e-Polymers **2009**, no. 147

http://www.e-polymers.org
ISSN 1618-7229

Synthesis and characterization of novel fluorinated polybenzoxazoles derived from 2,5-difluoroterephthalic acid

Xiao-Song Huang, [1] *Feng-Ling Qing* [1 2*]

[1*] College of Chemistry, Chemical Engineering and Biotechnology, and State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China; fax: 86-21-64166128; e-mail: flq@mail.sioc.ac.cn
[2]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 354 Fenglin Lu, Shanghai 200032, China

(Received: 06 January, 2009; published: 28 December, 2009)

Abstract: A new serious of fluorinated polybenzoxazoles (PBOs) were prepared from 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane together with 2,5-difluoroterephthalic acid (DFTA) and terephthalic acid by the one-pot polycondensation in polyphosphoric acid. The resulting PBOs showed good solubility in many common organic solvents and the thermal stability of PBOs was improved by the introduction of DFTA monomer.

Keywords: fluorinated polybenzoxazoles; 2,5-difluoroterephthalic acid.

Introduction

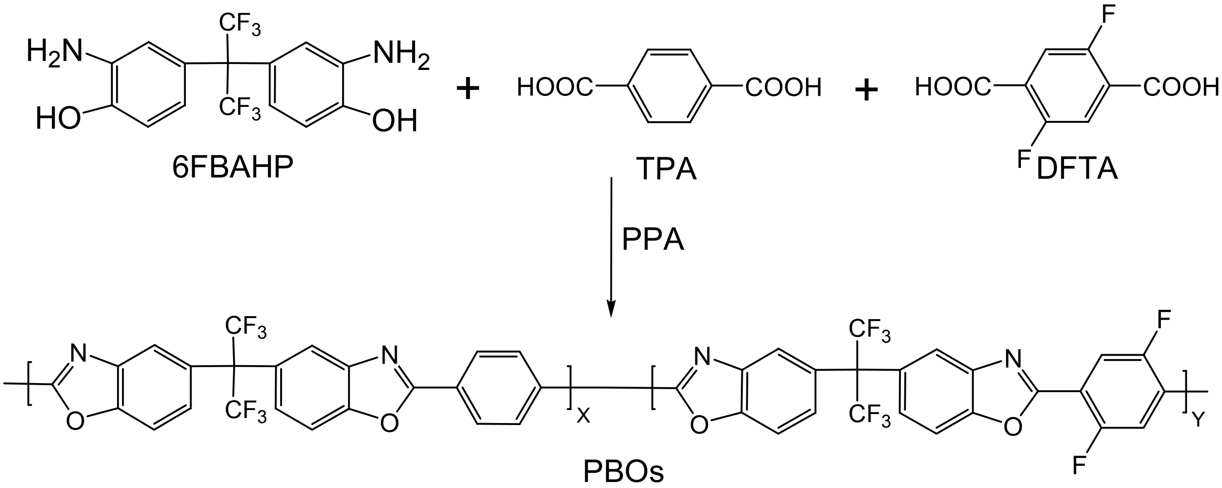
Aromatic polybenzoxazoles (PBOs) are a class of aromatic heterocyclic polymers that have excellent thermal stability, high mechanical properties, and good chemical resistance [1-4]. The excellent thermal stability and high flame resistance of PBOs make it the material of choice for high-temperature applications. However, PBOs are generally difficult to process because of their poor solubility in organic solvents. Consequently, versatile applications are limited. Thus, to allow for easier processing and fabricating, it is imperative that the solubility of PBOs in common solvents has to be increased. Many research groups have investigated the synthesis of amorphous soluble PBOs using fluorinated monomers and substituted terephthalic acids or aromatic diacids containing flexible linkages [5-9]. It is actually well-known that the incorporation of 2,2′-hexafluoroisopropylidene (6F) groups into the polymer backbone enhances the solubility of PBOs while preserving thermal oxidative stability to some extent [8, 10-11].

