Synthesis and Properties of Organosoluble Polynaphthalimides Bearing Ether Linkages and Phthalide Cardo Groups

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ABSTRACT: A series of organic-soluble polynaphthalimides (PNI) bearing flexible ether links and phthalide cardo group were synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) with 3,3-bis[4-(4-aminophenoxy)-3-methylphenyl]phthalide (BAMP) and its equimolar mixtures with other dietheramines by high-temperature solution polycondensation in *m*-cresol. The PNIs had moderate to high inherent viscosities in the range of 1.24–2.25 dL/g and could afford flexible and tough films with tensile strengths of 97–138 MPa by casting their *m*-cresol solutions. These PNIs exhibited high thermal stability, with glass transition temperature of 291°C–321°C, 10% weight-loss temperatures above 542°C, and char yields at 800°C in nitrogen higher than 56%. In comparison with PNIs without the BAMP component, these BAMP-modified PNIs revealed an enhanced solubility and film-forming capability. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1104–1109, 2007

Key words: 1,4,5,8-naphthalenetetracarboxylic dianhydride; polynaphthalimides; polyimides; phthalide; organosoluble; tough films

INTRODUCTION

Aromatic condensation polyimides have found wide applications in aerospace and microelectronics industries because of their excellent thermal stability, high mechanical strength, and superior chemical resistance.[1,2] Conventional/commercial polyimides are based on the phthalimide unit with a five-membered imide ring. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) is an accessible commercial tetrafunctional monomer useful for the preparation of polyimides with the six-membered imide ring.[3] The six-membered ring naphthenic polyimides (polynaphthalimides; PNI) derived from NTDA have found to demonstrate improved thermal and chemical (both acid and pure water) resistance when compared with conventional/commercial five-membered ring phthalic polyimides.[3,4] However, NTDA has not found wide application in polyimide synthesis; this is primarily associated with the problem concerning the synthesis of PNI having sufficiently high molecular weight and good processability. It was found that introduction of specific fragments such as hexafluoroisopropylidene, ether groups, and *m*-phenylene rings in the polymer backbone and/or phenoxy side groups ensured solubility of PNIs in organic solvents.[5,6] Recently, there has been much interest in the development of soluble sulfonated PNIs as materials for proton exchange membranes in polymer electrolyte fuel cells.[7–18] The PNIs were endowed with proton conductivity and solubility by the incorporation of sulfonic acid along the backbone.

We have previously reported that soluble polyimides could be prepared from 3,3-bis[4-(4-aminophenoxy)-3-methylphenyl]phthalide (BAMP; $\mathbf{I}_a$) and commercially available phthalic-type dianhydrides. Recently, we found that the PNI derived from BAMP and NTDA was also soluble in organic solvents and exhibited good film-forming ability. Good solubility of the BAMP polyimides is presumably due to the bulky pendent phthalide group. In this work, we describe the synthesis and related properties of new naphthenic copolyimides obtained from BAMP and aryl ether diamines. Here, BAMP was used as a solubility-enhanced component of the PNIs by introducing ether linkages into the main chain and bulky phthalide as side groups.

EXPERIMENTAL

Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA; TCI) and isoquinoline (Fluka) were used as received,

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*This author died on August 17, 2005, at the age of 75. This article is now dedicated to the memory of Prof. Chin-Ping Yang, who cherished research and publications as his lifetime joys.

