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Synthesis of Bis(amine anhydride)s for Novel High T_gs and Organosoluble Poly(amine imide)s by Palladium-Catalyzed Amination of 4-Chlorophthalide Anhydride

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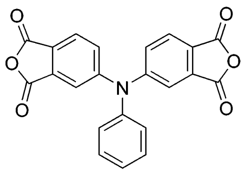
ABSTRACT: Two novel bis(amine anhydride)s, *N*,*N*-bis(3,4-dicarboxyphenyl)aniline dianhydride (**I**) and *N*,*N*-bis(3,4-dicarboxyphenyl)-*p*-*tert*-butylaniline (**II**), were synthesized from the palladium-catalyzed amination reaction of *N*-methyl-protected 4-chlorophthalic anhydride with arylamines, followed by alkaline hydrolysis of the intermediate bis(amine−phthalimide)s and subsequent dehydration of the resulting tetraacids. The X-ray structures of anhydride **I** and **II** were determined. The obtained dianhydride monomers were reacted with various aromatic diamines to produce a series of novel polyimides. Because of the incorporation of bulky, propeller-shaped triphenylamine units along the polymer backbone, all polyimides exhibited good solubility in many aprotic solvents while maintaining their high thermal properties. These polymers had glass transition temperatures in the range of 298−408 °C. Thermogravimetric analysis showed that all polymers were stable, with 10% weight loss recorded above 525 °C in nitrogen. The tough polymer films, obtained by casting from solution, had tensile strength, elongation at break, and tensile modulus values in the range of 95−164 MPa, 8.8−15.7%, and 1.3−2.2 GPa, respectively. The CO_2 permeability coefficients (P_{CO_2}) and permeability selectivity of CO_2 to CH_4 (P_{CO_2}/P_{CH_4}) of these polyimide membranes were in the range of 7.8−274 barrer and 19.2−45.3, respectively.

Introduction

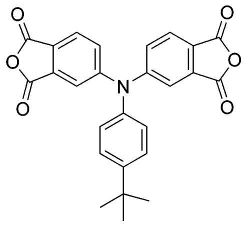
Aromatic polyimides(**PIs**) are well-established high performance materials originally developed for the aerospace industry. High thermal stability combined with chemical resistance and excellent electrical and mechanical properties of polyimides make them attractive as versatile high performance materials for a variety of applications such as electrics, coatings, composite materials and membranes.[1,2] However, most **PIs** also encounter processing difficulty because of their low solubility in common organic solvents and high melting or softening temperatures, which limited their applications. Therefore, significant synthetic efforts have been made to improve the processability and solubility of **PIs** with the retention of their attractive properties by the introduction of a new structure into the polymer backbone.

Aromatic dianhydrides are valuable building block for the preparation of **PIs** and a series of completely or partially ladderlike polyheteroarylenes. The simplest modification of the most widely used bis(phthalic anhydride)s to improve processability of polyimides is the introduction of single bonds[3] or “hinge” groups[4−8] between two fragments of phthalic anhydride. Such bis(phthalic anhydride)s are mainly prepared from 4-nitrophthalic anhydride or 4-chlorophthalic anhydride. For example, the bis(ether anhydride) used for Ultem poly(ether imide) can be prepared via the condensation of methyl 4-nitrophthalimide and Bisphenol A.[9] It has been generally recognized that flexible linkages or the bulky propylidene groups impart better solubility and melt-processing characteristics and improved toughness compared with polymers without these linkages. However, the decrease in mechanical properties on heating is almost always a consequence of the reduced chain stiffness or T_g. Another successful modification for increasing the solubility and processability of **PIs** is the introduction of bulky pendant phenyl groups into the polymer backbone.[10−18] The attachment of bulky lateral groups can impart an increase in T_g by restricting the segmental mobility, while providing an enhanced solubility because of decreased packing density and crystallinity. Combining these two structural modifications may minimize the tradeoff between poor processability and improved physical properties of highly aromatic polymers.[19−24]

To date, little is known about N-linked dianhydride and the corresponding poly(amine imide)s. The bis(amine anhydride)s such as **I** seem to be particularly attractive, because they combine several useful properties, such as bulky phenyl substituents, hindered rotation, and kinked backbone structure.



I



II

The unique structural feature of N-linked dianhydride prompt us to prepare and characterize a series of polyimides from the dianhydride **I** and **II**. In this article, we describe the synthesis of bis(amine anhydride)s and the corresponding **PIs**. Bis(amine anhydride)s was synthesized from the palladium-catalyzed amination reaction of *N*-methyl-protected 4-chlorophthalic anhydride with aniline and *p*-*tert*-butylaniline, respectively. It was expected that the introduction of triphenylamine structure

