Synthesis of High Molecular Weight Fluorinated Poly(phthalazinone ether)s by Self-Condensation of an AB-Type Monomer and by Condensation of AA Monomers with Decafluorobiphenyl

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Two kinds of fluorinated phthalazinone monomers have been successfully synthesized. The fluorinated AB-type phthalazinone monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2H)-one was prepared by reaction of 2-(hydroxybenzoyl)benzoic acid with 1-(pentafluorophenyl)hydrazine. The fluorinated biphenol phthalazinone monomer 2,2′-(perfluorobiphenyl-4,4′-diyl) -bis(4-(4-hydroxy-phenyl)-phthalazin-1(2H)-one) was synthesized by reaction of 2-(hydroxybenzoyl)benzoic acid with (perfluorobiphenyl-4,4′-diyl)bis (hydrazine). High molecular weight fluorinated poly(phthalazinone ether)s were obtained by self-condensation polymerization of the AB-type phthalazinone monomer under mild reaction conditions or by condensation of the fluorinated bisphthalazinone monomer with decafluorobiphenyl. Detailed structural characterization of these monomers and polymers was carried out by a combination of ^{1}H-NMR, ^{19}F-NMR, and FTIR. The self-condensation poly(phthalazinone ether) has a T_g of 316°C, and a $T_{d,-5\%}$ of 491°C.

The poly(phthalazinone ether)s derived from AA phthalazinone monomers and decafluorobiphenyl have a similar T_g, 220°C, and $T_{d,-5\%}$s higher than 467°C. These fluorinated poly(phthalazinone ether)s are soluble in many common solvents, and can be cast from chloroform solutions into tough, flexible films. These polymers cross-link to give insoluble polymers when heated for a short time at 300°C.

Keywords: A-B type monomer; self-condensation; poly(phthalazinone ether); decafluorbiphenyl; fluorinated

1 Introduction

Phthalazinone-containing polymers are a new class of high-performance heterocyclic-containing condensation polymers. The rigid unsymmetrical phenyl phthalazinone moiety in the polymer backbone gives them good solubility, and high rigidity. In 1993 we first reported the polymerization reaction by a direct N-C coupling reaction of 1,2-dihydro-4-(4-hydroxyphenyl)-1(*2H*)-phthalazinone **1** with activated dihalocompounds, e.g. bis(4-fluorophenyl)sulfone, to synthesize poly((1,2-dihydro-l-oxo(*2H*)-phthalazine-2,4-diyl)-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) (**2**) (Scheme 1) (1). Since then, a large effort has been devoted to synthesizing phthalazinone-containing polymers possessing good solubility and excellent thermal stability. Poly (phthalazinone ether)s (2–7) polyamides (4), and polyimides

(8) have been reported. These high-performance polymers have promising applications in the aerospace, electronics industries and as fuel cell membrane material.

Fluorinated polymers have unique properties, such as low dielectric constant, refractive index, optical loss, and moisture absorption and high thermoxidative and chemical stability. Many kinds of fluorinated polymers have been synthesized for applications, such as coatings for microelectronics and optical waveguide devices, gas-separation membranes, films, and matrix resins in fiber-reinforced composites (9–14). Fluorinated poly(arylene ether)s, with their characteristic excellent thermooxidative stability, high-T_g, and outstanding mechanical properties, have been utilized in the aerospace and electronics industries where high performance is required (14–17). The poly(phthalazinone ether)s, represented by poly(phthalazinone ether ketone)s and poly(phthalazinone ether sulfone)s, are a new class of poly(arylene ether)s with excellent thermooxidativity, high T_g, good solubility, and outstanding mechanical properties (1–7). Recently, some fluorinated poly(phthalazinone ether)s, synthesized from phthalazinone-containing monomers by

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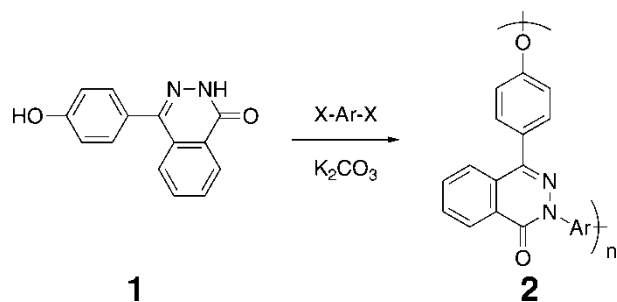
Sch. 1.   Synthesis of poly(phthalazinone ether) **2**.

reaction with perfluoro aromatics have been reported. Lu (18) synthesized a series of fluorinated polymers by polymerization of phthalazinone monomer **1** with perfluorobiphenyl. The molecular weight of the polymer was very low. Xiao (19) prepared a series of fluorinated poly(phthalazinone ether)s by reaction of a monofluorinated phthalazinone monomer with perfluorobiphenyl.

The self-condensation of AB-type monomers is an effective way to synthesize high molecular weight polymers. We previously reported (3) the synthesis of a series of AB-type phthalazinones. However, none of these AB monomers formed high molecular weight homopolymers, even under stringent conditions, because of premature precipitation of the polymer resulting from the high degree of crystallization of the oligomers. A preliminary report described the synthesis and polymerization of an A-B type monomer containing a pentafluorophenyl moiety **5** (20). This paper further describes the synthesis and polymerization of this fluorinated AB-type phthalazinone monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2H)-one **5**. Herein we also report the synthesis of the fluorinated biphenol phthalazinone monomer 2,2′-(perfluorobiphenyl-4,4′-diyl)bis(4-(4-hydroxyphenyl)-phthalazin-1(2H)-one). High molecular weight fluorinated poly(phtha1azinone ether)s were obtained by reaction of the phthalazinone monomer **1** and the fluorinated biphenol phthalazinone monomer with decafluorobiphenyl. All these fluorinated poly(phtha1azinone ether)s have good solubility in many kinds of common solvents and can be cast into clear, transparent, and tough films that have excellent thermal properties.