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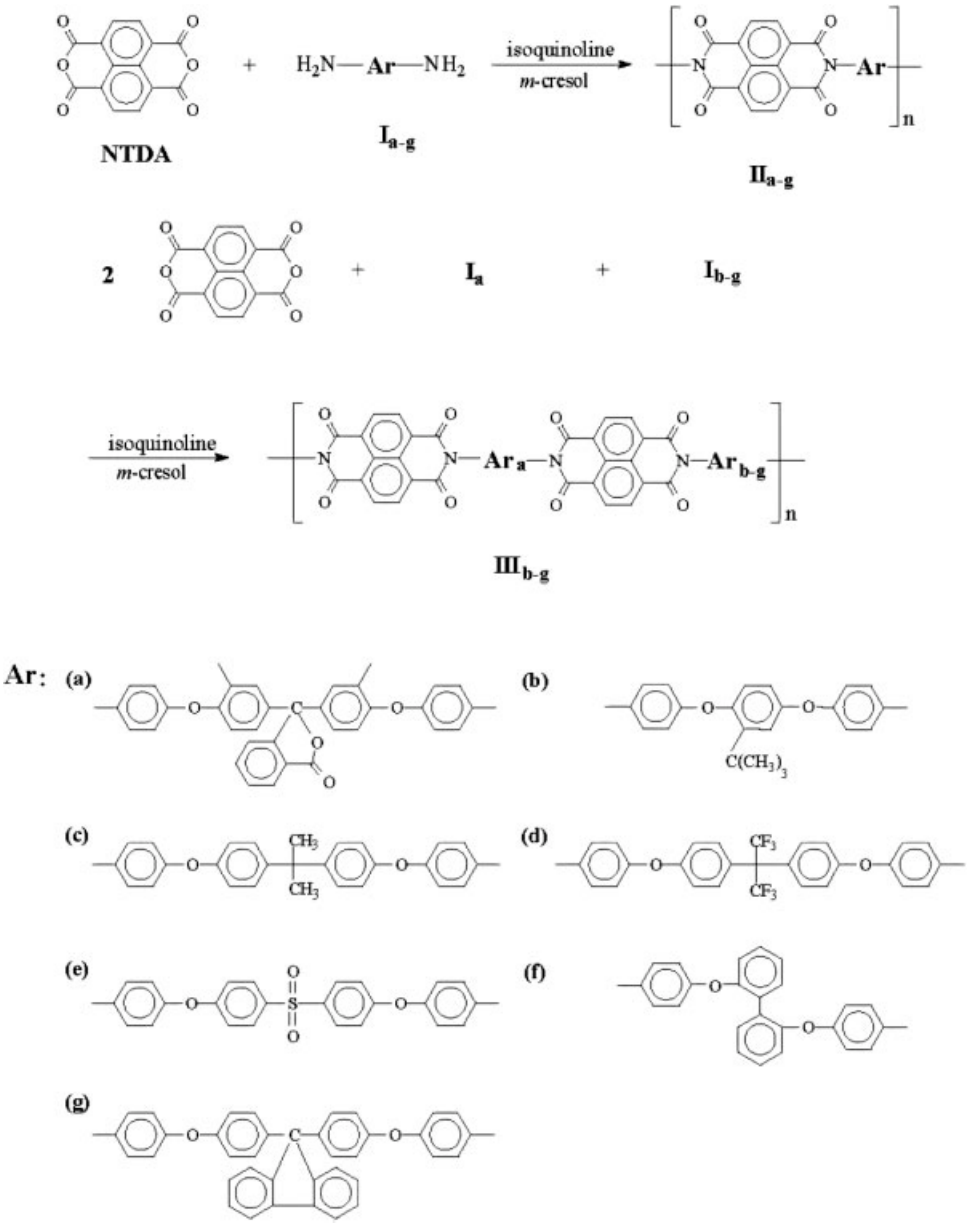

Scheme 1 Synthesis of Polynaphthalimides.

and 3,3-bis[4-(4-aminophenoxy)-3-methylphenyl]phthalide (I_a) (mp = 105–108°C),[19] 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (I_b) (mp = 129–130°C),[20] 2,2-bis(*p*-aminophenoxy)biphenyl (I_f) (mp = 157–158°C),[21] and 9,9-bis[4-(4-aminophenoxy)phenyl]-fluorene (I_g) (mp = 177–178°C)[22] were synthesized from the chloro-displacement reactions of 4-chloronitrobenzene with the corresponding aromatic diols in *N*,*N*-dimethylformamide (DMF) in the presence of potassium carbonate, followed by Pd/C-catalyzed hydrazine reduction. 2,2-Bis[4-(4-aminophenoxy)-phenyl]propane (I_c; Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (I_d; Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone (I_e; Chriskev) were used without further purification.

