

# Synthesis and Properties of Novel Poly(amide-imide)s Derived from 2,4-diaminotriphenylamine and Imide Ring-Preformed Dicarboxylic Acids

Sheng-Huei Hsiao<sup>1,\*</sup>, Chin-Ping Yang<sup>1</sup>, Chien-Wei Chen<sup>1</sup> and Guey-Sheng Liou<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei, Taiwan, Republic of China

<sup>2</sup>Department of Applied Chemistry, National Chi Nan University, Puli, Nantou, Taiwan, Republic of China

(\*Author for correspondence; Tel.: +886-2-25925252 ext. 2977; Fax: +886-2-25861939; E-mail: shhsiao@ttu.edu.tw)

Received 27 June 2004; accepted in revised form 27 October 2004

**Key words:** poly(amide imide)s, solubility, thermal properties, triphenylamine, triphenyl phosphite

## Abstract

2,4-diaminotriphenylamine (2) was synthesized via the cesium fluoride-mediated aromatic substitution reaction of 1-fluoro-2,4-dinitrobenzene with diphenylamine, followed by palladium-catalyzed hydrazine reduction. A series of poly(amide-imide)s (PAIs) with inherent viscosities of 0.38–0.46 dL/g were prepared by triphenyl phosphite-activated polycondensation from the diamine monomer 2 with various monoimide- and diimide-dicarboxylic acids. All of the PAIs were readily soluble in a variety of organic solvents and formed strong and tough films via solution casting. These PAIs have moderately high glass transition temperatures in the range of 168–274 °C and 10 % weight loss temperatures in excess of 447 °C in nitrogen or in air.

## 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. Imai has made an excellent review on the synthesis of PAIs [3]. As can be seen from the Imai's review, various approaches have been carried out successfully in the synthesis of PAIs. One of convenient and efficient synthesis of high-molecular-weights PAIs, developed by us in 1989–1990 [4–6], is the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines by means of the Yamazaki–Higashi phosphorylation technique [7]. The direct polycondensation route is a very useful laboratory method and avoids using moisture-sensitive acid chlorides, or 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 (2) and aromatic dicarboxylic acids [20]. As a continued study on polymers based on 2, this study explores the synthesis and basic characterization of several new PAIs having pendent diphenylamino groups by the polymerization of diamine 2 with various imide ring-preformed dicarboxylic acids. The presence of the bulky pendent diphenylamino group not only hinders close packing and between-chains interactions, but also preserves their structural rigidity. Hence, the obtained PAIs were expected to exhibit an enhanced solubility while retaining good thermal stability.

## Experimental

### General Directions

As reported in our recent publication [20], 2,4-diaminotriphenylamine (2; mp = 155–156 °C) was synthesized by hydrazine palladium-catalyzed reduction of 2,4-dinitrotriphenylamine (1) resulting from the condensation of 1-fluoro-2,4-dinitrobenzene with diphenylamine in the presence of cesium fluoride. According to the methods reported previously [4–6], monoimide-dicarboxylic acids 3a and 3b were

synthesized by condensation of trimellitic anhydride with *p*-aminobenzoic acid and *m*-aminobenzoic acid, respectively, and diimide-dicarboxylic acids 3c–3g were prepared by condensation of corresponding diamines with two equivalent amount of trimellitic anhydride. Commercially obtained calcium chloride was dried under vacuum at 150 °C for 6 h prior to use. Triphenyl phosphite (TPP) 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.

Elemental analyses were run in a Heraeus Vario-III analyzer. 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. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris 1 DSC differential scanning calorimeter in flowing nitrogen (20 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 at a scan rate of 10 °C/min with a penetration probe of 1.0 mm diameter under an applied constant load of 10 mN. 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<sup>3</sup>/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 five individual determinations 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 K<sub>α</sub> radiation ( $\lambda = 1.5418 \text{ \AA}$ , operating at 40 kV and 20 mA). The scanning rate was 3°/min over a  $2\theta$  range of 5–45°.