2   Experimental

2.1   Materials

2-(Hydroxybenzoyl)benzoic acid (**3**) was prepared by Ms. Antisar R. Hlil in our laboratory from phenolphthalein, and hydroxylamine as previously described (1). (Perfluorobiphenyl-4,4′-diyl)bis(hydrazine) was synthesized and purified according to the reported literature (21). 1-(Pentafluorophenyl)-hydrazine, hydrazine monohydrate, decafluorobiphenyl, phenolphthalein, hydroxylamine, potassium carbonate, were used as received. Reagent grade solvents *N*-methyl-2-pyrrolidinone

(NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1,1,2,2-tetrachloroethane (TCE), tetrahydrofuran (THF), CHCl$_3$, pyridine, sulpholane, absolute ethanol, benzene, were used as received.

2.2   Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer using CDCl$_3$ or DMSO-*d6* as solvent and tetramethylsilane as a reference. FTIR ATR spectra were obtained on a Perkin-Elmer FTIR spectrometer with a MIRACLE^{TM} ATR accessory with scan range $4000 \sim 525$ cm^{-1}, scan number 8, and resolution 4.0 cm^{-1}. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI-III TOF mass spectrometer with the instrument set in positive reflection mode to get higher resolution. The melting points were taken on a Fisher-Johns melting point apparatus at 70°C per minute or by DTA on a Seiko 5200 TG/DTA 220 instrument at a heating rate of 20°C/min. Monitoring the purity of the isolated monomers was done by high-performance liquid chromatography (HPLC, Milton Roy, CM 4000) with methanol as an eluent and a UV detector set at 254 nm. The T_g's of the polymers were obtained using a Seiko 5200 DSC 220 instrument at a heating rate of 20°C/min with a heating cooling heating circle scanning method. The T_g was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 5200 TG/DTA 220 instrument at a heating rate of 20°C/min under nitrogen. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. A water bath with a Julabo (Model type PC) heater was employed to control the temperature. Gel permeation chromatography (GPC) analyses were carried out on a Waters 510 HPLC equipped with 5 μm Phenogel columns (linear, 4×500 Å) arranged in a series with chloroform as a solvent and a UV detector at 254 nm.

2.2.1   4-(4-Hydroxyphenyl)-2-(pentafluorophenyl) phthalazin-1(2H)-one 5

2-(Hydroxybenzoyl)benzoic acid (**3**) (2.42 g, 0.01 mol) and 1-(pentafluorophenyl) hydrazine (**4**) (1.98 g, 0.01 mol) were heated in sulpholane (7 mL) at 110°C for 23 h. The reaction mixture was poured into hot water (50 mL) to give a pale ochre precipitate. The precipitate was filtered and washed thoroughly with water. The yield was 92.4%. The solid product was recrystallized from absolute ethanol to give colorless needles. ^{1}H-NMR (DMSO-*d6*): δ (ppm) 5.61 (m, 1H), 6.94−7.04 (s, 2H), 7.45−7.55 (s, 2H), 7.82−7.92 (S, 3H), 8.54−8.63 (m, 1H). ^{19}F NMR (CDCl$_3$): δ (ppm) −144.6 (2F), −153.4 (1F), and −162.1 (2F). Mp: 222°C. MALDI-TOF MS: 404.68 (M), 410.49 (M$^-$Li$^+$). HPLC (r.t.; purity): 2.78 (100%). FTIR (NEAT, cm^{-1}): 3237, 1645, 1610,

1572, 1512, 1473, 1335, 1284, 1269, 1228, 1201, 1172, 1078, 1038, 985, 946, 845, 809, 780, 745, 728, 688.

2.2.2 2,2′-(Perfluorobiphenyl-4, 4′-diyl)bis(4-(4-hydroxyphenyl)-phthalazin-1(2H)-one) 7

2-(Hydroxybenzoyl)benzoic acid **3** (2.42 g, 0.01 mol) and (perfluorobiphenyl-4,4′-diyl) -bis(hydrazine) **6** (1.79 g, 0.005 mol) were heated in absolute ethanol (10 mL) at reflux for 48 h. The product precipitated from the reaction system as a white precipitate. After boiling in a large amount of water, the purity of the chemical tested by HPLC showed only one peak belonging to the designed product. The yield was 57.2%. ^{1}H-NMR (DMSO-d6): δ (ppm) 6.90−6.96 (s, 4H), 7.47−7.52 (s, 4H), 7.85−7.90 (m, 2H), 8.00−8.10 (m, 4H), 8.45−8.50 (m, 2H), 9.94−9.96 (s, 2H). ^{19}F-NMR (CDCl$_3$): δ (ppm) −137.7 (4F), −144.3 (4F). MALDI-TOF MS: 773.39 (M), 779.19 (M$^-$Li$^+$). Mp: 378°C (DTA). HPLC (r.t.; purity): 2.86 (100%). FTIR (NEAT, cm^{-1}): 3272, 2360 (CO$_2$ peak), 1661, 1613, 1590, 1519, 1477, 1336, 1272, 1256, 1229, 1202, 1171, 1105, 977, 848, 785, 722, 686.

