

Synthesis of Polyimides Containing Fluorine for Pervaporation Separation of Toluene/n-Heptane Mixtures

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ABSTRACT: Four kinds of polyimides containing fluorine were successfully synthesized based on various dianhydrides including 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA), 4,4'-oxydiphthalic dianhydride (ODPA) and 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA), and various diamines including 2,2-bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (BDAF) and 2,2-bis[4-(4-aminophenoxy)phenyl] propylene (BAPP). The polyimides (6FDA-BAPP, 6FDA-BDAF, ODPA-BDAF, HQDPA-BDAF) were prepared according to a two-step method, low temperature polycondensation with total monomers content 15wt% in DMAc and next chemical imidization of viscous poly(amic acid)s. The polyimides thus obtained were characterized by FT-IR, NMR, DSC and so on. The results showed that the polyimides had expected structures, excellent thermal properties and good solubilities in strong polar solvents such as DMF, DMAc and NMP. Furthermore, the pervaporation (PV) performances of these polyimide membranes prepared by solution casting were investigated for separating aromatic from non-aromatic hydrocarbon. All the polyimide membranes showed permeabilities and selectivities towards toluene from n-heptane. Especially 6FDA-BDAF and 6FDA-BAPP membranes had better PV performances than others. And 6FDA-BDAF membranes had a specific permeation flux of $1.18 \text{ kg} \cdot \mu\text{m} / \text{m}^2 \cdot \text{h}$ and separation factor of 5.28, while 6FDA-BAPP membranes had $1.15 \text{ kg} \cdot \mu\text{m} / \text{m}^2 \cdot \text{h}$ and 3.43 for 20wt% toluene in the toluene/n-heptane mixtures at 85°C. With the feed temperatures increasing, the flux of the 6FDA-BDAF membranes was enhanced from $0.66 \text{ kg} \cdot \mu\text{m} / \text{m}^2 \cdot \text{h}$ to $1.18 \text{ kg} \cdot \mu\text{m} / \text{m}^2 \cdot \text{h}$, but the separation factor was reduced from 6.49 to 5.28.

Key words: synthesis, polyimide, membrane, pervaporation

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1. Introduction

In recent years, separation of organic-organic mixtures has been receiving more and more attentions. Especially the separation of aromatic/aliphatic mixtures is extensively studied for its industrial and environmental significance [1-2]. Pervaporation (PV) is an economical, clean and simple process compared with conventional technologies, which seems to be very suitable for this separation because it is based on not the relative volatility but difference in sorption and diffusion properties of the components towards membrane.

The key component of the pervaporation process is the membrane material, which determines the separation performances. Aromatic polyimides (PI) materials are well known for their excellent dielectric insulation properties and high heat and solvent resistance [3]. The polyimides have been attractive not only in the field of gas separation [4-7], but also in the pervaporation of aromatic/aliphatic mixtures [8-11].

The polyimide containing $-CF_3$ group derived from monomer like 6FDA, is found to have high free volume and restricted chain mobility, which is good for permselectivity of the membranes [12-13]. In this paper, four kinds of polyimides containing fluorine were synthesized via a two-step method. And the structures and properties of polyimides were characterized by FT-IR, NMR and other measurements. The pervaporation performances for toluene/n-heptane mixtures were also investigated.

2. Experimental

2.1 Materials

2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, 99%) was purchase from Fluka Chemical Co.. 2,2-bis [4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF, 99%), 2,2-bis [4-(4-aminophenoxy)phenyl] propypane (BAPP, 99%), 4,4'-oxydiphthalic dianhydride (ODPA, 99%) and 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA, 99%) were obtained from Shanghai EMST Electronic Material Co. Ltd.. All the dianhydrides and diamines were purified before use. N, N-dimethyl acetamide (DMAc) was distilled under reduced pressure over calcium hydride and stored over molecular sieves (4Å). Other reagents were used as received.

2.2 Synthesis of polyimides

All polyimides were prepared from the two-step route. A three-necked flask equipped with an addition funnel and a N_2 inlet was charged with a solution of diamine in DMAc, then dianhydride was added all at once. The mole ratio and solid content of diamine/dianhydride mixture were 1:1 and 15%, respectively. The reaction mixture was reacted for 8-12 h at room temperature in N_2 atmosphere providing a viscous polyamic acid solution. The chemical imidization was carried out with acetic anhydride and triethylamine at room temperature for 14-18 h. The reaction mixture was then added to distilled water. The precipitate was collected by filtration, washed

with water, and dried in vacuo at 160°C to obtain the polyimides solid.

