

SYNTHESIS AND CHARACTERIZATION OF ORGANO-SOLUBLE FLUORINATED POLYIMIDES FROM 4,4'-BIS(3-AMINO-5- TRIFLUOROMETHYLPHENOXY)-BIPHENYL AND VARIOUS AROMATIC DIANHYDRIDES*

Gui-long Wu^a, Jin-gang Liu^b, Zuo-bang Li^a, Zi-yi Ge^b, Lin Fan^b and Shi-yong Yang^{b**}

^a Institute of Polymer Science and Technology, Hebei University of Technology, Tianjin 300130, China

^b Laboratory of Advanced Polymer Materials, Center for Molecular Science, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China

Abstract An aromatic diamine monomer, 4,4'-bis(3-amino-5-trifluoromethyl phenoxy)-biphenyl (TFBPDA), was synthesized via the nucleophilic displacement reaction of 3,5-dinitrobenzotrifluoride and 4,4'-biphenol. The monomer was reacted with various aromatic dianhydrides via the high temperature polycondensation procedure to provide a series of polyimides. The polyimides, PI-1 to PI-4, show good solubility not only in aprotic solvents, such as *N*-methyl-2-pyrrolidinone and *N,N*-dimethylacetamide, but also in many common solvents, such as *m*-cresol, chloroform and cyclopentanone. PI-4, derived from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride and TFBPDA, was even soluble in toluene. Moreover, PI films exhibit good thermal stability, outstanding transparency in the visible light region and acceptable mechanical and electrical properties. The excellent combined properties of the polyimides make them as a good candidate for fabricating microelectronics.

Keywords: Diamine; Polyimide; Trifluoromethyl; Nucleophilic displacement; Solubility.

INTRODUCTION

The continuous advancement of microelectronics industry requires constant improvement in the processability of materials used to fabricate transistors, capacitors and other devices on the chips^[1–2]. The properties of particular interest for the materials used in the fabrication of chips include low processing temperatures, low dielectric constant, low moisture absorption, and high thermal and thermal-oxidative stability. Conventional aromatic polyimides, known for their excellent thermal and mechanical properties, could meet some of the criteria mentioned above and have been widely utilized as protecting or insulating films in integrated circuits (ICs) assembly. However, they are facing increasingly rising challenge on processability, especially on solubility. The rigid five-membered imide ring, on one hand, endows the polyimides with high thermal stability, but decreases their solubility at the same time^[3–4]. Therefore, the efforts aiming at modifying the rigid backbones of the polyimides without deteriorating the inherent properties have been one of the most remarkable topics in the polyimide researches. The modification have mainly focused on the synthesis of new monomers providing special features to the polyimides, such as lower intermolecular bonding, less molecular order, improved torsional mobility and so on. It could be summarized that: (1) the introduction of flexible substituents, such as $-\text{O}-$, $-\text{CH}_2-$, $-\text{SO}_2-$, *etc.* into the polyimide, (2) the introduction of bulky substituents, such as siloxane,

* This project is supported by the National Natural Science Foundation of China (NSFC) for distinguished Young Scholars (No. 59925310).

** Corresponding author: Shi-yong Yang (杨士勇), E-mail: public305@iccas.ac.cn

Received October 23, 2003; Revised December 3, 2003; Accepted December 8, 2003

cardo groups, hexafluoroisopropylidene, *etc.* into the polyimide, (3) the copolymerisation of two or more monomers, and (4) the use of meta-substituted monomers instead of para-substituted ones^[5–10].

In the present work, a *m*-substituted aromatic diamine 4,4'-bis(3-amino-5-trifluoromethyl phenoxy) biphenyl (TFBPDA) was synthesized via the nitro displacement reaction. The nucleophilic substitution reactions of aromatic nitro groups have been known for many years^[11–12]. Nitrobenzene derivatives with strong electron-withdrawing groups, such as cyano, *N*-substituted imide, keto and ester,^[13–15] could easily undergo the nitro displacement reactions. Among the activating groups, cyano group is the most effective, followed by *N*-substituted imide, keto and ester^[16]. Although many electron-withdrawing groups have been studied in the nitro displacement reactions, there are only a few reports in the literature on the reaction based on trifluoromethyl-substituted nitrobenzene.