2.2.3 General Procedure for the Synthesis of Fluorinated Poly(phthalazinone ether)s

Polymerization reactions were typically carried out in a dry 25 mL three-neck flask equipped with a stir-bar, a Dean-Stark trap fitted with a condenser, and a nitrogen inlet.

2.2.4 Synthesis of fluorinated poly(phthalazinone ether)s 8a-e from AB monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2H)-one (5)

2.2.4.1 Synthesis of fluorinated poly(phthalazinone ether) 8a.
Initially, a 25 mL dried flask was flushed with nitrogen and charged with 4-(4-hydroxyphenyl)-2-(pentafluorophenyl) phthalazin-1(2H)-one **5** 0.4043 g (1 mmol), K$_2$CO$_3$ 0.1036 g (0.75 mmol), DMAc (2.5 mL) and toluene (3 mL). The reaction mixture was heated to 135°C for 2 h to remove water generated in the reaction with toluene. The reaction temperature was then raised to reflux temperature of DMAc, and the toluene was removed completely. The reaction mixture was kept at reflux temperature for 7 h. After cooling, the mixture was diluted with 10 mL DMAc and poured into 150 mL of methanol containing 5 vol% of hydrochloric acid to precipitate out polymer. The resulting polymer was dissolved in chloroform (25 mL), filtered through a thin layer of Celite to remove the inorganic salts, and reverse precipitated with 150 mL of methanol. After filtering, drying in a vacuum oven at 80°C for 12 h, gave 0.272 g white powder. The yield was 68.9%.

2.2.4.2 Synthesis of fluorinated poly(phthalazinone ether) 8b, 8d.
A 25 mL dried flask was flushed with nitrogen and charged with 4-(4-hydroxyphenyl)-2-(pentafluorophenyl) phthalazin-1(2H)-one **5** 0.4043 g (1 mmol), K$_2$CO$_3$ 0.1036 g (0.75 mmol), DMAc (2.5 mL). The reaction mixture was heated to 100 $\sim$ 105°C for 24 h to carry out the polymerization reaction. After cooling, the mixture was diluted with 10 mL DMAc and poured into 150 mL of methanol containing 5 vol% of hydrochloric acid to precipitate out polymer. The resulting fibrous polymer **8d** was dissolved in chloroform (25 mL), filtered through a thin layer of Celite to remove the inorganic salts, and reverse precipitated with 150 mL of methanol. After filtering, drying in a vacuum oven at 80°C for 12 h, gave 0.328 g white powder. The yield was 83.1%. When the reaction time was increased to 48 h polymer **8b** was synthesized, yield of **8b** 75.4%.

2.2.4.3 Synthesis of fluorinated poly(phthalazinone ether) 8c, 8e.
A 25 mL dried flask was flushed with nitrogen and charged with 4-(4-hydroxyphenyl)-2-(pentafluorophenyl) phthalazin-1(2H)-one **5** 0.4043 g (1 mmol), K$_2$CO$_3$ 0.1036 g (0.75 mmol), DMAc (2.5 mL) and benzene (3 mL). The reaction mixture was heated to 100°C for 2 h to remove water generated in the reaction with benzene. The reaction mixture temperature was raised to 110°C, and the benzene was removed and the reaction mixture temperature was kept at that temperature for 4 h. After cooling, the mixture was diluted with 10 mL DMAc and poured into 150 mL of methanol containing 5 vol% of hydrochloric acid to precipitate out polymer. The resulting fibrous polymer **8e** was dissolved in chloroform (25 mL), filtered through a thin layer of Celite to remove the inorganic salts, and reverse precipitated with the addition of 150 mL of methanol. After filtering and drying in a vacuum oven at 80°C for 12 h, 0.3930 g of white powder was obtained. The yield was 99.7%. Lengthening the reaction time to 22 h, the polymer yield of **8c** was 99.6%.

2.2.5 Synthesis of fluorinated poly(phthalazinone ether) 10 from biphenol-like monomer 1,2-dihydro-4-(4-hydroxyphenyl)-1(2H)-phthalazinone (1) and decafluorobiphenyl (9)

A 25 mL dried flask was flushed with nitrogen and charged with 1,2-dihydro-4-(4-hydroxyphenyl)-1(2H)-phthalazinone **1** 0.2381 g (1 mmol), decafluorobiphenyl **9** 0.3375 g (1 mmol), K$_2$CO$_3$ 0.2072 g (1.5 mmol), DMAc 3 mL and benzene 3 mL. The reaction mixture was heated with benzene to 100°C for 2 h to remove water generated in the reaction. The reaction mixture temperature was then raised to 110°C, and the benzene was removed and the reaction mixture was kept at that temperature for 4 h. After cooling, the mixture was diluted with 10 mL DMAc and poured into 150 mL of methanol containing 5 vol% of hydrochloric acid to precipitate out polymer. The resulting fibrous polymer **10** was dissolved in chloroform (25 mL), filtered through a thin layer of Celite to remove the inorganic salts, and reverse precipitated with 150 mL of methanol. After filtering, drying in a vacuum oven at 80°C for 12 h, gave 0.468 g white powder. The yield was 87.8%.