2.3 Preparation of dense flat sheet membranes

Polyimides dense membranes were prepared by a casting method using a 3-5wt% solution of polyimides in DMAc. After allowing the polymer to dissolve in the DMAc overnight, the solution was filtered over a 25 µm metal filter to remove any impurities existing in the raw polymer material. The solution was subsequently cast on a glass plate. The specimens produced were thermally dried to remove the solvent and then stripped from the glass. The thickness of the obtained membrane was determined by a micro screw gauge and was found to be approximately 15~20µm.

2.4 Characterization of membrane materials and membranes

The polyimides were analyzed by Fourier transform infrared (FT-IR) spectra, and were recorded on a Nicolet IR560 spectrometer with polymer film. Spectra in the optical range of 400-4000 cm⁻¹ were obtained by averaging 32 scans at a resolution of 4cm⁻¹. The solubility was determined by dissolving the polyimides in several solvents at room temperature for 24 h. The inherent viscosities of the polyimides in DMAc solution (conc.0.5g/dl) were measured with a Ubbelohde viscometer at 30°C. 1H-NMR spectras were registered using a Varic ECA-600 spectrometer, using DMSO-d6 as a solvent. The ¹H chemical shifts were calibrated by using tetramethylsilane (TMS). Differential scanning calorimeter (DSC) was used to measure glass transition temperature (Tg). Samples of approximately 10 mg in weight were sealed in hermetic aluminum pans and scanned in the calorimeter with a heating rate 10°C/min in the range of 100-450°C under N₂ atmosphere. The physical properties of four polyimides were shown in the table.

Tab.1 Physical properties of four polyimides

Polyimides	Density(g/ml,25°C)	η _{inh} (dl/g)
6FDA-BDAF	1.353	0.82
6FDA-BAPP	1.301	0.59
ODPA-BDAF	1.365	1.05
HQDPA-BDAF	1.358	1.17

2.5 Pervaporation

The membrane separation performance was analyzed by pervaporation using special test equipment, as shown in Fig.1. The measurements were carried out for toluene/n-heptane (weight ratio: 20/80) mixtures. The concentrations of permeate and feed were analyzed by gas chromatography. The pervaporation performances were evaluated by the separation factor (α) and the permeation flux (F). The permeation flux was calculated using the expression:

$$F = \frac{Q}{(A \times T)} \quad (\text{kg/m}^2 \cdot \text{h})$$

Where Q (kg) is the total mass of permeate collected through the effective area of membrane (A, m²) during time T (h) after the state has been reached. In order to

compare the pervaporation characteristics of membranes having different membrane thicknesses, the normalized flux ($\text{kg}\cdot\mu\text{m}/\text{m}^2\cdot\text{h}$) was used.

The separation factor is defined by

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

Where Y_A and Y_B represent the weight fractions of toluene and n-heptane in the permeate, and X_A and X_B those in the feed, respectively.

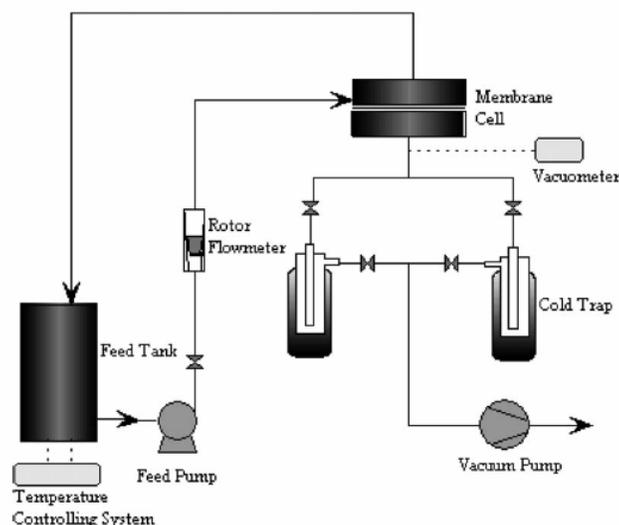
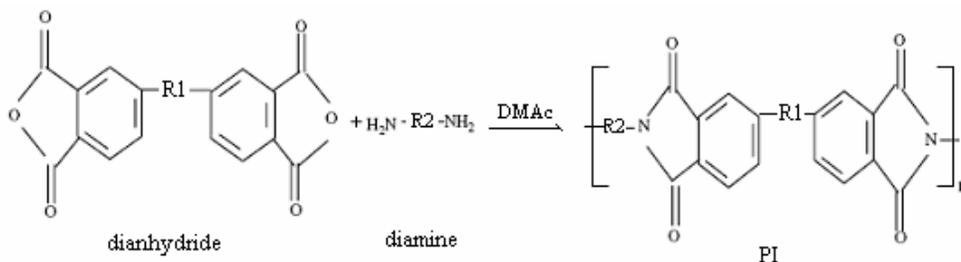


