

PERVAPORATION SEPARATION FOR TOLUENE/*n*-HEPTANE MIXTURE BY POLYIMIDE MEMBRANES CONTAINING FLUORINE*

Hong Ye, Ji-ding Li^{**}, Yang-zheng Lin, Jian Chen and Cui-xian Chen
Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract Five kinds of polyimides were synthesized using five dianhydrides (including 2,2-bis[4-(3,4-dicarboxyphenoxy)-phenyl] propane dianhydride (BPADA), 3,3',4,4'-diphenylsulfone-tetracarboxylic dianhydride (DSDA), 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA), 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA), and 4,4'-oxydiphthalic dianhydride (ODPA)) and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF) via the two-step method that included polyaddition to form the polyamic acid and subsequent chemical imidization at ambient temperature. The structures of polyimides were characterized by FTIR and NMR. The thermal properties were characterized by DSC and TGA. All five kinds of polyimides showed good thermal properties and solubility in organic solvents such as DMF, DMAc, NMP and THF at room temperature. The pervaporation (PV) experiments of polyimides for toluene/*n*-heptane mixture were carried out, and all the polyimides showed selective permeation towards toluene. The fluxes of 6FDA-BDAF, DSDA-BDAF, HQDPA-BDAF and ODPA-BDAF at 80°C were 1.08, 0.96, 1.77 and 0.10 kg·μm/(m²·h), and the separation factors were 5.44, 1.64, 1.28 and 11.44, respectively. The increasing feed temperature resulted in higher flux and lower separation factor of the 6FDA-BDAF membrane.

Keywords: Polyimide; Membrane; Pervaporation; Toluene.

INTRODUCTION

Pervaporation (PV) is a membrane separation process involving the partial vaporization of a liquid mixture through a membrane whose downstream side is usually kept under vacuum^[1]. It has been studied extensively because of the potential industrial utility for separation of azeotropic, close boiling, isomeric or heat-sensitive liquid mixtures. PV is considered to be a promising alternative to conventional energy intensive technologies like extractive or azeotropic distillation in liquid mixtures separation for being economical, safe and eco-friendly^[2–6]. The separation of compounds using PV method can be classified into three major fields viz. (i) dehydration of aqueous organic mixtures, (ii) removal of trace volatile organic compounds from aqueous solution and (iii) separation of organic/organic solvent mixtures. The separation of organic/organic mixtures, especially aromatic/aliphatic hydrocarbon mixtures is among the most important and difficult processes in petrochemical industry^[7, 8].

Polyimides are known for their excellent dielectric, adhesive and mechanical properties, dimension and thermal stability, and have been widely employed in microelectronic fields^[9–11]. However, their poor solubilities in organic solvents result in the difficult processings, thereby limit their extensive applications. The polyimides containing fluorine groups such as hexafluoroisopropylidene, trifluoromethyl or trifluoromethoxy groups were found to have increased free volume and improved solubilities^[12]. Furthermore, the polyimides containing

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^{**}Corresponding author: Ji-ding Li (李继定), E-mail: lijiding@mail.thu.edu.cn

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fluorine had potential as ideal materials not only in gas separation^[13], but also in pervaporation^[14–16]. Particularly, some studies showed that polyimides containing fluorine were attractive in the pervaporation separation of aromatic/aliphatic mixtures^[17, 18], but few studies focused on the relationship of structures and PV performances of polyimides containing fluorine.

In this paper, five kinds of organosoluble polyimides were prepared using dianhydrides (including 2,2-bis[4-(3,4-dicarboxyphenoxy)-phenyl] propane dianhydride (BPADA), 3,3',4,4'-diphenylsulfone-tetracarboxylic dianhydride (DSDA), 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA), 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA) and 4,4'-oxydiphthalic dianhydride (ODPA)) and one diamine of 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF) *via* the two-step method that included polyaddition to form the polyamic acid and subsequent chemical imidization at ambient temperature. The polyimide membranes were characterized by FTIR, NMR, DSC and TGA. The density and solubility of polyimides containing fluorine were investigated. The PV experiments of the polyimide membranes for toluene/*n*-heptane mixture were also carried out and the relationships of structures and PV performances of polyimides were discussed.

