Synthesis and Characterization of Phthalazinone Containing Poly(arylene ether)s, Poly(arylene thioether)s, and Poly(arylene sulfone)s via a Novel N−C Coupling Reaction

S. J. Wang,[‡] Y. Z. Meng,[*,†,‡] A. R. Hlil,[§] and A. S. Hay[§]

School of Physics & Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, P.O. Box 1122, Guangzhou 510650, P. R. China, and Department of Chemistry, McGill University, 801 Sherbrooke West, Montreal, Quebec, H3A 2K6, Canada

Received April 28, 2003; Revised Manuscript Received September 26, 2003

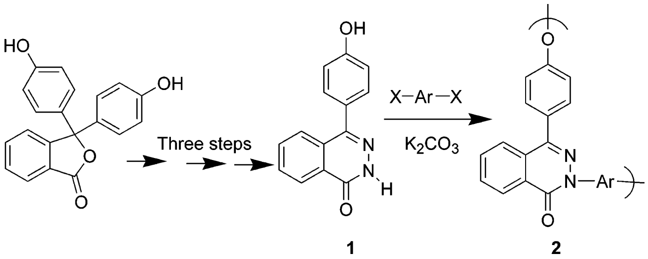
ABSTRACT: High molecular weight phthalazinone containing poly(arylene ether)s, poly(arylene thioether)s, and poly(arylene sulfone)s with very high glass transition temperatures were synthesized from a series of new bisphthalazinone monomers. Bisphthalazinone monomers **7a**−**c** and **8c** were synthesized from 2-(4-chlorobenzoyl)benzoic acid in high yields. Poly(arylene ether)s and poly(arylene thioether)s were synthesized in *N,N′*-dimethylacetamide (DMAc) in the presence of anhydrous K_2CO_3 by a nucleophilic substitution reaction between these bisphthalazinone monomers and activated difluoro compounds. The poly(arylene thioether)s were further oxidized to form poly(arylene sulfone)s, which would be very difficult, if not impossible, to synthesize by other method. All synthesized polymers have extremely high T_gs and thermal stability as determined from DSC and TGA analysis. Poly(arylene sulfone)s have the highest T_gs ranging from 288 to 333 °C. The poly(arylene ether)s and poly(arylene thioether)s described, having inherent viscosities in the range of 0.37−1.01 dL/g, are soluble in chlorinated solvents such as chloroform and could be cast into flexible films from solution. In contrast to their precursors, the poly(arylene sulfone)s described are not soluble in chloroform but are soluble in dipolar aprotic solvents such as DMAc.

Introduction

Poly(arylene ether)s, poly(arylene thioether)s and poly(arylene sulfone)s are three classes of high performance polymers that have attracted much attention as structural materials in automobile and electronic industries due to their excellent mechanical strength per unit weight, highly thermal stability, chemical resistance, and good insulating properties.[1] However, most high performance polymers are very difficult to be melt processed due to their highly rigid molecular structure. An alternative processing method for these polymers is the solution method. Therefore, the development of readily attainable precursors of high performance polymers that would produce soluble polymers will undoubtedly broaden the practical applications of these materials. In this sense, considerable research effort has been devoted to develop new polymers containing heterocyclic moieties since many of them possess outstanding mechanical strength and high thermooxidative stability because of their good solubility in common organic solvents. Accordingly, many kinds of heterocyclic polymers, such as poly(ether imide)s,[2] poly(aryl ether phenylquinoxaline)s,[3] and poly(aryl ether phthalazine)s,[4] have been synthesized.

Polymers with N−N bond in the polymer chain,[5] as well as polymers whose heterocyclic ring contains N−N linkage,[6] have been previously synthesized. However, there are very few reports about the synthesis of phthalazinone containing polymers in the literature. Imai reported the synthesis of polypyridazinophthalazines, which exhibit high thermal stabilities, from dibenzoylphthalic acids and bisarylhydrazines.[7]

Scheme 1. Synthesis of 1,2-Dihydro-4-(4-hydroxyphenyl)(2*H*)-phthalazin-1-one and Polymer 2



Methods to form the C−N bond in wholly aromatic compounds are limited to rather vigorous processes which are copper-mediated reactions.[8,9] A heterocyclic monomer, 1,2-dihydro-4-(4-hydroxyphenyl)(2*H*)-phthalazin-1-one (**1**), was synthesized from phenolphthalein via a multistep reaction years ago by Hay et al.[10,11] High-temperature polymers with excellent thermal and hydrolytic stability can be synthesized by polymerization with activated dihalo compounds (Scheme 1). The polymerization has been confirmed to proceed via a novel N−C coupling reaction by spectroscopic studies in previous works.[12] The result proved that the phthalazinone N−H groups behave like phenolic OH groups. Similarly, the compounds with two phthalazinone groups should react like bisphenols in nucleophilic aromatic substitution reactions. The resulting polymers would be expected to be thermally stable at high temperatures since similar polymers have been previously synthesized by an alternative route.[10] Yoshida extended the phthalazinone chemistry by synthesizing bisphthalazinones **3** that could be polymerized with activated diaryl compounds (Scheme 2).[13,14] However,

---

[*] Corresponding author. Telephone: +8620-84114113. Fax: +8620-85232337. E-mail: mengyz@yahoo.com.

