Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

polymer

Polymer 44 (2003) 7369–7376

www.elsevier.com/locate/polymer

Synthesis and characterization of a fluorinated phthalazinone monomer 4-(2-fluoro-4-hydroxyphenyl)-phthalazin-1(2*H*)-one and its polymers from polycondensation reactions

Shude Xiao[a,b,*], Jinyan Wang[a], Kun Jin[c], Xigao Jian[a], Qinji Peng[c]

[a]*Department of Polymer Science and Materials, Dalian University of Technology, P.O. Box 42, Zhongshan Rd. 158, Dalian 116012, People's Republic of China*
[b]*Department of Chemical Engineering, University of Waterloo, 200 University Ave. W., Waterloo, Ont., Canada N2L 3G1*
[c]*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Zhongshan Rd. 158, Dalian 116012, People's Republic of China*

Received 7 June 2003; received in revised form 23 September 2003; accepted 24 September 2003

Abstract

As a category of high performance polymers having good solubility and distinguished thermal properties, poly(phthalazinone ether)s received much attention for their applications in engineering plastics and membrane materials. 2-(2-Fluoro-4-hydroxybenzoyl)-benzoic acid (FHBBA) synthesized from 3-fluorophenol and phthalic anhydride reacted with hydrazine hydrate to form 4-(2-fluoro-4-hydroxyphenyl)-phthlazin-1(2*H*)-one (FDHPZ). Four polymers were prepared from polycondensation reactions of FDHPZ with 4,4′-difluorobenzophenone, bis(4-chlorophenyl) sulfone, 1,4-bis(4-fluorobenzoyl)-benzene and perfluorobiphenyl, respectively. All polymers show good solubility in common aprotic solvents and have excellent thermal properties investigated by DSC and TGA. FTIR and NMR spectra of FDHPZ, FHBBA, and polymers from FDHPZ were studied. Refractive indices (n_{TE}) of films on silicon substrates were measured with a Prism Coupler. These polymers have potentials as materials for optical waveguides.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Poly(aryl ether); Phthalazinone; Polycondensation

1. Introduction

Having outstanding comprehensive properties, heterocyclic polymers have attracted much attention from academic and commercial fields, and many of these polymers have been synthesized and used as high performance engineering plastics worldwide. Among this category of polymers, polyphthalazinones are known as common solvents soluble polymers with distinguished thermal stability [1–3]. Now a series of poly(phthalazinone ether)s such as poly(phthalazinone ketone) (PPEK), poly(phthalazinone sulfone) (PPES) and poly(phthalazinone sulfone ketone) (PPESK) have been synthesized and are commercially available [4,5]. As high performance polymers, they are widely used as engineering plastics and membrane materials [6–9]. The good solubility and excellent thermal properties are attributed to the fused ring system and non-coplanar conformation of the phthalazinone moieties in their backbones. 4-(4-Hydroxyphenyl)-phthlazin-1(2*H*)-one (DHPZ) that prepared from phenol and phthalic anhydride is the bisphenol-like monomer used in polycondensation reactions with activated dihalide monomers such as 4,4′-difluorobenzophenone or/and bis(4-chlorophenyl) sulfone to obtain high molecular weight polymers [10–13]. Side groups such as methyl and phenyl groups have been introduced into this monomer to obtain phthalazinone derivatives and their corresponding polymers [14–17]. Lianzhou Chen et al. synthesized a chlorinated phthalazinone monomer 4-(3-chloro-4-hydroxyphenyl)-phthalazin-1(2*H*)-one, and prepared polymers from this monomer with 4,4′-difluorobenzophenone [18,19]. This chlorinated poly(phthalazinone ketone) has a higher glass transition temperature and a lower 5% weight loss

---

[*] Corresponding author. Address: Department of Chemical Engineering, University of Waterloo, 200 University Ave. W., Waterloo, Ont., Canada N2L 3G1. Tel.: +1-519-888-4567x6153; fax: +1-519-746-4979.

E-mail addresses: sxiao@engmail.uwaterloo.ca (S. Xiao), jian4616@mail.dlptt.ln.cn (X. Jian).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.09.040

temperature than the original non-halogenated poly(phthalazinone ketone) [18,19].

In recent studies, fluorinated poly(aryl ether)s are used as materials for optical waveguides [20–23]. Fluorine atoms in these polymers lower refractive indices and reduce transmission losses caused from vibration absorption of C–H bonds [24–29]. To incorporate the excellent thermal properties and good solubility with the optical properties resulting from fluorine atoms in the polymers [30], this study focused on synthesis and characterization of a fluorinated phthalazinone derivative 4-(2-fluoro-4-hydroxyphenyl)-phthlazin-1(2*H*)-one (FDHPZ) and its polymers from polycondensation reactions with 4,4′-difluorobenzophenone, bis(4-chlorophenyl) sulfone, 1,4-bis(4-fluorobenzoyl)-benzene and perfluorobiphenyl. The monomer FDHPZ and its intermediate compound 2-(2-fluoro-4-hydroxybenzoyl)-benzoic acid (FHBBA) were characterized with FTIR and NMR spectra. The solubility and inherent viscosity of these polymers were measured, and their thermal properties and refractive indices (n_{TE}) were also studied.

