Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Gomurashvili, Zaza and Hay, Allan S.(2005) 'Aromatic Polyazines by a Copper-Amine Catalyzed Oxidative Polymerization Reaction', Journal of Macromolecular Science, Part A, 42: 2, 127 — 138

To link to this Article: DOI: 10.1081/MA-200046967

URL: http://dx.doi.org/10.1081/MA-200046967

Journal of Macromolecular Science®Part A—Pure and Applied Chemistry, 42:127–138, 2005
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ISSN 1060-1325 print/1520-5738 online
DOI: 10.1081/MA-200046967

Aromatic Polyazines by a Copper-Amine Catalyzed Oxidative Polymerization Reaction

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Benzophenone azine is a useful intermediate for hydrazine production. It can be formed in high yield by oxidation of benzophenoneimine in the presence of a copper-amine catalyst and dioxygen at low temperatures. We have used this method to synthesize aromatic polymers with azine linkages from six diketoimine monomers. The resulting polymers reached an average molecular weight of 10,000 and number average molecular weight of 6000 Daltons and were film forming materials.

Keywords oxidative coupling, diimines, Polyazines, hydrazones, aminodiphenylmethane

Introduction

Azines have proven useful as intermediates in the synthesis of hydrocarbons, amines, various heterocyclic systems and as ligands in transition metal compounds.[1,2] Benzophenone azine is an intermediate product in a process for hydrazine production by a catalytic oxidation process that involves the inexpensive starting materials, benzophenone, ammonia and molecular oxygen. In this method, benzophenoneimine is formed by the oxidative coupling of diphenylmethaneimine with oxygen in the presence of a copper catalyst. Hydrazine is obtained quantitatively by acid catalyzed hydrolysis and the formed benzophenone is recycled.[3–6] Copper-catalyzed formation of benzophenone azine was first reported[7] in 1959 and later improvements for industrial application have been reported.[8,9]

Benzophenone azine formation by oxidative coupling of benzophenone hydrazone with quinones[10] and N-bromosuccinimide[11] and bis(acetylacetanato) copper(II) complexes with oxygen[12] has also been reported. Recent studies in our laboratory demonstrated that benzophenone azine is also formed from aminodiphenylmethane by oxidative coupling presumably via the imine intermediate.

Catalytic oxidation with oxygen and a copper/amine catalyst has been extensively used in the manufacture of the engineering plastic poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO).[13–15] Similar catalyst systems have also been used in the synthesis of polydisulfides[16–18] poly(azo arylenes),[19,20] polyacetylenes,[21] and azoxyarylenes.[22]

In this paper we report on the copper/amine catalyzed oxidative formation of azines from imines for the synthesis of polymeric azines.

Received July 2004, Accepted August 2004

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Experimental

Materials

Solvents were purchased from commercial sources (Fisher Scientific, Aldrich Co) and purified by distillation using conventional methods and stored over 3-Å molecular sieves. CuCl, N,N,N′,N′-tetramethylethylenediamine (TMEDA), 1,8-diazabicyclo [5.4.0.]-undecene-7, (DBU), benzophenoneimine, aminodiphenylmethane, 1,4-dicyanobenzene, benzoyl chloride, diphenyl ether, all from Aldrich, were used as received or as otherwise stated. Benzophenone hydrazone,[23,24] 4,4′-oxybis(benzonitrile) (**1b**)[25] bis(4-cyanophenyl)sulfide[26] (**1c**), 1,1′-bis(4-benzoylphenyl)ether[27] (**4a**), 4,4′-dibenzoyldiphenyl ether dihydrazone[28] (**4b**) were synthesized as reported in the literature. Phenyllithium was prepared from bromobenzene as described[29] and used as the ether solution.

Measurements

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury 300 or 400 spectrometer. $CDCl_3$ was used as the solvent and tetramethylsilane as the internal standard. Melting points were taken on a Fisher-Johns melting point apparatus. Progress of the reactions was monitored by high performance liquid chromatography (HPLC, Milton Roy, CM4000) with methanol as an eluent and UV detector set at 254 nm. The GPC measurements were conducted with a Waters 510 system equipped with UV detector set at 254 nm. THF was used as the eluent and polystyrenes were used as standards. MALDI-TOF mass spectra were recorded with a Kratos Kompact MALDI-III TOF mass spectrometer with the instrument set in the positive reflection mode to get higher resolution. Electrospray ionization spectra were recorded with a Finnigan LCQ DUO Ion Trap Mass Analyzer fitted with API source and Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI) probes. Scan functions include: full scan MS (50-2000), full scan MS/MS, SIM, SRM and zoom scan. The samples were run in $CHCl_3$/methanol (1/20) using an ESI probe by infusion (10 μL/min) using an integrated syringe pump under data system control with capillary temperature of 200°C, needle voltage of 4.5 kv, sheath and auxilliary gas nitrogen and scan mode full MS and full MS/MS. Infrared spectra were recorded on a Bruker IFS 48 series FT-IR spectrometer from thin polymer films cast on the NaCl plate, or as KBr disc for monomeric compounds.