#### Synthesis of Poly(amide-imide)s

A typical example for the synthesis of 4e is as follows. A mixture of 0.548 g (1.0 mmol) of diimide-dicarboxylic acid 3e, 0.275 g (1.0 mmol) of diamine 2, 0.2 g of calcium chloride, 2 mL of NMP, 0.5 mL of pyridine, and 0.8 mL of triphenyl phosphite were heated with stirring at 120 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of methanol giving rise to a fiber-like precipitate that was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was quantitative. The inherent viscosity of the obtained polymer 4e was 0.45 dL/g as measured in *N,N*-dimethylacetamide (DMAc)-5 wt% LiCl at a concentration of 0.5 g/dL at 30 °C. IR (film): 3400 (amide N–H stretching), 1776, 1724 (imide C=O stretching), 1668 (amide C=O stretching), 1380 (imide C–N stretching), 1091, 725 cm<sup>-1</sup> (imide ring deformation). Anal. calcd. for PAI 4e C<sub>48</sub>H<sub>29</sub>N<sub>5</sub>O<sub>7</sub>(787.79)<sub>n</sub>: C, 73.18%; H, 3.71%; N, 8.89%. Found: C, 72.23%; H, 4.24%; N,

8.60%. The other PAIs of the 4 series were synthesized from diamine 2 and corresponding imide-dicarboxylic acids according to the same procedure as described above.

#### 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 thick were then stripped from the glass substrate.

## Results and Discussion

2,4-diaminotriphenylamine (2) was prepared from diphenylamine and 1-fluoro-2,4-dinitrobenzene according to a two-step procedure as shown in Scheme 1. A series of novel PAIs 4a–g bearing bulky pendent diphenylamino groups were synthesized from the polycondensation reactions of diamine 2 and various imide ring-containing dicarboxylic acids 3a–g using triphenyl phosphite as promoter in NMP in the presence of pyridine and calcium chloride. As shown in Table 1, the inherent viscosities of the resulting PAIs 4a–g were in the range of 0.38–0.46 dL/g. They could be readily dissolved in polar organic solvents, such as NMP, DMAc, DMF and DMSO, and could afford flexible and tough films by solvent casting. Thin films of PAIs 4a–g exhibited tensile strengths of 76–99 MPa, elongations to break of 7–12%, and initial moduli of 1.4–1.9 GPa.

The molecular structures of PAIs 4a–g were confirmed by IR spectroscopy and elemental analysis. The elemental analysis values were in good agreement with the calculated values of the proposed structures (Table 2), missing only the values found for the C-percentages that are always lower than the theoretical ones. That certainly can be attributed to the very aromatic nature of these polymers, which commonly leave a small coal residue in the standard conditions of microanalysis. Figure 1 shows the FTIR spectra of poly(amide-imide)s 4c and 4d. The infrared spectra show characteristic imide bands at 1778 and 1724 cm<sup>-1</sup> due to asymmetrical and symmetrical carbonyl stretching vibrations. Bands of amide groups appear at 3401 and 1677 cm<sup>-1</sup>.

The crystallinity of PAIs 4a–g was evaluated by WAXD measurements. It is found that all the PAIs exhibited essentially amorphous patterns. We can interpret the result by the presence of the pendent diphenylamino groups, which resulted in poor chain packing. The high solubility of these PAIs is also affected by the amorphous structure.

DSC, TMA and TGA were used to investigate the thermal properties of PAIs 4a to 4g. The results are summarized in Table 3. DSC experiments were conducted at a scan rate of 20 °C/min in nitrogen. Rapid cooling at –100 °C/min from 400 °C to 30 °C produced predominantly amorphous samples, so obvious *T<sub>g</sub>*'s of all the PAIs could easily be read in the subsequent heating traces. As listed in Table 2, PAIs 4a–g showed *T<sub>g</sub>*'s in the range of 168–274 °C, generally following the decreasing order of chain flexibility. As

Table 1. Inherent viscosity, thin film tensile properties, and solubility behavior of PAIs

Polymer code	$\eta_{inh}^a$ (dL/g)	Tensile properties <sup>b</sup>			Solubility in various solvents <sup>c</sup>							
		Strength to break (MPa)	Elongation to break (%)	Initial modulus (GPa)	NMP	DMF	DMAc	DMSO	Pyridine	<i>m</i> -cresol	THF	Chloroform
4a	0.39	80	7	1.4	+	+	+	+	+h	+h	–	–
4b	0.38	76	8	1.5	+	+	+	+	+h	+	–	–
4c	0.41	92	11	1.7	+	+	+	+	+h	+	±	–
4d	0.41	90	10	1.8	+	+	+	+	+h	+	±	–
4e	0.45	95	12	1.8	+	+	+	+	+h	+h	–	–
4f	0.46	99	11	1.9	+	+	+	+	+h	+h	±	–
4g	0.45	88	12	1.6	+	+	+	+	+h	+	±	–

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt% LiCl at 30 °C.

