Synthesis and Characterization of Highly Fluorinated Poly(phthalazinone ether)s Based on AB-Type Monomers

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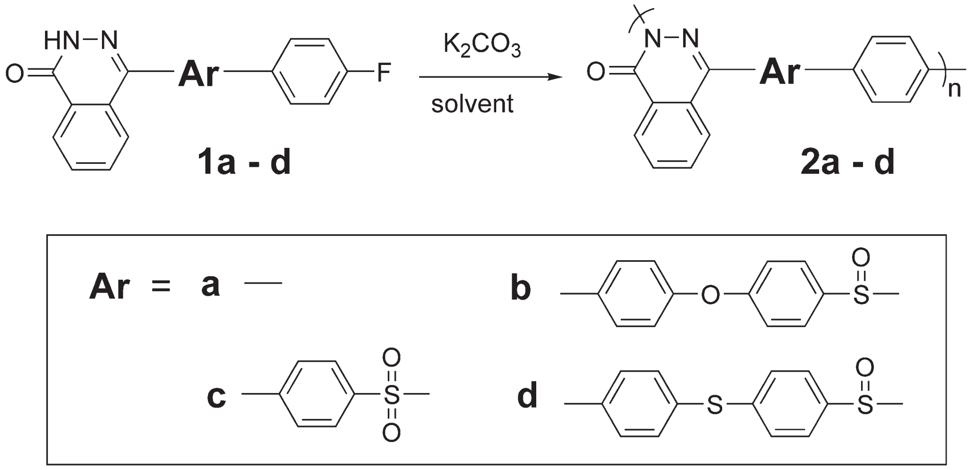
ABSTRACT: Four different fluorinated methyl- and phenyl-substituted 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(2H)-ones, AB-type phthalazinone monomers, have been successfully synthesized by nucleophilic addition–elimination reactions of methyl-substituted and phenyl-substituted 2-((4-hydroxy)benzoyl)benzoic acid with 1-(pentafluorophenyl)hydrazine. Under mild reaction conditions, the AB-type monomers underwent self-condensation polymerization reactions successfully and gave fluorinated poly(phthalazinone ether)s with high molecular weights. Detailed structural characterization of the AB-type monomers and fluorinated polymers was determined by ^{1}H NMR, ^{19}F NMR, FTIR, and GPC. The solubility, thermal properties, mechanical properties, water contact angles, and optical absorption of the polymers were evaluated. The polymers had high T_gs varying from 337 to 349 °C and decomposition temperatures ($T_{d,\ 25\ wt\ \%}$) above 409 °C. Tough, flexible films were cast from THF and chloroform solutions. The films showed excellent tensile strengths ranging from 70 to 85 MPa with good hydrophobicities with water contact angles higher than 95.5 °C. The polymers had absorption edges below 340 nm and very low absorbance per cm at higher wavelengths 500–2500 nm. These results indicate that the polymers are promising as high performance materials, for example, membranes and hydrophobic materials. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 1761–1770

KEYWORDS: AB type monomer; fluoropolymers; high performance polymers; hydrophobic material; step-growth polymerization

INTRODUCTION Phthalazinone-containing polymers, a new class of high-performance polymers containing heterocyclic moieties, have demonstrated good solubility, high rigidity, and excellent mechanical and thermal properties. These outstanding properties are strongly associated with the rigid unsymmetrical phenyl phthalazinone moieties in the polymers backbones. Poly((1,2-dihydro-1-oxo(*2H*)-phthalazine-2,4-diyl)-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene), the first phthalazinone-containing polymer, was published in 1993.[1] Since that time many phthalazinone-containing high-performance polymers, such as poly(phthalazinone ether)s,[2–30] polyamides,[31–33] polyimides,[34] and polyformal[35] with good solubility and excellent thermal stability have been synthesized. These high-performance polymers may have promising applications in passive optical waveguides,[5,13,14,36] ultrafiltration and nanofiltration membranes,[37,38] and functional membranes in the energy field, such as membranes for lithium-ion batteries,[39] anion exchange membrane materials for vanadium redox flow battery applications,[9,10] thin films for dielectric energy storage,[10] and proton exchange membrane materials for fuel cells.[11,15,19,21–23,26–28,40,41]

Highly fluorinated polymers such as polytetrafluoroethylene (Teflon) are very attractive in many applications, due to their high thermal and chemical stabilities, excellent optical and electronic properties, and special surface properties associated with their very low surface tension. However, the applications of fully fluorinated polymers usually are restricted by their poor processability.[42] Many partially fluorinated polymers with improved processability have been investigated.[43–49] Among them, fluorinated poly(arylene ether)s are one of the most important classes owing to high-T_g, excellent thermo oxidative stability, and outstanding mechanical properties and have been applied in the fields of aerospace and electronics industries where high performance is required.[46–49] Some fluorinated poly(phthalazinone ether)s have been reported in the past few years.[5,7,13,20,24] Xiao reported the preparation of fluorinated poly(phthalazinone ether)s by reaction of a monofluorinated



SCHEME 1 Synthesis of poly(phthalazinone ether)s from AB-type phthalazinone monomers **1a–d**.

phthalazinone monomer with commercially available aromatic dihalides and perfluorobiphenyl. All the polymers show good solubility in common aprotic solvents and have excellent thermal properties. The TE mode refractive indices of the polymers, ranging 1.5874–1.6888, endow them a potential as materials for optical waveguides.[5] Lu ran the polymerization of 4-(4′-hydroxyaryl)phthalazin-1(*2H*)-ones with perfluorobiphenyl but failed to give high molecular weight polymers.[24] Photo-cross-linking,[7] cross-linking techniques,[13] and self-condensation techniques[20] have been applied to improve the properties of the fluorinated poly(phthalazinone ether)s. Self-condensation of AB-type monomers is an effective way to synthesize high molecular weight polymers. We previously synthesized the AB-type phthalazinone monomers **1a–d** (Scheme 1).