2. Experimental

2.1. Materials

All solvents were reagent-grade and desiccated with anhydrous calcium chloride. Perfluorobiphenyl (PFBP, from Acros) and hydrazine hydrate (85 wt%) were used as received. 1,4-Bis(4-fluorobenzoyl)-benzene (BFBB) was recrystallized in *N*,*N*-dimethylacetamide (DMAc). 4,4′-Difluorobenzophenone (DFBP) and bis(4-chlorobenzene) sulfone (BCS) were purified from recrystallization in ethanol and dried in a vacuum oven for 24 h. All other chemicals were reagent-grade and used without further purification unless otherwise noted.

2.2. Instrumentation

^{1}H NMR and ^{13}C NMR spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 40 °C. ^{1}H NMR spectra were recorded in DMSO-d$_6$ solutions at a resonance frequency of 399.715 MHz and a 30° pulse, and a delay of 10 s were used to acquire the quantitative spectra. The DMSO-d$_6$ solution ^{13}C NMR spectra were carried out on the NMR spectrometer operating at 100.518 MHz for ^{13}C and a 30° pulse, and a delay of 6.2 s were used to acquire the quantitative spectra. The inherent viscosities of polymers were measured in NMP using an Ubbelohde viscosimeter at 25 °C. The apparent molecular weights of the polymers were determined by gel permeation chromatography (GPC) using THF at ambient temperature, and molecular weight calculations were based on polystyrene standards. Mass spectrum was given by HP 1100 High Performance Liquid Chromatography/Mass Selective Detector. Differential scanning calorimetry (DSC) analysis was performed on a Du Pont 2000 differential scanning calorimeter. Glass transition temperatures (T_g) were taken at the inflection point from the second heating curves. The melting points were recorded at the endothermic peaks of curves. Thermogravimetric analysis (TGA) was performed on the Perkin–Elmer 7 Series Thermal Analysis System. Dsecomposition temperatures (T_d) were recorded when the weight loss of the sample reached 5% in TGA. Samples for DSC and TGA were heated in a nitrogen atmosphere (50 ml/min) at a rate of 10 °C/min. FTIR Spectra were measured with a NICOLET-20DXB FTIR Spectrometer. Refractive indices of the polymers were measured at a wavelength of 632.8 nm using a Metricon M2010 Prism Coupler.

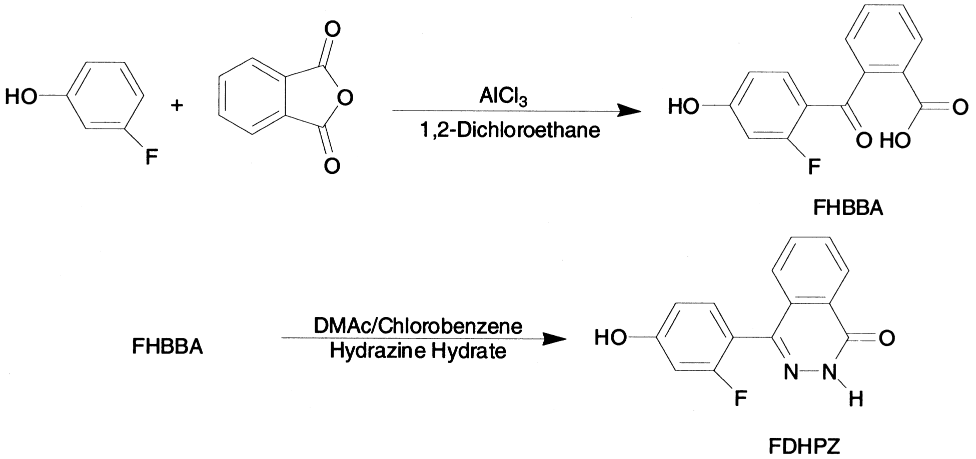
2.3. Preparation of the monomer and polymers

2.3.1. Preparation of FHBBA

3-Fluorophenol (11.2 g, 0.10 mol) and phthalic anhydride (14.8 g, 0.10 mol) was successively added into a three-necked flask charged with 1,2-dichloroethane (120 ml) below 0 °C. The resulting mixture was stirred intensively at room temperature until no hydrochloride could be seen from out of the reaction system. The mixture was poured into hydrochloric acid (15 wt%, 150 ml) containing crushed ice. The coarse compound 2-(2-fluoro-4-hydroxybenzoyl)-benzoic acid (FHBBA) (20 g, yield 80%) was obtained from steam distillation followed by filtration. This intermediate compound FHBBA could be purified from recrystallization in water. ^{1}H NMR (DMSO-d$_6$, δ ppm): 12.13, s, 1H; 7.36, d, 1H; 7.69, t, 1H; 7.62, t, 1H; 8.03, d, 1H; 6.72, d, 1H; 6.56, m, 1H; 7.14, t, 1H. ^{13}C NMR (DMSO-d$_6$, δ ppm): 166.09; 201.03; 126.67; 131.85; 129.45; 129.81; 129.43; 139.60; 117.57; 167.54, 165.00; 104.05, 103.82; 163.73, 163.59; 106.65, 106.42; 134.57, 134.45. m.p. (DSC): 169.26 °C. FTIR (NEAT, cm^{-1}): 3067, 1693, 1635, 1595, 1506, 1452, 1416, 1308, 1258, 1170, 1146, 1111, 981, 924, 843, 771, 716. MS peaks found (*m/z*): 259.0 $[M - H]^-$, 215.1 $[M - CO_2]$, 261.1 $[M + H^+]$, 283.1 $[M + Na^+]$, 299.1 $[M + K^+]$.

