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Synthesis of a High Molecular Weight Fluorinated Poly(phthalazinone ether) by Self-Condensation of an AB-Type Monomer

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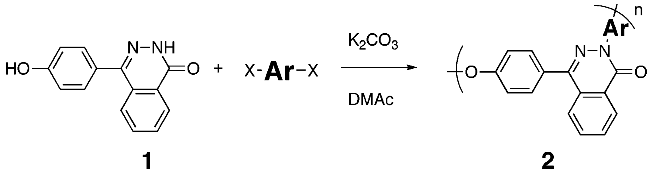
In 1993, we first described the polymerization of 1,2-dihydro-4-(4-hydroxyphenyl)-1(2*H*)-phthalazinone (**1**) with activated dihalo compounds, e.g., X−Ar−X = bis(4-fluorophenyl)sulfone, to synthesize poly((1,2-dihydro-l-oxo(2*H*)-phthalazine-2,4-diy1)-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) (**2**). The monomer **1** behaves like a biphenol to give a polymer with N−C linkages (Scheme 1).[1]

Since that time many phthalazinone-containing high-performance polymers, such as poly(phthalazinone ether)s,[2−7] polyamides,[8] and polyimides,[9] with good solubility and excellent thermal stability have been synthesized. 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 thermooxidative stability, high T_g, good solubility, and outstanding mechanical properties.[1−7] The introduction of the rigid unsymmetrical phenyl phthalazinone moiety into the polymer backbone gives good solubility and high rigidity to the polymer backbone.

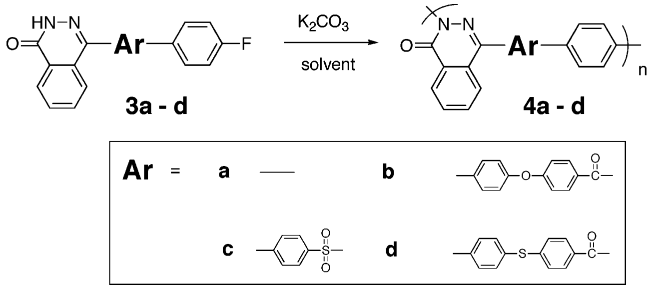
Fluorinated polymers have unique properties, such as low dielectric constant, refractive index, optical loss, and moisture absorption along with high thermoxidative and chemical stability.[10] Many kinds of fluorinated polymers aimed at various applications, such as films, coatings for microelectronics and optical devices, gas-separation membranes, and matrix resins in fiber-reinforced composites, have been synthesized.[11−15] Fluorinated poly(arylene ether)s are one of the most important classes owing to excellent thermooxidative stability, high T_g, and outstanding mechanical properties and have found applications in the fields of aerospace and electronics industries where high performance is required.[16−19] Recently some fluorinated poly(phthalazinone ether)s have been reported.[20,21] Lu synthesized a series of polymers by polymerization of phthalazinone monomer **1** with perfluorobiphenyl but failed to obtain high molecular weight polymers.[20] Xiao[21] reported the preparation 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 synthesized the AB-type phthalazinone monomers **3a−d** (Scheme 2).

Scheme 1. Synthesis of Poly(phthalazinone ether) 2



Scheme 2. Synthesis of Poly(phthalazinone ether)s from AB-Type Phthalazinone Monomers 3a−d



None of these AB monomers formed high molecular weight homopolymers **4a−d**, even under stringent conditions, because of premature precipitation of the polymer resulting from high degree of crystallization of the oligomers. This paper describes the synthesis and polymerization of the fluorinated AB-type phthalazinone monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2*H*)-one. A high molecular weight fluorinated poly(phtha1azinone ether) was successfully synthesized from this monomer. The fluorinated poly(phtha1azinone ether) has good solubility in many common solvents and could be cast into a clear, transparent, and tough film.

The fluorinated AB-type phthalazinone monomer 4-(4-hydroxyphenyl)-2-(penta fluorophenyl)phthalazin-1(2*H*)-one (**7**) was synthesized by reaction of 2-(hydroxybenzoyl)benzoic acid (**5**) with 1-(pentafluorophenyl)hydrazine (**6**) (Scheme 3).