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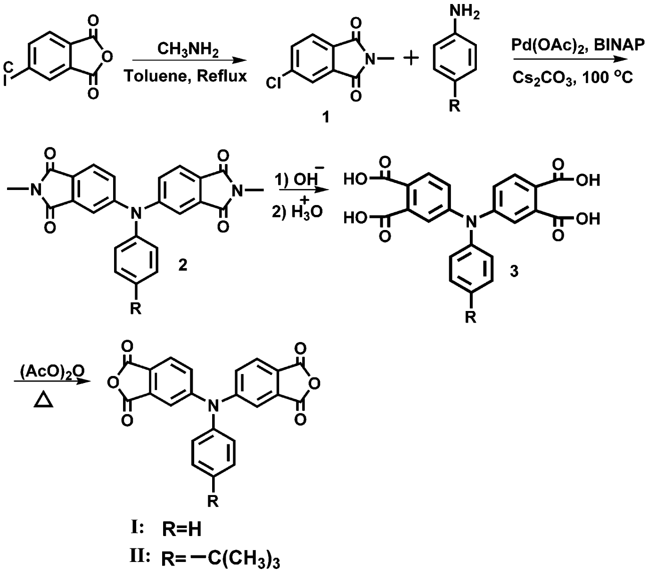
Scheme 1. Synthesis of Bis(amine anhydride) I and II



as an anhydride unit could improve the solubility of the **PIs** with retention of excellent thermal properties. A three-coordinated nitrogen induced kink structures is certainly responsible for lowering interchain interactions, thus improving the solubility of **PIs**. Furthermore, the Pd-catalyzed amination method provides a facile synthetic route to dianhydrides containing a variety of amines, and diamines moieties. Physical, thermal, and gas permeation properties of these **PIs** were also investigated.

Results and Discussion

Synthesis of Monomers and Polymers. The synthetic route of monomers is outlined in Scheme 1. Methyl 4-chlorophthalimide (**1**) was prepared from 4-chlorophthalic anhydride and methylamine. The 4-chlorophthalic anhydride was used rather than 4-bromophthalic anhydride because of the low cost of this regent. Bis(amine-phthalimide)s **2I** and **2II** were synthesized from the palladium-catalyzed amination reaction of **1** with aniline and *p-tert*-butylaniline in the yield of 84−92%. The amination reaction was carried out in DME in the presence of $Pd(OAc)_2$, BINAP, and Cs_2CO_3. In the first step, the coupling reaction generated a monosubstituted secondary arylamine. The accepted mechanism of the Pd-catalyzed amination involves a combination of aryl halides oxidative addition, production of an aryl amido species from the aryl halide complex, and reductive elimination of arylamine.[25] By inductive effect or by resonance, the electrowithdrawing carbonyl in the meta and para positions of the chloride substituent would favor the oxidative addition of the phthalimide chloride while the arylamine with electron-donating alkyl groups favor the reductive elimination. In the second step, the coupling of the secondary arylamines with **1** was sluggish due to the decreased activity and the steric hindrance of the secondary arylamines with the electrowithdrawing phthalimide groups.[26,27] Thus, the reactions required the use of high temperatures and long reaction times. 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**, **II**. Elemental analyses and IR and NMR spectroscopic techniques were used to identify the structures of the target dianhydride monomers. The representative C−H HMQC spectrum of the dianhydride monomer **II** is illustrated in Figure 1. Assignment of each proton is also given in this figure and this spectrum agrees well with the proposed molecular structure of **II**. Finally, we could obtain the single crystals of **I** and **II** by slow sublimation at 200 °C under vacuum and the crystal data are listed in Table S1 (Supporting Information). As shown in Figure 2, triphenylamine-containing dianhydrides display a three-dimensioned spatial configuration and the benzene rings of triphenylamine cores are not in the same plane. The torsional angles between the two phthalic anhydride rings are 58.4° for **I** and 48.6° for **II**. The density of **I** is appreciably higher than that of **II** (Table S1 and Table S2).

PIs were prepared by one-step polycondensation of the dianhydride **I** and **II** with a series of aromatic diamines in *m*-cresol using isoquinoline as catalyst (Scheme 2). The polymerizations were initially run at ambient temperature for 2 h. Then the temperature was raised slowly to 200 °C and maintained at that temperature for 24 h. Water formed during the imidization was continuously removed with a stream of nitrogen. In all of the reactions, a homogeneous, brown, clear viscous solution was formed. The **PIs** were obtained almost in quantitative yields (yields were above 95%) and had inherent viscosity values ranging between 0.63 and 1.81 dL/g (Table 1). The resulting **PIs** exhibited weight-average molecular weights and polydisperity in the ranges 5.4×10^4 to 24.9×10^4 and 1.93−3.39, respectively. The structure of **PIs** was confirmed by elemental analysis and IR spectroscopy. IR spectra of these **PIs** revealed the characteristic absorptions of imide groups occurred at 1772, 1722, 1378, and 744 cm^{-1} and did not show an amide carbonyl peak at 1650 cm^{-1}, indicating complete imidization during polycondensation. The ^1H and ^{13}C NMR spectrum of **PI IIb**, as shown in Figure 3, was consistent with its expected structure.

Polymer Characterization. The solubility behavior of these **PIs** was qualitatively tested in various organic solvent 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 dipolar solvents and in common organic solvents such as NMP, DMAc, and $CHCl_3$. It was noted the polymer **IIf** also showed good solubility in the tested solvents although it was derived from rigid diamine without flexible units. 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 pendant phenyl groups into polymer backbone, which retards dense chain packing and leads to a decreased chain−chain interaction. The packing-disruptive propeller-shaped triphenylamine unit in the bis(amine anhydride) moiety also contributed to the enhancement of solubility. As shown in Figure 2, the two adjacent planar anhydride components are kinked and connected to a three coordinated nitrogen. Thus, the resulting polymers should have a periodically twisted polymer backbone, and this would lower the chain packing and increase the solubility. Furthermore, the WAXD patterns for film specimens of these **PIs** revealed their amorphous character, which also explains the good solubility observed (Figure 4). The good solubility of these polymers in low boiling point solvents is a benefit to prepare the polymer films or coating at low processing temperature. The dense films of these **PIs** were prepared by the redissolution of powdered samples in DMAc, followed by the standard casting procedures.

