Synthesis of All-Aromatic Phthalazinone-Containing Polymers by a Novel N−C Coupling Reaction

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ABSTRACT: High molecular weight poly(phthalazinone)s with high glass transition temperatures were prepared by a novel N−C coupling reaction. New bis(phthalazinone) monomers (**5a**−**f**), such as 7,7′-oxobis[4-phenylphthalazin-1(2*H*)-one] (**5c**), were synthesized from the corresponding bis(phthalic anhydride)s (**3a**−**f**) in two steps. Other types of bis(phthalazinone) monomers (**8**, **9**) were synthesized from phthalic anhydride and diphenyl sulfide or diphenyl ether. AB-type phthalazinone monomers (**11a**, **12**−**14**) were also synthesized from phthalic anhydride. Poly(phthalazinone)s, having inherent viscosities of 0.3−0.4 dL/g, were prepared by the reaction of the bis(phthalazinone) monomers with an activated aryl halide such as bis(4-fluorophenyl) sulfone (**22**) in a dipolar aprotic solvent in the presence of potassium carbonate. AB-type phthalazinone monomers do not form high molecular weight polymers because of premature precipitation during the polymerization reaction. One of the AB-type phthalazinone monomers, 4-[4-((4-fluorophenyl)sulfonyl)phenyl]phthalazin-1(2*H*)-one, was successfully copolymerized with 4,4′-biphenol and bis(4-fluorophenyl) sulfone to form high molecular weight polymers. The copolymers showed higher glass transition temperatures (T_gs) as the phthalazinone ratio increased. All phthalazinone homopolymers except the Bisphenol A phthalazinone polymers show T_gs around 300 °C by differential scanning calorimetry. The decomposition temperatures for 5% weight losses in air and in nitrogen measured by thermogravimetric analysis are in the range of 480−530 °C. Polymers from the Bisphenol A phthalazinone monomer are soluble in chlorinated solvents such as chloroform. Other polymers are soluble in dipolar aprotic solvents such as *N*-methyl-2-pyrrolidinone. The soluble polymers can be cast into flexible films from solution.

Introduction

Considerable research has been carried out to develop new condensation polymers containing heterocyclic units since many of these polymers possess outstanding strength and moduli and are used predominantly as high temperature-resistant materials and fibers. Among the many heterocyclic polymers, polyimides[1] and polybenzimidazoles[2] have attracted commercial attention and have been widely studied. Numerous efforts to synthesize new heterocyclic polymers can be found in the literature. Many kinds of heterocyclic polymers, such as poly(ether imide)s,[3] poly(aryl ether phenylquinoxaline)s,[4] and poly(aryl ether benzoxazole)s,[5] have been synthesized by nucleophilic aromatic substitution reactions. In this case, the preformed heterocyclics are included in the monomer. Polymerization then takes place between an activated aryl halide and a nucleophile, such as a bisphenolate anion. In addition to these polymers, some new heterocyclic polymers, such as polyquinoline[6] and polyquinoxaline,[7] have been synthesized using heterocyclic formation as a polymerization reaction.

Polymers with the N−N bond in the polymer chain[8] as well as polymers whose heterocyclic ring contains the N−N linkage[9] 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 have high thermostabilities, from dibenzoylphthalic acids and bisarylhydrazines.[10]

Methods to form the carbon−nitrogen bond in aromatic systems are limited to rather vigorous processes which are copper-mediated reactions.[11,12] We have previously[13,14] described the synthesis of poly(1,2-dihydro-1-oxophthalazine-2,4-diyl-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) (**2**) by the reaction of 4-(4-hydroxyphenyl)phthalazin-1(2*H*)-one (**1**) with bis(4-fluorophenyl) sulfone (Scheme 1). In this polymerization reaction, the aza-nitrogen anion, formed by reaction with potassium carbonate, undergoes a displacement reaction with activated aryl halides. To the best of our knowledge, no polymerization reaction using the aza-nitrogen anionic displacement has been reported outside our laboratory. If the phthalazinone NH groups behave like phenolic OH groups, then compounds with two phthalazinone groups should react similarly to bisphenols in nucleophilic aromatic substitution reactions. The resulting polymers would be expected to be stable at high temperatures since similar structures have been previously synthesized by an alternative route.[10]

Results and Discussion

Monomer Synthesis. Three kinds of new phthalazinone monomers, bis(phthalazinone) monomers from diphthalic anhydrides, bis(phthalazinone) monomers from phthalic anhydride, and AB-type self-condensation phthalazinone monomers, were synthesized.

Bis(phthalazinone) monomers **5b**−**f** and 2,3,7,8-tetraazaanthracenediones **5a** were synthesized from the corresponding dianhydrides in two steps (Scheme 2). The first step is a Friedel−Crafts reaction between a series of dianhydrides and benzene. There are three possible isomers in the case of **5b**−**f**. In the case of **5a**, the two isomers, 4,6-dibenzoylphthalic acid and 2,5-dibenzoylphthalic acid, which formed in a ratio of 2:1, were separated by fractional recrystallization from glacial acetic acid. In the case of the anhydrides containing electron-withdrawing groups such as **3b**, **3d**, and **3e**, the acylinium ion para to the electron-withdrawing group is destabilized in the Friedel−Crafts reaction, favoring the formation of one isomer. The keto acids **4c** and **4f**, which are formed from dianhydrides containing electron-donating groups, **3c** and **3f**, are thermally unstable and cannot be purified. The crude

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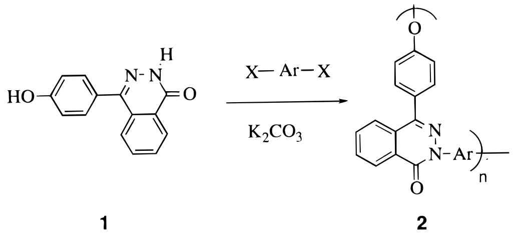
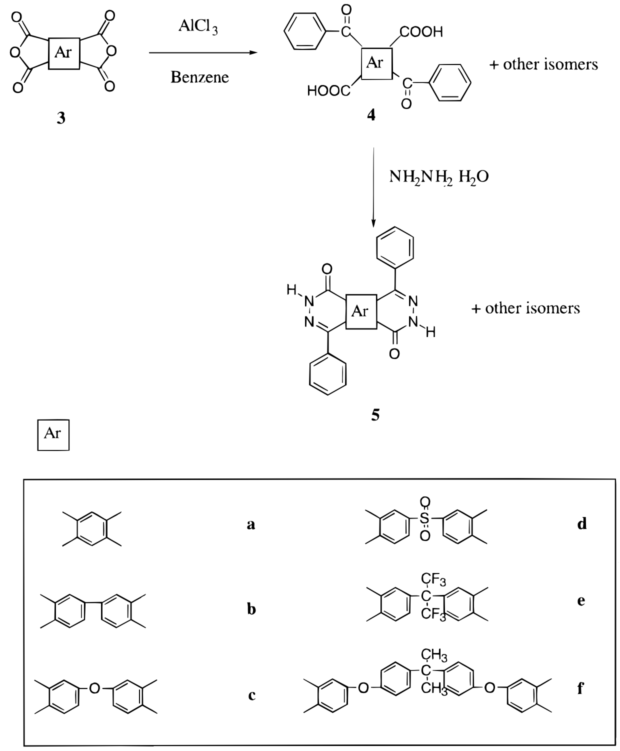
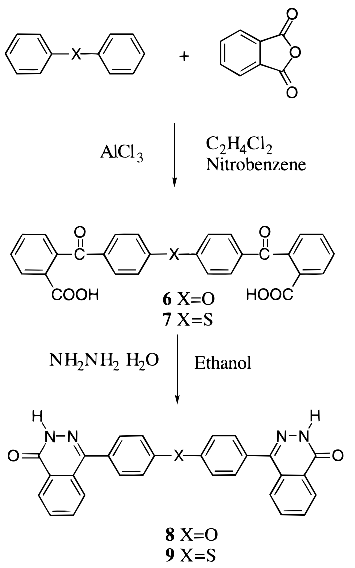
Scheme 1