Moreover, the diamine TFBPDA was polymerized with several aromatic dianhydrides, including 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). The effects of the meta structure and trifluoromethyl groups on the solution and film properties of the polyimides were mainly studied.

EXPERIMENTAL

Materials

3,5-Dinitrobenzotrifluoride, 4,4'-biphenol and anhydrous KF (Acros Organics Chemicals Co.) were used as received. 6FDA (Hoechst Celanese Corp.), BPDA, BTDA and ODPA (Beijing POME Corp.) were dried at 180°C in vacuo overnight prior to use. Commercially available *N*-methyl-2-pyrrolidinone (NMP), *N*, *N*-dimethylacetamide (DMAc), *N*, *N*-dimethylformamide (DMF), *m*-cresol, cyclopentanone (CPA), chloroform and toluene were purified by vacuum or normal distillation prior to use.

Measurements

Inherent viscosity was measured using a Ubbelohde viscometer with 0.5 g dL⁻¹ NMP solution at 30°C. FT-IR spectra were obtained with a Perkin-Elmer 782 Fourier transform spectrometer. Ultraviolet-visible (UV/Vis) spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. Prior to test, film samples were dried at 100°C for 1 h to remove the absorbed moisture. ¹H-NMR and ¹³C-NMR spectra were performed on a Varian Unity 200 spectrometer operated at 300 MHz in CDCl₃ or DMSO-*d*₆. DSC and TGA were recorded on a Perkin-Elmer 7 series thermal analysis system at a heating rate of 10 K/min. The electrical properties were measured on a Hewlett-Packard 4284A Presion LCR meter at room temperature.

Solubility was determined in the following manner: 1.5 g polyimide powder was mixed with 8.5 mL solvent at room temperature (15% solid), which was mechanically stirred in nitrogen for 24 h. The solubility was determined visually. Solubility is defined as a homogenous solution was obtained for a testing polymer, in which no phase separation, precipitation or gel formation is observed.

Water absorption was determined by immersing the polyimide film (3.0 × 1.0 × 0.005 cm³) in water at 25°C for 24 h, which was then dried immediately and weighted to determine the water uptakes.

Monomer Synthesis

4,4'-Bis(3-nitro-5-trifluoromethyl phenoxy) biphenyl

A 500 mL three-necked flask fitted with a mechanical stirrer, a thermometer and a nitrogen inlet was charged with a mixture of 3,5-dinitrobenzotrifluoride (23.61 g, 0.1 mol), 4,4'-biphenol (9.31 g, 0.05 mol), KF (3.49 g, 0.06 mol) and DMF (125 mL). The mixture was heated to reflux and maintained for 24 h. Then the reaction mixture was poured into 500 mL deionized water. The yellow precipitate was filtered out, washed thoroughly with boiling water, and dried under vacuo at 80°C overnight to afford the yellow powder TFBPDN (22.58 g, yield: 80%). The pure product was obtained by recrystallization twice from ethylene glycol monomethyl ether and water (2:1, V/V), m.p. 148.9°C (DSC peak temperature).

