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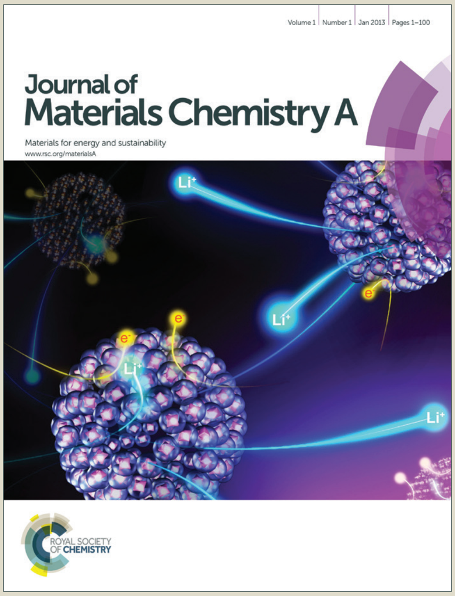

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ARTICLE TYPE

Synthesis, Characterization, and Gas Transport Properties of Novel Poly(amine imide)s Containing Tetraphenylmethane Pendant Groups

Hongchao Mao,[a,b] Suobo Zhang[a]*

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Two bis(amine anhydride) monomers containing tetraphenylmethane pendant groups were synthesized from palladium-catalyzed amination reaction of N-methyl-4-chlorophthal-imide with arylamines, followed by alkaline hydrolysis of the intermediate bis(amine imide)s and subsequent dehydration of the resulting tetraacids. These monomers were polymerized with appreciate aromatic diamines to obtain a series of novel poly(amine imide)s. The attained polymers exhibited good solubility in many aprotic solvents and had glass transition temperatures in the range of 310 to 395 °C. Thermogravimetric analysis showed that all polymers were stable, with 10% weight loss recorded above 510 °C in nitrogen. The surface areas of these novel poly(amine imide)s ranged from 78 to 290 m^2/g. Films obtained by casting exhibited a combination of relatively high permeability and modest good permselectivity with values close to the Robeson upper-bound for O_2/N_2 and CO_2/CH_4 gas pairs.

Introduction

Aromatic polyimides (PIs) are widely studied for use in gas separation owing to their good gas transport properties, exceptional chemical and thermal stability, as well as mechanical robustness among the various classes of polymers.[1,2] Their gas separation properties could be easily tuned by numerous combinations between diamines and dianhydrides.[3.4] In many cases, PIs with stiff backbone chains are considered as organic molecular sieves among polymeric membrane materials for gas separation due to their high selectivity. However, most of the PIs still fall below the Robeson upper-bound for important gas pairs (e.g., O_2/N_2, CO_2/N_2, and CO_2/CH_4),[5,6] and there is need for the polyimide materials that are both highly permeable and selective.[7-9] To obtain better performing PIs, an effective strategy is to introduce bulky and rigid groups into PIs, which tend to increase both polymer chain rigidity and free volume, what could be translated into a combination of high permeability and good selectivity.[10] Recently, J. de Abajo et al., prepared a series of copolyimides having adamantine ester pendant groups, and found that these copolyimides exhibited higher permeability and diffusion coefficients than the starting copolyimide governed by the internal free volume, which confirmed the positive effect of adamantane groups on improving the gas separation properties.[11] Park et al., reported a new platform of high performance polyimide based on 2,6-diaminotriptycene, which had internal free volume elements and thus led to the formation of high fractional free volume with proper cavity size to separate small gas molecules with high selectivity as high permeability.[12] Especially, the spirobisindane unit was also incorporated into the PIs, which inhabited the space-efficient packing of the polymer chains and led to a large amount of free volume. The free volume was accessible to probe molecules as for instance nitrogen and therefore they were considered to be microporous materials (PIMs).[13] The PIs containing spirobisindane moieties were first prepared by Zhang et al. in 2007,[14] and shortly thereafter PIM-PI membranes were reported that exhibited significantly higher permeability compared to conventional PI membranes.[15-17]

In our previous study, we reported the synthesis of a series of poly(amine imide)s based on two kinds of N-linked dianhydrides which were obtained from the Pd-catalyzed amination reaction of 4-chlorophthalimide with aniline and *p-tert*-butylaniline, respectively.[18] Because of the introduction of propeller-shaped tripenylamine groups in the dianhydride units, the resulting PIs exhibited good solubility in many aprotic solvents, good thermal resistance and exceptionally high glass transition temperatures.[19,20] Moreover, the Pd-catalyzed amination method provides a facile synthetic route to dianhydrides containing a variety of amines and diamines moieties.[18,21] That is, many useful physical and chemical properties in this kind of poly(amine imide)s could be tuned by using different dianhydrides from corresponding amines and diamines. Thus, from the perspective of obtaining the processable PIs possessing excellent gas separation properties and thermal stability, amines with bulky and rigid groups should be adopted to synthesize N-linked dianhydrides and corresponding poly(amine imide)s.

In the present paper, we describe the successful synthesis of novel poly(amine imide)s derived from two new N-linked dianhydrides containing bulky and rigid tetraphenylmethane moieties as pendant groups, which could stiff the polymer backbone by restricting the segmental mobility and give rise to high free volume through increasing inter-chain separation that are essential requirements for good gas separation property.[10,22-23] Additionally, the poly(amine imide) based on the diamine and dianhydride both containing tetraphenylmethane groups as pendant group was also prepared for further comparison. Physical, thermal, and gas separation properties of these novel poly(amine imide)s were studied. We expect that these poly(amine imide)s could be equipped with good gas separation properties, solubility and thermal stability.