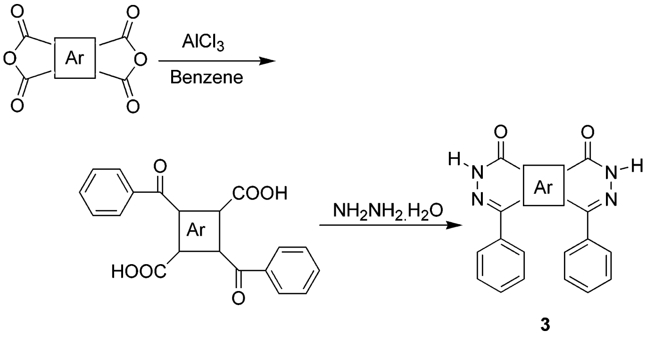
[†] Sun Yat-Sen University.

[‡] Chinese Academy of Sciences.

[§] McGill University.

10.1021/ma030246z CCC: $27.50

Scheme 2. Synthesis of Bisphthalazinone 3 from Aryl Dianhydride



many of the monomers that he synthesized were obtained in poor yields and many of the polymers were not very soluble since they had very rigid structures so that high molecular weight polymers were not obtained.

More recently, we have synthesized hydroxylphthalaznone monomer **1** from 2-(4-chlorophenylbenzoyl)benzoic acid (**4**),[15] which was synthesized previously via a Friedel–Crafts reaction and is commercially available. The chlorine group of 2-(4-chlorophenylbenzoyl)benzoic acid (**4**) was readily hydrolyzed to give **5** and, then, converted to hydroxylphthalazinone **1**. This approach is an easier and cheaper method to synthesize **1** when compared with previous synthetic methods from phenolphthalein by the reaction with hydrazine monohydrate.[16] Accordingly, high molecular weight polyphthalazinones have been synthesized from as-prepared **1**. The detailed synthetic procedure will be published else where.[15] Similarly, the chlorine group in **4** is expected to be easily displaced by other nucleophilic groups, such as bisphenolate and bisthiophenalate anion. In this work, several bisphthalazinone monomers were synthesized, and then, the phthalazinone containing poly(arylene ether)s and poly(arylene thioether)s have been obtained by polymerization with activated difluoro compounds. Moreover, the poly(arylene sulfone)s have been prepared by the oxidation of the corresponding poly(arylene thioether)s with hydrogen peroxide in acid medium.

Experimental Section

Materials. 2-(4-Chlorophenylbenzoyl)benzoic acid **4** was prepared from phthalic anhydride and chlorobenzene. 4,4′-oxybis(benzenethiol) was prepared according to reported procedures.[16] 4,4′-Dihydroxydiphenyl ether, 4,4′-isopropylidenediphenol (BPA) and 4,4′-(hexafluoroisopropylidene) diphenol (6F–BPA) were purchased from Aldrich Chemical Co. and used as received. 4,4′-Bis(4-fluorophenyl) sulfone (**9d**), 4,4′-difluorobenzophenone (**9e**), and 1,3-bis(4-fluorobenzoyl)benzene (**9f**) were obtained from Acros Chemical Inc. and recrystallized from toluene prior to use. Anhydrous potassium carbonate, hydrazine monohydrate, sulfuric acid, hydrogen peroxide 30% aqueous solution, reagent-grade *N*-methylpyrolidinone (NMP), *N*,*N*′-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO), were obtained from commercial sources and used as received unless otherwise noted.

Instrumentation. The ^{1}H NMR spectra were recorded with a Bruker NMR instrument (Model: DRX 400 MHz) using dimethyl-d_6 sulfoxide (DMSO-d_6) as a solvent and are listed in parts per million downfield from tetramethylsilane (TMS). Melting points were obtained using a melting point apparatus. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI–TOF–MS) analyses were performed on a Bruker Reflex MALDI–TOF–MS. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer for C, H, N, and S determinations. The glass transition temperatures (T_gs) were determined using a modulated TA DSC instrument (model MDSC 2910) at a heating rate of 20 °C/min under a nitrogen flow of 80 mL/min. The T_g values are reported from the second scan after first heating and quenching. The T_g was taken from the midpoint of the change in the slope of the baseline. The 5% weight loss temperatures were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 20 °C min^{-1} in N_2. Inherent viscosities (η_{inh}) of the synthesized polymers were obtained with a calibrated Ubbelohde viscometer. Measurements were performed in chloroform at 25 °C at a concentration of 0.5 g/dL. Gel permeation chromatography (GPC) analyses were carried out on a Waters 510 HPLC equipped with 5 μm Phenolgel columns (linear, 4 × 500 Å) arranged in series with chloroform as a solvent and a UV detector at 254 nm.

Preparation of BPA Containing Dicarboxylic Acid 5a. To a flask equipped with a Dean–Stark trap were added 2-(4-chlorobenzoyl)benzoic acid **4** (2.99 g, 11.5 mmol) and BPA (1.31 g, 5.7 mmol) and dissolved in a mixed solvent of DMAc (7 mL) and toluene (7 mL) under nitrogen atmosphere. When a homogeneous solution was obtained, potassium carbonate (1.65 g, 12 mmol) was introduced into it. The mixture was heated to reflux until no further water was produced. The remaining toluene was then removed by distillation and the reaction was maintained for another 12 h at 170 °C. After cooling, the resulting mixture was diluted with 50 mL of H_2O and poured into diluted HCl to precipitate the product. The resulting white powders were filtered, dried, and recrystallized from aqueous glacial acetic acid: Yield: 84% (3.2 g). Mp: 213-215 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 1.67 (s, 6H), 6.98–7.97 (m, 24H). MALDI–TOF–MS: single peak found, 676.81; calcd for $C_{43}H_{32}O_8$, 676.71.