FT-IR (KBr, cm^{-1}): 3108.2, 3063.9, 1593.0, 1549.2, 1448.5, 1350.0, 1239.7, 1179.5, 1142.9, 967.4 and 694.0. $^1\text{H-NMR}$ (300MHz, $\text{DMSO}-d_6$, δ): 7.24–7.27 (d; 4H), 7.79–7.82 (m; 4H), 7.86 (m; 2H), 7.98 (m; 2H) and 8.25 (s; 2H). $^{13}\text{C-NMR}$ (300MHz, CDCl_3 , δ): 114.5, 115.3, 117.0, 120.3, 120.4, 124.3, 129.1, 133.2, 133.6, 134.1, 137.5, 149.5, 154.1 and 159.2. MS (EI, m/e, percentage of relative intensity): 564 (M^+ , 100). Elemental analysis: calc. for $\text{C}_{26}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_6$: C, 55.33%; H, 2.50%; N, 4.96%. Found: C, 54.97%; H, 2.54; N, 4.78%.

4,4'-Bis(3-amino-5-trifluoromethyl phenoxy) biphenyl

A 500 mL three-necked flask fitted with a mechanical stirrer, a thermometer and a dropping funnel was charged with a mixture of TFBPDN (28.22 g, 0.05 mol), absolute ethanol (100 mL) and a catalytic amount of 5% palladium on activated carbon. The reaction mixture was heated to reflux and then hydrazine monohydrate (20 mL) diluted with ethanol (10 mL) was added dropwise over a period of 1.5 h. After the addition was completed, the reaction system was refluxed for 24 h. Then the mixture was filtered hot to remove the catalyst and the filtrate was cooled to room temperature. The precipitated white granular crystals was filtered out, washed with cold ethanol and dried under vacuo at 80°C overnight to afford TFBPDA (21.94 g, yield: 87%), m.p. 132.7°C (DSC peak temperature).

FT-IR (KBr, cm^{-1}): 3480.6, 3364.7, 1631.4, 1597.4, 1493.7, 1374.2, 1221.1, 1168.2, 1116.2, 1001.8 and 834.9. $^1\text{H-NMR}$ (300MHz, $\text{DMSO}-d_6$, δ): 5.74 (s; 4H), 6.37–6.39 (m; 4H), 6.60 (s; 2H), 7.09–7.12 (d; 4H) and 7.66–7.68 (d; 4H). $^{13}\text{C-NMR}$ (300MHz, $\text{DMSO}-d_6$, δ): 101.8, 105.4, 106.3, 120.1, 122.7, 126.3, 128.5, 129.9, 130.9, 131.3, 131.7, 132.1, 135.6, 151.6, 155.7 and 158.8. MS(EI, m/e, percentage of relative intensity): 504 (M^+ , 100). Elemental analysis: Calc. for $\text{C}_{26}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_2$: C, 61.91%; H, 3.60%; N, 5.55%. Found: C, 61.57%; H, 3.63; N, 5.49%.

Polymer Synthesis

A typical procedure for the preparation of the PI-1 was as follows.