General procedure for the preparation of PNIs

Phthalide-containing PNIs were prepared by reacting stoichiometric quantities of NTDA with various aryl ether diamines. The following procedure is for the preparation of PNI II_a and is representative for the preparation of all polymers. To a 50-mL round-bottom flask were added 0.5286 g (1.0 mmol) of BAMP (I_a), 0.2682 g (1.0 mmol) of NTDA, 3.0 mL of *m*-cresol, and three drops of isoqinuoline successively. The mixture was stirred at room temperature for 30 min, and then heated at 180°C for 10 h. After the reaction mixture was cooled to 80°C, an additional 2 mL of *m*-cresol was added to dilute the highly viscous solution, and then the polymer solution obtained was trickled into stirred methanol. The

TABLE I
Inherent Viscosity and Solubility of Polynaphthalimides

Polymer code	η_{inh}[a] (dL/g)	Solvent[b]							
		NMP	DMAc	DMF	DMSO	*m*-Cresol	Py	Dioxane	THF
$\mathbf{II}_a$	2.32	□	□	−	−	□	−	−	−
$\mathbf{II}_b$	0.75	−	−	−	−	+	−	−	−
$\mathbf{II}_c$	–	−	−	−	−	−	−	−	−
$\mathbf{II}_d$	0.67	+	−	−	−	○	−	−	−
$\mathbf{II}_e$	0.65	□	−	−	−	+	−	−	−
$\mathbf{II}_f$	–	−	−	−	−	−	−	−	−
$\mathbf{II}_g$	0.57	−	−	−	−	+	−	−	−
$\mathbf{III}_b$	1.88	□	○	−	−	□	□	−	−
$\mathbf{III}_c$	2.08	+	−	−	−	□	−	−	−
$\mathbf{III}_d$	2.25	□	○	−	−	□	□	□	−
$\mathbf{III}_e$	2.03	○	○	−	−	□	−	−	−
$\mathbf{III}_f$	1.37	−	−	−	−	□	+	−	−
$\mathbf{III}_g$	2.17	□	○	−	−	□	□	−	−

NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.
[a] Inherent viscosity (η_{inh}) measured at a polymer concentration of 0.5 g/dL in *m*-cresol at 30°C
[b] Solubility was determined at room temperature; □, soluble at 10%; ○, soluble at 5%; +, soluble at 1%; −, insoluble.

brown stringy precipitate was washed thoroughly with hot water and methanol, collected by filtration and dried *in vacuo* at 100°C for 10 h. Inherent viscosity of $\mathbf{II}_a$ was 2.32 dL/g, measured with a polymer concentration of 0.5 g/dL in *m*-cresol at 30°C. ^{1}H-NMR (500 MHz, DMSO-d_6, δ, ppm): 8.75 (4H, H_a), 8.08 (1H, H_j), 7.96 (1H, H_g), 7.92 (1H, H_h), 7.73 (1H, H_i), 7.51 (4H, H_b), 7.44 (2H, H_d), 7.33 (2H, H_f), 7.11 (4H, H_c), 7.06 (2H, H_e), 2.20 (6H, H_k). Films were cast as described below. Copolymers were prepared in a similar manner using 50 mol % of $\mathbf{I}_a$, 50 mol % of another diamine, and a stoichiometric amount of NTDA.

Film preparation

Thin films were cast from polyimide solutions in *m*-cresol (typically 10 wt % solid). The homogeneous solution was poured into a 9-cm-diameter glass culture dish, which was placed in 110°C oven over night to evaporate the solvent and to form a tack-free film. The films then were stage-dried to 250°C and held for 1 h. Polymer films were stripped off from the glass surface by soaking in water. The polymer films were further dried in vacuum at 200°C for 10 h.

Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a Heraeus VarioEL-III CHN analyzer. ^{1}H- and ^{13}C-NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at a 0.5 g/dL concentration in *m*-cresol with an Ubbelohde viscometer at 30°C. Mechanical properties of the films were measured on an Instron model 4400R tensile tester with a 5 kg load cell at a crosshead speed of 5 mm/min on strips approximately 30–60 μm thick and 0.5 cm wide with a 2-cm gauge length. An average of at least three replicates was used. Differential scanning calorimetry (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. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 at a scan rate of 10°C/min with 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. Measurements were carried out on 3–5 mg film samples heated in

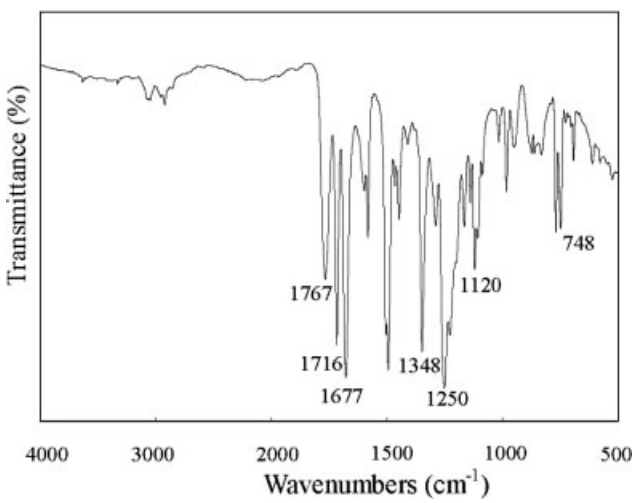

Figure 1 FTIR spectrum of polynaphthalimide $\mathbf{III}_b$.