The thermal properties of these polymers were assessed with thermogravimetric analysis (TGA) and dynamic mechanical thermal analyzer (DMTA-δ). Table 3 shows the thermal properties of **PIs** with the onset decomposition temperature (T_{onset}) and the temperature at 10% weight loss (T_{10}). Typical TGA thermograms **PI Ia** and **IIa** are shown in Figure 5. The

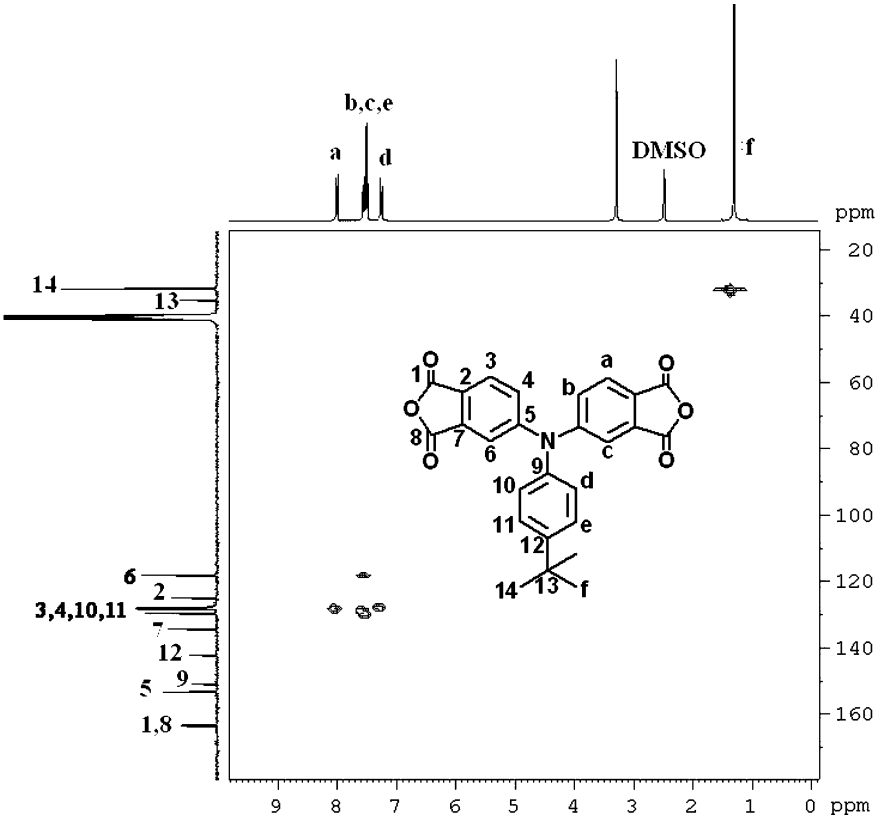


Figure 1. C−H HMQC spectrum of bis(amine anhydride) **II** in DMSO-d_6.

decomposition temperature (T_{10}) at a 10% weight loss of **PI IIa**−**IIf** were recorded in the range of 525−565 °C in nitrogen and in the range of 428−538 °C in air. The fluorinated **PI IIc** exhibited higher T_{10} values than its analogous **IIb** counterparts, and this increase may be a result of stronger C−F bonding of the CF_3 groups. The TGA results showed an excellent thermal stability of these **PIs**, even though they revealed high solubility. Generally, aromatic **PIs** have a tendency to form charge-transfer complexes and strong interchain packing. The chains interact with each other via a charge-transfer or electronic polarization mechanism. The amino functional groups may participate in the interactions of **PI** chains and become less vulnerable to thermooxidative reactions.

The glass transition temperatures (T_gs) of the **PIs** were not detectable by differential scanning calorimetry (DSC) in either normal or oscillating modes. The T_gs of the **PIs** containing triphenylamine units were also reported to be very weak or not detectable.[14] Therefore, the T_g value of the polymers was determined by DMTA using film samples. Figure 6 displays the dynamic storage modulus (E') and tan δ as a function of temperature for the **PI Ia**, **IIa**. Regarding the peak temperature in the tan δ curves as the T_g, the T_g values of these **PIs** ranged from 298 to 408 °C, depending on the diamine monomers used. Among all the **PIs** synthesized, polymer **IIf** showed the highest T_g of 408 °C, which can be attributed to the rigid diamine moieties in the polymer backbone. On the contrary, **PI Ia** showed the relatively lower T_g of 298 °C due to the relative flexible polymer chain. Upon comparison of commercial available **PI** (Ultem 1000 (G. E. Co.), T_g = 217 °C, Uplex-R, T_g = 266 °C[28]), it was observed that the triphenylamine unit can effectively enhance the glass transition temperature of the **PIs**. The mechanical properties of the **PIs** are summarized in Table 4. The polymer films had a tensile strength of 95−164 MPa, and elongation at break of 8.8−15.7%, and a tensile modulus of 1.3−2.2 GPa. Most of these polymer films exhibited high tensile strength, thus, they could be considered as strong materials.

Good solubility, rigidity, and a large free volume of the polymers are vital for application in gas separation membranes.[1,2] Bulky groups in the main chain generally tend to increase free volume and hence permeability coefficients. High chain stiffness is expected to result in relatively high permselectivities. In the present study, the **PIs** contain bulky *p-tert*-butylphenyl groups and a rigid main chain. Because of the unique properties of these **PIs**, it is of interest to investigate the gas separation behavior of these polymer membranes.