Fig.1 Pervaporation performances evaluating apparatus

3. Results and discussion

3.1 Characterization of membrane materials and membranes

The polyimides were prepared by the conventional two-step polymerization method, involving ring-opening polyaddition forming poly(amic acid) and subsequently chemical cyclodehydration (Fig.2). In order to obtain a high molecular weight poly(amic acid), the monomer purity and solvent dryness are extremely critical. In addition, the process of the monomer addition also plays an important role in successful polymerization. In our research, four polyimides, 6FDA-BDAF, 6FDA-BAPP, ODA-BDAF and HQDPA-BDAF, were Synthesized.



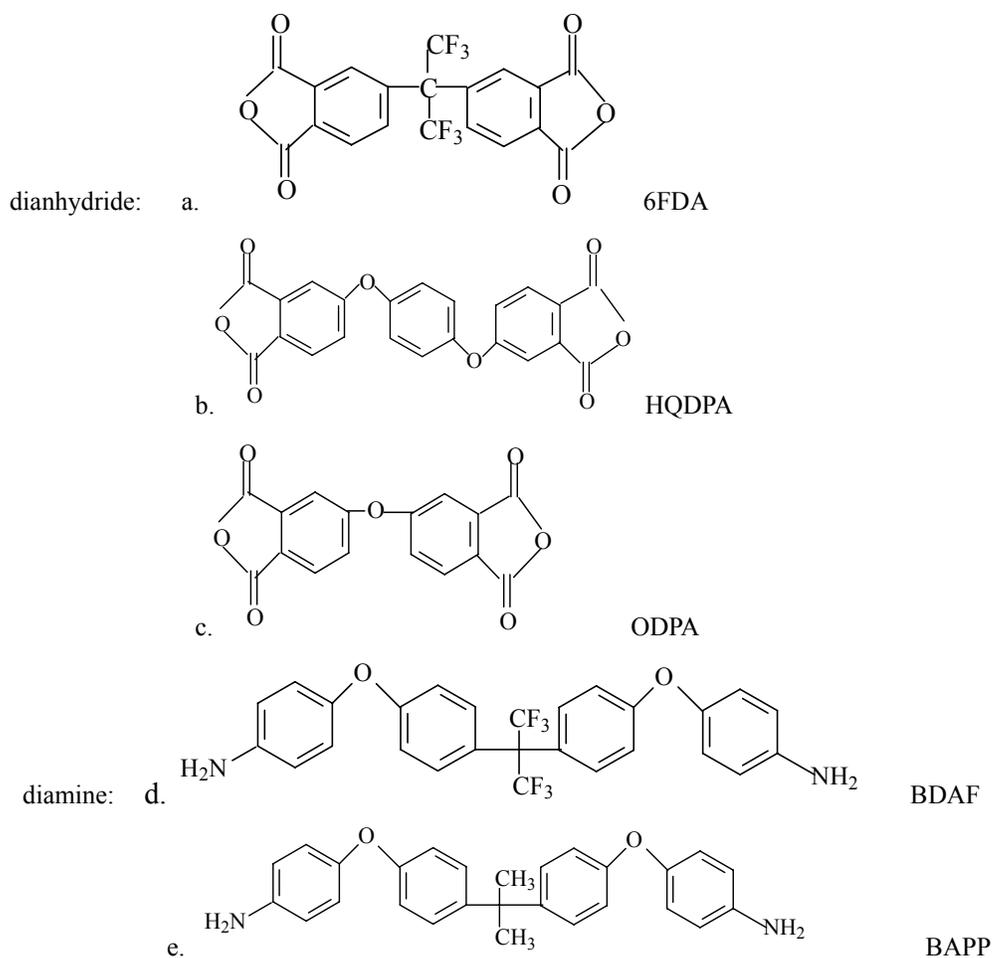


Fig.2 Synthesis of the polyimides

FT-IR measures were used to confirm a complete chemical imidization of the polyimides. As shown in the FT-IR spectrum, two polymers showed imide carbonyl peaks at 1780 cm^{-1} (C=O asymmetric stretching), at 1724 cm^{-1} (C=O symmetric stretching) and at 725 cm^{-1} (C=O banding), with the C–N stretching peak at 1365 cm^{-1} , but no amide groups near 3363 cm^{-1} (N–H stretching) and 1650 cm^{-1} (amide C=O strength), and this indicated that the polyimides had been well imidized.