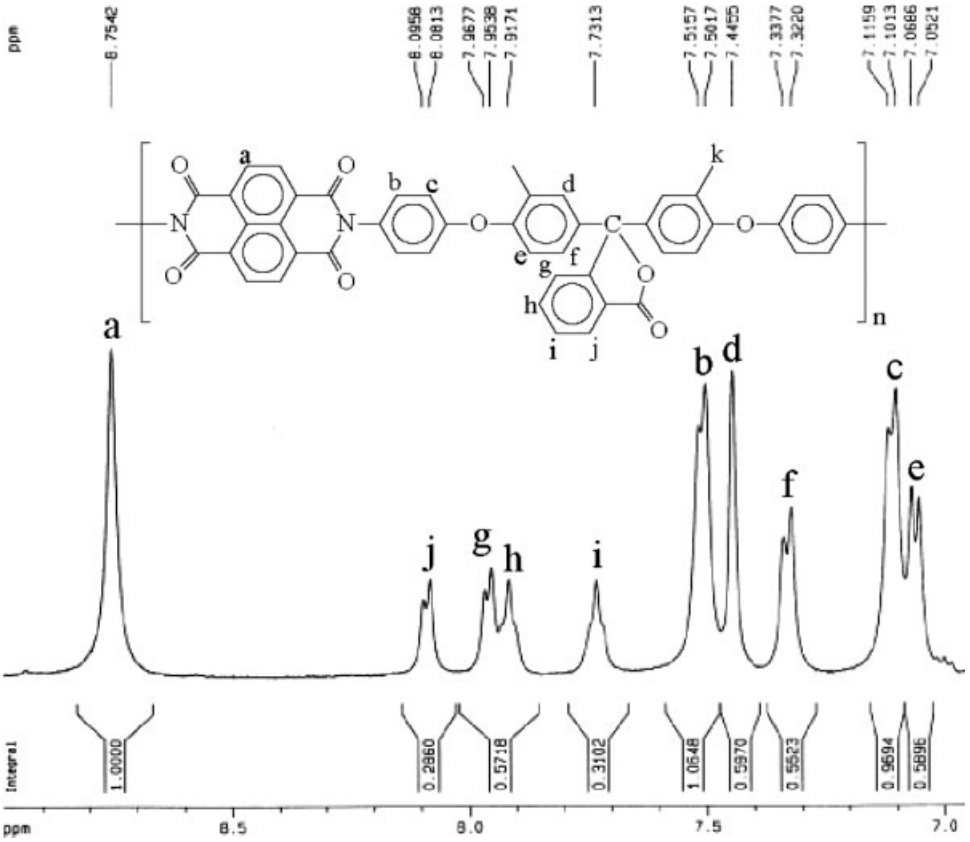

Figure 2 ^{1}H-NMR spectrum of polynaphthalimide $\mathbf{II_a}$ in DMSO-d_6. The signal arising from methyl protons (H_k) at δ = 2.20 ppm is not shown.

flowing nitrogen or air (30 cm^3/min) at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Synthesis of PNIs

As shown in Scheme 1, the PNI homopolymers $\mathbf{II}_{a-g}$ and copolymers $\mathbf{III}_{b-g}$ were prepared by the high-temperature solution polycondensation method. In this procedure, the dianhydride NTDA and the diamines were polymerized in *m*-cresol at 180°C, using isoquinoline as catalyst.[23] Under these conditions, chain growth and imidization essentially occur spontaneously. Depending on structure of the starting diamines, the polymerization reactions proceeded homogeneously or heterogeneously and led to the formation of the final PNIs. For the **II** series PNIs,

