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Synthesis of Polyimides Containing Fluorine and Their Pervaporation Performances to Aromatic/Aliphatic Hydrocarbon Mixtures

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Two kinds of polyimides containing fluorine were synthesized based on dianhydride of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and diamines including 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF) and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) using solution condensation and following chemical imidization. The structures of 6FDA-BDAF and 6FDA-BAPP were characterized by FT-IR, NMR, and XRD. Their glass transition temperatures characterized by DSC were in the range of 235–251°C, and the initial decomposition temperatures determined by TGA were over 540°C. The membranes of polyimide thus obtained were employed in pervaporation separation of aromatic/aliphatic mixtures. 6FDA-BDAF membranes obtained better separation performances than 6FDA-BAPP and had a flux of 0.66 kg · μm/m^2 · h and separation factor of 6.49 for toluene/n-heptane (20/80 wt.%) at 80°C. The effects of the fluorine group on polyimides properties and separation performances were investigated.

Keywords: polyimide; synthesis; pervaporation; aromatic hydrocarbon

1 Introduction

Naphtha is an important feedstock in the petrochemical industry and mainly composed of aromatic and aliphatic hydrocarbons. Aromatic hydrocarbons in naphtha are not only responsible for reduced efficiency of cracking process for ethylene production, but also potential threats of public health when naphtha is used for gasoline fraction. Recently, the separation of aromatics from aromatic/aliphatic hydrocarbon mixtures is receiving worldwide concern and extensively studied (1, 2). Traditionally, extractive distillation and azeotropic distillation are used to remove aromatic hydrocarbons present in naphtha (3–5). However, these conventional technologies often suffer from complicated processes and high operation costs, which are attributed to the post-treatment of additional azeotropic solvents. So there is a significant incentive to explore new processes for the separation.

Pervaporation (PV) is a promising alternative to the separation of aromatics from aromatic/aliphatic hydrocarbon mixtures. It offers many advantages, such as high separation efficiency, low energy consumption and simple operation (6–9). Furthermore, it is very suitable for the separation of azeotropic and close boiling mixtures, because the separation mechanism is not based on relative volatilitis but the difference in sorption and diffusion properties of feed components towards a membrane. The efficiency of the pervaporation process is mainly determined by membrane materials, so it is of great importance to improve new materials for pervaporation separation of aromatic/aliphatic hydrocarbon mixtures.

Polyimides (PI) are known for their excellent dielectric, adhesive, dimension, thermal stability and mechanical properties, and have been widely employed in the microelectronic fields (10–12). However, their poor solubilities in organic solvents result in difficult processing, thereby limiting their extensive applications. The polyimides containing fluorine groups such as hexafluoroisopropylidine, trifluoromethyl or trifluoromethoxy group were found to have increased free volume and improved solubilities (13). Furthermore, the polyimides containing fluorine had potential as ideal materials not only in gas separation (14–16), but also in pervaporation (17, 18). In particular, some studies showed that polyimides containing fluorine were attractive in the pervaporation separation of aromatic/aliphatic mixtures (19–21).

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In this paper, two kinds of novel polyimides with different fluorine content were synthesized. Their chemical structures and properties were characterized by FT-IR, NMR, DSC, etc., and pervaporation performances of the polyimide membranes were investigated for aromatic/aliphatic hydrocarbon mixtures and the effects of -CF_3 group on polyimides properties and separation performances for aromatic/aliphatic mixtures were discussed.

2 Experimental

2.1 Materials

2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (99%, Fluka Chemical Co.) was purified by sublimation. 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF, 99%) and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP, 99%) were obtained from Shanghai Ruitu Electronic Materials Co. Ltd. and dried under vacuum before use. N,N-dimethyl acetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). Other reagents (chemical reagent) were used as received.

2.2 Synthesis of Polyimides

The polyimides used in this paper were synthesized by a two-step method. The diamines and DMAc were poured into a three-necked flask equipped with an addition funnel and a N_2 inlet. After the diamines were completely dissolved, a stoichiometric amount of 6FDA was added all at once. The solution concentration was about 15% based on 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.

2.3 Membrane Preparation

Polyimide membranes were prepared by a casting method. The polyimides were dissolved in DMAc (unless otherwise specified) 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. The thickness of polyimide membranes was 15∼25 μm.

