Synthesis of High Molecular Weight Poly(phthalazinone ether)s by Ullmann C−N and C−O Condensation Reactions

Jinyan Wang,[†,‡] Yan Gao,[†] Antisar R. Hlil,[†] and Allan S. Hay*[,†]

Department of Chemistry, McGill University, 801 Sherbrooke Street W., Montreal, Quebec, H3A 2K6, Canada, and Department of Polymer Science & Materials, Dalian University of Technology, 158 Zhongshan Road, Dalian, 116012, P. R. China

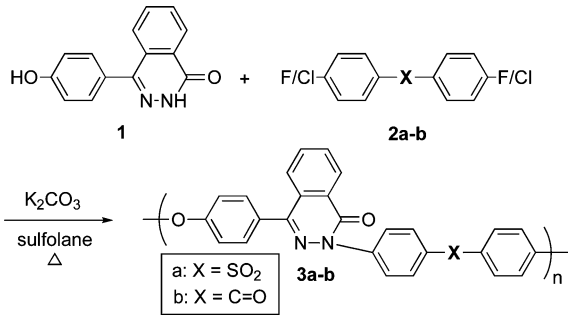
Received September 9, 2007
Revised Manuscript Received November 28, 2007

Introduction. The NH group in 1,2-dihydro-4-(4-hydroxyphenyl)-1-(2*H*)-phthalazinone (**1; DHPZ)** behaves like a phenolic OH group with the result that **DHPZ** can react with activated dihalo compounds to produce high molecular weight polymers via combined C−N and C−O condensation reactions. Poly(phthalazinone ether sulfone)s and poly(phthalazinone ether ketone)s were first successfully synthesized in 1993[1] by classical nucleophilic aromatic substitution reactions as shown in Scheme 1. Since then a family of high performance polymers has been developed from this monomer: poly(phthalazinone ether)s,[2−9] polyamides,[10,11] polyimides,[12,13] and polyesters.[14] They all possess excellent thermooxidative stability, high glass transition temperature, reasonable solubility and outstanding mechanical properties by virtue of the introduction of the rigid asymmetric phenyl phthalazinone moiety into the polymer backbone.

The Ullmann condensation is one of the most well-established reactions for aryl−oxygen and aryl−nitrogen bond formation. The order of ease of halide replacement is I > Br > Cl ≫ F. This is the reverse of the order of the activated halide for nucleophilic displacement polycondensation reactions. The harsh reaction conditions, however, have forced chemists to develop milder reaction conditions. Many modified synthetic methods have been reported for the formation of these bonds.[15,16] Most noteworthy among them are the use of cesium carbonate as the base in the presence of a catalytic amount of a copper(I) complex in the application of the reaction to a wider variety of functional groups, introduced by Buchwald and co-workers.[17] Other procedures involving various bases in combination with diverse copper species, ligands and temperature have been developed for the synthesis of small molecules.[18−21] There are also several reports about polyarylether formation via Ullmann C−O condensation reaction of various biphenols with dibromides in the presence of copper or cuprous salt with ligands.[22−24] To the best of our knowledge, no polymerization reaction via combined Ullmann C−O and C−N condensation reactions in a one-pot process has emerged. The similar reactivity of NH and OH groups in **DHPZ** in the nucleophilic displacement polycondensation reactions encouraged us to explore its use in an Ullmann condensation reaction. Herein we report our research results.

Results and Discussion. We initially utilized polycondensation conditions following Burgoyne's reaction protocol[25] that involved the reaction of the sodium salt of 9,9-bis(4-hydroxyphenyl)fluorene with dibromoarylene derivatives catalyzed by cuprous chloride with quinoline as complexing agent in benzophenone under nitrogen. Unfortunately, only a low molecular weight poly(phthalazinone ether) was obtained.

Scheme 1



In the preparation of the phthalazinone-containing poly(aryl ether sulfone) **3a** and poly(aryl ether ketone) **3b** (as shown in Scheme 1) by a classical nucleophilic polycondensation reaction, the reactions were conducted by first preparing the potassium salt of **DHPZ** in sulfolane using chlorobenzene for azeotropic removal of the water formed. Reaction with the activated halide at ca. 200 °C successfully gave the high molecular weight polymers. Using this methodology, to the solution of the potassium salt of **DHPZ** with 4,4′-dibromodiphenyl ether there was added freshly prepared CuCl/quinoline catalyst[25] (Scheme 2). Polymerization reactions were then carried out at different temperatures (Table 1).

