

Synthesis and Characterization of Novel Aromatic Polyimides from 1,4-Bis(4-aminophenyl)-2,3-diphenyl-naphthalene and Aromatic Tetracarboxylic Dianhydrides

Atsushi MORIKAWA[†] and Tadashi HATAKEYAMA

Department of Materials Science, Faculty of Engineering, Ibaraki University,
4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

(Received August 4, 1998)

ABSTRACT: New aromatic polyimides containing a tetraphenyl-naphthalene unit were synthesized from 1,4-bis(4-aminophenyl)-2,3-diphenyl-naphthalene and various aromatic tetracarboxylic dianhydride by the conventional two-step procedure that included ring-opening polyaddition in a polar amide-type solvent and subsequent thermal cyclic dehydration. These polyimides had inherent viscosities of 0.58–1.01 dl g⁻¹ and some polyimides were readily soluble in a wide range of organic solvents such as *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, pyridine and *m*-cresol on heating. The glass transition temperature of the polyimides ranged from 306 to 375°C, and 10% weight loss temperatures were 540–580°C in air.

KEY WORDS High Temperature Polyimides / Soluble Polyimides / 1,4-Bis(4-aminophenyl)-2,3-diphenyl-naphthalene / Thermal Behavior /

Aromatic polyimides are characterized by high glass transition temperatures (T_g) along with high decomposition temperatures and good mechanical properties. The only one major drawback is that they are insoluble in organic solvents and unprocessable after conversion from the polyamic acid, the precursor of polyimide, to the polyimide form. Several attempts have been made to improve the solubility of polyimides while maintaining the excellent thermal and mechanical properties.^{1–9} One attractive method to improve solubility is the introduction of bulky pendant phenyl group into the polyimide backbone, and a number of organic soluble polyimides having high T_g s have been successfully prepared by using aromatic diamines containing tetraphenylthiophene,^{10,11} tetraphenylfuran,¹² tetraphenylpyrrole,¹³ triphenylamine,¹⁴ triphenylbenzene,¹⁵ and tetraphenylquinquephenyl.¹⁶ Recently, we synthesized organic soluble polyamides having high thermal stability from 1,4-bis(4-aminophenyl)-2,3-diphenyl-naphthalene and various aromatic acid dicarboxylic acid chlorides.¹⁷ Therefore, soluble and thermally stable polyimide would be expected to be prepared from this diaminotetraphenyl-naphthalene. This paper describes the synthesis and characterization of novel polyimides by polymerization of the diamine with various aromatic tetracarboxylic dianhydrides, and the properties of polyimides such as solubility and thermal behavior are also discussed. The introduction of tetraphenyl-naphthalene unit into the polymer backbone was expected to increase the glass transition temperature due to the rigid terphenyl structure, as well as improve the solubility due to the bulky asymmetric structure.

EXPERIMENTAL

Materials

1,4-Bis(4-aminophenyl)-2,3-diphenyl-naphthalene (**I**) was synthesized according to the method reported previously.¹⁷ Pyromellitic dianhydride (**IIa**), 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (**IIb**), 3,3',4,4'-benzophe-

nonetetracarboxylic dianhydride (**IIc**), 4,4'-oxydiphthalic anhydride (**II'd**), and 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (**IIe**), were obtained commercially and purified by sublimation under reduced pressure. *N,N*-dimethylacetamide (DMAc) was purified by vacuum distillation with calcium hydride.

Polymerization

Polyimide IVa from I and IIa. In a three necked flask, 0.327 g (1.5 mmol) of solid **IIa** was added to a solution of 0.693 g (1.5 mmol) of diamine **I** in 7 ml of DMAc in one portion. The mixture was stirred at room temperature for 5 h under nitrogen. A part of the resulting viscous solution was poured into 200 ml methanol. The precipitated polymer was filtered, washed with hot methanol and dried under vacuum. The inherent viscosity of the polyamic acid (**IIIa**) in DMAc was 0.68 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30°C. The rest of the DMAc solution was cast onto a glass plate and the solvent was removed at 80°C. Thermal cyclodehydration of the polyamic acid was performed by heating at 100°C for 1 h, at 200°C for 1 h and 300°C for 1 h under vacuum. The IR spectrum (film) exhibited absorption band at 1780 and 1720 cm⁻¹ (C=O) and 1360 cm⁻¹ (C–N).