<sup>b</sup> Films were cast by slow evaporation of polymer solutions in DMAc. The cast films were dried under vacuum at 200 °C for 8 h prior to the tensile test.

<sup>c</sup> Qualitative solubility was tested with 10 mg sample in 1 mL solvent. +: soluble at room temperature; +h: soluble on heating; –: insoluble even on heating; ±: partially soluble at room temperature; NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

Table 2. Elemental analysis of poly(amide-imide)s

Polymer code	Formula (formula weight)	Calcd. (%)			Found (%)		
		C	H	N	C	H	N
4a	(C <sub>34</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>n</sub> (550.57) <sub>n</sub>	74.17	4.03	10.18	73.03	4.18	9.72
4b	(C <sub>34</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> ) <sub>n</sub> (550.57) <sub>n</sub>	74.17	4.03	10.18	73.21	4.16	10.08
4c	(C <sub>42</sub> H <sub>33</sub> N <sub>5</sub> O <sub>6</sub> ) <sub>n</sub> (703.75) <sub>n</sub>	71.68	4.73	9.96	70.35	4.69	9.15
4d	(C <sub>42</sub> H <sub>25</sub> N <sub>5</sub> O <sub>6</sub> ) <sub>n</sub> (695.69) <sub>n</sub>	72.51	3.62	10.07	71.46	3.84	9.85
4e	(C <sub>48</sub> H <sub>29</sub> N <sub>5</sub> O <sub>7</sub> ) <sub>n</sub> (787.79) <sub>n</sub>	73.18	3.71	8.89	72.23	4.24	8.60
4f	(C <sub>54</sub> H <sub>33</sub> N <sub>5</sub> O <sub>8</sub> ) <sub>n</sub> (879.88) <sub>n</sub>	73.71	3.78	7.96	72.34	3.95	7.74
4g	(C <sub>63</sub> H <sub>43</sub> N <sub>5</sub> O <sub>8</sub> ) <sub>n</sub> (998.06) <sub>n</sub>	75.82	4.34	7.02	74.29	4.59	7.00

Table 3. Thermal properties of PAIs

Polymer code	$T_g^a$ (°C)	$T_s^b$ (°C)	$T_d^c$ (°C)		Char yield <sup>d</sup> (wt %)
			In N <sub>2</sub>	In air	
4a	273	253	497	496	69
4b	264	253	494	481	71
4c	168	163	453	447	53
4d	274	262	531	524	63
4e	266	265	548	519	70
4f	257	254	542	516	65
4g	248	243	531	527	66