2.4 Characterization of Polyimides and Polyimide Membranes

The structures of polyimides were characterized by FT-IR spectra (Nicolet IR560) and ^{1}H-NMR and ^{19}F-NMR spectra using the solvent of DMSO-d_6 and a Varic ECA-600 spectrometer.

The molecular weights of the polyimides were determined by gel-permeation chromatography with tetrahydrofuran as a solvent and polystyrene as a standard sample. The inherent viscosities of the polyimides in DMAc solution (conc. 0.5 g/dl) were measured with a Ubbelohde viscometer at 30°C. Both polyimides of 6FDA-BDAF and 6FDA-BAPP were readily soluble in DMF, DMAc, NMP, DMSO and THF.

The glass transition temperature (Tg) of the polyimides was measured by differential scanning calorimeter (Seiko DSC6200) with a heating rate 10°C/min in the range of 100–450°C under N_2 atmosphere. Thermogravimetric analysis (TGA) was performed on a TGA-2050 thermal analyzer using a heating rate of 20°C/min in N_2 within the temperature range of 30–900°C.

The morphologies of the polyimides were characterized by a German Bruker D8 Advance X-ray diffractormeter (XRD) using CuKα. The mechanical properties of polyimide membranes were measured on an electronic universal testing machine (WDT-10) at room temperature with film specimens at a rate of 50 mm/min. The contact angles for water of polyimide membranes were determined by a OCA20 contact angle system (Data Physics Co.). 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, carbon tetrachloride.

Fraction free volume (*FFV*) of the polyimides was calculated using group contribution method (22) and defined as follows (23):

$$FFV = \frac{M/\rho - V_d}{M/\rho} \tag{1}$$

where M is the molecular weight of a polymer repeat unit, ρ is the measured density, and V_d is the estimated van der Waals volume.

Solubility parameter (δ) was estimated by a group contribution method and defined as follows (24):

$$\delta = (\delta_D^2 + \delta_P^2 + \delta_H^2)^{1/2} \tag{2}$$

where δ_D is a dispersive forces contribution, δ_P is a polar contribution, and δ_H is a hydrogen bonding contribution.

2.5 Pervaporation Experiments

The pervaporation performances of polyimide membranes were tested by using an apparatus developed in our laboratory as shown in Figure 1. The feed was heated and circulated from the feed tank (volume of 2.5×10^{-3} m^3) through the upstream side of the membrane cell by a pump with an adjustable function of flow rate. A membrane supported by a

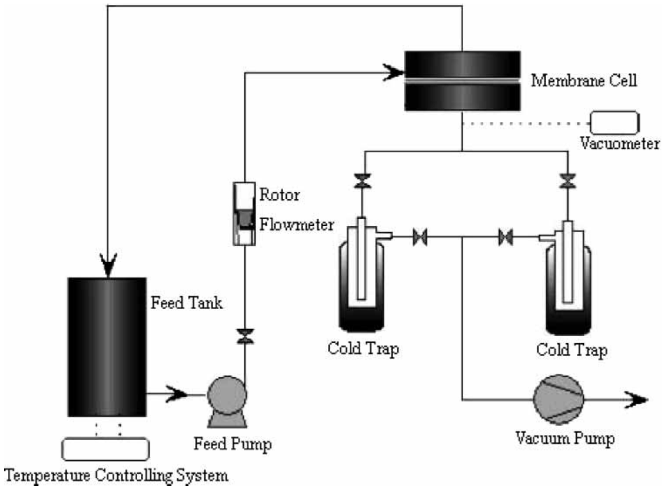

Fig. 1. Pervaporation performances test apparatus.

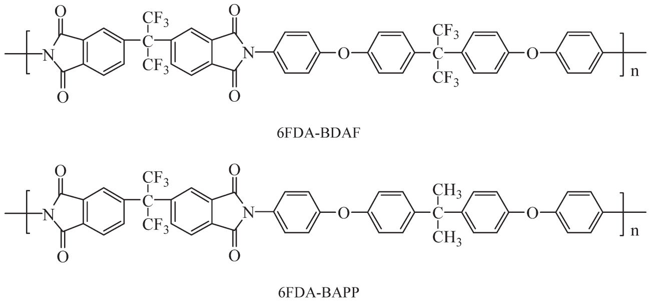

Fig. 2. Structures of 6FDA-BDAF and 6FDA-BAPP.

