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Synthesis and Characterization of Soluble Polyimides Derived from 4,4′-Diamino-3,3′-dimethyldiphenylmethane and Their Pervaporation Performances

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Two kinds of soluble polyimides were synthesized from 4,4′-diamino-3,3′-dimethyldiphenylmethane (DMMDA) and two dianhydrides (including BTDA, ODPA) via a two-step method, low temperature solution polycondensation and next chemical imidization. All polyimides were readily soluble in common polar solvent, such as DMF, DMAc and NMP. The polyimides were characterized by FT-IR, NMR, DSC, XRD and EA. The results showed that all of the polyimides revealed an amorphous nature and their inherent viscosities were 0.68–0.96 dlg^{-1}. The glass transition and melt temperature of these polyimides were determined by DSC and ranged from 224–283°C and 372–384°C, respectively. Thermogravimetric analysis indicated that these polyimides remained fairly stable up to a temperature around or below 400°C. Moreover, 10% mass losses were recorded at approximately 525°C in nitrogen atmosphere. They had a tensile strength in the range 89–137 MPa, and elongations breaking at around 10%. The pervaporation properties of the prepared polyimide dense membranes for ethanol/water mixtures were investigated at a different temperature and the average value of the separation factor and total permeation flux were 46–108 and 660–1380 g/m^{2}h, respectively.

Keywords polyimides, soluble, pervaporation, synthesis

Introduction

Polyimides (PIs) are a class of thermally stable polymers that are often prepared from dianhydride and diamine monomers. They are usually prepared by the so called two-step method in which a dianhydride and a diamine are allowed to undergo condensation polymerization to form a polyamic acid precursor and subsequently, the precursor is converted thermally or chemically to the final polyimide. They have a number of outstanding properties such as high thermo resistance, dimension stability, excellent electrical and mechanical properties (1–4). However, most polyimides suffer from processing problems

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Address correspondence to Jiding Li, Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China. Fax: 86-10-6277-0304; E-mail: lijiding@mail.tsinghua.edu.cn due to their insolubility. Thus, a variety of concepts for structural modifications such as flexible alkyl side chains, bulky lateral substituents, noncoplanar biphenylene moieties, as well as flexible alkyl or aryl ether spacers, have been used to enhance the solubility and lower the phase transition temperatures (5–7). In recent years, soluble polyimides have become very important and needed as solar cells and separation membranes (8–10).

Pervaporation (PV) is one of the membrane-separation processes that have been industrialized in many countries over the past decade. The attractiveness of this process lies in the fact that it offers an opportunity for the separation of organic liquid mixtures, especially in azeotropic solutions or organic contaminated industrial wastewater, in an energy saving, economical, and environmental protecting method (11). It is reported that polyimides have been one of the suitable membrane materials because of their excellent properties. Polyimide membranes show high selectivity in dehydration of alcohol at a wide range of water concentrations (12–14). Their high selectivity stems from high diffusion-selectivity due to their low free volume and the small size of water relative to alcohol. However, polyimide membranes showed lower permeation flux because they have very low free volume and low solubility.

In this work, diamine monomer with side methyl group was synthesized and used to prepare the soluble polyimides by way of a two-step method; preparation of poly(amic acid) followed by solution imidization. The chemical structure and physical properties of the two polyimides were characterized with FT-IR, NMR, XRD and DSC, etc. These polymers were subjected to thermal and mechanical property measurements. In addition, the polyimides membranes were prepared and their pervaporation performances for alcohol dehydration were also investigated.

Experimental

Materials

3,3′4,4′-benzophenontetracarboxylic dihydride (BTDA) was purchased from Acros Organics, Inc., 4,4′-oxydiphthlic dianhydride (ODPA) was obtained from Shanghai Synthesis Resin. All dianhydrides were purified by sublimation before use. DMMDA was synthesized in our laboratory and used to prepare polyimides.

N,N-dimethylformamide (DMF) was purified on distillation under reduced pressure over calcium hydride and stored over molecular sieves (4Å). Other reagents were used as received.

