

ORGANO-SOLUBLE FLUORINATED POLYIMIDES DERIVED FROM α,α -BIS(4-AMINO-3,5-DIMETHYLPHENYL)-4'-FLUOROPHENYL METHANE AND VARIOUS AROMATIC DIANHYDRIDES*

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Abstract Organo-soluble fluorinated polyimides were synthesized by the polycondensation of a new aromatic diamine α,α -bis(4-amino-3,5-dimethylphenyl)-4'-fluorophenyl methane with several aromatic dianhydrides. The one-step polymerization procedure was conducted at 180 °C in *m*-cresol, producing the polyimides with inherent viscosities of 0.68–0.76 dL g⁻¹. The polyimides could be soluble not only in polar aprotic solvents, such as *N*-methyl-2-pyrrolidinone, and *N,N*-dimethylacetamide, but also in common organic solvents, such as chloroform, cyclopentanone, *m*-cresol and so on. The polyimide films show excellent transparency with the UV-Vis cut-off lengths of 310–360 nm and light transmittances of higher than 80% in the visible region. In addition, the polyimides exhibit good thermal stability with an initial decomposition temperature (*T*_d) higher than 530 °C and have more than 60% of residual weight retentions at 700 °C.

Keywords: Fluorinated polyimides; Solubility; Thermal stability; Optical transparency.

INTRODUCTION

As the best-known heteroaromatic polymers, polyimides exhibit outstanding thermal and thermal-oxidative stability, excellent solvent resistance and good mechanical and electrical properties^[1–3]. These combined properties made them as good candidates to substitute the conventional structural materials, such as metal, ceramics and glass in many high performance applications. The heterocyclic five-membered imide ring, on one hand, imparts great rigidity to the polymer backbone and strong intermolecular interactions; but on the other hand, greatly decreases the solubility and processability of the polyimides. Usually, they could only be processed via their soluble precursor, poly(amic acid) (PAA) followed by thermal or chemical imidization. However, the most commonly used polyimide precursor, PAA solutions, were thermally and hydrolytically unstable. Therefore, they could only be stored in cold and dry environments, which greatly limit their extensive applications. In addition, the water released from the imidization reaction of PAA solutions often result in voids or pinholes in bulky materials. Thus, considerable researches have been carried out aiming at developing the polyimides that are processable in their imide form^[4–6].

It is well known that the increase in solubility, processability, transparency and the decrease in dielectric constant and water absorption could be achieved by the incorporation of fluorine atoms or fluoro-containing substituents into the polymer backbones by virtue of the special features of the C–F bond, such as high electronegativity, large bond energy, small polarizability and sometimes, the large free volume^[7–9]. On the other

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hand, the incorporation of fluorinated groups into the polyimides could often maintain the excellent inherent characters of the polymers, such as high thermal and mechanical properties. Therefore, the fluorinated polyimides have been one of the most active topics in functional polymer research fields.

Our research group have paid much attention to the fluorinated heteroaromatic polymers, including polyimides^[10–12], poly(amide imide)s^[13], polypyrrolones^[14] and poly(pyrrolone-imide)s^[15] in recent years and a series of researches covering the synthesis and characterization of new polymers and their applications in microelectronics have been carried out. Recently, Qian and his coworkers reported a photosensitive polyimide based on a diamine α,α -bis(4-amino-3,5-dimethyl phenyl)phenyl methane (BADP) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA)^[16]. The polyimide shows low water uptakes, good processability and photosensitivity, which makes it as a good candidate for the photoresist in fabricating microelectronics. As a continuation of the above work, a series of organo-soluble fluorinated polyimides based on a new diamine α,α -bis(4-amino-3,5-dimethylphenyl)-4'-fluorophenyl Methane (FMDA) and aromatic dianhydrides have been synthesized and characterized in the present work. Their solubility, transparency, thermal and mechanical properties were also studied.