Experimental Part

Materials

4-Chlorophthalic anhydride (99.2%) was purified by distillation. THF and bis(2-methoxy ethyl)ether were dried by refluxing over sodium distilled prior to use. Dimethyl sulfoxide (DMSO; ACROS) were dried over calcium hydride overnight, distilled under reduced pressure. Cesium carbonate (Cs_2CO_3) and cesium fluoride (CsF) was dried in vacuum at 150 °C for 24h prior to use. *m*-Cresol was dried over $CaCl_2$, then over molecular sieves, distilled under reduced pressure and stored under nitrogen in the dark. $Pd_2(dba)_3$ (Aldrich), 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos, Acoros), isoquinoline (Acoros), 4,4′-(hexafluor-oisopropylidene)dianiline (6FpDA, Aldrich), 2,4,6-trimethylbenzene-1,3-diamine (*m*-TMDA, Acros), Mg (Acros), 10% Pd/C (Aldrich), 4-fluoronitrobezene (Aldrich) were used as received. Other commercially available reagent grade chemicals were used without further purification. *N*-methyl-4-chlorophthalimide (**1**) were prepared as previously described.[18] 4-Tritylaniline, and 4-(tris(4-(tert-butyl)phenyl)methyl)aniline were synthesized according to the literatures.[24]

Measurement

^{1}H NMR spectra were measured at 300MHz on an AV300 spectrometer. FT-IR spectra were obtained with a Bio-Rad Digilab Division FTS-80 FT-IR spectrometer. Elemental analysis were performed on an Elemental Analysis MOD-1106. The X-ray diffraction data were collected on a SiemensP4 4-circle diffractometer at 293 K. The reduced viscosities were determined with an Ubbelohde capillary viscometer at 30 ± 0.1 °C on 0.5 gdL^{-1} concentrations of polymer in NMP. Thermogravimetric analysis (TGA) was performed in nitrogen or air atmosphere with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer DSC-7 system at a heating rate of 20 °C min^{-1} under air atmosphere. Volumetric gas adsorption was performed on an Autosorb-1 instrument (Quantachrome). Nitrogen adsorption isotherms at 77 K were measured in liquid-nitrogen baths.

Monomer synthesis

N′- Methyl-N,N-bis(3,4-phthalimide)-4-tritylaniline (2I)

A 250-mL three-necked flask was charged with **1** (18.26 g, 100.0 mmol), 4-tritylaniline (13.42g, 40.00 mmol), $Pd_2(dba)_3$ (0.46g, 0.5mmol), Xantphos (0.58g, 1mmol), Cs_2CO_3 (32.55g, 100mmol), and 60 mL of bis(2-methoxy ethyl)ether under nitrogen atmosphere and heated to 135 °C with stirring for 8 h. After cooling to room temperature, the resulting solution was poured into a mixture of ethanol/water. The precipitated yellow solid was collected by filtration, and then was washed with ethanol and water several times respectively, and dried in vacuum. The pure product **2I** was obtained by recrystallization from methanol and DMAc (2:1,v/v) in a yield of 81% (21.2 g). IR (KBr): 1767 and 1715 (C=O of imide), 1380 (C-N stretching), 742 cm^{-1} (C=O bending). ^{1}H (DMSO-d$_6$): 7.78-7.81 (d, 2H), 7.28-7.39 (m, 10H), 7.14-7.26 (m, 13H), 3.00 (s, 6H). Anal. Calcd for $C_{43}H_{31}N_3O_4$ (653.72): C, 79.00; H, 4.78; N, 6.43. Found: C, 78.85; H, 4.91; N 6.29.

N′-Methyl-N,N-bis(3,4-phthalimide)-4-(tris(4-(tert-butyl)phenyl)methyl)aniline (2II)

This compound was prepared from **1** and 4-(tris(4-(tert-butyl)phenyl)methyl)aniline using the same procedure as described above. The yield of **2II** was 86% (28.3g). IR (KBr): 1769 and 1716 (C=O of imide), 1376 (C-N stretching), 742 cm^{-1} (C=O bending). ^{1}H (DMSO-d$_6$): 7.70-7.73 (d, 2H), 7.49-7.52 (d, 2H), 7.25-7.34 (m, 8H), 7.24-7.19 (d, 2H), 7.06-7.11 (d, 6H), 6.95-7.03 (d, 2H), 2.99 (s, 6H), 1.31(s, 27H). Anal. Calcd for $C_{55}H_{55}N_3O_4$ (822.04): C, 80.34; H, 6.74; N, 5.11. Found: C, 80.11; H, 6.85; N 5.03.

N,N′-bis(3,4-dicarboxyphenyl)-4-tritylaniline dianhydride (I)

To a solution of 15% NaOH aqeous solution (60 mL) was added 13.1 g of compound **2I** (20 mmol). The mixture was refluxed for 48 h under nitrogen atmosphere after the solid was completely dissolved. After cooling to room temperature, the solution was adjusted to pH=1.0 with 6N HCl. The yellow precipitate was collected by filtration and dried in vacuum at 100 °C. The resulting tetracarboxylic acid was dissolved in acetic acid (25 mL) and acetic anhydride (25 mL). The solids were filtered without cooling and washed with petroleum ether, then dired at 100 °C under vacuum to give 8.53 g of yellow product in the yield of 68 %. IR (KBr): 1846 and 1763 (C=O of anhydride).^{1}H (CDCl$_3$): 7.88-7.93 (d, 2H), 7.57-7.61 (d, 2H), 7.48-7.55 (m, 2H), 7.19-7.38 (m, 17H), 7.02-7.07 (d, 2H). Anal. Calcd for $C_{41}H_{25}NO_6$ (627.64): C, 78.46; H, 4.01; N, 2.23. Found: C, 78.23; H, 4.15; N, 2.16.