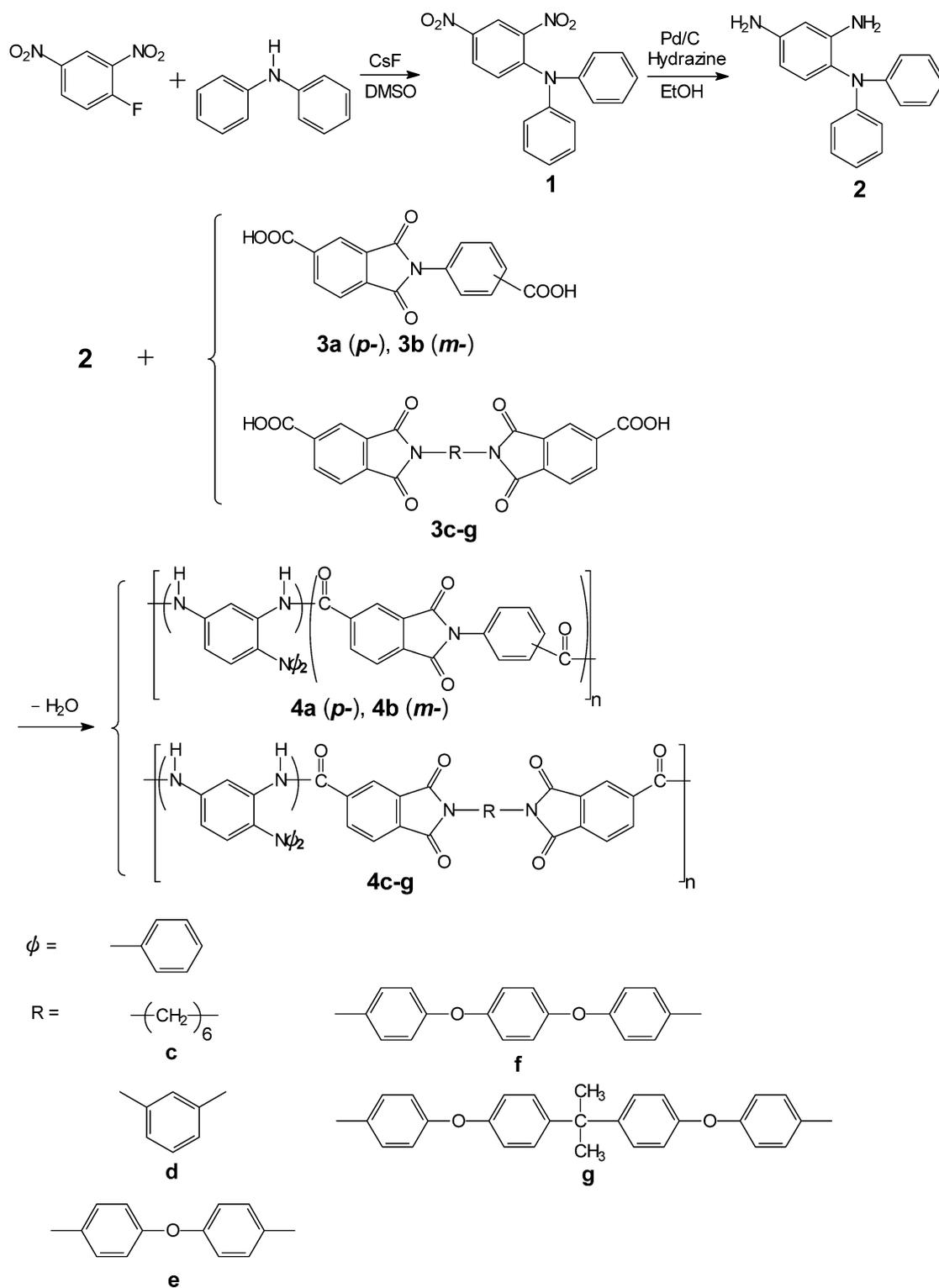
<sup>a</sup> The samples were heated from 30 to 400 °C at a scan rate of 20 °C/min followed by rapid cooling to 30 °C at –100 °C/min in nitrogen. The mid-point temperature of baseline shift on the subsequent DSC trace (from 30 to 400 °C at 20 °C/min) was defined as  $T_g$ .

<sup>b</sup> Softening temperature taken as the onset temperature of the probe displacement on the TMA trace. The samples were heated at 300 °C for 1 hr prior to the TMA test.

<sup>c</sup> 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 30 cm<sup>3</sup>/min.

<sup>d</sup> Residual weight percent at 800 °C in nitrogen.

expected, the semi-aromatic PAI 4c revealed the lowest  $T_g$  of 168 °C because of the flexible hexamethylene segments. All of these PAIs showed no well-defined melting endotherms up to the decomposition temperatures on the DSC curves. This result also supports the amorphous nature of these PAIs. The softening temperature ( $T_s$ ) (or apparent  $T_g$ ) of the PAI film samples were determined by the TMA method using a loaded penetration probe and were taken from the onset temperatures of the probe displacement on the TMA traces. As typical examples, the TMA thermograms of PAIs 4c and 4e are illustrated in Figure 2. In most cases, the  $T_s$  values obtained by TMA are comparable to the  $T_g$  values determined by DSC. The thermal stability of the PAIs was evaluated by TGA measurements in both air and nitrogen atmospheres. Typical TGA curves for PAI 4f are reproduced in Figure 3. The decomposition temperature ( $T_d$ ) at 10% weight losses in nitrogen and air atmospheres determined from the original TGA thermograms are given in Table 3. All PAIs exhibited a moderately high thermal stability with insignificant weight



Scheme 1.

