

## Synthesis of poly(aryl ether phenylquinoxaline) via Ullmann ether condensation of chlorine-substituted A-B quinoxaline monomers

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### Summary

An improved, less expensive route to a high-performance poly(aryl ether phenylquinoxaline) has been developed. Thus, an isomeric mixture of self-polymerizable (A-B) quinoxaline monomers, 2-(4-hydroxyphenyl)-3-phenyl-6-chloroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-chloroquinoxaline, was prepared by the condensation of 1,2-diamino-4-chlorobenzene with 4-hydroxybenzil. The mixture was polymerized at 200°C in benzophenone containing potassium carbonate and a freshly prepared copper(I)chloride/quinoline catalyst mixture. The polymer obtained displayed an intrinsic viscosity of 1.53 dl/g (*m*-cresol at 30.0±0.1°C) and a glass transition temperature of 252°C (DSC), similar to samples prepared previously from an analogous fluorine-substituted mixture.

### Introduction

Poly(phenylquinoxalines) (PPQs) are a well-established class of high-performance thermoplastics with high chemical and thermal stability [1,2]. However, they have not found wide-spread use primarily due to the high cost of the aromatic tetraamines and tetraketones used in their synthesis. In fact, the tetraketones are not commercially available. The polymerizations are also run in an undesirable solvent, i.e. *m*-cresol.

A recent approach to overcoming these problems has been to incorporate a quinoxaline moiety into a monomer, which is subsequently polymerized via aromatic nucleophilic substitution reactions. A self-polymerizable PPQ monomer that contains both a phenate nucleophile and a fluorine atom activated by a pyrazine ring for nucleophilic displacement has been prepared in this laboratory [3-5] and by Labadie and coworkers [6]. The A-B monomer, which exists as two isomers, 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline and 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline (**AB-F**), has been polymerized in *N*-methyl-2-pyrrolidinone (NMP) to high molecular weight. The polymer is soluble in NMP, in marked contrast to most PPQs, which are only soluble in phenolic and chlorinated solvents. The PPQ also

displays excellent mechanical and adhesive properties and shows considerable promise as a matrix resin for fiber-reinforced composites [7]. The objective of this research was to reduce the cost of this polymer and, thus, increase the chances of its commercialization, by replacing the relative expensive fluorine-substituted monomer mixture with a less expensive chlorine-substituted analog.

## Experimental

### *Materials*

Copper(I)chloride, Raney<sup>®</sup> nickel, trifluoroacetic acid, and 4-chloro-2-nitroaniline were used as received from Aldrich Chemical Co. Ethanol was used as received from McCormick Distillation Co. Potassium carbonate was dried at 100°C under reduced pressure overnight. Toluene was dried over magnesium sulfate. NMP was distilled from phosphorous pentoxide under reduced pressure. Quinoline was distilled from potassium hydroxide immediately before use. Benzophenone was recrystallized from toluene. 4-Hydroxybenzil was prepared as previously described [7]. Chloroform and hydrochloric acid were used as received from Fisher Chemical Co.

### *Synthesis of 1,2-diamino-4-chlorobenzene (2)*

To a Parr<sup>®</sup> bottle were added 4-chloro-2-nitroaniline (15.00 g, 0.08692 mol), ethanol (300 mL), and a 50% slurry of Raney<sup>®</sup> nickel/water (5.0 mL). The bottle was placed in a hydrogenation apparatus and agitated under hydrogen (60 psi) at room temperature for 4 h. The mixture was filtered through Celite<sup>®</sup>, and the residue rinsed with ethanol until the rinse was no longer colored. The filtrate was evaporated to dryness under reduced pressure. The residue was sublimed twice at 60°C to yield 11.04 g (89%) of a white powder (mp 72-73°C; lit. 72-73°C [8]), which was immediately used in the monomer synthesis.

### *Synthesis of AB-Cl (4)*

To a 500-mL, round-bottom flask equipped with a Claisen adapter, condenser, N<sub>2</sub> inlet, and an overhead stirrer were added 1,2-diamino-4-chlorobenzene (11.22 g, 0.07869 mol), 4-hydroxybenzil (17.80 g, 0.07868 mol), chloroform (232 mL), and five drops trifluoroacetic acid. The solution was stirred and heated at reflux under a N<sub>2</sub> blanket for 5 h. After the solution was allowed to cool to room temperature, it was transferred to a separatory funnel. The organic layer was washed with dilute hydrochloric acid, and then with water several times. The organic layer was evaporated to dryness under reduced pressure. The crude solid was recrystallized from toluene to yield 24.74 g (95%) of a bright yellow powder: mp 118 and 185°C (DSC); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 8.2-6.8 (m, Ar, 12H), 5.5 (s, OH, 1H). C<sub>20</sub>H<sub>13</sub>ClN<sub>2</sub>O (332.77): Calc. C 72.18, H 3.94, N 8.42, Cl 10.65. Found C 72.28, H 4.12, N 8.28, Cl 10.90.