2.2.6 Synthesis of fluorinated poly(phthalazinone ether) 11 from fluorinated biphenol phthalazinone monomer 2,2′-(perfluorobiphenyl-4,4′-diyl) -bis(4-(4-hydroxyphenyl)−phthalazin-1(2H)-one) (7) and decafluorobiphenyl (9)

A 25 mL dried flask was flushed with nitrogen and charged with 2,2′-(perfluorobiphenyl-4,4′-diyl)bis(4-(4-hydroxy phenyl)-phthalazin-1(2H)-one) **7** 0.3850 g (0.5 mmol), decafluoro-biphenyl **9** 0.1670 g (0.5 mmol), K₂CO₃ 0.1036 g (0.75 mmol), DMAc 3 mL and benzene 3 mL. The reaction mixture was heated to 100°C for 2 h to remove water generated in the reaction with benzene. The reaction mixture temperature was raised to 110°C, and the benzene was removed and the reaction mixture was kept at that temperature for 4 h. After cooling, the mixture was diluted with 10 mL DMAc and poured into 150 mL of methanol containing 5 vol% of hydrochloric acid to precipitate out polymer. The resulting fibrous polymer **11** was dissolved in chloroform (25 mL), filtered through a thin layer of Celite to remove the inorganic salts, and reverse precipitated with 150 mL of methanol. After filtering, drying in a vacuum oven at 80°C for 12 h, gave 0.4595 g white powder. The yield was 86.3%.

3 Results and Discussion

3.1 Monomer Synthesis

3.1.1 Fluorinated AB-type phthalazinone monomer4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2H)-one (5)

Compound **5** was synthesized by reaction of 2-(hydroxyben-zoyl)benzoic acid **3** with 1-(pentafluorophenyl)hydrazine **4** (Scheme 2). **3** was synthesized from phenolphthalein, and hydroxylamine as previously described (1). The condensation reaction of **3** with phenylhydrazine has been previously reported (22). 1-(Pentafluorophenyl)hydrazine has lower activity than phenylhydrazine because of the electron-withdrawing pentafluorophenyl group. The yield of **5** at a reaction temperature of 110°C for 2.5 h was 66.3%, and the reaction yield at 110°C for 1.5 h was 70.0%. At a reaction temperature of 155°C for 2.5, the yield was 86.6%, but the product was dark colored. The highest yield 92.4% was obtained at a lower temperature of 110°C and a longer
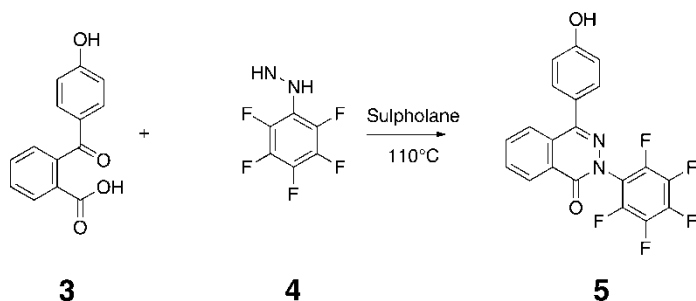
Sch. 2. Synthesis of AB-type phthalazinone monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2H)-one **5**.

reaction time of 23 h. The reaction mixture was poured into hot water to obtain a pale ochre precipitate. The solid product was recrystallized from absolute ethanol to give colorless needlelike crystals. The melting point of the product was 222°C by DTA at a heating rate of 20°C/min. ¹H and ¹⁹F-NMR spectra of fluorinated phthalazinone **5** were recorded using CDCl₃ as solvent, and tetramethylsilane and CFCl₃ as reference, respectively. The spectroscopic data shown in Figure 1 are consistent with the proposed structure. The ¹H-NMR (CDCl₃) spectrum showed a characteristic peak at δ 5.60 ppm for aryl hydroxyl group, and ¹⁹F-NMR (CDCl₃) spectrum clearly indicated three kinds of fluoro atoms of the pentafluorophenyl group at δ 144.6, δ 153.4, and δ 162.1 ppm, respectively, in a ratio of 2:1:2. The structure was confirmed by MALDI-TOF MS. The HPLC showed 100% purity.

3.1.2 Fluorinated biphenol phthalazinone monomer 2,2′-(perfluorobiphenyl-4,4′-diyl) -bis(4-(4-hydroxyphenyl)-phthalazin-1(2H)-one) (7)

Compound **7** was synthesized by reaction of 2-(hydroxyben-zoyl)benzoic acid (**3**) with (perfluorobiphenyl-4,4′-diyl)-bis (hydrazine) (**6**) (Scheme 3). The (perfluorobiphenyl-4,4′-diyl)bis(hydrazine) **6** has much lower activity than pentafluorophenylhydrazine because of the strong electron withdrawing octafluorobiphenyl group. In the reaction of pentafluorophenylhydrazine with **3** to give **6** the yield of **7** was 30.3% owing to some undetermined side reaction. At the reflux temperature of absolute ethanol for 24 h the yield was 51.4%. At longer reaction time, 48 h, the yield was increased to 57.2%. In absolute ethanol as reaction solvent, the product precipitated from the reaction system as white precipitate and the purification of the product was very simple. After boiling thoroughly in a large amount of water by HPLC only one peak belonging to the desired product was observed. The retention time of **7** was 2.86, mp 378 °C. ¹H-NMR and ¹⁹F- NMR spectra of the fluorinated phthalazinone 7 (Figure 2) were recorded using DMSO as solvent, and tetramethylsilane and CFCl₃ as reference, respectively. The spectroscopic data are in agreement with the proposed structure. ¹H-NMR (DMSO-d6): Aromatic signals δ (ppm) 6.90−6.96 (s, 4H), 7.47− 7.52 (s, 4H), 7.85−7.90 (m, 2H), 8.00−8.10(m, 4H), 8.45−8.50 (m, 2H), hydroxy signal 9.94−9.96 (s, 2H). The ¹⁹F-NMR (CDCl₃) spectrum clearly indicated two kinds of fluorine atoms for the octafluorobiphe-nyl group at δ 137.7, and δ 144.3 ppm, respectively, in a ratio of 1:1. MALDI-TOF MS: 773.39 (M), 779.19 (M⁻Li⁺). The calculated molecular weight is 770.12. MALDI-TOF MS and HPLC indicated 100% purity.

