

## Synthesis of novel poly(aryl ether amide)s containing the phthalazinone moiety

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Two novel heterocyclic diamine monomers: 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-aminophenoxy)phenyl]-(2H)-phthalazin-1-one and 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-(2H)-phthalazin-1-one were successfully synthesized using readily available heterocyclic bisphenol-like monomers through two steps in high yield. A series of novel poly(aryl ether amide)s containing the phthalazinone moiety with inherent viscosities of 1.16–1.67 dL/g were prepared by the direct polymerization of the novel diamines and aromatic dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents. The polymers were readily soluble in a variety of solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP), and pyridine. The polymers had high glass transition temperatures ( $T_g$ ) in the 291–329°C range.

**Keywords** Poly(aryl ether amide)s, phthalazinone, heterocyclic diamine, direct polymerization

### Introduction

High-performance aromatic polymers, such as aromatic polyamides and polyimides with high strength, stiffness, and thermal stability and chemical resistance would provide some useful applications. But their limited solubility requires extreme synthesis and processing conditions. For example, poly(*p*-phenylene terephthalamide), to form high-strength and high-modulus fibers (Kevlar®), must be processed from concentrated sulfuric acid at elevated temperatures.<sup>1</sup> Moreover, aromatic diamines which are commonly used for preparation of polyamides and polyimides, are light- and air-sensitive

materials and therefore difficult to purify and handle. Furthermore, some aromatic diamines have been found to be carcinogenic, and special care must be taken in handling these materials.<sup>2</sup> To overcome these limitations, structural modifications of the polymer backbone, such as the addition of bulky lateral substituents,<sup>3–6</sup> flexible alkyl side chains,<sup>7</sup> noncoplanar biphenylene moieties,<sup>8</sup> and organometallic complexation<sup>9</sup> have been utilized to modify the polymer properties by the design and preparation of new diamines.

Phthalazinone and its derivatives have been known for almost a century.<sup>10</sup> Until recently, Hay *et al.* first reported that Phthalazinone and its derivatives were bisphenol-like monomers which polymerize with the activated aryl dihalide monomers to give amorphous polymers with very high glass transition temperature and excellent thermostability, which are soluble in common organic solvents.<sup>11–15</sup> Heterocyclic rings in poly(aryl ether)s generally increase mechanical and adhesive properties as well as transition temperature ( $T_g$ ) of the polymers, while retaining thermal stability and processability.<sup>16</sup> Recently we have synthesized poly(aryl ether ketone)s and poly(aryl ether sulfone)s containing the phthalazinone moiety.<sup>14,15</sup> We first reported the synthesis of aromatic diamine and polyamides containing phthalazinone moiety.<sup>17</sup> The unique structural feature of the diamines lies in its unsymmetrical and non-coplanar conformation. Of particular interests are to investigate the effect of the unsymmetrical and non-coplanar but still rigid diamine functionality on the properties of the polymers. In this paper, we describe the synthesis of two novel diamines

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and a series of poly(aryl ether amide)s containing phthalazinone moiety.

## Experimental

### Materials and measurements

Unless specified otherwise, reagent-grade reactants and solvents were used as supplied. Pd-C(5%) was obtained from Dalian Institute of Chemical Physics, Chinese Academy of Sciences. 1-Methyl-2-pyrrolidinone and pyridine purified on distillation under reduced pressure over calcium hydride and stored over molecular sieves (4Å). Reagent-grade calcium chloride was dried under vacuum at 180°C for 6 h prior to use. Triphenyl phosphite was freshly vacuum-distilled before use. Dihydro-4-(4-hydroxyphenyl) (2*H*) phthalazin-1-one (**1a**) and dihydro-4-(4-hydroxy-3,5-dimethylphenyl) (2*H*) phthalazin-1-one (**1b**) were prepared according to the reported method.<sup>11,18</sup>

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Jeol FX 90Q or Bruker-400 instrument using tetramethylsilane as an internal reference. IR measurements were performed on Nicolet-20DXB spectrometer. Low and high-resolution mass spectra were obtained using Finnigan MAT/SS220 and Kratos Concept II H spectrometers, respectively. Melting points and the glass transition temperatures were obtained using a Serko 220C differential scanning calorimeter with a heating rate of 10°C/min in nitrogen. Intrinsic viscosities of all polymers were measured using an Ubbelohde dilution viscometer.