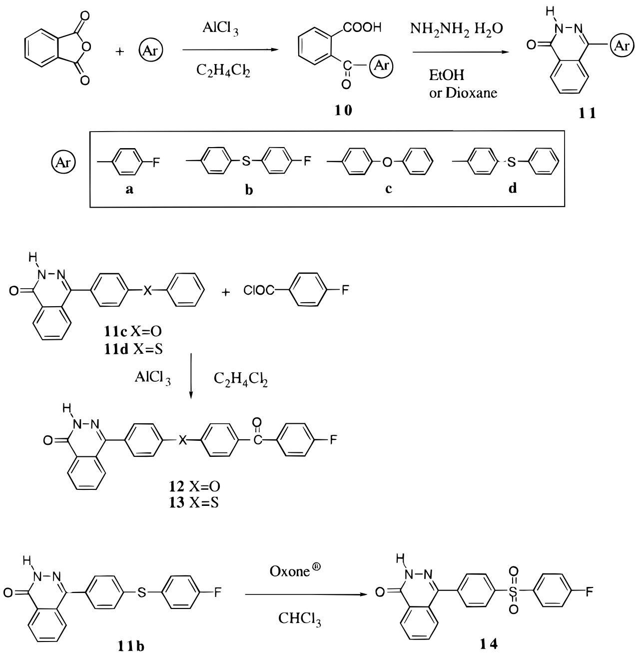
Scheme 2



Scheme 3



Scheme 4



products were directly reacted with hydrazine monohydrate. In the case of **4c** and **4f**, three isomers are thought to have formed based on the ^{1}H-NMR spectra and the melting points of the final product. The isomers were not separated and the mixture was reacted directly with hydrazine monohydrate to form the mixture of bis(phthalazinone)s. The other bis(phthalazinone) monomers **8** and **9** were synthesized from diphenyl sulfide or diphenyl ether and phthalic anhydride in two steps (Scheme 3). The Friedel–Crafts reaction proceeds at room temperature and monosubstitution takes place selectively as described by Wolfe and Stille.[6]

AB-type self-condensation phthalazinone monomers were synthesized from phthalic anhydride as shown in Scheme 4. Phthalic anhydride is reacted with fluorobenzene, 4-fluorophenyl sulfide, or diphenyl ether in the presence of anhydrous aluminum chloride at room temperature to form the corresponding keto acids **10a–d** in good yield, which are then reacted with hydrazine monohydrate affording the phthalazinones **11a-d**. Phthalazinone **11b** was oxidized by Oxone to form the phthalazinone **14** with a fluoride group, which is activated by sulfone toward nucleophilic substitution reaction. Phthalazinones **11c** and **11d** were reacted with 4-fluorobenzoyl chloride in the presence of anhydrous aluminum chloride, affording phthalazinones **12** and **13**, which have a 4-fluorobenzophenone moiety, in high yield.

Polymer Synthesis. The poly(phthalazinones)s were prepared by the reaction of the bis(phthalazinone) monomers **5a–f**, **8**, and **9** with either bis(4-fluorophenyl) sulfone (**22**), 4,4′-difluorobenzophenone (**23**), or 2,6-dichlorobenzonitrile (**24**) in a dipolar aprotic solvent (Scheme 5). **5f** was polymerized in *N*-methyl-2-pyrrolidinone (NMP) with toluene in the presence of potassium carbonate. The remaining monomers were polymerized in diphenyl sulfone (DPS) at higher temperatures. In the case of monomers **8** and **9**, longer reaction times were needed to obtain high molecular weight polymers, compared to monomers **5b**,**c**. The phthalazinone aza-nitrogen anions, which were formed via deprotonation by potassium carbonate, attack the activated aryl halides with elimination of the fluorides. High molecular weight polymers with inherent viscosities of 0.29–0.50 dL/g (see Table 1) were obtained for all polymers except **15a**, **15d**, **19**, and **20**. Polymers containing monomer **5f** in the polymer backbone are soluble in chloroform. Their inherent viscosities were 0.25–0.32 dL/g, with weight-average molecular weights in the range of 30 000–50 000 by GPC, compared to polystyrene standards (Table 1). In the case of **5a**, the

Scheme 5

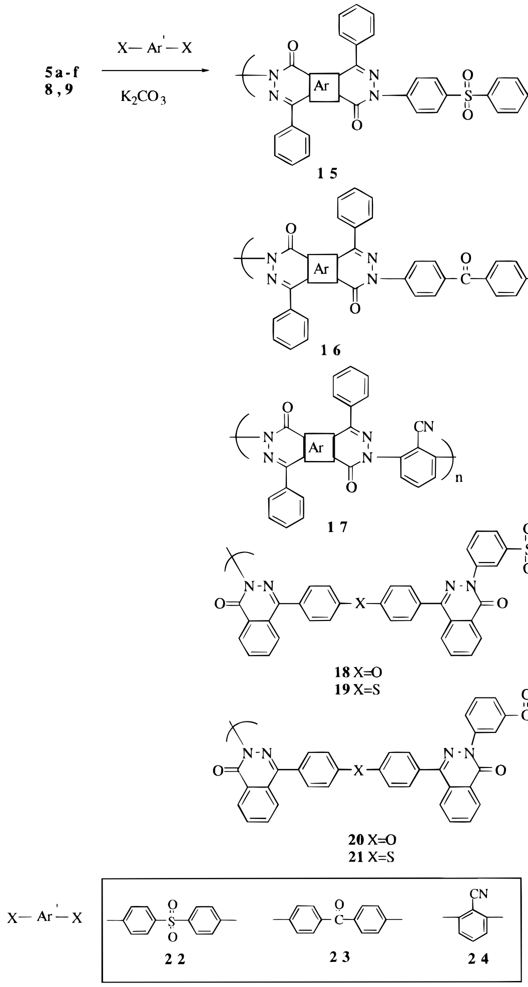


Table 1. Polymerization of the Biphthalazinone Monomers

polymer	solvent	temp (°C)	yield (%)	η_{inh}[b] (dL/g)	M_w[d]	M_n	PD
15a	DPS	310	99	0.18[c]			
15b	DPS	280	97	0.33			
15c	DPS	280	89	0.51			
15d	DPS	310	92	0.11			
15e	NMP	190	0[a)]				
15f	NMP	190	86	0.29	44000	15200	2.89
16c	DPS	230	96	0.42			
16f	NMP	190	81	0.32	51000	14900	3.42
	DPS	250	98	0.29			
17f	NMP	190	78	0.25	33000	8900	3.71
18	DPS	310	92	0.32			
19	DPS	310	91	0.21			
20	DPS	310	94	0.33			
21	DPS	310	94	0.19			

[a] Decomposition. [b] η_{inh} was measured at a concentration of 0.5 g/dL in NMP at 25 °C. [c] In concentrated sulfuric acid at 25 °C. [d] Molecular weight was determined by GPC in chloroform based on polystyrene standards.

