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Synthesis, characterization, and gas permeation properties of 6FDA-2,6-DAT/mPDA copolyimides

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Abstract The goal of this work is to explore new polyimide materials that exhibit both high permeability and high selectivity for specific gases. Copolyimides offer the possibility of preparing membranes with gas permeabilities and selectivities not obtainable with homopolyimides. A series of novel fluorinated copolyimides were synthesized with various diamine compositions by chemical imidization in a two-pot procedure. Polyamic acids were prepared by stoichiometric addition of solid dianhydride in portions to the diamine(s). The gas permeation behavior of 2,2'-bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydride(6FDA)-2,6-diamine toluene (2,6-DAT)/ 1,3-phenylenediamine (mPDA) polyimides was investigated. The physical properties of the copolyimides were characterized by IR, DSC and TGA. The glass transition temperature increased with increase in 2,6-DAT content. All the copolyimides were soluble in most of the common solvents. The gas permeability coefficients decreased with increasing mPDA content. However, the permselectivity of gas pairs such as H₂/N₂, O₂/N₂, and CO₂/CH₄ was enhanced with the incorporation of mPDA moiety. The permeability coefficients of H₂, O₂, N₂, CO₂ and CH₄ were found to decrease with the increasing order of kinetic diameters of the penetrant gases. 6FDA-2,6-DAT/mPDA (3:1) copolyimide and 6FDA-2,6-DAT polyimide had high separation properties for H₂/N₂, O₂/N₂, CO₂/CH₄. Their H₂, O₂ and CO₂ permeability coefficients were 64.99 Barrer, 5.22 Barrer, 23.87 Barrer and 81.96 Barrer, 8.83 Barrer, 39.59 Barrer, respectively, at 35°C and 0.2 MPa (1 Barrer = 10⁻¹⁰ cm³ (STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹) and their ideal permselectivities of H₂/N₂, O₂/N₂ and CO₂/CH₄ were 69.61, 6.09, 63.92 and 53.45, 5.76, 57.41, respectively. Moreover, all of the copolyimides studied in this work

exhibited similar performance, lying on or above the existing upper bound trade-off lines between permselectivity and permeability. They may be utilized for commercial gas separation membrane materials.

Keywords 2, 2'-bis(3, 4'-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), copolyimide, permeability, gas separation

1 Introduction

The use of polymeric materials for gas separations has gone from a laboratory curiosity to a commercial reality within the past several decades. Polymer membranes are considered to be an effective technology for the separation of gaseous mixtures due to their high separation efficiency, low operating costs and simple operating procedures. The development of novel polymer membranes with higher gas permeabilities and permselectivities has received a lot of attention [1–4]. Aromatic polyimides are considered to be one of the most important classes of high-performance polymers because of their excellent thermal, mechanical, and electrical properties, chemical resistance as well as outstanding gas selectivities for gas pairs such as O₂/N₂ and CO₂/CH₄. Polyimide glassy polymers have been recognized as one of the most promising candidates as a gas-separation material [5].

In general, polyimides are obtained from condensation polymerization of two monomers, *i.e.* dianhydride and diamine moieties. When a diamine and a dianhydride are added into a dipolar aprotic solvent such as *N,N*-dimethylacetamide, poly(amic acid) is obtained rapidly at ambient temperatures. The cyclodehydration of poly(amic acid)s to polyimides can be readily achieved by means of chemical dehydration at ambient temperature. Commonly used reagents are acid anhydrides in dipolar aprotic solvents or in the presence of tertiary amines. Among the dehydrating agents used were acetic anhydride, propionic anhydride, *n*-butyric anhydride, benzoic anhydride and others. Among the amine catalysts used were pyridine,

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methylpyridines, lutidine, *N*-methylmorpholine, trialkylamines and others [6]. Gas transport properties through the polyimide membrane have been investigated extensively. Commercially viable materials must have both high permeability and high selectivity for the gases separation of interest. However, there still exists a tradeoff relationship between gas permeability and permselectivity for polymeric membranes. In recent years, the structure/permeability/selectivity relationships of polymers have become the objective of systematic studies in order to achieve a high permeability and a high selectivity. Many studies indicate that the following structural modifications are required in order to enhance the selectivity and permeability of polyimides, and possibly also of other glassy polymers, toward light gases:

- 1) The backbone chains must be stiffened by inhibiting their intrasegmental (rotational) mobility
- 2) Intersegmental packing of the polymer chains must be simultaneously prevented
- 3) Interchain interactions must be weakened and, if possible, eliminated.