Table 5 summarizes the gas permeability coefficients of the polymer membranes. It is clear that the permeabilities of **PIs** correlate with their structures. The oxygen permeability coefficients (P_{O_2}) of **IIa** having a *tert*-butyl group at the para position of the phenyl ring was 5.16 barrer, which was higher than that of **Ia** (P_{O_2} = 1.4). Similar tendencies were observed with other gases; i.e., polymer **IIa** was more permeable to gases than was polymer **Ia**. Polymer **IIf** possessing four methyl groups at ortho position of the imide bond displayed the highest oxygen permeability among the present polymers, whose P_{O_2} value was 39.7 barrer. Polymer **IId**, which has two CF_3 groups at the diamine unit, also showed high oxygen permeability, whose P_{O_2} value was 16.5 barrer. This value was comparable with that of the reported fluorinated **PI** from 6FDA and the same diamine (6FDA:4,4′-(hexafluoroisopropylidene)diphthalic anhydride, P_{O_2} = 14.2 barrer).[22] The separation factors (α), based on ratios of pure gas permeability coefficients, are presented for O_2/N_2 and CO_2/CH_4 pairs in Table 5. Increase in permeability is generally known to be accompanied by decrease in permselectivity, which is consistent with the well-known permeability/selectivity tradeoff rule common in strongly size-sieving polymers. Polymer **IIa**−**IIf** exhibited increase permeabilities in all gas whereas slightly decrease in selectivity. To provide some perspective of the performance of the best **PIs** obtained to date, permeability/

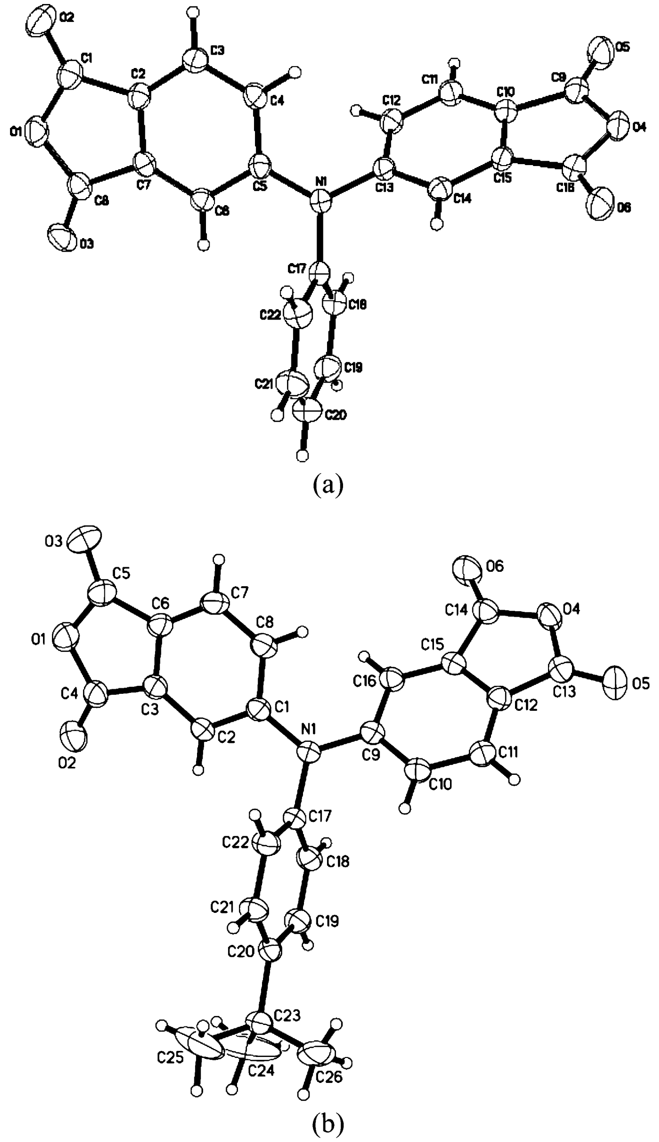


Figure 2. X-ray crystal structures of bis(amine anhydride)s **I** (a) and **II** (b) (hydrogens are omitted for clarity).

