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Synthesis of isomeric bis(amine anhydride)s for novel poly(amine imide)s by Pd-catalyzed amination of 4-chlorophthalic anhydride

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Abstract

Two novel bis(amine anhydride) monomers, *N*,*N*′-bis(3,4-dicarboxyphenyl)-1,4-phenylenediamine dianhydride **I** and *N*,*N*′-bis(3,4-dicarboxyphenyl)-1,3-phenylenediamine dianhydride **II**, were prepared via palladium-catalyzed amination reaction of 4-chloro-*N*-methylphthalimide with 1,4-phenylenediamine or 1,3-phenylenediamine, followed by alkaline hydrolysis of the intermediate bis(amine imide)s and subsequent dehydration of the resulting tetraacids. A series of new poly(amine imide)s were prepared from the synthesized dianhydride monomers with various diamines in NMP via conventional two-step method. FT-IR spectra of the poly(amine imide)s revealed that in the solid state, intermolecular and intramolecular hydrogen bonding (N–H···O=C) are present. These polymers had glass transition temperatures in the range of 250–295 °C. The 10% weight loss temperature of the resulting poly(amine imide)s ranged from 539 to 560 °C in nitrogen. The poly(amine imide)s have the peel strength values ranging from 283 to 358 N/m. The poly(amine imide)s films were found to be transparent, flexible, and tough. The films had a tensile strength, elongation at break, and tensile modulus in the ranges 102–152 MPa, 11.3–19.6%, and 1.04–2.08 GPa, respectively.

Keywords: Amination reaction; Polyimides; High-performance polymers

1. Introduction

Aromatic polyimides (PIs) are considered as a class of high-performance polymers that have been widely used for a variety of applications such as electrics, coatings, composite materials and membranes [1,2]. The use of PIs, in particular, can be attributed to their many favorable properties such as high thermooxidative stability, high mechanical strength, excellent electrical properties, and high chemical resistance. Conventionally, these materials are made through the condensation reaction of a dianhydride with a diamine giving soluble polyamic acids, followed by thermal or chemical imidization. A variety of new diamine and dianhydride monomers have been molecularly designed to satisfy the specific requirement for optional performance in special applications. A greater flexibility in the design and synthesis of aromatic diamines arises from the well-established chemistry of aniline and its derivatives [3]. Dianhydride monomers, 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 [4]. Two phthalic anhydrides can also be linked together through a variety of connectors, for instance O, S, CO, SO_2, and $C(CF_3)_2$ [5–9,14]. 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. However, the introduction of bulky and rigid linkages could improve solubility and processability of polyimides

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without sacrificing their thermal stability [10]. For example, in previous paper, we reported the synthesis of N-linked dianhydride and the corresponding poly(amine imide)s [11]. Because of the incorporation of bulky, propeller-shaped triphenylamine groups in the dianhydride units, the resulting polyimides exhibited good solubility in many aprotic solvents while maintaining their high thermal properties. As a continuation of this study, two new N-linked dianhydrides, *N*,*N*′-bis(3,4-dicarboxyphenyl)-1,4-phenylenediamine dianhydride (**I**) and *N*,*N*′-bis-(3,4-dicarboxyphenyl)-1,3-phenylenediamine dianhydride (**II**), were synthesized from the palladium-catalyzed amination reaction of 4-chloro-*N*-methylphthalimide with 1,4-phenylenediamine (PPD) and 1,3-phenylenediamine (MPD), respectively.

This paper deals with the synthesis and basic characterization of novel aromatic poly(amine imide)s derived from **I** or **II**.

These polymers can be considered as hybrid structure of polyimides and polyaniline. It was expected that the amino and carbonyl groups in poly(amine imide)s would result in intermolecular hydrogen bonds like in poly(arylene amide)s, such as Kevlar, leading to good thermal and mechanical properties that are essential requirements for high-performance polymers [12,13]. Functional amino groups on a PI backbone also serve as sites for further chemical modification, graft copolymerization, or cross-linking. Furthermore, the Pd-catalyzed amination method provides a facile synthetic route to dianhydrides containing a variety of diamine moieties. Physical, thermal, and gas permeation properties of these PIs were also investigated.

2. Experimental

2.1. Materials

Palladium(II) acetate (Aldrich) and bis(diphenylphosphino)-1,1′-binaphthyl (*rac*-BINAP) (Aldrich) were used as received. Cesium carbonate (Cs_2CO_3) was dried in vacuum at 150 °C for 24 h prior to use. 4-Chlorophthalic anhydride (99.2%) was purified by distillation. 1,3-Phenylenediamine (MPD), 1,4-phenylenediamine (PPD) and 4,4′-oxydianiline (ODA) were purified by sublimation under vacuum. 4,4′-Methylenedianiline (MDA), 3,3′-dimethyl-4,4′-methylenedianiline (DMMDA), and 2,2′-dimethyl-4,4′-biphenylenediamine (DMB) were purified by recrystallization from ethanol prior to use. 1,4-Bis(4-aminophenoxy)benzene (TPEQ) was synthesized according to the literature [14]. 1,2-Dimethoxyethane (DME) was dried by refluxing over sodium and distilled prior to use. *N*-Methyl-2-pyrrolidone (NMP) was purified by stirring over phosphorous pentoxide for 5 h, then distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves in the dark. Other commercially available reagent grade chemicals were used without further purification.

