

Synthesis of Novel Poly(aryl ether amide)s Containing the Phthalazinone Moiety

Lin CHENG^{1*}, Xi Gao JIAN²

¹Department of Materials Science & Engineering, Wuhan Institute of Chemical Technology,
Wuhan 430074

²Department of Polymer Science & Materials, DaLian University of Technology, DaLian 116012

Abstract: 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 from readily available heterocyclic bisphenol-like monomers in two steps in high yield. A series of novel poly(aryl ether amide)s containing the phthalazinone moiety were successfully prepared by the direct polymerization of the novel diamines and aromatic dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents.

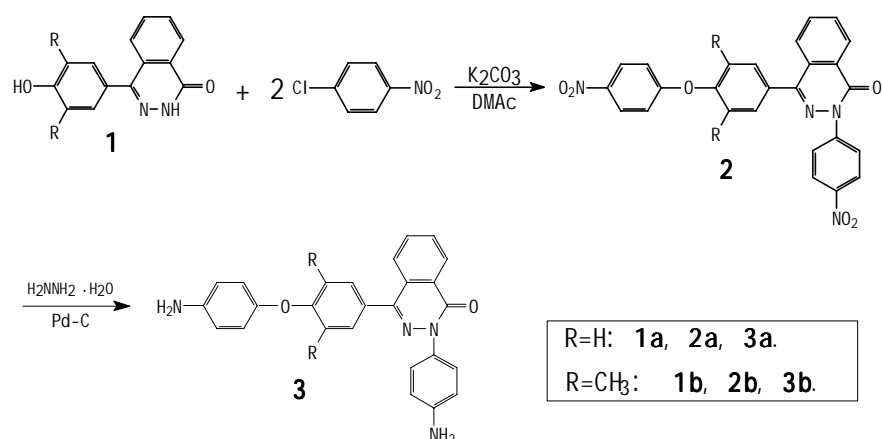
Keywords: Poly(aryl ether amide)s, phthalazinone, direct polymerization, heterocyclic diamine.

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. Phthalazinone and its derivatives have been known for almost a century¹. Recently Hay *et al.*^{2,3} first reported that phthalazinone and its derivatives were bisphenol-like monomers which can be polymerized 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. 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 processability⁴. More recently we have synthesized poly(aryl ether ketone)s and poly(aryl ether sulfone)s containing the phthalazinone moiety^{5,6}. In this letter, we extend our investigation to the synthesis of novel polyamides containing phthalazinone moiety.

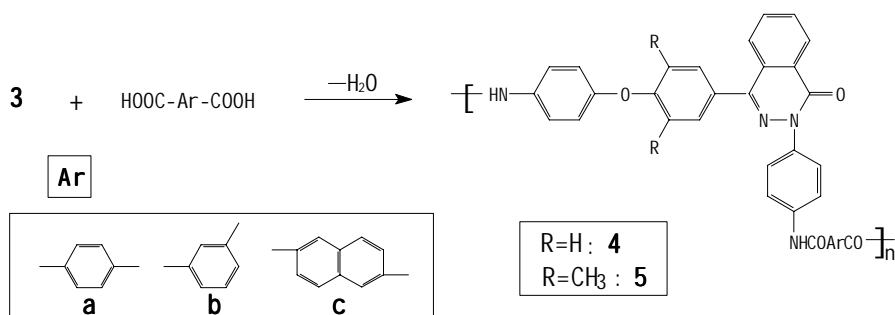
Two novel noncoplanar and asymmetric diamine: 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-aminophenoxy)phenyl](2H)phthalazin-1-one (**3a**) and 1,2-dihydro-2-(4-amino-phenyl)-4-[4-(4-aminophenoxy)-3,5-dimethylphenyl](2H)phthalazin-1-one (**3b**), were synthesized by condensation of asymmetric heterocyclic bisphenol-like **1a** and **1b** with *p*-chloronitrobenzene in the presence of potassium carbonate respectively, giving corresponding Dinitro-compound **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 **2** and diamine **3** were confirmed by FTIR, ^1H - and ^{13}C -NMR, 2D-NMR, MS, including HRMS^{7, 8}. All the obtained data agree with the proposed structures.

Scheme 1



Scheme 2



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**)⁹. Almost quantitative yields of the polyamides (**4a-c**) and (**5a-c**) were obtained. Spectroscopic data, together with intrinsic viscosity and T_g measurements, confirming the structures of polyamides is 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**.