These AB monomers failed to form high molecular weight homopolymers **2a–d**, even under stringent conditions, because the high degree of crystallization of the oligomers resulted in the premature precipitation of the polymers.[3] Later, we introduced the fluorine atoms into the AB-type monomer to improve the solubility of the oligomer to enable formation of the high molecular weight polymers. The fluorinated poly(phtha1azinone ether) has good solubility in many common solvents and could be cast into a clear, transparent, and tough films.[20]

In this paper, we design a series of new fluorinated AB-type phthalazinone monomers containing methyl or phenyl side groups. Herein the synthesis and polymerizations of these fluorinated AB-type phthalazinone monomers have been investigated. High molecular weight fluorinated poly(phthalazinone ether)s were obtained by the self-condensations of the AB-type monomers. All these fluorinated poly(phthalazinone ether)s have good solubility in some common solvents and can be cast into clear, transparent, and tough films that have excellent thermal and mechanical properties, high hydrophobicity, characteristic optical properties.

EXPERIMENTAL

Materials

2-((4-hydroxy)benzoyl)benzoic acids (**3a–d**) were synthesized as outlined in Cheng's work.[18] m-Cresol (>98%), *o*-cresol (>98%), 2,3-xylenol (>97%), 2,6-xylenol (>98%), and *o*-phenylphenol (>98%) were purchased from Aldrich Chemical Co. and used as received. 1-(Pentafluorophenyl) hydrazine was purchased from TCI Chemical Co. Anhydrous potassium carbonate was used as received. Reagent grade solvents *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), 1,1,2,2-tetrachloroethane (TCE), $CHCl_3$, sulpholane, pyridine, ethanol, glacial acetic acid, benzene, toluene, methanol were obtained from commercial sources and used as received.

Characterizations

^{1}H NMR and ^{19}F NMR spectra were measured with a Bruker AVANCE 400S with deutrated dimethyl sulfoxide (DMSO-d_6) or deuterated chloroform ($CDCl_3$) as a solvent, and tetramethylsilane (TMS) and $CFCl_3$ as internal references, respectively. FT-IR spectra were recorded on a Bruker Tensor 27 instrument. Gel permeation chromatography (GPC) analyses were carried out on a Waters 510 HPLC equipped with 5 μm phenol gel columns (linear, 4× 500 Å) arranged in series with chloroform as a solvent, a UV detector at 254 nm and polystyrenes as standards. The system was operated at 25 °C with a flow of 1 mL min^{-1} solvent. Melting points were taken on a XT4A melting point testing apparatus at 70 °C per minute. The solubility of the polymers was determined with 2 mg of a polymer in 3 mL of a solvent. Thermogravimetric analysis (TGA) was carried out using with a TAINC SDT Q600 thermogravimetric analyzer at a heating rate of 20 °C per minute from 30 to 700 °C under a protective nitrogen atmosphere (100 mL min^{-1}). The T_gs of the polymers were obtained using a Netzsch DSC 204C DSC instrument at a heating rate of 20 °C min^{-1} 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 mechanical properties of the membranes were measured with a SANS Electromechanical Universal Testing Machine (UTM6000) at a stretching speed of 50 mm min^{-1} at 25 °C. The data were evaluated with SANS Power Test-SOOC software.

Water Contact Angle

The films were vacuum-dried at 100 °C for 24 h prior to the water contact angle measurements. Contact angle was detected with an Optical Contact Angle Measuring Device DSA100, and the size of the water droplet is 4 μL. The measurements ran five trials for each membrane.

Optical Absorption

The optical absorbance was determined using a Perkin Elmer Lambda 950 UV–vis–NIR spectrophotometer (200–2500 nm) for free standing films. The measured value of absorbance was divided by the film thickness to obtain a value of optical absorbance per cm.

Synthesis of AB-Type Monomer 4-(3′,5′-Dimethyl-4′-Hydroxyphenyl)-2-(Pentafluorophenyl)phthalazin-1(*2H*)-one (4a)

2-(3′,5′-Dimethyl-4′-hydroxybenzoyl)benzoic acid **3a** (2.70 g, 0.01 mol) and 1-(pentafluorophenyl) hydrazine (1.98 g, 0.01 mol) were heated in sulpholane (7 mL) at 125 °C for 23 h in a flask equipped with a magnetic stirrer and a condenser. After cooling down 15 mL of ethanol was added into the reaction mixture and the reaction mixture was poured into 80 mL of hot water to give a dark brown precipitate. The precipitate was filtered and washed with water thoroughly. The yield was 86.5%. The solid product was recrystallized from a mixture of DMAc/EtOH = 1/5(v/v) to give pale yellow needle crystals. ^{1}H NMR (DMSO-d_6, δ, ppm): 2.19–2.28 (s, 6H), 7.20–7.25 (s, 2H), 7.86-7.90 (d, 1H), 7.98–8.08 (m, 2H), 8.25–8.45(d, 1H), 8.73–8.75(s, 1H). ^{19}F NMR (DMSO-d_6, δ, ppm): −145.9 (2F), −152.3 (1F), and −161.9 (2F). Mp:266 °C.

