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Synthesis and properties of novel poly(amide-imide)s containing pendent diphenylamino groups

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Abstract

A new dicarboxylic acid, 2,4-bis(*N*-trimellitoyl)triphenylamine, bearing two preformed imide rings was synthesized from the condensation of 2,4-diaminotriphenylamine and trimellitic anhydride at 1:2 molar ratio. A series of poly(amide-imide)s (PAIs) with inherent viscosities of 0.38–0.66 dl/g were prepared by triphenyl phosphite-activated polycondensation from the diimide–dicarboxylic acid with various aromatic diamines. All the resulting PAIs were readily soluble in a variety of organic solvents and formed strong and tough films via solution casting. These PAIs have useful levels of thermal stability associated with moderately high glass-transition temperatures (259–314 °C) and 10% weight loss temperatures in excess of 530 °C in nitrogen or in air.

Keywords: Poly(amide–imide)s; 2,4-Diaminotriphenylamine; Diimide–diacid; Triphenyl phosphite; Thermally stable polymers

1. Introduction

Polyimides are one of the most important class of thermally stable polymers [1,2], which are well known for their high-performance properties but have one major disadvantage of typically being insoluble and unprocessable after conversion from the poly(amic acid) to the polyimide form. Replacement of polyimides by copolyimides such as poly(amide–imide)s (PAIs) may be useful in modifying the intractable nature of polyimides. PAIs contain both amide and cyclic imide units along the polymer chain and hence constitute a polymer class with average properties between aromatic polyamides and polyimides. This class of polymers seems to provide a favorable balance between processability and performance.

PAIs can be synthesized readily by general synthetic methods similar to those for both aromatic polyamides and polyimides. Various approaches have been carried out successfully in the synthesis of PAIs [3]. One of convenient and efficient synthesis of high-molecular-weight PAIs is the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines by means of the Yamazaki–Higashi phosphorylation technique [4], developed by us in 1989–1990 [5–7]. The direct polycondensation route is a very useful laboratory method and avoids using moisture-sensitive acid chlorides, or

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isocyanates [8–10]. In addition, this synthetic approach to PAIs can offer us the option of introduction of specific segments between amide or imide groups. The properties of PAIs can be readily modified by the incorporation of different segments. Thus, a number of novel PAIs have been readily prepared using this convenient technique by us and others [11–19]. Very recently, we have reported a series of soluble, thermally stable aromatic polyamides derived from 2,4-diaminotriphenylamine (**1**) and aromatic dicarboxylic acids [20]. As a continuation of our efforts in preparing easily processable high-performance polymers, this study explores the synthesis and basic characterization of a new class of PAIs having pendent diphenylamino groups by the polymerization of the bistrimellitimide of **1** with various aromatic diamines. The presence of the bulky pendent diphenylamino group not only hinders close packing and interchain interactions between polymers, but also preserves their structural rigidity. Hence, the obtained PAIs were expected to exhibit an enhanced solubility while retaining good thermal stability.

2. Experimental

2.1. Reagents and solvents

2,4-Diaminotriphenylamine (**1**; mp = 155–156 °C) was synthesized in a two-step procedure starting from the nucleophilic fluoro-displacement of 1-fluoro-2,4-dinitrobenzene with diphenylamine in the presence of cesium fluoride. The synthetic details and characterization data of compound **1** have been reported in a recent paper [20]. All of the commercially available aromatic diamines **3a** to **3g** were of high purity and were used without further purification. Commercially obtained calcium chloride was dried under vacuum at 150 °C for 6 h prior to use. Triphenyl phosphite was purified by distillation under reduced pressure. *N*,*N*-Dimethylformamide (DMF), pyridine, and *N*-methyl-2-pyrrolidone (NMP) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle.