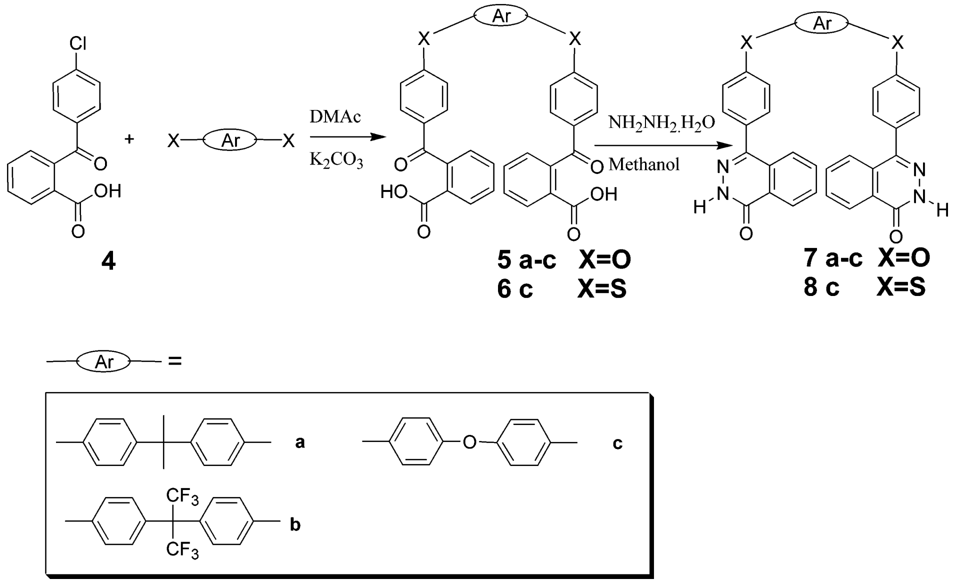
Preparation of BPA Containing Bisphthalazinone 7a. To a flask equipped with a Dean–Stark trap containing 3.34 g (5 mmol) of **5a** and 100 mL of methanol was slowly introduced 0.25 g (5 mmol) of hydrazine monohydrate. The reaction mixture was refluxed and stirred for 24 h at this temperature. At the beginning of the reaction, the reaction mixture appeared as a white emulsion. The mixture became clearer and clearer stepwise during the heating. The white colored compound **7a** started to precipitate out from the solution after 6 h. The reaction mixture was cooled and the precipitates were collected by filtration. The crude product was recrystallized from DMF as white powders: Yield: 97%. Mp: 320 °C. ^{1}H NMR (400 MHz DMSO-d_6) δ (ppm): 1.67 (s, 6H), 7.05 (d, 4H), 7.13 (d, 4H), 7.30 (d, 4H), 7.58 (d, 4H), 7.87 (d, 2H), 7.90 (m, 4H), 8.31(d, 2H), 12.82 (s, 2H). MALDI–TOF–MS: single peak found, 669.00; calcd for $C_{43}H_{32}N_4O_4$, 668.74. Anal. Calcd for $C_{43}H_{32}N_4O_4$ (%): C, 77.23; H, 4.82; N, 8.38. Found: C, 76.54; H, 5.01; N, 8.30.

Preparation of 6F–BPA Containing Dicarboxylic Acid 5b. This compound was prepared by the reaction of 2-(4-chlorobenzoyl)benzoic acid with 6F-BPA in the presence of anhydrous potassium carbonate using the same procedure described for **5a**. The crude product was recrystallized from aqueous glacial acetic acid: Yield: 87%. Mp: 245 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.13 (d, 4H), 7.20 (d, 4H), 7.40 (m, 6H), 7.64–7.72 (m, 8H), 7.98 (d, 2H). MALDI–TOF–MS: single peak found, 784.96; calcd for $C_{43}H_{26}F_6O_8$, 784.65.

Preparation of 6F-BPA Containing Bisphthalazinone 7b. Compound **7b** was synthesized by reacting keto acid **5b** with hydrazine monohydrate in methanol using the same procedure described for **7a**. The crude product was recrystallized from DMF as white powders: Yield: 98%. Mp: 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.22 (d, 4H), 7.27 (d, 4H), 7.42 (d, 4H), 7.65 (d, 4H), 7.73 (m, 2H), 7.90 (m, 4H), 8.34 (m, 2H), 12.85 (s, 2H). MALDI–TOF–MS: single peak found, 776.48; calcd for $C_{43}H_{26}F_6N_4O_4$, 776.68. Anal. Calcd for $C_{43}H_{26}F_6N_4O_4$ (%): C, 66.50; H, 3.37; N, 7.21. Found: C, 63.91; H, 3.89; N, 6.88.

Preparation of Biphenyl Ether Containing Dicarboxylic Acid 5c. This compound was prepared by the reaction of 2-(4-chlorobenzoyl)benzoic acid with 4,4′-dihydroxydiphenyl ether using the same procedure described for **5a**. The crude product was recrystallized from aqueous glacial acetic acid:

Scheme 3. Synthesis of Bisphthalazinone Monomers 7a−c and 8c



Yield: 85%. Mp: 120 °C. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.11−8.34 (m, 24H). MALDI−TOF−MS: single peak found, 650.87; calcd for $C_{40}H_{26}O_9$, 650.63.