EXPERIMENTAL

Materials

Triethylamine, acetic anhydride, carbon tetrachloride, ethanol, toluene, *n*-heptane, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and chloroform (CHCl₃) were obtained from Beijing Yili Chemicals Co. Ltd., and DMAc was purified on distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 nm). 2,2-Bis[4-(3,4-dicarboxyphenoxy)-phenyl] propane dianhydride (BPADA), 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA), 4,4'-oxydiphthalic dianhydride (ODPA) and 2,2-bis[4-(4-aminophenoxy)-phenyl] hexafluoropropane (BDAF) were obtained from Shanghai Ruitu Electronic Materials Co. Ltd.. 3,3',4,4'-Diphenylsulfone-tetracarboxylic dianhydride (DSDA) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) were obtained from Fluka Chemical Co. All the five dianhydrides were purified by sublimation, and the diamine of BDAF was dried under vacuum before using.

Synthesis of Polyimides Containing Fluorine

The polyimides used in this paper were synthesized by a two-step method. The diamine and DMAc were poured into a three-necked flask equipped with an addition funnel and a N₂ inlet. After the diamine was completely dissolved, the stoichiometric amount of dianhydride was added all at once. The solution concentration was about 15% based on the monomer weight. The condensation polymerization was carried out for at least 8 h at room temperature to give a viscous polyamic acid solution. Then the chemical imidization was carried out with excessive acetic anhydride as the dehydrating agent and triethylamine as the catalyst at room temperature for 14–16 h. The molar ratio of acetic anhydride to the amic acid of poly(amic acid) was 2 and that of triethylamine was 0.3. The final polyimide solution was poured into distilled water. The precipitate was collected by filtration, washed with water, and dried in vacuum at 150°C for 24 h.

Preparation of Homogeneous Polyimide Membranes

Polyimide membranes were prepared by a casting method. The polyimides were dissolved in the solvent to form 5 wt% membrane solutions, and then filtered over a 25 µm metal filter to remove any impurities existing in the raw polymer materials. The solutions thus obtained were subsequently cast on glass plates and thermally dried to remove the solvent. Finally the resulting membranes were stripped from the glass in water. In this study, the thicknesses of polyimide membranes were all 12–22 µm.

Characterization of Homogeneous Polyimide Membranes

The structures of polyimides were characterized by FT-IR spectra (Nicolet IR560), ¹H-NMR and ¹⁹F-NMR spectra using the solvent of DMSO-*d*₆ and a Varic ECA-600 spectrometer. The inherent viscosities of the

polyimides in DMAc solution (conc. 0.5 g/dL) were measured with an Ubbelohde viscometer at 30°C. The glass transition temperature (T_g) of the polyimides was measured by using a differential scanning calorimeter (Seiko DSC6200) with a heating rate 10 K/min in the range of 100–450°C under N₂ atmosphere. Thermogravimetric analysis (TGA) was performed on a TGA-2050 thermal analyzer using a heating rate of 20 K/min in N₂ within the temperature range of 30–900°C. The thicknesses of the polyimide membranes were determined by using a micro screw gauge. The density was measured by a floating method using mixtures of ethanol and carbon tetrachloride.

Solubility Measurements

The solubility measurements were carried out in DMF, DMAc, NMP, DMSO, THF, CHCl₃ and the feed mixture of PV experiments viz. toluene and *n*-heptane mixture (the mass fraction of toluene was 20%), and the concentration of polyimides in different mixtures was 15% by weight. According to the state of the mixtures after kept at ambient temperature for 24 h, the solubilities of polyimides in the solvents were divided into four types: (1) soluble, *i.e.*, the polyimide dissolved in the solvent completely and the mixture became homogeneous, (2) soluble after heating, *i.e.*, the polyimide could dissolve in the solvent completely after heating the mixture to 40°C, (3) swelling, *i.e.*, the mixture became a gel, and (4) non-soluble, the polyimide could not dissolve in the solvent.