TABLE II
Elemental Analysis of the Polynaphthalimides

Polymer code	Formula of repeat unit (formula weight)		Elemental analysis (%)		
			C	H	N
$\mathbf{II}_a$	$(C_{48}H_{28}N_2O_8)_n$	Calcd	75.78	3.71	3.68
	$(760.76)_n$	Found	75.19	3.20	3.23
$\mathbf{III}_b$	$(C_{84}H_{52}N_4O_{14})_n$	Calcd	75.20	3.91	4.18
	$(1341.36)_n$	Found	74.40	4.04	4.04
$\mathbf{III}_c$	$(C_{89}H_{54}N_4O_{14})_n$	Calcd	76.17	3.88	3.99
	$(1403.43)_n$	Found	76.05	3.95	3.80
$\mathbf{III}_d$	$(C_{89}H_{48}N_4O_{14}F_6)_n$	Calcd	70.73	3.20	3.71
	$(1511.37)_n$	Found	69.47	3.32	3.44
$\mathbf{III}_e$	$(C_{86}H_{48}N_4O_{16}S_1)_n$	Calcd	72.47	3.39	3.93
	$(1425.40)_n$	Found	71.74	3.53	3.55
$\mathbf{III}_f$	$(C_{86}H_{48}N_4O_{14})_n$	Calcd	75.88	3.55	4.12
	$(1361.35)_n$	Found	75.25	3.65	3.73
$\mathbf{III}_g$	$(C_{99}H_{56}N_4O_{14})_n$	Calcd	77.94	3.70	3.67
	$(1211.05)_n$	Found	77.42	3.81	3.53

TABLE III
Tensile Properties of Polynaphthalimide Films

Polymer code	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
$\mathbf{II}_a$	123	32	2.3
$\mathbf{III}_b$	127	13	2.8
$\mathbf{III}_c$	124	9	2.6
$\mathbf{III}_d$	101	14	2.2
$\mathbf{III}_e$	97	7	2.2
$\mathbf{III}_f$	97	5	2.8
$\mathbf{III}_g$	138	11	3.0

only $\mathbf{II}_a$ was produced with high inherent viscosity (2.32 dL/g) and could be cast into the flexible and tough film. Less favorable results were obtained from reactions of NTDA with other diamines. In most cases, an early precipitation occurred, which retarded further polymerization, because of the insolubility of the resulting PNI. However, all the reactions of NTDA with equimolar mixtures of diamine $\mathbf{I}_a$ and any another diamine of $\mathbf{I}_{b–h}$ proceeded homogeneously and led to the formation of highly viscous polymer solutions. Slow pouring these polymer solutions into stirred methanol resulted in tough fiber-like precipitates, which could be cast from their solutions in *m*-cresol to form transparent, light brown, and flexible films. This indicated the formation of high-moleculor-weight polymers; as shown in Table I, the **III** series PNIs exhibited high inherent viscosities in the range of 1.24–2.25 dL/g. The successful syntheses of these PNIs could be attributed to their improved solubility caused by the incorporation of bulky phthalide cardo groups in the polymer backbones.

The chemical structure of the PNIs was confirmed by FTIR and proton NMR spectroscopy. For example, the FTIR spectrum of PNI $\mathbf{III}_b$ is presented in Figure 1. The strong absorption bands around 1767 and 1716 cm^{-1} are assigned to the stretch vibration of carbonyl groups of imide rings. The peak at around 1677 cm^{-1} is peculiar to the lactone carbonyl groups, and the strong absorption bands around 1250 cm^{-1} is attributed to the aryl ether bonds. Figure 2 illustrates the ^{1}H-NMR spectrum of PNI $\mathbf{II}_a$ in DMSO-d_6. Aromatic protons were well assigned to the chemical structure of this PNI. In addition to IR and NMR spectra, the elemental analysis results of PNIs also generally agreed with the calculated values for the proposed structures (Table II).

Polymer solubility

The solubility of the PNIs was tested in various organic solvents, and the results are also summarized in Table I. For the **II** series PNI homopolymers, only $\mathbf{II}_a$ is soluble at a concentration of 10% in *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), and *m*-cresol. The other **II** series PNIs are sparingly soluble or insoluble in the tested solvents. The better solubility of $\mathbf{II}_a$ than the other **II** series PNIs can be explained by the introduction of bulky, solubilizing phthalide group into the polymer backbone. Copolymerization of NTDA with equimolar mixtures of $\mathbf{I}_a$ and $\mathbf{I}_{b–g}$ produced the **III** series PNIs with an enhanced solubility. As shown in Table I, all the **III** series PNIs are soluble at a concentration of 10% in *m*-cresol, and most of them are soluble at 5 or 10 wt % in NMP and DMAc. Therefore, diamine $\mathbf{I}_a$ can be used as a solubility-enhancer in the preparation of soluble PNIs.