2.3.2. Preparation of FDHPZ

2-(2-Fluoro-4-hydroxybenzoyl)-benzoic acid (FHBBA) (26 g, 0.10 mol), DMAc (20 ml) and chlorobenzene (200 ml) were added into a three-necked flask equipped with a dropping funnel, and the mixture was heated to reflux. Then hydrazine hydrate (30 ml, 85 wt%) was carefully dropped into the mixture. The reaction was stopped in 2 h and was cooled to the room temperature. The precipitate was filtered and washed with anhydrous ethanol to obtain coarse compound 4-(2-fluoro-4-hydroxyphenyl)-phthlazin-1(2*H*)-one (FDHPZ). It was purified by recrystallization in DMAc and washed with anhydrous ethanol, then dried under vacuum at 120 °C for 24 h. About 20 g refined 4-(2-fluoro-4-hydroxyphenyl)-phthlazin-1(2*H*)-one (FDHPZ) were obtained (yield 78%). ^{1}H NMR



Scheme 1. Procedures for preparation of FDHPZ.

(DMSO-d_6, δ ppm): 12.69, s, 1H; 7.46, d, 1H; 7.86, m, 1H; 7.82, m, 1H; 8.33, d, 1H; 6.71, d, 1H; 6.77, d, 1H; 7.27, t, 2H; 10.31, s, 1H. ^{13}C NMR (DMSO-d_6, δ ppm): 159.03; 141.98; 126.06; 133.18; 131.92; 125.61; 127.40; 129.49; 113.08, 112.92; 161.37, 158.93; 102.69, 102.46; 159.87, 159.75; 111.79; 131.23. m.p. (DSC): 322.01 °C. FTIR (NEAT, cm^{-1}): 3272, 3155, 3073, 1633, 1590, 1546, 1514, 1459, 1365, 1302, 1232, 1162, 1127, 976, 962, 845, 807, 787, 743.

2.3.3. *Preparation of polymers*

Polymer FDHPZ/BFBB, for instance, was prepared from the following procedures: under the protection of nitrogen, FDHPZ (0.5125 g, 2 mmol), 1,4-bis(4-flurobenzoyl)-benzene (BFBB) (0.6446 g, 2 mmol), and anhydrous K_2CO_3 (0.44 g, 4.5 mmol) were added into a three-necked flask equipped with a Dean–Stark trap and charged with DMAc (4.0 ml) and toluene (3 ml). The mixture was heated to flux at 150 °C, and 3 h later toluene was piped out, then the reaction temperature was increased to 160 °C. When the reaction system became viscous, it was poured into excess ethanol to end the reaction of polycondensation.

It took about 3 h, 4 h, 8.5 h at the temperature of 160 °C to obtain polymers FDHPZ/BFBB, FDHPZ/DFBP and FDHPZ/BCS, respectively.

As of the polymer FDHPZ/PFBP, the polycondesation was carried out in a flask equipped with a Dean–Stark trap under the protection of nitrogen in *N*,*N*-dimethylacetamide (DMAc) under 120 °C. FDHPZ (1.2812 g, 5 mmol), perfluorobiphenyl (PFBP) (1.7040 g, 5.1 mmol), and anhydrous potassium carbonate (1.1 g, 7.5 mmol) were added into DMAc (14 ml) and benzene (4 ml). The mixture was maintained refluxing at 100 °C for 1 h. After benzene was removed, the reaction system was kept at 120 °C for 5 h. Then the viscous solution was poured into excess ethanol to give a white polymer.

All polymers were treated in boiling water for 1 h, then refined by precipitating their NMP solutions in excess ethanol, and treated in boiling water again. The filtered polymers were dried under vacuum at 160 °C for 24 h.

FTIR data for FDHPZ/BFBB (Film, cm^{-1}): 3058, 3009, 1666, 1596, 1496, 1413, 1308, 1270, 1250, 1221, 925, 753. FTIR data for FDHPZ/DFBP (Film, cm^{-1}): 3066, 3009, 1670, 1597, 1498, 1308, 1273, 1245, 1219, 1164, 1132, 929, 754. FTIR data for FDHPZ/BCS (Film, cm^{-1}): 3075, 1670, 1642, 1586, 1487, 1409, 1324, 1264, 1242, 1154, 1106, 975, 833, 756. FTIR data of FDHPZ/PFBP (Film, cm^{-1}): 3021, 1694, 1619, 1489, 1261, 1243, 1154, 1130, 979, 757, 724, 691. ^{1}H NMR spectra data of FDHPZ/PFBP (DMSO-d_6, δ ppm): 8.48, 8.03, 7.61, 7.47, 7.30.

3. Results and discussion

3.1. *Intermediate FHBBA and monomer FDHPZ*

3.1.1. *Synthesis of FHBBA and FDHPZ*

As a fluorinated derivative, FDHPZ was prepared from 3-fluorophenol and phthalic anhydride using the same method as DHPZ was synthesized (Scheme 1). The traditional synthesizing route for DHPZ is a multi-step procedure [10,11], while the method used in this paper is only a two-step one and easily carried out with a high yield [31]. In the first step, aluminium (III) chloride was used as the catalyst in the Friedel–Crafts acylation reaction of 3-fluorophenol and phthalic anhydride to obtain 2-(2-fluoro-4-hydroxybenzoyl)-benzoic acid (FHBBA) [32]. However, because of the existence of the electron-withdrawing fluorine atom attached to phenol, the yield is a little lower. The intermediate compound FHBBA can dissolve in hot water, so water was used as a solvent for recrystallization, but it is not necessary to purify this intermediate in this step. To form the phthalazinone structure in FDHPZ, hydrazine hydrate was used in the final step. Recrystallization in DMAc is indispensable to obtain the pure monomer FDHPZ for the following polycondensation reactions.