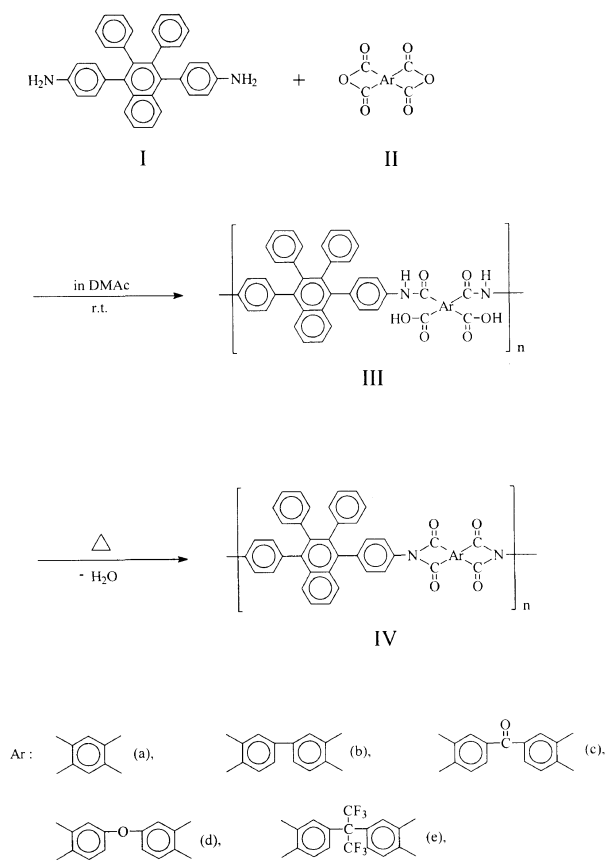
Anal. Calcd for (C₄₄H₂₄N₂O₄)_n: C, 81.97%; H, 3.75%; N, 4.35%. Found: C, 81.90%; H, 3.66%; N, 4.28%.

Other polymers were synthesized by similar procedure.

Measurement

¹H and ¹³C NMR spectra and IR spectra were recorded on a JNM-GSX-400 FT-NMR spectrometer and Shimadzu Spectro Photometer IR 435, respectively. X-Ray diffraction was performed with a Rigaku RAD-B System. Differential scanning calorimetry (DSC) and thermogravimetry (TG) used a Rigaku Thermal Analysis Station TAS 100 and TG 8110, respectively, and the measurements were made at a heating rate of 10°C min⁻¹ in air and nitrogen.

[†] To whom correspondence should be addressed.



Scheme 1.

Table I. Synthesis of polyamic acids and polyimides

Dianhydride	Polyamic acid ^a		Polyimide ^b	
	Code	η_{inh}^c dl g ⁻¹	Code	η_{inh}^d dl g ⁻¹
IIa	IIIa	0.68	IVa	0.59
IIb	IIIb	1.03	IVb	1.01
IIc	IIIc	0.83	IVc	0.75
IIId	IIIId	0.62	IVd	0.58
IIe	IIIe	0.90	IVe	0.81

^a Polymerization was carried out with 1.5 mmol each monomer in 7.0 ml of DMAc at room temperature for 5 h under nitrogen. ^b Thermal conversion was performed by heating at 100°C for 1 h, at 200°C for 1 h and 300°C for 1 h under vacuum. ^c Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C. ^d Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

RESULTS AND DISCUSSION

Polymer Synthesis

Aromatic polyimides **IVa–IVe** were synthesized by the usual two-step procedure which involved the ring-opening polyaddition of diamine to aromatic tetracarboxylic dianhydride **IIa–IIe** and the subsequent thermal cyclodehydration as shown in Scheme 1.

In the first step, ring-opening polyadditions were carried out in DMAc at room temperature, leading to the formation of polyamic acids having inherent viscosities of 0.65–1.03 dl g⁻¹ in DMAc (Table I). The polymerization proceeded in homogeneous solution in the reaction media (DMAc), and the viscosity of the

Table II. Solubility of aromatic polyimides

Solvent	Polymer				
	IVa	IVb	IVc	IVd	IVe
<i>N</i> -Methyl-2-pyrrolidone	–	–	+	+	+
<i>N,N</i> -Dimethylacetamide	–	–	+	+	+
<i>N,N</i> -Dimethylformamide	–	–	+	+	+
<i>m</i> -Cresol	–	–	+	+	+
Pyridine	–	–	+	+	+

^a Solubility: ++, soluble at room temperature; +, soluble on heating; –, insoluble.

polyamic acids were rather high.