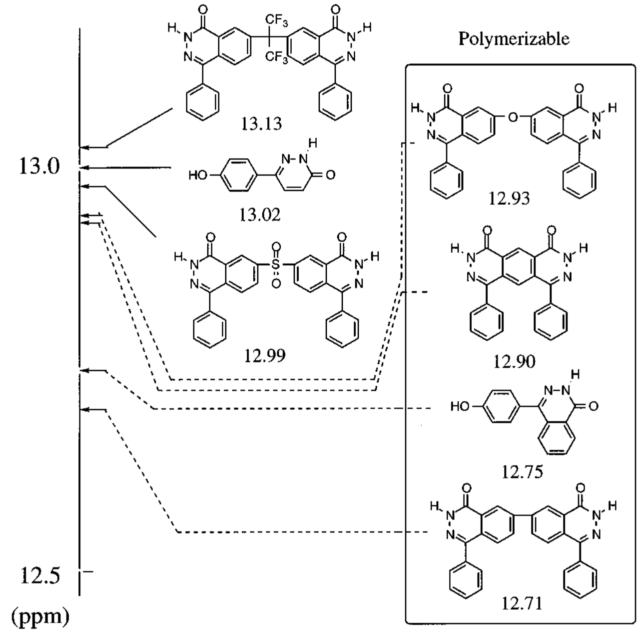
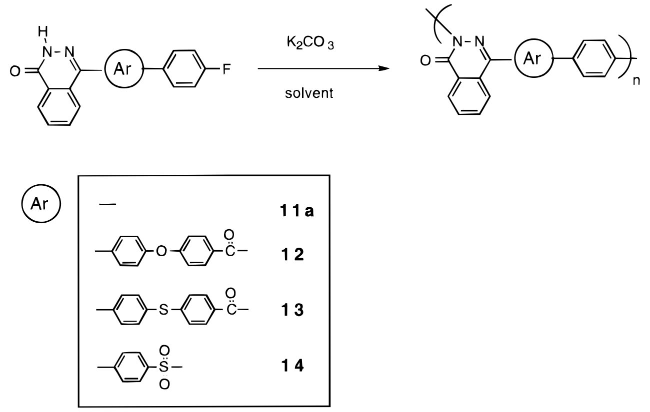


Figure 1. ^{1}H-NMR chemical shifts of the acidic protons of the phthalazinone monomers in DMSO-d_6.

Scheme 6



polymerization reaction was carried out for each of the separated isomers; however, neither of them formed high molecular weight polymers, presumably due to their insolubility. The mixture of the isomers obtained from **3a** gave higher molecular weight polymer than the polymer from the separated single isomer. However, the structure of **5a** is so rigid that even in the reaction with **22**, which should form the most soluble polymer, the insoluble oligomer precipitated out at an early stage of the polymerization reaction. When 4,4′-difluorobenzophenone **23**) was reacted with the bis(phthalazinone) monomers, insoluble oligomer also precipitated out of the reaction mixture before high molecular weight polymer formed, except for monomers **5c** and **5f**. When 2,6-dichlorobenzonitrile (**24**) was used as a monomer, only **5c** formed a high molecular weight polymer. The monomers containing electron-withdrawing groups, such as **5d** and **5e**, do not form high molecular weight polymers. Monomer **5d** formed only oligomers during the polymerization reaction, and monomer **5e** decomposed during the reaction regardless of the reaction conditions used. The electron-withdrawing group makes the NH group more acidic and consequently the resulting anion becomes less nucleophilic, thereby limiting the polymerization reaction. The H chemical shift of the acidic NH proton of the phthalazinone monomers can be used as a measure of their reactivity (Figure 1).

AB-type phthalazinone monomers **11a**, **12**, **13**, and **14** were polymerized in DPS, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), and 1-cyclohexyl-2-pyrrolidinone (CHP) at 250−300 °C (Scheme 6). Because of high crystallinities of the polymers, premature precipitation took place. The inherent viscosities of formed polymers are less than 0.15 dL/g in concentrated sulfuric acid. None of them formed high molecular weight polymers even when stringent conditions,

Scheme 7

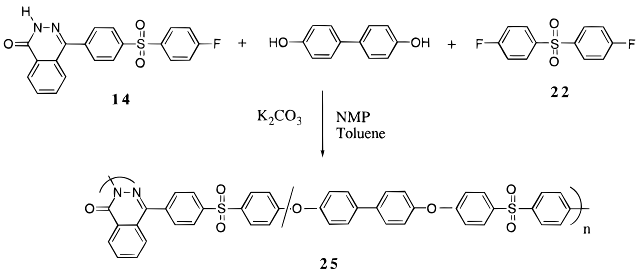


Table 2. Copolymerization of 14 with 4,4′-Biphenol

14 (%)	yield (%)	η_{inh}[a] (dL/g)	M_n[c]	M_w	PD	T_g[d] (°C)	solubility
0	90	0.48	17000	63400	3.7	240	$CHCl_3$
20	91	0.46	8900	35000	3.9	273	$CHCl_3$
50	89	0.31				323	NMP
100	87	0.11[b]				422	H_2SO_4

[a] Inherent viscosity was measured at a concentration of 0.5 g/dL in NMP at 25 °C. [b] In concentrated sulfuric acid at 25 °C. [c] Molecular weight was determined by GPC in chloroform based on polystyrene standards. [d] Second scan at a heating rate of 20 °C min^{-1}.

Table 3. Thermal Properties of Phthalazinone Polymers

polymer	T_g[a] (°C)	TGA[b] (°C) air	TGA[b] (°C) N_2
15a	*c*	478	488
15b	344	478	479
15c	310	485	499
15f	221	471	489
16c	286	512	497
16f	195	465	486
17c	301	531	526
17f	200	469	501
18	295	477	476
19	279	465	471
20	301	467	468
21	281	459	461

[a] T_g was determined by DSC at a heating rate of 20 °C min^{-1} under nitrogen (160 mL min^{-1}); the values were reported from the second scan. [b] Reported for 5% weight loss at a heating rate of 20 °C min^{-1} under air or nitrogen (flow rate 200 mL min^{-1}). [c] Not detected.