2.2. Monomer synthesis

2.2.1. N,N′-Bis(N-methylphthalimido)-1,4-phenylenediamine (2I)

A flame-dried Schlenk flask was charged with **1** (18.6 g, 95.0 mmol), 1,4-phenylenediamine (5.40 g, 50.0 mmol), $Pd(OAc)_2$ (0.225 g, 1.00 mmol), *rac*-BINAP (0.623, 1.00 mmol), Cs_2CO_3 (35.8 g, 110 mmol) and 70 mL of 1,2-dimethoxyethane (DME) under nitrogen atmosphere and heated to 100 °C with stirring for 6 h. After cooling to room temperature, the reaction mixture was poured into a mixture of ethanol/water. The precipitate was filtered, and washed with hot water and ethanol for three times. The pure product **2I** was obtained.

Yield: 88%. FT-IR (KBr pellet, cm^{-1}): 3321 (N–H stretching), 1759 (asymmetry C=O stretching), 1688 (symmetry C=O stretching). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 9.09 (s, 2H), 7.61–7.64 (d, 2H), 7.24–7.25 (m, 6H), 7.18–7.22 (d, 2H), 2.98 (s, 6H). Anal. Calcd for $C_{24}H_{18}N_4O_4$ (426.42): C, 67.60%; H, 4.25%; N, 13.14%. Found: C, 68.19%; H, 4.48%; N, 13.34%.

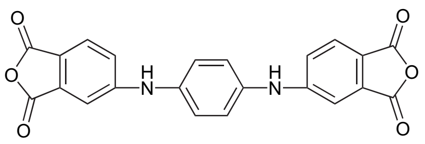
2.2.2. N,N′-Bis(N-methylphthalimido)-1,3-phenylenediamine (2II)

This compound was prepared from **1** and 1,3-phenylenediamine using the same procedure as described above.

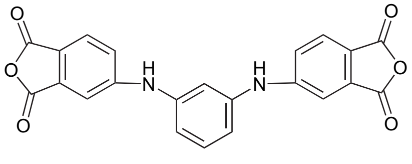
Yield: 87%. FT-IR (KBr pellet, cm^{-1}): 3327 (N–H stretching), 1765 (asymmetry C=O stretching), 1702 (symmetry C=O stretching). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 9.17 (s, 2H), 7.66–7.69 (d, 1H), 7.35–7.38 (d, 2H), 7.33–7.34 (d, 2H), 7.28–7.32 (dd, 2H), 7.03–7.04 (d, 1H), 6.89–6.92 (dd, 2H), 2.98 (s, 6H). Anal. Calcd for $C_{24}H_{18}N_4O_4$ (426.42): C, 67.60%; H, 4.25%; N, 13.14%. Found: C, 67.88%; H, 4.59%; N, 13.10%.

2.2.3. N,N′-Bis(3,4-dicarboxyphenyl)-1,4-phenylenediamine dianhydride (I)

To a 15% NaOH aqueous solution (60 mL) was added 17.1 g of compound **2I** (40.0 mmol). The mixture was refluxed for 24 h under nitrogen atmosphere after the solid was completely dissolved. After cooling to room temperature, the solution was adjusted to pH = 1.0 with 6 N HCl. The green precipitate was collected by filtration and dried in vacuum at 100 °C. The resulting tetracarboxylic acid was dissolved in



I



II

50 mL acetic anhydride and then refluxed for 6 h. The solids were filtered without cooling and washed with petroleum ether, then dried at 100 °C under vacuum to give 10.2 g of brown product.

Yield: 66%. FT-IR (KBr pellet, cm^{-1}): 3327 (N–H stretching), 1836 (anhydride asymmetry C=O stretching), 1766 (anhydride symmetry C=O stretching). ^1H NMR (300 MHz, DMSO-d_6, ppm): 9.48 (s, 2H), 7.83–7.86 (d, 2H), 7.36–7.40 (dd, 2H), 7.33–7.34 (m, 6H). Anal. Calcd for $C_{22}H_{12}N_2O_6$ (400.34): C, 66.00%; H, 3.02%; N, 7.00%. Found: C, 66.00%; H, 3.33%; N, 7.33%.

2.2.4. *N,N′-Bis(3,4-dicarboxyphenyl)-1,3-phenylenediamine dianhydride (**II**)*

This compound was prepared from **2II** using the same procedure as described above.

Yield: 64%. FT-IR (KBr pellet, cm^{-1}): 3354 (N–H stretching), 1837 (anhydride asymmetry C=O stretching), 1762 (anhydride symmetry C=O stretching). ^1H NMR (300 MHz, DMSO-d_6, ppm): 9.54 (s, 2H), 7.86–7.89 (d, 2H), 7.42–7.47 (m, 5H), 7.10–7.11 (d, 1H), 7.01–7.04 (dd, 2H). Anal. Calcd for $C_{22}H_{12}N_2O_6$ (400.34): C, 66.00%; H, 3.02%; N, 7.00%. Found: C, 65.63%; H, 3.32%; N, 6.94%.