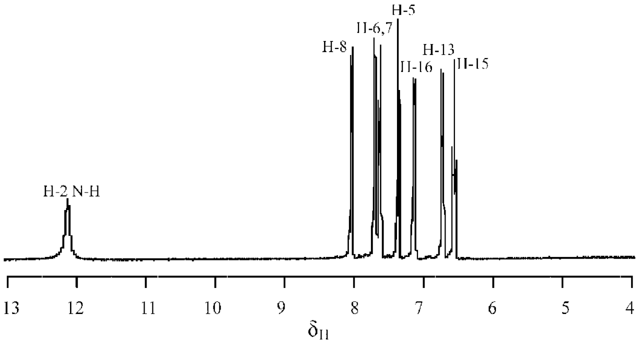


Fig. 1. ^{1}H NMR of FHBBA in DMSO-d$_6$.

Table 1
Assignments for protons and carbons for FHBBA and FDHPZ

No.	FHBBA, ^{1}H δ (ppm)	FHBBA, ^{13}C δ (ppm)	FDHPZ, ^{1}H δ (ppm)	FDHPZ, ^{13}C δ (ppm)
1	/	166.09	/	159.03
2	12.13, s, 1H	/	12.69, s, 1H	/
4	/	201.03	/	141.98
5	7.36, d, 1H	126.67	7.46, d, 1H	126.06
6	7.69, t, 1H	131.85	7.86, m, 1H	133.18
7	7.62, t, 1H	129.45	7.82, m, H	131.92
8	8.03, d, 1H	129.81	8.33, d, 1H	125.61
9	/	129.43	/	127.40
10	/	139.60	/	129.49
11	/	117.57	/	113.08, 112.92^{a}
12	/	167.54, 165.00^{a}	/	161.37, 158.93^{a}
13	6.72, d, 1H	104.05, 103.82^{a}	6.71, d, 1H	102.69, 102.46^{a}
14	/	163.73, 163.59^{a}	/	159.87, 159.75^{a}
15	6.56, m, 1H	106.65, 106.42^{a}	6.77, d, 1H	111.79
16	7.14, t, 1H	134.57, 134.45^{a}	7.27, t, 2H	131.23
17	–^{b}	/	10.31, s, 1H	/

[a] Double peaks.
[b] Not found.

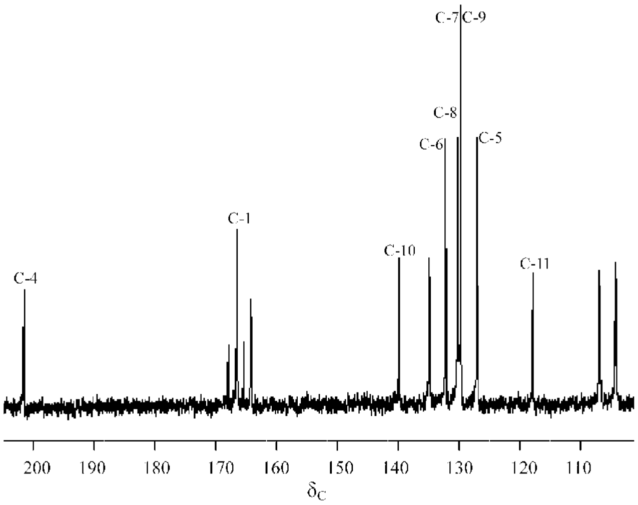


Fig. 2. ^{13}C NMR of FHBBA in DMSO-d$_6$.

3.1.2. Characterization of FHBBA and FDHPZ

The intermediate compound FHBBA and the monomer FDHPZ were purified from recrystallization for characterization. From fragments found in MS spectrum, the molecular weight calculated for FHBBA is 260.0. In the FTIR spectrum of FHBBA, the absorption peak of C=O is found at 1693 cm^{-1}, and absorption peaks of aromatic rings occur at 1595, 1506 and 1452 cm^{-1}. In the FTIR spectrum of FDHPZ, the absorption peak at 1633 cm^{-1} is due to the stretching vibration of C=O, and absorption peaks at 1590, 1514 and 1459 cm^{-1} are attributed to the vibration of aromatic rings.

NMR technologies, gCOSY, gHSQC and gHMBC have been used to assign protons in ^{1}H NMR spectra (Fig. 1 for FHBBA and Fig. 3 for FDHPZ) and carbon atoms in ^{13}C NMR spectra (Fig. 2 for FHBBA and Fig. 4 for FDHPZ). The full assignments are listed in Table 1. Because of the ^{19}F atoms in FHBBA, NMR peaks for C-12, C-13, C-14, C-15 and C-16 split into double peaks in ^{13}C NMR spectrum of FHBBA, and the same happens at NMR peaks for C-11, C-12, C-13 and C-14 in ^{13}C NMR spectrum of FDHPZ. In ^{1}H NMR spectrum of FHBBA, the NMR peak of O–H can not be found, but it is reasonable considering the acidic condition of the DMSO-d$_6$ solution resulting from the carboxyl group in FHBBA. These NMR data have confirmed the anticipated structures for FHBBA and FDHPZ (Fig. 5).