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 a temperature between 65°C and 85°C using a thermostat. The effective area of the membrane was 2.2×10^{-3} m^2. Vacuum on the permeate side was maintained below 500 Pa and was monitored with a digital vacuometer. Two cold traps were set in parallel allowing 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, $kg \cdot \mu m/m^2 \cdot h$) as defined in (3) to compare pervaporation performances of membranes with different thickness.

$$J = \frac{Q}{A \cdot T} \cdot l \tag{3}$$

where Q (kg) is the total mass of permeate collected through the effective area of membrane (A, m^2) during time T (h), l is membrane thickness.

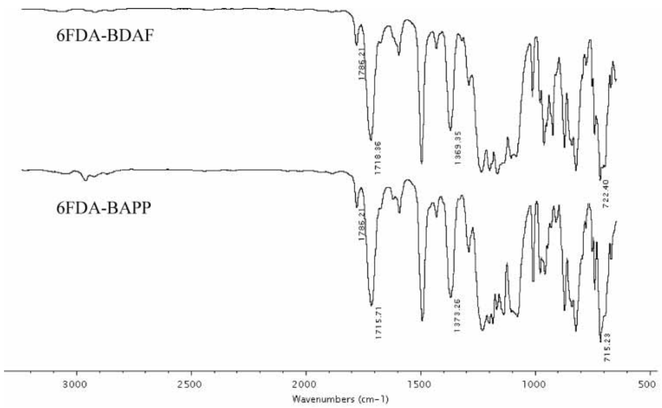

Fig. 3. FT-IR spectra of 6FDA-BDAF and 6FDA-BAPP.

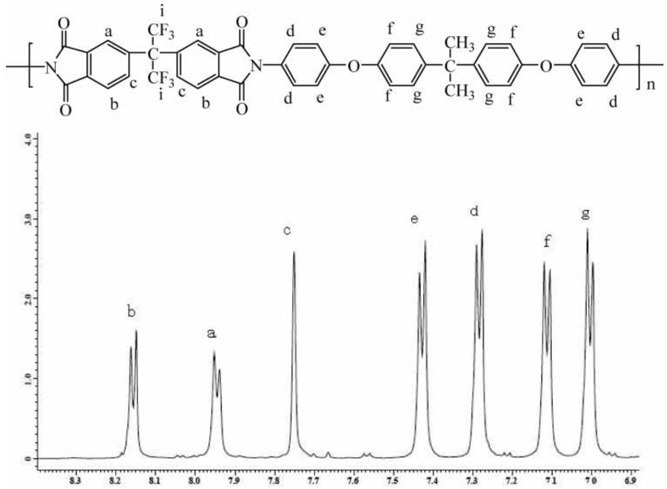

Fig. 4 ^{1}H-NMR spectra of 6FDA-BAPP.

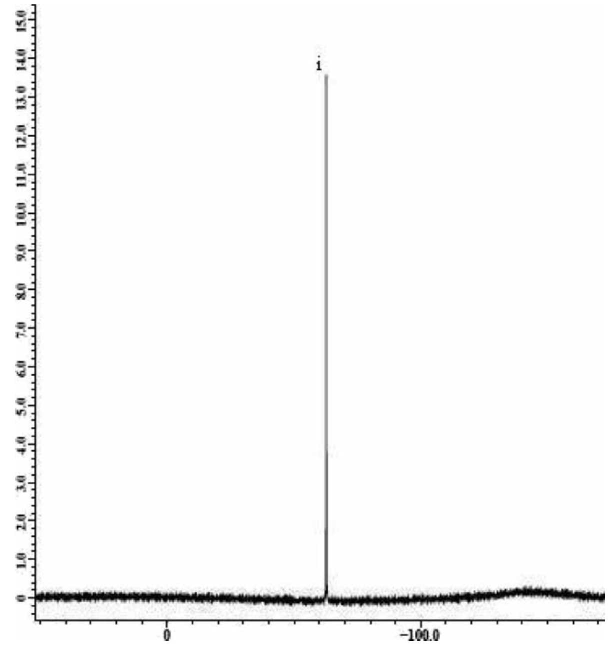

Fig. 5. ^{19}F-NMR spectra of 6FDA-BAPP.