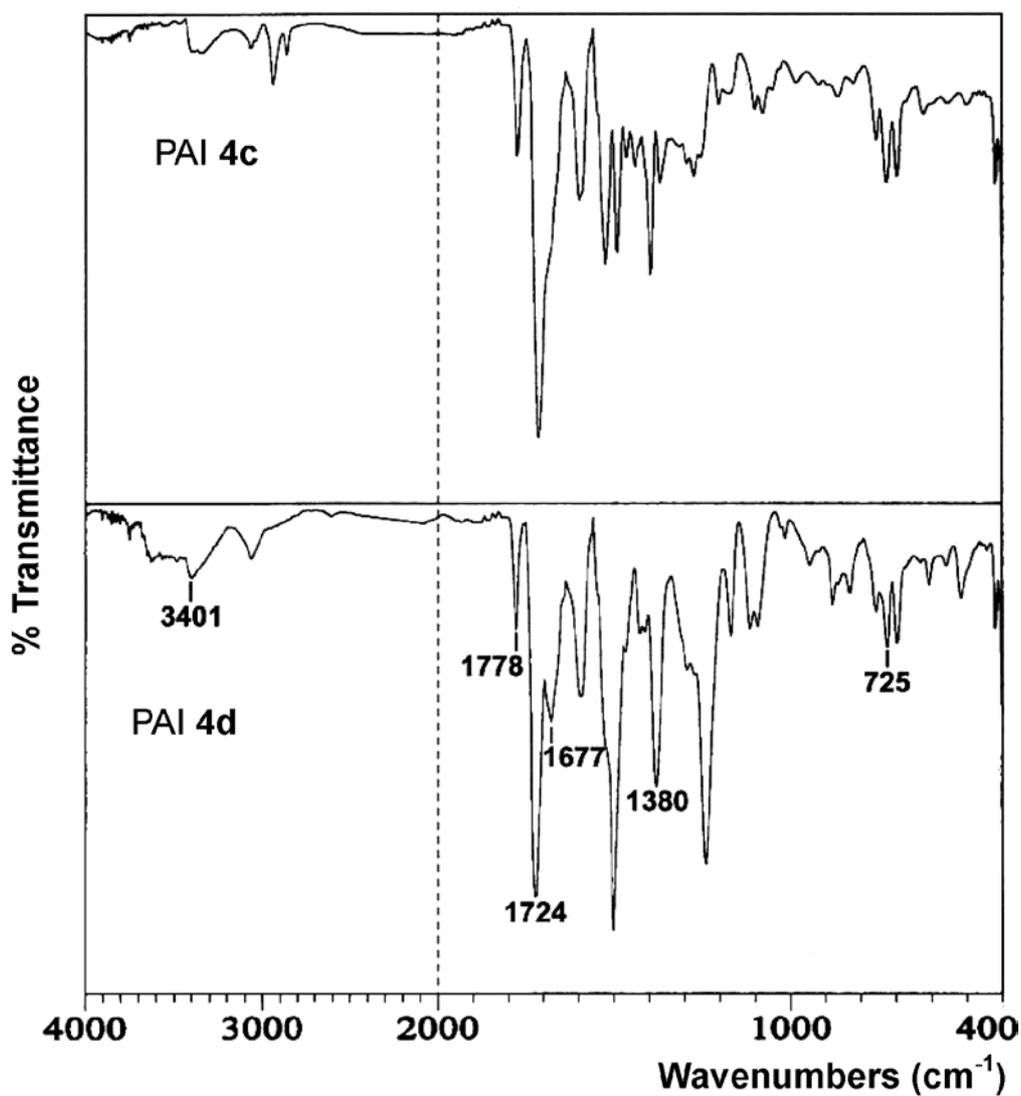


Figure 1. Thin-film FTIR spectra of poly(amide-imide)s 4c and 4d.