3.2. Polymers from FDHPZ

3.2.1. Synthesis of poly(alylene ether)s

Poly(alylene ether)s including poly(ether sulfone)s,

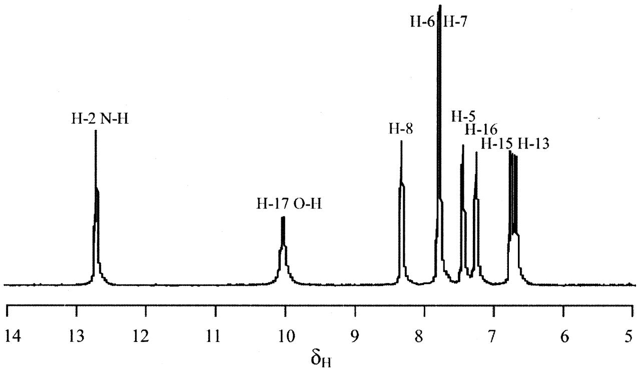


Fig. 3. ^{1}H NMR of FDHPZ in DMSO-d$_6$.

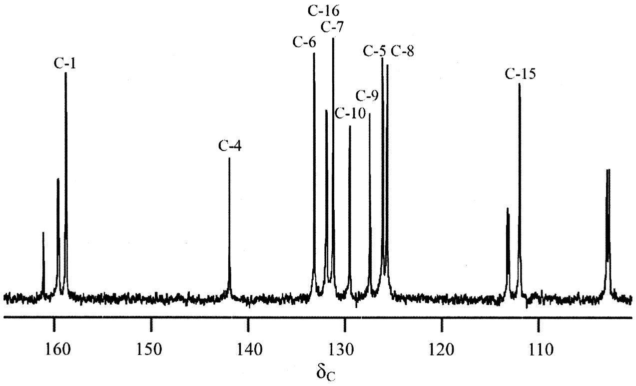


Fig. 4. ^{13}C NMR of FDHPZ in DMSO-d$_6$.

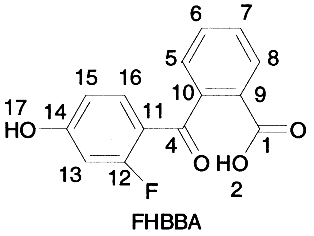
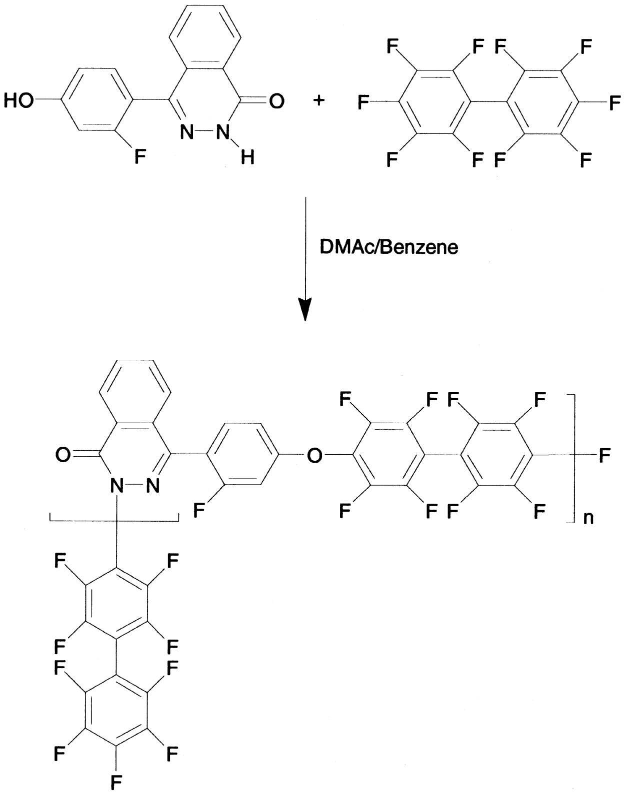


Fig. 5. NMR assignments for FHBBA and FDHPZ.

poly(ether ketone)s are commonly prepared from nucleophilic aromatic substitution polycondensation in aprotic solvents such as DMSO and sulfolane [33–35]. In these reactions, anhydrous potassium carbonate was used as a catalyst to react with the active hydrogen atoms of the hydroxy groups in the bisphenols. As a bisphenol-like monomer, FDHPZ has two active hydrogen atoms O–H and N–H that can react with potassium carbonate, so polymers can be formed from an N–C coupling reaction with activated dihalogenated monomers through polycondensation. Polymers can be easily prepared from FDHPZ with 1,4-bis(4-fluorobenzoyl)-benzene, 4,4′-difluorobenzophenone and bis(4-chlorobenzene) sulfone in DMAc at 160 °C (Scheme 2) using toluene to remove water produced in polycondensation. After removal of water, It took about 3, 4, 8.5 h at 160 °C to obtain high molecular weight polymers FDHPZ/BFBB, FDHPZ/DFBP and FDHPZ/BCS, respectively. This proved the known fact that BFBB, DFBP and BCS have different polycondensation reactivity when they react with bisphenol monomers on the same conditions [35], that is, BFBB > DFBP > BCS, which results from the difference in the electron-withdrawing effects between carbonyl groups and sulfone groups, and at same time