3.2 Polymer Synthesis

3.2.1 Fluorinated poly(phthalazinone ether) 8

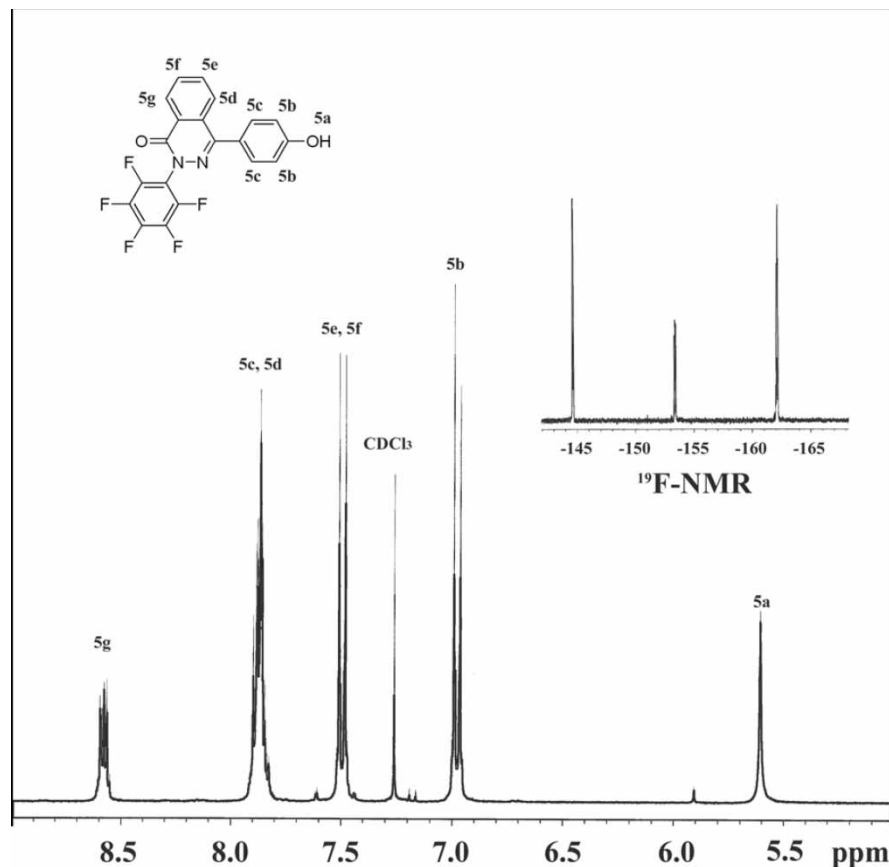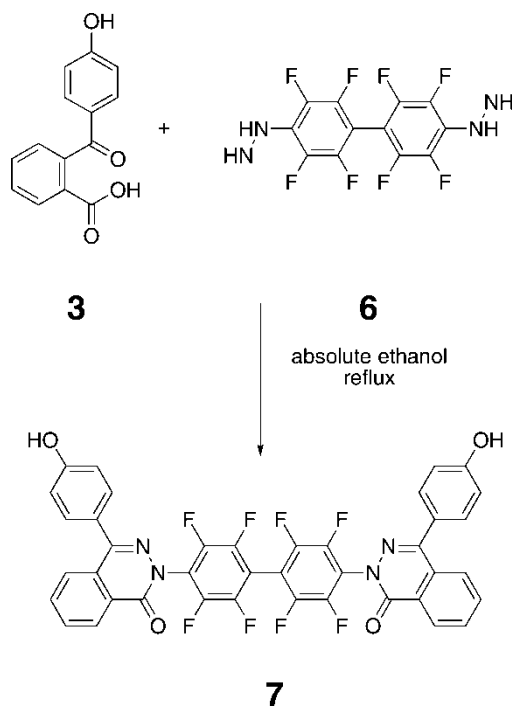The fluorinated polymer **8** was synthesized by self-condensation of AB-type pentafluorinated phthalazinone

Fig. 1. ¹H and ¹⁹F NMR spectra of AB monomer fluorinated phthalazinone **5**.