2,5-Difluoroterephthalic acid (DFTA) was a very useful fluorinated monomer for the preparation of high performance thermoplastics [12-15]. Recently, we have developed a new synthetic route for DFTA [16]. In this paper, we describe the synthesis and characterization of a new serious of fluorinated polybenzoxazoles derived from 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6FBAHP) and DFTA. It was expected that the introduction of DFTA monomer may enhance the thermal stability of the resulting polybenzoxazoles while the existence of 2,2’-hexafluoroisopropylidene (6F) groups improve the solubility in organic solvents. This study was undertaken to investigate the influence of the chemical structure of PBOs on their thermal and physical properties.

Results and discussion

Synthesis of polybenzoxazoles

6FBAHP was combined with mixtures of TPA and DFTA taken in various proportions to form a series of fluorinated benzoxazole copolymers (Scheme 1). The *X* and *Y* value was controlled by the starting monomers with molar ratios varying from 0/100, 25/75, 50/50, 75/25 and 100/0.



Scheme 1. Synthesis of fluorinated benzoxazole copolymers.

Tab. 1. Components and Yield of fluorinated PBOs

Polymer	X (%)	Y (%)	Yield (%)
PBOs-1	0	100	89
PBOs-2	25	75	91
PBOs-3	50	50	90
PBOs-4	75	25	92
PBOs-5	100	0	91

Different components and yields of fluorinated benzoxazole copolymers are listed in Table 1. The chemical structures of the resulting PBOs were characterized by FT-IR and ^{1}H NMR spectroscopy. Figure 1 depicts the FTIR spectra of PBOs-3. It can be seen that the complete cyclization was confirmed by the disappearance of C=O stretching bands at 1780-1650 cm^{-1} and the appearance of a absorption bands at 1620 cm^{-1} coming from the oxazole ring. The characteristic absorption peaks were also observed at 3071 cm^{-1} for the aromatic C–H stretching, 1201, 1135 cm^{-1} for the

C–F stretching in the CF_3 group, 1254 cm^{-1} for the aromatic C-F stretching. Figure 2 compares the different ^1H NMR spectra among PBOs-1, PBOs-3 and PBOs-5. It shows that the chemical shifts of all protons agree well with the proposed polymers structures. Signal at 8.70 ppm was assigned to protons H_4 of TPA while protons H_5 of DFTA appeared at 8.34 ppm. Signals appeared from 7.81-8.35 are assigned to protons H_3, H_2 and H_1 of 6FBAHP.

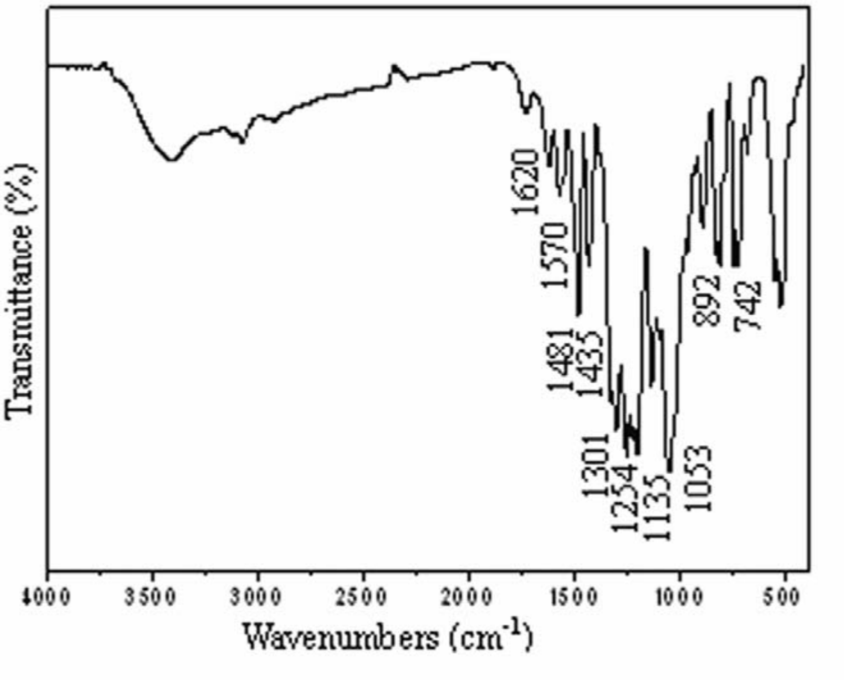


Fig. 1. FT-IR spectra of PBOs-3.