EXPERIMENTAL

Materials

2,6-Dimethyl aniline and 4-fluorobenzaldehyde (Acros Corp.) were purchased and used as received. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA) (Beijing POME Corp.) and 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) (Hoechst Celanese Corp.) were recrystallized from acetic anhydride and dried under vacuum at 160 °C for 10 h before use. Commercially available *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *m*-cresol, cyclopentanone (CPA), γ -butyrolactone (γ -BL), chloroform and toluene were purified by distillation prior to use.

Monomer Synthesis

α,α -Bis(4-amino-3,5-dimethylphenyl)-4'-fluorophenyl methane

To a mixture of 24.24 g (0.2 mol) of 2,6-dimethyl aniline and 50 mL deionized water placed in a 500 mL three-necked flask fitted with a mechanical stirrer, a thermometer, a nitrogen inlet and a dropping funnel, 23.68 g of 37% hydrochloric acid was added gradually. With vigorous stirring, 13.01 g (0.105 mol) of 4-fluorobenzaldehyde was added dropwise over 1 h after the temperature of the reaction mixture was rose to 50 °C. After standing for another 0.5 h, the reaction mixture was heated to reflux for 10 h. Then, the solution was cooled to room temperature followed by neutralization with a solution of 5% sodium hydroxide (200 mL). The pale blue precipitate was filtered and dried under vacuo at 80 °C overnight. The product FMDA was purified by recrystallization twice from absolute ethanol and the yield was 25.71 g (76.8%), m.p. 170.0 °C (DSC peak temperature). FT-IR (KBr, cm^{-1}): 3480.2, 3434.4, 3397.3, 3346.8, 3033.4, 2965.2, 2924.4, 2850.7, 1624.3, 1601.9, 1488.6, 1307.4, 1223.9, 1155.5 and 844.4. ¹H-NMR(300MHz, DMSO-*d*₆, δ): 2.01 (s; 12H), 4.37 (s; 4H), 5.13 (s; 1H), 6.52 (s; 4H) and 7.05–7.07 (d; 4H). MS (electron ionization, *m/e*, percentage of relative intensity): 348 (M⁺, 100). Elemental analysis: Calc. for C₂₃H₂₅FN₂: C, 79.28%; H, 7.23%; N, 8.04%. Found: C, 79.11%; H, 7.29%; N, 7.95%.

Polymer Synthesis

The synthesis of the polyimides could be representively illustrated by the synthesis of PI-1.

To a solution of 3.4846 g (10 mmol) of FMDA in 33 mL *m*-cresol placed in a 250 mL three-necked flask fitted with a mechanical stirrer, a nitrogen inlet and a Dean-Stark trap was added 2.9422 g BPDA (10 mmol) in three portions. After the reaction mixture was stirred in nitrogen for 0.5 h, a mixture of toluene (36 mL) and isoquinoline (catalytic amount) was added. The reaction mixture was heated to 180 °C and maintained for 5 h. During the reaction, the toluene-water azeotrope was distilled out of the system. After cooled to room

temperature, the viscous solution was poured slowly into excess of ethanol to yield silky precipitate. The precipitate was collected and dried at 80°C under vacuum overnight. The yield was 6.17 g (96%). The inherent viscosity of the polymer in NMP was 0.76 dL·g⁻¹ at a concentration of 0.5 g·dL⁻¹ at 30°C. FT-IR (film, cm⁻¹): 1778.7, 1723.4 and 1370.2.

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.

Measurements

FT-IR spectra were obtained with a Perkin-Elmer 782 Fourier transform spectrometer. 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. Inherent viscosity was measured using a Ubbelohde viscometer with 0.5 g·dL⁻¹ NMP solution at 30°C. ¹H-NMR was performed on a Varian Unity 200 spectrometer operating at 300 MHz in 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. Solubility was determined as follows: 1.5 g polyimide resin was mixed with 8.5 mL solvent at room temperature (15% solid content), which was mechanically stirred in nitrogen for 24 h. The tensile properties were performed on 6.0 mm-wide specimens in accordance with GB1447-83 at a rate of 5 mm·min⁻¹. The electrical properties were measured on a Hewlett-Packard 4284A Presion LCR meter at room temperature. Water uptakes were 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.