Some aromatic polyimides that contain $-\text{C}(\text{CF}_3)_2-$ groups in their dianhydride moieties (*e.g.*, the 6FDA-based polyimides) have been found to be considerably more gas-selective than other glassy polymers with comparable permeabilities. 6FDA (hexafluorodianhydride)-based polyimides consistently deviate from the general relationship between permeability and permselectivity by showing systematically higher permselectivities at values of permeability equivalent to other polymers [7–9]. Fluorine-containing polyimides have received a great deal of attention because fluorine often lowers the thermal-expansion coefficient and gives increased solubility and lowers the dielectric constant. The most practical approach is to introduce flexible linkages between the aromatic rings in the diamine and dianhydride. Modified polyimides with flexible bonds that provide improved solubility have been successfully commercialized. Some of 6FDA polyimides have been employed to fabricate high performance membranes.

There are some methods to tailor the properties of polymers: blending, surface modification and copolymerization. Blending has been widely used in polymer modification. In heterogeneous blends, the morphology of the biphasic structure and the nature of the interface are the governing factors that affect the gas transport properties. In homogenous miscible blends, the gas transport properties are, however, highly dependent on the strength of the interactions between the two components. For membrane applications, blending modification would involve complicated phase behavior in membrane fabrication, as most polymers are immiscible. Membranes formed from crosslinked polyimides have improved environmental stability and superior gas selectivity than the corresponding uncrosslinked polyimide. But crosslinking reaction usually results in decreased solubility in organic

solvents as well as very high glass-transition temperatures. These properties make the materials difficult to fabricate by conventional techniques. To overcome these limitations, several kinds of structural modifications have been adopted. One direction was structural modifications of the polymer backbone such as the addition of bulky lateral substituents, flexible alkyl side chains and non-coplanar biphenylene moieties, and kinked comonomers have been utilized to modify the polymer properties, either by lowering the interchain interactions or by reducing the stiffness of the polymer backbone. Copolyimides offer the possibility of preparing membranes with gas permeabilities and selectivities not obtainable with homopolyimides. One may be able to tailor their gas separation properties by varying the monomer ratio [10–14].

This study investigated the relationship between the permeabilities and component ratios of 6FDA-mPDA and 6FDA-2,6-DAT. The reason for choosing these polyimides is that 6FDA-2,6-DAT has a little higher permeability, but a relatively low selectivity for a specific gas pair, while 6FDA-mPDA has a higher selectivity with a relatively low permeability. It is possible that a copolyimide can be made with a better combination of permeability and selectivity than either of the homopolymers for gas separation applications.

2 Experiments

2.1 Materials

The dianhydride monomer used in this study was 2,2'-bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). This monomer was obtained from Clariant Chemicals Co., Ltd., which was purified by vacuum sublimation. The diamine monomers used were: 2,6-diamine toluene (2,6-DAT) obtained from Sinopharm chemical reagent Co., which was purified by vacuum sublimation, and 1,3-phenylenediamine(mPDA) was obtained from Acros Organics Ltd., which was purified by recrystallization. *N*-Methyl-2-pyrrolidone (NMP) was purchased from Acros Organics Ltd. NMP was purified by vacuum distillation. Acetic anhydride and triethylamide were received from the Shenyang Chemical Reagent Factory and Shantou Xilong Chemical Factory, respectively, which were purified by distillation under nitrogen. Methanol was obtained from the Shenyang Chemical Reagent Factory and used as received.