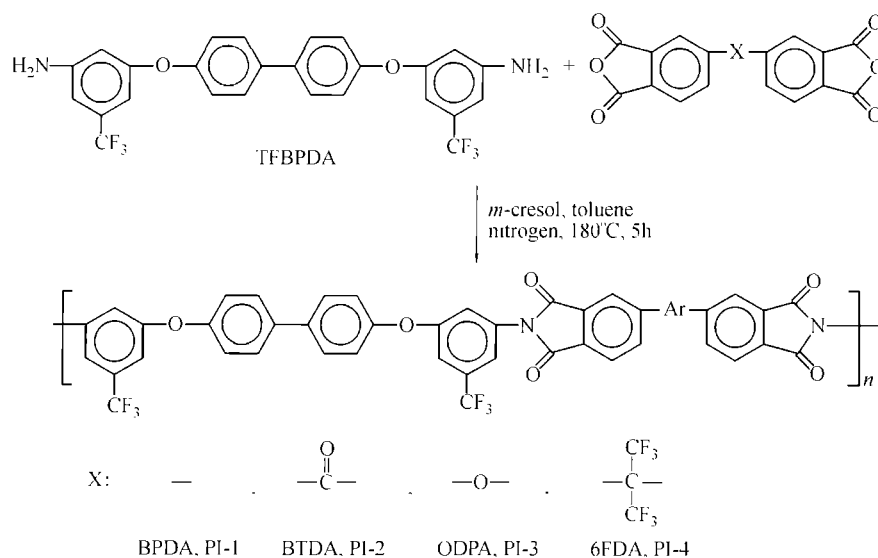
In a 250 mL three-necked flask fitted with a mechanical stirrer, a nitrogen inlet and a Dean-stark trap was charged with a mixture of TFBPDA (5.0443 g, 10 mmol) and *m*-cresol (28 mL). After the mixture was cooled to 10–15°C, BPDA (2.9422 g, 10 mmol) was added in three portions with vigorous stirring. After the addition was completed, additional *m*-cresol (20 mL) was added. The reaction mixture was stirred in nitrogen for 2 h to afford a clear solution, and then a mixture of toluene (56 mL) and isoquinoline (catalytic amount) was added. The reaction mixture was heated to 180°C and maintained at this temperature for 5 h. During the heating, toluene-water azeotrope was distilled out of the system. A viscous polyimide solution was obtained after the reaction mixture was cooled to room temperature, and then the viscous solution was poured slowly into 500 mL ethanol to yield a silky precipitate. The precipitate was collected and dried at 80°C under vacuo overnight to afford a light-yellow silky resin (5.49 g, yield: 93%). The inherent viscosity of the polymer in NMP was 0.94 dL g^{-1} at a concentration of 0.5 $\text{g} \cdot \text{dL}^{-1}$ at 30°C. FT-IR (film, cm^{-1}): 1779.8, 1726.3 and 1380.8.

PI-2–PI-4 were prepared in the same manner as PI-1 except that BPDA was replaced by BTDA for PI-2, ODPA for PI-3 and 6FDA for PI-4.

RESULTS AND DISCUSSION

Polymer Synthesis

The polyimides were prepared by one-step procedure starting from diamine TFBPDA and aromatic tetracarboxylic dianhydride through the high temperature imidization as shown in Scheme 1. The inherent viscosities of the polyimides PI-1–PI-4 are in the range of 0.86–0.94 dL g^{-1} , indicating these molecular weight of the PIs are sufficient to form flexible and tough films. The identification of the PIs was performed by the FT-IR spectra as shown in Fig. 1. For example, the characteristic bands at 1768 and 1720 cm^{-1} , which are commonly attributed to the ν_{asyCO} and ν_{symCO} of the imide and the bands at 1381 cm^{-1} , which is assigned as the absorption band of C–N group verify the formation of imide structure. Crystallinity of the polyimide films was examined by wide-angle X-ray diffraction pattern. As shown in Fig. 2, all the polymers show an amorphous pattern, which might be attributed to the incorporation of flexible bonds, such as –O– and –CF₃– in the polyimide backbones.