Synthesis of 4,4′-Diamino-3,3′-dimethyldiphenylmethane (DMMDA)

o-Toluidine (100 g) and 30% concentrated hydrochloric acid (108 g) were added to a 500 mL, three-necked flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel, and the mixture was heated to 60°C; this was followed by the addition of 21.4 g of a 38 wt% aqueous formaldehyde solution. The mixture was stirred for 4 h and was gradually elevated to 90°C for another 4 h. After cooling, the reaction mixture was carefully neutralized to pH 7 with a 25% aqueous NaOH solution. After the product was collected by filtration and washed with warm water, it was recrystallized from an aqueous ethanol solution to give 86.5 g white crystals.

Mp: 157–158°C. IR (KBr): 3431, 3348, 2912, 2850, 1623, 1503, 1435, 1276, 825, 774 cm^{-1}. ^{1}H NMR (300 MHz, DMSO, δ, ppm): 2.04 (s, 3H), 3.52 (s, 2H), 4.56 (s, 2H), 6.50 (d, 1H), 6.67 (d, 2H).

Synthesis of Polyimides from BTDA, ODPA and DMMDA

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 DMF, then dianhydride was added all at once. The mole ratio and solid content of diamine/dianhydride mixture were 1:1 and 12%, 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 an ethanol solution. The precipitate was collected by filtration, washed with water, and dried *in vacuo* at 160°C to obtain the polyimides solid.

Dense Flat Sheet Membranes

Polyimides dense membranes were prepared by a casting method using a 12 wt% solution of polyimides in DMF. After allowing the polymer to dissolve in the DMF 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 using a 200 μm casting knife. The specimens produced were dried *in vacuo* for 2 days at 150°C to remove the solvent. The thickness of the obtained membrane was determined by using a micro screw gauge and was found to be approximately 20 μm.

Measurements

The polyimides were analyzed by Fourier transform infared (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 4 cm^{-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.0.5 g/dl) were measured with a Ubbelohde viscometer at 30°C. ^1H NMR spectra were registered using a Varic ECA-600 spectrometer, using DMSO-d_6 as a solvent. The ^1H chemical shifts were calibrated by using tetramethylsilane (TMS). Elemental analyses were carried out with Elementar Vario-EL elemental analyzer. Differential scanning calorimeter (DSC) was used to measure glass transition temperature (T_g). Samples of approximately 6–7 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 N_2 atmosphere. Thermogravimetric analyses (TGA) were 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. Mechanical properties of the film were measured on an TS-2000 at room temperature with film specimens at the rate of 5 mm/min.

Pervaporation Performance

The membrane separation performance was analyzed by pervaporation using special test equipment (15). The measurements were carried out for an ethanol solution (93.56 wt%) at 60, 70, and 80°C, respectively. 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 separation factor is defined by:

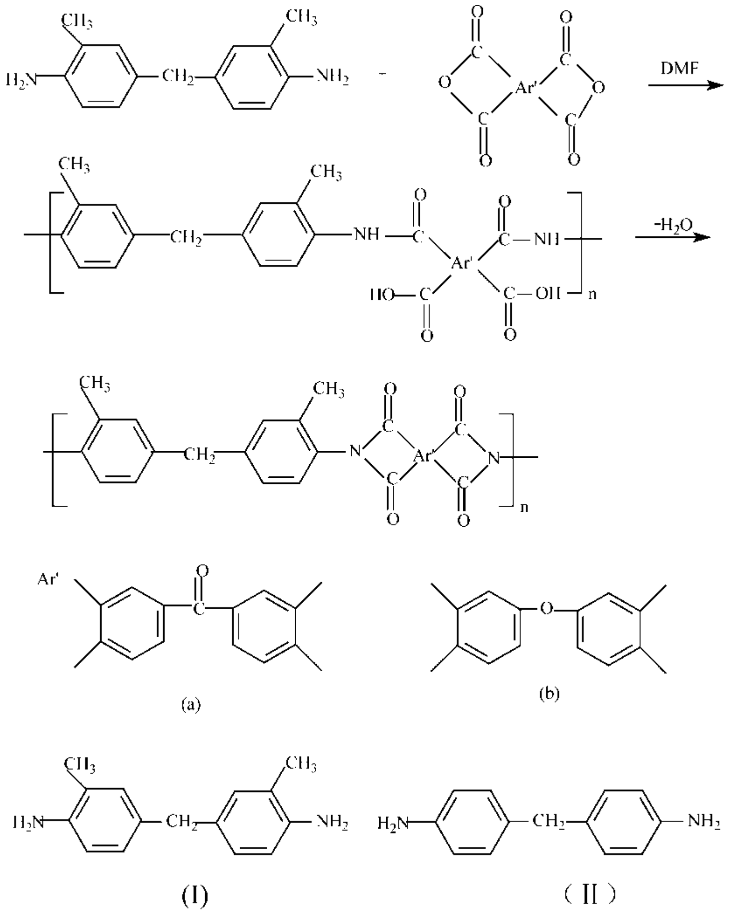
$$\alpha = \frac{Y_0 \cdot X_w}{X_0 \cdot Y_w}$$