### *Polymerization of AB-Cl in DPS/Toluene*

To a 100-mL, round-bottom flask equipped with an overhead stirrer, a N<sub>2</sub> inlet and a Dean-Stark trap were added AB-Cl (4.00 g, 0.012 mol), sodium bicarbonate (1.34 g, 0.016 mol), cuprous oxide (0.13 g, 0.0018 mol), diphenylsulfone (20 g) and 20 mL of

toluene. The mixture was stirred and heated at 150°C for 4 h during which time the water of condensation was collected in the Dean-Stark trap. Toluene was removed by distillation as the reaction mixture was heated to 180°C for 1 h and then at 320°C for 1 h. The hot dark-brown mixture was added dropwise to 1 L of a rapidly-stirred 1:1(v/v) acetone/acetic acid mixture. The powder that precipitated was collected by filtration, dried under reduced pressure and reprecipitated from chloroform with methanol. The fibrous, off-white polymer was collected by filtration, dried in air and then stirred in refluxing methanol and in refluxing water. The product, which was obtained in quantitative yield, was dried at 180°C under reduced pressure for 20 h.

#### *Preparation of CuCl/quinoline catalyst [9]*

To a 50-mL, round-bottom flask equipped with a Claisen adapter, overhead stirrer, and N<sub>2</sub> inlet were added quinoline (20 mL) and copper(I)chloride (3.00 g). The mixture was stirred under a N<sub>2</sub> blanket for 48 h and used immediately.

#### *Polymerization of AB-Cl in Benzophenone/Toluene*

To a 100-mL, 3-neck, round-bottom flask equipped with an overhead stirrer, N<sub>2</sub> inlet, Dean-Stark trap, condenser, and N<sub>2</sub> outlet were added AB-Cl (8.50 g, 0.0255 mol), potassium carbonate (4.24 g, 0.0307 mol), benzophenone (21.25 g), and toluene (25 mL). The mixture was stirred and heated at 160°C for 5.5 h under a N<sub>2</sub> flow to aid in the azeotropic removal of water. The mixture was then heated at 170°C and the N<sub>2</sub> flow increased to remove the toluene. The mixture was heated to 200°C, and the copper(I)chloride/quinoline catalyst (2 mL) was added. The polymerization mixture was allowed to stir at 200°C for 24 h. The highly viscous mixture was poured while hot into 600 mL of a 5/1 (v/v) methanol/acetic acid solution. The gray, fibrous polymer was collected by filtration and reprecipitated twice from chloroform with methanol. The off-white, fibrous polymer was stirred overnight in refluxing methanol and overnight in refluxing water and then dried at 180°C under reduced pressure. A quantitative yield of product was obtained.

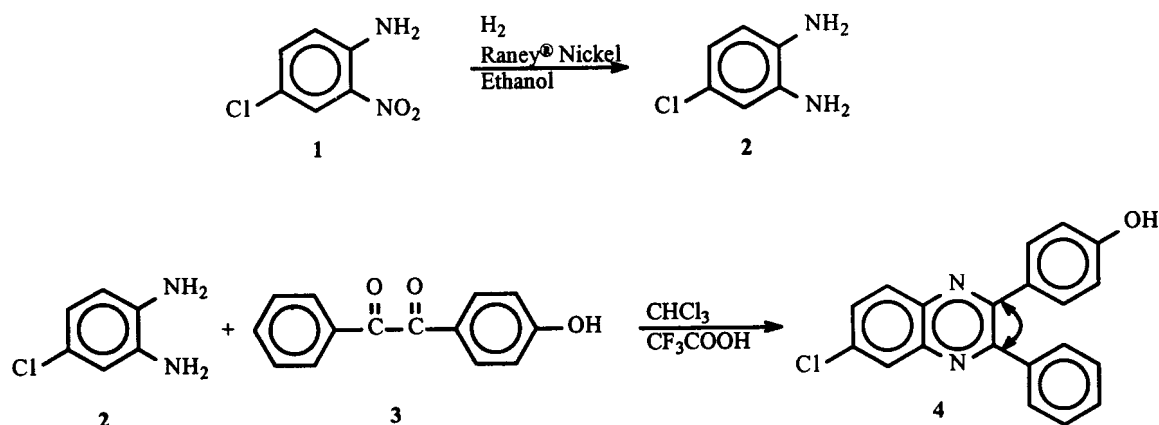
#### *Measurements*

Differential scanning calorimetric (DSC) analyses were performed under nitrogen at a heating rate of 10°C/min using a DuPont Model 2910 thermal analyzer equipped with a DSC cell. Thermogravimetric analyses were performed under nitrogen and air at a heating rate of 10°C/min using a TA Instruments Model 2950 thermogravimetric analyzer. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectrum was obtained with a Varian Gemini 200 NMR Spectrometer at 200 MHz in CDCl<sub>3</sub> using tetramethylsilane as an internal standard. Intrinsic viscosities were determined with a Cannon-Ubbelohde #200 viscometer. Flow times were recorded for *m*-cresol solutions with polymer concentrations of approximately 0.5 g/dL, to 0.25 g/dl, at 30.0 ± 0.1°C. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Inc.