Synthesis of AB-Type Monomer 4-(2′, 3′-Dimethyl-4′-Hydroxyphenyl)-2-(Pentafluorophenyl)phthalazin-1(*2H*)-one (4b)

2-(2′,3′-Dimethyl-4′-hydroxybenzoyl)benzoic acid **3b** (2.70 g, 0.01 mol) and 1-(pentafluorophenyl) hydrazine (1.98 g, 0.01 mol) were heated in sulpholane (7 mL) at 125 °C for 23 h in a flask equipped with a magnetic stirrer and a condenser. Working up the reaction mixture by the same procedure used for **4a** gave a pale ochre precipitate **4b**. The yield was 76.0%. The solid product was recrystallized from absolute ethanol to give light brown needle crystals. ^{1}H NMR (DMSO-d_6, δ, ppm): 1.99 (s, 3H), 2.14 (s, 3H), 6.80-6.83 (d, 1H), 7.0–7.04 (d, 1H), 7.36–7.42 (d, 1H), 7.63–8.05 (d, 2H), 8.40–8.46 (d, 1H), 9.64 (s, 1H). ^{19}F NMR (DMSO-d_6, δ, ppm): −145.2 (1F), 146.5 (1F), −152.6 (1F), −161.7 (1F), and −162.0 (1F). Mp: 218 °C.

Synthesis of AB-Type Monomer 4-(3′-Methyl-4′-Hydroxyphenyl)-2-(Pentafluorophenyl)-Phthalazin-1(*2H*)-one (4c)

2-(3′-Methyl-4′-hydroxybenzoyl)-benzoic acid **3c** (2.56 g, 0.01 mol) and 1-(pentafluorophenyl) hydrazine (1.98 g, 0.01 mol) were heated in sulpholane (7 mL) at 125 °C for 23 h in a flask equipped with a magnetic stirrer and a condenser. Working up the reaction mixture by the same procedure used for **4a** gave a pale ochre raw precipitate **4c**. The yield was 89.1%. The solid product was recrystallized from a mixture solution of absolute ethanol/water (3/1(v/v)) to give light brown needle crystals. ^{1}H NMR (DMSO-d_6, δ, ppm): 2.19 (s, 3H), 6.92–6.98 (d, 1H), 7.23–7.37 (m, 2H), 7.84–7.90 (d, 1H), 7.99–8.07 (m, 2H), 8.38–8.50 (d, 1H), 9.83 (s, 1H). ^{19}F NMR (DMSO-d_6, δ, ppm): −145.8 (2F), −152.5 (1F), and −161.8 (2F). Mp:233 °C.

Synthesis of AB-Type Monomer 4-(3′-Phenyl-4′-Hydroxyphenyl)-2-(Pentafluorophenyl)-phthalazin-1(*2H*)-one (4d)

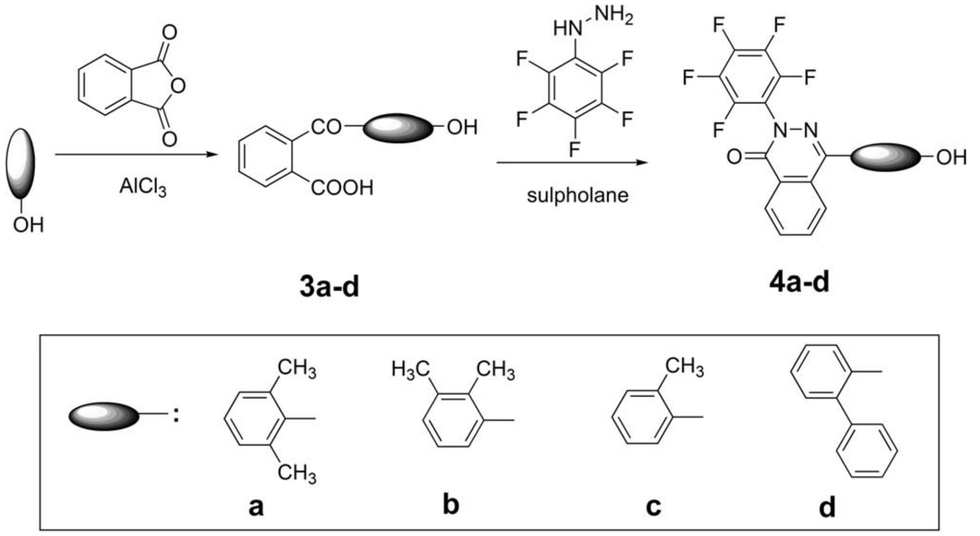
2-(3′-Phenyl-4′-hydroxybenzoyl)benzoic acid **3d** (3.19 g, 0.01 mol) and 1-(pentafluorophenyl) hydrazine (1.98 g, 0.01 mol) were heated in sulpholane (7 mL) at 125 °C for 23 h in a flask equipped with a magnetic stirrer and a condenser. After adding 25 mL of ethanol into the reaction mixture, the reaction mixture was poured into 100 mL of hot water to give an ochre precipitate. The precipitate was filtered and washed thoroughly with water. The yield was 80.1%. The solid product was recrystallized from H_2O/EtOH = 1/4(v/v) to give a light brown powder. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.14–7.16 (d, 1H), 7.30–7.32 (s, 1H), 7.40–7.44 (m, 2H), 7.47–7.52 (d, 2H), 7.60–7.62 (m, 2H), 7.95–8.08 (m, 3H), 8.44–8.46 (m, 1H), 10.14 (s, 1H). ^{19}F NMR (DMSO-d_6, δ, ppm): −145.7 (2F), −152.5 (1F), and −161.7 (2F). Mp:222 °C.

Synthesis of Fluorinated Poly(phthalazinone ether) 5a

Initially, a 25 mL dried flask was flushed with nitrogen and charged with 4-(3′,5′-dimethyl-4′-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(*2H*)-one **4a** 0.4323 g (1 mmol), K_2CO_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. Then toluene was then removed completely with a strong N_2 flux. The reaction mixture temperature was maintained for 2 h. After cooling, the mixture was diluted with 5 mL DMAc and poured into 150 mL of methanol containing 5 vol % of hydrochloric acid to precipitate out the polymer. The resulting polymer was dissolved in chloroform (25 mL), filtered through a thin layer of celite to remove the inorganic salts, and reversed precipitated into 150 mL of methanol. After filtering, drying in a vacuum oven at 80 °C for 12 h, gave 0.396 g of white fiber. The yield was 99.5%. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.38(s, 6H), 7.32 (s, 2H), 7.77–7.79 (d, 1H), 7.85–7.89 (m, 2H), 8.56–8.58 (m, 1H). ^{19}F NMR ($CDCl_3$, δ, ppm): −145.5 (2F), −158.3 (2F).