Table 1. Physical properties of 6FDA-BDAF and 6FDA-BAPP

Polyimide	$\overline{Mw}$ (g/mol)	$\overline{Mw}/\overline{Mn}$	Density (g/ml)	Inherent viscosity (dl/g)	Contact angle	Tensile stress (MPa)	Elongation (%)
6FDA-BDAF	102100	2.77	1.353	0.82	79.0	83.62	7.17
6FDA-BAPP	61330	2.34	1.301	0.59	81.7	66.31	8.74

$\overline{Mw}$: weight-average molecular weight; $\overline{Mn}$: number-average molecular weight.

The selectivity of membrane was demonstrated by the separation factor and defined as:

$$\alpha = \frac{Y_A \cdot X_B}{X_A \cdot Y_B} \tag{4}$$

where Y_A and Y_B represent the weight fractions of aromatic and aliphatic hydrocarbons in the downstream permeate, and X_A and X_B represent those in the feed mixture, respectively.

3 Results and Discussion

3.1 *Structure Characterization of the Polyimides Containing Fluorine*

The structures of 6FDA-BDAF and 6FDA-BAPP synthesized in this study were shown in Figure 2. The difference between 6FDA-BDAF and 6FDA-BAPP was that 6FDA-BDAF had two more fluorine substitutions -CF_3 instead of -CH_3 group compared to 6FDA-BAPP.

The degrees of imidization of 6FDA-BDAF and 6FDA-BAPP were measured by FT-IR and shown in Figure 3. As demonstrated in FT-IR spectra, the characteristic polyimide absorption bands of 6FDA-BDAF and 6FDA-BAPP were found at around 1785 cm^{-1} (C═O asymmetric stretching), 1718 cm^{-1} (C═O symmetric stretching), 720 cm^{-1} (imide ring deformation) and 1370 cm^{-1} (C-N stretching), with the disappearance of absorption band near 3363 cm^{-1} (N-H stretching) and 1650 cm^{-1} (amide C═O strength). It was shown that the complete imidization of two polyimides was achieved. 6FDA-BAPP also showed absorption band at 2960 cm^{-1} (-CH_3 asymmetric stretching).

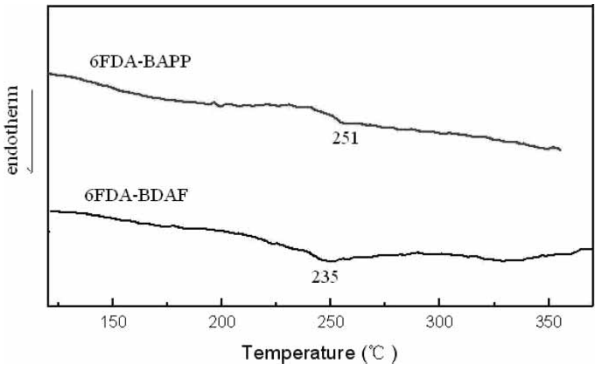

Fig. 6. DSC curves of 6FDA-BDAF and 6FDA-BAPP.

The ^{1}H-NMR spectra of 6FDA-BAPP was shown in Figure 4. The aromatic protons were detected around 7.1–8.2 ppm depending on the position in the aromatic ring as expected. All hydrogen peaks in the ^{1}H-NMR were in good agreement with the proposed polymer structure as indicated in Figure 4.

Besides, the ^{19}F-NMR analysis of 6FDA-BAPP was given in Figure 5. A single characteristic peak was observed indicating the same chemical environment of F atom in 6FDA-BAPP, which provided more evidence for successful synthesis of polyimide containing fluorine.

The physical properties of 6FDA-BDAF and 6FDA-BAPP, including the molecular weight, inherent viscosity, density, contact angle and mechanical properties were shown in Table 1.

3.2 *Properties of the Polyimides Containing Fluorine*

3.1.1 *Thermal Properties of the Polyimides Containing Fluorine*

The glass transition temperatures of 6FDA-BDAF and 6FDA-BAPP were determined by DSC (Figure 6). As shown in DSC curves, the glass transition temperature (Tg) of 6FDA-BDAF was 235°C and that of 6FDA-BAPP was 251°C.