In the second step, the thermal conversion of the polyamic acids to polyimides was performed by heating precursor polymers in the form of film successively at 100°C for 1 h, at 200°C for 1 h and 300°C for 1 h under vacuum. The inherent viscosities of the polyimides formed were high enough in the range of 0.58–1.01 dl g⁻¹, in concentrated sulfuric acid (Table I), and hence these polyimides gave tough films except **IVa** and **IVb**. Polyimide **IVa** and **IVb** gave only brittle films. This might be due to the rigid structures of carboxylic dianhydrides **IVa** and **IVb**.

The formation of polyimides were confirmed by appearance of absorption bands at around 1770 cm⁻¹ and 1720 cm⁻¹ (C=O) and at about 1360 cm⁻¹ (C–N) characteristic of imide group in the IR spectra. Elemental analysis values were in close agreement with those calculated values, thus also supporting polyimide formation.

Polymer Properties

Table II lists qualitative solubility of the tetraphenyl-naphthalene containing aromatic polyimides. All polyimides were insoluble in organic solvents at room temperature. Polyimides **IVc**, **IVd**, and **IVe** having connecting groups were soluble in *N*-methyl-2-pyrrolidone, DMAc, pyridine and *m*-cresol on heating. Interestingly, the polyimide never precipitated in spite of the insolubility at room temperature when the hot solution was cooled to room temperature. However, polyimides, **IVa** and **IVb**, having rigid structures barely swelled and were insoluble in these solvents even on heating. In spite of the bulky structure, the solubility of these tetraphenyl-naphthalene-based polyimides was lower than that of aromatic polyimides having similar phenyl-pendant structures such as tetraphenylthiophene, tetraphenylfuran, tetraphenylpyrrole, tetraphenylethylene, triphenylamine, and triphenylphosphine, previously reported to be soluble in *N*-methylpyrrolidone (NMP) at room temperature.¹⁸ The presence of hetero-atoms such as O, N, and S in diamine component of polyimide is expected to increase the solubility due to polar interaction with the solvents. Thus, the absence of hetero-atoms as well as the rigid terphenyl structure is the possible cause of the relatively low solubility of the present polyimides. X-Ray diffraction studies of present polyimides showed that they were amorphous.

The thermal behavior of these polyimides was evaluated by TG and DSC. Figure 1 shows typical DSC and TG curves of Polyamide **IVa**, and the glass transi-

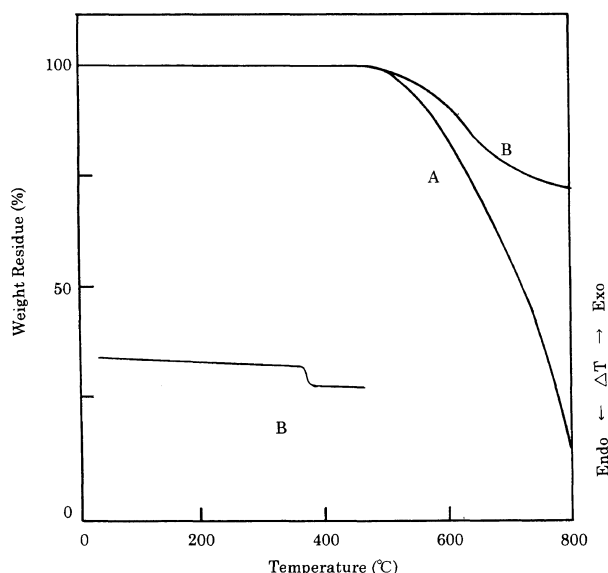


Figure 1. DSC and TG curves for polyamide IVa at heating rate of $10^{\circ}\text{C min}^{-1}$ in (A) air and (B) nitrogen.