Synthesis of Fluorinated Poly(phthalazinone ether) 5b

Initially, a 25 mL dried flask was flushed with nitrogen and charged with 4-(2′,3′-dimethyl-4′-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(*2H*)-one **4b** 0.4323 g (1 mmol), K_2CO_3 0.1036 g (0.75 mmol), DMAc (2.5 mL), and benzene (3 mL). The reaction mixture was heated to 110 °C for 2 h to remove water generated in the reaction with benzene. After most of benzene was removed, the reaction mixture was kept weakly refluxing for 4 h. After cooling, the mixture was diluted with 5 mL DMAc and poured into 150 mL of methanol containing 5 vol % of hydrochloric acid to



SCHEME 2 Synthesis of phthalazinone-containing AB monomers **4a–d**.

precipitate out the polymer. The resulting polymer was dissolved in chloroform (25 mL), filtered through a thin layer of celite to remove the inorganic salts, and reversed precipitated into 150 mL of methanol. After filtering, drying in a vacuum oven at 80 °C for 12 h, gave 0.405 g of white fiber. The yield was 99.6%. ^{1}H NMR (CDCl$_3$, δ, ppm): 2.22 (s, 3H), 2.46 (s, 3H), 6.69–6.78 (s, 1H), 7.14–7.19 (m, 1H), 7.40–7.42 (m, 1H), 7.74–7.90 (s, 2H), 8.59 (s, 1H). ^{19}F NMR (CDCl$_3$, δ, ppm): −144.0 (1F), −145.7 (1F), −154.6 (2F). The other polymers **5c** and **5d** were synthesized in the similar way to **5b**.

Syntheses of Fluorinated Poly(phthalazinone ether) 5c

Replacing **4b** with 4-(3′-methyl-4′-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(*2H*)-one **4c** 0.4183 g (1 mmol) ran the self-polycondensation and working up the reaction mixture similar to the procedure for **5b**. The yield was 99.7%. ^{1}H NMR (CDCl$_3$, δ, ppm): 2.52 (s, 3H), 6.85–6.89 (d, 1H), 7.38–7.40 (m, 1H), 7.53 (s, 1H), 7.80–7.84 (m, 1H), 7.88–7.89 (m, 2H), 8.58–8.61 (m, 1H). ^{19}F NMR (CDCl$_3$, δ, ppm): −144.5 (2F), −154.4 (2F).

Synthesis of Fluorinated Poly(phthalazinone ether) 5d

Replacing **4b** with 4-(3′-phenyl-4′-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(2H)-one **4d** 0.4804 g (1 mmol) and working up the reaction mixture similar way to **5b** gave 0.457 g white fibrous polymer **5d**. The yield was 99.5%. ^{1}H NMR (CDCl$_3$, δ, ppm): 6.99–7.05 (m, 1H), 7.33–7.45 (m, 2H), 7.52–7.56 (m, 1H), 7.64–7.71 (m, 3H), 7.87 (s, 3H), 8.57–8.59 (m, 1H). ^{19}F NMR (CDCl$_3$, δ, ppm): −145.1 (2F), -153.7 (2F).

RESULTS AND DISCUSSION

Synthesis of Fluorinated AB-Type Phthalazinone Monomers 4a–d

In our previous work, the fluorinated AB-type phthalazinone monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(*2H*)-one was synthesized by reaction of 2-((4-hydroxy)-benzoyl)benzoic acid with 1-(pentafluorophenyl)hydrazine at a reaction temperature of 110 °C for 23 h to give a high yield of 92.4%.[20] Herein the AB-type new monomers **4a-d**, methyl or phenyl substituted 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(*2H*)-one, were synthesized by reactions of the derivates of 2-((4-hydroxy)benzoyl)benzoic acid **3a–d** with 1-(pentafluorophenyl)hydrazine under varying reaction conditions (Scheme 2 and Table 1). The key step in the cyclic reactions is the nucleophilic addition–eliminations between ketone and hydrazine groups. The nucleophilic addition-elimination activities of the ketone groups are weakened by the electron donating effect and steric hindrance effect of side groups. The yields of **4a–d** are a bit lower than that of the phthalazinone monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(2H)-one without side groups. In the nucleophilic addition-elimination of **3a** and 1-(pentafluorophenyl) hydrazine, the yield of **4a** increases with increases in reaction temperature and reactant concentration until the temperature is higher than 130 °C when the color of **4a** deepens with the increasing temperature. The optimum synthesis conditions for **4a** are reaction temperature of 125 °C, reaction time of 23 h with a reactant concentration of 1.25 M. **4b–c** synthesized under the same conditions. **4b** gave the lowest yield due to the obvious steric hindrance effect of the methyl group ortho to the ketone group.