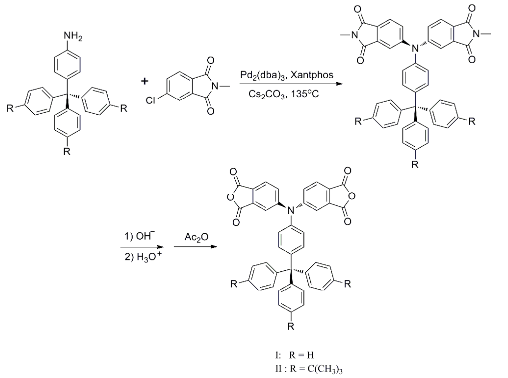
,N′-bis(3,4-dicarboxyphenyl)- 4-(tris(4-(tert-butyl)phenyl)methyl)aniline dianhydride (II)

This compound was prepared from **2II** using the same procedure as described above. The yield of **II** was 62% (9.87 g). IR (KBr): 1848 and 1764 (C=O of anhydride). ^{1}H (CDCl$_3$): 7.90-7.96 (d, 2H), 7.60-7.65 (d, 2H), 7.52-7.58 (m, 2H), 7.26-7.36 (m, 8H), 7.00-7.14 (m, 8H), 1.31(s, 27H). Anal. Calcd for $C_{53}H_{49}NO_6$ (795.96): C, 79.97; H, 6.20; N, 1.76. Found: C, 79.85; H, 6.29; N, 1.68.

4,4′-Diamino-4-tritylaniline (c)

In a 250 mL round-bottom flask equipped with a stirring bar, a mixture of 16.8 g (0.05 mol) of 4-tritylaniline, 14.3 g (0.1 mol) of 4-fluoronitrobenzene, and 15.2 g (0.1 mol) of CsF in 100 mL of dimethyl sulfoxide (DMSO) was heated with stirring at 140 °C for 12 h. After cooling, the mixture was poured into 300 mL of water, and the precipitate was collected by filtration and then washed thoroughly with water. Recrystallization from methanol yielded 18.8 g of 4,4′-dinitro-4-tritylaniline as yellow crystals in 65% yield. ^{1}H (DMSO-d$_6$): 8.13-8.17 (d, 4H), 7.20-7.31 (m, 15H), 7.14-7.18 (d, 4H), 7.02-7.06 (d, 4H).

In a 300 mL round-bottom flask, 11.5 g (0.02 mol) of dinitro compound obtained above, 0.2 g of 10 wt % Pd/C, 10 mL of hydrazine monohydrate, and 100 mL of ethanol was heated at a reflux temperature for 12 h. The solution was filtered hot to remove Pd/C. After cooling, the mixture was poured into 400 mL



Scheme 1 Synthesis of Bis(amine anhydride) **I** and **II**

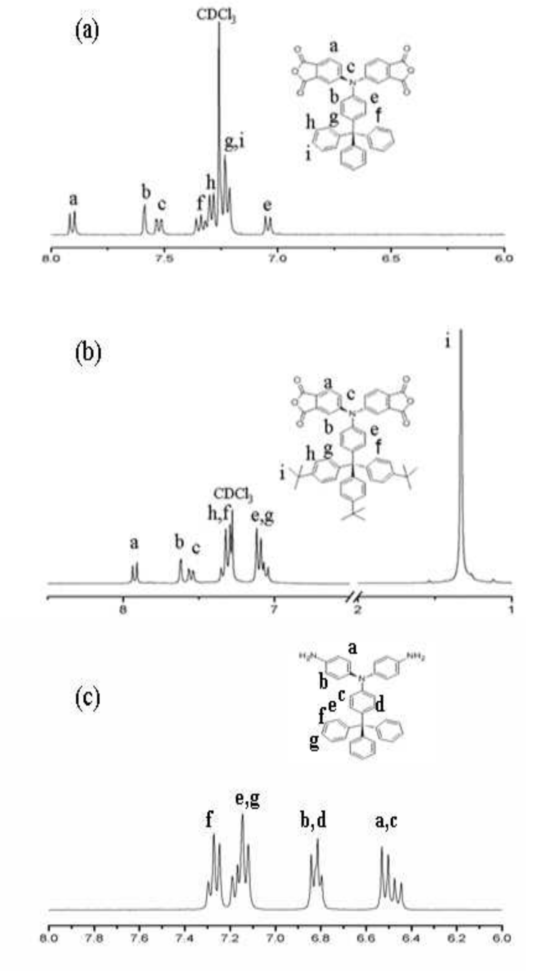


Fig. 1 (a) ^{1}H NMR spectra of bis(amine anhydride) **I** in CDCl$_3$ (b) ^{1}H NMR spectra of bis(amine anhydride) **II** in CDCl$_3$ (c) ^{1}H NMR spectra of diamine **c** in DMSO-d_6

of water and the precipitate was collected by filtration, and then dried in vacuum to afford 9.4 g (91% yield) of diamine as pale purple powder. ^{1}H (DMSO-d$_6$): 7.23-7.31 (m, 6H), 7.11-7.21 (m, 9H), 6.78-6.86 (m, 6H), 6.49-6.55 (d, 4H), 6.43-6.47 (2H). Anal. Calcd for $C_{37}H_{31}N_3$ (517.66): C, 85.85; H, 6.04; N, 8.12. Found: C, 85.22; H, 6.29; N, 8.49.

Polymer synthesis

A typical polymerization procedure is as follows: a 100 mL completely dried, three-necked flask was charged with equimolar amounts of each monomer (1.00 mmol of the dianhydride and 1.00 mmol of the diamine) and 10 mL of m-cresol which was equipped with a mechanical stirrer, nitrogen inlet and outlet. The reaction mixture was stirred at room temperature for 2 h until complete dissolution of solids and then heated to 80^{o}C for 4 h. After a few drops of isoquinoline were added, the mixture was heated with stirring at 200 ^{o}C for 24 h. Water formed during the imidization was continuously removed by the steady flow of nitrogen. At the end of the reaction, the mixture was cooled and poured into 50 mL of methanol. The polymer was collected by filtration, washed with methanol for several times. Further purification involved the precipitation of a THF solution in methanol, Soxhlet extraction with methanol for 2 days and a vacuum drying at 100 ^{o}C for 24 h thus leading to a yellow solid as the products.