RESULTS AND DISCUSSION

Polymer Synthesis

Generally, polyimides could be prepared by the polycondensation of an aromatic diamine with dianhydride via a two-step procedure to form a precursor, poly(amic acid), followed by thermal or chemical imidization to afford the final polyimide.

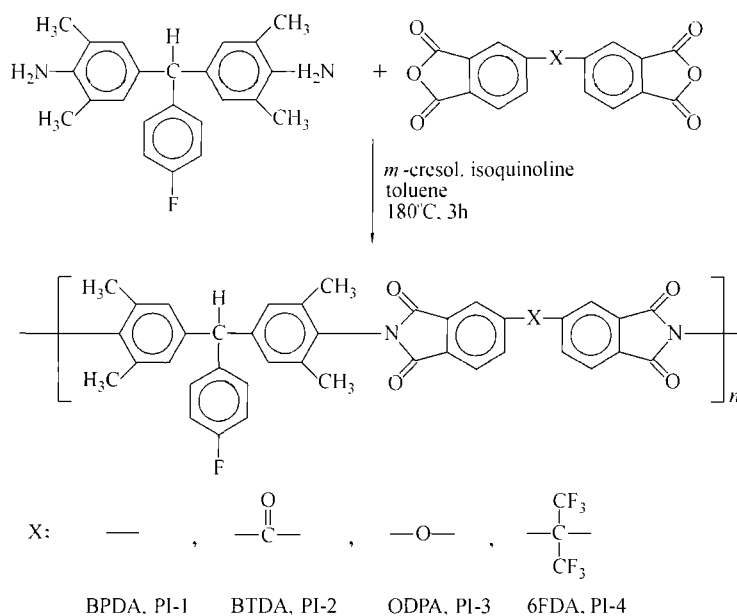
In the present work, an alternative route for the preparation of organo-soluble polyimides, that is, one-step high temperature solution polycondensation procedure was adopted (Scheme 1). In this procedure, the diamine was commonly first added in *m*-cresol containing a catalytic amount of isoquinoline and stirred under a nitrogen atmosphere at room temperature to obtain a clear solution. Then, a stoichiometric quantity of dianhydride was added in batches with a solid content of about 15% (W/W). Toluene, performing as the azeotropic agent with water produced in the imidization reaction, was added after a viscous solution was obtained. Then the reaction mixture was heated slowly to 180°C, during which the azeotrope was distilled out of the reaction system. The reaction was maintained at 180°C for 3–5 h and then cooled to room temperature to obtain a brown viscous polyimide solution. The silky polyimide resin could be obtained by carefully precipitating the polyimide solution with methanol.

After being dried in vacuum oven, the silky resin was dissolved in common solvents, such as NMP, DMAc, DMF, chloroform, THF and so on, with a solid content of 15% (W/W) to give a homogeneous polyimide solution, showing inherent viscosities of 0.68–0.76 dL·g⁻¹ (Table 1). The flexible polyimide films, PI-1–PI-4, were cast from the PI solutions on glass substrates followed by thermally baking with the corresponding conditions. The curing procedure was dependent on the boiling points of the solvents used.

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	0.72	++	++	++	++	++	+h	–
PI-2	0.68	++	++	++	++	++	++	–
PI-3	0.76	++	++	++	++	++	++	+h
PI-4	0.73	++	++	++	++	++	++	++

^a ++: Soluble at room temperature; +h: Soluble at heating; –: Insoluble



Scheme 1 Synthesis of the polyimides PI-1–PI-4 via one-step procedure

Figure 1 shows the FT-IR spectra of polyimide films. The vibrational absorption bands at about 1780 and 1720 cm^{-1} , assigned to the ν_{asyCO} and ν_{syCO} of imide groups, appear in all of the polymers. And absorption band at about 1383 cm^{-1} was assigned to the $\nu_{\text{C-N}}$ of imide structure. X-ray diffraction patterns of polyimide films are shown in Fig. 2, which indicate that the polyimide films are amorphous polymers.