Synthesis of Dinitriles

The three bisnitriles **6d–f**, were synthesized by the same procedure. A general procedure is given for the synthesis of 4,4-[isopropylidenebis(1,4-phenylene)dioxy]dibenzonitrile (**6e**). 4,4′-Isopropylidenediphenol (13,7 g, 60 mmol) and K_2CO_3 (10 g; 72.5 mmol) were suspended in 125 mL of a DMF/toluene mixture (vol. ratio 4 : 1) and heated to 150°C under nitrogen using a Dean-Stark trap to remove the water by azeotropic distillation. After collecting the theoretical amount of water, 4-fluorobenzonitrile (15.1 g; 125 mmol) was added and heating continued at 170°C for 5 h. DMF was removed under reduced pressure. A white solid was collected and washed with water and ethanol. Recrystallization from methanol gave white needles of **6e** in 79% yield, mp 123–124°C (m.p. lit.[30] 124°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.59 (d, 4H), 7.27 (d, 4H), 7.00 (m, 8H), 1.72 (s, 6H).

1,4-Bis(p-cyanophenoxy)benzene (6d): The reaction of hydroquinone with 4-fluorobenzonitrile gave white crystals in 86% yield, after recrystallization from acetonitrile. Mp 213°C which corresponds to the reported value.[31] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.61 (d,4H), 7.10 (d,4H), 7.02 (m,8H).

4,4′-[[1,1′-Biphenyl]-4,4′-diylbis(oxy)]bisbenzonitrile (1f): Reaction of the potassium salt of 4,4′dihydroxybiphenyl with 4-fluorobenzonitrile gave white flakes in 92% yield. After recrystallization from chloroform/methanol it had mp 236°C. IR (KBr) ν (cm^{-1}): 2223 ($C{\equiv}N$), 1595 (phenyl), 1245 (C–O–C). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.61 (t, 8H), 7.14 (d, 4H), 7.06 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.53, 154.50, 137.24, 134.30, 128.91, 120.92, 118.98, 118.23, 106.30. MALDI-TOF MS: 388 Da.

Preparation of Bisketimines 7a–f: All operations involving organometallic reagents were carried out in dry solvents and under a nitrogen atmosphere. The reactions were carried out following the general procedure developed by Lee.[32]

To a −70°C chilled mixture of 8 mmols of dinitrile in 50–60 mL of freshly distilled diethyl ether there was added, dropwise, 18 mmols of phenyllithium in ether solution using a syringe through a rubber septum. Stirring with cooling for 30 min gave a red solution. After removing the cooling bath, the reaction mixture was allowed to warm to room temperature and left at that temperature for 6 h. A yellow salt, the diketiminolithium, precipitated out of the solution. To this mixture, 50–60 mL of water was added carefully. The red solution immediately turned to colorless, forming a white precipitate that gradually dissolved into the ether layer. The ether layer was separated, washed with saline water, dried over anhydrous magnesium sulfate and filtered. The filtrate evaporated and the crude product recrystallized. The yields obtained were in the 60–75% range.

1,4-Dibenzimidoylbenzene (7a): Yield 72% after crystallization from cyclohexane. Mp 102–104°C (m.p. lit[32] 100–102°C), b.p. 175–180°C/0.015T. MALDI-TOF MS: 284 (M^+) Da. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.7, 130.7, 128.6.

4,4′-Dibenzoyldiphenylether diimine (7b): Yield 78% after crystallization from toluene/cyclohexane (1 : 2). M.p. 134–136 °C. MALDI-TOF MS: 376.5 (M^+) Da. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.64 (s, NH), 7.69–7.42 (m, Ar), 7.11–7.06 (m, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.5, 158.7, 149.9, 134.7, 130.7, 130.4, 128.6, 128.4, 119.9, 118.8.