Mechanical properties of PNI films

Transparent and flexible films of PNIs $\mathbf{II}_a$ and $\mathbf{III}_{b–h}$ were cast from their solutions in *m*-cresol. The tensile properties of these polymer films are collected in Table III. They had strengths at break of 97–138 MPa, elongations to break of 7%–14%, and initial moduli of 2.2–3.0 GPa, indicating that they are strong materials.

Thermal properties

DSC, TGA, and TMA were used to evaluate the thermal properties of the polymers. The thermal behavior data of all the PNIs are summarized in Table IV. DSC analysis of the polymer powders or films was carried out by heating the samples to 400°C, air-cool-

TABLE IV
Thermal Properties of Polynaphthalimides

Polymer code	T_g (°C)[a]	T_s (°C)[b]	T_{10} (°C)[c] In N_2	T_{10} (°C)[c] In air	Char yield (%)[d]
$\mathbf{II}_a$	305	308	563	553	59
$\mathbf{II}_b$	345	–	594	519	56
$\mathbf{II}_c$	348	–	603	563	59
$\mathbf{II}_d$	354	–	610	591	61
$\mathbf{II}_e$	368	–	587	567	58
$\mathbf{II}_f$	370	–	594	570	53
$\mathbf{II}_g$	373	–	632	570	64
$\mathbf{III}_b$	291	308	542	554	62
$\mathbf{III}_c$	317	322	559	570	57
$\mathbf{III}_d$	319	331	572	583	60
$\mathbf{III}_e$	312	316	545	563	56
$\mathbf{III}_f$	310	314	569	584	58
$\mathbf{III}_g$	317	327	574	592	66

[a] Midpoint temperature of the baseline shift on the second heating DSC traces, with a heating rate of 20°C/min.
[b] Softening temperature taken as the onset temperature of the probe displacement on the TMA trace at a heating rate of 10°C/min. The film samples were heated at 350°C for 1 h prior to the TMA experiments.
[c] Temperatures at which 10% weight loss were recorded by TG at a heating rate of 20°C/min.
[d] Residual weight (%) when heated to 800°C in nitrogen.

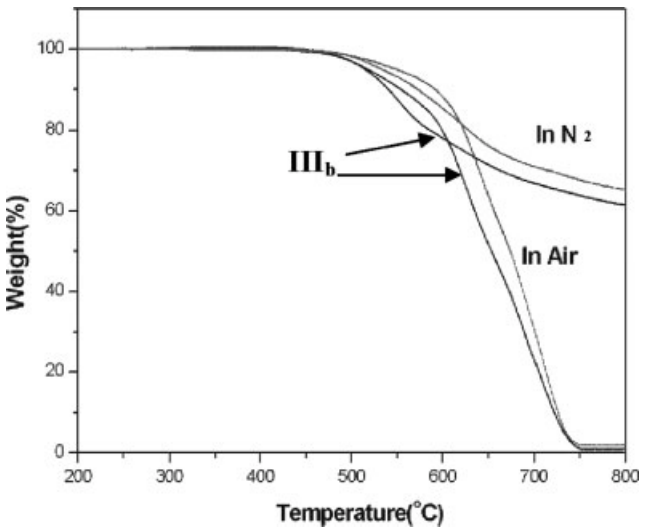

Figure 3 TGA curves for polynaphthalimides **III**$_b$ and **III**$_g$.

ing to room temperature, and then reheating to 400°C. Glass transition temperature (T_g) of all the PNIs could be easily read in the second heating DSC traces. PNIs **II**$_{a–g}$ exhibited T_g values in the range of 305°C–373°C. The relatively lower T_g value of **II**$_a$ compared to the other polymers in this series could be explained by the presence of the phthalide cardo group along the polymer chain, resulting in an increased free volume. PNIs **III**$_{b–g}$ showed T_g values between 291°C and 319°C. The softening temperatures (T_s) of the polymer films were also measured with TMA by the penetration method. The T_s value was read from the onset temperature of the probe displacement on the TMA trace. In most cases, the T_s values obtained by TMA are comparable to the T_g values observed by the DSC experiments.