As depicted in Table 2, the synthesized polybenzoxazoles had relatively low inherent viscosities (0.74-1.17) while the homopolymers (PBOs-1, 5) had a higher value than the copolymers (PBOs-2, 3, 4) and this can be further confirmed by the GPC results. The molecular weights of the PBOs determined by GPC in THF using polystyrene as standard are in the range of 41400-52800 for M_n and 87000-108200 for M_w with the M_w/M_n values of 2.02-2.14.

Tab. 2. Intrinsic Viscosity and GPC results of fluorinated PBOs.

Polymer	$[\eta]^a$	$M_n \times 10^{-4b}$	$M_w \times 10^{-4b}$	$(M_w/M_n)^b$
PBOs-1	1.17	5.28	10.82	2.05
PBOs-2	0.74	4.14	8.77	2.12
PBOs-3	0.91	4.65	9.67	2.08
PBOs-4	0.83	4.41	9.43	2.14
PBOs-5	1.01	5.12	10.34	2.02

[a] MSA, 30°C, 0.25g/dL.
[b] GPC in THF vs. polystyrene at 35°C.

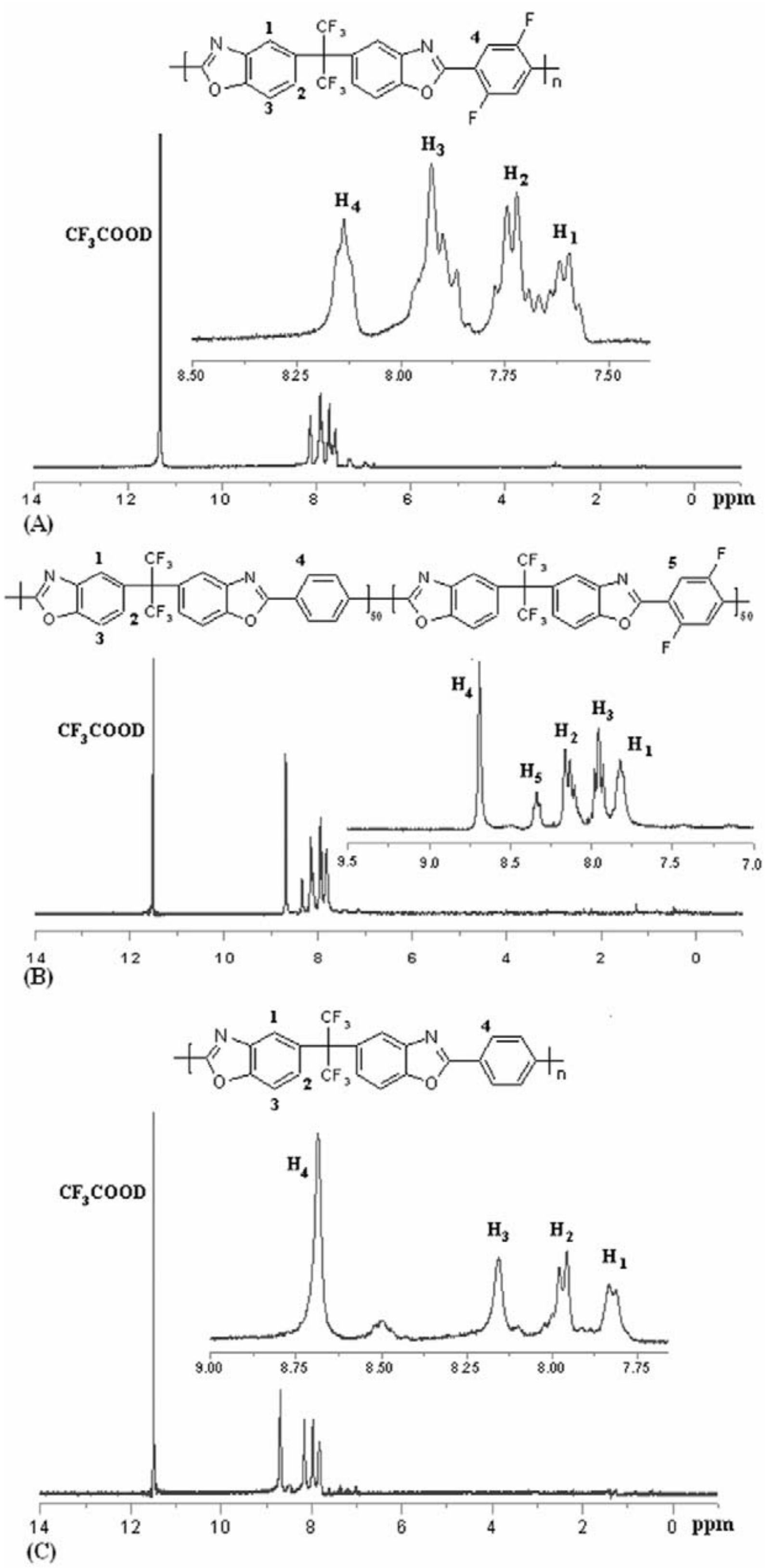


Fig. 2. ^{1}H NMR spectra of PBOs-1 (A), PBOs-3 (B) and PBOs-5 (C) in CF_3COOD.

Thermal Properties of PBOs