The 2-(hydroxybenzoyl)benzoic acid (**5**) was synthesized from phenolphthalein and hydroxylamine as previously described.[1] The condensation reaction of **5** with phenylhydrazine was reported by Paventi.[22] The 1-(pentafluorophenyl)hydrazine has lower activity than phenylhydrazine because of the electron-withdrawing pentafluorophenyl group. Longer reaction times and increasing the reaction temperature significantly improved the yield. At a reaction temperature of 110 °C for 2.5 h the yield obtained was 66.3%, whereas at reaction temperature of 155 °C for 2.5 h the yield was 86.6%. The highest yield, 92.4%, was obtained at 110 °C for 23 h. The reaction mixture was poured into hot water to give a pale ochre-colored precipitate. The solid product was recrystallized from absolute ethanol to give colorless needlelike crystals, mp 222 °C. ^{1}H and ^{19}F NMR spectra of the fluorinated phthalazinone were recorded on a Varian Mercury 300 spectrometer using $CDCl_3$ as solvent and tetramethylsilane and $CFCl_3$ as reference, respectively. The spectroscopic data are in agreement with the proposed structure. The ^{1}H NMR ($CDCl_3$) spectrum showed a characteristic peak at δ 5.60 ppm for the aryl hydroxyl group, and the ^{19}F NMR ($CDCl_3$) spectrum (Figure 1a) clearly indicated three kinds of fluorine atoms for the pentafluorophenyl group at δ 144.6, δ 153.4, and δ 162.1 ppm, respectively, in a ratio of 2:1:2. MALDI−TOF MS: 404.68 (M), 410.49 (M^-Li^+). The calculated molecular weight is 404.04. MALDI−TOF MS and HPLC indicated 100% purity.

Fluorinated poly(phthalazinone ether) **8** was synthesized by self-condensation of the AB-type fluorinated phthalazinone monomer **7** in dimethylacetamide (DMAc) using excess of K_2CO_3 (Scheme 3).

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 7−20 h. High molecular weight fluorinated poly(phthalazinone ether) was not obtained. The film

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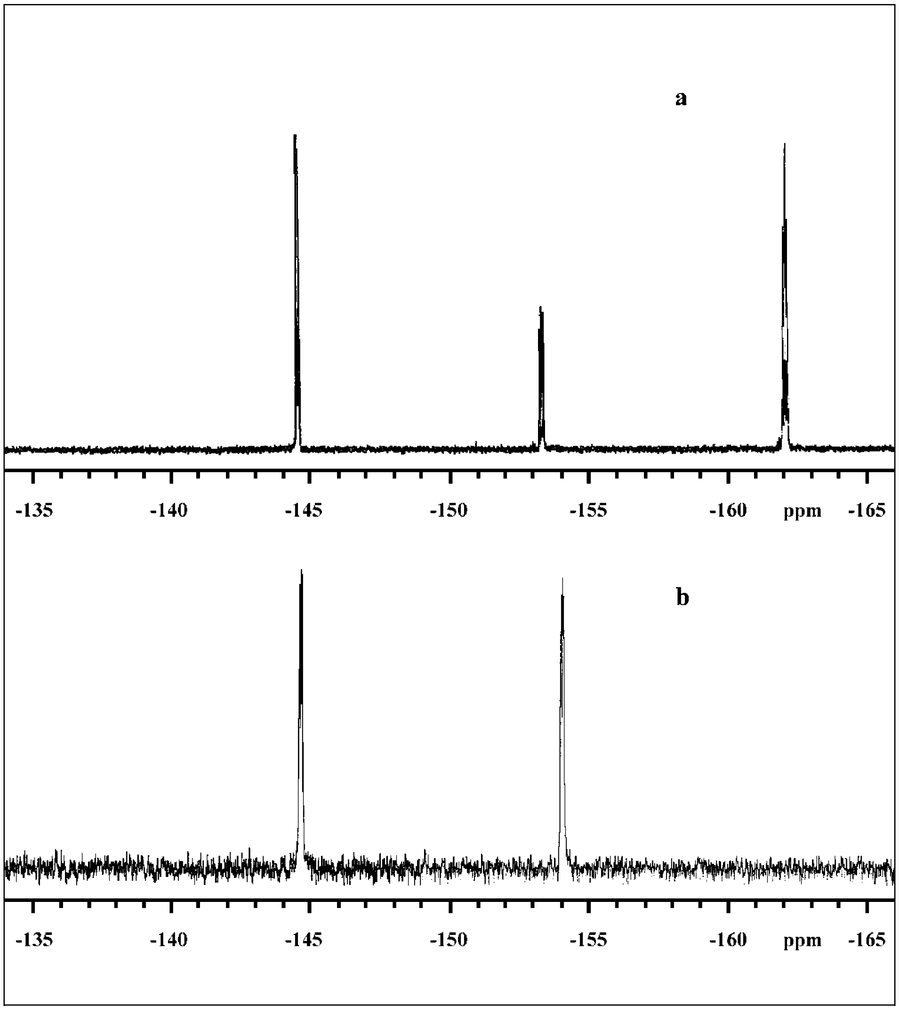

Figure 1. ^{19}F NMR spectra of (a) fluorinated phthalazinone monomer **7** and (b) fluorinated poly(phthalazinone ether) **8**.