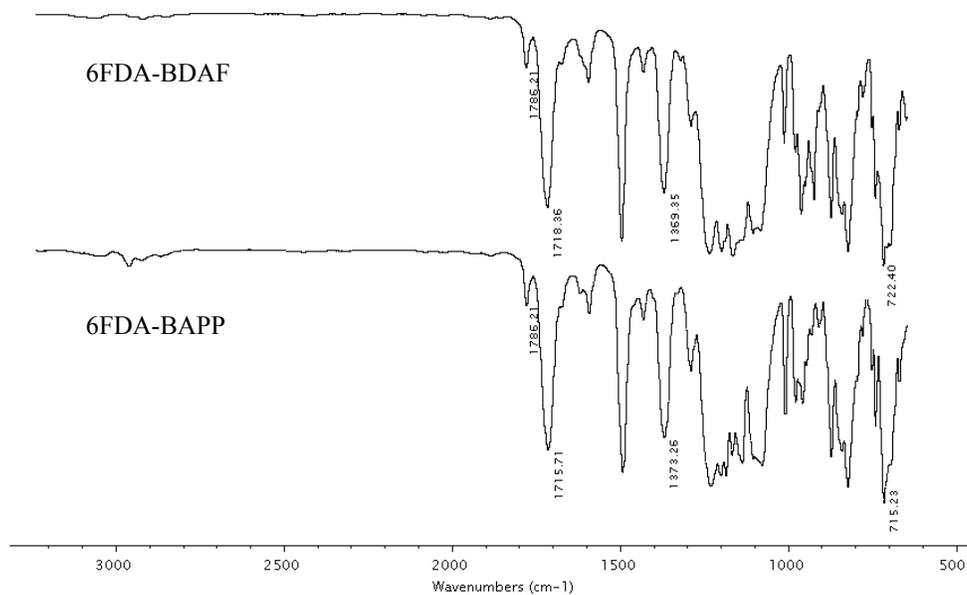


Fig. 3 FI-IR spectrum of two polyimides

NMR measures were used to obtain more information about the structures of the polyimides. Fig.4 shows the $^1\text{H-NMR}$ spectra of 6FDA-BDAF in DMSO- d_6 . As expected, the aromatic protons were detected around 7.2–8.2 ppm, depending on the position in the aromatic ring. The aromatic carboxylic acid proton and aromatic amide proton peak (10.5 ppm) completely disappeared, which meant that the poly(amic acid) was completely converted into polyimide. On the other hand, all hydrogen peaks in the $^1\text{H NMR}$ were in good agreement with the proposed polymer structure. In $^{19}\text{F-NMR}$ analysis (Fig.5), two characteristic peaks were observed at -62.7786 and -63.3344 ppm, providing evidence for the successful synthesis of 6FDA-BDAF.

