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Azoxyarylene compounds and polymers by a copper-pyridine catalyzed oxidative coupling reaction

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Summary

Azoxyarylene compounds can be quantitatively formed by oxidative coupling of N-arylhydroxylamines in the presence of a copper-pyridine catalyst and dioxygen. This new method was utilized to synthesize a poly(azoxy arylene). Polymer **5** obtained has a weight average molecular weight of 6,500 and a number average molecular weight of 4,400.

Introduction

Copper-amine catalysts have been extensively used in the manufacture of the important engineering plastic poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO).(1,2) This catalyst system has also been used in the synthesis of polydisulfides,(3-5) poly(azo arylene)s,(6,7) and polyacetylenes.(8) The mechanism for the oxidative coupling reaction has been recently revisted.(9-11) Herein, we wish to report a new oxidative coupling reaction catalyzed by a copper-pyridine catalyst in the presence of dioxygen, namely the oxidative coupling of N-arylhydroxylamines to form azoxyarylene compounds.

Experimental Section

^{1}H-NMR and ^{13}C-NMR were performed on a Varian Unity 300 NMR instrument. GPC analysis was performed using Phenomenex Phenogel columns and a Beckman 160 UV detector. THF was used as the eluent and polystyrenes were used as standards. Elemental analyses were performed by Desert Analytics, Tucson, Arizona.

Nitrobenzene, hydrazine monohydrate, 2,2'-isopropylidene-bisphenol (bis-phenol A, BPA), 4-fluoronitrobenzene, pyridine, CuCl, and 5% Rh/C were purchased from commercial sources and used as received. N-Phenylhydroxylamine **la** was prepared according to a literature procedure(12). The preparation of N-(4-phenoxyphenyl)hydroxylamine **1b** has also been reported previously (13), as has the synthesis of the bis-p-nitrophenyl ether of bis-phenol A **3**. (14)

*Synthesis of Azoxybenzene **2a**.*
A 25 mL three neck round bottom flask equipped with a condenser, a magnetic stirrer and an dioxygen inlet was charged with 0.05g of CuCl (0.5 mmol) and 5.0 mL of pyridine. The

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mixture was vigorously stirred for 15 min with dioxygen bubbling directly into the reaction mixture. Then, 1.0 g (9.2 mmol) of N-phenylhydroxylamine **la** dissolved in 5.0 mL of pyridine was added to the reaction mixture in one portion. The reaction temperature increased immediately by 5 °C. The resulting mixture was stirred for 30 min and then poured into 100 mL of water to precipitate out the product, which was collected by filtration. The product was recrystallized from ethanol and dried at room temperature under vacuum for 48 h, 0.87 g of green yellow crystal was obtained. Yield, 96 %. M. p.: 33-35°C (lit.(15) 35 - 6 °C). FT-IR (KBr): 1470 cm^{-1} (-N=N(O)-).

Synthesis of Azoxy-bis(4-phenoxybenzene) ***2b***

The synthesis was carried as described above. The amount of N-(4-phenoxyphenyl)hydroxylamine **1b** used was 2.0 g and 1.62 g of azoxy-bis(4-phenoxybenzene) was obtained after recrystallization from ethanol. Yield: 85 %. M. p.: 88-90 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm), 8.27 (t, 4H), 7.42 (m, 4H), 7.20 (m, 2H), 7.06 (m, 8H). ^{13}C-NMR ($CDCl_3$): δ (ppm), 160.4, 158.3, 156.1, 143.1, 139.4, 130.1, 129.9, 127.7, 124.5, 124.1, 124.0, 119.9, 119.7, 117.9, 117.6, 113.0. Elemental analysis (%): Cald.: C, 75.38; H, 4.74; N, 7.33; Found: C, 75.32; H, 4.56; N, 7.51. MS (m/z): 382 (M^+). FT-IR (KBr): 1467 cm^{-1} (-N=N(O)-).

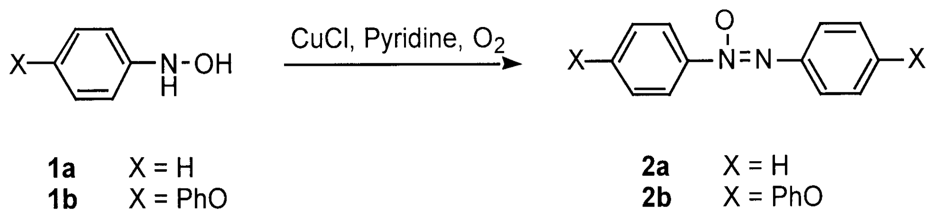
Polymerization reaction.

A 100 mL three neck round bottom flask equipped with a condenser and a magnetic stirrer was charged with 0.1 g of 5 % Rh/C, 5.0 g (0.011 mol) of **3**, and 25 mL of THF. The reaction flask was placed in an ice water bath and 1.2 g of hydrazine monohydrate was added dropwise over 10 min. After stirring at room temperature for 2h, the mixture is dried with anhydrous sodium sulfate and filtered. The solution is concentrated to about 5 mL and immediately added to the copper-pyridine catalyst system. The copper-pyridine system was formed by 0.20 g of CuC and 25 mL of pyridine with dioxygen bubbled in directly. The reaction temperature increased immediately by 5 °C. The resulting mixture was stirred for 1 h and then poured into 200 mL of methanol containing 5 mL of conc. HCl solution to precipitate out the product, which was collected by filtration. The powder was collected by filtration and purified once more by dissolving in 30 mL of chloroform and precipitate out from methanol. Yield, 86 %. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm), 8.27 (d, 4H), 7.26 (m, 4H), 7.04 (m, 8H). FT-IR (KBr): 1462 cm^{-1} (-N=N(O)-).