Membrane preparation

A solution of 5-8 wt % solution of the given polymer in *N,N*-dimethylacetamide was prepared by stirring the mixture for overnight, and filtered through a 0.2 μm syringe filter to remove the nondissolved materials and dust particles. Film cast onto the glass plate from the clear solution and dried at 80^{o}C for 12 h, after which the membrane was dried in a vacuum oven (60 ^{o}C for 2 h, 120 ^{o}C for 8 h and 220 ^{o}C for 10 h).

Gas permeability measurement

Gas permeation measurements were performed using a constant-volume/variable-pressure method at a feed pressure of 1atm and a feed temperature of 25^{o}C. The permeability was determined in the sequence of O_2, N_2, CH_4, and CO_2. The design of the permeation apparatus and the experimental procedure are described in detail elsewhere. The permeability coefficient of all gases was calculated by:

$$P = DS = 10^{10}\,\frac{V_d l}{ARTp_{up}}\left(\frac{dp}{dt}\right)$$

Where P is the permeability coefficient of a membrane to gas inbarrers (1 barrer =10^{-10} cm^3 [STP] cm cm^{-2} s^{-1} cm Hg^{-1}), P_{up} is the upstream pressure (cmHg), *dp/dt* is the steady-state permeate-side pressure increase (cmHg/s), V_d is the calibrated permeate volume (cm^3), l is the membrane thickness (cm), A is the effective area of the film (cm), R is the universal gas constant (0.278 cm^{3}cmHg/(cm^3(STP)K)), T is the absolute temperature (K). The apparent diffusion coefficient D (cm^2/s) of the polymer membrane was calculated by $D = l^2/6\theta$, where θ is the time lag of the permeability measurement. The solubility coefficient S (cm^3 (STP)/(cm^{3}cmHg)) was obtained from the relationship $S=P/D$.

Mixed gas permeability coefficients were measured using a constant pressure/variable volume system equipped with a gas chromatograph. The measuring temperature was 25°C. The concentrations of each gas were detected using a gas chromatograph equipped with a thermal conductivity detector. The mixed-gas selectivity was calculated by the ratio of downstream(y) and upstream (x) mole fraction of the two gases by the following equation:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j}$$

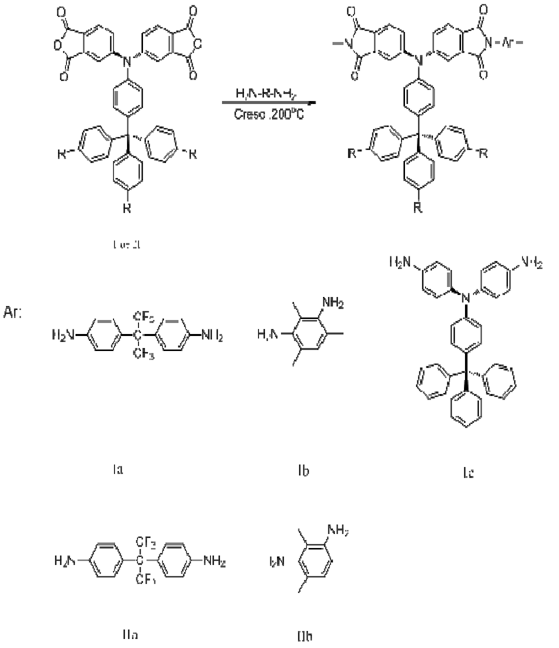
Where y_i and y_j are the mole fractions of components *i* and *j* respectively in the downstream, x_i and x_j are the mole fractions of components *i* and *j* respectively in the upstream.

Results and discussion

synthesis and characterization of monomer and polymer

The synthetic route of bis(amine anhydride) monomers is outlined in Scheme 1. The key step of this route was the coupling reaction to give the tripenylamine moieties. We have previously described the bis(amine-phthalimide)s by means of a palladium-catalyzed amination reaction of **1** with aniline and *p-tert*-butylaniline, respectively.[18] The amination reaction was carried out in 1,2-Dimethoxyethane (DME) in the presence of $Pd(OAc)_2$, BINAP, and Cs_2CO_3. However, our initial attempt to prepare the bis(amine-phthalimide)s **2I** and **2II** according to the synthesis method we described above resulted in rather low yields. In view of this, a modified synthesis method was developed. In this method, the $Pd_2(dba)_3$ and Xantphos were used as catalysts instead of Pd $(OAc)_2$ and BINAP, which increased the reactivity of the arylamines with **1**. Besides, using bis(2-methoxy ethyl)ether as solvent allowed the use of higher reaction temperature than that of DME, which was highly required for this reaction. According to the modified synthesis method, bis(amine-phthalimide)s **2I** and **2II** could be obtained in high yields and relatively short reaction time. The resulting bis(amine-phthalimide)s were hydrolyzed in an alkaline solution to obtain the bis(amine diacid)s. The bis(amine diacid)s were then cyclodehydrated to the bis(amine anhydride) **I** and **II**. Diamine monomer **c** was prepared by the condensation of 4-tritylaniline with 4-fluoronitrobenzene, followed by hydrazine Pd/C catalytic reduction. Elemental analyses, IR and NMR spectroscopic techniques were used to identify the structures of the target monomers. The proposed structure of these target monomers were confirmed by ^{1}H NMR spectra as shown in Fig.1. Assignment of each proton is also given in this figure and this spectrum agrees well with the proposed molecular structures.