2.3. *Synthesis of poly(amine amic acid)s and poly(amine imide)s*

Poly(amine imide)s were prepared by reacting equal mole of *N,N′*-bis(3,4-dicarboxyphenyl)-1,4-phenylenediamine dianhydride **I** or *N,N′*-bis(3,4-dicarboxyphenyl)-1,3-phenylenediamine dianhydride **II** with various diamines via a two-step procedure. Poly(amine imide)s syntheses are exemplified by specific synthesis of **IIb** from the condensation of **II** and ODA. To a 100-mL three-neck round-bottom flask equipped with magnetic stirrer, nitrogen inlet, 0.2003 g of ODA (1.0 mmol) and 3.4 g of dried NMP were added. After the diamine had dissolved completely, 0.4004 g of *N,N′*-bis (3,4-dicarboxyphenyl)-1,3-phenylenediamine dianhydride **II** (1.0 mmol) was added to the stirred solution of ODA in NMP (3.4 g) quickly. The solid content of the solution was 15% (w/w). The reaction mixture was stirred in nitrogen at room temperature for 48 h to afford a viscous brown solution. The obtained poly(amic acid) (PAA) solution was filtered through a 0.2 μm Teflon syringe filter to eliminate any particulates that might affect the quality of the cured film. The purified PAA solution was poured on a leveled clean glass plate. The poly(amine imide) thin film was obtained by drying the PAA solution for 2 h in an oven at 80 °C, and then thermally curing at 150, 250, and 300 °C for 1 h each in vacuum. The **IIb** film, which was brown in color, was obtained by immersing the glass plate in warm water.

Other poly(amine imide)s films were prepared by a procedure similar to that mentioned above, except that ODA was replaced by MDA (**IIa**), DMMDA (**IIc**), TPEQ (**IId**) or DMB (**IIe**) or *N,N′*-bis(3,4-dicarboxyphenyl)-1,3-phenylenediamine dianhydride **II** was replaced by *N,N′*-bis(3,4-dicarboxyphenyl)-1,4-phenylenediamine dianhydride **I** (**Ia–e**).

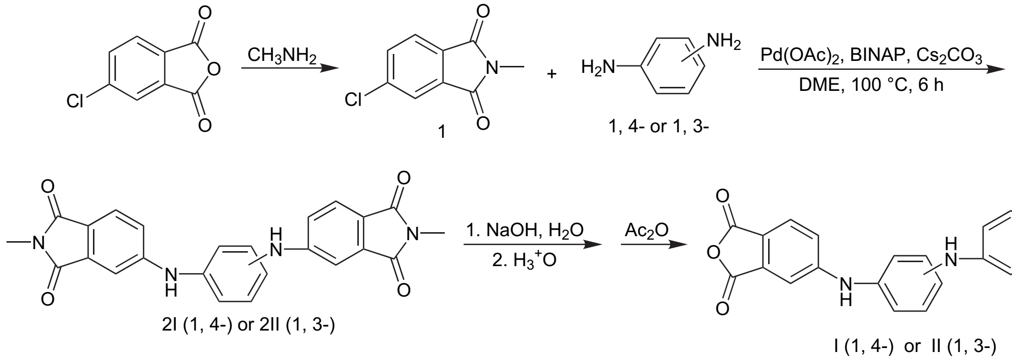
2.4. *Measurements*

The FT-IR spectra were recorded on a Bio-Rad Digilab Division FTS-80 spectrometer. ^1H NMR spectra were measured at 300 MHz on a Bruker AV300 spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed on an Elemental Analyses MOD-1106. The inherent viscosities were determined at a 0.5% concentration of polymer in NMP with an Ubbelohde capillary viscometer at 30(±0.1) °C. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC-7 system at a heating rate of 20 °C/min under nitrogen atmosphere. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific™) in a tension mode at a heating rate of 3 °C/min and a frequency of 1 Hz from room temperature. Thermogravimetric analysis (TGA) was carried out with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. The coefficients of thermal expansion (CTEs) of the poly(amine imide) films were determined by thermal mechanical analysis (TMA) with a DuPont 9900 thermomechanical analyzer at a heating rate of 5 °C/min from 25 to 250 °C and taken as the mean between 40 and 180 °C. The mechanical properties of the films were measured on a mechanical tester Instron-1211 at a speed of 5 mm/min at 25 °C. Peel tests were performed at room temperature using a tensile testing machine equipped with a 180°-peel fixture. Wide-angle X-ray diffraction measurements were performed at room temperature using a Rigaku D/max-2500 X-ray diffractometer with a Cu Kα ($\lambda = 0.154$ nm) source, operated at 40 kV and 250 mA. The scanning rate was 4°/min over a range of $2\theta = 10–40°$.