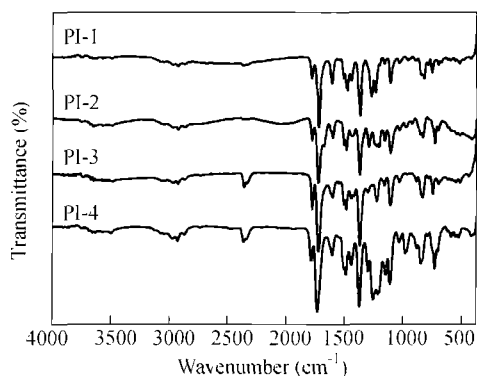


Fig. 1 FT-IR spectra of the polyimide films PI-1–PI-4

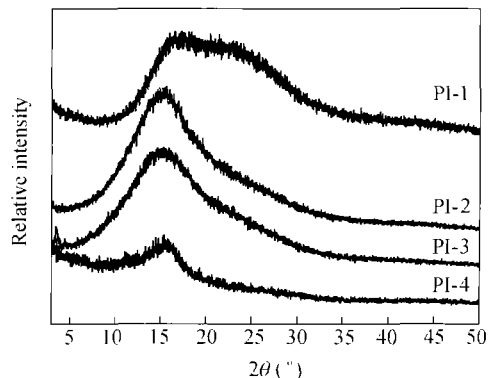


Fig. 2 Wide-angle X-ray diffraction patterns of the polyimide films

Solubility of Polyimide

The solubility of polyimides in various organic solvents, such as NMP, DMAC, *m*-cresol, CHCl_3 , γ -BL, CPA and toluene were tested. As seen from the results shown in Table 1, the polyimides show excellent solubility at room temperature not only in polar aprotic solvents such as NMP, and DMAc, but also in common solvents, such as chloroform, CPA, *m*-cresol and so on. The difference in solubility of the four polyimides could only be identified from toluene. PI-4 is soluble in toluene at room temperature, but PI-3 could only be soluble in hot toluene. However, PI-1 and PI-2 couldn't be soluble in toluene in any conditions. The excellent solubility of FMDA-based PIs is mainly attributed to the bulky fluoro-substituted phenyl group and the methyl groups in the backbone of FMDA. The large free volumes occupied by these substituents bestow good solubility and processability on PIs. From the view point of industrial processing, the good solubility of PIs in some solvents

with moderate boiling points, such as CPA (b.p. 130–131 °C), could greatly extend their applications, especially in the high-temperature-sensitive 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 polyimides possess good thermal properties with $T_d = 530.7$ – 570.8 °C and $T_{10\%} = 538.7$ – 574.4 °C. According to the $T_{10\%}$ temperature, which is often regarded as the criterion of thermal stability of the high temperature polymers, the thermal stability of PIs decreases in the order of PI-1 > PI-3 > PI-4 > PI-2. This order was consistent with their structure rigidity and intermolecular interactions. The residual weight ratios (R_w s) of polyimides at 700 °C lie in the range of 61–74%. The high thermal stability might be attributed to the rigid backbone structures of the polymers.

Table 2. Thermal properties of the polyimides

PI	T_g (°C)	T_d (°C) ^a	$T_{5\%}$ (°C) ^a	$T_{10\%}$ (°C) ^a	R_w (%) ^b
PI-1	315.0	545.9	493.7	574.4	74
PI-2	300.5	530.7	425.4	538.7	66
PI-3	322.2	570.8	472.4	559.6	70
PI-4	344.6	543.4	507.6	554.9	61

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

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

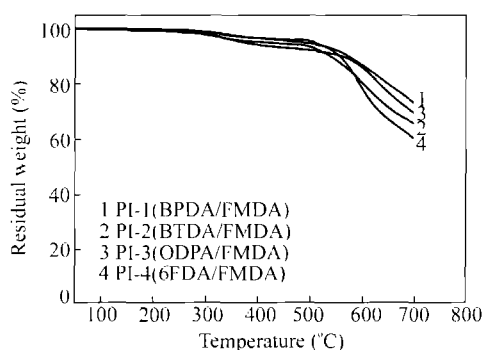


Fig. 3 TGA curves of the polyimides (heating rate: 10 K/min)