PIs were prepared by a one-step, high-temperature solution polycondensation, according to Scheme 2. The polymerizations were carried out in m-cresol using isoquinoline as catalyst. The polymerizations were initially run at the ambient temperature for 2 h and at 80°C for 4 h. Then, the mixture was heated to 200°C and kept for 24 h. Water formed during the imidization was continuously removed with a stream of nitrogen. The PIs were obtained in high yields and had inherent viscosity values ranging between 0.41 and 0.63 dL/g (Table 1). The elemental analyses agreed quite well with calculated values for the proposed structures of PIs. The resulting PIs exhibited weight-average molecular weights and polydisperity in the ranges 4.53×10^4 to 6.76×10^4 and 2.01-3.15, respectively. The chemical structure of PIs was also characterized by ^{1}H NMR and FT-IR. IR spectra of these PIs revealed the characteristic absorptions of imide groups occurred at 1772, 1722, 1378, and 744 cm^{-1}, whereas no signals associated with polyamic acid (higher than 3000 cm^{-1}) were observed. The ^{1}H NMR spectrum of PI **Ia**, as shown in Fig. 2, was consistent with its expected structure.



Scheme 2 Synthesis of Poly(amine-imide)s

Table 1 Inherent viscosity, molar masses, elemental analysis of poly(amine-imide)s

Polymers	η^a(dL/g)	GPC^b			Elemental analysis (%)		
		Mw×10^4	PDI		C	H	N
Ia	0.63	4.53	2.23	Calcd	72.49	3.80	4.53
				Found	72.30	389	4.42
Ib	0.56	6.51	2.01	Calcd	80.73	5.01	5.65
				Found	84.55	5.19	5.58
Ic	0.46	4.80	2.52	Calcd	84.30	4.90	5.04
				Found	84.45	4.99	4.95
IIa	0.48	4.68	3.15	Calcd	74.51	5.42	3.83
				Found	74.33	5.56	3.71
IIb	0.41	6.76	2.09	Calcd	81.64	6.74	4.61
				Found	81.25	6.88	4.48

[a] Inherent viscosity measured was at a concentration of 0.5 g dL^{-1} in NMP at 30 °C. [b] With respect to polystyrene standards, with THF as the eluent.

polymer properties

The solubility of the polymers was tested in various solvents and the results are summarized in Table 2. All PIs from **I** or **II** were readily soluble with a 10% solid content both in strong dipolare solvents and in common organic solvents such as NMP, CH_2Cl_2, $CHCl_3$, and THF. In general, these polymers revealed an enhanced solubility as compared with conventional aromatic PIs. This can be attributed in part to the incorporation of bulky tetraphenylmethane groups, which disrupted the intermolecular attraction forces in the polymer. Also, the propeller-shaped triphenylamine moieties in the bis(amine anhydride) contributed to the enhancement of solubility, which twisted the polymer backbone, resulting in noncoplanar, rigid, and contorted conformation capable of efficiently hindering the chain packing. The good solubility of these PIs in low boiling point solvents is a benefit to prepare the polymer films or coating at low processing temperature. The crystallinity of these PIs was evaluated by wide-

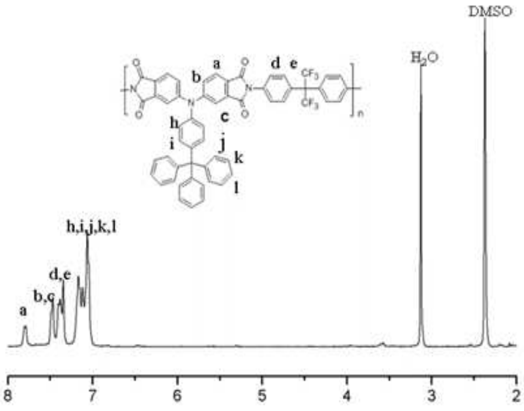


Fig. 2 ^{1}H NMR spectrum of poly(amine imide) **Ia** in DMSO-d_6

Table 2 Solubility[a] of Poly(amine-imide)s

Polymers	$CHCl_3$	THF	DMSO	NMP	DMAc	Acetone
Ia	+	+	+	+	+	–
Ib	+	+	+	+	+	–
Ic	+	+	+	+	+	–
IIa	+	+	+	+	+	–
IIb	+	+	+	+	+	–

[a] '+' easily soluble, '–' insoluble

angle X-ray diffraction experiments (WXRD). The results indicated that the polymers were essentially amorphous, further revealing that the bulky pendant groups disturbed the packing of the polymers which had excellent solubility.

The thermal properties of these polyimides were investigated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 3). The *Tg* values of these polyimides ranged from 310°C to 397°C, depending on the diamine monomers used. The polymer **Ib** and **IIb** showed the highest *T*g among all the PIs associated with the rigid diamine moieties in the polymer backbone. Upon comparison of commercial available PI (Ultem 1000 (G. E. Co.), *T*g = 217 °C, Uplex-R, *T*g = 266 °C), it was observed that the tetraphenylmethane groups can effectively enhance the glass transition temperature of the PIs. In addition, it was noteworthy that the PI **Ic** exhibited higher *Tg* than that of PI **Ia** containing two bulky $C(CF_3)_2$ groups and based on the same dianhydride, which further confirmed the effect of tetraphenylmethane groups on restricting polymer segmental mobility and thus increase their *T*g. All the polymers indicated no clear melting endotherms up to the decompostition temperatures on the DSC thermograms, which supported the amorphous nature of these PIs.