PV Experiments

The pervaporation performances of polyimide membranes were tested by using an apparatus developed in our laboratory as shown in Fig. 1. The feed was heated and circulated from the feed tank (volume of $2.5 \times 10^{-3} \text{ m}^3$) through the upstream side of the membrane cell by a pump with adjustable function of flow rate. A membrane supported by a porous sintered stainless steel in the permeate side was mounted in the pervaporation cell. The measurements were carried out for aromatic/aliphatic hydrocarbon mixtures in which the content of aromatic hydrocarbon was 20 wt%. The feed mixture was maintained at temperature between 65°C and 85°C using a thermostat. The effective area of the membrane was $2.2 \times 10^{-3} \text{ m}^2$. Vacuum on the permeate side was maintained below 500 Pa and monitored with a digital vacuumeter. Two cold traps were set in parallel to allow the collection of permeate without rupture of the vacuum. The concentrations of permeate and feed mixture were analyzed by gas chromatography. The permeability was evaluated by the normalized flux (J , kg·μm/(m²·h)) as defined in Eq. (1) to compare pervaporation performances of membranes with different thickness.

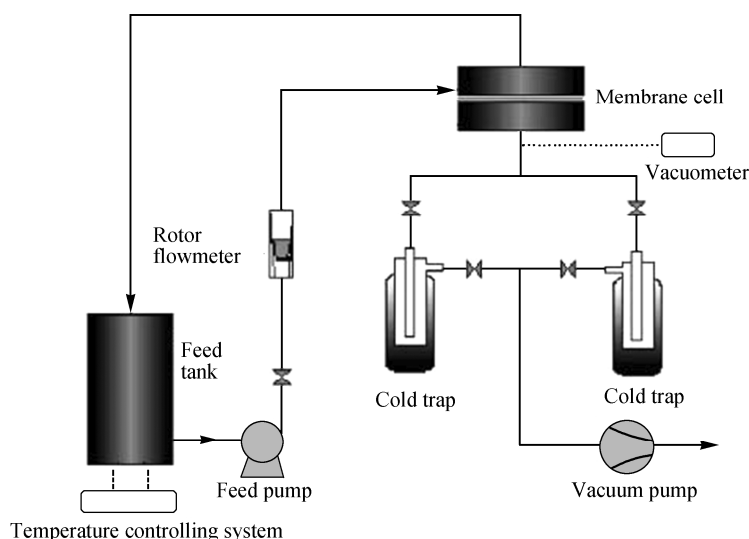


Fig. 1 Pervaporation performances test apparatus

The ^1H -NMR spectrum of 6FDA-BDAF is shown in Fig. 4. The aromatic protons were detected around $\delta = 7.1$ – 8.2 depending on the position in the aromatic ring as expected. The assignment of each proton was also given in Fig. 4 according to the position and intensity of the peaks. And these peaks were in good agreement with the proposed polymer structures.