2.2. Synthesis of 2,4-bis(*N*-trimellitoyl)triphenylamine (2)

A mixture of 9.5 g (50 mmol) of trimellitic anhydride (TMA) and 6.6 g (24 mmol) of 2,4-diaminotriphenylamine (**1**) were dissolved in 80 ml of dry DMF at 60 °C and stirred for 1 h. About 80 ml of toluene was then added, and the mixture was heated with reflux for 3 h until about 0.9 ml of water was distilled off azeotropically under a Dean-Stark trap. Heating was continued to distill off the residual toluene. After cooling, the yellow precipitate was isolated by filtration and washed with methanol. The obtained crude product was purified by recrystallization from DMF/methanol and dried in vaccum to afford 12.4 g (83% yield) of diimide–diacid **2**; mp = 309–310 °C (by DSC, at a scan rate of 2 °C/min).

IR (KBr): 3500–3100 cm^{-1} (carboxyl O–H), 1785, 1724 cm^{-1} (imide C=O), 1683 cm^{-1} (carboxyl C=O), 1365 cm^{-1} (imide C–N), 1096, 713 cm^{-1} (imide ring deformation). ANAL. Calcd for $C_{36}H_{21}N_3O_8$ (623.58): C, 69.34%; H, 3.39%; N, 6.74%. Found: C, 68.93%; H, 3.61%; N, 7.41%. ^{1}H NMR (DMSO-d_6, δ, ppm) (for the peak assignments, see Fig. 1): 8.44 (H_e), 8.33 (H_d), 8.29 (H_f), 8.11 (H'_e), 8.06 (H'_d), 7.83 (H'_f), 7.58 (H_b), 7.55 (H_a), 7.34 (H_c), 7.09 (H_h), 6.90 (H_g), 6.85 (H_i).

2.3. Synthesis of poly(amide–imide)s

As a typical example, PAI **4a** was prepared as follows: A mixture of 0.790 g (1.25 mmol) of diimide–diacid **2**, 0.248 g (1.25 mmol) of 4,4′-methylenedianiline (**3a**), 0.8 g of calcium chloride, 8 ml of NMP, 1.5 ml of pyridine, and 0.8 ml of triphenyl phosphite was heated with stirring at 100 °C for 3 h. The obtained polymer solution was trickled into 300 ml of methanol with stirring to afford a fiber-like precipitate. The precipitate was collected, washed thoroughly with methanol and hot water, and dried to give 0.97 g (99%) of PAI **4a**. The inherent viscosity of polymer **4a** was 0.63 dl/g, measured at a concentration of 0.5 g/dl in DMAc at 30 °C. IR (film): 3392 cm^{-1} (N–H amide), 1779, 1724 cm^{-1} (imide C=O), 1671 cm^{-1} (amide C=O), 1089, 725 cm^{-1} (imide ring deformation). ANAL. Calcd for $(C_{49}H_{31}N_5O_6$ $(785.82)_n$: C, 74.89%; H, 3.98%; N, 8.91%. Found: C, 71.24%; H, 4.50%; N, 9.07%.

The other PAIs were synthesized by an analogous procedure described above.

2.4. Film preparation

A solution of 0.7 g of a PAI sample was dissolved in 10 ml of hot DMAc. The homogeneous solution was poured into a 9 cm glass Petri dish, which was placed in a 90 °C oven overnight for the slow release of the solvent and then dried in vacuo at 200 °C for 8 h. The flexible PAI films with 60–70 μm in thickness were then stripped from the glass substrate.

2.5. Instruments and characterization methods

Elemental analyses were run in a Heraeus Vario-III analyzer. ^{1}H NMR spectra were measured on a Jeol EX-400 spectrometer using DMSO-d_6 as the solvent and tetramethylsilane as internal reference. Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. The inherent viscosities were determined at a concentration of 0.5 g/dl in DMAc using a Cannon–Fenske viscometer at 30 °C.