Typcical TGA curves for PI **Ia** and **IIa** were illustrated in Fig.3. All of the polyimides exhibited a similar TGA pattern with no significant weight loss below 450 °C in nitrogen atmosphere. The 10% weight-loss temperatures of the polyimides in nitrogen were recorded in the range of 510-525 °C. The TGA results showed an excellent thermal stability of these PIs, even though they revealed high solubility. The char yields of these polymers in nitrogen atmosphere were more than 57% at 800 °C, which could be ascribed to their high aromatic content.

The mechanical properties of the PIs were summarized in Table 4. These films had a tensile strength of 95-110 MPa, elongation at break of 4.9-8.0 %, and a tensile modulus of 1.3-1.7 GPa.

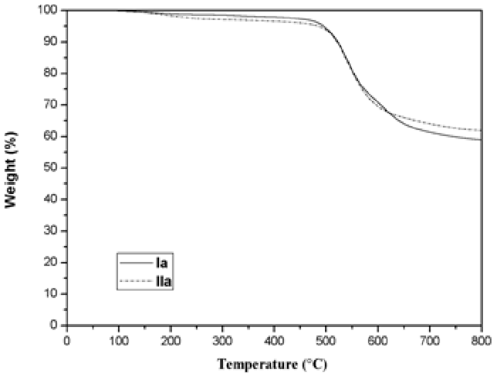


Fig. 3 TGA diagram of poly(amine imide)s **Ia** and **IIa** in nitrogen.

Table 3 Thermal properties of the poly(amine imide)s.

Polymers	T_g[a] (°C)	T_5[b] (°C)	T_{10}[c] (°C)	Char yields[d] (%)
Ia	310	495	522	59.9
Ib	395	493	531	57.5
Ic	329	483	510	63.1
IIa	312	486	523	61.8
IIb	393	502	525	59.1

From the second trace of DSC measurements conducted at a heating rate of 20°C min^{-1}. [b] 5% weight loss temperature in TGA at 10°C min^{-1} heating rate. [c] 10% weight loss temperature in TGA at 10°C min^{-1} heating rate. [d] Weight retain at 800°C.

To evaluate the free volume imparted by the rigid and bulky tetraphenylmethane groups, BET surface area measurements were carried out. Fig.4 showed the N_2 sorption isotherms of the PIs based on the dianhydrides **I** and **II**. The steep increase at high relative pressure showed the presence of an additional large outer surface area of very small particles and the corresponding interparticle volume. However, the nitrogen uptake in the low pressure regime (p/p_0 <0.2), especially for the PIs based on the dianhydride **II,** indicated the contribution of inherent microporisity. Calculations suggested that the pore sizes of these PIs were in the mesoporous range when using NLDFT anlysis; however, as the restricted access of N_2 molecules within the narrow microporosity could lead to an underestimation of the porosity in this size range, nitrogen sorption should be used as a qualitative analytical tool for the determination of micropores in soft matter, rather than as a quantitative one.[25] Additionally, these PIs exhibited significant hysteresis between adsorption and desorption, even at low relative pressures, which could be associated with the plasticization and swelling in a microporous structure.[26]

The results of the nitrogen sorption measurements were summarized in Table 5. The PI **IIa** and **IIb** containing the larger pendant group exhibited a surface area of 225 m^2/g and 290 m^2/g respectively, whereas the PIs including **I** as the dianhydride exhibit relatively lower surface areas ranged from 78 to 181 m^2/g. In comparison with PIs based on 6FpDA, the PIs from m-TMDA showed higher surface area which could be associated with methyl groups adjacent to the nitrogen of the imide group that severely restricts rotation about the C-N bond and thus prevented dense chain packing. However, it was unexpected that PI **Ic** containing the tetraphenylmethane groups in both diamine and

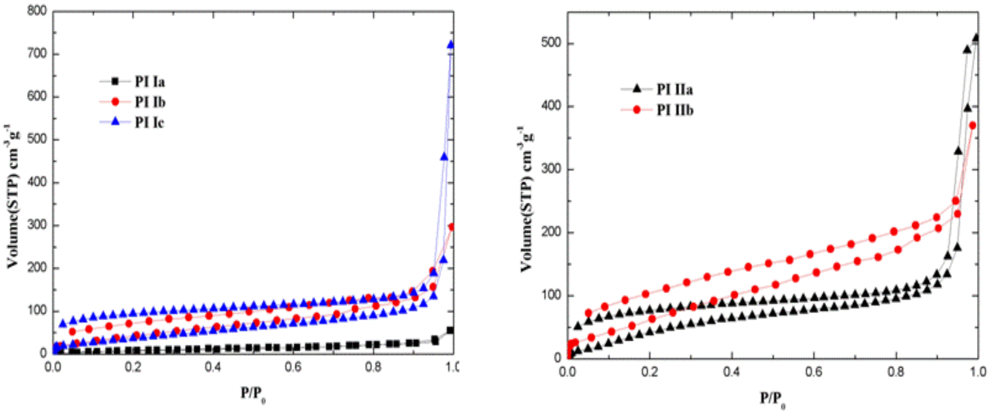


Fig. 4 Nitrogen sorption isotherms of poly(amine imide)s measured at 77 K

Table 4 Mechanical properties of the poly(amine imide) membranes.