Table III. Thermal behavior of aromatic polyimides

Polymer	T_g^a °C	T_{10}^b		Char yield ^c %
		In air °C	In nitrogen °C	
IVa	375	573	624	74
IVb	360	578	632	75
IVc	339	575	615	73
IVd	306	557	625	71
IVe	322	543	595	65

^a Determined by DSC in nitrogen at a heating rate of $10^{\circ}\text{C min}^{-1}$.

^b Temperature at which 10% weight loss was recorded by TG at a heating rate of $10^{\circ}\text{C min}^{-1}$. ^c Char yield in nitrogen at 800°C by TG.

tion temperatures (T_g) and 10% weight loss temperature (T_{10}) are summarized in Table III. The present polyimides had relatively high T_g in the range of $306\text{--}375^{\circ}\text{C}$, and as high glass transition temperature as tetraphenylthiophene-based polyimide, which was the most thermally stable polymer in the aromatic polyamide having similar phenyl pendant structure, which had been previously reported.¹⁹ Polyimides IVa and IVb having rigid symmetric structures had higher T_g than polymers with unsymmetric one and flexible connecting group.

None of the present polyimides lost weight below 470°C in air or nitrogen, and T_{10} in air and nitrogen were in the range of $543\text{--}578^{\circ}\text{C}$ and $595\text{--}632^{\circ}\text{C}$, respectively. More than 65% weight was retained even

at 800°C in nitrogen for these polyimides. These results indicate high thermal stability of the present polyimides. On the basis of T_{10} , these tetraphenyl-naphthalene-based polyimides had as high thermal stability as tetraphenylthiophene-based polyamide, which was the most thermally stable polymer in the aromatic polyimide having similar phenyl pendant structure previously reported.¹⁹

CONCLUSION

New aromatic polyimides containing tetraphenyl-naphthalene unit were synthesized from 1,4-bis(4-aminophenyl)-2,3-diphenyl-naphthalene and various aromatic tetracarboxylic dianhydrides by the conventional two-step procedure that included ring-opening polyaddition and subsequent cyclodehydration. The polyimides formed had high inherent viscosities, and were characterized as polyimides with both high T_g s of $306\text{--}375^{\circ}\text{C}$ and high thermal stability. Some of the polyimides were soluble in polar solvents on heating.

REFERENCES

- V. V. Korshak, S. V. Vinogradova, and Y. S. Vygodskii, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C11**, 45 (1974).
- G. R. Husk, P. E. Cassidy, and K. L. Gebert, *Macromolecules*, **21**, 1234 (1988).
- F. Akutsu, S. Kuze, K. Matsuo, K. Naruchi, and M. Miura, *Makromol. Chem., Rapid Commun.*, **11**, 673 (1990).
- S. Z. D. Cheng, S. K. Lee, J. S. Barley, S. L. C. Hsu, and F. W. Harris, *Macromolecules*, **24**, 1883 (1991).
- T. Matsuura, Y. Hasuda, S. Nishi, and N. Yamada, *Macromolecules*, **24**, 5001 (1991).
- S. Z. D. Cheng, F. E. Arnold, Jr., A. Zhang, S. L. C. Hsu, and F. W. Harris, *Macromolecules*, **24**, 5856 (1991).
- N. Biolley, M. Gregoire, T. Pascal, and B. Sillion, *Polymer*, **32**, 3256 (1991).
- S. Ando, T. Matsuura, and S. Sasaki, *Macromolecules*, **25**, 5858 (1992).
- R. Giesa, U. Keller, P. Eiselt, and H.-W. Schmidt, *J. Polym. Sci., Appl. Polym. Symp.*, **26**, 421 (1975).
- Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2189 (1984).
- H.-J. Jeong, A. Kobayashi, M. Kakimoto, and Y. Imai, *Polym. J.*, **26**, 373 (1994).
- H.-J. Jeong, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 39 (1991).
- H.-J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 1691 (1991).
- Y. Oishi, M. Ishida, M. Kakimoto, Y. Imai, and T. Kurosaki, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1027 (1992).
- I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules*, **31**, 1236 (1998).
- I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules*, **31**, 515 (1998).
- A. Morikawa and T. Hatakeyama, *Polym. J.*, **31**, 66 (1999).
- Y. Imai, *High Perform. Polym.*, **7**, 337 (1995).