3. Results and discussion

3.1. *Monomer synthesis*

The synthetic route of monomers is outlined in Scheme 1. 4-Chloro-*N*-methylphthalimide (**1**) was prepared from 4-chlorophthalic anhydride and methylamine [11]. 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 1,4-phenylenediamine (PPD) and 1,3-phenylenediamine (MPD) in the yield of 87–88%. The amination reaction was carried out in DME in the presence of $Pd(OAc)_2$, BINAP, and Cs_2CO_3. 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 [15]. By inductive effect or by resonance, the electron-withdrawing carbonyl in the *meta* and *para* positions of chloride substituent would favor the oxidative addition of the phthalimide chloride while the arylamine with electron-donating alkyl groups favor the reductive elimination. The resulting bis(amine-phthalimide)s were hydrolyzed in an



Scheme 1. Synthesis of bis(amine anhydride) monomers **I** and **II**.

alkaline solution to obtain the bis(amine diacid)s. The bis(amine diacid)s were then cyclodehydrated to the bis(amine anhydride)s **I** and **II**. Elemental analyses, IR and NMR spectroscopic techniques were used to identify the structures of the target dianhydride monomers. The FT-IR spectra of amino-containing dianhydride monomers **I** and **II** show characteristic absorptions at 3327 and 3354 cm^{-1} due to the N–H stretching of a secondary amino group, respectively (Fig. 1). In addition, the asymmetric and symmetric absorptions of carbonyl (C=O) for **I** and **II** are observed at 1836, 1837 and 1766, 1762 cm^{-1}, respectively. The ^{1}H NMR spectra of **I** and **II** is illustrated in Fig. 2. Assignment of each proton is also given in this figure and this spectrum agrees well with the proposed molecular structure of **I** and **II**.

3.2. Preparation of poly(amine imide)s

Two series PIs were prepared from aromatic dianhydrides and diamines via the soluble poly(amic acid) (PAA) precursors, followed by thermal imidization at elevated temperatures (Scheme 2). The reaction of bis(amine anhydride)s with the diamines at the ambient temperature gave a viscous poly(amic acid) solution. All poly(amic acid)s (**Ia–e** and **IIa–e**) had inherent viscosities in the range of 0.43–0.76 dL/g in NMP (Table 1). Flexible and tough poly(amine imide) films were obtained by drying the PAA solution for 2 h in an oven at 80 °C, and then thermally cured at 150, 250, and 300 °C for 1 h each in vacuum, followed by immersion in warm water. The successful thermal conversion from PAAs to PIs can be confirmed by the FT-IR spectra shown in Fig. 3. In this figure,

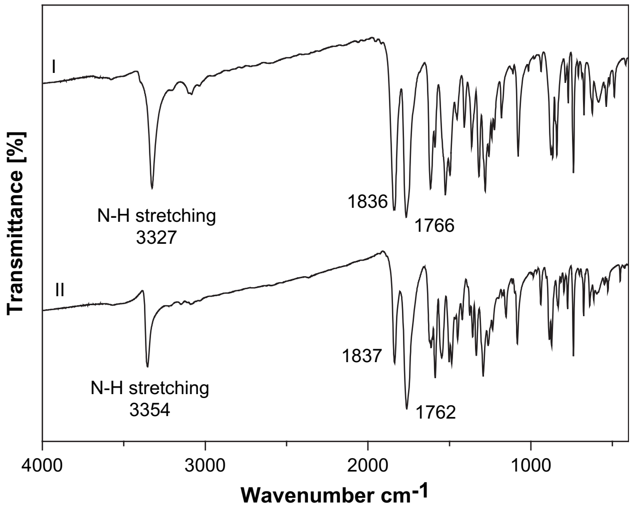


Fig. 1. FT-IR spectra of bis(amine anhydride) monomers **I** and **II**.