Table 4. Solubilities[a] of Poly(phthalazinone)s

polymer	solvent: sulfuric acid	*m*-cresol	TCE[b]	chloroform	NMP
15a	+	−	−	−	−
15b	+	+	−	−	+
15c	+	+	−	−	+
15f	+	+	+	+	+
16c	+	+	−	−	+ −
16f	+	+	+	+	−
17c	+	+	−	−	+ −
17f	+	+	+	+ −	+
21	+	+ −	−	−	−
22	+	+ −	−	−	−
23	+	+ −	−	−	−
24	+	+ −	−	−	−

[a] Solubility: +, soluble at room temperature; + −, partially soluble; −, insoluble. [b] TCE, *sym*-tetrachloroethane.

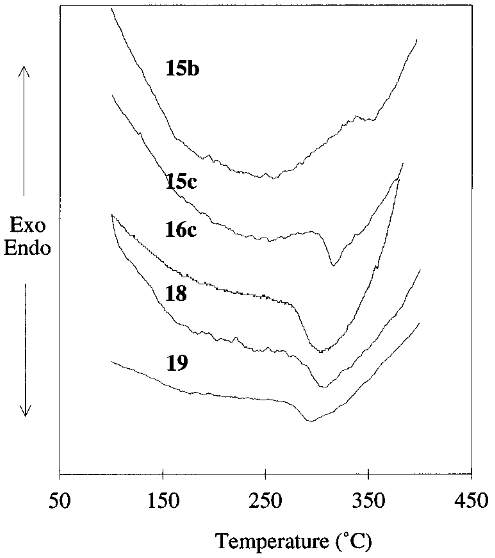


Figure 2. DSC analysis of polymers **15b**, **15c**, **16c**, **18**, and **19** under an atmosphere of nitrogen.

such as 300 °C in DPS, were used. The polymer from the AB monomer **12**, which is lower molecular weight, has the same empirical formula as the polymer formed from **1** and **23**, which is high molecular weight (Scheme 1). The latter polymer, which formed from two monomers, contains head-to-head linkages and head-to-tail linkages, so that the crystallinity was reduced by the random arrangement of the two monomers' linkages. The amorphous polymer is soluble in sulfolane at 220 °C and formed high molecular weght polymer without premature precipitation. We attempted to copolymerize monomer **11a** with 4,4′-biphenol and bis(4-fluorophenyl) sulfone (**22**); however, only low molecular weight oligomers formed. The fluoride group in this monomer is unreactive and high molecular weight polymer was not formed. Monomer **14**, however, could be successfully copolymerized with 4,4′-biphenol and **22** to form high molecular weight polymer (Scheme 7, Table 2). This suggests that the reactivity of the aza-nitrogen anion of the phthalazinone is comparable to that of the biphenol. The copolymers have higher T_gs and lower solubilities as the amount of **14** increases.

Polymer Characterizations and Properties. Polymers with the BPA linkage are soluble in chlorinated solvents such as chloroform. The remaining polymers are soluble in solvents such as NMP or *m*-cresol. A few are soluble only in concentrated sulfuric acid (Table 4).

Polymers with flexible ether linkages, such as **15c** and **16c**, were solution cast into flexible films from *m*-cresol, and **15f** was cast into flexible films from 1,1′,2,2′-tetrachloroethane. Polymer **15a** is only soluble in a solvent such as concentrated sulfuric acid. All the polymers obtained showed characteristic phthalazinone CO stretching at 1650 cm^{-1} in their IR spectra. The IR spectra of **15a** (both of the polymers from separated isomers) were identical to the polymers which were synthesized by another route.[10]

The glass transition temperatures (T_gs) listed in Table 3 were measured by differential scanning calorimetry (DSC). Typical DSC curves for poly(phthalazinone)s are shown in Figure 2. The poly(phthalazinone)s showed very high T_gs around 300 °C except the Bisphenol A phthalazinone polymers. The T_g of polymer **15a** was not detectable by DSC. Thermal stabilities of the poly(phthalazinone)s were determined by thermogravimetric analysis (TGA) (Figure 3). All the poly(phthalazinone)s showed a similar pattern of decomposition with no weight loss below 400 °C in either air or nitrogen. The temperatures for 5% weight loss were observed between 480 and 530 °C.

Young's moduli for polymers **15b**, **15c**,**15f** and **16c** are given in Table V. All polymers have Young's moduli in the range 1.75−2.21 GPa at 25 °C. These values are

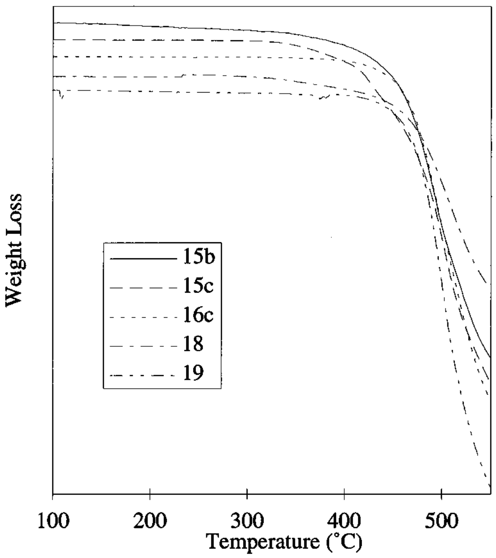


Figure 3. TGA thermogram (weight loss vs temperature) for polymers **15b**, **15c**, **16c**, **18**, and **19** under an atmosphere of nitrogen.

Table 5. Mechanical Properties of Phthalazinone Polymers

	Young's modulus (GPa)		
polymer	20 °C	200 °C	tan δ (°C)
15b	2.15	1.26	238
15c	1.81	1.29	279
15f	1.75	1.11	200
16c	2.21	1.44	265

typical for engineering thermoplastics. When films of these polymers are heated, they maintain good mechanical properties in the GPa range above 200 °C. The T_gs of polymers as measured from the tan δ are lower than the values measured by DSC due to the mild mechanical deformations inherent in the testing method.[15]

Conclusions

A new class of monomers, bis(phthalazinone)s, have been prepared in two steps in good yields from readily available compounds. They were reacted with a series of activated aryl halides to give high molecular weight novel poly(phthalazinone)s in a one-step reaction involving the formation of an N−C bond. The formed polymers have high glass transition temperatures and excellent thermostabilities. AB-type phthalazinone monomers also have been prepared and successfully copolymerized with poly(ether sulfone), affording polymers with higher T_gs.