Preparation of Biphenyl Ether Containing Bisphthalazinone 7c. Compound **7c** was prepared by the reaction of keto acid **5c** with hydrazine monohydrate in methanol using the same procedure described for **7a**. The crude product was recrystallized from DMF as a white powder: Yield: 97%. Mp: 335 °C. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.12−7.20 (m, 12H), 7.58−7.60 (m, 6H), 7.89−7.91 (m, 4H), 8.32 (m, 2H), 12.82 (s, 2H). MALDI−TOF−MS: single peak found, 642.91; calcd for $C_{40}H_{26}N_4O_5$, 642.66. Anal. Calcd for $C_{40}H_{26}N_4O_5$ (%): C, 74.76; H, 4.08; N, 8.72. Found: C, 74.66; H, 4.10; N, 8.76.

Preparation of Oxybis(benzenethiol) Containing Dicarboxylic Acid 6c. This compound was prepared by the reaction of 2-(4-chlorobenzoyl)benzoic acid with 4,4′-oxybis(benzenethiol) in the presence of anhydrous potassium carbonate using the same procedure described for **5a**. The reaction mixture should be protected with a nitrogen flow because the thiophenol is easily oxidized. The crude product was recrystallized from aqueous glacial acetic acid: Yield: 95%. Mp: 208 °C. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.17−7.97 (m, 24H). MALDI−TOF−MS: single peak found, 682.80; calcd for $C_{40}H_{26}O_7S_2$, 682.76.

Preparation of Oxybis(benzenethiol) Containing Bisphthalazinone 8c. Compound **8c** was prepared by the reaction of keto acid **6c** with hydrazine monohydrate in methanol using the same procedure described for **7a**. The crude product was recrystallized from DMF as a white powder: Yield: 98%. Mp: 298 °C. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.17 (d, 4H), 7.36 (d, 4H), 7.57 (m, 8H), 7.68 (m, 2H), 7.88 (m, 4H), 8.32 (m, 2H), 12.85 (s, 2H). MALDI−TOF−MS: single peak found, 674.95; calcd for $C_{40}H_{26}N_4O_3S_2$, 674.79. Anal. Calcd for $C_{40}H_{26}N_4O_3S_2$ (%): C, 71.20; H, 3.88; N, 8.30; S, 9.50. Found: C, 71.35; H, 3.78; N, 8.45; S, 9.70.

General Procedure for the Synthesis of Poly(arylene ether)s and Poly(arylene thioether)s. Poly(arylene ether)s and poly(arylene thioether)s were synthesized in a dry 25 mL three-neck flask equipped with a nitrogen inlet, a Dean−Stark trap fitted with a condenser, and a magnetic stirrer. A typical procedure for the synthesis of the polymers is given as follows.

Polymer **10ad** is selected as an example. To a dried flask containing 0.254 g of bis(4-fluorophenyl) sulfone **9d** (0.0010 mol) were introduced 0.6687 g (0.0010 mol) of bisphthalazinone monomer **7a**, 6 mL of toluene, 6 mL of DMAc, and 0.1935 g of anhydrous potassium carbonate (0.0014 mol). The resulting mixture was slowly heated to reflux (145 °C) with stirring. A strong nitrogen flow was maintained to azeotrope off the water formed with toluene. After 2 h of dehydration, the temperature was increased to 170−180 °C (oil bath temperature) by stepwise removing toluene from the Dean−Stark trap. After 20 h polymerization, the solution was cooled to 100 °C followed by diluting with 4 mL of DMAc and, thereafter, precipitated into methanol (200 mL) containing a few drops of concentrated HCl. The resulting fibrous polymer was redissolved in chloroform (40 mL), filtered to remove the inorganic salts, and precipitated into 200 mL of methanol. The purified product in the form of fine white fiber was dried at 130 °C under vacuum for 24 h. A total of 0.865 g of polymer **10ad** was obtained in high yield of 89%.

Anal. Calcd for polymer **10ad** $(C_{55}H_{38}N_4O_6S)_n$ (%): C, 74.81; H, 4.34; N, 6.35; S, 3.63. Found: C, 74.91; H, 4.54; N, 6.25; S, 3.66.

General Procedure for the Synthesis of Poly(arylene sulfone)s.[17,18] Polymer **12cd** is taken as an example. The synthesis was conducted in a 25 mL round-bottom flask. The poly(arylene thioether) **11cd** (0.5 g) was suspended in 10 mL of 90% formic acid by magnetic stirring. The mixture was then heated to 50 °C and 5 g of 30% aqueous hydrogen peroxide was dropwise added. After the reaction was stirred for 6 h, the product was filtered, washed with methanol, and dried at 130 °C under vacuum for 24 h to give poly(arylene sulfone) **12cd**.

Results and Discussion

Monomer Synthesis. Dicarboxylic acids **5a−c** containing an ether linkage were synthesized from 2-(4-chlorophenylbenzoyl)benzoic acid **4** in two steps as shown in Scheme 3. First, the keto dicarboxylic acids **5a−c** were prepared by the nucleophilic substitution reaction of **4** with different biphenols under the same conditions as the formation of poly(arylene ether)s.[19−22] The bisphthalazinone monomers **7a−c** can be then synthesized from **5a−c** and hydrazine monohydrate in refluxing methanol. Figure 1 shows the H−H cosy NMR spectrum of bisphthalazinone monomer **7b**, indicating the structure of **7b** as shown in Scheme 3.