where Y_0 and Y_w represent the weight fractions of organic solvent and water in the permeate, and X_0 and X_w in the feed, respectively.

Results and Discussion

Monomer Synthesis

DMMDA was easily synthesized from the condensation of o-toluidine with formaldehyde in the presence of HCl. The key procedure was the first step and the mole ratio of o-toluidine/HCl should be in the range of 0.95 to 1 at 50–60°C. The chemical structures of DMMDA were identified by FT-IR and ^{1}H NMR. The results were in good agreement with the proposed structure of DMMDA.



Scheme 1.

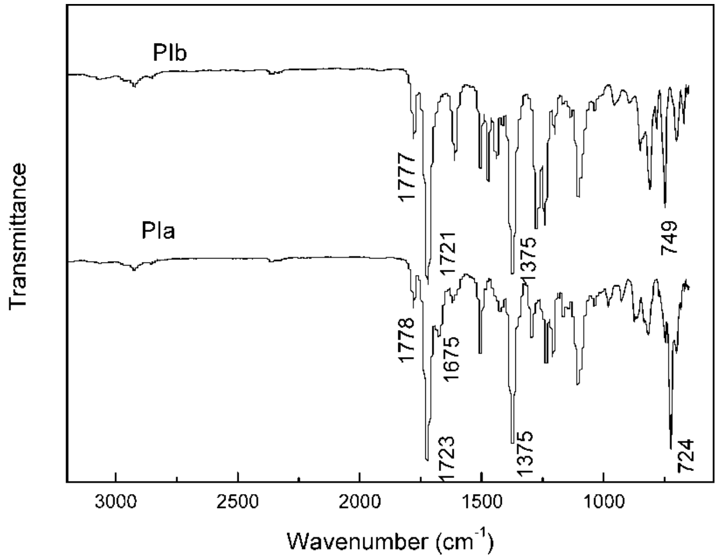


Figure 1. FT-IR spectra of two polyimides.

Synthesis and Structure Characterization of Polyimides

The polyimides were prepared by the conventional two-step polymerization method, as shown in Scheme 1, involving ring-opening polyaddition forming poly(amic acid) and