Figure 1 displays ^{1}H NMR and ^{19}F NMR spectra of the fluorinated phthalazinones **4a–d**. The spectroscopic data are in agreement with the proposed structures. ^{1}H NMR of **4a** (DMSO-*d$_6$*): δ (ppm) methyl signal 2.19–2.28 (s, 6H), aromatic signals 7.20–7.25 (s, 2H), 7.86–7.90 (d, 1H), 7.98–8.08 (m, 2H), 8.25-8.45(d, 1H), hydroxyl signal 8.73–8.75 (s, 1H). ^{19}F NMR spectrum of **4a** clearly indicates three kinds of fluorine atoms of the pentafluorophenyl group at δ 145.9, δ 152.3 and δ 161.9 ppm, respectively, in a ratio of 2:1:2. In the ^{1}H NMR spectrum of **4b** the methyl signals divide into

TABLE 1 The Nucleophilic Addition–Elimination Reactions of the Derivatives of 2-(Hydroxybenzoyl)benzoic Acid **3a–d** and 1-(Pentafluorophenyl)hydrazine

Benzoic acid	Conv. (m)	Temp. (°C)	Time (h)	Yield (%)	Color of product
3a	1.25	120	23	84.6	Pale yellow
	1.25	125	23	86.5	Yellow
	1.25	125	6	85.8	Yellow
	1.00	125	6	78.2	Yellow
	1.25	130	23	87.0	Light brown
	1.25	150	23	87.9	Brown
3b	1.25	125	23	76.0	Light brown
	1.00	125	6	68.5	Light brown
3c	1.25	125	23	89.1	Light brown
	1.00	125	6	78.1	Light brown
3d	1.25	125	23	80.1	Light brown

two groups at δ 1.99 (s, 3H) and δ 2.14(s, 3H) owing to the position effects of the electron donating conjugation and the electron withdrawing effect of the hydroxyl group. Fluorine signals around δ 146 and 161.9 ppm split into two peaks in ^{19}F NMR spectrum of **4b** because of the σ–π hyperconjugation of the asymmetrical methyl groups. The ratio of the fluorine signals is 1:1:1:1:1. Fluorine signals in ^{19}F NMR spectra of **4c–d** demonstrate three kinds of fluorine atoms in the pentafluorophenyl group in a ratio of 2:1:2 because of the pentafluorophenyl groups located at the meta-position of the methyl and phenyl groups. Hydroxyl signals in the ^{1}H NMR spectra of **4b–c** move to high a chemical shift area due to the reduced electron donating σ–π hyperconjugation of the ortho-methyl groups. Especially in the case of **4d**, hydroxyl signal appear at the highest chemical shift area because of the electron withdrawing π–π conjugation of phenyl group.

In the FTIR spectrum of A–B-type monomer **4a** (Fig. 2), it has two kinds of functional groups hydroxyl group and C–F. The wide signal near 3300 cm^{-1} is contributed by the absorption of –OH. And the signal assigned to C–F appears at 1078 cm^{-1}. The characteristic signal of —C=N— in the phthalazinone moiety appears at 1518 cm^{-1} overlapped with aromatic rings signals. The absorption peak assigned to —C=O occurs at 1649 cm^{-1}. The characteristic signal of methyl group appears at 2972 cm^{-1}. Monomers **4b–c** containing methyl groups demonstrate similar absorptions. In the case of **4d** with the phenyl side group, the characteristic signal of methyl group disappears and the signal of phenyl group appears at 3066 cm^{-1}.

Synthesis of Fluorinated Poly(phthalazinone ether)s 5a–d

As depicted in Scheme 3, the fluorinated poly(phthalazinone ether) **5a–d** were synthesized via the self-condensations of new AB-type phthalazinone monomers **4a–d**. Herein the new phthalazinone monomers **4a–d** are the derivatives of 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(*2H*)-one with varying side groups. The optimum self-condensation conditions for 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(*2H*)-one to give high molecular weight polymer has been published in our previous work.[20] We ran the self-condensations of the AB-type new phthalazinone monomers **4a–d** under the same conditions as 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)-phthalazin-1(*2H*)-one (Table 2). All the monomers except **4a** gave high molecular weight polymers. Polymer **5d** has the lowest molecular weight because the

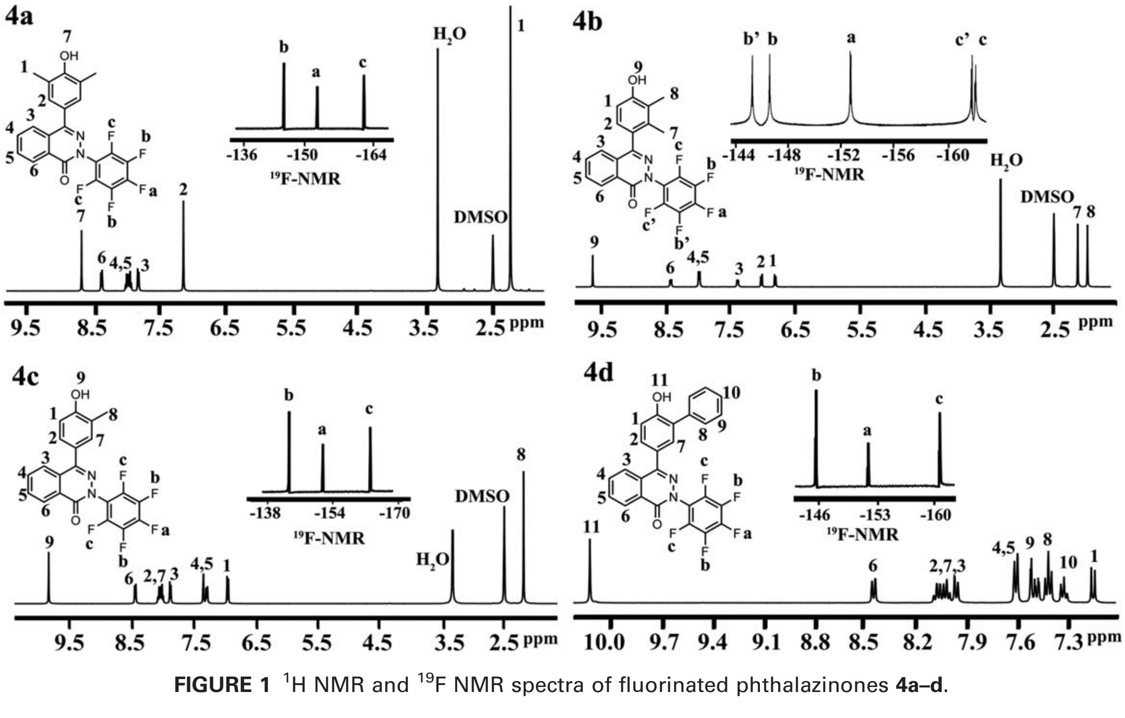


FIGURE 1 ^{1}H NMR and ^{19}F NMR spectra of fluorinated phthalazinones **4a–d**.