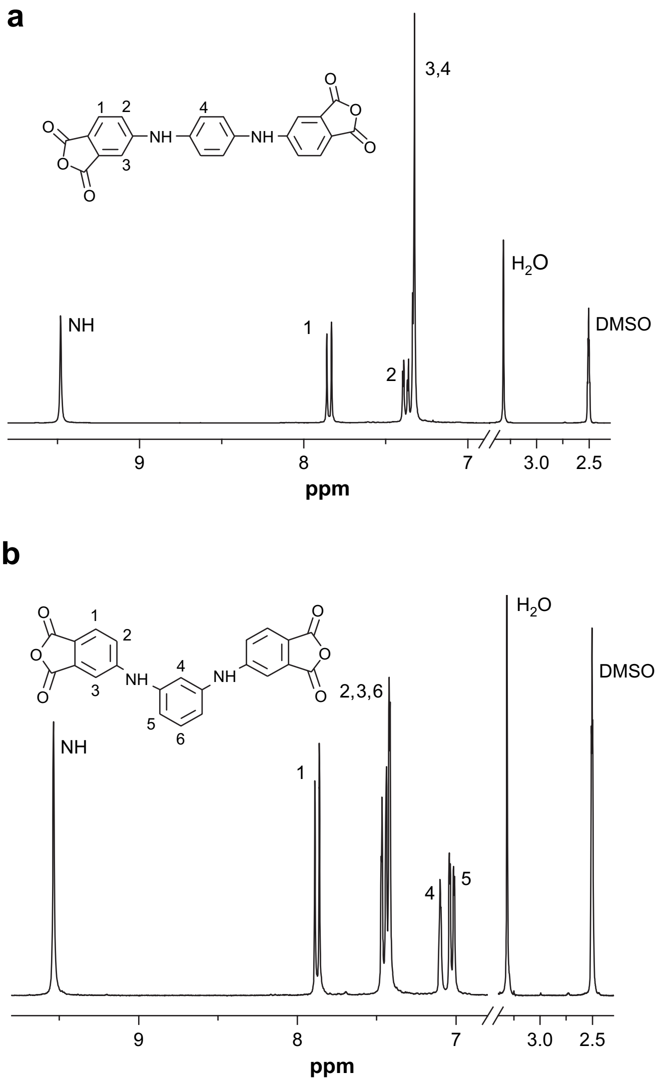
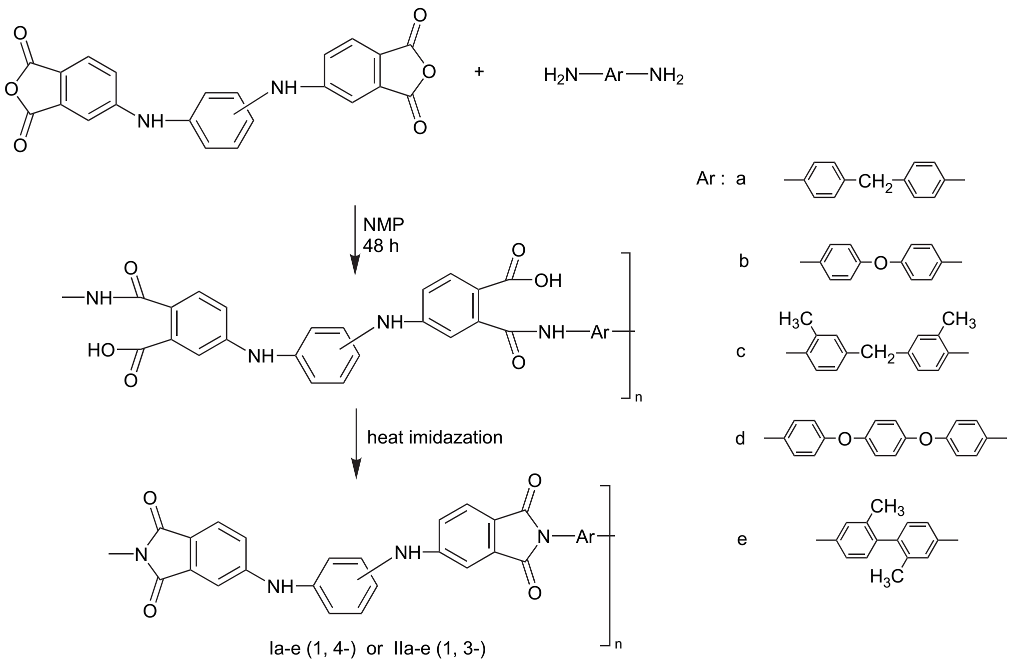


Fig. 2. ^{1}H NMR spectra of (a) **I** and (b) **II** in DMSO-d_6.



Scheme 2. Synthesis of poly(amine imide)s.

no peaks due to the C═O stretching of the amide groups (1650 cm^{-1}) are observed. Hydrogen bonding interactions of polymers have frequently been studied by FT-IR spectroscopy [16,17]. Since the hydrogen bond between N–H and carbonyl oxygen of imide group weakened the force constant of C═O double bond, the carbonyl adsorption was found to shift toward a lower wave-number. As listed in Table 1, Ultem poly(ether imide) exhibited the characteristic absorption bands of the imide ring near 1772 and 1722 cm^{-1} (asymmetrical and symmetrical C═O stretching vibration). Due to the presence of hydrogen bonding interactions, the poly(amine imide)s show the characteristic absorption bands of the imide ring down to 1765 and 1700 cm^{-1}. Obviously, because of hydrogen bonding, a significant broadening of the absorption frequency of the bands γ_{NH} (3345–3357 cm^{-1}) are observed. All poly(amine imide)s have poor solubility in common organic solvents such as DMF, NMP, DMAc, and DMSO, due to the hydrogen bonding interaction.

Table 1
Synthesis and characterization of poly(amine imide)s

Polymer	Yield (%)	η_{inh}[a] (dL/g)	γ_{NH}[b] (cm^{-1})	$\gamma_{C=O}$[b] (cm^{-1})	
				Asymmetric	Symmetric
Ia	97	0.43	3355	1765	1699
Ib	99	0.56	3347	1765	1701
Ic	97	0.50	3345	1766	1703
Id	99	0.62	3355	1766	1697
Ie	98	0.64	3357	1767	1701
IIa	98	0.49	3352	1766	1700
IIb	99	0.58	3346	1767	1700
IIc	97	0.48	3348	1765	1701
IId	99	0.76	3356	1767	1702
IIe	98	0.68	3354	1766	1702

[a] Measured with PAA at a concentration of 0.5 g/dL in NMP solution at 30 °C.
[b] FT-IR (film).