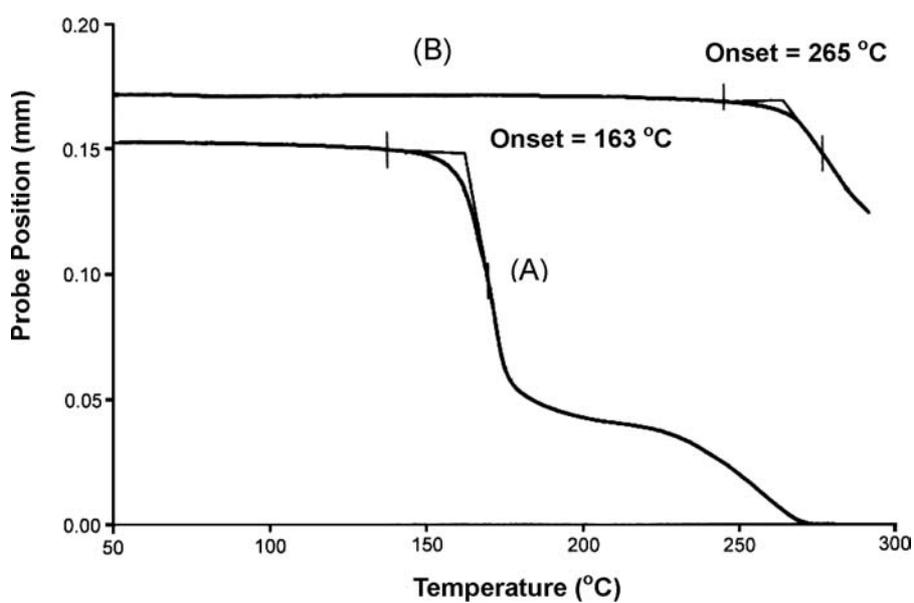


Figure 2. TMA thermograms of poly(amide-imide)s 4c (curve A) and 4e (curve B) with a heating rate of 10  $^{\circ}\text{C}/\text{min}$ .