Similarly, the thioether bonds containing bisphthalazinone monomer **8c** can be prepared by the reaction of 2-(4-chlorophenylbenzoyl)benzoic acid (**4**) with 4,4′-oxybis(benzenethiol) as shown in Scheme 3. 4,4′-Oxybis(benzenethiol) was synthesized from diphenyl ether according to the reported procedure.[20] In the presence of potassium carbonate, the thiophenoxide anions formed

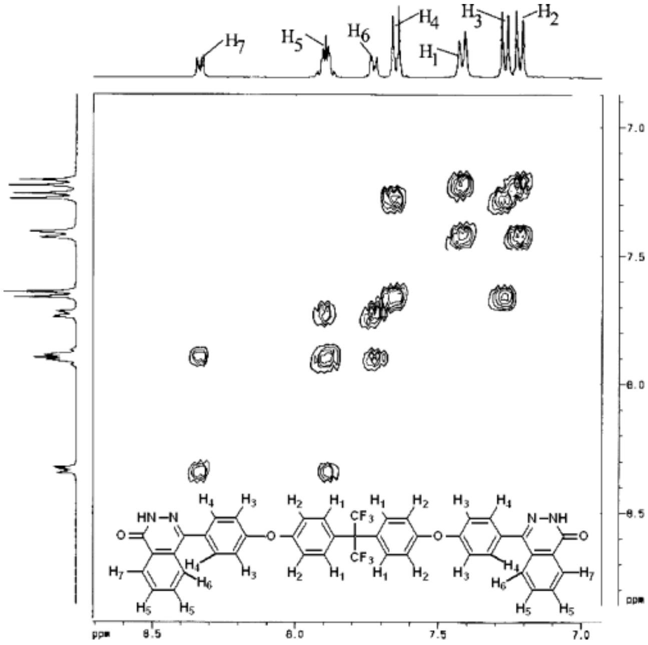


Figure 1. H−H cosy NMR spectrum of bisphthalazinone monomer **7b**.

are nucleophiles with higher activity than phenoxide, and therefore, can replace the reactive chlorine group of 2-(4-chlorophenylbenzoyl)benzoic acid (**4**). However, more careful attention should be paid to protect the reaction under nitrogen atmosphere because thiophenoxide anions can be easily oxidized during the reaction. The keto acid **6c** was synthesized in 10 h at 140 °C under the same condition as the syntheses of **5a**−**c**. Finally, monomer **8c** was obtained in high yield after the reaction of **6c** with hydrazine monohydrate in refluxing methanol.

All bisphthalazinone monomers are soluble in dipolar aprotic solvents such as DMSO and DMAc. To obtain high molecular weight polymers, the synthesized monomers have to be recrystallized from DMAc or DMF.

Syntheses of Poly(arylene ether)s and Poly(arylene thioether)s. As depicted in Scheme 4, poly(arylene ether)s and poly(arylene thioether)s were synthesized by the reaction of bisphthalazinone monomers **7a**−**c** or **8c** with 4,4′-bis(4-fluorophenyl) sulfone (**9d**), 4,4′-difluorobenzophenone (**9e**), or bis(4-fluorobenzoyl)-benzene (**9f**) in a dipolar aprotic solvent of DMAc.[19−20] During the polymerization, the aza-nitrogen anion that formed by the reaction with potassium carbonate, underwent a displacement reaction with activated aryl halides. In this case, the phthalazinone =NH groups of phthalazinone monomers behave like phenolic −OH groups.

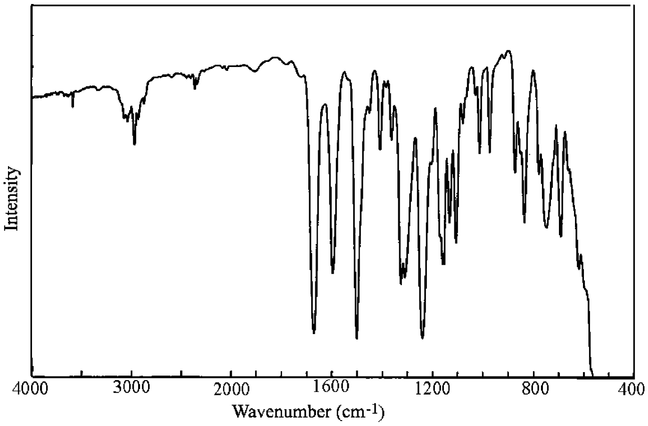


Figure 2. FTIR spectrum of polymer **10ad**.