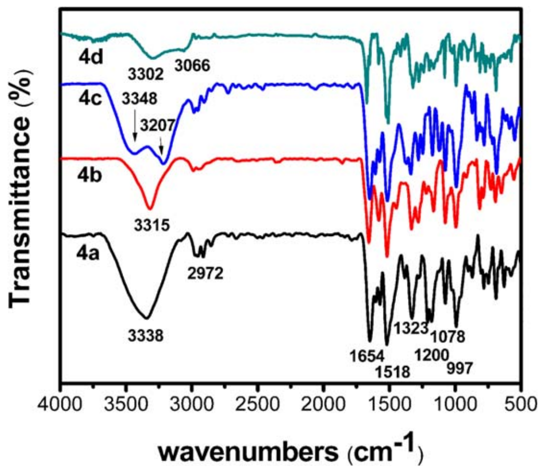


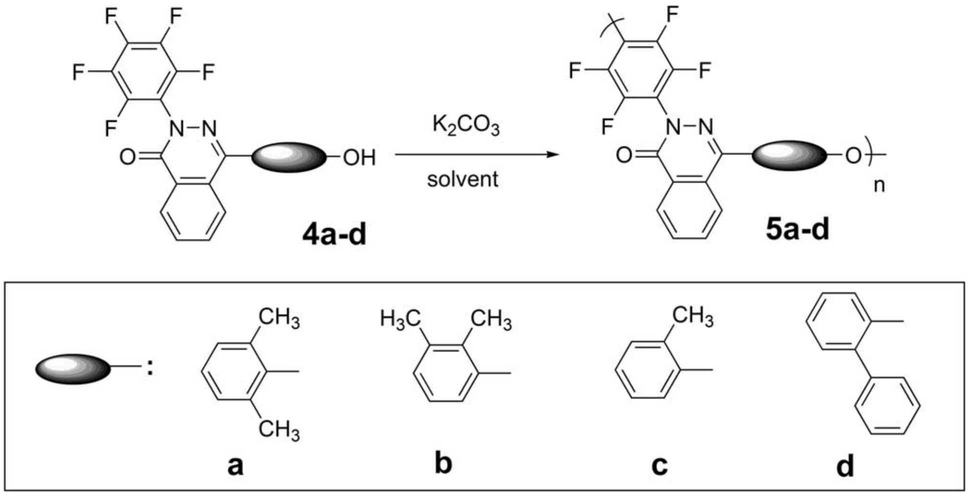
FIGURE 2 FT-IR spectra of fluorinated phthalazinones **4a–d**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

negative π–π conjugation of the phenyl group lowers the reactivity of the phenoxide anion. Polymer **5c** has the highest molecular weight due to the positive electron donating σ–π hyperconjugation of the ortho methyl group of the phenol ring that increase the reactivity of the phenol salt. Polymer **5a** has the lowest molecular weight due to the low polymerization temperature. By changing the solvent to DMAc/toluene to run the polymerization at the higher temperature of 135–140 °C, high molecular weight polymer **5a** was successfully synthesized with a narrow polydispersity of 1.52.

The ^{1}H NMR and ^{19}F NMR spectra of the fluorinated poly(-phthalazinone ether)s (Fig. 3) were recorded using $CDCl_3$ as solvent. The spectroscopic data are in agreement with the proposed structures. Obviously, the hydroxyl signal and the *para* fluorine signal disappear in the ^{1}H NMR and ^{19}F NMR spectra of the polymers respectively. The FTIR spectra of the polymers are shown in Figure 4. The peaks at 3000–3600 disappeared in the polymer FTIR spectra. This agrees well with the results of the ^{1}H NMR and ^{19}F NMR.

Solubility

The solubility of the polymers **5a–d** in common aprotic organic solvents is listed in Table 3. They show excellent solubility in DMAc, THF, $CHCl_3$, TCE, NMP, and pyridine. A reasonable explanation is that the twisted noncoplanar bulky phthalazinone architectures and flexible ether bonds interfere with the compact packing of the backbones and give a larger free volume. The other explanation is that the introduction of strong polar moieties pentafluorophenyl group strengthens the polarity of the polymer backbones. In addition, the pendant side groups also have effects on the solubility of these polymers because of variations of the conformation of the polymer backbone. Polymer **5b** is soluble in sulpholane and polymer **5c** partially soluble, while



SCHEME 3 Synthesis of Fluorinated Poly(Phthalazinone Ether)s **5a–d**.

TABLE 2 Self-Condensation of AB-Type Phthalazinone Monomers **4a–d**

Polymer	Polymerization tem.(°C) time^{-1} (h)	Solvent	Yield (%)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	M_w/M_n
5a	105–110/4	DMAc/benzene	98.6	7,836	42,398	5.41
	135–140/4	DMAc/toluene	99.5	169,739	257,607	1.52
5b	105–110/4	DMAc/benzene	99.6	52,020	67,692	1.30
5c	105–110/4	DMAc/benzene	99.7	111,431	171,696	1.54
5d	105–110/4	DMAc/benzene	99.5	35,815	98,541	2.75