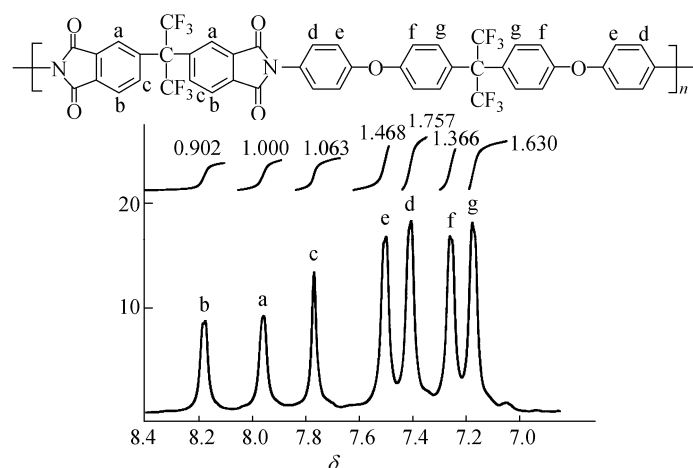


Fig. 4 ^1H -NMR spectrum of 6FDA-BDAF

Besides, the ^{19}F -NMR analysis of 6FDA-BDAF is given in Fig. 5. The two sharp peaks were observed at $\delta = -63.3344$ and -62.7786 . The peak at $\delta = -63.3344$ owed to the fluorine in 6FDA, and the signal at -62.7786 ascribed to the fluorine in BDAF. This result provided another evidence for the successful synthesis of 6FDA-BDAF. The other kinds of synthesized polyimides containing fluorine in this study also obtained the expected structures.

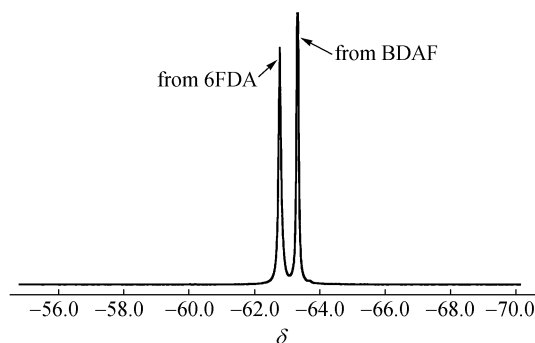


Fig. 5 ^{19}F -NMR spectrum of 6FDA-BDAF

Properties of Polyimide Membranes

The physical and thermal properties of the polyimides are shown in Table 1. For the polyimides with the same diamine of BDAF, the values of density increased following the order of BPADA, 6FDA, DSDA, HQDPA and ODP. To some extent, the density symbolized the package level of polymer chains. And the lower the value of the density was, the looser the package of polymer chains was. The side groups of $-\text{CH}_3$ and $-\text{CF}_3$ in BPADA and 6FDA acted as factors and did not allow efficient packing by steric hindrance, thereby reducing the packing density. The bridge groups of dianhydride including sulfone in DSDA and phenoxy in HQDPA also seemed to disrupt chain packing, but their effects on densities were weaker than side groups.

The polyimides synthesized in this study also exhibited high thermal properties as shown by T_g and T_d listed in Table 1. DSDA-BDAF obtained the highest T_g (256°C) among the five polyimides, because the sulfone groups provided the strong interaction between the polymer chains. Although the side groups like $-\text{CH}_3$

and $-\text{CF}_3$ in BPADA and 6FDA produced the steric hindrance for the mobility of polymer chains, their approximately symmetric configuration in structure would facilitate the rotation of polymer segments and result in the lower T_g . The thermal decomposition temperature (T_d) over 500°C also could be observed in Table 1, which indicated that all of these polyimides containing fluorine showed excellent thermal stabilities, and could be used at high temperature.

Table 1. Properties of the polyimides

Polyimides	Density (g/mL)	Inherent viscosity (dL/g)	T_g (°C)	T_d (°C)
BPADA-BDAF	1.287	0.56	178	537
6FDA-BDAF	1.316	0.82	235	565
DSDA-BDAF	1.348	0.53	256	540
HQDPA-BDAF	1.358	1.17	243	522
ODPA-BDAF	1.399	1.05	220	517

Solubility of Polyimides

The solubilities of polyimides in organic solvents such as NMP, DMAc, DMF, and DMSO were investigated. And the results are shown in Table 2. It could be seen that all polyimides were easily dissolved in polar nonproton solvents such as DMF, DMAc and NMP, and in weakly polar solvents such as THF at room temperature. The good solubilities of the polyimides were attributed to the large side groups of $-\text{CF}_3$ from BDAF, which were also advantageous for the membrane preparation. The BPADA-BDAF showed good solubility in almost all solvents shown in Table 2, which could be explained from the viewpoint of molecular structure. BPADA-BDAF had not only the side groups such as $-\text{CF}_3$ or $-\text{CH}_3$, but also the more tortuous structure such as phenoxy in the backbones than the others. These groups could enlarge intersegmental distance and facilitate the diffusion of solvent into polymer, which was in agreement with the lowest density of BPADA-BDAF in Table 1.