Figure 2 shows the FTIR spectrum of poly(arylene ether) **10ad**. It can be seen that the absorption due to the carbonyl group (*O*=*C*−N=) clearly appears at 1666 cm^{-1} in the polymer with a lactam structure, but is completely absent in the lactim structure where an absorption due to −O−*C*=*N*− appears at about 1610 cm^{-1}.[22] The FTIR spectra of other polymers give the same results as polymer **10ad**, demonstrating that the synthesized poly(arylene ether)s and poly(arylene thioether)s have main-chain structures as shown in Scheme 4. The aza-nitrogen anions (=N^-), which were produced by reacting with potassium carbonate, can attack the activated aryl halides with the elimination of corresponding fluorides. High molecular weight poly(arylene ether)s and poly(arylene thioether)s with inherent viscosities ranging from 0.37 to 1.01 dL/g (Table 1) were obtained. As can be seen in the table, all synthesized polymers are soluble in common organic solvents such

Scheme 4. Synthesis of Poly(arylene ether)s 10a−c and Poly(arylene thioether) 11c

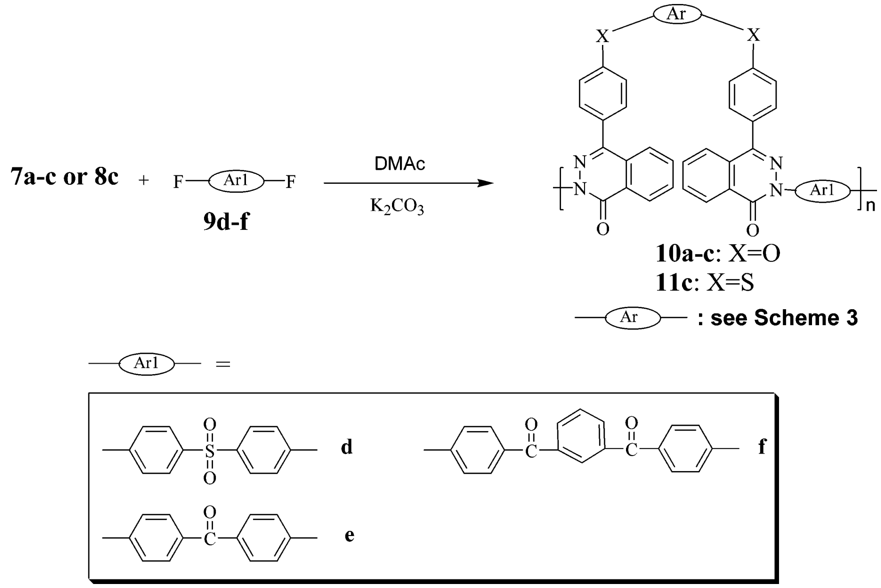


Table 1. Properties of the Bisphthalanone Containing Polymers

polymer	η_{inh} [a] (dL/g)	M_n [c]	M_w	P_d	T_g [e]	TGA (5%)[f]
10ad	0.64	27 716	53 706	1.93	230	490
10ae	0.67	38 845	85 492	2.2	250	494
10af	0.91	37 852	93 547	2.4	235	506
10bd	0.65	32 835	62 720	1.9	273	522
10be	0.37	25 071	50 320	2.0	254	518
10bf	0.41	31 112	55 299	1.77	232	514
10cd	0.42	24 066	47 522	1.97	260	418
10ce	0.45	55 326	115 823	2.01	235	503
10cf	0.68	16 824	36 525	2.17	227	465
11cd	0.57	48 642	88 428	1.81	259	465
11ce	0.40	20 497	41 856	2.04	237	507
11cf	1.01	63 403	151 167	2.38	229	505
12cd	0.69[b]	*d*	*d*	*d*	333	505
12ce	0.41[b]	*d*	*d*	*d*	306	500
12cf	0.73[b]	*d*	*d*	*d*	288	495

[a] η_{inh} was measured at a concentration of 0.5 g/dL in chloroform at 30 °C. [b] Or in NMP at 30 °C. [c] Molecular weight was determined by GPC in chloroform with polystyrene as standard. [d] Not obtained. [e] T_g was determined by DSC at a heating rate of 20 °C min^{-1} under nitrogen. [f] Reported for 5% weight loss temperature at a heating rate of 20 °C under nitrogen.

as chloroform because of the existence of flexible —O— or —S— linkages in the backbone of these polymers. Also due to these flexible linkages, high molecular weight polymers, ranging from 12 000 to 150 000 determined by the GPC technique were achieved as shown in Table 1.

Poly(arylene sulfone)s. It is well-known that aryl thioethers can be readily oxidized to produce aryl sulfones. A typical example is the synthesis of poly(1,4-phenylene sulfone) by the oxidation of poly(thio-1,4-phenylene) with hydrogen peroxide in acid medium.[16,20] By using the same method, the poly(arylene thioether)s were oxidized to produce poly(arylene sulfone)s. With the advances in synthetic methods for the preparation of poly(arylene thioether)s,[21,22] many poly(arylene sulfone)s can be synthesized via this reaction, which can otherwise not be easily synthesized via other methods. This is because it is rather difficult to obtain high molecular weight poly(arylene sulfone)s due to their poor solubilities. In this work, poly(arylene thioether)s containing bisphthalazinone moiety were also readily oxidized into poly(arylene sulfone)s with hydrogen peroxide in 90% formic acid.

As depicted in Scheme 4, a series of poly(arylene sulfone)s were obtained after 6 h of reaction at 50 °C. The completion of the oxidation was followed and confirmed by ^{1}H NMR. Owing to the strong electron-withdrawing property of the sulfone group, the proton signals adjacent to the sulfone groups shifted to a much lower field compared with their precursor. A comparison of ^{1}H NMR spectra of **11ce** and **12ce** is shown in Figure 3. Any sulfoxide groups present in the polymers would result in a strong exothermal peak showing up in the DSC scans. However, the DSC scans for the poly(arylene sulfone) **12c** (synthesis shown in Scheme 5) showed the absence of such an exothermal peak, indicating the absence of the sulfoxide group formed due to incomplete oxidation. The DSC traces for polymers **12cd**, **12ce**, and **12cf** are shown in Figure 4, respectively.