Higher polymerization temperature facilitated the formation of higher molecular weight polymer. The highest molecular weight polymer **5a3**, measured relative to polystyrene by gel permeation chromatography (GPC) in $CHCl_3$ as solvent on a Water 510 HPLC, was obtained at a reaction temperature of 190−195 °C. Raising the polymerization temperature to above 200 °C gave some gelation. This was presumably due an oxidative coupling reaction of end-capped phenol groups by traces of oxygen catalyzed by cuprous ion at the higher reaction temperatures.[26] The resulting polymer was isolated by precipitation in methanol followed by redissolving in chloroform and reverse precipitation with acetone. The polymer **5a3** had an inherent viscosity of 0.58 dL/g in NMP at 30 °C and was soluble in chloroform, *N*,*N*-dimethylacetamide (DMAC), NMP, and DMSO at room temperature (Table 2). A tough, flexible film was cast from its solution in chloroform. A glass transition temperature (T_g) of 240 °C was detected by differential scanning calorimetry (DSC) and the temperature of 5% weight loss under nitrogen was higher than 500 °C, measured by thermogravimetric analyses (TG), indicating its excellent thermal stability. The soluble portion of polymer obtained at 200−205 °C had similar properties.

A series of polymers from **DHPZ** and the five other dibromides were then prepared under the above-described reaction conditions (Table 2). High molecular weight polymers with inherent viscosities of 0.32−0.63 dL/g in NMP at 30 °C were formed with the exception of polymers **5c** and **5d**, that prematurely came out of the solution during the reaction. Although the inherent viscosity of polymer **5b1** is lower than that of polymer **5a3**, its film cast from chloroform was still flexible and tough. Polymer **5b1**and **5g** have solubilities similar to polymer **5a3**, and their GPC analysis was carried out. Methyl groups in polymers **5e** and **5f** improved their solubility in the

* Corresponding author. Email: allan.hay@mcgill.ca.
† McGill University.
‡ Dalian University of Technology.

10.1021/ma702039a CCC: $40.75
Published on Web 12/22/2007

Scheme 2

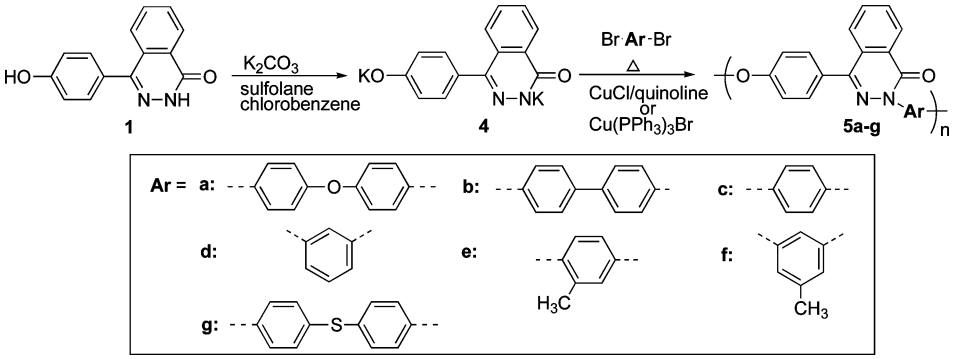


Table 1. Synthetic Conditions for Preparation of Poly(phthalazinone Ether)s

polymer[a]	reaction *T* (°C)	GPC M_n (kDa)	GPC M_w (kDa)	GPC PDI	film
5a1	170−175	7.3	25.3	3.49	fragile
5a2	180−185	9.0	39.4	4.37	fragile
5a3	190−195	18.4	51.5	2.79	tough[b]
5a4	200−205	14.5	42.7	2.96	tough[c]

[a] After 4 h of dehydration, the reaction mixture was cooled to 80 °C, then the stoichiometric amount of 4,4′-dibromodiphenyl ether was added. The mixture was heated to the temperature listed in Table 1 (oil bath) with the addition of freshly prepared CuCl/ quinoline catalyst. The reaction was maintained at this temperature for 17 h with stirring. With the addition of more CuCl, the reaction was continued for another 24 h. The solution was quenched in a mixture of methanol and dilute hydrochloric acid. The resulting polymer was purified by reverse precipitation from chloroform/ acetone. [b] Will withstand several 180° bends. [c] Soluble portion (70%).