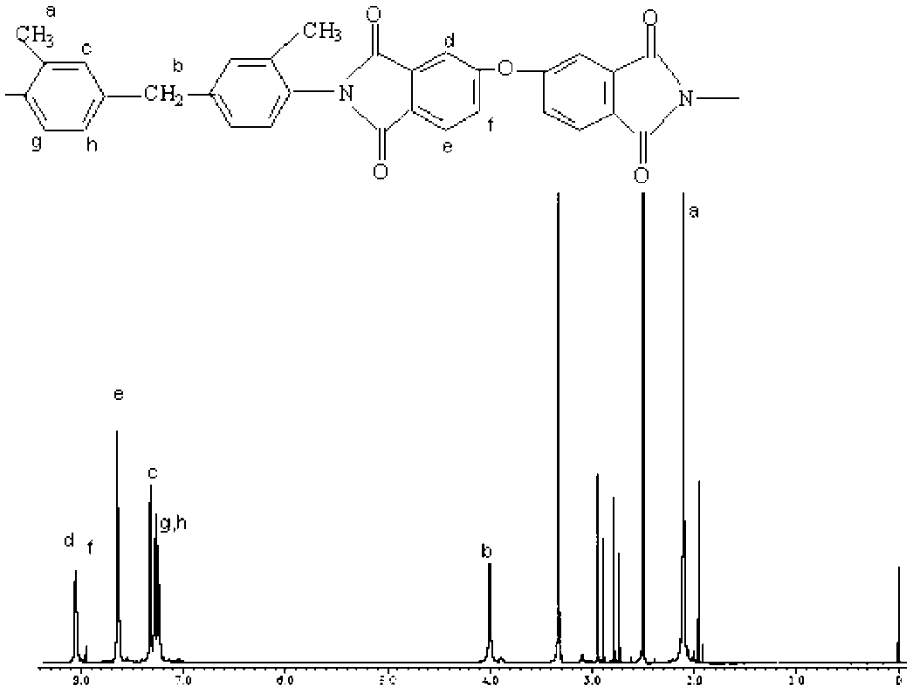


Figure 2. ^{1}H-NMR of ODPA-DMMDA.

Table 1
Elemental analysis of two polyimides

Polymer	η_{inh} (dl g^{-1})^a	Elemental analysis (%) C	H	N
Ia	0.68			
	Calcd	74.99	3.93	5.47
	Found	73.81	4.28	5.75
Ib	0.96			
	Calcd	74.39	4.03	5.60
	Found	72.86	4.19	5.80

[a] Measured in DMAc at a concentration of 0.5 g dl^{-1} at 30°C.

subsequently, chemical cyclodehydration. The polyamic acid precursors were prepared by adding the dianhydride to the diamine solution gradually according to equimolar ratio, and then chemical conversion of poly(amic acid)s with a mixture of acetic anhydride and triethylamine is processed at room temperature to obtain polyimides. 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. The complete imidization of the polyimides was conformed by FT-IR spectra (Figure 1). 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 (N–H stretching) and 1650 cm^{-1} (amide C=O strength), and this indicated that the polyimides had been fully imidized (16). Figure 2 shows the ^1H NMR spectra of PIa in DMSO-d_6. As expected, the aromatic protons were detected around 7.2–8.2 ppm, depending on the oposition in the aromatic ring. The aromatic

Table 2
Solubility of two polyimides

Solvent	Polymer Ia	Ib	IIa	IIb
DMF	S	S	I	I
DMSO	S	S	P	P
NMP	S	S	I	I
DMAc	S	S	I	I
m-Cresol	S	S	P	P
Chloroform	S	S	I	I
Toluene	I	I	I	I
THF	I	I	I	I
H_2SO_4	S	S	S	S

At RT for 24 h, S: soluble, I: insoluble P: partially soluble.

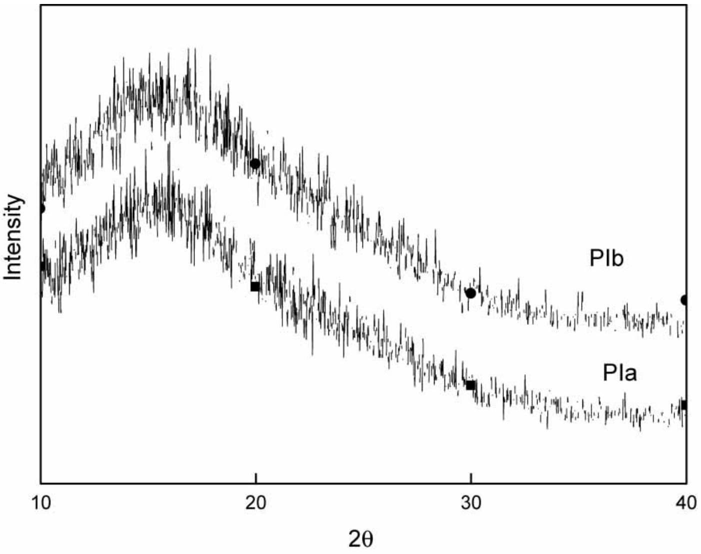


Figure 3. DSC thermogram of two DMMDA based polyimides.