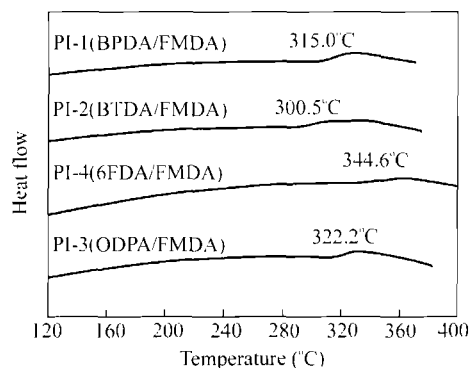


Fig. 4 DSC curves of the polyimides (heating rate: 10 K/min)

It could also be seen from the DSC curves shown in Fig. 4 that all the polyimides exhibit no crystallization or melting transition in the DSC measurement. In addition, the polyimides show exceptionally high T_g s at 300.5–344.6 °C, which might be attributed to the substitution of methyl groups in the position ortho to an imide ring increasingly restrict the rotation of nitrogen atom along the phenyl ring, resulting in more rigid polymer chains, which in turn increase the T_g s of the polymers. PI-4 (6FDA/FMDA) has the highest glass transition temperature (344.6 °C), due to the steric hindrance of the bulky hexafluoroisopropylidene group in the dianhydride moiety. PI-2 (BTDA/FMDA) and PI-3 (ODPA/FMDA) have intermediate T_g values of 300.5 °C and 322.2 °C, respectively, which was in good correspondence with their intermediate rigidity and intermolecular interactions.

Mechanical and Electrical Properties

Table 3 shows the mechanical and electrical properties of the polyimides. The tensile properties of PI-1–PI-4 films were measured with an Instron instrument at 25 °C. The polyimide films have tensile strengths of 82.4–95.2 MPa, elongation at break of 9–12%, and tensile modulus of 0.84–1.13 GPa, demonstrating that the polyimide films are strong and flexible. The surface resistance (R_s) and volume resistance (R_v) of the films are at the level of 10^{14} Ω and 10^{15} $\Omega \cdot \text{cm}$, respectively, indicating that the polyimide films have good dielectric properties.

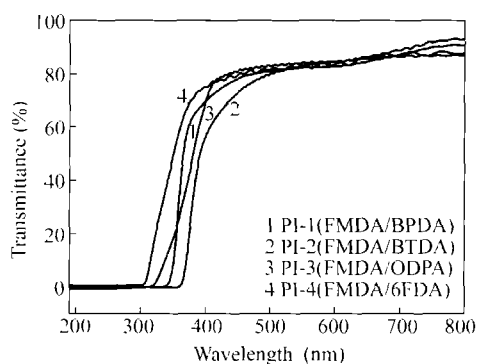
Table 3. Mechanical and electrical properties of the polyimides^a

PI	E_B (%)	T_S (MPa)	T_M (GPa)	$R_S \times 10^{14}$ (Ω)	$R_V \times 10^{15}$ ($\Omega \cdot \text{cm}$)
PI-1	9	82.4	0.84	4.4	4.8
PI-2	10	84.6	1.02	5.1	2.1
PI-3	12	95.2	1.13	6.3	7.2
PI-4	11	94.3	1.07	6.6	7.4

^a E_B : Elongation at break; T_S : Tensile strength; T_M : Tensile modulus R_V : Volume resistance; R_S : Surface resistance

Optical Properties

The transparency of the polyimide films was determined by UV-Vis measurement (Fig. 5) and the optical data for the films are listed in Table 4. It could be seen from the data that the UV cutoff wavelength and transmittance at 500 nm decrease with the increasing of fluorine content of the PIs. For example, PI-4, which has the highest fluorine content, shows the best transparency with UV cutoff wavelength of 310 nm and 83% of transmittance at 500 nm. The other three films, which have same fluorine contents, show quite similar optical transparency. However, PI-2 film has much higher UV cutoff length than the other two films, which could be explained as the presence of the polar carbonyl group in the polymer structure.

