NOTES

A Novel Class of Organosoluble and Strictly Alternating Poly(amine-amide-imide)s Containing Triphenylamine Units in the Main Chain

Guey-Sheng Liou[†] and Sheng-Huei Hsiao[*,†]

Department of Applied Chemistry, National Chi Nan University, 1 University Road Puli, Nantou Hsien 545, Taiwan, Republic of China
[*]*Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 104, Taiwan, Republic of China*

Among the various heterocyclic polymers that have been investigated for high-performance applications, aromatic polyimides are used widely in the semi-conductor and electronic-packaging industry because of their outstanding thermally stability, good insulation properties with low dielectric constant, good adhesion to common substrates, and superior chemical stability.[1,2] However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms due to their high melting or glass transition temperatures and their limited solubility in organic solvents. Therefore, a great deal of effort has been expended to try to improve the processing characteristics of the relatively intractable polymers.[3−8] These studies include introducing flexible segments into the polymer chain; replacing symmetrical aromatic rings by unsymmetrical ones, which leads to a reduction in crystallinity; introducing bulky pendant groups to minimize crystallization; and forming a noncoplanar structure, thereby making crystallization impossible. In addition, it is well-known that the synthesis of poly(amide-imide)s can offer a compromise between excellent thermal stability and tractability.[9] On the other hand, incorporation of a bulky pendant phenyl group into a polymer backbone is known to increase solubility and processability of polyimides without sacrificing high thermal stability.[10−13] Nevertheless, little is known about aromatic polyimides having a phenyl-pendant aromatic amine unit in the polymer backbone, that is, poly(amine-imide)s. The only example was the poly(amine-imide)s derived from 4,4′-diaminotriphenylamine and various aromatic tetracarboxylic dianhydrides.[14]

Recently, we have designed new triphenylamine-containing poly(amine-amide)s having 1,4-phenylene backbone to elucidate the effect of backbone structure on properties of poly(amine-amide)s.[15] This study explores the synthesis and basic characterization of a series of new strictly alternating aromatic poly(amine-amide-imide)s containing the triphenylamine unit by the polymerization of *N,N′*-bis(4-aminophenyl)-*N,N′*-diphenyl-1,4-phenylenediamine[15] with various imide ring-preformed dicarboxylic acids. It is quite likely that the triphenylamine-containing poly(amine-amide-imide)s will possess electro- and photochemical properties as well as high thermal stability because of the triphenylamine conjugated system. Thus, these triphenylamine-containing poly(amine-amide-imide)s may be applied in organic electroluminescent elements because light-emitting triarylamine derivatives[16−18] and triarylamine-containing polymers[19,20] are reputed to be a hole-transporting layer material and show increasing potential as active components for a wide range of electronic and optoelectronics devices.

EXPERIMENTAL

Materials

According to the methods reported previously,[21−24] imide-dicarboxylic acids **1a** and **1b** were synthesized by condensation of trimellitic anhydride with glycine and *p*-aminobenzoic acid, respectively, and diimide-dicarboxylic acids **1c–1f** were prepared by condensation of corresponding diamines with two equivalent amount of trimellitic anhydride. *N,N′*-Bis(4-aminophenyl)-*N,N′*-diphenyl-1,4-phenylenediamine (**2**)(mp 261–262°C) was synthesized by hydrogen or hydrazine Pd/C-catalyzed

[†]To whom correspondence should be addressed (E-mail: gsliou@ncnu.edu.tw, shhsiao@ttu.edu.tw).

reduction of N,N'-bis(4-nitrophenyl)-N,N'-diphenyl-1,4-phenylenediamine resulting from the condensation of N,N'-diphenyl-1,4-phenylenediamine with 4-fluoronitrobenzene in the presence of potassium carbonate or sodium hydride. The synthetic details of diamine **2** have been reported in a recent paper.[15] Commercially obtained anhydrous calcium chloride was dried under vacuum at 150 °C for 6 h. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure. Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), N,N-demethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

General Polymer Synthesis

Typical procedures for the synthesis of triphenylamine-based poly(amine-amide-imide) **3g** are as follows. A mixture of 0.4426 g (1.0 mmol) of diamine **2**, 0.5482 g (1.0 mmol) of the diimide-diacid **1g**, 0.4 g of calcium chloride, 0.7 mL of TPP, 1.0 mL of pyridine, and 4 mL of NMP was heated with stirring at 105 °C for 3 h. The polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy, fiber-like precipitate which was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C; yield 0.945 g (99%). The inherent viscosity of the obtained poly(amine-amide-imide) **3g** was 0.62 dL g^{-1}, measured at a concentration of 0.5 g dL^{-1} in N,N-dimethylacetamide (DMAc), containing 5 wt% LiCl at 30 °C.