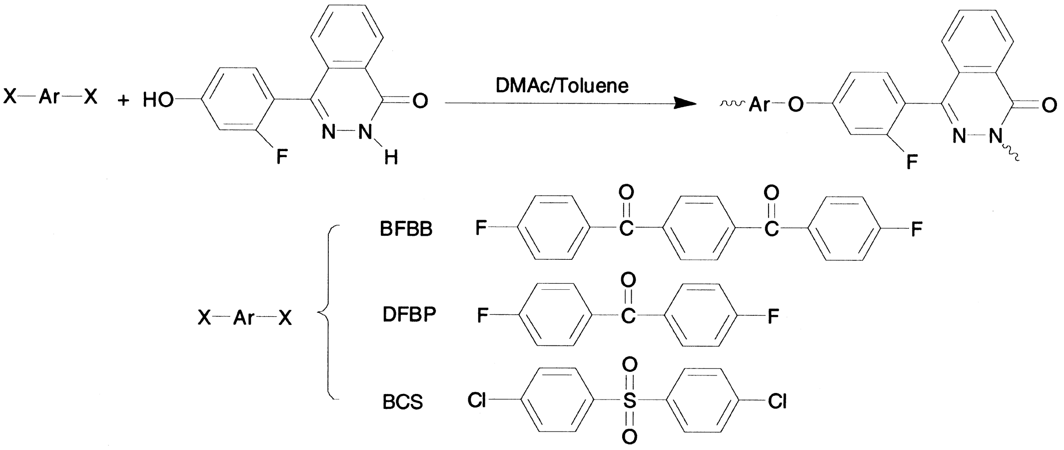


Scheme 3. Polycondensation reaction of FDHPZ with PFBP.

Table 2
Solubility the fluorinated poly(aryl ether)s

Polymers	CHCl$_3$	DMAc	DMF	DMSO	NMP	TCE	THF	Py	Sulfolane
FDHPZ/BFBB	+	+	+	++	+	+	+	+	++
FDHPZ/DFBP	+	++	++	±	+	+	±	++	++
FDHPZ/BCS	−	++	++	−	++	−	±	±	−
FDHPZ/PFBP	+	+	+	++	++	+	+	+	++

Key: + soluble; ++ soluble when heated; ± partially soluble; − insoluble.



Scheme 2. Polycondensation reactions of FDHPZ with BFBB, DFBP and BCS.

Table 3
Thermal properties and refractive indices of polymers

Polymer	T_g[a] (°C)	T_{d5}[a] (°C)	Film thickness (μm)	Refractive index[b] (n_{TE})
FDHPZ/BFBB	287	537	–	–
FDHPZ/DFBP	253	534	3.7246	1.6888
FDHPZ/BCS	~283	505	5.1792	1.6641
FDHPZ/PFBP	253	534	0.8652	1.5874

[a] In nitrogen atmosphere.
[b] Measured at 632.8 nm.

Table 4
Inherent viscosity and molecular weight of the polymers

Polymer	Inherent viscosity[a] (dl/g)	M_n[b]	M_w[b]	PDI
FDHPZ/BFBB	0.38	8892	12998	1.46
FDHPZ/DFBP	0.53	11432	15238	1.33
FDHPZ/BCS	0.97	6875[c]	9622[c]	1.40
FDHPZ/PFBP	0.50	11702	21725	1.86

[a] Measured in NMP at 25 °C.
[b] Measured by GPC in THF at the ambient temperature.
[c] Partially soluble in THF, so these values are smaller than the actual ones.

Table 5
FTIR data for polymers

Absorption	Ar-H (cm^{-1})	C=O (cm^{-1})	Aromatic rings (cm^{-1})	C–O–C (cm^{-1})
FHBBA	3067	1693	1595, 1506, 1452	–
FDHPZ	3073	1633	1590, 1514, 1459	–
FDHPZ/BFBB	3058, 3009	1666	1596, 1496	1250
FDHPZ/DFBP	3066, 3009	1670	1597, 1498	1245
FDHPZ/BCS	3075	1670	1586, 1487	1242,
FDHPZ/PFBP	3021	1694	1619, 1489	1243

from the difference between detachability of fluorine atoms and that of chlorine atoms.

It has been reported that the condensation reaction of perfluorobiphenyl mainly occurs at the para position to give linear polymers on mild reaction conditions, otherwise it may occurs at *ortho* positions that easily leads to crosslinking polymers [20–23]. Therefore in this reaction, to avoid the tendency of crosslinking, the temperature was lowered below 130 °C and the molar fraction of the two monomers FDHPZ and PFBP is 1:1.02. A white polymer having inherent viscosity of 0.50 dl/g in NMP at 25 °C was successfully obtained from the polycondensation reaction on the described conditions (Scheme 3).

3.2.2. Solubility and thermal properties of polymers

The solubility of the polymers in common aprotic organic solvents was measured and is listed in Table 2. They show excellent solubility in DMAc, DMF and NMP, which leads to the good processibility. And as a result, it is easy to prepared films by spin coating with these solvents. Though the phthalazinone moieties in the polymers are aromatic and rigid, there is a dihedral angle between phthalazinone and the attached phenyl group. This asymmetric and non-coplanar formation makes polymers' chains twisting, which results in good solubility, though there are no other flexible bonds except –O– in the chains. These features of the polymers, however, retain their good thermal stability. Thermal properties of these polymers (showed in Table 3) were investigated with DSC and TGA. The glass transition temperatures T_gs are in the range of 253 °C to 287 °C, and the decomposition temperatures for 5% weight loss T_{d5}s are all above 500 °C. All these show they have distinguished thermal stabilities and they can be used at a temperature of above 250 °C.