Results and Discussion

Oxidative coupling reaction of N-arylhydroxylamines.

The oxidative coupling reaction of N-arylhydroxylamine to form azoxyarylene compounds in the presence of a copper-pyridine catalyst and dioxygen is a fast reaction. Once the reactant was added to the catalytic system, the intensive green color due to the formation of copper(II)pyridine complex disappeared immediately and temperature increased by ~ 5 °C. As the reaction proceeded, the reaction mixture became green in color again and remained stable. After stirring at room temperature for 30 min, the reaction mixture was poured into water to precipitate out crystalline azoxy compounds. The products were obtained in quantitative yields.



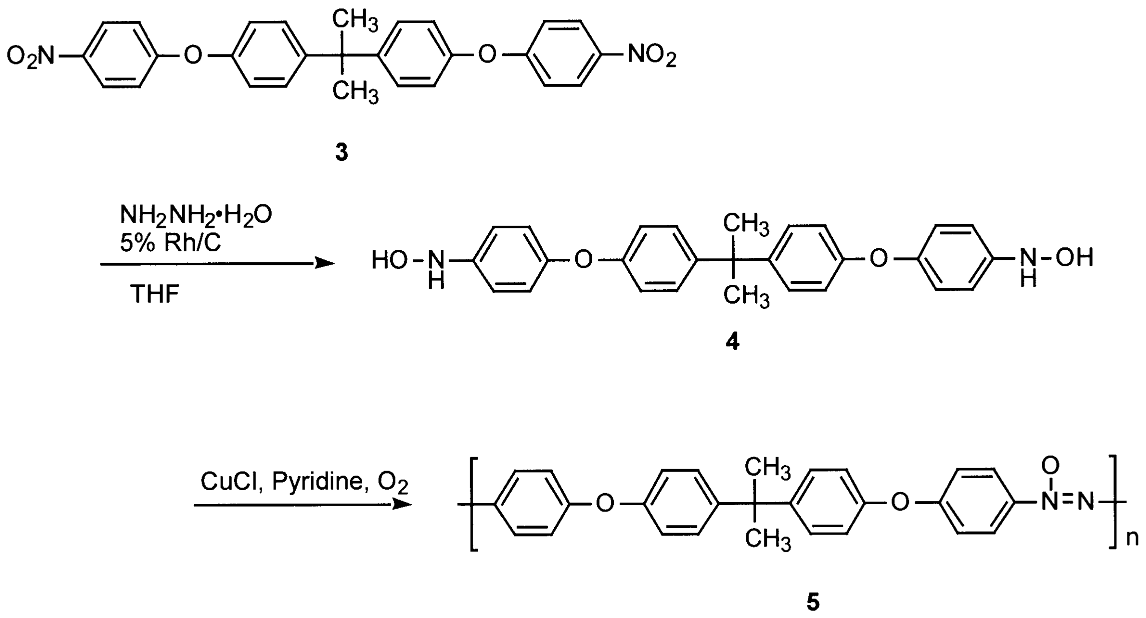
1a X = H
1b X = PhO
2a X = H
2b X = PhO

(1)

It should be pointed out that the starting materials, N-arylhydroxylamines, do not necessarily have to be isolated and purified. They can be used directly in the solution after the reduction of the precursor nitrocompounds simply by filtering off the catalyst.

Poly(azoxy arylene)s by oxidative coupling reaction of N-arylhydroxylamines.

Encouraged by the above results, we set out to synthesize a poly(azoxy arylene) by this novel oxidative coupling reaction. A number of azoxy group-containing aromatic polyesters have been reported to exhibit liquid crystalline behavior.(16) Poly(azoxy arylene ether)s have been previously synthesized by a nucleophilic substitution reaction and their properties have been briefly studied.(17)



3

4

5

(2)

By the present oxidative coupling reaction, polymer **5** was obtained in high yield starting from the bis-nitro compound 3 without the isolation of the intermediate **4**. The bis-nitro compound **3** was simply prepared from BPA and 4-fluoronitrobenzene in DMF in the presence of anhydrous potassium carbonate, followed by recrystallization from ethanol.(14) The reduction to the bishydroxylamine derivative **4** was carried out in THF using hydrazine monohydrate in the presence of Rh/C catalyst. At the end of reaction, the reaction mixture was filtered and concentrated. The resulting solution was added to the copper-pyridine solution in one portion with the bubbling of dioxygen. The polymerization took place immediately as evidenced by the color change. The solution was stirred at room temperature for 60 min and poured into 150 mL of methanol containing 5 mL of conc. HCl solution to precipitate the polymer which was collected by filtration. The polymer had a weight average molecular weight of 6,500 and a number average molecular weight of 4,400.

N,N'-Dihydroxyl-1,4-phenylenediamine, which can be recrystallized from cyclohexane/methylene chloride, failed to form polymer in these reaction conditions. Oxidation of this compound forms reddish low molecular weight material. This behavior has also been observed for the attempted oxidative coupling of 1,4-phenylenediamine which also failed to yield high molecular weight poly(azo phenylene).(7) 1,2-Phenylenediamine has been reported to form *cis,cis*-mucononitrile in the presence of a copper-pyridine catalyst and dioxygen.(18) Because N,N'-dihydroxyl-1,4-phenylenediamine has a much lower oxidation potential than 1,4-phenylenediamine and 1,2-phenylenediamine, it is not surprising that high molecular weight polymers could not be obtained.

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