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

PI	Fluorine content (%)	Transmittance at 500 nm (%)	UV cutoff wavelength (nm)	Water uptakes (%)
PI-1	3.13	78	336	0.36
PI-2	2.99	76	368	0.51
PI-3	3.05	79	322	0.34
PI-4	17.58	83	310	0.29

In addition, the water uptakes of PI films show the similar trends as the transparency. For instance, the water uptakes of the polymers increase with the decreasing fluorine contents, that is, PI-2 (0.51) > PI-1 (0.36) $\approx$ PI-3 (0.34) > PI-4 (0.29). This trend was mainly because of the hydrophobic features of the fluoro-containing groups.

CONCLUSION

A series of new fluoro-containing polyimides have been synthesized from the multi-methyl-substituted fluorinated diamine FMDA and aromatic dianhydrides. The bulky fluoro-substituted phenyl and methyl groups endowed the PIs with high solubility in common organic solvents and great transparency in the visible light region. Moreover, the polyimide films show low water uptakes, high thermal stability, and good mechanical and electrical properties. With these excellent combined properties, these materials have great potential applications in fabricating microelectronic devices.

REFERENCES

- 1 Ghosh, M.K. and Mittal, K.L. (Eds.). "Polyimide: Fundamental and Applications", Marcel Dekker, New York, 1996, p.759–814
- 2 Wilson, D., Stenzenberger, H.D. and Hergenrother, P.M. (Eds.). "Polyimides", Chapman & Hall, New York, 1990, p.227–251
- 3 Mittal, K.L., "Polyimides: Synthesis, Characterization and Applications", Plenum, New York, 1986, p. 1
- 4 Yagci, H., Ostrowski, C. and Mathias, L.J., J. Polym. Sci., Part A: Polym. Chem., 1999, 37: 1189
- 5 Hsieu, Y.S., Yang, C.R., Hwang, G.Y. and Lee, Y.D., Macromol. Chem. Phys., 2001, 202: 1394
- 6 Jeong, K.U., Jo, Y.J. and Yoon, T.H., J. Polym. Sci., Part A: Polym. Chem., 2001, 39: 3335
- 7 Hsiao, S.H., Yang, C.P. and Chung, C.L., J. Polym. Sci., Part A: Polym. Chem., 2003, 41: 2001
- 8 Bes, L., Rousseau, A., Boutevin, B., Mercier, R. and Kerboua, R., Macromol. Chem. Phys., 2001, 202: 2954
- 9 Banerjee, S., Madhra, M.K., Salunke, A.K. and Maier, G., J. Polym. Sci., Part A: Polym. Chem., 2002, 40: 1016
- 10 Liu, J.G., He, M.H., Li, Z.X., Qian, Z.G., Wang, F.S. and Yang, S.Y., J. Polym. Sci., Part A: Polym. Chem., 2002, 40: 1572
- 11 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
- 12 Xie, K., Liu, J.G., Zhou, H.W., Zhang, S.Y., He, M.H. and Yang, S.Y., Polymer, 2001, 42: 7267
- 13 Li, Z.X., Fan, L., Ge, Z.Y., Wu, J.T. and Yang, S.Y., J. Polym. Sci., Part A: Polym. Chem., 2003, 41: 1831
- 14 Liu, J.G., Wang, L.F., Yang, H.X., Li, H.S., Li, Y.F., Fan, L. and Yang, S.Y., J. Polym. Sci., Part A: Polym. Chem., 2004, 42(8): 1845–1856
- 15 Shang, Y.M., Fan, L., Gao, S.Q., Hu, A.J. and Yang, S.Y., High Perform. Polym., accepted, 2004, 16(1): 39–54
- 16 Qian, Z.G., Ge, Z.Y., Li, Z.X., He, M.H., Liu, J.G., Pang, Z.Z., Fan, L. and Yang, S.Y., Polymer, 2002, 43: 6057