Thermal properties of PBOs were evaluated by means of differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA). The results are listed in

Table 3. DSC was used to determine the glass transition temperatures of polymers with a heating rate of 10 °C/min in nitrogen. The glass-transition temperature of the PBOs ranged from 303 °C to 319 °C. Figure 3 illustrated a typical DSC curve of PBOs-3. A clear T_g at 311°C was taken from the midpoint of the heat capacity. Figure 4 showed the initial thermal decomposition temperature of 522 °C for PBOs-3. Meanwhile, the residual weight ratio at 800 °C is also summarized in Table 3. As expected, PBOs-1 presents the best thermal stability (T_d=541 °C) owing to the highest portion of DFTA monomer. The results of thermal analysis demonstrate that the resulting PBOs should hold excellent thermal stability, which would facilitate their application.

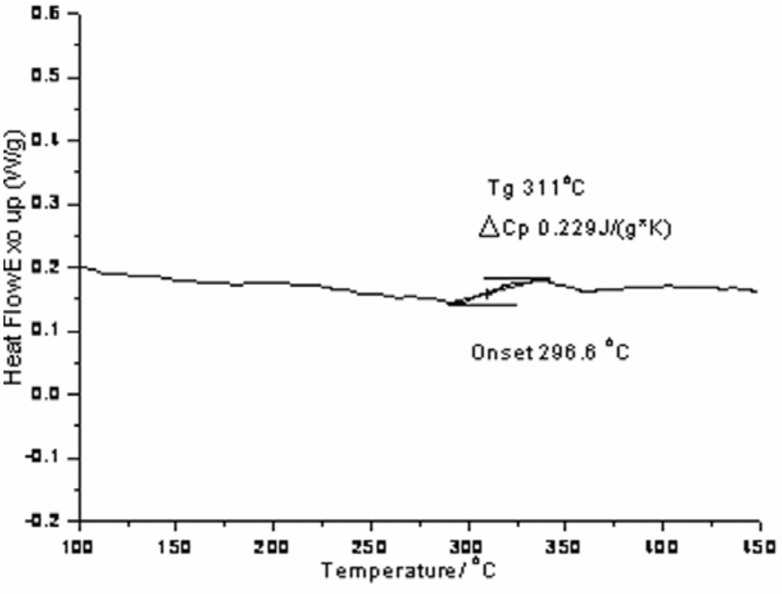


Fig. 3. DSC curves of PBOs-3 in nitrogen.