IR (film): 3310 (N–H stretching), 1790, 1720 (imide carbonyl stretching), and 1670 cm^{-1} (amide carbonyl stretching). ELEM. ANAL. Calcd. for $(C_{60}H_{38}N_6O_7)_n$ $(954.99)_n$: C, 75.46%; H, 4.01%; N, 8.80%. Found: C, 73.29%; H, 4.09%; N, 8.50%.

Preparation of Poly(amine-amide-imide) Films

A solution of polymer was made by dissolving about 0.7 g of the poly(amine-amide-imide) sample in 10 mL of DMAc. The homogenous solution was poured into a 9 cm glass Petri dish, which was placed in a 90 °C oven overnight to slowly release the solvent, then the film was stripped off from the glass substrate and further dried *in vacuo* at 160 °C for 8 h. The obtained films had about 80–100 μm in thickness and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Measurements

Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. Elemental analyses were run in a PerkinElmer model 2400 C–H–N analyzer. The inherent viscosities were determined at a concentration of 0.5 g dL^{-1} in DMAc 5 wt% LiCl using a Cannon-Fenske viscometer at 30 °C. 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^{-1}) at a heating rate of 20 °C min^{-1}. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris 1 differential scanning calorimeter in flowing nitrogen (20 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1}. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 at a scan rate of 10 °C min^{-1} with a penetration probe of 1.0 mm diameter under an applied constant load of 10 mN. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered copper K_α radiation (40 kV, 15 mA), and the scanning rate was 2° min^{-1}. Measurements were performed with film specimens of about 0.1 mm in thickness. An Instron universal tester model 1130 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^{-1} 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.

RESULTS AND DISCUSSION

Polymer Synthesis

A series of new triphenylamine-based poly(amine-amide-imide)s **3a**–**3h** were synthesized from diamine **2** with imide-diacids (**1a**, **1b**) and diimide-diacids (**1c**–**1h**) by the direct phosphorylation polycondensation reaction using triphenyl phosphite and pyridine as condensing agents (Scheme 1). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polymers precipitated in a tough fiber-like form when slowly pouring the resulting polymer solutions into stirring methanol. These poly(amine-amide-imide)s were obtained in almost quantitative yield with inherent viscosities in the range of 0.37–0.80 dL g^{-1} measured in DMAc 5 wt% LiCl, as shown in Table I. Most of the poly(amine-amide-imide)s could be solution cast into flexible and tough films, indicative of the formation of high molecular weight polymers. The formation of poly(amine-amide-imide)s was confirmed by elemental analysis and infrared spectroscopy. Elemental analyses are in a good agreement with the proposed structures, missing only the values found for the C-percentages that are always lower than the theoretical
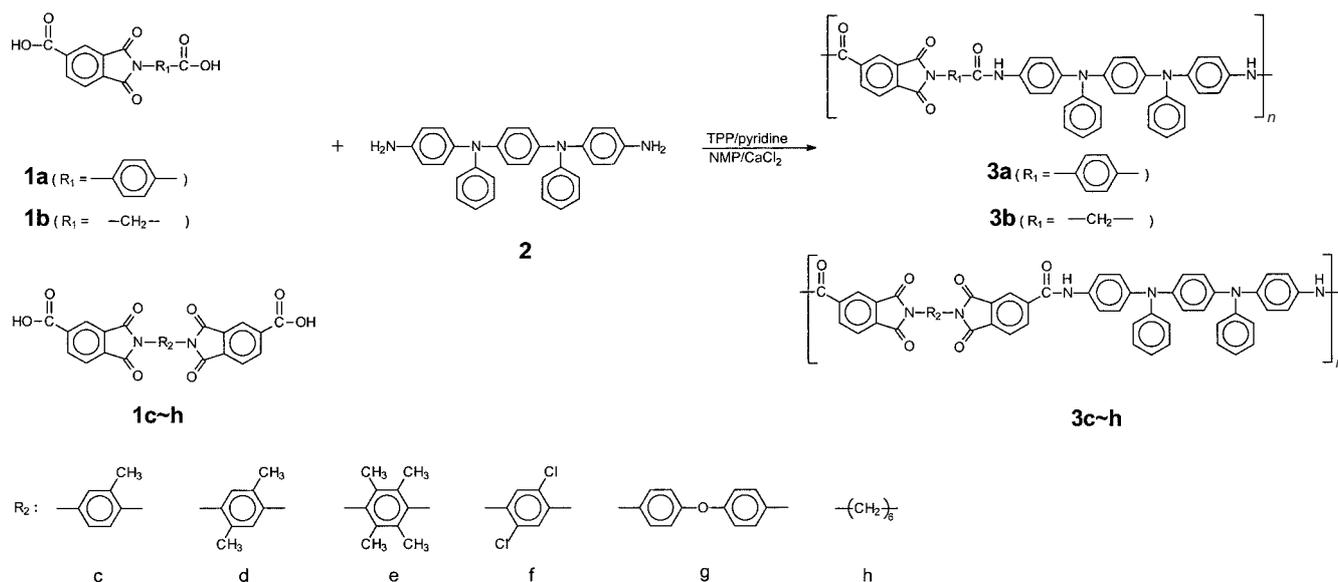
Scheme 1. Synthesis of triphenylamine-containing poly(amide-imide).