Scheme 1 Synthesis of the polyimides via one-step procedure

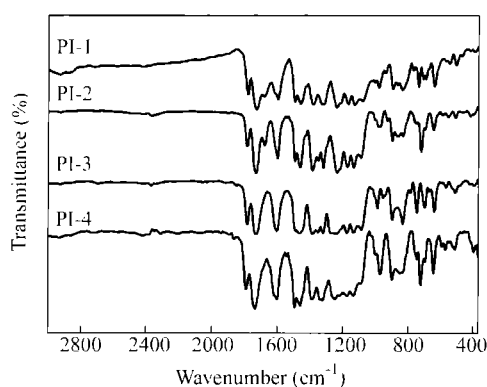


Fig. 1 FT-IR spectra of polyimide films PI-1–PI-4

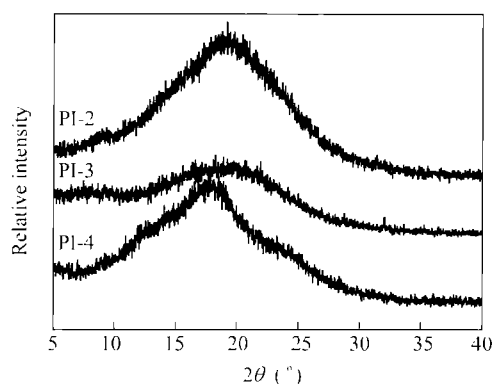


Fig. 2 Wide-angle X-ray diffraction patterns of polyimide films

Polymer Solubility

The solubility of polyimides was tested qualitatively in various solvents (Table 1). It was found that all the PIs, even in their imide forms, were soluble not only in polar aprotic solvents, such as NMP and DMAc, but also in many common solvents, such as *m*-cresol, CPA and chloroform. The excellent solubility of the PIs in the solvents could be attributed to the amorphous nature of the polymer structures. The PI-4 exhibit the best solubility and it can be soluble even in toluene, probably due to the presence of flexible trifluoromethyl groups in the TFBPDA moiety and bulky hexafluoroisopropylidene substituents in the dianhydride moiety. The relatively poor solubility of PI-1 could be explained as the strong intermolecular interaction caused by the conjugation of biphenyl groups in the polymer structures.

Table 1. Inherent viscosity and solubility of the polyimides

PI	η_{inh} (dL/g)	Solvents ^a						
		NMP	DMAc	<i>m</i> -Cresol	CPA	γ -BL	CHCl ₃	Toluene
PI-1	0.94	++	++	++	+h	+h	+h	-
PI-2	0.92	++	++	++	++	+h	++	+h
PI-3	0.89	++	++	++	++	++	++	+h
PI-4	0.86	++	++	++	++	++	++	++

^a ++ Soluble at room temperature; +h Soluble at heating; - Insoluble

The superior solubility of the PIs in common solvents, especially in the solvents with moderate boiling point and polarity, such as CPA (b.p. 130–131 °C), makes the polyimides possibly to be used in the fabrication of microelectronic devices. For example, in the assembly of liquid crystal display devices (LCDs), polyimide film is often used as the alignment film^[17]. Because conventional polyimides are insoluble, their soluble precursors (PAAs) are often used, which are then thermally converted in situ to the fully-imidized polyimides at 250–350 °C. The high curing temperature often causes severe damage for thermal sensitive electronic devices. For instance, in the thin film transistor (TFT) driven active matrix liquid crystal display device (TFT-LCD), the color filter is highly thermal-sensitive, and the performance of which will deteriorate after exposing to high temperature (> 180 °C). Hence, the polyimides developed in the present work might find wide applications in the high-tech fields.

Thermal Properties

The thermal properties of the PIs were evaluated by TGA and DSC measurement. It could be seen from the TGA curves shown in Fig. 3 and the thermal data listed in Table 2 that the polyimide films begin to decompose at 560 °C and they nearly maintain more than 60% of the original weight at 700 °C. The 10% weight loss temperatures of the films are in the range of 564.6–599.3 °C and decrease in the order of PI-3 > PI-1 > PI-4 > PI-2. However, as shown in Fig. 4, the T_g s of the films exhibit different changing order, that is PI-1 > PI-4 > PI-2 > PI-3. Interestingly, PI-3, derived from ODPDA and TFBPDA, shows the highest T_d , $T_{10\%}$ and R_w , but the lowest T_g . This property might be attributed to the existence of flexible and thermal-stable ether bond in the dianhydride moiety.