The elemental analysis of the poly(amine imide)s showed that in all cases the determined carbon and nitrogen contents were lower than the calculated ones for the proposed structures. This possibly was caused by the hygroscopic nature of the amino groups of these polymers. The uptake of water was in the range of 1.82–4.02% as calculated from the weight change of the vacuum-dried polymer samples after they were exposed to air at room temperature for 12 h. Therefore, the measured elemental analysis values were corrected by elimination of the amount of absorbed water (Table 2). Similar to the study performed on hygroscopic polyaramides [18], the experimental data were then in good agreement with the calculated ones.

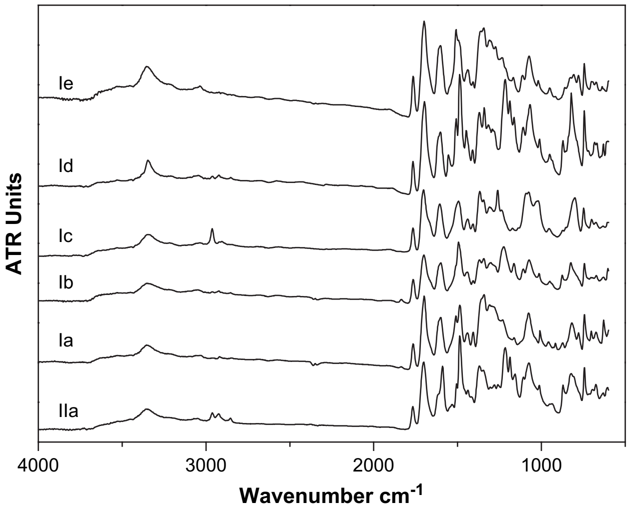


Fig. 3. FT-IR spectra of poly(amine imide) films.

Table 2
Elemental analysis for poly(amine imide)s

Polymer code	Formula (mol. wt%)[c]	Elemental analysis[a] (%)				Moisture uptake[b]
			C	H	N	
Ia	$(C_{35}H_{22}N_4O_4)_n$ $(562.59)_n$	Calculated	74.72	3.94	9.96	3.65
		Found	71.82	4.12	9.50	
		Corrected	74.44	3.97	9.85	
Ib	$(C_{34}H_{19}N_4O_5)_n$ $(563.55)_n$	Calculated	72.46	3.40	9.94	4.02
		Found	69.46	3.52	9.28	
		Corrected	72.25	3.38	9.65	
Ic	$(C_{37}H_{26}N_4O_4)_n$ $(590.64)_n$	Calculated	75.24	4.44	9.49	3.14
		Found	72.58	4.55	9.12	
		Corrected	74.86	4.41	9.41	
Id	$(C_{40}H_{23}N_4O_6)_n$ $(655.65)_n$	Calculated	73.28	3.54	8.55	2.88
		Found	71.07	3.62	8.10	
		Corrected	73.12	3.52	8.33	
Ie	$(C_{36}H_{24}N_4O_4)_n$ $(576.62)_n$	Calculated	74.99	4.20	9.72	2.41
		Found	73.10	4.25	9.44	
		Corrected	74.86	4.15	9.67	
IIa	$(C_{35}H_{22}N_4O_4)_n$ $(562.59)_n$	Calculated	74.72	3.94	9.96	3.28
		Found	72.15	4.09	9.59	
		Corrected	74.52	3.96	9.90	
IIb	$(C_{34}H_{19}N_4O_5)_n$ $(563.55)_n$	Calculated	72.46	3.40	9.94	3.78
		Found	69.36	3.60	9.36	
		Corrected	71.98	3.46	9.71	
IIc	$(C_{37}H_{26}N_4O_4)_n$ $(590.64)_n$	Calculated	75.24	4.44	9.49	2.90
		Found	73.02	4.49	9.15	
		Corrected	75.14	4.36	9.42	
IId	$(C_{40}H_{23}N_4O_6)_n$ $(655.65)_n$	Calculated	73.28	3.54	8.55	2.51
		Found	71.25	3.58	8.28	
		Corrected	73.04	3.49	8.49	
IIe	$(C_{36}H_{24}N_4O_4)_n$ $(576.62)_n$	Calculated	74.99	4.20	9.72	1.82
		Found	73.22	4.24	9.57	
		Corrected	74.55	4.16	9.74	

[a] For C and N corrected value: found value × (100% + moisture uptake %). For H corrected value: found value × (100% − moisture uptake %).

[b] Moisture uptake (%) = $(W - W_0)/W_0 \times 100\%$, where W is the weight of polymer sample after standing at room temperature and W_0 is the weight of polymer sample after drying in a vacuum at 100 °C for 12 h.

[c] In g/mol.

3.3. Polymer properties

The thermal properties of the poly(amine imide)s were examined by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) experiments and dynamic mechanical thermal analyzer measurements (DMTA). Table 3 summarizes the thermal properties of PIs with the onset decomposition temperature (T_{onset}) and the temperature at 10% weight loss (T_{10}). Typical TGA thermograms of polymers **Ib** and **IIb** are shown in Fig. 4. The

Table 3
Thermal and mechanical properties of poly(amine imide)s

Polymer	T_g (°C)		T_{onset}[c] (°C)	T_{10}[d] (°C)	Tensile strength (MPa)	Tensile modulus (Gpa)	Elongation at break (%)
	DSC[a]	DMTA[b]					
Ia	254	268	482	558	123	1.54	16.3
Ib	280	296	484	560	132	1.72	16.7
Ic	260	275	460	541	116	1.31	15.4
Id	252	258	485	559	107	1.15	17.6
Ie	295	310	459	550	152	2.08	11.3
IIa	251	266	480	556	119	1.51	16.4
IIb	279	295	485	557	125	1.70	17.2
IIc	256	270	456	539	114	1.25	15.3
IId	250	254	482	557	102	1.04	19.6
IIe	286	307	458	548	140	1.99	11.8

[a] From the second trace of DSC measurements conducted at a heating rate of 20 °C/min.