Table I. Inherent viscosity and elemental analysis of poly(amine-amide-imide)s

Polymer code	η_{inh} (dL g)[a]	Formula (Formula weight)	Calcd (%) C	Calcd (%) H	Calcd (%) N	Found (%) C	Found (%) H	Found (%) N
3a	0.52	$(C_{46}H_{31}N_5O_4)_n$ $(717.78)_n$	76.97	4.35	9.76	73.93	4.38	9.42
3b	0.37	$(C_{41}H_{29}N_5O_4)_n$ $(655.71)_n$	75.10	4.46	10.68	71.21	4.46	10.08
3c	0.66	$(C_{55}H_{36}N_6O_6)_n$ $(876.92)_n$	75.33	4.14	9.58	71.87	4.12	9.15
3d	0.60	$(C_{56}H_{38}N_6O_6)_n$ $(890.95)_n$	75.49	4.30	9.43	72.46	4.64	8.85
3e	0.80	$(C_{58}H_{42}N_6O_6)_n$ $(919.00)_n$	75.80	4.61	9.14	73.01	4.76	8.85
3f	0.60	$(C_{54}H_{32}Cl_2N_6O_6)_n$ $(931.79)_n$	69.61	3.46	9.02	67.14	3.52	8.74
3g	0.62	$(C_{60}H_{38}N_6O_7)_n$ $(954.99)_n$	75.46	4.01	8.80	73.29	4.09	8.50
3h	0.46	$(C_{54}H_{42}N_6O_6)_n$ $(870.96)_n$	74.47	4.86	9.65	72.72	4.92	9.56

[a]Measured at a concentration of 0.5 g dL^{-1} in DMAc 5 wt% LiCl at 30 °C.

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. The IR spectra of the poly(amine-amide-imide)s exhibited characteristic absorptions for imide ring at around 1790 and 1720 cm^{-1}, characteristic of the symmetrical and asymmetrical carbonyl stretching vibration. Bands of amide groups appeared at near 3400–3300 cm^{-1} (N–H) and 1670 cm^{-1}(C=O), supported the formation of the amide linkages.

Properties of Polymers

The X-ray diffraction studies of the triphenylamine-based poly(amine-amide-imide)s indicated that all the polymers were essentially amorphous. The solubility behavior of these polymers was tested qualitatively, and the results are listed in Table II. All the poly(amine-amide-imide)s were soluble in polar solvents such as NMP, DMAc, and DMF. Most of them were also soluble in *m*-cresol and hot DMSO. Their high solubility and amorphous nature can be attributed to the introduction of bulky, twisted, three-dimensional triphenylamine unit along the polymer backbone, which resulted in increased chain distance and decreased chain interaction. Thus, the excellent solubility makes the present polymers potential candidates for practical applications in spin-on and casting processes.