Experimental Section

Materials. Tetramethylene sulfone (sulfolane) and 1,1,2,2-tetrachloroethane (TCE) were used as obtained from Aldrich. Diphenyl sulfone and 2,6-dichlorobenzonitrile (**24**) (Aldrich) were recrystallized from ethanol. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (**3b**), 1,2,4,5-benzenetetracarboxylic dianhydride (**3a**), diphenyl sulfide, diphenyl ether, phthalic anhydride, 4,4′-difluorobenzophenone (**23**), and 4,4′-bis(4-fluorophenyl) sulfone (**22**) were used as obtained from Aldrich. Anhydrous aluminum chloride and anhydrous potassium carbonate were obtained from Omega. 4,4′-Oxydi[phthalic anhydride] (**3c**) and 4,4′-sulfonyldi[phthalic anhydride] (**3d**) were obtained from Chriskev Co. Inc. 2,2′-(Hexafluoroisopropylidene)bis[phthalic anhydride] (**3e**) was obtained from Hoechst Co. 4-Fluorobenzoyl chloride was obtained from Lancaster. Bisphenol A dianhydride (**3f**) was kindly donated by General Electric Co. All common solvents were obtained from Caledon and used as received unless otherwise noted.

Characterization. The melting points of the monomers were obtained using a Fisher-Johns melting point apparatus or a Mettler FP800 DSC and are uncorrected. The ^{1}H-NMR spectra were measured with a JEOL 270 instrument using dimethyl-d_6 sulfoxide (DMSO-d_6) as a solvent. The chemical shifts were calibrated using tetramethylsilane (TMS). The chemical shift (δ) and coupling constant (J) data are quoted in ppm and hertz, respectively. Infrared spectra were recorded using an IR Analect AQS-18 FT-IR spectrometer. Glass transition temperatures (T_gs) were obtained using a Seiko 220 DSC instrument at a heating rate of 20 °C min^{-1} in N_2 (160 mL/min). The T_g values were reported from the second scan. The T_g was taken from the midpoint of the change in the slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 20 °C min^{-1} in N_2 and air (200 mL/min) and the values reported are for 5% weight loss. Inherent viscosity (η_{inh}) data were obtained with a calibrated Ubbelohde viscometer. Measurements were made in NMP or H_2SO_4 at 25 °C at a concentration of 0.5 g/dL. Thermomechanical studies were performed on a Seiko 120 thermomechanical analyzer thermal stress−strain analyzer (TMA/SS) with a heating rate of 3 °C min^{-1}. Films for the thermomechanical analyzer were cast from *m*-cresol or 1,1′,2,2′-tetrachloroethane at 145 °C and dried under vacuum at 150 °C for 4 h and at 200 °C for 24 h.

Synthesis. 4,6-Dibenzoylisophthalic Acid (DBIA) or 2,5-Dibenzoylphthalic Acid (DBTA) (4a). 4,6-Dibenzoylisophthalic acid (DBIA) and 2,5-dibenzoylphthalic acid (DBTA) were synthesized according to the reported procedure by the Friedel−Crafts reaction of pyromellitic dianhydride with benzene in the presence of anhydrous aluminum chloride. Two isomers were separated by fractional recrystallization from aqueous methanol. DBIA: yield 42%; mp 328 °C (DSC) (lit.[5] mp 318 °C). DBTA: yield 18%; mp 285−287 °C (lit. mp[15] 277−278 °C).

1,8-Diphenyl-2,3,6,7-tetraazaanthracene-4,5-dione (5). To 3.74 g (0.01 mol) of DBTA (DBIA or a mixture of two isomers) and 100 mL of ethanol was added 0.50 g (0.01 mol) of hydrazine monohydrate. The reaction mixture was heated to reflux and stirred for 4 h. A white powder precipitated, which was washed with water and then methanol and dried under reduced pressure at 80 °C: yield 89%; mp 330 °C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.58−7.69 (m, 10H), 8.55 (m, 2H), 12.89 (s, 2H); IR (KBr) 1670 cm^{-1}; MS (*m/e*, relative intensity (%)) 365.9 (M$^+$, 100). Anal. Calcd for $C_{22}H_{14}O_2N_2$: C, 72.12; H, 3.85; N, 15.29. Found: C, 72.84; H, 3.85; N, 15.75.

4,8-Diphenyl-2,3,6,7-tetraazaanthracene-1,5-dione (5a): yield 92%; mp >400 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.58−7.69 (m, 10H), 8.55 (m, 2H), 12.89 (s, 2H); IR (KBr) 1655 cm^{-1}; MS (*m/e*, relative intensity (%)) 365.9 (M$^+$, 100). Anal. Calcd for $C_{22}H_{14}O_2N_2$: C, 72.12; H, 3.85; N, 15.29. Found: C, 72.67; H, 3.80; N, 15.82.

Mixture of Two Isomers (5): yield 97%; mp 330 °C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.58−7.69 (m, 10H), 8.55 (m, 2H), 12.89 (s, 2H); IR (KBr) 1670 cm^{-1} ($\nu_{C=O}$); MS (*m/e*, relative intensity (%)) 365.9 (M$^+$, 100). Anal. Calcd for $C_{22}H_{14}O_2N_2$: C, 72.12; H, 3.85; N, 15.29. Found: C, 72.03; H, 3.83; N, 15.30.

3,3′-Dibenzoyl-1,1′-biphenyl-4,4′-dicarboxylic Acid (4b). In a 500 mL three-neck, round-bottom flask equipped with a mechanical stirrer and a water-cooled condenser were added 3,3′,4,4′-biphenyltetracarboxylic dianhydride (**3b**) (8.82 g, 0.03 mol), anhydrous aluminum chloride (19.99 g, 0.15 mol), and 200 mL of benzene freshly distilled from sodium. The reaction mixture was heated to reflux with vigorous stirring and held at this temperature for 16 h. The hot reaction mixture was poured onto 300 g of crushed ice containing 5 mL of concentrated HCl. The white granular mass was filtered, washed with water, and dissolved in warm dilute potassium hydroxide solution. After filtration to remove a little insoluble matter, the keto acids were precipitated with dilute HCl. The white powder was filtered, dried, and recrystallized from glacial acetic acid: yield 81.0% (10.93 g); mp 255−257 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.50 (m, 4H), 7.65 (m, 6H), 7.76 (d, J_2

= 8.15, 2H), 8.42 (dd, J_3 = 1.97, J_2 = 8.14, 2H), 8.54 (d, J_3 = 1.97, 2H).

4,4′-Diphenyl-1,1′-biphthalazin-1(2*H*),1′(2′*H*)-dione (5b). Biphthalazinone monomers **5b** were prepared by the reaction of keto acid **4b** with hydrazine monohydrate in methanol using the procedure described for **5a**. The crude product was recrystallized from glacial acetic acid: yield 88% (9.46 g); white powder, mp 385 °C (DSC endothermic peak); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.51−7.89 (m, 10H), 8.35 (m, 2H), 8.50 (m, 2H), 8.70 (s, 2H), 12.71 (s, 2H); MS (m/e, relative intensity (%)) 442.48 (M^+, 100). Anal. Calcd for $C_{28}H_{18}N_4O_2$: C, 76.01; H, 4.10; N, 12.66. Found: C, 74.40; H, 4.13; N, 12.66.