2.2 Synthesis of 6FDA-2,6-DAT/mPDA polyimides

The homo- and co-polyimides were synthesized by a two-step method. Polyamic acids (PAA) were prepared by stoichiometric addition of solid 6FDA, in portions, to the diamine(s) contained in NMP. PAA solutions were made up to 20% solids. Reaction mixtures were stirred with a

mechanical EUROSTAR power control-visc stirrer in a nitrogen atmosphere at ambient temperature for 5 h. Then polyamic acids were imidized to form polyimides. The cyclization was achieved by chemical imidization under nitrogen purge at ambient temperature for 20 h through the addition of acetic anhydride (dehydrating agent) and triethylamine (catalyst). The polymer solution was precipitated with ethanol and then washed three times by ethanol and dried at 200°C in vacuum oven for 24 h. The example of synthesis of 6FDA-2,6-DAT/mPDA copolyimide is shown as Fig. 1.

2.3 Preparation of dense membranes

All polyimides were prepared as dense films. These films were obtained by a casting method. The appropriate amount of polyimides was dissolved in dry NMP to form 8 wt% solutions, and then filtered to remove non-dissolved materials and dust particles. After being degassed for 1 h, the polyimides solution was poured into a casting ring on leveled clean glass plates at 80°C. The whole plate was covered with a hood with a small gap to allow the solvent to slowly evaporate for about 12 h. Subsequently, the films were removed from the glass plates. The nascent films were dried in a vacuum oven at 100°C for 4 h to remove the residual solvent. The temperature was gradually increased at a heating rate of 1 K/min from 80°C to 250°C, and each membrane was annealed at 250°C for 24 h. The films were slowly cooled in an oven from 250°C to room temperature and then were stored in a desiccator for further tests and studies.

2.4 Characterization methods

2.4.1 FTIR

The FTIR-ATR is applied to confirm the polyimides formation from polyamic acids. The IR spectra for dense films were obtained by using a Thermo Nicolet NeXUS FTIR spectrometer. The scanning range was from 4000 cm^{-1} to 400 cm^{-1} .

2.4.2 DSC and TGA

Glass transition temperature (T_g) was determined from the second heating cycle by using a Mettler Toledo DSC822 differential scanning calorimetry (DSC). Temperature scanning including heating and cooling modes was in the range of 100–400°C with a rate of ± 5 K/min in nitrogen atmosphere. The 5% weight loss temperatures of copolyimides in dense film form were examined from ambient temperature to 900°C at a heating rate of 10 K/min by using a SHIMADZU DT-20B thermogravimetric analyzer in nitrogen atmosphere, and a sample size of 10 ± 1 mg was used.

2.4.3 Solubility

The solubility of copolyimides was evaluated using the following method: copolyimide powder of 20 mg was added into 1 mL of the solvent and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, the solubility was characterized.