As mentioned above, Most of the poly(amine-amide-

Table II. Solubility and thin film tensile properties of poly(amine-amide-imide)s

Polymer	Solubility[a]							Tensile properties of the polymer films[b]		
	NMP	DMAc	DMF	DMSO	m-Cresol	THF	CHCl₃	Tensile strength	Elongation to break	Initial modulu
								MPa	%	GPa
3a	+	+	+	+h	–	–	–	113	12	2.6
3b	+	+	+	+	–	–	–	–	–	–
3c	+	+	+h	+h	+	–	–	90	10	2.4
3d	+	+	+	+h	+	–	–	96	7	2.4
3e	+	+	+	+h	+	–	–	104	33	1.8
3f	+h	+h	+h	+	–	+	–	–	–	–
3g	+	+	+	+h	–	–	–	107	11	2.1
3h	+	+	+h	–	+h	–	–	101	10	2.1

[a]+, Soluble at room temperature; +h, soluble on heating; and –, insoluble even on heating. [b]Films were cast by slow evaporation of polymer solutions in DMAc. The film specimens were dried *in vacuo* at 160 °C for 8 h prior to the tensile test.

Table III. Thermal properties of poly(amine-amide-imide)s

Polymer	T_g (°C)[a]	T_s (°C)[b]	T_d at 5% weight loss (°C)[c]		T_d at 10% weight loss (°C)[c]		Char yield[d] (wt %)
			In N₂	In air	In N₂	In air	
3a	296	295	493	498	572	564	74
3b	243	244	416	409	466	465	69
3c	296	299	497	491	576	551	72
3d	285	283	488	485	542	539	70
3e	306	310	498	492	566	546	72
3f	270	257	432	444	520	522	66
3g	290	287	528	518	607	587	73
3h	220	217	460	442	491	482	67

[a]Glass-transition temperature, taken as the midpoint temperature of the baseline shift on the second DSC heating trace (scan rate = 20 °C min⁻¹) after rapid cooling from 400 °C. [b]Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace at a heating rate of 10 °C min⁻¹. The film samples were heated at 300 °C for 30 min prior to the TMA experiments. [c]Decomposition temperature, recorded *via* TGA at a heating rate of 20 °C min⁻¹ and a gas-flow rate of 30 cm³ min⁻¹. [d]Residual weight percentage at 800 °C in nitrogen.

imide)s could be solution-cast into smooth, flexible, and tough films. These films were subjected to tensile testing, and the results are also given in Table II. The tensile strengths, elongations to break, and initial moduli of these films were in the ranges of 90–113 MPa, 7–33%, and 1.8–2.6 GPa, respectively.

DSC and TMA were used to evaluate the thermal transitions of these poly(amine-amide-imide)s. Each sample was subjected to two subsequent DSC heating runs with 20 °C min⁻¹, the first from 40 to 400 °C after which the sample was cooled down with a programmed cooling rate of −200 °C min⁻¹ to 40 °C, followed by a second heating run with an end temperature of 400 °C. The first run was aimed to eliminate any possible volatiles such as the absorbed moisture and the residual solvent in the samples. The quenching procedure led to predominantly amorphous samples. Reheating produced neat DSC thermograms in the second run, and a clear heat capacity jump attributable to a glass transition could be observed in every case. As shown in Table III, the poly(amine-amide-imide)s **3a**–**3h** had T_g's of 220–306 °C, follow-

ing the decreasing order of chain flexibility. As expected, the semi-aromatic poly(amine-amide-imide) **3h** revealed the lowest T_g of 200 °C because of the flexible hexamethylene unit. All the polymers showed no well-defined melting endotherms up to the decomposition temperatures on the DSC thermograms. This result also supports the amorphous nature of these triphenylamine-containing poly(amine-amide-imide)s. The softening temperatures (T_s) (may be referred as apparent T_g) of the poly(amine-amide-imide) 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. In almost all cases, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments.