4,5′-Sulfonylbis[2-benzoylbenzoic acid] (4d). This compound was prepared by the Friedel−Crafts reaction of 4,4′-sulfonyl bis[phthalic anhydride] (**3d**) with benzene in the presence of anhydrous aluminum chloride using the procedure described for **4b**: yield 55.5%; light yellow powder, mp 289−291 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.52 (m, 4H), 7.66 (m, 6H), 7.76 (d, J_2 = 8.15, 2H), 8.43 (dd, J_2 = 8.03, J_3 = 1.97, 2H), 8.56 (d, J_3 = 1.99, 2H).

7,7′-Sulfonylbis[4-phenylphthalazin-1(2*H*)-one] (5d). Biphthalazinone monomers **5d** were prepared by the reaction of keto acid **4d** with hydrazine monohydrate in methanol using the procedure described for **5a**. The crude product was recrystallized from glacial acetic acid: yield 91.0%; white powder, mp 346.4 °C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.52−7.61 (m, 10H), 7.87 (m, 2H), 8.45 (m, 2H), 8.83 (s, 2H), 13.20 (s, 2H); MS (*m*/*e*, relative intensity (%)) 506 (M^+, 100). Anal. Calcd for $C_{28}H_{18}N_4O_4S$: C, 66.39; H, 3.58; N, 11.06. Found: C, 65.90; H, 3.49; N, 11.31.

4,5′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis[2-benzoylbenzoic acid] (4e). This compound was prepared by the Friedel−Crafts reaction of 2,2′-(hexafluoroisopropylidene)bis[phthalic anhydride] (**3e**) with benzene in the presence of anhydrous aluminum chloride using the procedure described for **4b**.

This compound is partially soluble in benzene. After the reaction mixture was poured onto crushed ice containing concentrated HCl, benzene was removed by distillation and the white granular mass remaining in the hot liquid was filtered. It was then treated by the same procedure as for **4b** and **4d**: yield 39.8%; white powder, mp 224−226 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.5−7.8 (m, 14H), 8.08 (s, 2H).

7,7′-(1,1,1,3,3,3-Hexafluoropropane-2,2-diyl)bis[4-phenylphthalazin-1(2*H*)-one] (5e). Biphthalazinone monomer **5e** was prepared by the reaction of keto acid **4e** with hydrazine monohydrate in methanol using the procedure described for **5a**. The crude product was recrystallized from glacial acetic acid: yield 94%; white powder, mp 353 °C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) 7.51−7.61 (m, 10H), 7.84 (m, 4H), 8.37 (s, 2H), 13.13 (s, 2H); MS (*m*/*e*, relative intensity (%)) 594.08 (M^+, 6.5), 593.08 (33.9), 592.08 (100). Anal. Calcd for $C_{31}H_{18}F_6N_4O_2$: C, 62.84; H, 3.06; N, 9.46. Found: C, 61.29; H, 3.29; N, 9.50.

Bisphenol A Bis[benzoylbenzoic Acid] (4f). Bisphenol A 4,4′-di[phthalic anhydride] (10.40 g, 0.02 mol) was suspended in 500 mL of freshly sodium-distilled benzene in a 1 L round-bottom, three-neck flask equipped with a condenser and a mechanical stirrer. To this was added slowly 13.33 g (0.10 mol) of anhydrous aluminum chloride at room temperature. The resulting dark red suspension was heated to 65−70 °C and stirred for 3 h. The resulting black solution was poured onto 500 mL of crushed ice. After the ice melted, the white powder was filtered off and washed with chloroform repeatedly. The washed chloroform and benzene layers were put together, and the solvents were removed under reduced pressure at 25 °C. The resulting brown powder was dried in vacuo at 25 °C. A total of 4.50 g of brown powder was obtained. This compound reacts at 40 °C to form an insoluble residue. All attempts to recrystallize it failed. An endothermic peak starts at 40 °C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 1.62 (s, 6H), 7.10−8.00 (m, 24H).

Bisphenol A 7,7′-Bis[4-phenylphthalazin-1(2*H*)-one] (5f). This compound was prepared by the reaction of keto acid **4f** with hydrazine monohydrate in methanol using the procedure described for **5a**. The crude product was recrystallized from toluene and methanol alternately, and 5−6 recrystallizations were needed to obtain monomer grade purity material: $_1$H-NMR (DMSO-d_6) 1.62 (s, 6H), 8.02−8.24 (m, 22.6H), 8.34 (d, J_2 = 8.69, 1.4H), 12.79 (s, 1.3H), 12.82 (s, 0.7H) Because there are three isomers, interpretation of the peaks was not carried out. No effort was made to separate the isomers. MS (*m*/*e*, relative intensity (%)) 669 (M^+, 15), 370.99 (100). Anal. Calcd for $C_{43}H_{32}N_4O_4$: C, 77.23; H, 4.82; N, 8.38. Found: C, 76.83; H, 4.77; N, 8.51.

4,5′-Oxybis[2-benzoylbenzoic acid] (4c). In a 1 L round-bottom, three-neck flask equipped with a condenser and a mechanical stirrer, 6.20 g (0.02 mol) of 4,4′-oxydi[phthalic anhydride] (**3c**) was suspended in 500 mL of benzene freshly distilled from sodium. To this was added slowly 13.33 g (0.10 mol) of anhydrous aluminum chloride at room temperature. The reaction mixture was heated to reflux and stirred for 24 h. The reaction mixture was a white slurry at the beginning, then a sticky light yellow residue separated, and finally a viscous black half solid formed. The benzene was decanted and the black partial solid was poured into 1 L of crushed ice water. The white powder (18.2 g) was obtained after filtration and drying at room temperature in vacuo. This compound reacts at about 40 °C to form an insoluble residue. All attempts to recrystallize it failed. ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.19−7.25 (m, 2H), 7.34−7.38 (m, 2H), 7.45−7.62 (m, 2H), 8.01−8.09 (m, 2H).

7,7′-Oxybis[4-phenylphthalazin-1(2*H*)-one] (5c). This compound was prepared by the reaction of keto acid **4c** with hydrazine monohydrate in methanol using the procedure described for **5a**. The crude product was recrystallized from NMP: overall yield 44%; mp 290, 310, 324 °C (DSC endothermic peaks); ^{1}H-NMR (DMSO-d_6) 7.29 (d, J_3 = 2.54, 1.2H), 7.47−7.85 (m, 12H), 8.40−8.45 (d, J_2 = 8.67, 1H), 12.91 (s, 0.8H), 12.90 (s, 1.2H). Because of the three isomers, interpretation of the peaks was not done. No effort was made to separate the isomers. MS (*m*/*e*, relative intensity (%)) 457.94 (M^+, 100)). Anal. Calcd for $C_{28}H_{18}N_4O_3$: C, 73.35; H, 3.96; N, 12.22. Found: C, 72.52; H, 3.12; N, 11.63.

4,4′-Bis(2-carboxybenzoyl)diphenyl Ether (6). This compound was synthesized from diphenyl ether and phthalic anhydride according to Wolfe et al.:[6] yield 68%; mp 261−263 °C (lit. mp 263−267 °C); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.16 (d, J_2 = 8.88, 4H), 7.42 (d, J_2 = 8.10, 2H), 7.68 (m, 8H), 7.99 (d, J_2 = 8.10, 2H).