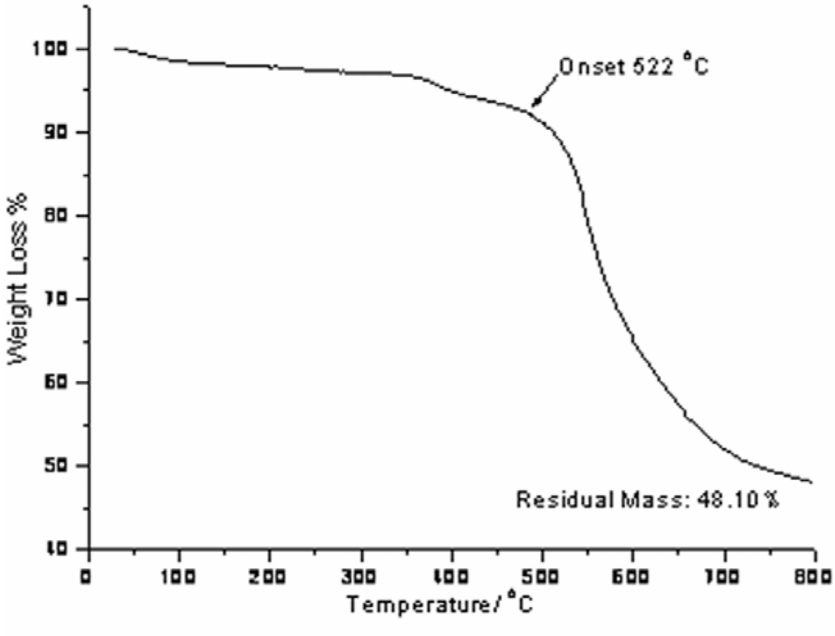
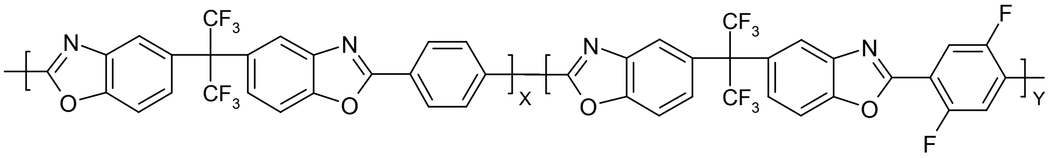


Fig. 4. TGA curves of PBOs-3 in nitrogen.

Tab. 3. Thermal properties of fluorinated PBOs



Polymer	X (%)	Y (%)	T_g [a] (%)	T_d [a] (°C)	R_w [b] (%)
PBOs-1	0	100	303	541	47
PBOs-2	25	75	306	520	46
PBOs-3	50	50	311	522	48
PBOs-4	75	25	316	526	38
PBOs-5	100	0	319	531	35

[a] DSC and TGA at 10°C/min in N_2.
[b] Residual weight retention at 800°C.

Solubility

The solubility behavior of the resulting polymers was examined. As summarized in Table 4, all the polymers were soluble in MSA, TFAA and THF at room temperature. The PBOs can also dissolve well when heated in polar solvents such as NMP, DMSO and DMAc. The good solubility of PBOs can be attributed to the introduction of bulky trifluoromethyl groups which inhibit efficiently the PBOs from forming regular chain structure and increase the molecular polarity correspondingly. Therefore, the resulting PBOs molecule tends to contain a high free volume, thus exhibiting excellent solubility in organic solvents.

Tab. 4. Solubility of fluorinated PBOs.

Polymer	Solvent [a]							
	MSA	TFAA	THF	DMSO	DMAc	NMP	Acetone	Chloroform
PBOs-1	+ +	+ +	+ +	+	+	+	—	—
PBOs-2	+ +	+ +	+ +	+	+	+	—	—
PBOs-3	+ +	+ +	+ +	+	+	+	—	—
PBOs-4	+ +	+ +	+ +	+	+	+	—	—
PBOs-5	+ +	+ +	+ +	+	+	+	—	—

[a] ++: soluble at room temperature; +: soluble on heating; -: insoluble even on heating. MSA: Methanesulfonic acid; TFAA: trifluoroacetic acid; NMP: N-methyl-2-pyrrolidone; DMAc: N,N-dimethylacetamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

Morphology

All the WAXD patterns of the PBOs shown in Figure 5 have two major diffraction peaks at the interplanar spacing corresponding to around 2θ=15° (~0.58 nm, labelled as peak A) and 2θ=25° (~0.35 nm, labeled as peak B). The periodicity for peak A stands for the side-to-side distance between two neighbouring polymer chains. For PBO, its side-to-side distance is 0.55 nm (2θ=16°), corresponding to the (200) plane

[17]. The diffraction peak B stands for the face-to-face distance between two neighbouring polymer chains. The face-to-face distance for PBO is 0.336 nm (2θ= 26.5°), corresponding to the (010) plane [18]. As depicted in Figure 5, there is a shift in both peaks for fluorinated PBOs compared with PBO, indicating an increase in the interplanar spacing for PBOs because the flexible BAHP6F segments affect the rigid-chain ordered structure of PBO.