[b] Measured by DMTA at 1 Hz and at a rate of 3 °C/min.

[c] Onset decomposition temperature in TGA at 10 °C/min heating rate.

[d] Temperature at 10% weight loss in TGA at 10 °C/min heating rate.

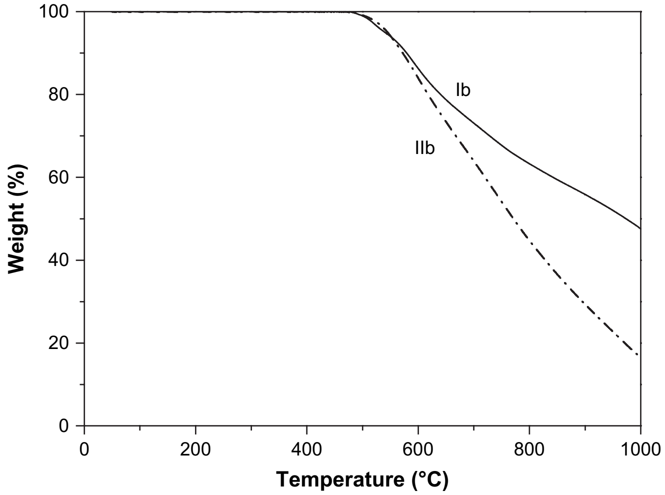


Fig. 4. TGA diagram of poly(amine imide)s **Ib** and **IIb** in nitrogen.

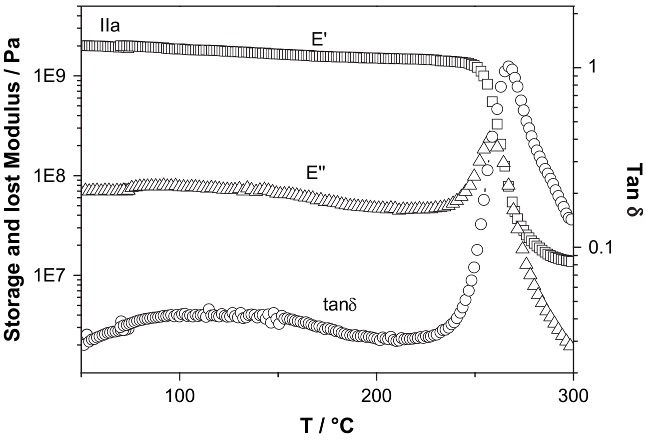


Fig. 5. Dynamic modulus as function of temperature of **IIa**.

decomposition temperature (T_{10}) at a 10% weight loss of **Ia–e** and **IIa–e** was recorded in the range of 539–560 °C in nitrogen. The TGA results showed an excellent thermal stability of these PIs, even though they contain the functional amino groups in the backbone. 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 determined by differential scanning calorimetry (DSC) with a heating rate of 20 °C/min in nitrogen. The T_g of polymers could be read in the second heating trace of DSC. The T_g of polyimides was in the range of 250–295 °C, which depended on the chemical structure of aromatic diamine component. As can be expected, polyimides **Ie** and **IIe** exhibited the highest T_g due to the rigid biphenyl diamine. Polyimides **Id** and **IIe** obtained from TPEQ diamine showed the lowest T_g because of the presence of two flexible ether linkages between the phthalimide units. Polyimides **Ia–e** obtained from 1,4-phenylenediamino linked dianhydride showed slightly higher T_g than those (**IIa–e**) from 1,3-phenylenediamino linked dianhydride and the same diamines. These polyimides also displayed higher T_g than those from bis(ether dianhydride) connected by 1,4-phenoxy, or 1,3-phenoxy linkages. For example, T_g value of **Ib** is about 35 °C higher than that of poly(ether imide) from 1,4-bis(3,4-dicarboxyl-phenoxy)benzene dianhydride and ODA [19]. This behavior is attributed to the formation of strong intermolecular complexes. Fig. 5 displays the dynamic storage modulus (E') and loss modulus (E'') as a function of temperature of **IIa**. On the basis of tan δ peaks, the glass transition relaxation was observed at about 266 °C, which is slightly higher than that measured by DSC. The E' curve of **IIa** shows a small decrease just prior to the glass transition.