4,4′-Oxybis[4-(1,4-phenylene)phthalazin-1(2*H*)-one] (8). Compound **6** (4.68 g, 0.01 mol) was reacted with 0.50 g (0.01 mol) of hydrazine monohydrate in dioxane at reflux for 24 h. At the beginning of the reaction, the reaction mixture was a white emulsion which on heating cleared up. After 2 h a white powder started to come out. The reaction mixture was cooled down and the precipitate was collected by filtration. A total of 4.17 g of **8** was obtained after recrystallization from glacial acetic acid as a white powder: yield 91%; mp 390 °C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) 7.00−8.00 (m, 14H), 8.20−8.50 (m, 2H), 12.90 (s, 2H); MS (*m*/*e*, relative intensity (%)) 455.99 (M^+, 100). Anal. Calcd for $C_{28}H_{18}N_4O_3$: C, 73.35; H, 3.96; N, 12.22. Found: C, 72.38; H, 4.23; N, 11.96.

4,4′-Bis(2-carboxybenzoyl)diphenyl sulfide (7). This compound was prepared using the procedure described for **6**: yield 80.9%; mp 281−283 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.05−7.25 (m, 10H), 7.30−8.00 (m, 4H), 8.20−8.30 (m, 2H).

4,4′-Thiobis[4-(1,4-phenylene)phthalazin-1(2*H*)-one) (9). This compound was prepared using the procedure described for **8**: yield 94.9%; mp 380 °C (DSC); ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.64 (m, 8H), 7.72 (m, 2H), 7.90 (m, 4H), 8.36 (m, 2H), 12.78 (s, 2H); MS (*m*/*e*, relative intensity (%)) 474 (M^+, 0.5), 460 (1.0), 307 (38.4). Anal. Calcd for $C_{28}H_{18}N_4O_2S$: C, 70.87; H, 3.82; N, 11.81. Found: C, 70.33; H, 3.85; N, 11.48.

2-[(4-Fluorophenyl)carbonyl]benzoic Acid (10a). Phthalic anhydride (25 g, 0.17 mol), fluorobenzene (108 mL, 1.16 mol), and anhydrous aluminum chloride (50 g, 0.375 mol) were placed in a 1 L three-neck, round-bottom flask equipped with a mechanical stirrer. The reaction mixture was heated to reflux over 30 min. The color changed from yellow to red brown and finally dark brown. The reaction mixture was stirred for 1 h and then cooled to room temperature. The minimum amount of water (ca. 20 mL) was added to the dark-colored solution, and the black solution turned to a light yellow slurry with generation of HCl. The precipitates were added to 20 mL of concentrated HCl and then washed twice with water. The yellow powder was dissolved in warm dilute KOH solution. The small amount of insoluble material was filtered off and the filtrate was acidified with concentrated HCl (ca. 10 mL). A white powder precipitated out. The powder was filtered and recrystallized from toluene−petroleum ether: yield 40% (16.4 g); white needles, mp 141−143 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.31 (m, 2H), 7.42 (d, $J_2 = 8.64$, 1H), 7.62−7.78 (m, 4H), 7.96 (d, $J_2 = 8.64$, 1H).

4-(4-Fluorophenyl)phthalazine-1(2*H*)-one (11a). Acid **10a** (4.80 g, 0.015 mol) and hydrazine monohydrate (0.75 g, 0.015 mol) were heated in methanol (50 mL) at reflux for 6 h. A white powder precipitated from solution. After cooling to room temperature, it was collected by filtration and recrystallized from aqueous acetic acid: yield 90%; white needles, mp 279−281 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.34−7.40 (m, 2H), 7.61−7.66 (m, 3H), 7.85−7.92 (m, 2H), 8.30−8.34 (m, 1H), 12.89 (s, 1H); MS (*m*/*e*, relative intensity (%)) 239.85 (M$^+$, 100), 238.85 (95.2). Anal. Calcd for $C_{14}H_9FN_2O$: C, 70.00; H, 3.78; N, 11.66. Found: C, 70.00; H, 3.80; N, 11.73.

(4-Fluorophenyl) Phenyl Sulfide. This material was prepared by the reaction of copper(I) benzenethiolate with 4-bromofluorobenzene according to Peach:[15] yield 67%; b.p. 171 °C (3.2 kPa).

2-[(4-((4-Fluorophenyl)thio)phenyl)carbonyl]benzoic Acid (10b). To an ice-cooled mixture of phthalic anhydride (5.92 g, 0.04 mol) and (4-fluorophenyl) phenyl sulfide (8.16 g, 0.04 mol) in 80 mL of 1,2-dichlorobenzene was added anhydrous aluminum chloride (10.67 g, 0.08 mol). The temperature was raised gradually to room temperature. The reaction mixture, a reddish black solution, was stirred for 30 and then poured into 400 mL of crushed ice and 20 mL of concentrated HCl, forming a white emulsion. The water layer was decanted off and the solvent was evaporated from the organic layer. The resulting white powder was recrystallized from aqueous acetic acid: yield 77% (10.92 g); white powder, mp 159−161 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.18 (d, $J_2 = 8.40$, 2H), 7.32 (d, $J_2 = 7.80$, 2H), 7.38 (d, $J_2 = 5.70$, 2H), 7.53 (d, $J_2 = 8.40$, 2H), 7.58−7.75 (m, 3H), 7.97 (d, $J_2 = 7.16$, 1H).

4-[4-((4-Fluorophenyl)thio)phenyl]phthalazine-1(2*H*)-one (11b). This material was prepared by the reaction of **10b** with hydrazine monohydrate in methanol using the procedure described for **11a**. The crude product was recrystallized from aqueous acetic acid: yield 88%; colorless needles, mp 244−246 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.13−7.19 (m, 1H), 7.21−7.39 (m, 2H), 7.42−7.71 (m, 4H), 7.85−7.94 (m, 2H), 8.33 (m, 1H), 12.87 (s, 1H).

4-[4-((4-Fluorophenyl)sulfonyl)phenyl]phthalazine-1(2*H*)-one (14). Phthalazinone **11b** was added to a vigorously stirred suspension of wet alumina (2.0 g) and Oxone (1.23 g, 2.0 mmol) in chloroform (10 mL). The mixture was heated at reflux for 12 h. The mixture was cooled and the solids were washed thoroughly with warm chloroform. Removal of solvent afforded crude sulfone, which was recrystallized from aqueous acetic acid: yield 82%; mp 268−269 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.45−7.52 (m, 2H), 7.62−7.69 (m, 1H), 7.84−7.95 (m, 4H), 8.22−8.25 (m, 4H), 8.32-8.39 (m, 1H), 12.98 (s, 1H); MS (*m*/*e*, relative intensity (%)) 379.88 (M$^+$, 100). Anal. Calcd for $C_{20}H_{13}N_2O_3S$: C, 63.15; H, 3.44; N, 7.36. Found: C, 62.83; H, 3.22; N, 6.99.