Polymer	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at break (%)
Ia	110	1.5	7.8
Ib	95	1.4	7.6
Ic	104	1.7	8.0
IIa	97	1.4	5.2
IIb	101	1.3	4.9

Table 5 Results of nitrogen sorption measurements

Polymers	S_{BET}^{a}(m^2/g)	S_{Lang}^{b}(m^2/g)	$V_{0.9}$^{c}(cm^3/g)
Ia	78	113	0.09
Ib	181	342	0.39
Ic	152	335	0.18
IIa	225	406	0.19
IIb	290	572	0.32

[a] Apparent surface area calculated over the relative pressure range P/P$_0$ =0.1–0.2 using the BET method. [b] Apparent surface area calculated over the relative pressure range P/P$_0$ =0.1–0.2 using the Langmuir method. [c] Total pore volume (P/P$_0$ =0.9).

dianhydride structures also exhibited lower surface area than that of PI **Ib**, which also confirmed that the stiffness of main chains was the governing factor for obtaining polymeric materials with high free volume. Comparatively, the surface areas of these PIs with bulky pendant groups were relatively lower than that of PIM-PIs, which usually contained highly rigid spiro-centers in the main chains.[15-16,25] Nevertheless, viewed from another perspective, these PIs exhibited higher surface areas than most bulky PIs (40-68 m^2/g) and this could be attributed directly to the free-volume generating properties of the tetraphenylmethane as pendant groups.[27,28]

Gas separation properties

Gas permeation properties of the polyimide membranes were measured at 25°C and 1atm. The pure gas permeability coefficients and separation factors based on ratios of pure gas permeability coefficients were summarized in Table 6. Owing to the relatively high free volume confirmed by the BET surface area measurements, these membranes were more permeable than that of commercially available PIs. For example, the CO_2 permeability coefficients of these membranes were in the range of 59-427 barrer, whereas the Matrimid 5218 have CO_2 permeability of 8.7 barrer.[29] The permeability coefficient of these poly(amine imide)s were related to their surface areas. Since the PI **IIb** have the highest surface areas among them, it exhibited the highest gas permeability coefficient for all the gases tested.

The O_2/N_2 and CO_2/CH_4 selectivity coefficients were in the range 3.90–5.01 and 16.2–26.7 respectively. Following the trade-off relationship between selectivity vs. permeability, the PI **IIb** with the high surface area and gas permeability coefficient also exhibited the relatively low permselectivity coefficient among them.

The pressure-dependent mixed gas tests were also performed to investigate the gas separation performance of these PIs, which may differ from that of pure gases especially for strongly adsorbing species such as CO_2. Fig.5 showed the permeation of the mixed gas of 80:20 CO_2/N_2 for PI **Ia-c** membranes. It was seen from Fig.5a that the CO_2 permeability decreased with increasing partial pressure for all polymers tested and declined by almost 14-17% at CO_2 partial pressure of 5 bar. This was due to the filling of Langmuir sorption sites, as predicted by the dual mode sorption mechanism.[30] On the other hand, the N_2 permeability changed little at the same pressure. As a result, the overall mixed gas selectivity also decreased with increasing CO_2 partial pressure (Fig.5c), which agreed with the general tendency for mixed gas pressure-selectivity for polymer membranes.

Fig.6 and Fig.7 described gas permeability and selectivity of the polyimide membranes for CO_2/CH_4 and O_2/N_2 compared to upper bounds established by Robeson.[5,6] Data from the PIs based on N-linked dianhydrides from *p-tert*-butylaniline are also included for comparison. Although all the PIs fell slightly below the present upper bound limit for O_2/N_2 gas pair, in comparison with the poly(amine imide)s based on N-linked dianhydrides from *p-tert*-butylaniline, the new obtained poly(amine imide)s showed better combination of permeability and selectivity because they were placed closer to the upper bound line. For CO_2/CH_4 gas pair, the PI **IIa** was located on the 1991 upper

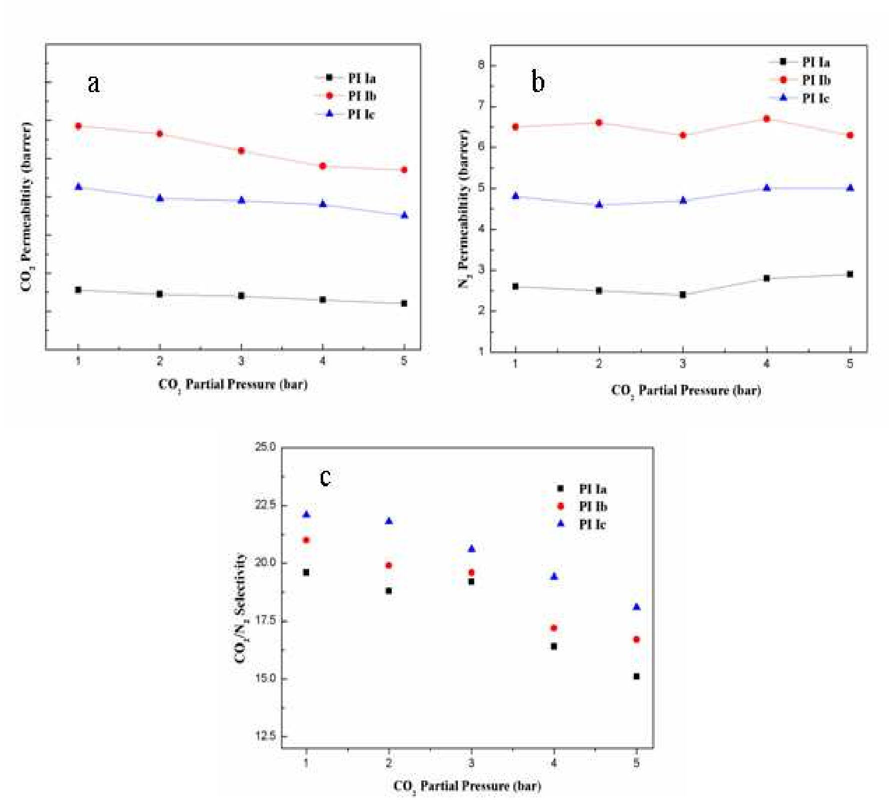


Fig. 5 Mixed gas permeation using a 80/20 CO_2/N_2 at 25° C: (a) CO_2 permeability, (b) N_2 permeability, and (c) CO_2/N_2 separation factor.