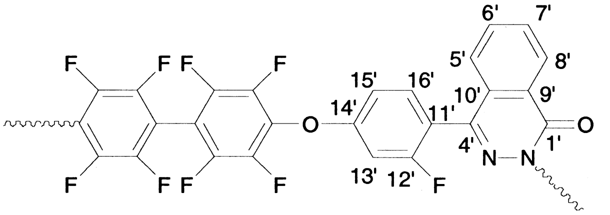


Fig. 6. ^1H NMR assignment for the FDHPZ moiety in polymer FDHPZ/PFBP.

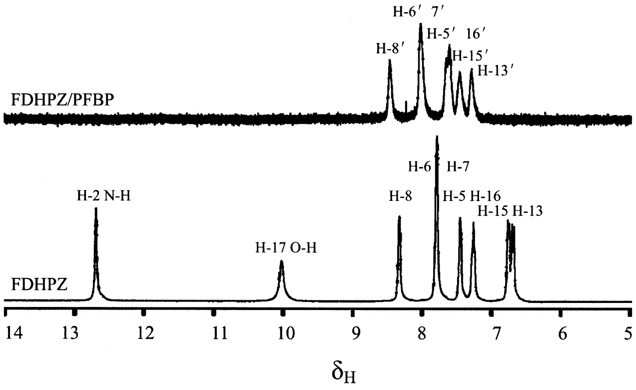


Fig. 7. Comparison of ^1H NMR spectra of FDHPZ and polymer FDHPZ/PFBP.

The inherent viscosity and molecular weight of polymers are listed in Table 4. The value of molecular weight for FDHPZ/BCS appears to be very small, which results from the poor solubility in THF that was used as the solvent in GPC. FDHPZ/PFBP has a large PDI (M_w/M_n) which implies that there is a large range of molecular weight.

3.2.3. FTIR and NMR of polymers

FTIR spectra data of the polymers have been studied and are listed in Table 5. The stretching vibration absorption of Ar-H can be found in the range of 3100–3000 cm^{-1}, and that of carbonyl groups including acyl groups in the lactam structure of phthalazinone moieties occurs from 1690 to1660 cm^{-1}. The IR absorption at 1619–1586 and

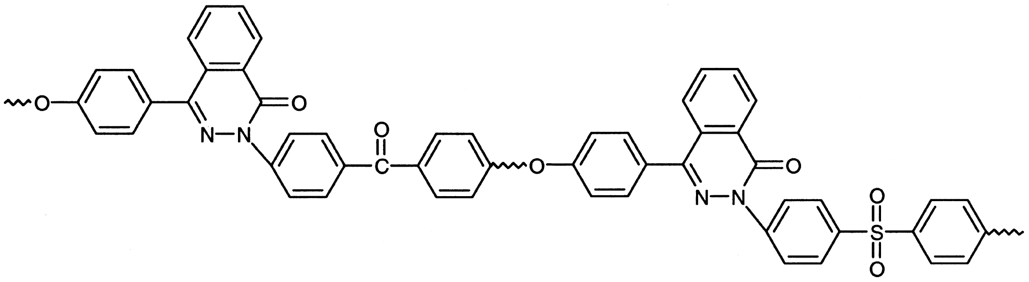


Fig. 8. Non-fluorinated phthalazinone-containing polymer PPESK.

1498–1487 cm^{-1} is caused from the vibration of aromatic rings in the polymers' backbones. The absorption near 1245 cm^{-1} is contributed to the existence of C–O–C bonds in the samples, which can, in some points, demonstrates the formation of the polymers. The absorption at 1324 cm^{-1} in the FTIR spectrum of FDHPZ/BCS confirms the existence of sulfone groups in this polymer.

Because of the peculiarity of hydrogen atoms in polymer FDHPZ/PFBP, ^{1}H NMR spectrum was measured in DMSO-d_6. It makes the proton assignments (Fig. 6) for ^{1}H NMR easy and clear that there are no C–H bonds in the PFBP moiety of the repeating unit. The NMR peaks at 12.96 ppm (N–H) and 10.31 ppm (O–H) in monomer FDHPZ do not exist in polymer FDHPZ/PFBP, and all the other peaks shift to lower fields comparing the monomer FDHPZ (showed in Fig. 7).

3.2.4. Films preparation and refractive indices

To prepare films on the silicon substrates, NMP was used as the solvent to give 15–20 wt% solutions that were filtered by 0.45 μm syringe filters. Films were prepared by spin coating on silicon disks for 30 s with a speed of 800 rpm and the acceleration of 1500 rpm/s. These films were heated from 50 to 200 °C at a nonlinear heating rate for 30 min, then they were treated at 200 °C for 20 min followed by cooling spontaneously to 88.5 °C. Films could be readily prepared from FDHPZ/DFBP, FDHPZ/BCS and FDHPZ/PFBP except FDHPZ/BFBB.

Films with good appearance could not be prepared from FDHPZ/BFBB, so its refractive index could not be obtained. Refractive indices of the other polymers measured at a wavelength of 632.8 nm by a Prism Coupler are listed in Table 3. The TE mode refractive indices of the three polymers are in the range of 1.5874–1.6888. The n_{TE} of the non-fluorinated polymer PPESK (S:K = 1:1, Dalian Polymer New Materials Co. Ltd.) as shown in Fig. 8 is 1.6794, which is much greater than that of FDHPZ/PFBP which has a much higher fluorine content.