2-[(4-Phenoxyphenyl)carbonyl]benzoic Acid (10c). This material was prepared by the reaction of phthalic anhydride with diphenyl ether in 1,1,2,2-tetrachloroethane−nitrobenzene mixed solvent (volume ratio 5:1) according to Stille's procedure. The crude product was recrystallized from aqueous acetic acid: yield 74%; white needles, mp 161−163 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.04 (d, $J_2 = 8.69$, 2H), 7.13 (d, $J_2 = 7.83$, 2H), 7.26 (t, $J_2 = 7.70$, 1H), 7.39−7.50 (m, 2H), 7.60−7.78 (m, 5H), 8.00 (d, $J_2 = 7.29$, 1H).

4-(4-Phenoxyphenyl)phthalazine-1(2*H*)-one (11c). This material was prepared by the reaction of **10c** with hydrazine monohydrate in methanol using the procedure described for **11b**. The crude product was recrystallized from aqueous acetic acid: yield 89%; white needles, mp 244−245 °C; ^{1}H-NMR (270 MHz, DMSO-d_6) δ 7.15 (m, 5H), 7.45 (m, 2H), 7.59 (m, 2H), 7.71 (m, 1H), 7.92 (m, 2H), 8.31 (m, 1H), 12.83 (s, 1H).

4-[4-(4-[(4-Fluorophenyl)carbonyl]phenoxy)phenyl]phthalazine-1(2*H*)-one (12). To an ice-cooled mixture of 4-fluorobenzoyl chloride (3.32 g, 0.021 mol) and anhydrous aluminum chloride (5.33 g, 0.04 mol) in 150 mL of 1,2-dichloroethane was added 6.28 g (0.020 mol) of phthalazinone **11c**. The yellow slurry turned into a red-brown solution. The temperature was raised gradually to room temperature. The reddish black solution was stirred for 24 h. The reaction mixture was poured into 200 mL of crushed ice and 10 mL of concentrated HCl. The resulting white powder was filtered, washed with methanol, and recrystallized from aqueous acetic acid: 80% yield (0.70 g); mp 277−281 °C; ^{1}H-NMR (DMSO-d_6) δ 7.20−7.40 (m, 7H), 7.63−7.90 (m, 8H), 8.33 (m, 1H), 12.88 (s, 1H); MS (*m*/*e*, relative intensity (%)) 436 (M$^+$, 2.9), 314 (100). Anal. Calcd for $C_{27}H_{17}N_2O_3$: C, 74.30; H, 3.93; N, 6.42. Found: C, 73.95 ; H, 3.98 ; N, 6.39.

2-[4-(Phenylthio)phenyl)carbonyl]benzoic Acid (10d). This material was prepared by the reaction of phthalic anhydride with phenyl ether in 1,1,2,2-tetrachloroethane−nitrobenzene mixed solvent (volume ratio 5:1) according to Stille's procedure. The crude product was recrystallized from aqueous acetic acid: yield 78%; white needles, mp 128−129 °C; ^{1}H-NMR (DMSO-d_6) δ 7.24 (d, $J_2 = 8.40$, 2H), 7.42−7.72 (m, 10H), 7.97 (d, $J_2 = 7.29$, 1H).

4-[4-(Phenylthio)phenyl]phthalazine-1(2*H*)-one (11d). This material was prepared by the reaction of **10b** with hydrazine monohydrate in methanol using the procedure described for **11a**. The crude product was recrystallized from aqueous acetic acid: yield 95%; colorless needles, mp 244−246 °C; ^{1}H-NMR (DMSO-d_6) δ 7.43−7.56 (m, 7H), 7.58−7.63 (m, 2H), 7.68−7.73 (m, 1H), 7.87−7.92 (m, 2H), 8.32-8.35 (m, 1H), 12.86 (s, 1H).

4-[4-((4-[(4-Fluorophenyl)carbonyl]phenyl)thio)phenyl]phthalazine-1(2*H*)-one (13). This material was prepared by the reaction of **11d** with *p*-fluorobenzoyl chloride in the presence of anhydrous aluminum chloride in 1,2-dichloroethane using the procedure described for **13**. The crude product was recrystallized from aqueous acetic acid: 79% yield; white needles, mp 268−270 °C; ^{1}H-NMR (DMSO-d_6) δ 7.37−7.49 (m, 7H), 7.18−7.95 (m, 8H), 8.33−8.37 (m, 1H), 12.92 (s, 1H); MS (*m*/*e*, relative intensity (%)) 452.94 (M$^+$, 26.5), 451.94 (85.1), 329.96 (100.00). Anal. Calcd for $C_{27}H_{17}FN_2O_4S$: C, 71.67; H, 3.79; N, 6.19. Found: C, 71.38; H, 3.81; N, 6.14.

General Procedure for the Preparation of Phthalazinone Polymers. Polymerizations were typically carried out in a dry 50 mL three-neck flask equipped with a stirbar, a Dean−Stark trap fitted with a condenser, and a nitrogen inlet.

(1) Polymerization of Phthalazinone Monomer 5f (Example: Polymer 15f). To a dried flask containing 0.254 g of bis(4-fluorophenyl) sulfone (**22**) (0.0010 mol), 0.669 g (0.0010 mol) of phthalazinone monomer **5f**, 6 mL of toluene, and 4 mL of NMP was added 0.152 g of anhydrous potassium carbonate (0.0011 mol). The resulting mixture was heated to reflux (130 °C) with stirring. A strong flow of nitrogen was maintained to azeotrope off the water formed with toluene. After 2 h of dehydration, the temperature was increased to 190 °C by bleeding toluene from the Dean−Stark trap. After 10 h the solution was cooled to 100 °C, diluted with 10 mL of TCE, and precipitated into methanol (200 mL) containing a few drops of concentrated HCl. The resulting fibrous polymer was dissolved in chloroform (40 mL), filtered through a thin layer of Celite to remove the inorganic salts, and reverse precipitated into 200 mL of methanol. After drying under reduced pressure at 80 °C, 0.759 g of light yellow powder **15f** (yield 86%) was obtained.

(2) Polymerization of Phthalazinone Monomers in DPS (Example: Polymer 15c). To a 50 mL three-neck flask were added **5c** (0.4586 g, 0.001 mol), anhydrous potassium carbonate (0.1510 g, 0.0011 mol), bis(4-fluorophenyl) sulfone (**22**) (0.2542 g, 0.001 mol), and DPS (4.32 g). The reaction mixture was stirred at 150 °C for 6 h. The water that formed was removed by purging with nitrogen. The reaction mixture temperature was raised to 200 °C for 6 h and finally to 280 °C for 24 h. The mixture, a dark-colored viscous liquid, was added to acetone (100 mL) and acetic acid (2 mL), and the tan-colored fibrous polymer separated out. It was dissolved in 7 mL of hot NMP, filtered through a thin layer of Celite, precipitated into methanol, filtered, and dried to give 0.569 g of polymer **15c** (yield 89%).

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