Physical property characterization of the films prepared from the poly(amic acid) solution is summarized in Table 4. The coefficient of thermal expansion (CTE) of the poly(amine imide) ranged from 9.8 to 20.6 ppm/°C (Table 3). These values are generally low and in the region desired to match most substrates encountered in electronics (metals like copper or aluminum, ceramics like silica or alumina). CTEs are associated with the rigidity and linearity of the polymer chain, which affect the chain packing. Polyimides with low CTE are generally based on rod-like or nearly rod-like backbones. Most notable of these is the polyimide prepared from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and *p*-phenylene diamine (PPD) (e.g., DuPont's Pyralin™ PI-2611). This polyimide has an excellent balance of mechanical and physical properties and has an in-plane CTE of 4 ppm/°C matching that of silicon. Among all synthesized PIs, **Ie** showed the lowest CTE of 9.8 ppm/°C, which is comparable with that of BPDA/PPD. The low CTE of **Ie** is rationalized as due to the rigid backbone and the intermolecular hydrogen bonding interactions.

The film samples of the poly(amine imide)s showed tensile strengths of 102–152 MPa, elongations at break of 11.3–19.6%, and tensile modulus of 1.04–2.08 GPa. Most of the polymers showed tough and strong behavior. The adhesion test to copper was conducted by a 180°-peel test. The results of the adhesion test summarized in Table 4 show that the poly(amine imide)s have the peel strength values ranging from 283 to 358 N/m. All the poly(amine imide)s have better adhesion properties than that of Kapton, which has a peel strength of less than 100 N/m without adhesion promoter. The relatively higher peel strength values is most likely due to the formation of a stable copper complex through copper and the N–H group of amino unit in the poly(amine imide)s.

The crystallinity of the poly(amine imide)s was evaluated by wide-angle X-ray diffraction experiments. All the polymers exhibited Gaussian distributions, which indicated an amorphous morphology, as shown in Fig. 6. These results were supported by the absence of crystalline melting peaks in the DSC measurements. The most prominent WAXD peak in the amorphous glassy polymer spectra is often used to estimate the average interchain spacing distance (*d*-spacing). The *d*-spacing values were calculated with Bragg's equation by reported methods and are compiled in Table 4. Regardless of the

Table 4
Physical properties of poly(amine imide)s

Polymer	CTE[a] (ppm/°C)	Peel strength[b] (N/m)	*d*-spacing	Polymer	CTE[a] (ppm/°C)	Peel strength[b] (N/m)	*d*-spacing
Ia	17.7	289	4.92	**IIa**	17.7	288	4.82
Ib	18.5	291	4.87	**IIb**	18.6	290	4.78
Ic	19.4	330	5.03	**IIc**	19.5	327	4.95
Id	20.6	285	4.76	**IId**	20.6	283	4.70
Ie	9.8	358	5.15	**IIe**	9.9	355	5.07

[a] Determined from TMA measurements conducted at a heating rate of 5 °C/min from 25 to 250 °C and taken as the mean between 40 and 180 °C.

[b] The adhesion test to copper was conducted by a 180°-peel test.

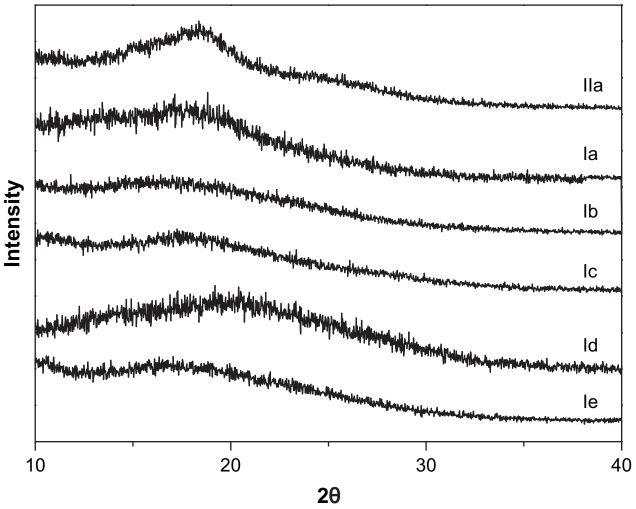


Fig. 6. Wide-angle X-ray diffractograms of poly(amine imide)s.

composition, all the polymers exhibited a structureless morphology. This was because that the dianhydride monomers have a hinged amino linkage.

4. Conclusions

N,*N*′-Bis(3,4-dicarboxyphenyl)-1,4-phenylenediamine dianhydride **I** and *N*,*N*′-bis(3,4-dicarboxyphenyl)-1,3-phenylenediamine dianhydride **II**, two novel isomeric amino-containing dianhydride monomers, were synthesized successfully from 1,4-phenylenediamine or 1,3-phenylenediamine and 4-chloro-*N*-methylphthalimide. A series of poly(amine imide)s were prepared from condensation of the novel amino-containing dianhydride with various aromatic diamines in NMP, followed by thermal imidization. The poly(amine imide)s exhibited good thermal and thermooxidative stabilities with a glass transition temperature of 250–295 °C and 10% weight loss temperature of 539–560 °C in nitrogen. The poly(amine imide)s have the peel strength values ranging from 283 to 358 N/m. The transparent, flexible and tough poly(amine imide)s films obtained exhibited good mechanical properties, with a tensile strength and tensile modulus in the ranges 102–152 MPa and 1.04–2.08 GPa, respectively, as well as elongation at break 11.3–19.6%. These good combinations of properties can make the poly(amine imide)s attractive for practical applications.

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