Tabl. 5. Physical properties of fluorinated PBOs.

Polymer	λ_{cut}^{a}(nm)	T_{450}^{b} (%)	T_{500}^{b} (%)	2θ(degree)	d-spacing (nm)
PBOs-1	390	50	73	15.12	0.586
				24.10	0.369
PBOs-2	385	59	80	15.30	0.578
				25.28	0.352
PBOs-3	382	62	82	15.34	0.577
				25.06	0.355
PBOs-4	380	65	84	14.90	0.594
				25.37	0.351
PBOs-5	379	68	85	15.50	0.571
				25.50	0.349

[a] UV cutoff wavelength. [b] Transmittance at 450 nm and 500 nm.

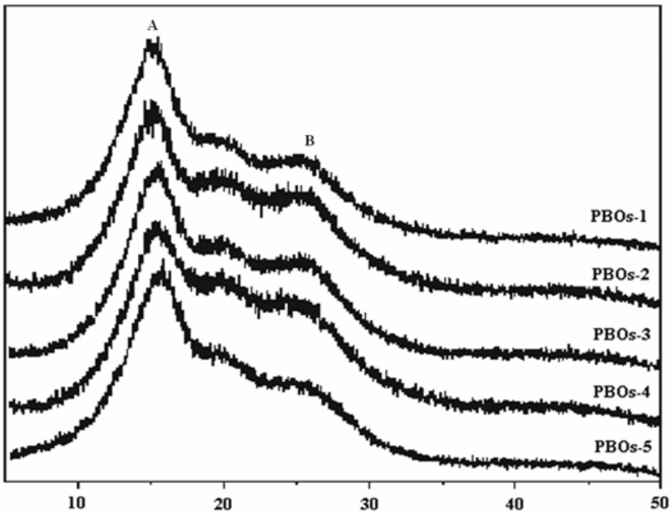


Fig. 5. Wide-angle X-ray diffraction patterns of fluorinated PBOs.

Optical properties

The transparency of the fluorinated PBOs films was evaluated by UV-vis spectra measurement. As can be seen from Figure 6, all the PBOs films showed good transparency in visible region. The cut off wavelength increased with an increase of DFTA content in PBOs. For example, PBOs-1, which had the highest fluorine content had a cut off UV wavelength of 390 nm and 73% of transmittance at 500 nm (Table 5). PBOs-5, on the other hand, had a blue-shift of 11 nm and 85% of transmittance at 500 nm. The high transparency of PBOs films might be attributed to the strong electronegativity of fluorine atoms which efficiently reduce the formation of inter- or intramolecular charge-transfer complexes.

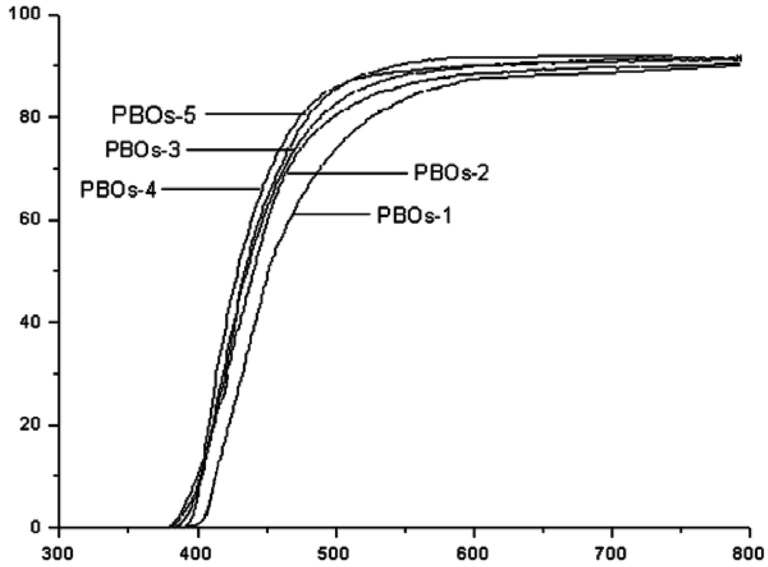


Fig. 6. UV-vis spectra of fluorinated PBOs films.