The thermal stabilities of 6FDA-BDAF and 6FDA-BAPP were investigated by TGA as shown in Figure 7. 6FDA-BDAF and 6FDA-BAPP underwent 10% weight loss (T_{10}) at 545°C and 543°C, the fastest weight loss at 565°C and 548°C. Furthermore, the residual weight fractions at 900°C

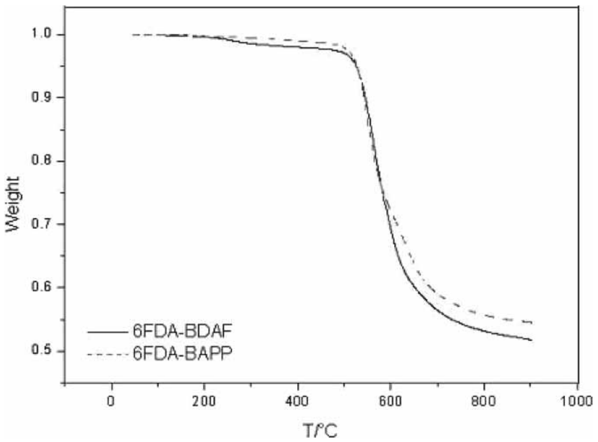

Fig. 7. TGA thermograms of 6FDA-BDAF and 6FDA-BAPP.

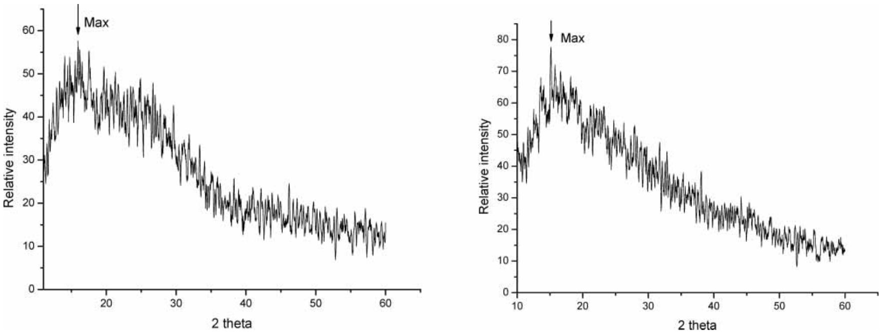

Fig. 8. XRD spectra of two polyimides (left figure: 6FDA; right figure: 6FDA-BAPP).

Table 2. The mean intersegmental distance of 6FDA-BDAF and 6FDA-BAPP

PI	2θ	d-spacing (Å)
6FDA-BDAF	15.92	5.56
6FDA-BAPP	15.18	5.83

Table 3. Effects of fluorine content and different feed mixtures on pervaporation performances

PI	Fluorine content (wt.%)	Feed mixture (80°C)	J ($kg \cdot \mu m/m^2 \cdot h$)	α
6FDA-BDAF	25.21	toluene/n-heptane	1.08	5.44
		benzene/n-heptane	1.20	3.10
6FDA-BAPP	14.31	toluene/n-heptane	0.54	4.67
		benzene/n-heptane	0.34	2.64

of two polyimides were 51.8% and 54.5%, respectively as shown in Figure 7.

6FDA-BDAF had two more trifluoromethyl (CF_3) groups than 6FDA-BAPP, while thermal properties of polyimides were not greatly affected by the number of CF_3 groups. Besides, thermal properties of the polyimides with fluorine groups were as excellent as those without fluorine groups such as ODPA-BAPP with Tg of 215°C and T_{10} of 555°C (25). That was probably because aromatic rings and imide groups in the backbones were mainly responsible for the mobility and chemical stability of the polymer chains, while the effects of side groups like -CF_3 and -CH_3 were small.

3.1.2 Morphology of 6FDA-BDAF and 6FDA-BAPP

The morphologies of 6FDA-BDAF and 6FDA-BAPP were investigated by XRD as shown in Figure 8. Both spectras of polyimide membranes displayed a broad band around $2\theta = 15^\circ$ indicating the amorphous structures due to the disrupted chain packing. The mean intersegmental distance that was represented by d-spacing were calculated from the XRD spectra and listed in Table 2. 6FDA-BDAF showed smaller d-spacing than 6FDA-BAPP, which was in agreement with larger density listed in Table 1. The probable reason was that the hindrance effect of the -CF_3- groups would increase the interactions between polymer chains.