## **Results and discussion**

The self-polymerizable quinoxaline mixture of 2-(4-hydroxyphenyl)-3-phenyl-6-chloroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-chloroquinoxaline (**AB-Cl,4**),

was prepared by a route similar to that used previously to prepare the fluorine-substituted monomer mixture (Scheme 1). In this case, 4-chloro-2-nitroaniline (**1**) was used in place of 4-fluoro-2-nitroaniline. This starting material is approximately 30 times less expensive than 4-fluoro-2-nitroaniline [10]. Initial attempts to reduce **1** using hydrogen and palladium on activated carbon led to the formation of not only 1,2-diamino-4-chlorobenzene (**2**), but also 5-20% of 1,2-diaminobenzene. Palladium on activated carbon has been reported not only to be effective in the reduction of nitro groups, but also in the dehalogenation of aryl chlorides [11]. However, Raney<sup>®</sup> nickel has been found to be a poor catalyst for the dehalogenation of aryl chlorides, especially with low catalyst to substrate ratios [11]. The reduction of **1** with hydrogen and this catalyst provided **2** in 89% yield without any apparent side reactions. Intermediate **2** was then condensed with 4-hydroxybenzil (**3**) in chloroform containing trifluoroacetic acid to give a 95% yield of **AB-Cl** (**4**). The DSC thermogram of the monomer mixture contained two melting endotherms similar to those of other **AB** quinoxaline monomer mixtures [12].



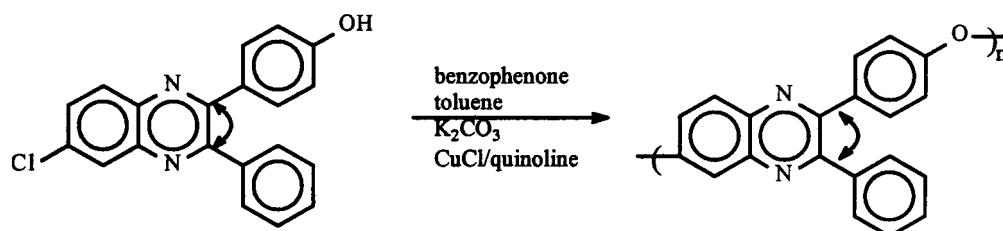
**Scheme 1.** Synthesis of **AB-Cl** (**4**)

The initial attempts at the polymerization of **AB-Cl** were carried out in NMP/toluene mixtures containing potassium carbonate according to the procedure previously used for the polymerization of **AB-F** [7]. However, only low molecular weight polymers were obtained. Several modified procedures in which the temperature profiles were varied also failed to produce polymer. A polymerization in diphenylsulfone (DPS) containing potassium carbonate at 320°C was also unsuccessful. It is well-known that the polymerization of activated aryl chlorides via aromatic nucleophilic substitution reactions is difficult, particularly when the chloro groups are activated by relatively weak withdrawing groups, such as the pyrazine ring [13-15].

Hence, it was decided to attempt the polymerization using Ullman ether coupling reactions. In the initial run, the polymerization of **AB-Cl** was carried out using Ullman conditions developed at ICI [16]. Thus, the monomer mixture was stirred in a DPS/toluene mixture containing sodium bicarbonate and cuprous oxide. The reaction mixture was heated at 150°C for 4 h, at 180°C for 1 h and finally at 320°C for 1 h. Although the initial polymerization yielded a polymer with an intrinsic viscosity of 1.03 dl/g (*m*-cresol at 30.0±0.1°C), several subsequent attempts to reproduce these results were unsuccessful.

During the course of this work, new Ullmann ether coupling conditions were developed for the polymerization of non-activated aryl dichlorides with diphenols [9].

Thus, the polymerization of **AB-Cl** was carried out under these conditions. Treatment of **AB-Cl** with a freshly prepared copper(I)chloride/quinoline catalyst mixture in benzophenone containing potassium carbonate at 200°C afforded a high molecular weight PPQ (Scheme 2). The intrinsic viscosity of the sample was 1.53 dl/g (*m*-cresol at 30.0±0.1°C), which is very close to the highest value obtained on samples prepared from **AB-F** (1.64 dl/g) [7]. DSC analysis showed that the  $T_g$  was 252°C, essentially identical to that previously reported [7]. The FTIR spectrum was identical to that obtained on samples prepared from **AB-F**. The polymerization results were also quite reproducible.



**Scheme 2.** Polymerization of **AB-Cl**

## Conclusions

**AB-Cl** can be polymerized under Ullman ether coupling conditions to high molecular weight polymer. The key to obtaining good and reproducible results appears to be the use of a freshly prepared catalyst mixture of copper(I)chloride and quinoline. It is speculated that this provides a sufficient amount of cuprous ion to affect the polymerization.

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