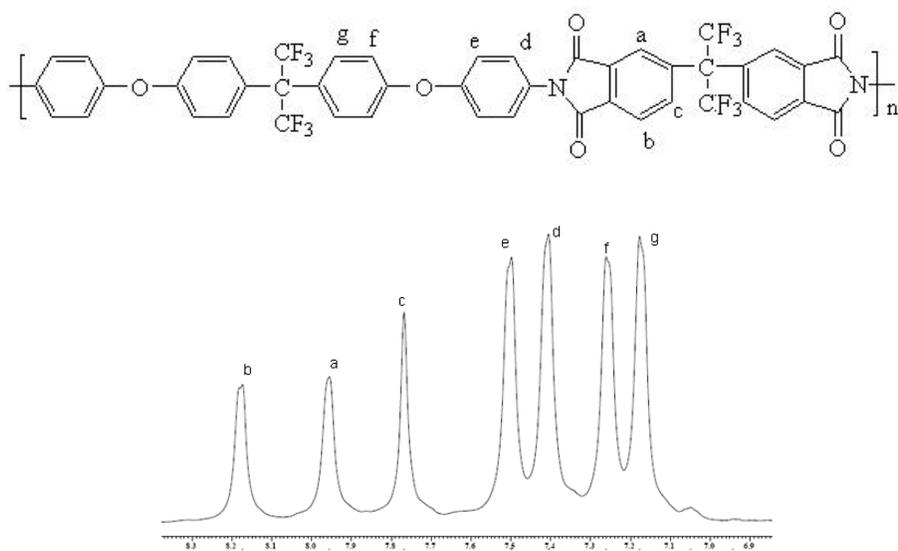


Fig. 4 $^1\text{H-NMR}$ spectrum of 6FDA-BDAF

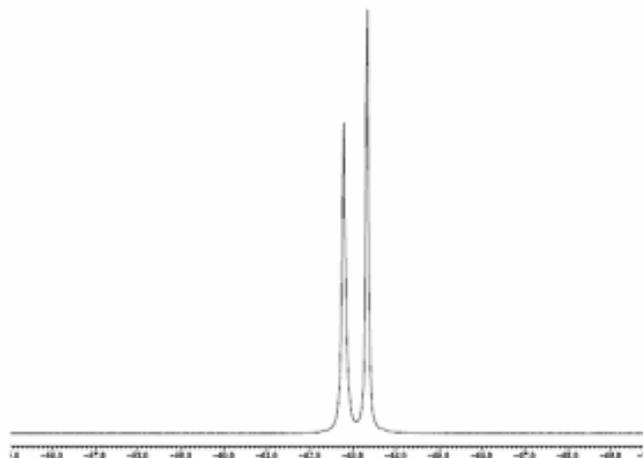


Fig. 5 ¹⁹F-NMR spectrum of 6FDA-BDAF

The solubility of polyimides in various solvents was investigated and the results were shown in Tab.2. Due to the existence of trifluoromethyl, methyl and flexible ether group into the polymer backbone, they exhibited an excellent solubility toward test solvents.

Tab.2. Solubility of two polyimides

PI	DMF	DMAc	NMP	DMSO	THF	Chloroform	Toluene	Feed mixture
6FDA-BDAF	S	S	S	S	S	S	W	I
6FDA-BAPP	S	S	S	S	S	S	W	I
ODPA-BDAF	S	S	S	W	S	S	I	I
HQDPA-BDAF	S	S	S	W	S	S	I	I

Note: *weight ratio: toluene/n-heptane=20/80, test temperature: 90°C, S: soluble,

I: insoluble; W: swelled

The thermal properties of four polyimides were investigated as listed in Tab.3. The polyimides showed high Tg for their large side groups such as -CH₃ or -CF₃ and high density of benzene rings.

Tab.3 Thermal properties of four polyimides

PI	Tg (°C)
6FDA-BDAF	235
6FDA-BAPP	251
HQDPA-BADF	243
ODPA-BADF	220

3.2 Pervaporation

Four polyimide dense membranes were prepared for the pervaporation of toluene/n-heptane and the results were listed in Tab.4. The results showed that toluene could be separated from toluene/n-heptane mixture in priority. Among all the homogeneous polyimide membranes, 6FDA-BDAF possessed the best overall separation performance. When the toluene content in the feed was 20wt%, its membrane with a thickness of 18 microns had a separation factor of 5.44 and the total flux of 1.08 kg· $\mu\text{m}/\text{m}^2\cdot\text{h}$, which was mostly owed to proper affinity of $-\text{CF}_3$ group to aromatics. The results in Tab.5 indicated the effects of feed temperature on pervaporation performances of 6FDA-BADF membranes. With the temperature increasing, the total flux of polyimide membranes increased, but the separation factor was reduced. It can be explained by enhancement of mobility of polymer chain under higher temperature.

Tab.4 PV performances of PI membranes (85°C)

PI	Membrane thickness (μm)	Total flux ($\text{kg}\cdot\mu\text{m}/\text{m}^2\cdot\text{h}$)	Separation factor
6FDA-BDAF	17	1.18	5.28
6FDA-BAPP	12	1.15	3.43
ODPA-BDAF	14	0.10	11.44
HQDPA-BDAF	15	1.77	1.28

Tab.5 Effects of feed temperature on pervaporation performances of 6FDA-BADF membranes

Temperature (°C)	Total Flux ($\text{kg}\cdot\mu\text{m}/\text{m}^2\cdot\text{h}$)	Permeate toluene content (wt%)	Separation factor
65	0.66	62.97	6.49
70	0.81	62.90	6.46
75	0.87	59.95	5.64
80	1.08	59.14	5.44
85	1.18	58.35	5.28

4. Conclusions

A series of soluble polyimides containing fluorine were successfully synthesized via a two-step method and characterized by FT-IR, NMR and DSC in this research. The pervaporation experiments showed that all the polyimides thus obtained could selectively separate toluene from toluene/n-heptane mixture. It was noticeable that 6FDA-BDAF membranes showed better PV performances than the other polyimides with the total flux of 1.08 kg· $\mu\text{m}/\text{m}^2\cdot\text{h}$ and separation factor of 5.44 at 85°C with

toluene content 20wt% in the feed mixture. And it was found that with the feed temperatures increasing, the flux of the membranes was enhanced from 0.66 kg·μm/m²·h to 1.18 kg·μm/m²·h, but the separation factor was reduced from 6.49 to 5.28.

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