Table 2. Solubility of the polyimides^a

PI	DMF	DMAc	NMP	DMSO	THF	Chloroform	Toluene	Mixture ^b
BPADA-BDAF	++	++	++	±	++	+	++	+
6FDA-BDAF	++	++	++	++	++	++	±	—
DSDA-BDAF	++	++	++	++	++	++	±	—
HQDPA-BDAF	++	++	++	±	++	++	—	—
ODPA-BDAF	++	++	++	+	++	++	—	—

^a++ Soluble; + Soluble after heating the mixtures to 40°C; ± Swelling; — Non-soluble;

^bMixture is the toluene/*n*-heptane mixture used in PV experiments and the mass fraction of toluene is 20%

On the other hand, the toluene was obviously not the good solvent for the polyimides except for BPADA-BDAF as shown in Table 2. Especially, most of the polyimides were insoluble in the feed mixtures containing 20 wt% toluene. It suggested that they could be used in pervaporation test of this study with enough resistance of swelling.

PV Performance of Polyimides

The PV performances of four polyimides of 6FDA-BDAF, DSDA-BDAF, HQDPA-BDAF and ODPA-BDAF for toluene/*n*-heptane mixture were investigated with the results listed in Table 3. All the polyimide membranes exhibited toluene selectivity.

Among these four polyimide membranes, the ODPA-BDAF membranes exhibited the lowest flux but the highest separation factor. There were no substitute groups like $-\text{CF}_3$ in the backbone of ODPA. Thereby the best packing of polymer chain was obtained over the other polyimides and revealed by the highest density as shown in Table 1. The higher packing density would restrict the swelling of membranes and resulted in the lower flux and higher selectivity. Both of the HQDPA-BDAF and ODPA-BDAF had the structure of phenoxy and $-\text{CF}_3$. But the separation factor of ODPA-BDAF was much higher than that of HQDPA-BDAF. That could be explained from the affinity to toluene and molecular structure of polyimide membranes. From the viewpoint of affinity, HQDPA-BDAF had more benzene rings in polymer chains than ODPA-BDAF, so it could be

speculated that HQDPA-BDAF membranes had better affinity to toluene than ODPa-BDAF. That was advantageous for the selective separation of toluene. But from the viewpoint of polymer structures, the additional phenoxy groups would make the polymer chain more tortuous and flexible, which also would provide the more free volume for the small molecules to penetrate and increase the permeability of HQDPA-BDAF membranes. Furthermore, the “structure effect” seemed to be a predominant factor, thus the much higher flux and lower separation factor were obtained from HQDPA-BDAF than ODPa-BDAF.

Table 3. Pervaporation performances of polyimide membranes at 80°C

Polyimides	J (kg·μm/(m ² ·h))	α	c_t^a (%)
6FDA-BDAF	1.08	5.44	56.95
DSDA-BDAF	0.96	1.64	29.08
HQDPA-BDAF	1.77	1.28	24.24
ODPA-BDAF	0.10	11.44	74.09

^a c_t is the concentration of toluene in permeate

The 6FDA-BDAF membranes were preferable for separation of toluene/*n*-heptane mixture on consideration of permeability and selectivity. They obtained the flux of 1.08 kg·μm/(m²·h) and the separation factor of 5.44. The —CF₃ groups in 6FDA not only facilitated the diffusion of penetrants due to the disrupted chain packing, but also provided the good affinity to toluene due to electronegative C—F bonds. Meanwhile DSDA-BDAF membranes obtained the unsatisfactory separation performance, and that was probably resulted from lower molecular weight as suggested by inherent viscosity (see Table 1) than other polyimides.