The thermal stability of these poly(amine-amide-imide)s was studied by TGA. Some thermal behavior data determined from original thermograms poly(amine-amide-imide) **3** in both air and nitrogen atmospheres are also tabulated in Table III. The wholly aromatic poly(amine-amide-imide)s showed good thermal stability, with 10% weight loss temperature being

recorded above 522 °C in air or nitrogen. As expected, the polymers containing aliphatic segments, such as polymers **3b** and **3h**, revealed a lower thermal stability; they began to decompose around 400°C. The amount of carbonized residue (char yield) at 800°C of these poly(amine-amide-imide)s in nitrogen atmosphere was 66–74%, indicating high flame-retardant characteristics. It also can be noticed that there is a large window between T_g or T_s and the decomposition temperature of each poly(amine-amide-imide), which could be advantageous in the processing of these polymers by thermoforming technique.

CONCLUSIONS

A series of new triphenylamine-containing aromatic poly(amine-amide-imide)s have been successfully synthesized by the direct phosphorylation polycondensation reaction from the diamine, N,N′-bis(4-aminophenyl)-N,N′-diphenyl-1,4-phenylenediamine, and various imide ring-preformed dicarboxylic acids. Because of the presence of the bulky triphenylamine unit, all the poly(amine-amide)s were amorphous, had good solubility in many polar aprotic solvents, and exhibited excellent thin film forming capability. Good solubility, moderate T_g or T_s values suitable for molding, and good thermal stability and mechanical properties make these triphenylamine-based poly(amine-amide-imide)s as promising processable high-performance polymeric materials.

REFERENCES

1. M. K. Ghosh, K. L. Mittal, Ed., "Polyimides: Fundamentals and Applications" Marcel Dekker, New York, N.Y., 1996, pp 309–341.
2. D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, Ed., "Polyimides" Chapman and Hall, New York, N.Y., 1990, pp 227–251.
3. Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2189 (1984).
4. Y. Imai, *React. Funct. Polym.*, **30**, 3 (1996).
5. S. H. Hsiao, G. S. Liou, and S. H. Chen, *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 1657 (1998).
6. G. S. Liou, *J. Polym. Sci. Part. A: Polym. Chem.*, **36**, 1937 (1998).
7. G. S. Liou, M. Maruyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 2021 (1998).
8. S. H. Hsiao and C. T. Li, *Macromolecules*, **31**, 7213 (1998).
9. (a) C. P. Yang, G. S. Liou, C. C. Yang, and N. W. Tseng, *Polym. Bull.*, **42**, 1 (1999).
   (b) C. P. Yang, G. S. Liou, C. C. Yang, and S. H. Chen, *Polym Bull.*, **43**, 21 (1999).
   (c) C. P. Yang, G. S. Liou, S. Y. Chang, and S. H. Chen, *J. Appl. Polym. Sci.*, **73**, 271 (1999).
10. Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2189 (1984).
11. H. J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **29**, 39 (1991).
12. H. J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **29**, 1691 (1991).
13. G. S. Liou and S. H. Hsiao, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 2564 (2002).
14. Y. Oishi, M. Ishida, M. Kakimoto, Y. Imai, and T. Kurosaki, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 1027 (1992).
15. G. S. Liou, S. H. Hsiao, M. Ishida, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 2810 (2002).
16. C. W. Ko and Y. T. Tao, *Synth. Met.*, **126**, 37 (2002).
17. B. E. Koene, D. E. Loy, and M. E. Thompson, *Chem. Mater.*, **10**, 2235 (1998).
18. Y. Shirota, K. Okumoto, and H. Inada, *Synth. Met.*, **111–112**, 387 (2000).
19. A. Wu, M. Kakimoto, and Y. Imai, *Supramol. Sci.*, **3**, 3 (1996).
20. J. Lu, A. R. Hlil, Y. Sun, and A. S. Hay, *Chem Mater.*, **11**, 2501 (1999).
21. C. P. Yang and S. H. Hsiao, *Makromol. Chem.*, **190**, 2199 (1989).
22. S. H. Hsiao and C. P. Yang, *J. Polym. Sci. Part A: Polym. Chem.*, **28**, 1149 (1990).
23. G. S. Liou, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 4141 (1999).
24. G. S. Liou, *Macromol. Chem. Phys.*, **201**, 1141 (2000).
25. N. Yamazaki, M. Matsumoto, and F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1373 (1975).