Conclusions

In summary, a new serious of fluorinated polybenzoxazoles derived from 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6FBAHP) together with 2,5-difluoroterephthalic acid (DFTA) and terephthalic acid (TPA) were synthesized and characterized. All polymers show high glass transition temperatures, excellent thermal stability and solubility in various common organic solvents. The introduction of DFTA monomer to the polymer backbone is not only responsible for enhancing the thermal stability but also is partially responsible for imparting low colour to the PBOs films by reducing charge transfer complex formation. The good combined properties have made them good potential candidates for high-tech applications.

Experimental part

Materials

2,2-Bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6FBAHP) was obtained from Zigong Longxiang Chemical Co., Ltd. Terephthalic acid (TPA), 84% poly(phosphoric acid) (PPA) and methanesulfonic acid (MSA) were obtained from Sinopharm Chemical Reagent Co., Ltd. Other reagents or materials were used as received.

Measurements

Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. Gas chromatography/mass spectrometry (GC/MS) was recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. ^{1}H NMR (400 MHz) spectra was recorded on a **Bruker** AV 400 spectrometer system. CF_3COOD were used as the solvents and chemical shifts reported were internally referenced to Me_4Si (0 ppm) for ^{1}H nuclei. Differential scanning calorimetry (DSC) was conducted on a NetZSch (German) DSC 204 F1 system under nitrogen calibrated with indium and zinc standards. The specimen was heated from 25 to 450 ^{o}C at a heating rate of 10 ^{o}C/min. Dynamic thermo-gravimetric analysis (TGA) was performed on NetZSch (German) TGA 209 F1 system on powder samples at a heating rate of 10 ^{o}C/min under nitrogen atmosphere from 25 to 800 ^{o}C. Ultraviolet-Visible (UV-vis) spectra were recorded on a Hitachi U-3310 spectrophotometer at room temperature. The wide-angle X-ray diffraction (XRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu/Kα1 radiation, operated at 40 kV and 300 mA.

Synthesis of 2,5-Difluoroterephthalic acid (DFTA)

The synthesis of 2,5-difluoroterephthalic acid (DFTA) has been previously described [16].

Synthesis of polybenzoxazoles(PBOs)

The general procedure for the synthesis of PBOs homo and copolymers is illustrated by the synthesis of PBOs-3.

Into a 250-mL flask equipped with a mechanical stirrer and a nitrogen inlet and outlet, there were placed 0.831 g (0.005mol) of TPA, 1.011 g (0.005 mol) of DFTA, 3.663 g (0.01 mol) of 6FBAHP and 34.33g of 84% PPA (polyphosphoric acid). The resultant mixture was heated slowly to 100 °C in an oil bath, and that temperature was maintained for 24 h. The temperature was then raised slowly to 140 °C for 4 h, 160 °C for 6 h, and finally 200 °C for 24 h. The viscous polymerization solution (yellow in colour) was allowed to cool to room temperature before precipitation into water (1000 mL). The resulting fibrous precipitate was filtered and washed with ammonium hydroxide and then with a copious amount of water, and finally dried in vacuum at 110 °C.

PBOs-1: IR (v, KBr,): 3076, 1620, 1481, 1198, 1255, 1198, 1132, 959 cm^{-1}. ^{1}H NMR (CF_3COOD, 400MHz, ppm): δ8.34 (s, 2H), 8.16-8.10(m, 2H), 7.98-7.93(m, 2H), 7.83-7.81(m, 2H).

PBOs-2: IR (v, KBr,): 3074, 1620, 1479, 1257, 1197, 1132, 959 cm^{-1}. ^{1}H NMR (CF_3COOD, 400MHz, ppm): δ8.70 (s, 1H), 8.35-8.33(m, 1.5H), 8.16-8.10 (m, 2H), 7.98-7.93(m, 2H), 7.83-7.81(m, 2H).