3.2 Pervaporation Performances

3.2.1 Effects of Fluorine Content and Different Feed Mixtures

The effects of fluorine content of polyimides and different feed mixtures on pervaporation performances were illustrated in Table 3. As expected, both polyimides containing fluorine showed selective permeation towards aromatic hydrocarbons.

Table 4. Fraction of free volume (FFV) and solubility parameters (δ) of feed components and polyimides

Compound	V_d (cm^3/mol)	FFV (%)	Solubility parameter ($(MPa)^{1/2}$) δ_D	δ_P	δ_H	δ
Benzene	89.4	—	18.4	0	2.0	18.6
Toluene	106.8	—	18.0	1.4	2.0	18.2
n-Heptane	147.4	—	15.3	0	0	15.3
6FDA-BDAF	517	27.00	21.67	7.01	5.70	23.48
6FDA-BAPP	469	29.73	23.16	7.72	5.99	25.14

V_d: van der Waals volume; δ: Hansen solubility parameter, δ_D: dispersive forces contribution, δ_P: polar contribution, δ_H: hydrogen bonding contribution.

Table 5. Effect of casting solvent on pervaporation performances

Solvent	Molar volume (cm^3/mol)	Boiling point (°C)	J ($kg \cdot \mu m/m^2 \cdot h$)	α
DMF	77.04	153	0.64	3.52
DMAc	92.35	165	1.08	5.44
NMP	96.06	204	1.27	4.36

Membrane: 6FDA-BDAF; Feed: toluene/n-heptane mixture (20/80 wt.%) (80°C).

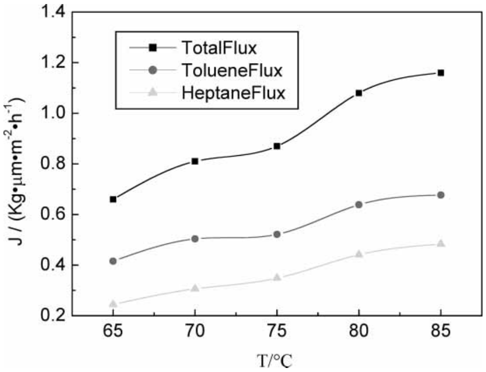

Fig. 9. Effect of feed temperature on permeability of 6FDA-BDAF membrane for toluene/n-heptane mixture.

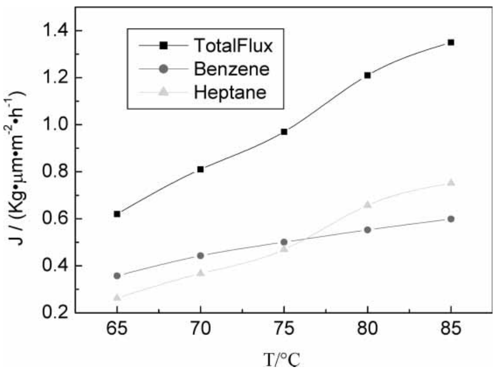

Fig. 11. Effect of feed temperature on permeability of 6FDA-BDAF membrane for benzene/n-heptane mixture.

It could be explained in terms of solubility parameters shown in Table 4. The solubility parameters indicated that the hydrogen bonding component (δ_H) of benzene and toluene were stronger than that of n-heptane. Besides, the solubility parameters of aromatics were closer to the polyimides than n-heptane. Therefore, aromatic hydrocarbons showed stronger affinity to polar macromolecules than aliphatic hydrocarbons, and a polymer such as polyimide possessing polar groups facilitated the solution and diffusion of aromatics in the membrane.

It also can be seen from Table 3 that the polyimide membranes derived from 6FDA-BDAF obtained better pervaporation performances than those from 6FDA-BAPP under the same feed mixture. In particular, the total flux of the 6FDA-BDAF membrane was found to be about 2 times that of 6FDA-BAPP when the feed mixture was a toluene/n-heptane mixture.

That could be explained from two sides. On one hand, the surfaces of 6FDA-BDAF membranes had more polarity than those of 6FDA-BAPP, as characterized by contact angle data shown in Table 1, which was more advantageous to the sorption of aromatic hydrocarbon molecule in feed mixture. On the other hand, as presented in Table 4, the solubility parameters of aromatic compounds were closer to 6FDA-BDAF in contrast to 6FDA-BAPP, which indicated more favorable solubility of aromatics in membranes. The better aromatic affinity of 6FDA-BDAF was probably due to more fluorine content from -CF_3 groups in the structures, which was because there were great interactions between electronegative C-F bond and benzene ring.