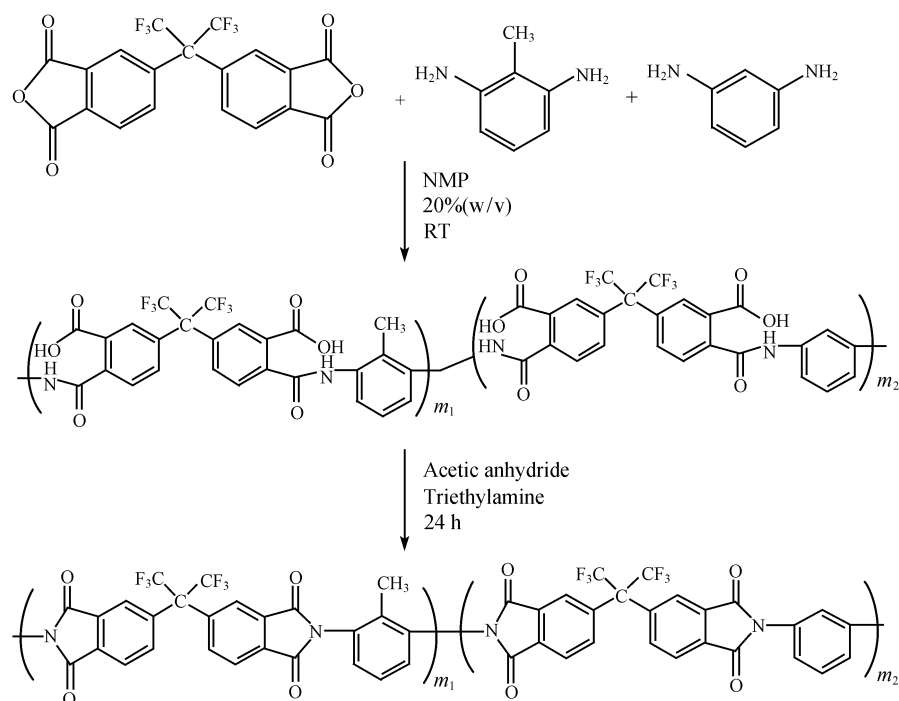


Fig. 1 Reaction scheme of copolyimides

2.4.4 Measurements of gas permeability

The gas transport properties were measured by using the variable pressure (constant volume) method. Permeation properties of H₂, O₂, N₂, CO₂ and CH₄ were measured. Ultrahigh-purity gases (99.99%) were used for all experiments. The membrane was mounted in a permeation cell prior to degassing the whole apparatus. Permeant gas was then introduced on the upstream side, and the permeant pressure on the downstream side was monitored using a MKS-Baratron pressure transducer. From the known steady-state permeation rate, pressure difference across the membrane, permeable area and film thickness, the permeability coefficient was determined (pure gas tests). The gas permeability coefficient, P (cm³ (STP) cm/cm² s cmHg), was determined by the following equation:

$$P = \frac{1}{760} \times \frac{V}{A} \times \frac{273.15}{273.15 + T} \times \frac{L}{760p} \times \frac{dp}{dt} \quad (1)$$

where A is the membrane area (cm²), L is the membrane thickness (cm), p is the upstream pressure (cmHg), V is the downstream volume (cm³), T is the absolute temperature (K), and dp/dt is the permeation rate (cmHg/s). The gas permeabilities of polymer membranes were characterized by a mean permeability coefficient with units of Barrer. 1 Barrer = 10⁻¹⁰ cm³ (STP)·cm/(cm²·s·cmHg).

The ideal permselectivity of a dense membrane for gas A to gas B is defined as follows:

$$\alpha_{A,B} = \frac{P_A}{P_B} \quad (2)$$

3 Results and discussion

3.1 FTIR spectra

Figure 2 shows the FTIR-ATR spectra of the 6FDA-2,6-DAT/mPDA polyimides dense films. It can be seen that the peaks at 1728 cm⁻¹ and 1787 cm⁻¹ correspond to the symmetric and asymmetric $\nu_{C=O}$ of imide respectively. The peak observed at 1358 cm⁻¹ was assigned to ν_{C-N} and the 1064 cm⁻¹ was assigned to imide ring. Moreover, there wasn't any peak around 3300 cm⁻¹ (N—H and —OH), that means the imidation was complete [15].

Table 1 Glass transition temperature and 5% weight loss temperature of copolyimides

PI	$T_g/^\circ\text{C}$	T_g (Calculated)/ $^\circ\text{C}$	5 wt% loss $T/^\circ\text{C}$
6FDA-2,6-DAT	334	—	531
6FDA-2,6-DAT/mPDA (3:1) ^a	327	325.57	533
6FDA-2,6-DAT/mPDA (1:1) ^a	319	317.26	537
6FDA-2,6-DAT/mPDA (1:3) ^a	310	309.07	540
6FDA-mPDA	301	—	548