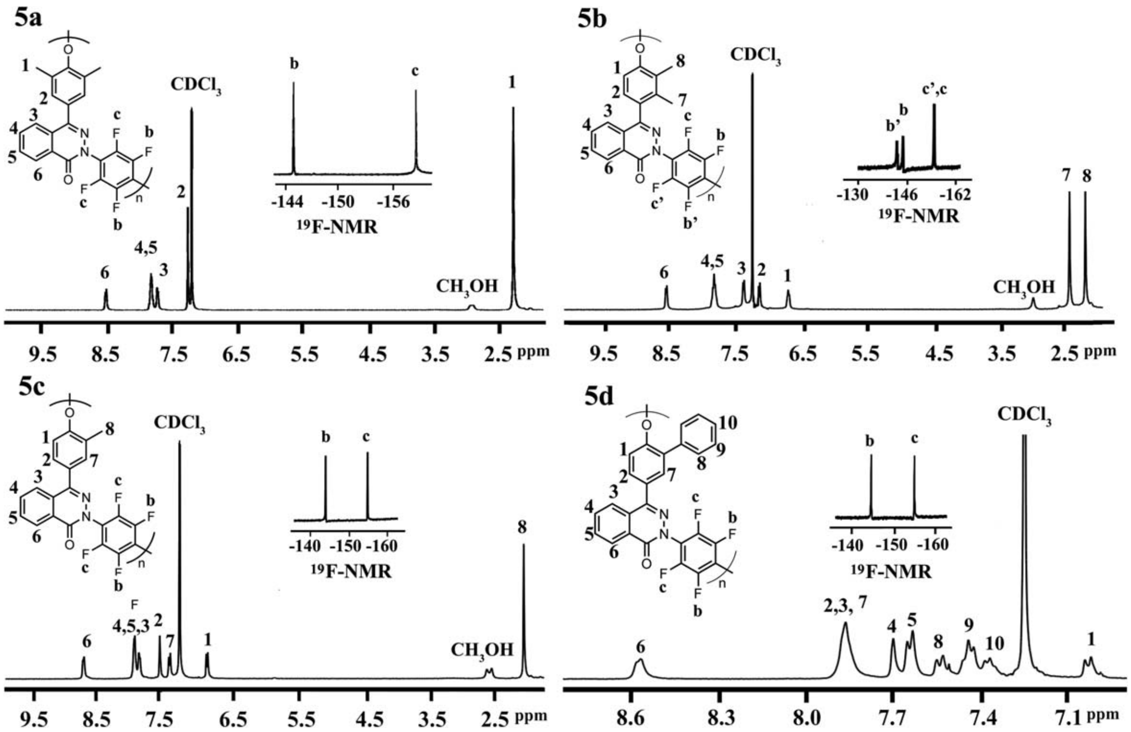


FIGURE 3 ^{1}H NMR and ^{19}F NMR spectra of fluorinated poly(phthalazinone ether)s **5a–d**.

their counterparts **5a** and **5b** are insoluble. All of these polymers could be cast into tough, flexible, and colorless or nearly colorless films. These properties are promising for practical applications in the field of membranes.

Thermal Properties

All the fluorinated poly(phthalazinone ether)s **5a–d** show high T_gs as listed in Table 4, as measured by a differential scanning calorimeter. When compared with the fluorinated poly(phthalazinone ether) without side group, polymers **5a–d** demonstrate a distinct increase in T_g higher than 22 °C indicating that the introduction of the bulky side group increases the rigidity of the polymer backbones.

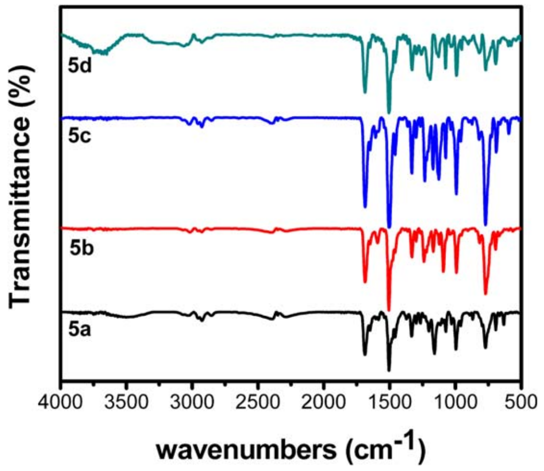


FIGURE 4 FT-IR spectra of fluorinated poly(phthalazinone ether)s **5a–d**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The initial weight losses of the fluorinated poly(phthalazinone ether)s **5a–d** were observed in the temperature range of 403–423 °C, which is significantly lower than that of polymer without side group (491 °C).[20] Table 4 also summarizes the decomposition temperatures of polymers **5a–d** as determined by TGA, plotted in Figure 5. Evidently, polymer **5d** with a phenyl side group has a higher T_d value than **5a–c** containing methyl groups. This instability could be attributable to the oxidation of the C–H bonds in the methyl group, followed by decarboxylation and decarbonylation reactions. Moreover, all the polymers display char yields above 70% in nitrogen at 600 °C. This excellent thermal stability could be ascribed to crosslinking of these polymers and the high aromatic ring content of the polymer backbones.

Mechanical Properties

Mechanical properties of the polymers membranes are summarized in Table 5. All the fluorinated poly(phthalazinone

TABLE 3 Solubility of Fluorinated Poly(phthalazinone ether)s **5a–d**

	DMAc	THF	CHCl$_3$	TCE	NMP	Pyridine	Sulpholane
5a	++	+	++	++	++	++	–
5b	++	++	++	++	++	++	+
5c	++	++	++	++	++	++	±
5d	++	++	++	++	+	++	–

++, Fully soluble at room temperature; +, soluble; ±, partially soluble; −, insoluble.

TABLE 4 Thermal Properties of Fluorinated Poly(phthalazinone ether)s **5a–d**

Polymer	T_g (°C)^a	$T_{d\ (-5\ wt\ \%)}$ (°C)^a	$T_{d\ (-10\ wt\ \%)}$ (°C)^b	600 °C Residue (%)^c
5a	342	408	433	71
5b	337	415	434	71
5c	348	409	433	72
5d	349	451	478	77
8e[20]	315	491	-	-

[a] Reported for 5% wt loss at a heating rate 20 °C min^{-1} under nitrogen flow rate 80 mL min^{-1}.