Table 2. Properties of Poly(phthalazinone ether)s

polymer	GPC M_n (kDa)	GPC PDI	η_{inh}[b] (dL/g)	T_g[c] (°C)	$T_{d-5\%}$[d] (°C, N_2)	solubility[e]
5a3	18.4	2.79	0.58	240	521	$CHCl_3$, NMP DMAC, DMSO
5b1[a]	12.0	2.70	0.32	284	519	$CHCl_3$, NMP DMAC, DMSO
5b2[a]	4.5	2.84	0.10	282	510	$CHCl_3$, NMP DMAC, DMSO
5c			*f*	248		
5d				247		
5e	*g*		0.63	293	493	NMP (heating)
5f			0.61	244	484	NMP (heating)
5g	25.4	3.77	0.58	237	510	$CHCl_3$, NMP DMAC, DMSO

[a] Reaction conditions : **5b1:** catalyst : CuCl/quinoline; **5b2**: catalyst: $Cu(PPh_3)_3Br$. [b] Inherent viscosity was measured at a concentration of 0.5 dL/g in NMP at 30 °C. [c] Second scan at a heating rate of 10 °C/min under N_2 flow rate 160 mL/min. [d] 5% weight loss at a heating rate of 20 °C/min under N_2. [e] At room temperature. [f] Insoluble in NMP. Solubility in chloroform too low to be detected by GPC.

reaction solvent with the result that high molecular weight polymers were readily formed. Polymer **5b1** has a higher T_g than polymer **5a3** due to its more rigid main chain, and polymers **5a3** and **5g** showed similar T_gs as expected with their similar structures. The lower T_gs of polymer **5c** and **5d** are attributed to their lower molecular weights. Polymer **5e** exhibited the highest T_g. The temperatures for 5% weight loss in nitrogen were in the range of 484 to 521 °C, indicating their excellent thermal stabilities. The structures of polymers **5a3, 5b1,** and **5e** were confirmed by proton NMR (400 MHz in $CDCl_3$).[27]

A number of other catalysts were screened and it was found that Venkataraman's air stable homogeneous copper catalyst $Cu(PPh_3)_3Br$ for the cross-coupling of aryl bromides with phenols or amides[28] showed reasonable activity in the synthesis of small molecules. Difunctional aryl ether oligomers (C−O coupling) had been synthesized using this method by Laskoski.[23] The reaction between **DHPZ** and 4,4′-dibromobiphenyl was then performed at around 190 °C with 20 mol % of $Cu(PPh_3)_3Br$ and K_2CO_3 as the base in sulfolane after dehydration as usual. Using this protocol, polymer **5b2** with inherent viscosity 0.10 dL/g in NMP at 30 °C was produced. Its number-average molecular weight was only 4.5 kDa even after the polymerization reaction time was prolonged to 72 h. A lower polymerization reaction temperature 150 °C was used on the assumption that the catalyst $Cu(PPh_3)_3Br$ is sensitive to the higher temperature. The film of the resulting polymer cast in chloroform was still brittle.

In conclusion, a new class of high molecular weight poly(phthalazinone ether)s has been successfully synthesized via the Ullmann condensation reaction of 1,2-dihydro-4-(4-hydroxyphenyl)-1-(2*H*)-phthalazinone (**1**) and unactivated aromatic dibromides catalyzed by cuprous chloride with quinoline as ligand. The polymers have T_gs of more than 237 °C and $T_{d-5\%}$s of more than 484 °C. They are soluble in common organic solvents and can be cast into tough and flexible films. The catalyst $Cu(PPh_3)_3Br$ was less effective for the formation of polymers derived from **DHPZ** with unactivated aromatic dibromides. Further work is in progress for their application in optical waveguides.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada and partially supported by China Scholarship Council.