^a In a molar ratio of diamines in a diamine mixture

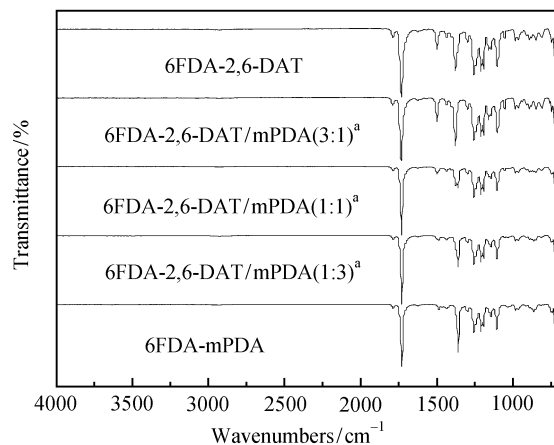


Fig. 2 FTIR-ATR spectra

3.2 Thermal Properties

All the copolyimides were assumed to be random copolymers because of the presence of a single glass transition temperature (T_g) in DSC traces (Table 1). Glass transition temperature increased with increase in 2,6-DAT content. The presence of methyl groups in 2,6-DAT moiety hinders the rotation of the phenyl ring of 2,6-DAT, whereas the phenyl ring of comonomer mPDA moves easily as there is no substitute group in its phenyl ring. A simple method to predict the glass transition temperature of random copolymers by the Fox equation is shown below [16]:

$$\frac{1}{T_g} = \frac{m_1}{T_{g1}} + \frac{m_2}{T_{g2}} \quad (3)$$

where m_1 and m_2 are the weight fractions, and T_{g1} and T_{g2} are the glass transition temperatures of homopolymers. Figure 3 compares the glass transition temperatures obtained from the DSC experiments and calculated from Fox equation. For the copolymers, the T_g s from experiments accord with those calculated from Fox equation. It may be due to the interaction between the two polymer segments. Temperature at which 5% weight loss is observed in nitrogen atmosphere is also given in Table 1. Copolyimides exhibit a single decomposition starting at a temperature above 500°C. The thermal stability generally decreases with increasing 2,6-DAT content.

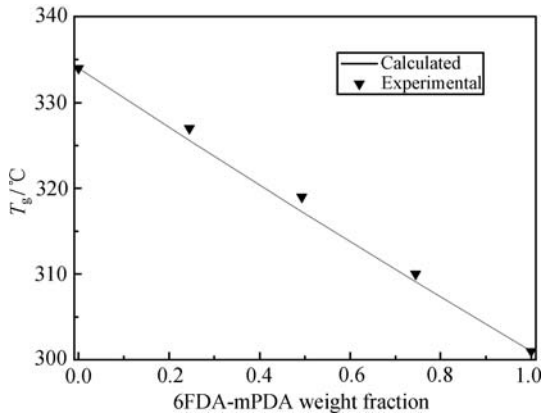


Fig. 3 T_g of 6FDA-2,6-DAT/mPDA copolyimides

3.3 Solubility

6FDA-2,6-DAT/mPDA polyimides were soluble in common solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), NMP, tetrahydrofuran (THF) and chloroform at ambient temperature, but were insoluble in acetone and methanol. Solubility level was not affected by copolymer composition.

3.4 Gas transport properties

The gas permeability coefficients, ideal selectivity of 6FDA-2,6-DAT/mPDA series polyimides for different gases measured at 35°C and 0.2 MPa are summarized in Table 2. It can be seen that the gas permeability coefficients decrease with the addition of mPDA, while the permselectivity of the gas pairs such as H_2/N_2 , O_2/N_2 and CO_2/CH_4 increased considerably. The gas permeability coefficients decrease in the following sequence: $P(H_2) > P(CO_2) > P(O_2) > P(N_2) > P(CH_4)$, which agrees well with the increasing order of kinetic diameters of the gas molecules. The gas transport properties of commercial polyimide Matrimid[®] 5218 and polyetherimide Ultem[®] 1000 are listed in Table 2 for comparison [20, 10].

The permeability coefficients of copolyimides can be calculated from the equation by Hopfenberg and Paul [17]:

$$\ln P_{\text{copolyimide}} = \phi_1 \ln P_1 + \phi_2 \ln P_2 \quad (4)$$

where ϕ is the volume fraction, $P_{\text{copolyimide}}$ and P are the permeability coefficients for copolyimide and homopolyimide respectively (subscripts 1 and 2 indicated the two homopolymers).