The thermal stability of these PNIs was evaluated by TGA. Typical TGA curves of PNIs **III**$_b$ and **III**$_g$ are shown in Figure 3. All the PNIs showed high thermal stability; they did not show significant decomposition before 500°C in both air and nitrogen atmospheres. The temperatures for 10% weight loss (T_{10}) of PNIs **III**$_{b–h}$ in nitrogen and air atmospheres stayed within 542°C–574°C and within 554°C–592°C, respectively. All polymers showed char yields at 800°C in nitrogen higher than 56%. TGA traces of PNIs **III**$_{b–h}$ showed a slower decomposition rate in air than in nitrogen at earlier stages, probably due to free radical formation on the methyl sites of the BAMP component, leading to crosslinking.

CONCLUSIONS

Novel organosoluble PNIs were successfully synthesized by the incorporation of the phthalide-containing dietheramine BAMP component. The obtained PNIs could afford flexible and ductile films with good mechanical properties and high thermal stability. These properties suggest the potential usefulness of these novel polyimides in high-tech applications.

References

1. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds. Polyimides; Blackie: Glasgow, 1990.
2. Ghosh, M. K.; Mittal, K. L., Eds. Polyimide: Fundamentals and Applications; Marcel Dekker: New York, 1996.
3. Rusanov, A. L. Adv Polym Sci 1994, 111, 115.
4. Genies, C.; Mercier, R.; Sillion, B.; Pettand, R.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 5097.
5. Rusanov, A. L.; Bulycheva, E. G.; Elshina, L. B.; Askadskiy, A. A.; Nesmeyanov, A. N.; Vlasov, U. N.; Rogozhnikova, O. Y. Polym Prepr (Am Chem Soc Div Polym Chem) 1998, 39, 853.
6. Rusanov, A. L.; Tartakovskiy, V. A.; Shevelev, S. A.; Dutov, M. D.; Vatsadse, I. A.; Serushkina, O. V.; Komarova, L. A.; Prigozhina, M. P.; Bulycheva, E. G.; Elshina, L. B. Polymer 2000, 41, 5021.
7. Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 359.
8. Fang, J. H.; Guo, X. X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. Macromolecules 2002, 35, 9022.
9. Guo, X. X.; Fang, J. H.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. Macromolecules 2002, 35, 6707.
10. Yin, Y.; Fang, J. H.; Cui, Y. F; Tanaka, K.; Kita, H.; Okamoto, K. Polymer 2003, 44, 4509.
11. Yin, Y.; Fang, J.; Tatsuya, W.; Kazuhiro, T.; Kita, H.; Okamoto, K. J Mater Chem 2004, 14, 1062.
12. Yin, Y.; Yamada, O.; Suto, Y.; Mishima, T.; Tanka, K.; Kita, H.; Okamoto, K. J Polym Sci Part A: Polym Chem 2005, 43, 1545.
13. Hu, Z. X.; Yin, Y.; Chen, S. W.; Yamada, O.; Tanakak, K.; Kita, H.; Okamoto, K. J Polym Sci Part A: Polym Chem 2006, 44, 2862.
14. Yasuda, T.; Miyatake, K.; Hirai, M.; Nanasawa, M.; Watanabe, M. J Polym Sci Part A: Polym Chem 2005, 43, 4439.
15. Einsla, B. R.; Hong, Y. T.; Kim, Y. S.; Wang, F.; Gunduz, N.; McGrath, J. E. J Polym Sci Part A: Polym Chem 2004, 42, 862.
16. Lee, C.; Sundar, S.; Kwon, J.; Han, H. J Polym Sci Part A: Polym Chem 2004, 42, 3612.
17. Lee, C.; Sundar, S.; Kwon, J.; Han, H. J Polym Sci Part A: Polym Chem 2004, 42, 3621.
18. Yang, S. J.; Jang, W.; Lee, C.; Shul, Y. G.; Han, H. J Polym Sci Part B: Polym Phys 2005, 43, 1455.
19. Yang, C. P.; Tang, S. Y. J Polym Sci Part A: Polym Chem 1999, 37, 455.
20. Yang, C. P.; Hsiao, S. H.; Yang, H. W. Macromol Chem Phys 1999, 200, 1528.
21. Hsiao, S. H.; Yang, C. P.; Lin, C. K. J Polym Res 1995, 2, 1.
22. Yang, C. P.; Lin, J. H. J Polym Sci Part A: Polym Chem 1993, 31, 2153.
23. Piroux, F.; Mercier, R.; Picq, D.; Espuche, E. Polymer 2004, 45, 6445.