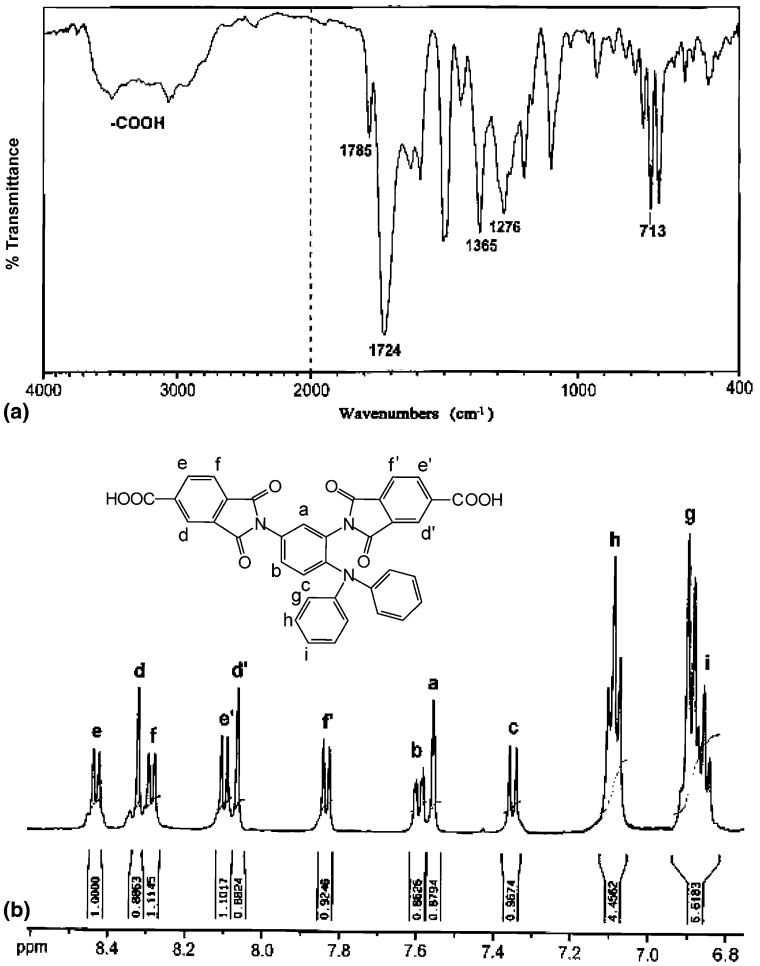


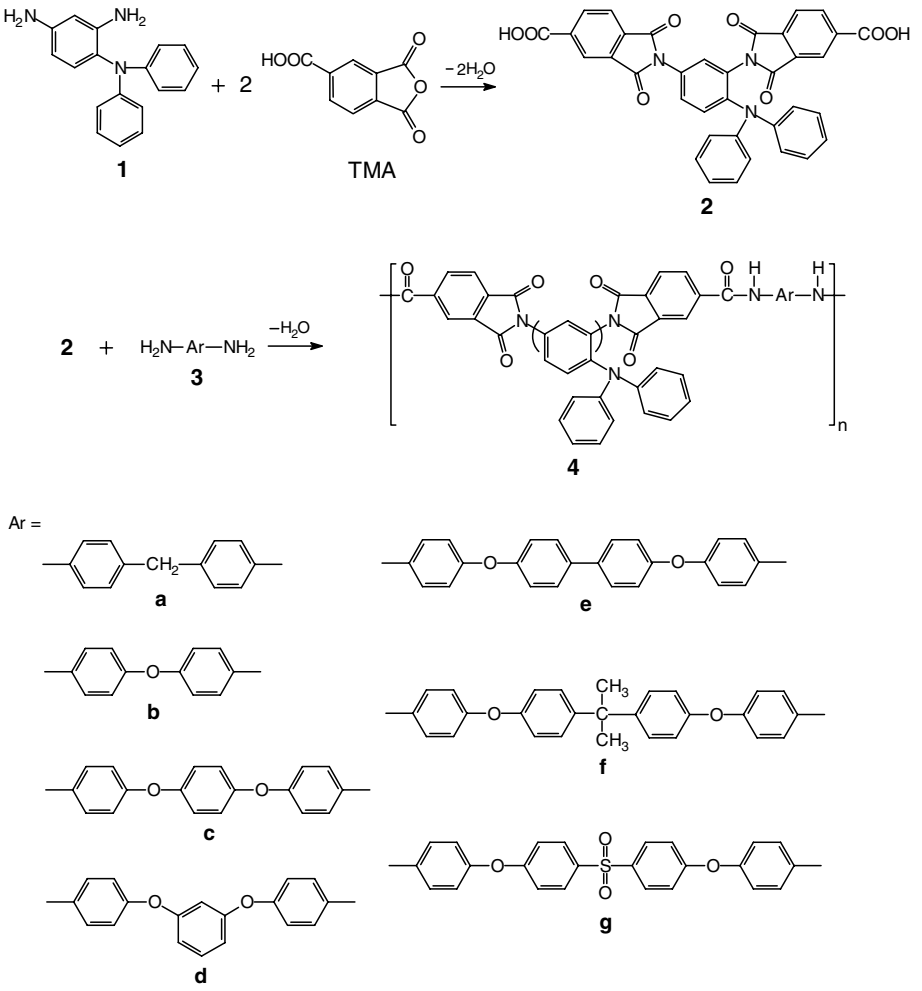
Fig. 1. (a) IR spectrum and (b) ^{1}H NMR spectrum (in DMSO-d_6) of 2,4-bis(*N*-trimellitoyl)triphenylamine (**2**).