Sch. 3. Synthesis of the fluorinated biphenol phthalazinone monomer 2,2′-(perfluorobiphenyl-4,4′-diyl)-bis(4-(4-hydroxyphenyl)-phthalazin-1(2*H*)-one) **7**.

monomer **5** in a dipolar aprotic solvent DMAc using excess of K_2CO_3 (Scheme 4). The properties are given in Table 1. Initially, the reaction mixture was kept at 135°C for 2 h to remove the water generated in the reaction with toluene using a Dean-Stark trap, and then the temperature was raised to the reflux temperature of DMAc for 7 h. After working up, the fluorinated poly(phthalazinone ether) **8a** with an inherent viscosity of 0.28 dL/g was obtained. Owing to the low molecular weight, the film cast from **8a** was brittle. Lengthening the polymerization to 20 h gave gelation. Presumably, at the high reaction temperature the AB monomer acts as polyfunctional material by displacement of other fluorine atoms. Mercer (17) disclosed that hexafluorobenzene reacted with biphenol monomers to produce high molecular weight fluorinated polymers at a temperature of 60−80°C and reaction times varying from 24 to 72 h. The fluoro group in the *para* position of the pentafluorobenzene group may have similar activity as hexafluorobenzene. When the polymerization reaction was run at a lower temperature, 105−110°C for 48 h, a high molecular weight polymer **8b** with inherent viscosity 0.41 dL/g, was obtained. When the reaction was carried out for 22 h at the same temperature with removal of the water a polymer **8c** with inherent viscosity 0.48 dL/g was obtained. At 105−110°C for 24 h in a DMAc/benzene mixture with removal of water a high
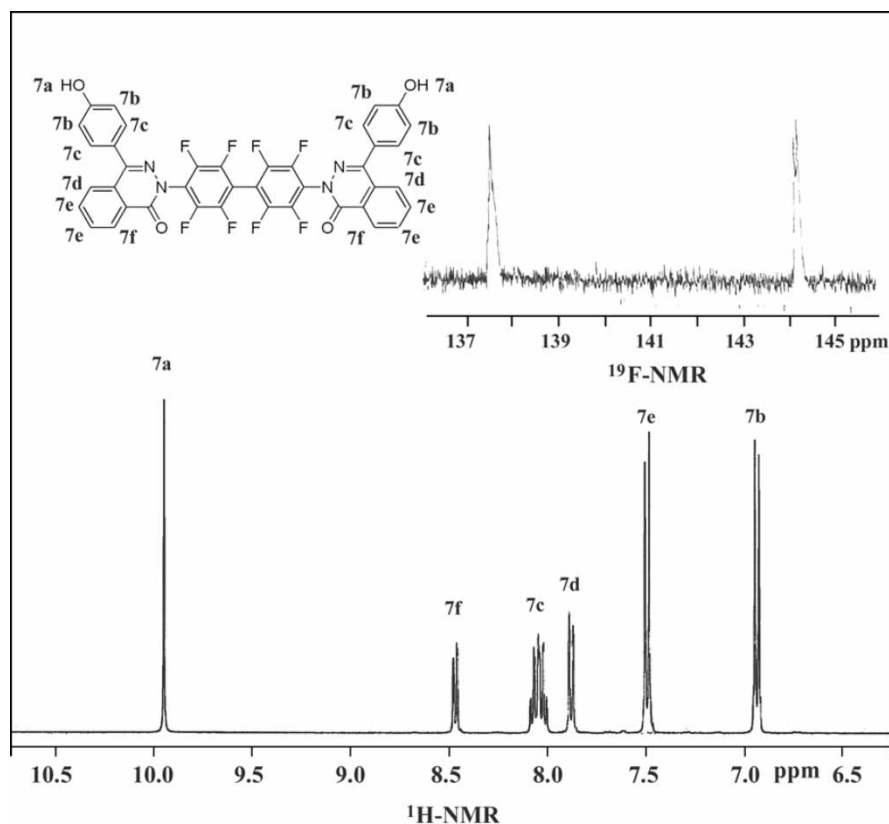
Fig. 2. ^{1}H and ^{19}F NMR spectra of fluorinated biphenol phthalazinone monomer.

molecular weight polymer **8e** with an inherent viscosity of 0.55 dL/g was obtained. (Table 1) The ^{19}F-NMR spectra of fluorinated poly(phthalazinone ether) **8** indicated there were two kinds of fluorines in the backbone with the exact ratio 1:1 (Figure 3), at δ 144.6 and δ 154.0 ppm, respectively. There was no discernible difference in the spectra of the various polymers, **8a**–**8e**. Figure 4 shows the ^{1}H-NMR spectrum of **8** with the assignments.

The GPC results for the fluorinated poly(phthalazinone ether) **8** obtained at various polymerization conditions are shown in Figure 4. Both polymer and low molecular weight cyclic or linear oligomers are observed. Because the AB monomer concentration of the above described polymerizations was only 13.3%, the reaction should favor the formation of cyclics. A bimodal molecular weight distribution for **8a** was observed with a large peak corresponding to cyclic or linear oligomers. Dehydration increases the polymerization rate significantly and **8c** and **8e,** that were prepared with azeotropic removal of water, displayed narrower peaks in the high molecular region compared with **8b** and **8d**. A comparison of the GPC plot for **8b** with that of **8d**, or the plot of **8c** with that of **8e**, indicated that the peaks assigned to high molecular weight polymers shift to the lower molecular weight region and those peaks assigned to oligomers move to higher molecular weight along with an increased peak broadening.