Scheme 2. Synthesis of Poly(amine−imide)s

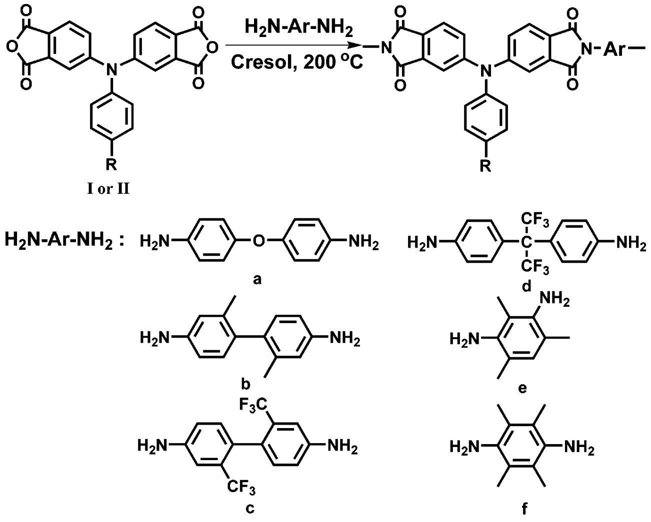


Table 1. Preparation and Elemental Analysis of Poly(amine−imide)s

PI no.	η_{inh} (dL/g)[a]	GPC[b] $M_w \times 10^4$	GPC[b] PDI	anal. (%)	C	H	N
Ia	1.08	24.9	2.73	calcd	74.31	3.48	7.65
				found	74.11	3.60	7.46
Ib	1.24	20.2	2.12	calcd	77.69	3.26	7.55
				found	77.45	3.43	7.50
Ic	1.11	15.6	2.52	calcd	65.07	1.82	6.32
				found	64.86	1.98	6.21
Id	0.91	17.7	2.24	calcd	65.50	2.08	6.19
				found	65.33	2.24	6.07
IIa	0.63	19.2	1.93	calcd	75.36	4.49	6.94
				found	75.09	4.66	6.78
IIb	1.06	12.2	3.06	calcd	77.78	5.06	6.80
				found	77.52	5.24	6.67
IIc	0.85	19.0	2.05	calcd	66.21	3.47	5.79
				found	66.00	3.63	5.67
IId	1.12	20.5	3.39	calcd	66.58	3.68	5.68
				found	66.34	3.85	5.59
IIe	0.76	5.45	2.62	calcd	75.66	5.26	7.56
				found	75.41	5.45	7.43
IIf	1.81	21.3	2.46	calcd	75.90	5.49	7.38
				found	75.72	5.66	7.24

[a] Inherent viscosity measured at a concentration of 0.5 g/dL in NMP at 30 °C. [b] With respect to polystyrene standards, with $CHCl_3$ as the eluent.

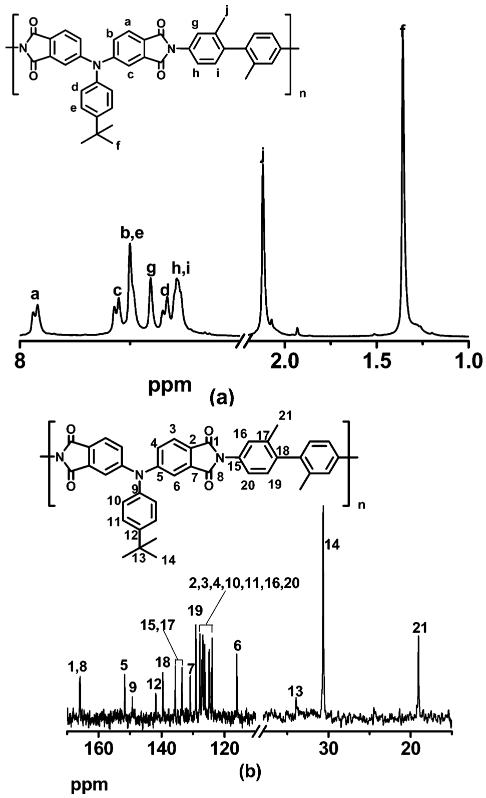


Figure 3. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of poly(amine−imide) **IIb** in DMSO-d_6.

selectivity maps are present in Figure S7 for CO_2/CH_4 pair. The solid lines represent the upper bound lines of Robeson's. The polymers in this study all fall below the upper bound. However, in comparison with the conventional **PIs** 6FDA−ODA, BPDA−ODA (BPDA: 3,3′,4,4′-biphenyltetracarboxylic dianhydride),[29] the present **PIs** showed the large improvements in gas-separation performance as evidenced by their tradeoff points close to the Robesion's 1991 upper bound line.

Experimental Section

Materials. 4-Chlorophthalic anhydride (99.2%) was purified by distillation. 1,2-Dimethoxyethane (DME) was dried by refluxing over sodium and distilled prior to use. *m*-Cresol was dried over $CaCl_2$, then over 4 Å molecular sieves, distilled under reduced pressure and stored under nitrogen in the dark. $Pd(OAc)_2$ (Aldrich),

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

	solvent[b]								
PI no.	acetone	DOA	THF	$CHCl_3$	DMF	DMAc	DMSO	NMP	*m*-cresol
Ia	−	−	−	+	±	+	±	+	+
Ib	−	+	+	+	+	+	+	+	+
Ic	−	+	+	+	+	+	+	+	+
Id	−	+	+	+	+	+	+	+	+
IIa	−	+	+	+	+	+	+	+	+
IIb	−	+	+	+	+	+	+	+	+
IIc	−	+	+	+	+	+	+	+	+
IId	−	+	+	+	+	+	+	+	+
IIe	−	+	+	+	+	+	+	+	+
IIf	−	+	+	+	+	+	+	+	+

[a] Solubility: +, soluble; ±, partially soluble; −, insoluble. [b] DMF, *N*,*N*-dimethylformamide; DMAc, *N*,*N*-dimethylacetamide; NMP, *N*-methylpyrrolidone; DMSO, dimethyl sulfoxide; DOA, 1,4-dioxane.