The ideal permselectivity of the copolyimides can be calculated from the equation:

$$\ln \frac{P_A}{P_B} = \phi_1 \ln \frac{P_{A1}}{P_{B1}} + \phi_2 \ln \frac{P_{A2}}{P_{B2}} \quad (5)$$

where $\frac{P_A}{P_B}$ is the calculated result of ideal permselectivity for copolyimide; $\frac{P_{A1}}{P_{B1}}$ and $\frac{P_{A2}}{P_{B2}}$ are the ideal permselectivities for homopolymer 1 and 2 in gas A and B respectively.

Figure 4 shows the effect of 6FDA-mPDA content on the permeability coefficient of 6FDA-2,6-DAT/mPDA copolyimides. A comparison for the permeability coefficients obtained from experiments and calculated

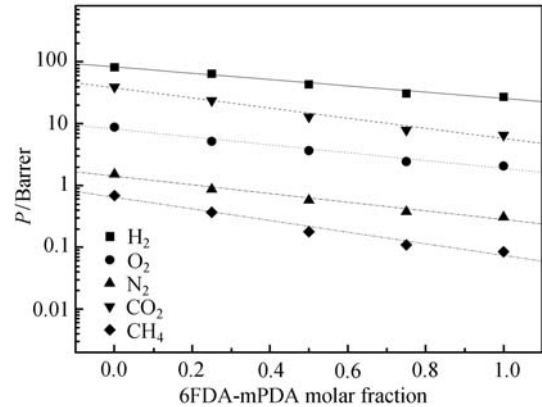


Fig. 4 Effect of 6FDA-mPDA content on the permeability coefficients

Table 2 Gas Permeability 6FDA-TMPDA/mPDA polyimides at 35°C, 0.2 MPa

PI	P/Barrer					α		
	H_2	O_2	N_2	CO_2	CH_4	H_2/N_2	O_2/N_2	CO_2/CH_4
6FDA-2,6-DAT	81.96	8.83	1.53	39.59	0.69	53.45	5.76	57.41
6FDA-2,6-DAT ^a	102	10.3	1.83	34.0	–	59.7	5.04	–
6FDA-2,6-DAT/mPDA(3:1)	64.99	5.22	0.87	23.87	0.37	69.61	6.09	63.92
6FDA-2,6-DAT/mPDA(1:1)	43.56	3.67	0.58	12.94	0.18	78.36	6.33	71.13
6FDA-2,6-DAT/mPDA(1:3)	31.02	2.45	0.38	7.96	0.11	82.50	6.52	72.35
6FDA-mPDA	27.32	2.08	0.31	6.55	0.085	89.31	6.81	77.07
Matrimid [®] 5218 Polyimide ^b	22.5 ^d	1.32	0.18	–	–	122 ^e	7.2	–
Ultem [®] 1000 Polyetherimide ^c	9.4 ^d	0.41	0.05	–	–	184 ^e	8.0	–

¹ Barrer = $10^{-10} \text{ cm}^3 (\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$, ^a data from reference [19]; ^b tested at 25°C; ^c tested at 35°C; ^d permeability coefficient for He; ^e ideal selective factor for He/ N_2

from semilogarithmic equation (4) is also given in Fig. 4. Figure 5 is the effect of 6FDA-mPDA content on the permselectivities of 6FDA-2,6-DAT/mPDA copolyimides. The broken line in Fig. 5 illustrates the results calculated from Eq. (5). The permeability coefficients and the ideal permselectivities from experiments are in good accordance with the predicted values as the same dependency as Refs. [18, 19].