carboxylic acid proton and aromatic amide proton peak (10.5 ppm) completely disappeared, which means that the poly(amic acid) was completely converted into polyimide. On the other hand, all hydrogen peaks in the ^{1}H NMR were in good agreement with the proposed polymer structure. In addition to IR and NMR spectra, the elemental analysis values of these polyimides listed in Table 1 were in agreement with their calculated values for the proposed structure.

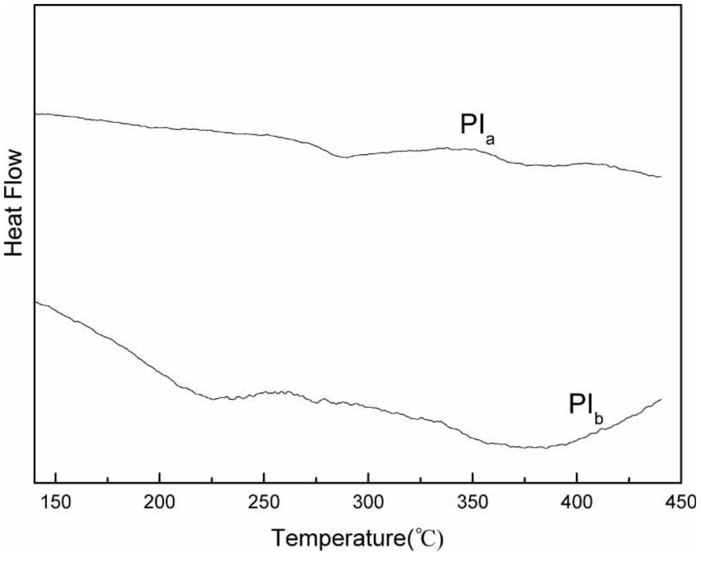


Figure 4. The thermal stability of two polyimides.

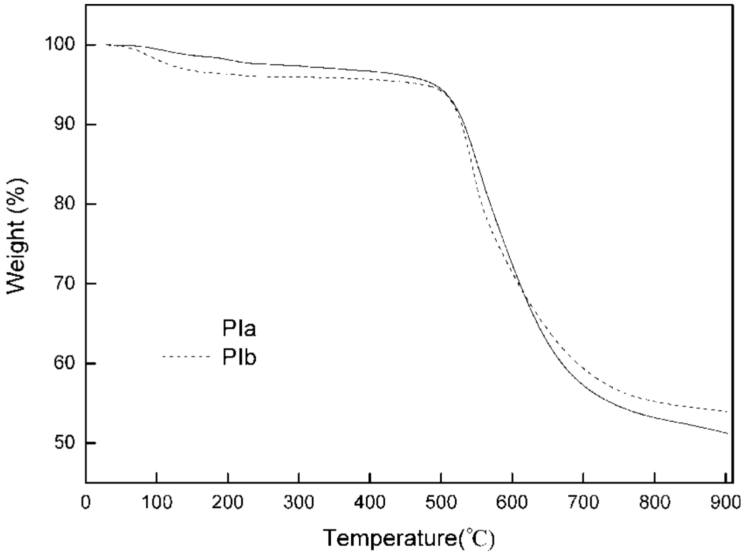


Figure 5. Wide-angle x-ray diffractograms of two polyimides.