Supporting Information Available: Text giving experimental and characterization information and figures showing ^1H NMR spectra for poylmers **5a3** and **5b1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Berard, N.; Hay, A. S. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1993**, *34*, 148−149.
(2) Yoshida, S.; Hay, A. S. *Macromolecules* **1995**, *28*, 2579−2581.
(3) Meng, Y. Z.; Jian, X. G.; Xu, Y.; Qu, M. J.; Hay, A. S. *Chin. Polym. Mater. Sci. Eng.* **1994**, *10*, 85−88.
(4) Yoshida, S.; Hay, A. S. *Macromolecules* **1997**, *30*, 2254−2261.
(5) Meng, Y. Z.; Hay, A. S.; Jian, X. G.; Tjong, S. C. *J. Appl. Polym. Sci.* **1997**, *66*, 1425−1432.
(6) Ding, Y.; Hlil, A. R.; Hay, A. S. *Polym. Prepr.* (*Am. Chem. Soc. Div. Polym. Chem.*) **1997**, *38*, 187−188.
(7) Meng, Y. Z.; Hay, A. S.; Jian, X. G.; Tjong, S. C. *J. Appl. Polym. Sci.* **1998**, *68*, 137−143.
(8) Liu, Y. J.; Jian, X. G.; Liu, S. J. *J. Appl. Polym. Sci.* **2001**, *82*, 823−826.
(9) Wang, S. J.; Meng, Y. Z.; Hlil, A. R.; Hay, A. S. *Macromolecules* **2004**, *37*, 60−65.
(10) Cheng, L.; Jian, X. G.; Mao, S. Z. *J. Polym. Sci., Part A*: *Polym. Chem.* **2002**, *40*, 3489−3496.
(11) Cheng, L.; Jian, X. G. *J. Appl. Polym. Sci.* **2004**, *92*, 1516−1520.

(12) Wang, J. Y.; Jian, X. G.; Xiao, S. D. *Chin. Chem. Lett.* **2001**, *12*, 593−594.
(13) Wang, J. Y.; Liao, G. X.; Liu, C.; Jian, X. G. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6089−6097.
(14) Gao, Y. R.; Wang, J. Y.; Liu, C.; Jian, X. G. *Chin. Chem. Lett.* **2006**, *17*, 140−142.
(15) Lindley, J. *Tetrahedron* **1984**, *40*, 1433−1456.
(16) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400−5449.
(17) Marcoux, J. F.; Doye, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 10539−10540.
(18) Palomo, C.; Oiarbide, M.; Lopez, R.; Gomez-Bengoa, E. *Chem. Commun. 1998*, 2091−2092.
(19) Gujadhur, R. K.; Venkataraman, D.; Kintigh, J. T. *Tetrahedron Lett.* **2001**, *42*, 4791−4793.
(20) Cristau, H. J.; Cellier, P. P.; Hamada, S.; Spindler, J. F.; Taillefer, M. *Org. Lett.* **2004**, *6*, 913−916.
(21) Kunz, K.; Scholz, U.; Ganzer, D. *Synlett* **2003**, *15*, 2428−2439.
(22) Zhang, J. G.; Wang, H. Q.; Li, X. Y. *Polymer* **2006**, *47*, 1511−1518.
(23) Laskoski, M.; Dominguez, D. D.; Keller, T. M. *J. Polym. Sci., Part A, Polym. Chem.* **2006**, *44*, 4559−4565.
(24) Choi, B. K.; Yamamoto, T. *J. Appl. Polym. Sci.* **2006**, *102*, 1763−1767.
(25) Burgoyne, W. F.; Robeson, L. M.; Vrtis, R. N. US Patent 5,874,-516, 1999, Feb.
(26) Hay, A. S. *Prog. Polym. Sci.*, **1999**, *24*, 45−80.
(27) Polymer **5a3** ($CDCl_3$, 400MHz): δ 8.59 (m, 1H), 7.80 (s, 3H), 7.70 (s, 2H), 7.59 (d, 2H, J = 8.0 Hz), 7.00−7.26 (m, 8H); Polymer **5b1** ($CDCl_3$, 400MHz): δ 8.63 (m, 1H), 7.83 (s, 5H), 7.73−7.57 (m, 6H), 7.20 (m, 4H); Polymer **5g** ($CDCl_3$, 400MHz): δ 8.59 (m, 1H), 7.78 (s, 3H), 7.68−7.59 (m, 4H), 7.46−7.35 (m, 4H), 7.13 (m, 2H), 7.03 (m, 2H).
(28) Gujadhur, R. K.; Bates, C. G.; Venkataraman, D. *Org. Lett.*, **2001**, *3*, 4315−4317.

MA702039A