Differential scanning calorimeter (DSC) was performed on a PerkinElmer Pyris 1 DSC differential scanning calorimeter in flowing nitrogen (20 cm^3/min) at a heating rate of 20 °C/min. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on 3–5 mg samples heated in flowing nitrogen or air (30 cm^3/min) at a heating rate of 20 °C/min. An Instron universal tester model 4400R with a load cell 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm width, 6 cm length, and about 0.1 mm thickness), and an average of at least three replicates was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer with a graphite monochromator, using nickel-filtered Cu Kα radiation (λ = 1.5418 Å, operating at 40 kV and 20 mA). The scanning rate was 3°/min over a 2θ range of 5–45°.

3. Results and discussion

3.1. Synthesis of diimide–diacid 2

2,4-Bis(*N*-trimellitoyl)triphenylamine (**2**), the diimide–diacid monomer, was prepared via a two-stage procedure that included ring-opening addition of the diamine **1** with two equivalent amounts of trimellitic anhydride, followed by cyclodehydration to the diimide–diacid by means of toluene–water azeotropic distillation (Scheme 1). The molecular structure of **2** was confirmed by elemental analysis and IR and ^{1}H NMR spectrometry. The IR and ^{1}H NMR spectra of diimide–diacid **2** are illustrated in Fig. 1. The characteristic absorption bands in its IR spectrum and the proton



Scheme 1. Synthesis of bistrimellitimide **2** and poly(amide–imide)s **4a–g**.

resonance peaks of diimide–diacid **2** were in a good agreement with the expected molecular structure.

3.2. Polymer synthesis

A series of novel PAIs **4a–g** were prepared from the polycondensation reactions of diimde–diacid **2** with various aromatic diamines **3a–g** using triphenyl phosphite and pyridine as condensing agents (Scheme 1). As shown in Table 1, the series of PAIs **4a–g** had inherent viscosities of 0.42–0.66 dl/g. All of these PAIs could be solution cast into flexible and tough films with good tensile properties. These results indicated the formation of high-molecular-weight polymers. The structures of PAIs **4a–g** were confirmed by elemental analysis and IR spectroscopy. Representative IR spectra of PAIs **4a** and **4b** are shown in Fig. 2. The IR spectra of these PAIs exhibited characteristic absorptions for the imide ring and amide groups as described in Section 2.