The fluorinated poly(phthalazinone ether)s **10**, **11** were prepared by the reaction of 4-(4-hydroxylphenyl)phthalazin-(2*H*)-one **1**, and 2,2′-(perfluorobiphenyl-4,4′-diyl)-bis(4-(4-hydroxyphenyl)-phthalazin-1(2*H*)-one) **7** with decafluorobiphenyl **9** in DMAc with benzene in the presence of excess potassium carbonate (Scheme 5). In the case of monomers **1** and **9**, Lu (18) first used N-methylpyrrolidinone (NMP) and sulpholane as solvent at about 200°C and got insoluble polymers. Even after they changed the solvent to DMAc and ran the polymerization reaction at 160°C, they obtained soluble polymer with an inherent viscosity of only 0.20 dL/g.
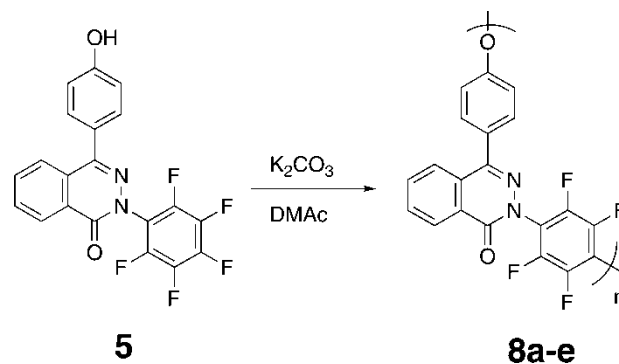
Sch. 4. Synthesis of the fluorinated poly(phthalazinone ether) **8**.

Table 1. Self-condensation of AB-type phthalazinone monomer 5 under various polymerization conditions and polymerization of AA monomers with decafluorobiphenyl

No.	Polymerization T(°C)/time(h)	Solvent	Yield (%)	$\eta_{inh}{}^{a}$ (dl/g)	Mn^{b}	Mw^{b}
8a	170−175/7	DMAc/Toulene	68.9	0.28	4100	42300
8b	105−110/48	DMAc	75.4	0.41	3700	38500
8c	105−110/22	DMAc/Benzene	99.6	0.48	10700	139300
8d	105−110/24	DMAc	83.1	0.53	7300	76600
8e	105−110/4	DMAc/Benzene	99.7	0.55	15300	163300
10	105−110/4	DMAc/Benzene	87.8	0.58	19700	167200
11	105−110/4	DMAc/Benzene	86.3	0.39	11400	110700

[a]Inherent viscosity was measured at a concentration of 0.2 g/dL in CHCl₃ at 25°C.
[b]Molecular weight was determined by GPC in chloroform based on polystyrene standards at room temperature.

We used the same polymerization conditions used for fluorinated AB phthalazinone monomer **5** for the preparation of **8**. High molecular weight polymer **10** with an inherent viscosity of 0.58 dL/g was obtained. Comparing the inherent viscosities of polymer **8e**, **10**, and **11**, synthesized under the same polymerization conditions, the polymer **11** has the lowest molecular weight. Lower monomer concentration results generally results in cyclics and the peak corresponding to oligomers of **8e** is larger than those of polymer **10** and **11**

(Figure 5), obtained at relatively higher monomer concentrations of 16.2%, and 15.5%, compared with 13.3% for **8e**.

3.3 Polymer Characterization and Properties

Fluorinated poly(phthalazinone ether)s **8**, **10**, **11** have good solubility in common solvents, such as DMAc, DMF, DMSO, NMP, TCE, THF, CHCl₃, pyridine, and sulpholane. Tough, flexible films were obtained by solution casting

Fig. 3. ¹H and ¹⁹F NMR spectra of fluorinated poly(phthalazinone ether) **8**.

Fig. 4. GPC curves of fluorinated poly(phthalazinone ether) **8** synthesized under various polymerization conditions.

Fig. 5. GPC curves of fluorinated poly(phthalazinone ether)s synthesized from various monomers.

Sch. 5. Synthesis of the fluorinated poly(phthalazinone ether)s **10**, **11**.
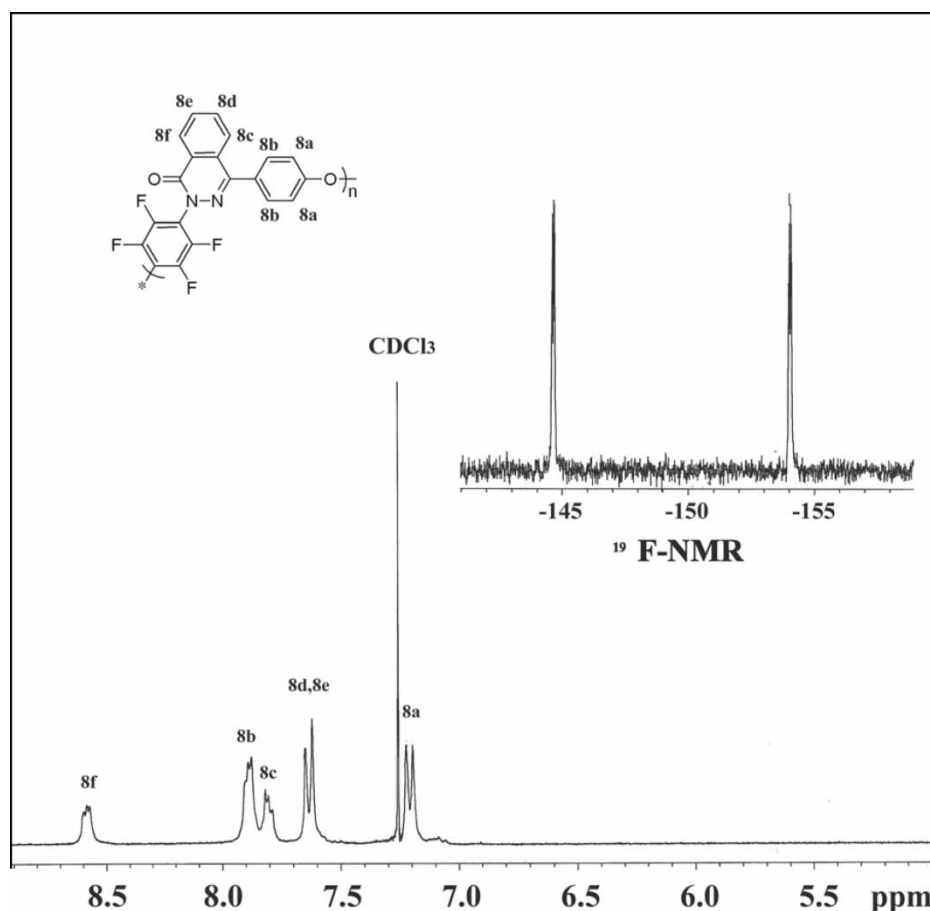
Table 2. Thermal properties of fluorinated poly(phthalazinone ether)s