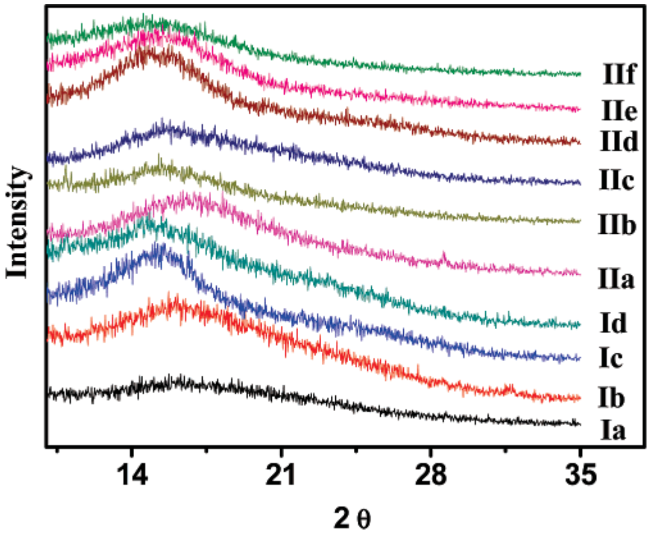


Figure 4. WAXD diffraction patterns of poly(amine−imide)s.

Table 3. Thermal Properties of Poly(amine−imide)s

PI no.	T_g (°C) DMTA[a]	T_{onset} (°C)[b]		T_{10} (°C)	
		N_2	air	N_2	air
Ia	298	540	519	565	538
Ib	351	492	515	525	462
Ic	311	558	571	575	574
Id	314	529	537	552	536
IIa	300	514	443	533	506
IIb	362	503	430	525	468
IIc	317	510	434	541	492
IId	307	515	425	540	486
IIe	397	492	412	543	457
IIf	408	514	401	527	428

[a] The glass transition temperatures (T_g) were measured by DMTA at 1 Hz and at a rate of 4 °C/min. [b] The weight loss temperature was recorded by TGA at a heating rate of 10 °C/min.

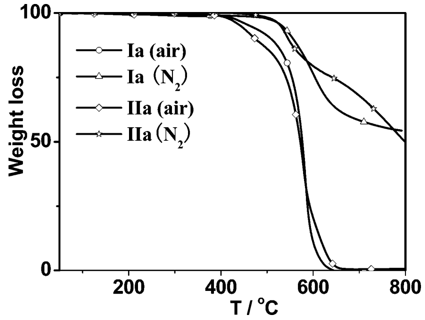


Figure 5. TGA curves of typical poly(amine−imide)s **Ia** and **IIa**.

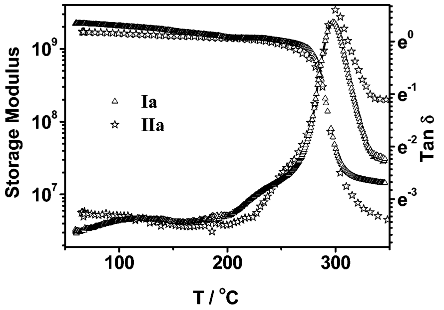


Figure 6. Dynamic modulus as a function of temperature for poly(amine−imide) **Ia** and **IIa**.

Table 4. Mechanical Properties of Poly(amine−imide)s

PI no.	film properties[a]	tensile strength (MPa)	tensile modulus (GPa)	elongation at break (%)
Ia	tough flexible	126	2.1	15.2
Ib	tough flexible	116	2.1	29.0
Ic	tough flexible	94.5	2.2	6.0
Id	tough flexible	105	2.1	8.1
IIa	tough flexible	103	1.7	12.4
IIb	tough flexible	164	2.2	11.4
IIc	tough flexible	127	2.0	14.1
IId	tough flexible	104	1.3	15.7
IIe	tough flexible	95	1.3	8.8
IIf	tough flexible	110	1.5	13.5

[a] Cast from 5% (w/v) DMAc solutions.

bis(diphenylphosphino)-1,1′-binaphthyl(*rac*-BINAP, Acros), 4-*tert*-butylaniline (Acros), isoquinoline (Acros), 4,4′-oxydianiline (ODA, Aldrich), 2,2′-dimethyl-4,4′-biphenyldiamine (DMBA, Aldrich), 2,2′-bis(trifluoromethyl)benzidine (TFMB, TCI), 4,4′-(hexafluoroisopropylidene)dianiline (6FDA, Aldrich), 2,4,6-trimethylbenzene-1,3-diamine (*m*-TMDA, Acros), and 2,3,5,6-tetramethylbenzene-1,4-diamine (TMDA, Aldrich) were used as received. Other commercially available reagent grade chemicals were used without further purification.

Measurements. ^1H and ^{13}C NMR spectra were measured at 400 MHz on a AV 400 spectrometer. The FT-IR spectra were obtained using a BRUKER Vertex 70 spectrometer. Elemental analyses were performed on an elemental analysis FLASH-EA-1112 series. The X-ray diffraction data were collected on a SiemensP4 4-circle diffractometer at 293 K. The inherent viscosities were determined at a 0.5% concentration of polymer in NMP with an Ubbelohde capillary viscometer at 30 (±0.1 °C). The molecular weight measurements were performed on a Tosoh INC HLC-8220 GPC (30 mg mL^{-1} chloroform solution as an eluent) and calibrated by the standard polystyrenes. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Rigaku Max 2500 V PC X-ray diffractometer (Japan). The mechanical properties of the films were measured on a mechanical tester Instron-1211. The thermogravimetric analysis (TGA) results were obtained in air and in nitrogen with a Perkin-Elemer TGA-2 thermogravimetric analyzer, and the experiments were carried out with (5 mg samples) at a heating rate of 10 °C/min. The dynamic mechanical property of the polymer