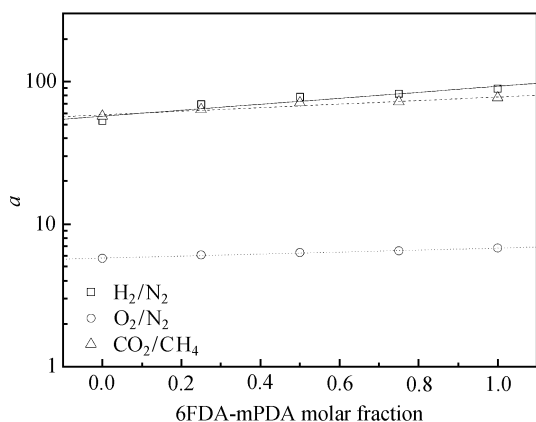


Fig. 5 Effect of 6FDA-mPDA content on the ideal selectivity

There is a general relationship reported in the literatures that as the permeability of gas A increases, its selectivity decreases. In 1991, Robeson reported trends that are applicable to all permeation measurements. The boundary is defined as the “upper bound”, which is the upper limit of gas separation performance for current state of the art membranes [21]. The gas separation properties of polymer exceeding or approaching the “upper bound” are suitable for commercial application. The performances of 6FDA-2,6-DAT/mPDA copolyimides are compared to the “upper bound” trade-off lines (Figs. 6–8). As shown, all of the copolyimides exhibit gases separation performance, near, lying on or above the upper bound limit.

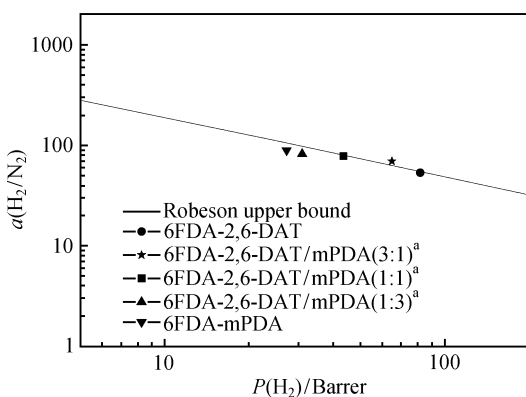


Fig. 6 Performances of 6FDA-2,6-DAT/mPDA polyimides compared to H_2/N_2 trade-off limit

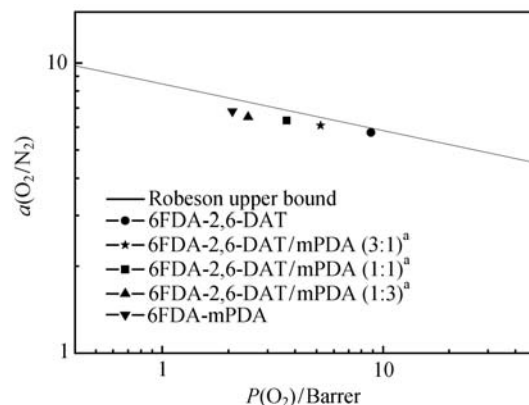


Fig. 7 Performances of 6FDA-2,6-DAT/mPDA polyimides compared to O_2/N_2 trade-off limit

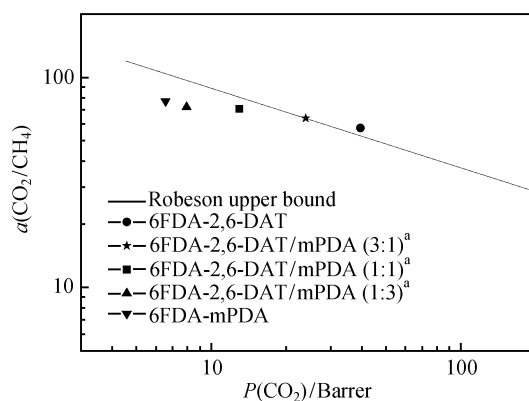


Fig. 8 Performances of 6FDA-2,6-DAT/mPDA polyimides compared to CO_2/CH_4 trade-off limit

4 Conclusion

6FDA-2,6-DAT/mPDA copolyimides were investigated systematically by varying the diamine ratios. All the copolyimides were soluble in most of the common solvents. The gas permeability coefficients decreased with increasing mPDA content. However, the permselectivity of gas pairs such as H_2/N_2 , O_2/N_2 , CO_2/CH_4 was enhanced with the incorporation of mPDA moiety. The permeability coefficients of H_2 , O_2 , N_2 , CO_2 and CH_4 were found to decrease with the increasing order of kinetic diameters of the penetrant gases. Moreover, all of the prepared copolyimides in this work exhibited performance close to, lying on or above the existing upper bound trade-off lines between permselectivity and permeability.

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