Effect of Feed Temperature on 6FDA-BDAF Membranes

The 6FDA-BDAF membranes were chosen to carry out the pervaporation experiments under different temperatures in order to investigate the temperature dependence of PV performances. As shown in Table 4, the increasing feed temperature resulted in higher flux and lower separation factor of 6FDA-BDAF membranes. The higher temperature brought the increase of the mobility and flexibility of polymer chains, which increased the free volume of polymer. All of these would promote the diffusion of small molecules through the polymer membrane. Furthermore, the dependence of permeability of feed components on temperature is portrayed in Fig. 6. It was found that the permeability of 6FDA-BDAF membranes decreased exponentially with reciprocal of feed temperature following an Arrhenius type relation shown as follows:

$$J = J_0 e^{-\frac{E_a}{RT}} \quad (3)$$

Where J is the flux of membranes, J_0 is pre-exponential factor, E_a is the activation energy of permeation for feed components, T is the feed absolute temperature and R is the gas constant.

Table 4. Effect of feed temperature on pervaporation performance

Feed temperature (°C)	Toluene content in permeate (wt%)	J (kg·μm/(m ² ·h))	α
65	62.97	0.66	6.49
70	62.19	0.81	6.47
75	59.95	0.87	5.64
80	59.14	1.08	5.44
85	58.35	1.16	5.28

The permeation activation energy of PV could be evaluated from the slopes, and the results are listed in Table 5. The activation energy decreased following the order of $E_{a,h} > E_{a,m} > E_{a,t}$. That was to say, the partial permeation flux of *n*-heptane was more sensitive to the change of feed temperature. It implied that the *n*-heptane flux increased more quickly than the toluene flux with the increased operating temperature. And it would result in the decrease of the separation factor of 6FDA-BDAF membranes with the operating temperature increasing as shown in Table 4.

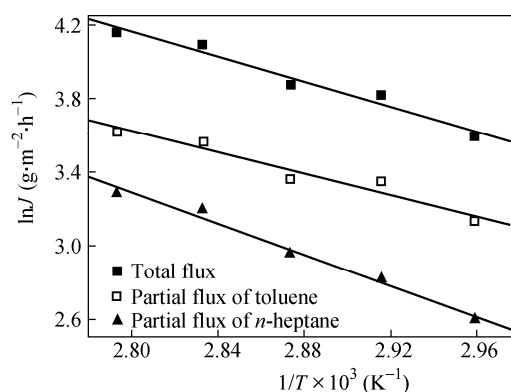


Fig. 6 Dependence of permeability of feed components on temperature

Table 5. Activation energy (kJ/mol) of penetrants in 6FDA-BDAF membranes

E_a	$E_{a,m}$	$E_{a,t}$	$E_{a,h}$
Value	28.40	24.09	35.09

$E_{a,m}$: the activation energy of feed mixture; $E_{a,t}$: the activation energy of toluene;
 $E_{a,h}$: the activation energy of n-heptane

CONCLUSIONS

Five kinds of polyimide membranes containing fluorine were prepared using the dianhydrides (including BPADA, DSDA, HQDPA, ODPA and 6FDA) and BDAF. These polyimide materials showed good solubilities and excellent thermal stabilities. Besides, all the polyimide membranes in this study showed selective permeation towards toluene in toluene/n-heptane mixture during PV experiments. The fluxes of 6FDA-BDAF, DSDA-BDAF, HQDPA-BDAF and ODPA-BDAF at 80°C were 1.08, 0.96, 1.77 and 0.10 kg·μm/(m²·h), respectively, and the separation factors were 5.44, 1.64, 1.28 and 11.44, respectively. The increasing feed temperature resulted in higher flux and lower separation factor of 6FDA-BDAF membranes.

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