Table 6 Pure gas permeabilities[a] and selectivities (α) of the poly(amine imide)s at 25 °C and 1 atm.

Polymer	Permeabilities (barrer)				selectivities (α)	
	$P(O_2)$	$P(N_2)$	$P(CO_2)$	$P(CH_4)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/CH_4)$
Ia	14.7	2.93	59.5	2.23	5.01	26.7
Ib	29.3	6.40	153	6.74	4.21	22.7
Ic	25.8	5.54	117	5.01	4.68	23.5
IIa	33.8	7.93	198	8.61	4.26	23.0
IIb	71.1	18.2	427	26.2	3.90	16.2

[a] P is permeability coefficient; units: 1 Barrer=10^{-10} cm^3 [STP] cm cm^{-2} s^{-1} cm Hg^{-1}.

bound, exhibiting the best gas separation performance among them. All these results confirmed the positive effect of the tetraphenylmethane groups on improving the gas separation properties. Nevertheless, most of these PIs still could not outperform the PIM-PIs usually containing the spirobisindane units in the main chain, which tend to lie on or even beyond the 1991 upper bound. The result might be due to the relatively less rigid polymer chains of these PIs than that of the PIM-PIs, which was also reflected by their relatively lower apparent BET surface area. Similar results have revealed that a systematic increase in backbone rigidity is required to obtain better gas separation properties.[10,23,31] Therefore, the polymer design could be optimized by preparing derivatives of dianhydride **I** and **II** that could further stiff the backbones, such as the dianhydrides from the amines with methyl substituents adjacent to the amine group,[32] to improve the gas separation performance. The synthesis of such poly(amine imide)s is planned.

Conclusion

Two novel bis(amine anhydride)s monomers with rigid and bulky tetraphenylmethane pendant groups, have been prepared via Pd-catalyzed amination reaction of *N*-methyl-4-chlorophthal-imide with 4-tritylaniline, 4-(tris(4-(tert-butyl)phenyl)methyl)aniline, respectively. A series of poly(amine imide)s were obtained from such bis(amine anhydride) monomers and aromatic diamines. The tetraphenylmethane pendant groups endowed the resulting polymers with high thermal stability, high *T*g's and excellent solubility in common organic solvents such as chloroform and THF. These poly(amine imide)s exhibited high internal free volume confirmed by the BET surface area measurements and thus led to relatively high gas permeability coefficients, greater than commercially available PIs. On the other hand, the restricted segmental mobility of the polymer backbone contributed to the modest good permselectivities. In particular, the highest permeability (427 barrers) of the PI **IIb** for CO_2 was achieved and the PI **IIa** lied on the 1991 boundary limit for CO_2/CH_4 gas pair. Thus, they are materials with promising performance for air or natural gas purification. These studies help to emphasize the importance of the restriction of chain conformational for the PIs with bulky and rigid pendant groups obtaining excellent gas separation performance. Further studies are aimed at optimizing polymer design by preparing novel bis(amine anhydride)s from corresponding amines which could impart polymer with higher free volume or even characteristics similar to a polymer of

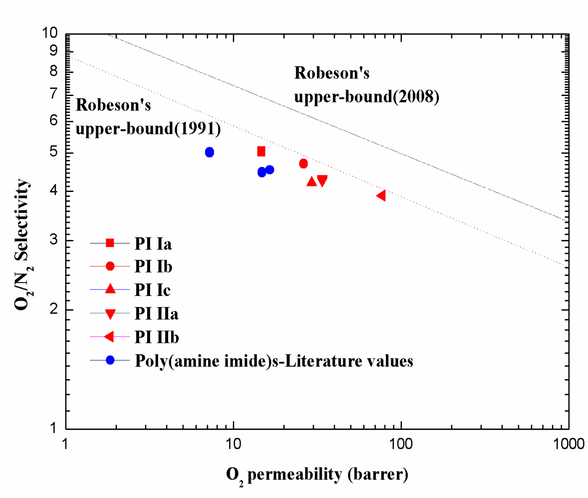


Fig. 6 Robeson plot[5,6] for a comparision of O_2/N_2 selectivity *vs.* O_2 permeability coefficients of the PIs with some other polymers reported earlier, values taken form ref. 18.

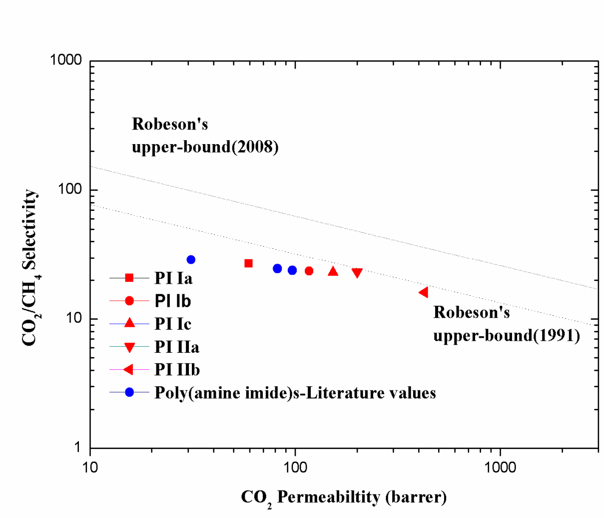


Fig.7 Robeson plot[5,6] for a comparision of CO_2/CH_4 selectivity *vs.* CO_2 permeability coefficients of the PIs with some other polymers reported earlier, values taken form ref. 18.

intrinsic microporosity and thus further improve their gas separation properties.

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Notes and references

[a] *Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.*
[b] *School of Chinese Academy of Sciences, Beijing 100049, China.*
** Corresponding author. Fax: +86 431 85262117; Tel: +86 431 85262118; E-mail: sbzhang@ciac.ac.cn*

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