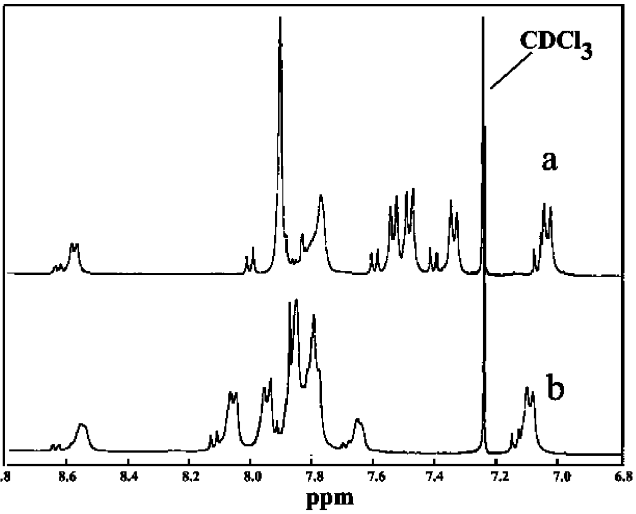


Figure 3. Comparison between ^{1}H NMR of poly(arylene thioether) and poly(arylene sulfone)s: (a) polymer **11ce**; (b) polymer **12ce**.

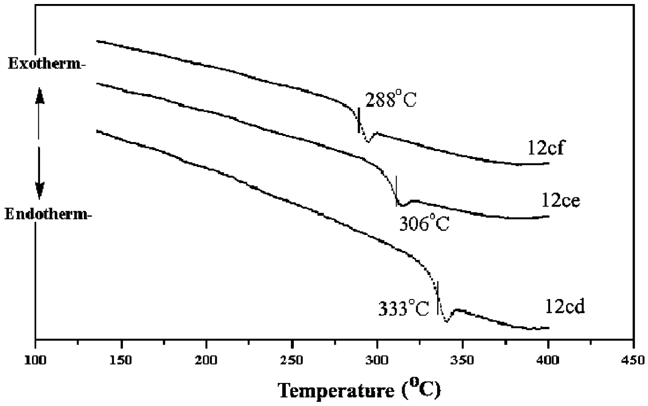
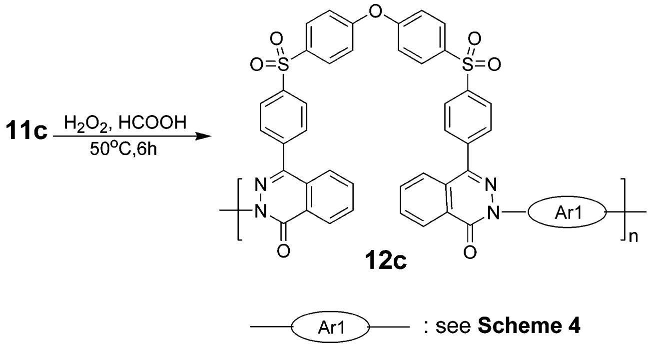


Figure 4. DSC traces for poly(arylene sulfone)s **10c**.

Scheme 5. Synthesis of Poly(arylene sulfone) 12c from Poly(arylene thioether) 11c



Properties of the Synthesized Polymers. It has been well documented that the wholly aromatic polymers including poly(arylene ether)s and poly(arylene thioether)s exhibit excellent mechanical properties. Therefore, poly(arylene ether)s containing phthalazinone moiety also showed superior mechanical properties.[12b] Because of the flexible linkages in the polymer backbone, the poly(arylene ether)s and poly(arylene thioether)s are generally soluble in common organic solvents and can be cast into transparent and tough films from chloroform. However, the poly(arylene sulfone) **12c** is not soluble in chlorinated solvents due to its very rigid sulfone linkages compared with its poly(arylene thioether) precursor. Nevertheless, the poly(arylene sulfone) **12c** can be dissolved in dipolar aprotic solvents such as NMP.

The glass transition temperatures (T_gs) of the polymers listed in Table 1 were determined by differential scanning calorimetry (DSC). Typical DSC traces for these poly(arylene sulfone)s are depicted in Figure 4.

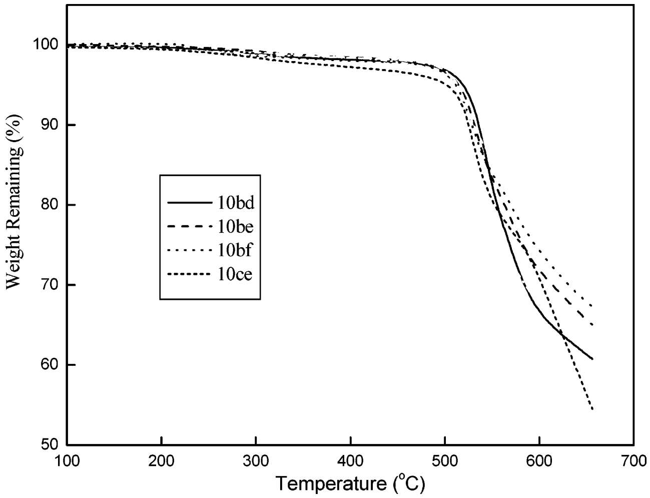


Figure 5. TGA thermogram curves for polymers **10bd**, **10be**, **10bf**, and **10ce** under nitrogen atmosphere.