Table 5. Permeability Coefficients and Ideal Separation Factors Measured at 30 °C and 1 atm

	permeabilities (barrer)[a]				permselectivities ($a_{A/B}$)	
PI no.	P_{O_2}	P_{N_2}	P_{CO_2}	P_{CH_4}	P_{CO_2}/P_{CH_4}	P_{O_2}/P_{N_2}
Ia	1.36	0.19	7.770	0.17	45.29	7.16
IIa	5.16	0.95	31.10	1.14	27.25	5.43
IIb	7.22	1.44	31.10	1.06	29.23	5.03
IIc	14.82	3.30	82.32	3.31	24.84	4.48
IId	16.50	3.64	97.51	4.06	24.02	4.53
IIe	34.74	8.57	198.04	10.32	20.71	4.41
IIf	39.71	9.00	274.01	13.23	19.18	4.05

[a] Permeability values are given in units of barrers, where 1 barrer = 10^{-10}cm^3 (STP) cm/(cm^2 s cmHg).

films was measured on a Rheometric-Scientific dynamic mechanical thermal analyzer (DMTA-δ) at a frequency of 1 Hz and at a rate of 4 °C/min. Gas permeability for the polymer membrane with about 20−25 μm of thickness were measured with a conventional permeability apparatus, which consists of upstream and downstream parts separated by a membrane.

X-ray Structure Determinations of I and II. The single crystals of dianhydride **I** and **II** were grown during sublimation at 200 °C under vacuum. All measurements were made on a SiemensP4 4-circle diffractometer at 293 K under monochromatized Mo KR radiation ($\lambda = 0.71073$ Å). Dianhyride **I** crystallized in a monoclinic system with space group $P2_1/c$, $F_w = 385.32$, $a = 10.213(6)$ Å, $b = 11.940$ (8) Å, $\beta = 108.717(9)°$, $c = 15.310(10)$ Å, and $V = 1768.4(19)$ Å^3 with $Z = 4$ for $D_{calcd} = 1.447$ mg/m^3. Least-squares refinement based on 4478 independent reflections converged to final $R_1 = 0.0387$ and $R_w = 0.0860$. Dianhyride **II** crystallized in a triclinic system with space group $P1$, $F_w = 441.42$, $a = 9.978(6)$ Å, $\alpha = 116.13°$, $b = 10.346(6)$ Å, $\beta = 92.572(7)°$, $c = 11.746(7)$ Å, and $V = 1087.2(11)$ Å^3 with $Z = 2$ for $D_{calcd} = 1.348$ mg/m^3. Least-squares refinement based on 4478 independent reflections converged to final $R_1 = 0.0666$ and $R_w = 0.1566$. The structures of compounds **I** and **II** were solved by direct methods using SHELXTL revision 5.1 program.

Monomer Syntheses. *N*-Methyl-4-chlorophthalimide (1). A 91.2 g (0.5 mol) sample of of 4-chlorophthalic anhydride and 600 mL of toluene were added to a 1 L three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser. The reaction mixture was stirred at room temperature until complete solubilization of 4-chlorophthalic anhydride. Then, 77.58 g of aqueous methylamine solution (ca. 23.25 g, 0.75 mol of methylamine) were dropped in the flask. The mixture was heated with stirring at 140 °C for 5 h during which time the water was azeotropically removed. Then, the mixture was cooled to room temperature. The precipitated white crystals were filtered out and dried to give 80.2 g of the product (yield, 82%; mp, 135−136 °C). IR (KBr): 1781 and 1726 (C═O of imide), 1369 (C−N stretching), 744 cm^{-1} (C═O bending). ^{1}H NMR (DMSO-d_6): δ 8.06 (1H, s), 8.01−8.04 (1H, m), 7.78−7.81 (1H, d), 3.04 (3H, s). Anal. Calcd for $C_9H_6ClNO_2$: C, 55.26; H, 3.09; N, 7.16. Found: C, 55.13; H, 3.18; N, 7.11.

***N*′-Methyl-*N*,*N*-bis(3,4-phthalimide)aniline (2I).** A flame-dried Schlenk flask was charged with **1** (18.26 g, 100.0 mmol), aniline (3.88 g, 41.67 mmol), Pd(OAc)$_2$ (0.23 g, 1 mmol), *rac*-BINAP (0.79 g, 1.25 mmol), Cs_2CO_3 (32.55 g, 100 mmol), and 60 mL of 1,2-dimethoxyethane under nitrogen atmosphere and heated to 100 °C with stirring for 36 h. After cooling to room temperature, the reaction mixture was poured into 200 mL of methanol. The precipitate was filtered, washed with hot water. The pure product **2I** was obtained by recrystallization from methanol and DMAc (2:1, v/v) in a yield of 84% (14.4 g). Mp: 264−266 °C. IR (KBr): 1768 and 1719 (C═O of imide), 1383 (C−N stretching), 742 cm^{-1} (C═O bending). ^{1}H NMR (DMSO-d_6): δ 7.78−7.81 (2H, d), 7.48−7.51 (2H, d), 7.27−7.34 (6H, t), 3.00 (6H, s). Anal. Calcd for $C_{24}H_{17}N_3O_4$ (411.4): C, 70.07; H, 4.16; N, 10.21. Found: C, 69.67; H, 4.21; N, 10.16.