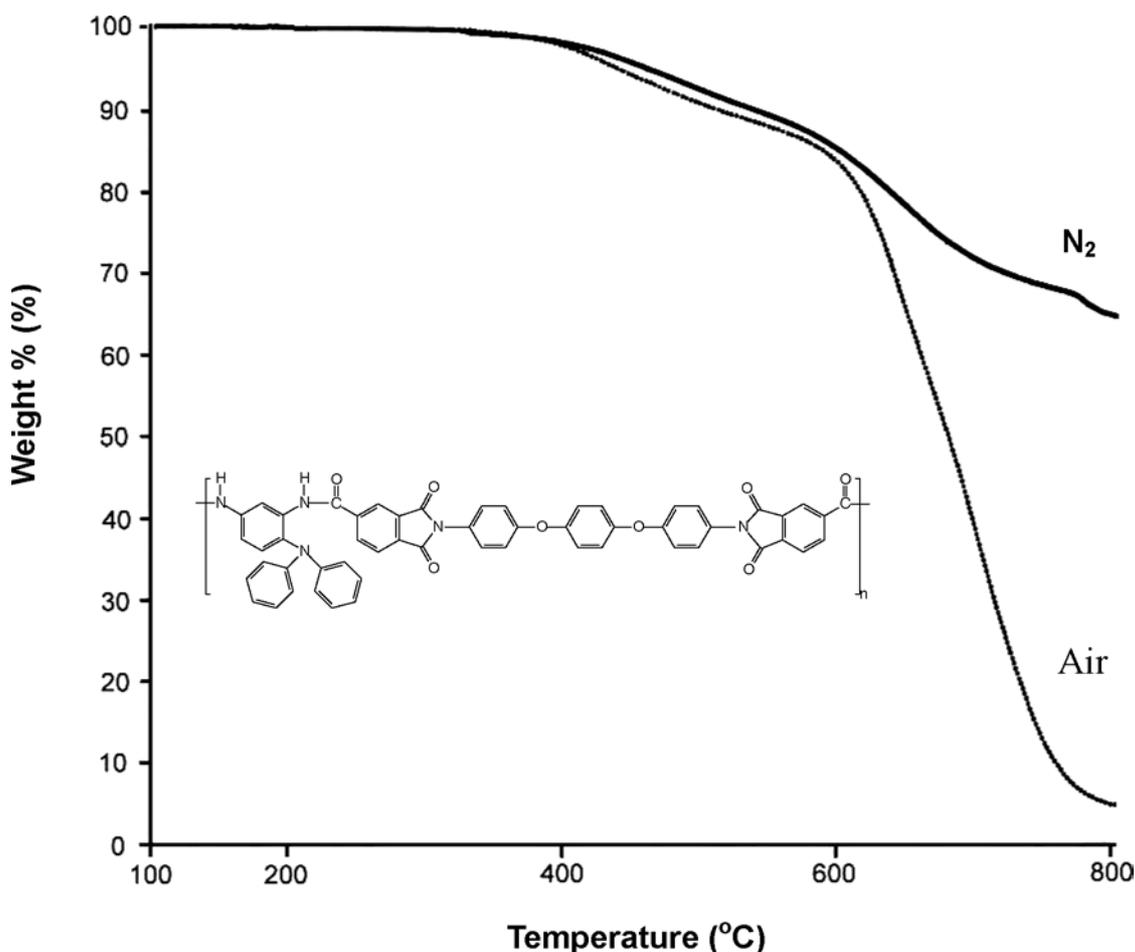


Figure 3. TGA curves of poly(amide-imide) 4f with a heating rate of 20 °C/min.

loss up to temperatures of approximately 400 °C in both air and nitrogen atmosphere, and the anaerobic char yield at 800 °C for these PAIs was in the 53–71% range.

## Conclusions

A series of new PAIs having moderate inherent viscosities were successfully prepared by phosphorylation polyamidations from 2,4-diaminotriphenylamine with various imide ring-preformed dicarboxylic acids. 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.

## References

1. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, Eds., *Polyimides*, Blackie, Glasgow and London 1990.
2. M. K. Ghosh and K. L. Mittal, Eds., *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, 1996.
3. Y. Imai, in *Polyimides: Fundamentals and Applications*, M. K. Ghosh and K. L. Mittal, Eds., Marcel Dekker, New York, 1996, pp. 49–70.
4. C.-P. Yang and S.-H. Hsiao, *Makromol. Chem.*, **190**, 2119 (1989).
5. S.-H. Hsiao and C.-P. Yang, *J. Polym. Sci. Part A: Polym. Chem.*, **28**, 1149 (1990).
6. S.-H. Hsiao and C.-P. Yang, *Makromol. Chem.*, **191**, 155 (1990).
7. N. Yamazaki, M. Matsumoto and F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1373 (1975).
8. W. Wrasidlo and A. M. Augl, *J. Polym. Sci. Polym. Chem. Ed.*, **7**, 321 (1969).
9. J. L. Nieto, J. G. de la Campa and J. de Abajo, *Makromol. Chem.*, **183**, 557 (1982).
10. J. G. de la Campa, J. de Abajo and J. L. Nieto, *Makromol. Chem.*, **183**, 571 (1982).
11. C.-P. Yang, S.-H. Hsiao and H.-C. Hsiao, *J. Appl. Polym. Sci.*, **71**, 823 (1999).
12. C.-P. Yang, R.-S. Chen and C.-C. Huang, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 2421 (1999).
13. C.-P. Yang, R.-S. Chen and C.-D. Chen, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 775 (2001).
14. C.-P. Yang, R.-S. Chen and M.-J. Wang, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 1092 (2004).
15. Z. X. Li, L. Fan, Z. Y. Ge, J. T. Wu and S. Y. Yang, *J. Polym. Sci. Part A: Polym. Chem.*, **41**, 1831 (2003).
16. D.-J. Liaw, P.-N. Hsu, W.-H. Chen and B.-Y. Liaw, *Macromol. Chem. Phys.*, **202**, 1483 (2001).
17. D.-J. Liaw, P.-N. Hsu and B.-Y. Liaw, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 63 (2001).
18. A. Banihashemi and H. Behniafar, *Polym. Int.*, **52**, 1136 (2003).
19. H. Behniafar and A. Banihashemi, *Eur. Polym. J.*, **40**, 1409 (2004).
20. S.-H. Hsiao, C.-W. Chen and G.-S. Liou, *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 3302 (2004).