No.	Polymerization T(°C)/time(h)	Solvent	T_g^a (°C)	T_g^b (°C)	$T_{d(-5wt)\%}^c$ (°C)
8a	170–175/7	DMAc/Toulene	315	342	436
8b	105–110/48	DMAc	309	346	472
8c	105–110/22	DMAc/Benzene	314	345	483
8d	105–110/24	DMAc	316	329	485
8e	105–110/4	DMAc/Benzene	316	315	491
10	105–110/4	DMAc/Benzene	220	220, 326	467
11	105–110/4	DMAc/Benzene	220	220, 330	475

[a] T_g of fluorinated poly(phthalazinone ether) was determined by DSC at a heating rate of 20°C/min under nitrogen flow rate 160 mL/min, the values were reported from the first scan

[b] T_g values of fluorinated poly(phthalazinone ether) were reported from the second scan after heating to 400°C.

[c] Reported for 5% wt loss at a heating rate 20°C/min under nitrogen flow rate 80 mL/min.

from chloroform. Thermogravimetric measurements indicated these fluorinated poly(phthalazinone ether)s have excellent thermal stability (Table 2). Fluorinated poly(phthalazinone ether) **8** with various molecular weights have 5% wt losses under N_2 higher than 436°C. The highest molecular weight polymer **8e** had the highest $T_{d,-5\%}$, 491°C, with the lowest molecular weight polymer **8a** having a $T_{d,-5\%}$ of 436 °C. The glass transition temperatures (T_g's) of the fluorinated poly(phthalazinone ether) **8** (Table 2, T_g^a) by DSC were higher than 308°C with the highest T_g, 316°C, for the highest molecular weight polymer, **8e**. The polymers were all heated to 400°C and the T_gs were measured again. The T_g of the highest molecular weight polymer, **8e,** remained about the same but all the others increased significantly, indicating that some crosslinking may have occurred. These results, along with the TGA, and GPC results, indicate that the lower molecular weight polymers contain more functional groups that react at lower temperatures. All of the polymers when heated to 250°C for 120 min or to 300°C for 5 min became insoluble in chloroform at room temperature and were also insoluble in o-dichlorobenzene when heated to 180°C. A film made from **8e** swelled approximately 100% but remained flexible. Polymer **10**, **11** had the same T_g of 220°C. $T_{d,-5\%}$s of them were 467°C, 475°C, respectively. When polymers **10**, **11** were heated to 400°C, they showed two separate T_{g_s}. The first T_g was the same as the linear backbone. The higher Tg may then be due to the crosslinked polymer.

4 Conclusions

The fluorinated AB-type phthalazinone monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(*2H*)-one **5** and the fluorinated bisphenol phthalazinone monomer 2,2′-(perfluorobiphenyl-4,4′-diyl)bis(4-(4-hydroxyphenyl)-phthalazin-1(2H)-one) **7** have been synthesized successfully by reaction of 2-(hydroxybenzoyl)benzoic acid **2** with 1-(pentafluorophenyl)hydrazine **4** and (perfluorobiphenyl-4,4′-diyl)bis(hydrazine) **6**. A high molecular weight fluorinated poly

(phthalazinone ether) **8** with good solubility in common solvents was obtained by self-condensation polymerization of AB-type phthalazinone monomer **5** under mild reaction conditions. High molecular weight fluorinated poly(phthalazinone ether)s **10, 11** have been synthesized from phthalazinone monomer **1** and fluorinated biphenol phthalazinone monomer **7** with decafluorobiphenyl. These fluorinated poly(phthalazinone ether)s can be cast from chloroform solutions into tough, flexile films. Polymer **8** has a T_g of 316°C, a $T_{d-5\%}$ of 491°C. The polymer **10**, **11** have similar T_g of 220°C because of the same backbone. The $T_{d-5\%}$s of polymers **10**, **11** are 467°C, 475°C, respectively. These fluorinated poly(phthalazinone ether)s polymers are soluble in many common solvents. They crosslink to give insoluble polymers when heated for a short time at 300°C. This characteristic makes the novel perfluorinated poly(phthalazinone ether)s potentially useful in the electronic articles, and aerospace industry application, where high performance needed.

5 Acknowledgements

6 References

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