***N*′-Methyl-*N*,*N*-bis(3,4-phthalimide)-*p*-*tert*-butylaniline (2II).** This compound was prepared from **1** and 4-*tert*-butylaniline using the same procedure as described above. The yield of **2II** was 92% (17.92 g). Mp: 219−220 °C. IR (KBr): 1767 and 1711 (C═O of imide), 1378 (C−N stretching), 742 cm^{-1} (C═O bending). ^{1}H NMR (DMSO-d_6): δ 7.77−7.80 (2H, d), 7.50−7.53 (2H, d), 7.30−7.34 (4H, t), 7.19−7.21 (2H, d), 2.99 (6H, s), 1.31 ppm (9H, s). Anal. Calcd for $C_{28}H_{25}N_3O_4$ (467.52): C, 71.93; H, 5.39; N, 8.99. Found: C, 71.67; H, 5.45; N 8.90.

***N*,*N*-Bis(3,4-dicarboxyphenyl)aniline Dianhydride (I).** To a solution of **2I** (14.03 g, 30 mmol) in 50 mL of H_2O was slowly added KOH aqueous solution (8.4 g KOH in 20% solution). The solution was heated at reflux for 24 h. After cooling to room temperature, the solution was adjust to pH = 1.0 with 6 N HCl. The yellow precipitate was collected by filtration and dried in vacuum at 100 °C. The resulting tetracarboxylic acid was dissolved in 20 mL of acetic anhydride, and the solution was refluxed for 4 h. The yellow solids were filtered and washed with toluene after the solution was cooled to room temperature, and then dried at 100 °C under vacuum to give 9.26 g of yellow product in the yield of 70%. Mp: 242−244 °C. FT-IR (KBr): 1847 and 1765 cm^{-1} (C═O of anhydride). ^{1}H NMR (DMSO-d_6): δ 8.01−8.04 (2H, d), 7.51−7.58 (6H, m), 7.40−7.45 (1H, t), 7.34−7.36 (2H, d). ^{13}C NMR (DMSO-d_6): δ 162.8, 162.3, 152.6, 151.1, 144.1, 133.6, 130.8, 129.0, 127.6, 127.3, 124.4, 117.5. Anal. Calcd for $C_{22}H_{11}NO_6$ (385.33): C, 68.57; H, 2.88; N, 3.64. Found: C, 68.22; H, 2.93; N, 3.59.

***N*,*N*-Bis(3,4-dicarboxyphenyl)-*p*-*tert*-butylaniline Dianhydride (II).** This compound was prepared from **2II** using the similar procedure as described above. The yield of **II** was 62%. Mp: 230−231 °C. FT-IR (KBr): 1842 and 1772 cm^{-1} (C═O of anhydride). ^{1}H NMR (DMSO-d_6): δ 7.90−7.93 (2H, d), 7.45−7.48 (2H, d), 7.39−7.42 (4H, m), 7.15−7.18 (1H, d), 1.21 ppm (9H, s). ^{13}C NMR (DMSO-d_6): δ 163.8, 163.2, 153.6, 151.1, 142.3, 134.6, 129.8, 128.5, 128.2, 128.0, 125.2, 118.3, 35.4, 31.9. Anal. Calcd for $C_{26}H_{19}NO_6$ (441.12): C, 70.74; H, 4.34; N, 3.17. Found: C, 70.66; H, 4.52; N 3.14.

Preparation of Polymers. Polyimide **Ia** is given as an example: Diamine **a** (0.200 g, 1 mmol) and dianhydride **I** (0.385 g, 1 mmol) were first dissolved in 10 mL of *m*-cresol in a 100 mL three-neck round-bottom flask. The flask was purged with nitrogen and then the reaction mixture was stirred at room temperature for 30 min until complete dissolution of solids. After a few drops of isoquinoline were added, the mixture was heated with stirring at 200 °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 precipitated into 50 mL of ethanol. The polymer that precipitated was collected by filtration, washed with ethanol for several times and dried in a vacuum oven at 200 °C for 24 h. The yield was 97%(0.53 g). All of the other polyimides (**Ib**−**Id** and **IIa**−**IIf**) were prepared using a similar procedure.

Preparation of Dense Film. A 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. The solution was then poured into a casting ring on a leveled clean glass plate. The casting films were dried in an oven for 12 h at 80 °C, and the film samples were dried under vacuum for 2 h at 150 °C followed by 24 h at 220 °C in order to ensure complete removal of solvent.

Conclusion

Two novel bis(amine anhydride)s were successfully prepared via Pd-catalyzed amination reaction of *N*-methyl-4-chlorophthalimide with aniline, and *p*-*tert*-butylaniline, respectively. A series of poly(amine imide)s with high molecular weights were obtained from such bis(amine anhydride) monomers and various diamines. Because of the presence of the bulky triphenylamine unit, these poly(amine imide)s showed high thermal stability with high T_g's, good mechanical properties, and high solubility in common organic solvents such as chloroform and THF. Gas transport properties of these polyimides for CO_2, CH_4, O_2, and N_2 have been investigated. It is shown that the introduction of the bulky triphenylamine dianhydride unit onto aromatic polyimides can improve gas transport properties by increasing permeability with only minor decreases in permselectivity. Thus, these new polyimides could be considered as newly processable and for varied uses in high performance polymer.

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Supporting Information Available: Tables of crystal data of bis(amine anhydride) **I** and **II** and figures showing the permselectivity for carbon dioxide/methane vs carbon dioxide permeability of poly(amine-imide)s, ^{1}H NMR spectra of **I** ,**2I**, and **2II**, ^{13}C NMR spectrum of **I**, TGA curves of poly(amine−imide) **Ib−d** and **IIb−f**, and DMTA curves of poly(amine−imide) **Ib−d** and **IIb−f**, and a table of FT-IR data of poly(amine-imide)s. This material is available free of charge via the Internet at http://pubs.acs.org.

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