3.3. Properties of poly(amide–imide)s

The WAXD studies of PAIs **4a–g** indicated that all of these polymers were essentially amorphous. The qualitative solubility of these PAIs is also reported in Table 1. All of them were soluble in aprotic dipolar solvents such as NMP, DMAc, DMF, and DMSO, and even in less polar solvents like *m*-cresol and pyridine. Their high solubility and amorphous nature can be attributed to the introduction of bulky, packing-disruptive diphenylamino pendent groups along the polymer backbone. Therefore, the excellent solubility makes these polymers potential candidates for practical applications in spin-on and casting processes.

All of the PAIs could be solution cast into transparent, flexible and tough films. These films exhibited good mechanical properties with tensile strengths of 83–121 MPa, elongations to break of 8–12%, and initial moduli of 1.8–2.2 GPa.

Table 1
Inherent viscosity, thin film tensile properties, and solubility behavior of poly(amide–imide)s

Polymer code	η_{inh}[a] (dl/g)	Tensile properties[b]			Solubility in various solvents[c]						
		σ (MPa)	ε (%)	E (GPa)	NMP	DMAc	DMSO	DMF	*m*-Cresol	Pyridine	THF
4a	0.63	110	11	2.1	+	+	+	+	+h	+	–
4b	0.66	121	12	2.2	+h	+h	+	+	+h	+h	–
4c	0.46	91	10	1.9	+	+	+h	+	+h	+	–
4d	0.64	117	11	2.1	+	+	+	+	+h	+	–
4e	0.44	86	8	1.8	+	+	+h	+	+h	+h	–
4f	0.63	113	10	2.1	+h	+	+h	+	+h	+	–
4g	0.42	83	8	1.9	+	+	+h	+	+h	+h	–

[a] Measured at a concentration of 0.5 g/dl in DMAc containing 5 wt.% LiCl at 30 °C.
[b] Films were cast by evaporation of polymer solutions in DMAc. The cast films were dried under vacuum at 150 °C for 6 h prior to the tensile test. σ: Strength to break; ε: elongation to break; E: initial modulus.
[c] Qualitative solubility was tested with 10 mg sample in 1 ml solvent. +: Soluble at room temperature; +h: soluble on heating; –: insoluble even on heating. NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

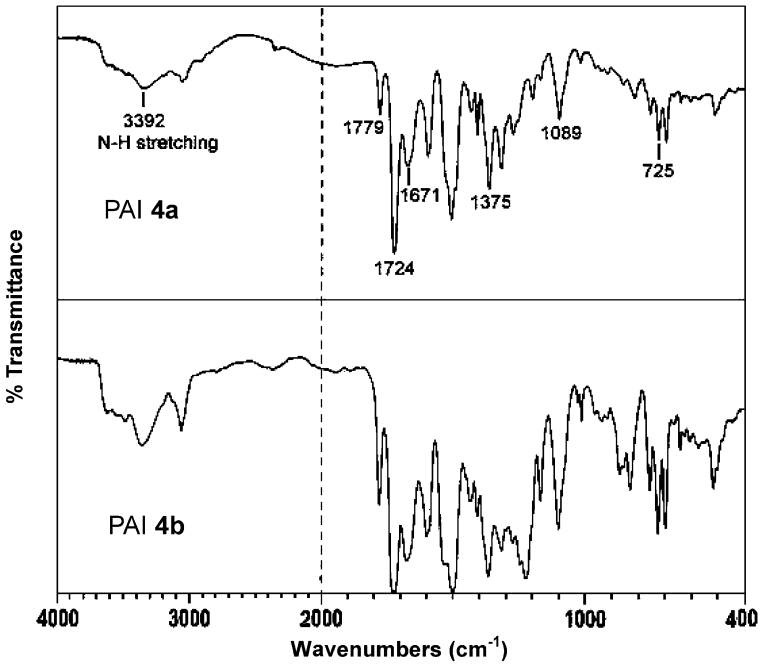


Fig. 2. Thin film FTIR spectra of poly(amide–imide)s **4a** and **4b**.