[b] Reported for 10% wt loss at a heating rate 20 °C min^{-1} under nitrogen flow rate 80 mL min^{-1}.

[c] Char yield, calculated as the percentage of the solid residue after heating from room temperature to 600 °C in nitrogen.

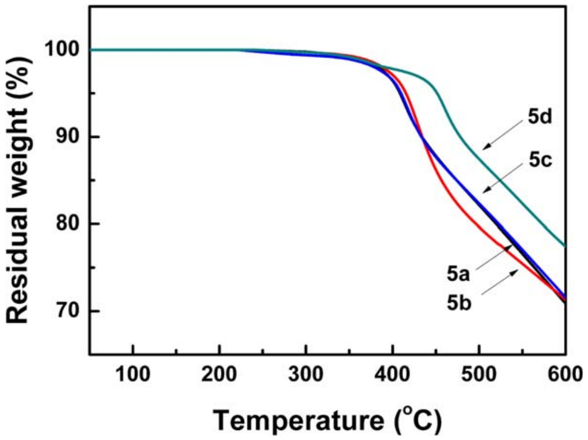


FIGURE 5 TG curves of fluorinated poly(phthalazinone ether)s **5a–d**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ether)s **5a–d** show high tensile strength ranging from 70 to 85 MPa. Their Young's moduli vary from 1.83 to 2.46 Gpa. Elongations at break are below 10.3%. These results indicate that these polymers have excellent mechanical properties.

Contact Angles

The surface tensions of the fluorinated poly(phthalazinone ether)s **5a–d** films were characterized by water contact angle measurements, and the results are shown in Figure 6. The films were coated on glass slides from THF solutions. The water contact angles of the polymer **5a–d** films are higher than 95.5°, indicating high hydrophobicities.

TABLE 5 Mechanical Properties of Fluorinated Poly(phthalazinone ether)s **5a–d**

Polymer	Tensile strength (Mpa)	Elongation at break (%)	Modulus (Gpa)
5a	85.4	10.3	2.46
5b	74.2	9.62	2.01
5c	73.2	9.32	2.35
5d	70.0	4.37	1.83

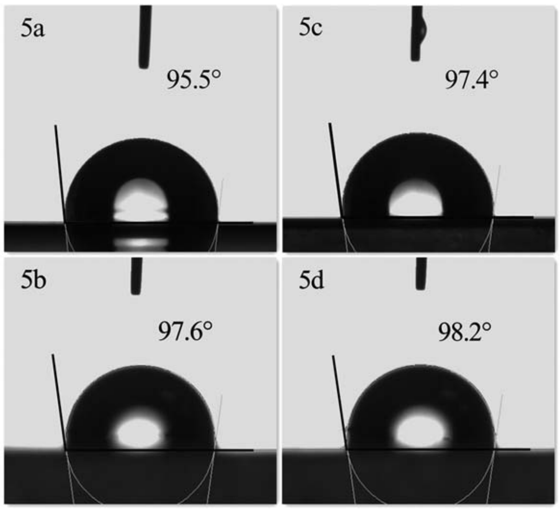


FIGURE 6 Contact angles of fluorinated poly(phthalazinone ether)s **5a–d** (THF).

Optical Absorption

The UV–vis–NIR absorption spectra of the fluorinated poly (phthalazinone ether)s **5a–d** films are shown in Figure 7. These polymers have similar optical absorption properties. The absorption edges of these polymers are at wavelengths below 340 nm and the Abs/cm are very low at higher wavelengths 500–2500 nm. They show slight differences in optical absorption at wavelengths ranging from 340 to 500 nm. Polymer **5a** with two symmetric methyl groups gives the lowest absorbance per cm.

CONCLUSIONS

AB-type phthalazinone monomers from methyl or phenyl substituted 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2H)-one **4a–d** have been synthesized by

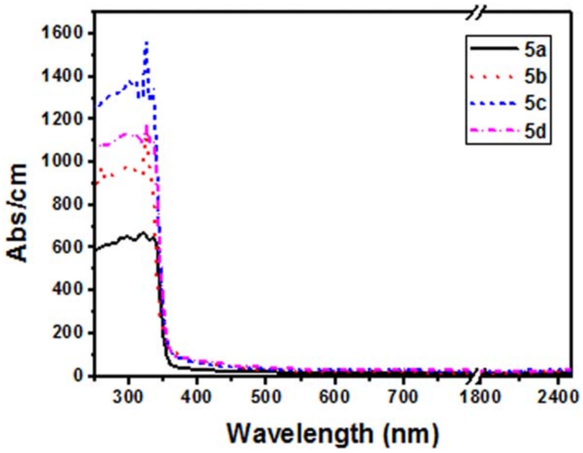


FIGURE 7 UV–vis–NIR absorption spectra of fluorinated poly (phthalazinone ether)s **5a–d**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nucleophilic addition–elimination reactions of derivatives of 2-((4-hydroxy)benzoyl)benzoic acid with (pentafluorophenyl)hydrazine. Under mild reaction conditions, high-molecular weight fluorinated poly(phthalazinone ether)s **5a–d** with good solubility in common solvents were fabricated by self-condensation of the AB-type phthalazinone monomers **4a–d**. Tough, flexible films were obtained from chloroform solutions by the solution cast method. The polymers have T_gs varying from 337 to 349 °C and $T_{d(-5\ wt\ \%)}$s higher than 409 °C. The tensile strength of the films rang from 70 to 85 MPa. **5a–d** films obtained from THF solutions indicate high hydrophobicities with water contact angles higher than 95.5 °C. The polymers have absorption edges below 340 nm and very low absorbance per cm at higher wavelengths 500–2500 nm. These results indicate that polymers **5a–d** are promising candidates as high-performance materials, for example, membranes and hydrophobic materials.

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