Scheme 3. Synthesis of AB-Type Phthalazinone Monomer 4-(4-Hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2*H*)-one 7 and Fluorinated Poly(phthalazinone ether) 8

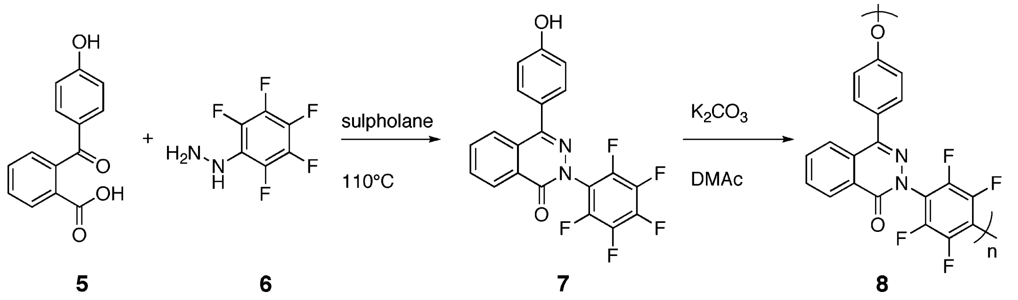

Table 1. Properties of Fluorinated Poly(phthalazinone ether) 8 from AB Monomer 7 under Various Polymerization Conditions

no.	polymerization T (°C)/time (h)	solvent	yield (%)	η_{inh}[a] (dL/g)	T_g[b] (°C)	T_g[c] (°C)	T_d(−5 wt %)[d] (°C)
8a	170−175/7	DMAc/toluene	68.9	0.28	315	342	436
8b	105−110/48	DMAc	75.4	0.41	309	346	472
8c	105−110/22	DMAc/benzene	99.6	0.48	314	345	483
8d	105−110/24	DMAc	83.1	0.53	316	329	485
8e	105−110/4	DMAc/benzene	99.7	0.55	316	315	491

[a] Inherent viscosity was measured at a concentration of 0.2 g/dL in $CHCl_3$ at 25 °C. [b] Heating rate of 20 °C/min under nitrogen flow rate 160 mL/min, values from the first scan. [c] T_g from the second scan after heating to 400 °C. [d] 5% weight loss at a heating rate of 20 °C/min under nitrogen, flow rate 80 mL/min.

cast from the polymer **8a** prepared at 170 °C for 7 h with an inherent viscosity of 0.28 dL/g (Table 1) was brittle.

Prolonging the polymerization time to 20 h gave gelation, presumably because the AB monomer behaves as a polyfunctional material. 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. Better results were obtained (**8d**; η_{inh} 0.53 dL/g) at 105−110 °C for 24 h, and when the reaction was carried out at this temperature in a DMAc/benzene mixture to remove water, a high molecular weight polymer **8e** with an inherent viscosity of 0.55 dL/g was obtained. The ^{19}F NMR spectra of fluorinated poly(phthalazinone ether) **8** indicated there were two kinds of fluorines in the backbone with exact ratio 1:1 (Figure 1b), at δ 144.6 and δ 154.0 ppm. There was no discernible difference in the spectra of the various polymers, **8a**−**8e**.

Fluorinated poly(phthalazinone ether) **8** has good solubility in solvents such as DMAc, DMF, DMSO, NMP, TCE, THF, $CHCl_3$, pyridine, and sulfolane. A tough, flexible film was obtained by solution casting from chloroform. The glass transition temperatures (T_g's) of the fluorinated poly(phthalazinone ether)s (Table 1, T_g^b) 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 cross-linking may have occurred. TGA measurements indicated excellent thermal stability (Table 1) with the various molecular weight polymers having 5% weight 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. These results, along with the DSC results, indicate that the lower molecular weight polymers contain functional groups that react at lower temperatures. All of the polymers when heated 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 ∼100% but remained flexible. This phenomenon is under investigation.

In conclusion, the AB-type phthalazinone monomer 4-(4-hydroxyphenyl)-2-(pentafluorophenyl)phthalazin-1(2*H*)-one (**7**) has been synthesized by reaction of 2-(hydroxybenzoyl)benzoic acid with 1-(pentafluorophenyl)hydrazine. A high molecular weight fluorinated poly(phthalazinone ether) **8** with good solubility in common solvents was obtained by self-condensation of the AB-type phthalazinone monomer **7** under mild reaction conditions. The polymer can be cast from chloroform solution into a tough, flexible film. The polymer has a T_g of 316 °C and a $T_{d,-5\%}$ of 491 °C and is soluble in many common solvents. The polymer cross-links when heated for a short time at 300 °C.

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