMPD/BTFBz(1/3) < NTDA-TrMPD/BTFBz(1/2) < NTDA-TrMPD/BTFBz(1/1), which is just consistent with the order of their V_F values. The membranes with higher V_F values possess more spaces for gas transport, and therefore higher diffusion coefficients were obtained. NTDA-TrMPD/BTFBz(3/1) is an exception of which diffusion coefficient is lower than that of NTDA-TrMPD/BTFBz(1/1) despite the slightly larger V_F of the former. At present, we cannot give a reasonable explanation. From this table, it can also be seen that no clear relationship exists between the polyimide structures and their solubility coefficients. Moreover, for all the membranes the solubility coefficient values are in the order: $S_{N2} \approx S_{O2} < S_{CH4} << S_{CO2}$, while the diffusivity coefficients are in the order: $D_{CH4} < D_{N2} \approx D_{CO2} < D_{O2}$. As a result, as shown in **Table 6**, for O_2/N_2 gas pair the diffusivity selectivity is mainly responsible for the permselectivity of all the copolyimde membranes. In contrast, for CO_2/N_2 gas pair the solubility selectivity is the main factor which contributes to the permselectivity. For CO_2/CH_4, both the solubility selectivity and the diffusivity selectivity significantly contribute to the permselectivity.

Table 5. Gas solubility coefficients and diffusion coefficients of the copolyimides membranes derived from NTDA, PMDA, TrMPD and BTFBz at 35 °C and 2 atm.

Polyimide	S (10^{-2} cm^3(STP)cm^{-3}cmHg^{-1})				D (10^{-8} cm^{2}s^{-1})			
	N_2	O_2	CO_2	CH_4	N_2	O_2	CO_2	CH_4
NTDA-TrMPD/BTFBz(3/1)	2.55	3.07	45.8	5.18	20.1	56.0	21.7	13.2

NTDA-TrMPD/BTFBz(1/1)	1.49	1.81	27.9	5.18	30.6	90.8	33.3	8.3
NTDA-TrMPD/BTFBz(1/2)	1.83	2.52	33.7	5.89	10.7	27.3	12.0	3.12
NTDA-TrMPD/BTFBz(1/3)	1.63	2.09	31.1	4.74	6.12	19.1	7.1	1.98
PMDA-TrMPD/BTFBz(1/1)	0.92	1.04	19.5	2.53	4.78	16.2	9.2	1.57

Table 6. Solubility selectivity and diffusivity selectivity of the copolyimides membranes derived from NTDA, PMDA, TrMPD and BTFBzat 35 °C and 2 atm.

Polyimide	D_{O_2}/D_{N_2}	S_{O_2}/S_{N_2}	D_{CO_2}/D_{N_2}	S_{CO_2}/S_{N_2}	D_{CO_2}/D_{CH_4}	S_{CO_2}/S_{CH_4}
NTDA-TrMPD/BTFBz(3/1)	2.8	1.2	1.1	18.0	1.6	8.8
NTDA-TrMPD/BTFBz(1/1)	3.0	1.2	1.1	18.7	4.0	5.4
NTDA-TrMPD/BTFBz(1/2)	2.6	1.4	1.1	18.4	3.9	5.8
NTDA-TrMPD/BTFBz(1/3)	3.1	1.3	1.2	19.1	3.6	6.6
PMDA-TrMPD/BTFBz(1/1)	2.3	1.8	0.9	22.9	3.5	7.1

It is interesting to compare the gas separation performance of the present copolyimide membranes with those of other polymeric membranes reported in literature. The solid line in **Fig. 5** are the latest upper bound for CO_2/CH_4 separation, presented by Robeson in 2008 [4]. It can be seen that theNTDA-TrMPD/DDBT(1/1) and NTDA-TrMPD/BTFBz(1/1) displayed excellent CO_2/CH_4 separation performance of which selectivity/permeability coefficient plots almost reach to the upper bound.
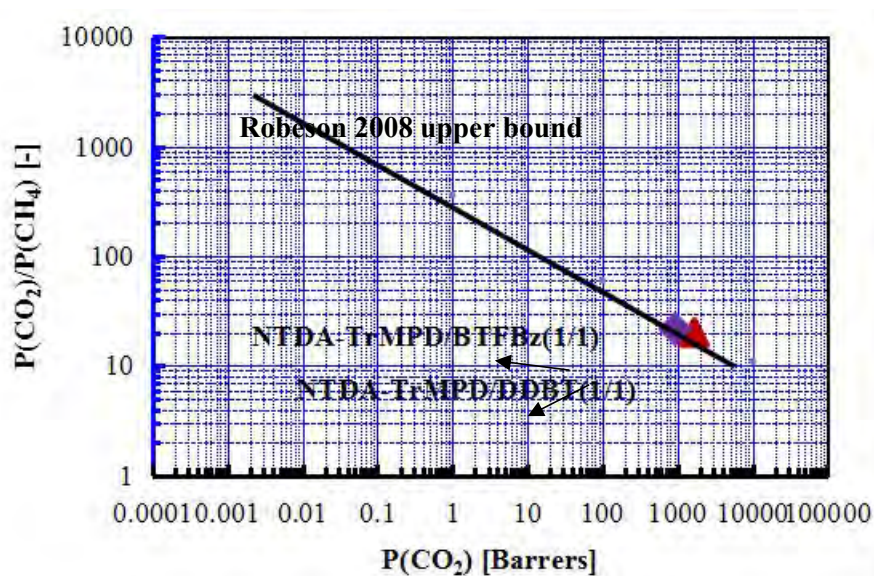
Fig. 6. Comparison of CO2/CH4 separation performances for various polymeric membranes.

4.CONCLUSIONS

A series of novel organo-soluble six-membered ring copolyimideshave been synthesized by random copolymerization of NTDA and various aromatic diamines in *m*-cresol. Copolymerization is very effective for improvement of polyimide solubility. The relationship between polyimide chemical structures and gas separation performances was systematically investigated. Polyimides with highly rigid backbone tend to have high gas permeability coefficients. NTDA-TrMPD/DDBT(1/1) and NTDA-TrMPD/BTFBz(1/1) membranes exhibited excellent separation performance for CO_2/CH_4 gas pair which almost reached the latest upper bound reported by

Robeson in 2008.

Acknowledgments

References

[1] D. Sek, A. Wanic, E. Schab-Balcerzak, J. Polym. Sci., Part A: Polym. Chem. 33 (1995) 547-554.

[2] D. Sek, A. Wanic, E. Schab-Balcerzak, J. Polym. Sci., Part A: Polym. Chem. 35 (1997) 539-545.

[3] Y. Tsuda, M. Kojima, J. M. Oh, Polym. J. 38 (2006) 1043-1054.

[4] L. M. Robeson, J. Membr. Sci. 320 (2008) 390–400.