Table 2. Thermal properties of the polyimides

PI	T_g (°C)	T_d (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	R_w (%) ^b
PI-1	233.0	576.4	517.5	579.5	62
PI-2	197.7	566.6	470.3	564.6	64
PI-3	181.3	581.5	537.9	599.3	66
PI-4	213.3	562.0	497.8	566.8	57

^a T_d : Onset decomposition temperature; $T_{5\%}$, $T_{10\%}$: Temperatures at 5% and 10% weight loss

^b Residual weight retention (R_w %) at 700 °C

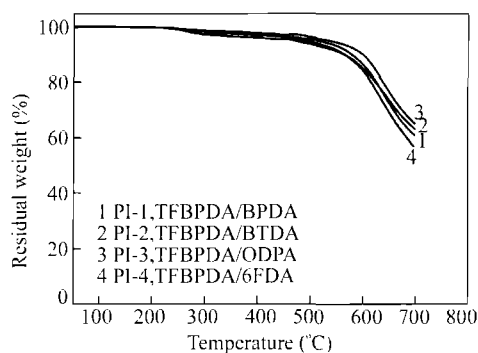


Fig. 3 TGA curves of the polyimides (heating rate: 10 K/min)

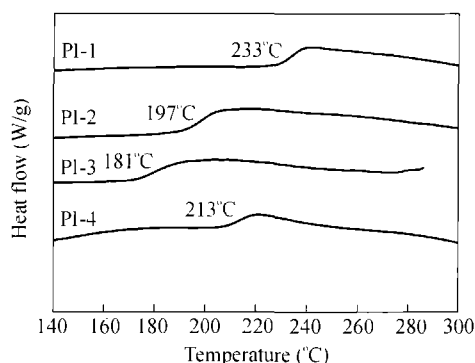


Fig. 4 DSC curves of the polyimides (heating rate: 10 K/min)

Mechanical and Electrical Properties

The tensile and electrical properties of the polyimide films are shown in Table 3. The polyimide films show high tensile strength up to 114.3 MPa and tensile modulus up to 1.85 GPa. The elongation values of films are in the range of 8–12%, indicating the flexible character of the films. Moreover, the polyimide films exhibit high insulating properties with surface and volume resistance of 10^{14} and 10^{15} level, respectively. The excellent insulating properties make it possible to use the films as passivation layer and interlayer dielectric film in the chip fabrications.

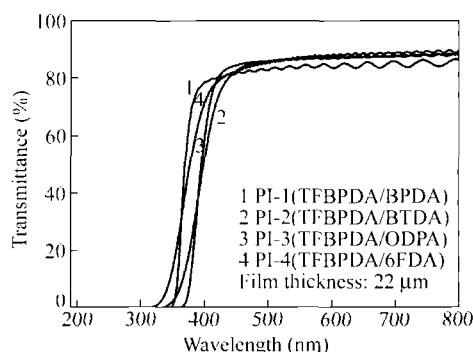
Table 3. Mechanical and electrical properties of the polyimides^a

PI	E_B (%)	T_S (MPa)	Y_M (GPa)	$R_S \times 10^{14}$ (Ω)	$R_V \times 10^{15}$ ($\Omega \cdot \text{cm}$)
PI-1	8	83.2	1.28	7.6	3.2
PI-2	9	98.6	1.32	4.3	2.1
PI-3	12	109.2	1.85	5.7	3.6
PI-4	11	114.3	1.83	6.2	3.9

^a E_B : Elongation at break; T_S : Tensile strength; Y_M : Young's modulus; R_V : Volume resistance; R_S : Surface resistance

Optical Properties

Figure 5 depicts the UV-Vis spectra of the PI films and the cutoff wavelengths observed from the spectra are listed in Table 4. All the fluorinated polyimides exhibit high transmittance values and light colours in the visible light region. For example, PI-4 shows cutoff wavelength at 323 nm and 85% of transmittance at 500 nm. By comparison, 6FDA and ODPA produce more transparent and light-coloured polyimides (PI-4 and PI-3) than BPDA (PI-1) and BTDA (PI-2). This result is mainly attributed to the decrease of the formation of intermolecular charge-transfer-complex (CTC) between the electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The bulky and electron-withdrawing $-\text{CF}_3$ group, on one hand, decreased the CTC formation through the steric hindrance and inductive effect; on the other hand, they weakened the intermolecular cohesive force due to the lower polarizability of the C—F bond. The effect of fluorine contents on the optical properties of PI films can be obviously observed from the data listed in Table 4. The cutoff wavelengths of the films decrease approximately with the increase of fluorine contents in the order of PI-2 > PI-1 > PI-3 > PI-4. The transmittance values at 500 nm changes adversely.