### Synthesis of monomers

**Preparation of 2a** A 500mL-three-necked flask containing **1a** (23.8 g, 0.1 mol), *p*-chloronitrobenzene (34.6 g, 0.22 mol), potassium carbonate (33 g, 0.24 mol), DMAc (200 mL), toluene (70 mL), was equipped with a mechanical stirrer, a Dean-Stark trap, a water condenser, a thermometer, and a nitrogen inlet. Under an atmosphere of nitrogen, the mixture was heated and maintained at 140°C for 5–6 h to remove all water by means of azeotropic distillation with toluene. The temperature was then increased to 150°C to remove toluene for 1 h and then cooled. The mixture was then poured into an ethanol-water mixture (1:1 V/V, 300 mL). The precipitate was collected on a filter and crys-

tallized from DMF to give yellow solid (44.2 g, yield: 92%), mp, 235–236°C. IR (cm<sup>-1</sup>): 1112(w, N—N), 1262(m, C—O—C), 1346, 1509(s, NO<sub>2</sub>). EI-MS (*m/z*, relative intensity %): 480(M<sup>+</sup>, 100).

**2b** was prepared by the similar procedure of **2a**. **2b**: yellow solid, mp: 210–211°C, yield: 93%. IR (cm<sup>-1</sup>): 1685(s, C = O), 1608(m, C = N), 1511, 1346(s, NO<sub>2</sub>), 1111(m, N—N). EI-MS (*m/z*, relative intensity %): 508(M<sup>+</sup>, 100). <sup>1</sup>H NMR (δ, DMSO-*d*<sub>6</sub>): 8.55–7.60(m, 10H), 7.45–7.52(m, 2H), 7.05–7.13(m, 2H), 2.15(s, 6H, CH<sub>3</sub>).

**Preparation of 3a** The dinitro compound **2a** (33.6 g, 0.07 mol), Pd-C (5%, 0.8 g), and ethylglycol monomethyl ether (500 mL), were introduced into a three-necked flask to which hydrazin monohydrate (175 mL) was added dropwise over 1 h at reflux temperature (about 105°C). After the addition was completed, the reaction was continued at reflux temperature for another 10 h. The mixture was then filtered and recrystallized from ethylglycol monomethyl ether to remove Pd-C. After cooling, the product was obtained as the pale yellow crystals (mp: 260–261°C, yield: 95%). IR (cm<sup>-1</sup>): 1104(w, N—N), 1224(m, C—O—C), 1606(m, C = N), 1657(s, C = O), 3336, 3368, 3403, 3432(m, N—H). EI-MS (*m/z*, relative intensity %): 420(M<sup>+</sup>, 100). HRMS: Calcd: 420.1588, Found: 420.1603, <sup>1</sup>H NMR (δ, DMSO-*d*<sub>6</sub>): 5.10(brs, 4H, NH<sub>2</sub>), 6.65(d, *J* = 8.65 Hz, 4H), 6.85(d, *J* = 8.64 Hz, 2H), 6.99(d, *J* = 8.68 Hz, 2H), 7.26(d, *J* = 8.64 Hz, 2H), 7.57(d, *J* = 8.72 Hz, 2H), 7.75(m, 1H), 7.90(m, 2H), 8.40(m, 1H).

**3b** was prepared by the analogous procedure of **3a**. **3b**: pale yellow crystals (mp: 282–283°C, yield: 91%). IR (cm<sup>-1</sup>): 3408, 3334(m, N—H), 2919(w, CH<sub>3</sub>), 1650(s, C = O), 1114(m, N—N). EI-MS (*m/z*, relative intensity %): 448(M<sup>+</sup>, 100%), <sup>1</sup>H NMR (δ, DMSO-*d*<sub>6</sub>): 8.40(m, 1H, H-8), 7.80–6.50(m, 13H, ArH), 5.20(brs, 2H, NH<sub>2</sub>), 4.61(brs, 2H, NH<sub>2</sub>), 2.15(s, 6H, CH<sub>3</sub>).