All polymers had T_gs greater than 230 °C. Owing to the incorporation of the rigid sulfone group, the T_gs of these poly(arylene sulfone)s are significantly (60−74 °C) higher than those of their poly(arylene thioether) precursors (Table 1). For example, poly(arylene thioether) **11ce** has a T_g of 237 °C, while poly(arylene sulfone) **12ce** has a T_g of 306 °C. Poly(arylene sulfone) **12cd** exhibits the highest T_g of 333 °C. Besides the very high T_gs of these polymers, they still maintain the good solubility in organic solvents for easier solution processability.

The TGA thermograms of the poly(phthalazinone)s are shown in Figure 5. All these polymers exhibited a similar pattern of decomposition with slight weight loss below 450 °C. These phthalazinone moiety containing poly(arylene ether)s, poly(arylene thioether)s and poly(arylene sulfone)s possess highly thermal stabilities with 5% weight loss temperatures higher than 500 °C.

Conclusions

A series of bisphthalazinone monomers were successfully synthesized from 2-(4-chlorobenzoyl) phthalic acid. These new monomers behave like biphenols when reacting with activated aryl halides. High molecular weight phthalazinone containing poly(arylene ether)s and poly(arylene thioether)s were prepared from the bisphthalazinones and activated aryl halides via the formation of N−C bonds. The poly(arylene thioether)s can be oxidized to produce poly(arylene sulfone)s by using hydrogen peroxide. All these phthalazinone-containing polymers possess very high glass transition temperatures and excellent thermostabilities. The poly(arylene ether)s and poly(arylene thioether)s are soluble in chlorinated solvents such as chloroform, while the poly(arylene sulfone)s are only soluble in dipolar aprotic solvents such as *N*,*N*′-dimethylacetamide.

Acknowledgment. We thank the National High Technology Research & Development 863 Program (Grant No: 2003AA302410), the Natural Sciences & Engineering Research Council of Canada, the Natural Science Foundation of China (Grant No. 50203016), the Guangdong Natural Science Foundation of China (Project Grant No. 000941, Key Project Grant No. 010525, and Team Project Grant No. 015007), and the Guangdong Province Sci & Tech Bureau (Key Strategic Project Grant No. A1100402) for financial support of this work.

References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker Inc.: New York, 1980.
(2) White, D. M.; Takekoshi, T.; Williams, F. J., II; Relles, M.; Donahue, P. E., II; Klopfer, I.; Loucks, G. R.; Manello, J. S.; Mathews, R. O.; Schluenz, R. W. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1981**, *19*, 1635.
(3) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1990**, *23*, 1561.
(4) Singh, R.; Hay, A. S. *Macromolecules* **1992**, *25*, 1033.
(5) Ghassemi, H.; Hay, A. S. *Macromolecules* **1993**, *26*, 5824.
(6) Jain, S. R.; Sridhara, K.; Thangarathesvaran, P. M. *Prog. Polym. Sci.* **1993**, *18*, 997.
(7) Imai, Y.; Ueda, M.; Aizawa, T. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1976**, *14*, 2797.
(8) For example: Bacon, R. G. R.; Karim, A. *J. Chem. Soc., Perkin. Trans. 1* **1972**, 272.
(9) Recent example of N-arylation: Stabler, S. R.; Jahangir *Synth. Commun.* **1994**, *24* (1), 123.
(10) Berard, N.; Hay, A. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1), 148.
(11) Paventi, M.; Chan, K. P. *Pure Appl. Chem.* **1996**, *A33* (2), 133.
(12) (a) Meng, Y. Z.; Tjong, S. C.; Wang, S. J.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **2002**, *40*, 1441. (b) Meng, Y. Z.; Hlil, A. R.; Hay, A. S. *J. Polym. Sci., Part A* **1999**, *37*, 1781−1788.
(13) Yoshida, S.; Hay, A. S. *Macromolecues* **1997**, *30*, 2254−61.
(14) Yoshida, S.; Hay, A. S. *Macromolecues* **1995**, *28*, 2579−81.
(15) Wang, S. J.; Meng, Y. Z.; Tjong, S. C.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **2003**, *41*, 2481−2490.
(16) Ding, Y.; Hay, A. S. *J. Macromol. Sci.—Pure Appl. Chem.* **1997**, *A34* (3), 405−415.
(17) Mulhaupt, R.; Glatz, F. P.; Schultze, J. D.; Springer, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 203.
(18) Ding, Y.; Hlil, A. R.; Hay, A. S. *J. Polym. Sci., Part A: Polym Chem.* **1998**, *36*, 1201.
(19) Meng, Y. Z.; Abu-Yousef, I. A.; Hlil, A. R.; Hay, A. S. *Macromolecules* **2000**, *33*, 9185−9191.
(20) Meng, Y. Z.; Tjong, S. C.; Hay, A. S.; Wang, S. J. *J. Polym. Sci., Part A: Polym Chem. Ed.* **2001**, *39*, 3218−3226.
(21) Ding, Y.; Hay, A. S. *Macromolecules* **1997** *30*, 5612.
(22) Ding, Y.; Hay, A. S. *Macromolecules* **1997**, *30*, 2527.

MA030246Z