4. Conclusion

A new fluorinated bisphenol-like monomer, 4-(2-fluoro-4-hydroxyphenyl)-phthlazin-1(2*H*)-one (FDHPZ) was synthesized from 3-fluorophenol, phthalic anhydride and hydrazine hydrate. FDHPZ and its intermediate 2-(2-fluoro-4-hydroxybenzoyl)-benzoic acid were characterized by NMR and FTIR spetra. Fours polymers FDHPZ/DFBP, FDHPZ/BCS, FDHPZ/BFBB and FDHPZ/PFBP were prepared from polycondensation reactions with 4,4′-difluorobenzophenone (DFBP), bis(4-chlorophenyl) sulfone (BCS), 1,4-bis(4-fluorobenzoyl)-benzene (BFBB) and perfluorobiphenyl (PFBP), respectively. To avoid crosslinking, the polycondensation between FDHPZ and PFBP was carried out on mild conditions, and a multifluorinated poly(phthalazinone ether) FDHPZ/PFBP was successfully obtained. These polymers show good solubility in common aprotic organic solvents. The T_g and T_{d5} measured by DSC and TGA show distinguished thermal properties of these polymers. Films of 0.8–5.2 μm in thickness were prepared by spin coating from the 15–20 wt% NMP solutions on silicon substrates. Their TE mode refractive indices were measured with a Prism Coupler. The thermal and optical properties indicate that they are promising as materials for optical communications.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (NSFC) General Project No. 50143013.

References

[1] Liu YJ, Jian XG, Liu SJ. J Appl Polym Sci 2001;82:823–6.

[2] Meng YZ, Hlil AR, Hay AS. J Polym Sci Polym Chem 1999;37:1781–8.

[3] Meng YZ, Hay AS, Tjong SC. J Appl Polym Sci 1998;68:137–43.

[4] Hay AS, Meng YZ, Zheng HB, Jian XG. CHN Patent Appl No 93109179 1993.

[5] Hay AS, Meng YZ, Zheng HB, Jian XG. CHN Patent Appl No 93109180 1993.

[6] Liao GX, Jian XG, Guo XY, Wang JY. Chin Chem Lett 2002;13(7):607–8.

[7] Gao Y, Robertson GP, Guiver MD, Jian XG. J Polym Sci Polym Chem 2003;41:497–507.

[8] Xiao GY, Sun GM, Yan DY, Zhu PF, Tao P. Polymer 2002;43:5335–9.

[9] Zhang SH, Yang DL, Jian XG. Chem J Chin Univ 2002;23(12):2382–5.

[10] Berard N, Paventi M, Chan KP, Hay AS. Macromol Symp 1994;77:379–88.

[11] Yoshida S, Hay AS. Macromolecules 1995;28(7):2579–81.

[12] Yoshida S, Hay AS. Macromolecules 1997;30(8):2254–61.
[13] Jian XG, Zhu XL, Chen LZ. J Dalian U Technol 1999;39(5):629–34.
[14] Jian XG, Zhu XL, Chen LZ. Chem J Chin Univ 2001;22(11):1932–5.
[15] Chen LZ, Jian XG. Polym Mater Sci Engng 2000;16(5):158–60.
[16] Chen LZ, Jian XG, Wang ZY. Polym Mater Sci Engng 2001;17(4): 44–7.
[17] Chen LZ, Jian XG, Guo XY. Chin Plast Ind 1999;27(2):31–2.
[18] Chen LZ, Jian XG, Gao X, Zhang SH. Chin J Appl Chem 1999;16(3): 106–8.
[19] Jian XG, Chen LZ, Zhu XL. Chin J Mater Res 2001;15(5):500–4.
[20] Lee HJ, Lee EM, Lee MH, Oh MC, Ahn JH, Han SG, Kim HG. J Polym Sci Polym Chem 1998;36:2881–7.
[21] Lee HJ, Lee MH, Oh MC, Ahn JH, Han SG. J Polym Sci Polym Chem 1999;37:2355–61.
[22] Kim JP, Lee WY, Kang JW, Kwon SK, Kim JJ, Lee JS. Macromolecules 2001;34(22):7817–21.
[23] Ding JF, Liu FT, Li M, Day M, Zhou M. J Polym Sci Polym Chem 2002;40:4205–16.
[24] Matsuura T, Ando S, Sasaki S. Fluoropolymers 2: properties. New York: Plenum Press; 1999. p. 305–50.
[25] Ando S, Kaino T, Sasaki S. Fluoropolymers 2: properties. New York: Plenum Press; 1999. p. 277–303.
[26] Han K, Lee HJ, Rhee TH. J Appl Polym Sci 1999;74:107–12.
[27] Bosc D, Rousseau A, Morand A, Benech P, Tedjini S. Opt Mater 1999;13:205–9.
[28] Lv CL, Cui ZC, Yang B. Chin J Appl Chem 2001;18(5):342–6.
[29] Liu JH, Liu HT, Cheng YB. Polymer 1998;39(22):5549–52.
[30] Kim JJ, Kang JW. Proc SPIE-Int Soc Opt Engng 1999;3799: 202–13.
[31] Cheng L, Jian XG, Mao SZ. J Polym Sci Polym Chem 2002;40: 3489–96.
[32] Olah GA. Friedel–Crafts and related reactions, III acylation and related reactions, part 1. New York: Wiley; 1964. Chapter XXXIV.
[33] Mercer FW, Fone MM, McKenzie MT. J Polym Sci Polym Sci 1997; 35:521–6.
[34] Garcia C, Lozano AE, De La Campa JG, De Abajo J. J Polym Sci Polym Chem 2002;40:2601–8.
[35] Hergenrother PM, Jensen BJ, Havens SJ. Polymer 1988;29:358–69.