**Fig. 5** UV-Vis spectra of the polyimide films**Table 4.** Optical properties and water uptakes of the polyimides

PI	Fluorine content (%)	Transmittance at 500 nm (%)	UV cutoff wavelength (nm)	Water absorption (%)
PI-1	14.95	80	349	0.31
PI-2	14.42	82	368	0.34
PI-3	14.64	83	333	0.28
PI-4	24.98	85	323	0.22

The water absorption of PI films lies in the range of 0.22–0.34% and their variation follows the similar rule for the optical properties. The low water absorption values of PI films could be attributed the hydrophobic features of the trifluoromethyl groups.

CONCLUSION

An aromatic fluorinated diamine monomer TFBPDA was synthesized via the nucleophilic displacement reaction of 3,5-dinitrobenzotrifluoride. A series of polyimides were prepared by reacting the aromatic diamine with aromatic dianhydrides. Characterization results indicate that the polyimides have good solubility not only in

strong aprotic solvents, but also in many common solvents. Flexible films could be obtained by casting the fully-imidized polymer solution followed by thermal baking at moderate temperatures. The polyimide films, with glass transition temperatures at 181–233 °C, show good thermal stability at elevated temperature. Optical transparency measurement of the polymer films indicates that they have cut-off wavelengths at 323–368 nm.

REFERENCES

- 1 Mittal, K.L., "Polyimide and Other High Temperature Polymers: Synthesis, Characterization and Applications", ed. Zeist, VSP BV, 2003, p. 447–458
- 2 Wilson, D., Stenzenberger H.D. and Hergenrother P.M., "Polyimides", Chapman & Hall, New York, 1990, p. 227–251
- 3 Yada, N., Polym. Adv. Tech., 1997, 8: 215
- 4 Liaw, D.J., Liaw, B.Y. and Su, K.L., Polym. Adv. Tech., 1999, 10: 13
- 5 Ayala, D., Lozano, A.E., Abajo, J.D. and Campa, J.G.D.C., J. Polym. Sci., Part A: Polym. Chem., 1999, 37: 805
- 6 Madhra, M.K., Salunke, A.K., Banerjee, S. and Prabha, S., Macromol. Chem. Phys., 2002, 203: 1238
- 7 Yagci, H., Ostrowski, C. and Mathias, L.J., J. Polym. Sci., Part A: Polym. Chem., 1999, 37: 1189
- 8 Han, K., You, K., Jang, W.H. and Rhee, T.H., Macromol. Chem. Phys., 2000, 201: 747
- 9 Liaw, D.J. and Liaw, B.Y., Macromol. Chem. Phys., 1999, 200: 1326
- 10 Mikroyannidis, J.A., J. Polym. Sci., Part A: Polym. Chem., 1999, 37: 15
- 11 Bennett, J.F. and Zahler, R.E., Chem. Rev., 1951, 49: 273
- 12 Heath, D.R. and Wirth, J.G., 1973, US Patent, 3763210
- 13 Caswell, L. and Kao, T., J. Heterocycl. Chem., 1966, 3: 333
- 14 Beck, J.R., J. Org. Chem., 1972, 37: 3224
- 15 Beck, J.R., J. Org. Chem., 1973, 38: 4086
- 16 Takekoshi, T., Polym. J., 1987, 19: 191
- 17 Liu, J.G., Li, Z.X., Wu, J.T., Zhou, H.W., Wang, F.S. and Yang, S.Y., J. Polym. Sci., Part A: Polym. Chem., 2002, 40: 1583