### Polymerization

A typical example of polycondensation is shown as follows:

Polymer **4a** from **3a** and terephthalic acid: A mixture of diamine **3a** (1.0504 g, 2.5 mmol), terephthalic acid (0.418 g, 2.5 mmol), calcium chloride (0.45

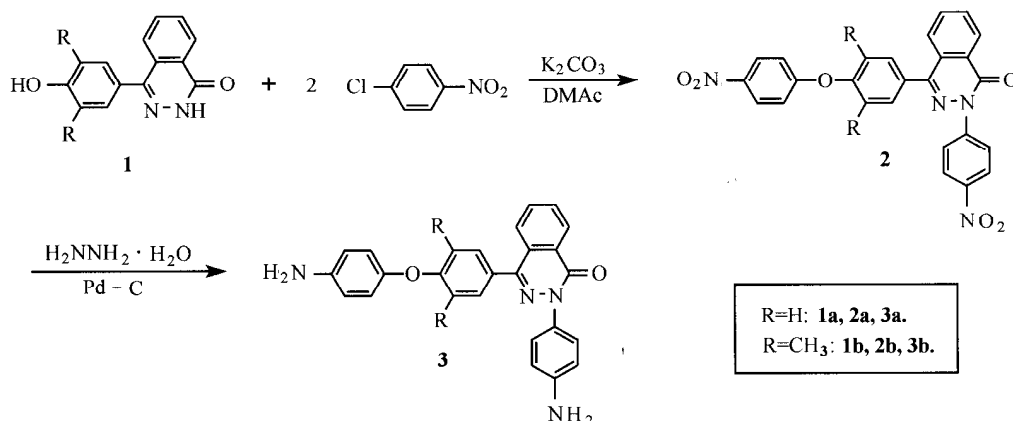
g), NMP (5 mL), pyridine (1.4 mL), and triphenyl phosphite (1.4 mL), was heated with stirring at 100°C for 3 h under nitrogen. The obtained polymer solution was slowly poured into methanol (500 mL) with constant stirring, producing fibrous precipitate. After being washed thoroughly with methanol and hot water, the product was collected on a filter, and dried at 100°C under vacuum. The yield was 98%.

All other polymers were prepared by similar manner as mentioned above.

## Results and discussion

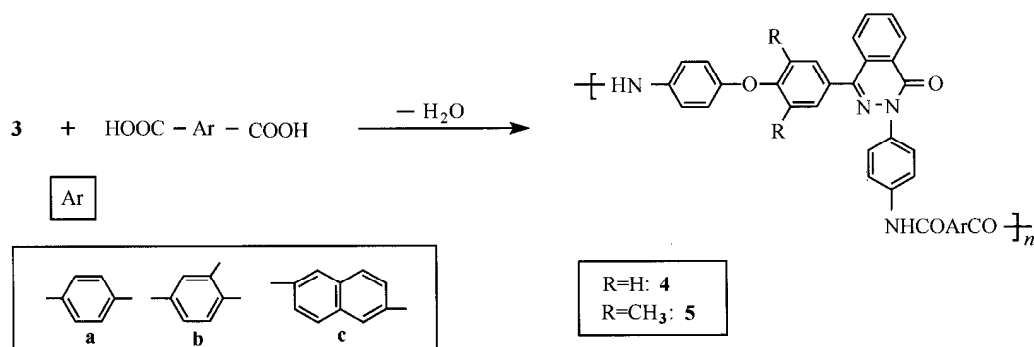
Two novel noncoplanar and asymmetric diamines:

Scheme 1



The direct polycondensation of the diamine **3** with the aromatic diacids was undertaken successfully according to the phosphorylation method first reported by Yamazaki for the synthesis of polyamides (Scheme 2).<sup>19</sup>

Scheme 2



1, 2-dihydro-2-(4-aminophenyl)-4-[4-(4-aminophenoxy)phenyl]-(2*H*)-phthalazin-1-one (**3a**) and 1, 2-dihydro-2-(4-aminophenyl)-4-[4-(4-aminophenoxy)-3, 5-dimethylphenyl]-(2*H*)-phthalazin-1-one (**3b**), were synthesized on condensation of asymmetric heterocyclic bisphenol-like **1a** and **1b** with *p*-chloronitrobenzene in presence of potassium carbonate respectively, giving corresponding dinitro compounds **2a** and **2b** (Scheme 1), followed by reduction with hydrazine monohydrate/Pd-C. Unlike commonly used diamines, compound **3a** and **3b** are quite stable on exposure to light and air. The structures of the dinitro compounds **2** and diamine **3** were confirmed by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR, 2D-NMR, EI-MS, including HRMS. All the obtained data agree with the proposed structures.

Almost quantitative yields of the polyamides **4a-c** were obtained. Spectroscopic data, together with intrinsic viscosity and *T<sub>g</sub>* measurements, confirming the structures of polyamides, are given in Table 1. Almost all polyamides

were soluble in polar aprotic solvents such as NMP, DMF, DMAc, DMSO and even in pyridine. Transparent

and flexible films were easily prepared by solution casting from DMAc solution of each polymer **4** and **5**.

**Table 1** Synthesis and characterization data of the polymer (**4a–c** and **5a–c**)

Polymer	$[\eta]^a$	Yield (%)	$^1\text{H NMR}$ ( $\delta_{\text{H}}$ , 90 MHz)	IR ( $\text{cm}^{-1}$ )	$T_g^b$ ( $^{\circ}\text{C}$ )
<b>4a</b>	1.43	98	6.89–8.51(m, 20H, ArH), 10.21–10.39(brs, 2H, NH)	3310(m, N-H), 1658(s, amide I), 1604(m, C=N)	329
<b>4b</b>	1.26	98	6.99–8.65(m, 20H, ArH), 10.32–10.49(brs, 2H, NH)	3308(m, N-H), 1668(s, amide I), 1607(m, C=N)	314
<b>4c</b>	1.51	96	6.71–8.72(m, 22H, ArH), 10.39–10.48(brs, 2H, NH)	3314(m, N-H), 1668(s, amide I), 1604(m, C=N)	ND <sup>c</sup>
<b>5a</b>	1.38	98	2.15(s, 6H, CH <sub>3</sub> ), 6.81–8.59(m, 18H, ArH), 10.21–10.49(brs, 2H, NH)	3305(m, NH), 1657(s, amide I), 1602(m, C=N)	291
<b>5b</b>	1.16	97	2.15(s, 6H, CH <sub>3</sub> ), 6.80–8.63(m, 18H, ArH), 10.19–10.51(brs, 2H, NH)	3334(m, NH), 1667(s, amide I), 1607(m, C=N)	ND
<b>5c</b>	1.67	99	2.15(s, 6H, CH <sub>3</sub> ), 6.80–8.71(m, 18H, ArH), 10.20–10.51(brs, 2H, NH)	3320(m, NH), 1652(s, amide I), 1605(m, C=N)	ND

<sup>a</sup> Measured at a concentration of 0.5 g/L in NMP at 25 $^{\circ}\text{C}$ ; <sup>b</sup> From DSC measurements conducted at a rate of 10 $^{\circ}\text{C}/\text{min}$  in nitrogen

<sup>c</sup> No  $T_g$  was observed in DSC trace.

In conclusion, novel amorphous poly(aryl ether amide)s containing the phthalazinone moiety with high molecular weights were prepared using the phosphorylation method. The polymers showed outstanding thermal stability, good solubility and film-forming property. Further preparation of a series of poly(aryl ether amide) containing the phthalazinone moiety is in progress.

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