PBOs-3: IR (v, KBr,): 3071, 1620, 1481, 1254, 1201, 1135, 892 cm^{-1}. ^{1}H NMR (CF_3COOD, 400MHz, ppm): δ8.70 (s, 2H), 8.35-8.33 (m, 1H), 8.16-8.10 (m, 2H), 7.98-7.93(m, 2H), 7.83-7.81(m, 2H).

PBOs-4: IR (v, KBr,): 3072, 1620, 1478, 1254, 1196, 1135, 958 cm^{-1}. ^{1}H NMR (CF_3COOD, 400MHz, ppm): δ8.69 (s, 3H), 8.35-8.33 (m, 0.5H), 8.16-8.10 (m, 2H), 7.98-7.93(m, 2H), 7.83-7.81(m, 2H).

PBOs-5: IR (v, KBr,): 3070, 1620, 1478, 1227, 1198, 1137, 960 cm^{-1}. ^{1}H NMR (CF_3COOD, 400MHz, ppm): δ8.70 (s, 4H), 8.15(s, 2H), 7.97-7.95(m, 2H), 7.83-7.81(m, 2H).

Film casting

The light yellow PBOs solution in THF with a solid content of 15 wt.% was filtered through a 0.2 mm Teflon syringe filter to eliminate any particulates that might affect the quality of the cured film. The purified PBOs solution was spin-coated on a glass plate (20×20 mm), and the thickness of the PBOs coating was controlled at 20-30 μm by adjusting the spin rate.

Acknowledgements

We are grateful to National Natural Science Foundation of China, the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT0526) and Shanghai Municipal Scientific Committee for the financial support.

References

[1] Holmes, G.A.; Rice, K.; Snyder, C. R. *J. Mater. Sci.* **2006**, 41, 4105.
[2] Chae, H.G.; Kumar, S. *J. Appl. Polym. Sci.* **2006**, 100, 791.
[3] Hu, X.D.; Jenkins, S.E.; Min, B.G.; Polk, M.B.; Kumar, S. *Macromol. Mater. Eng.* **2003**, 288, 823.
[4] So, Y.H. *Prog. Polym. Sci.* **2000**, 25, 791.
[5] Wolfe, J. F.; Arnold, F. E. *Macromolecules*. **1981**, 14, 909.
[6] Ueda, M.; Sugita, H.; Sato, M. *J. Polym. Sci. Part A: Polym. Chem.* **1986**, 24, 1019.
[7] Evers, R. C.; Arnold, F. E.; Helminiak, T. E. *Macromolecules.* **1981**, 14, 925.
[8] Hilborn, J. G.; Labadie, J. W.; Hedrick, J. L. *Macromolecules.* **1990**, 23, 2854.
[9] Smith, J. G.; Connell, J. W.; Hergenrother, P. M. *Polymer.* **1992**, 33, 1742.
[10] Maglio, G.; Palumbo, R.; Tortora, M. *J. Polym. Sci. Part A: Polym. Chem*. **2000**, 38, 1172.
[11] Johnson, R. A. ; Mathias, L. J. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, 33, 1901.
[12] Cassidy, P.E.; Reddy, V.S. *React. Funct. Polym.* **1996**, 30, 141.
[13] Person, D.; Cassidy, P. E.; Fitch, J. W.; Kono, K.; Ueda, M. *React. Funct. Polym.* **1996**, 30, 229.
[14] Kim, J. H.; Bang, S. W.; Kim, Y. J. *Bull. Korean Chem. Soc.* **2000**, 21, 896.
[15] Kim, J. H.; Kim, Y. J.; Won, J. C.; Choi, K. Y. *J. Appl. Polym. Sci.* **2004**, 92, 178.
[16] Huang, X. S.; Qing, F. L. J. *Fluorine Chem* **2008**, 129, 1076.
[17] Wang, S. F.; Wu, P. P.; Han, Z. W. *J. Mater. Sci.* **2004,** 39, 2717.
[18] Fratini, A. V. ; Lenhert, P. G. ; Resch, T. J. ; Adams, W. W. *Mater. Res. Soc. Symp. Proc.* **1989**134, 431.