Besides, higher separation factors of polyimide membranes were obtained towards toluene than benzene as shown in Table 3. Toluene had more polarity as seen from δ_P in Table 4 than benzene, so it likely had better affinity to polar membrane materials such as polyimides.

3.2.2 *Effect of Casting Solvent on Pervaporation Performances*

The effects of casting solvents on pervaporation performances were tested as in Table 5. The result showed that the

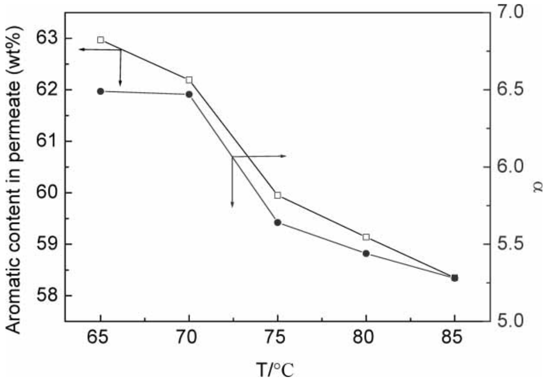

Fig. 10. Effect of feed temperature on selectivity of 6FDA-BDAF membrane for toluene/n-heptane mixture.

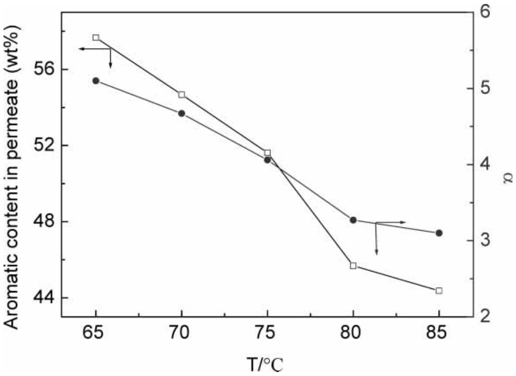

Fig. 12. Effect of feed temperature on selectivity of 6FDA-BDAF membrane for benzene/n-heptane mixture.

total flux increased with the molar volume of solvents increasing. So the solvent imprints left in membrane were likely controlled by the molar volume of solvent molecules.

3.2.3 Effect of Feed Temperature on Pervaporation Performances of 6FDA-BDAF Membranes

The effects of feed temperature on permeability of 6FDA-BDAF membranes were shown in Figures 9 and 11, and temperature dependence of selectivity was portrayed in Figures 10 and 12. All results showed increased flux and decreased separation factor with feed temperature increasing. The decreasing extent of separation factor in benzene/n-heptane mixture was comparatively more than toluene/n-heptane mixture, which could be due to rapidly increasing of n-heptane flux with temperature (see Figure 11). The increased flux was caused by the enhanced mobility of the polymer segments, while the decrease selectivity was attributed to the increasing degree of swelling of the polyimide membranes with increased temperature.

4 Conclusions

The novel polyimides containing fluorine, 6FDA-BDAF and 6FDA-BAPP, were successfully synthesized via solution condensation and chemical imidization. The polyimides thus obtained were revealed an amorphous structure and good solubility in DMF, DMAc, and NMP. The glass transition temperatures and initial decomposition temperatures of 6FDA-BDAF and 6FDA-BAPP were determined over 230°C and 540°C respectively. Both membranes of 6FDA-BDAF and 6FDA-BAPP showed selective permeation towards aromatic hydrocarbons in pervaporation separation of aromatic/aliphatic hydrocarbon mixtures. The polyimide membranes derived from 6FDA-BDAF showed better pervaporation performances than those from 6FDA-BAPP, and the flux of $0.66\ \mathrm{kg} \cdot \mu\mathrm{m/m^2} \cdot \mathrm{h}$ and separation factor of 6.49 for toluene/n-heptane mixture at 65°C were obtained. The increasing feed temperature resulted in higher flux and lower separation factor of 6FDA-BDAF membrane. Furthermore, the separation factor of 6FDA-BDAF was decreased a little for toluene/n-heptane mixture instead of obviously in benzene/n-heptane mixture with temperature increasing.

5 Acknowledgements

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