The thermal properties of these PAIs determined by DSC and TGA are reported in Table 2. The glass-transition temperatures (T_gs) values of these PAIs were observed in the 259–314 °C range, depending on the structure of the diamine component and increasing with the decreasing chain stiffness. As expected, PAIs **4f** and **4g** derived from long-chain flexible diamines revealed relatively lower T_g values. The TGA curves of a representative PAI **4b** in both air and nitrogen atmospheres are reproduced in Fig. 3. The TGA data indicate that these PAIs had fairly high thermal stability. None of the PAIs showed a significant weight loss up to 450 °C in nitrogen or air, and the decomposition temperatures (T_ds) at 10% weight loss of these polymers stayed within 549–571 °C in nitrogen and within 539–561 °C in air. They left more than a 65% char yield at 800 °C in nitrogen. The high char yields of these PAIs can be attributed to their high aromatic contents.

Table 2
Thermal properties of poly(amide–imide)s

Polymer code	T_g[a] (°C)	T_d[b] (°C)		Char yield[c] (wt.%)
		In N_2	In air	
4a	310	564	551	72
4b	314	571	556	70
4c	294	565	560	67
4d	287	570	561	69
4e	294	570	551	70
4f	262	553	539	66
4g	259	549	543	65

[a] The samples were heated from 30 to 400 °C at a scan rate of 20 °C/min followed by rapid cooling to 30 °C at −100 °C/min in nitrogen, after which the samples were reheated from 30 °C to 400 °C at a scan rate of 20 °C/min. The midpoint temperature of baseline shift on the heating DSC trace was defined as T_g.

[b] Decomposition temperature at which a 10 wt.% loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm^3/min.

[c] Residual weight percent at 800 °C in nitrogen.

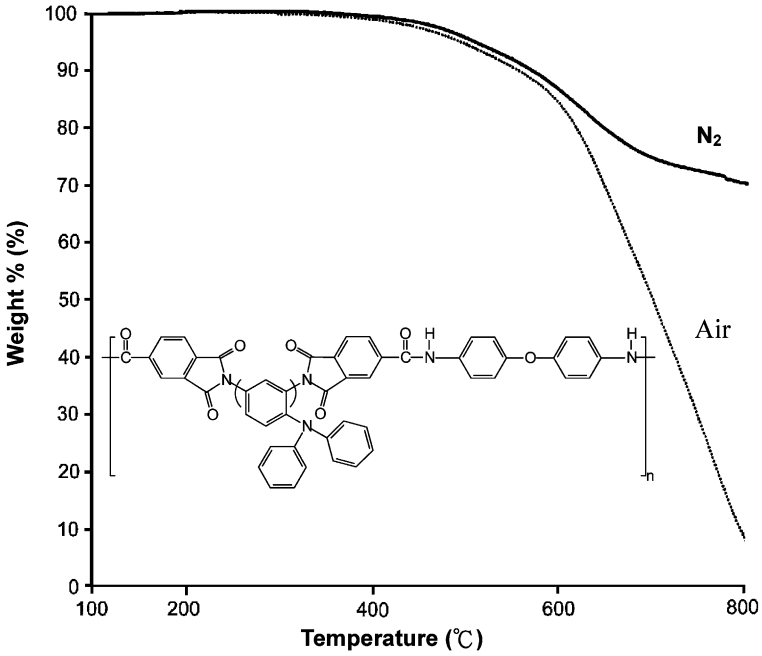


Fig. 3. TGA curves of poly(amide–imide) **4b** with a heating rate of 20 °C/min.

4. Conclusions

2,4-Bis(*N*-trimellitoyl)triphenylamine has been synthesized and used an a new PAI building block. PAIs having moderate inherent viscosities were successfully prepared by phosphorylation polyamidations from the diimide–diacid with various aromatic diamines. Because of the presence of bulky pendent diphenylamino group, these polymers were essentially amorphous and showed excellent solubility in many polar aprotic solvents. All of them could be cast into transparent and flexible films. Good solubility, moderate T_g or T_s values, and high thermal stability and mechanical strengths make these PAIs as promising processable high-performance polymeric materials.

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