The solubility of polyimides in various solvents was investigated and the results are summarized in Table 2. Due to the incorporation of a side methyl group in diamine and flexible ether or ketone group into the polymer backbone, they have exhibited an excellent solubility toward test solvents. DMMDA-based polyimides showed good solubility in aprotic polar solvents such as NMP, DMAc, DMSO, and DMF at room temperature, but showed bad solubility in THF. Since all of the polyimides prepared in this investigation showed good solubility in DMAc, the intrinsic viscosity was measured in DMAc at 30°C. The intrinsic viscosity of DMMDA-based polyimides ranged from 0.68–0.96 dl/g, as shown in Table 1.

Thermal and Mechanical Properties of Two Polyimides

The wide-angle X-ray diffractograms of polyimides are given in Figure 3. Polyimide containing benzophenone moiety showed a little crystallinity, whereas ODPA-DMMDA polyimides showed amorphous patterns. There were no significant differences in crystallinities between the two polyimides. The possible reason is that the presence of noncoplanar conformation decreases the intermolecular forces between the polymer chains, subsequently causing a decrease in crystallinity.

Table 3
Thermal characterization of polyimides

Polymer	T_g (°C) DSC	T_d (°C) In N_2	Loss 10 wt% T (°C)	Residue (wt%) (In N_2, 900°C)
Ia	283	514	525	51.3
Ib	224	517	524	53.5

Table 4
Mechanical properties of two polyimides

Polymer	Tensile stress (MPa)	Elongation (%)	Moludus (GPa)
Ia	89	11.2	1.75
Ib	137	9.1	2.63

The thermal properties of both polyimides were investigated by DSC and TGA, as shown in Figures 4 and 5, and the thermal behavior data of polyimides were summarized in Table 3. Glass transition temperatures (T_g) of polyimides determined by means of differential scanning calorimeter, were found to be in the range of 224–283°C, depending on the structure of polymers.

The results of TGA analyses showed an excellent thermal stability of the synthesized polyimides. The two polyimides do not decompose around or below 400°C in nitrogen atmosphere. Their decomposition temperatures of 10% mass loss were about 525°C in nitrogen and the char yields at 900°C in nitrogen atmosphere not exceed 52%. The TGA data suggests high thermal stability of the stiff naphthalene structure.

The mechanical properties of the polyimides films prepared by the chemical imidization are summarized in Table 4. The polyimide films had a tensile strength of 89–137 Mpa, elongation at break of about 10%, and initial modulus of 1.75–2.63 Gpa. Two of the polymer films exhibited high tensile strength, high modulus and low elongation; thus, they could be considered as tough and flexible materials.

Pervaporation Performances

Pervaporation test was carried out with the polyimides dense membranes. The pervaporation performances of the membranes and the effect of the test temperatures are demonstrated in Table 5. It has been shown that there are many differences for the separation factors and the total flux between PIa and PIb. At the same test temperature, the separation factor of PIa is higher than that of PIb, which indicated that the polyimide membranes containing carbonyl group showed higher pervaporation selectivity than that of containing ether group. In addition, the separation factor decreases while the total flux increases as increasing operating temperature for PIa, but for PIb both the separation factor and the total flux become higher as increasing operating temperature. The above results are related with both fractional free volume and the mobility of the polymer.

Table 5
Pervaporation performances of polyimides dense membranes at different temperatures

	60°C		70°C		80°C	
Polymer	α	F (g/(m^{2}h))	α	F (g/(m^{2}h))	α	F (g/(m^{2}h))
Ia	116	325	104	634	96	983
Ib	38	1241	44	1447	57	1473

Conclusions

The diamine DMMDA was successfully prepared this study in high purity and high yields in, and moderate to high molecular weights of soluble polyimides were obtained. These polyimides are amorphous and exhibited excellent solubility. The T_g values of the DMMDA-based polyimides were 283 and 224, respectively. Two polyimides exhibit good thermal stability and mechanical properties. Thus, these polyimides are promising soluble high-temperature membrane materials. In addition, polyimide membranes were prepared and used for pervaporation dehydration. The separation factor and permeation flux were 46–108 and 660–1380 $g/m^2 h$, respectively for pervaporation 93.56 wt% ethanol solution.

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