In summary, novel amorphous poly (aryl ether amide)s containing the

phthalazinone moiety with high molecular weights were prepared through the phosphorylation method. The polymers showed outstanding thermal stability, good solubility and film-forming properties. Preparation of a series of poly (aryl ether amide) containing the phthalazinone moiety is in progress.

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

polymer	$[\eta]^a$	Yield(%)	$^1\text{H-NMR } \delta(\text{ppm}, 90\text{MHz})$	IR (cm^{-1})	$T_g^b(\text{°C})$
4a	1.43	98	6.9-8.5(m,20H,Ar-H)	3310(N-H) 1658(amide I)	329
			10.2-10.4(d,2H,N-H)	1604(C=N)	
4b	1.26	98	7-8.65(m,20H,Ar-H)	3308(N-H) 1668(amide I)	314
			10.3-10.5(d,2H,N-H)	1607(C=N)	
4c	1.51	96	6.7-8.7(m,22H,Ar-H)	3314(N-H) 1668(amide I)	ND ^c
			10.4-10.5(d,2H,N-H)	1604(C=N)	
5a	1.38	98	2.15(s,6H,CH ₃)	3305(N-H) 1657(amide I)	291
			6.8-8.59(m,18H,Ar-H)	1602(C=N)	
			10.2-10.5(d,2H,N-H)		
5b	1.16	97	2.15(s,6H,CH ₃)	3334(N-H) 1667(amide I)	ND
			6.8-8.6(m,18H,Ar-H)	1607(C=N)	
			10.2-10.5(d,2H,N-H)		
5c	1.67	99	2.15(s,6H,CH ₃)	3320(N-H) 1652(amide I)	ND
			6.8-8.7(m,20H,Ar-H)	1605(C=N)	
			10.2-10.5(d,2H,N-H)		

^aMeasured at a concentration of 0.5gL^{-1}

^bFrom DSC measurements conducted at a rate of $10\text{°C}/\text{min}$ in nitrogen

^cNo T_g was observed in DSC trace

Acknowledgments

The Project was supported by the National Natural Science Foundation of China and authors also extend our thanks to Prof. Z. Y. Wang and Dr. H. B. Zheng at Carleton University for recording the NMR spectra and HRMS.

References and Notes

- W. R. Vaughan, *Chem. Rev.*, **1948**, 43, 448.
- N. Berard, A. S. Hay, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, 34, 148.
- Y. Z. Meng, X. G. Jian, A. S. Hay *et al* *Chin. Polym. Mater. Sci. Eng.* **1994**, 10(6), 34
- C. G. Herbert, R. G. Bass, K. A. Waston, *et al* *Macromolecules*, **1996**, 29, 7709.
- Y. Z. Meng, A. S. Hay, X. G. Jian *et al* *J. Appl. Polym. Sci.*, **1997**, 66, 1425.
- Y. Z. Meng, A. S. Hay, X. G. Jian *et al* *J. Appl. Polym. Sci.*, **1998**, 68, 137.
- Compound **3a**: mp: 260-261 °C, yield: 95%, IR (cm^{-1}): 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^+ , 100%). HRMS: Calcd: 420.1588, Found: 420.1603, $^1\text{H-NMR } (\delta \text{ ppm } 400\text{MHz DMSO-}d_6)$: 5.10 (brs, 4H, -NH₂) 6.65 (d 4H) 6.85 (d, 2H) 6.99 (d, 2H) 7.26 (d, 2H) 7.57 (d,

- 2H) 7.83 (d, 2H) 8.40 (d-d, 1H), ^{13}C -NMR (δ ppm 100MHz DMSO- d_6):159.72, 157.84, 148.16, 145.81, 145.62, 144.95, 133.46, 131.79, 130.96, 130.66, 128.40, 128.16, 128.11, 126.82, 126.64, 121.13, 116.14, 114.93, 114.87, 113.03.
8. Compound **3b**: mp: 282-283°C, yield: 91%, IR (cm^{-1}): 3408, 3334 (m, N-H) 2919 (w, CH_3) 1650 (s, C=O) 1114 (m, N-N), EI-MS (m/z, relative intensity %): 448 (M^+ , 100%), ^1H -NMR (δ ppm 90MHz DMSO- d_6): 2.15 (s, 6H, CH_3) 4.6 (brs, 2H, NH_2) 5.2 (brs, 2H, NH_2) 8-6.5 (m, 13H, Ar-H) 8.4 (d-d, 1H).
9. N. Yamazaki, M. Matsumoto, F. Higashi, *J. Polym. Sci.*, **1975**, 13, 1373.

Received 11 November 1999

Revised 3 January 2000