Bis(4-benzoylphenyl)sulfide diimine (7c): Yield 81% after crystallization from toluene/cyclohexane (5/95), m.p. 107–109°C. MALDI-TOF MS: 392.5 (M^+) Da. IR(KBr) ν (cm^{-1}): 3270 (N–H), 1653 (C=N), 1590 (phenyl). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.73 (s, NH), 7.54–7.39 (m, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 177.6, 149.9, 138.2, 130.8, 130.6, 129.7, 128.7, 128.4.

4,4′-Bis-[1,4-diphenoxybenzene]-benzenemethanimine (7d): White crystals, mp 139–140°C from toluene. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.58 (s, broad N*H*). 7.61–7.42 (m, 14H), 7.09 (s, 4H), 6.90 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.5, 159.9, 152.4, 139.9, 133.9, 130.7, 130.4, 128.6, 128.4, 121.4, 117.45. MALDI-TOF MS: 468.6 (M^+) Da.

Bisimine 7e: The viscous product was concentrated in 110 mL of hot cyclohexane. Impurities precipitated out first, which were removed by filtration. A yellow amorphous solid was collected after evaporation of the filtered solution. Yield 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61 (t, 8H), 7.17 (d, 4H), 7.06 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.6, 159.8, 154.2, 130.6, 130.6, 130.3, 128.9, 128.6, 128.4, 127.5, 127.3, 119.3, 117.9, 42.6 31.4. Dry HCl gas was bubbled into the ether solution of **2e** to give a white crystalline salt, which was washed with ether and dried under vacuum. M.p. 171–174°C. IR(KBr) ν (cm^{-1}): 3300–2500 (broad, NH·HCl salt), 1650 (C=N), 1598 (phenyl), 1244 ($C(CH_3)_2$).

Bisimine 7f: White crystals were collected from toluene in 75% yield. M.p. 210–212°C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.62 (s. broad N*H*), 7.58–7.42 (m, 16H), 7.40 (d, 4H), 7.12 (d, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 177.6, 159.6, 155.9, 136.5, 130.6, 130.4, 128.6, 128.4, 120.1, 118.1. MALDI-TOF MS: 544 (M^+) Da.

Model Oxidative Polymerization Reactions

Model polymerization reactions were carried out under oxygen as described below. Into a cylindrical glass reactor equipped with a vibromixer stirrer and oxygen inlet tube was placed 0.055 g (0.56 mmol) of powdered CuCl, 5 mL of dry chlorobenzene, 0.33 mL (2.24 mmol) of TMEDA and the mixture was stirred for 15 min. while oxygen was bubbled into the mixture. The complex of Cu(I) was converted to Cu(II). After the catalyst was prepared the reactor was placed into an oil bath preheated to 95°C. Vigorous stirring was continued, and there was added 0.6 g of dried magnesium sulfate and the solution of 5.5 mmol of the diimine in 10 mL of chlorobenzene. The reaction mixture gradually changed from a dark blue-green color to yellow. The resulting mixture was stirred for 50 min and then poured into 200 mL of methanol containing 4 mL of ammonium hydroxide, to precipitate out the product, that was collected by filtration. The product was purified by redissolving in 15 mL of chloroform, filtering through Celite, and precipitating out in methanol. Molecular weights of polymers were characterized by GPC and these values and yields are summarized in Tables 1–2.

Results and Discussion

Model Oxidation Study

Three different classes of compounds form benzophenone azine **1** by oxidative coupling: benzophenone imine **2**, benzophenone hydrazone **3**, and aminodiphenyl methane **4**. (Sch. 1)

Table 1
Synthesis of model polyazine **9d** by oxidative coupling of bisimine **7d**

#	Temperature	Monomer/ catalyst	Reaction time (min)	M_n[a]	M_w[a]	Yield[b] (%)
1	85	100	120	—	—	0
2	85	50	120	—	—	0
3	85	20	50	4,700	7,700	74
4	85	10	50	6,200	10,000	84
5	85	4	50	5,200	8,500	81
6	60	10	60	3,400	3,700	62

[a] From GPC measurements.

[b] After second precipitation Tg of #3 and #5 samples were 127°C; TGA 95%, (N_2), 388°C.

Table 2
Yields and molecular weights of polyazines **9a–f***

Polymer	M_n[a]	M_w[a]	Yield[b] (%)
9a	2,600	3,600	52
9b	2,300	2,800	45
9b[c]	2,500	3,300	54
9c	2,400	3,100	68
9e	3,000	3,900	72
9e[d]	2,400	3,200	78
9f[e]	2,200	2,900	71

*Polymerization reactions performed at 85°C, in chlorobenzene, for 50 min. Cu to Monomer ratio: 1/10.

[a] From GPC measurements.

[b] Yields were entered after second precipitation.

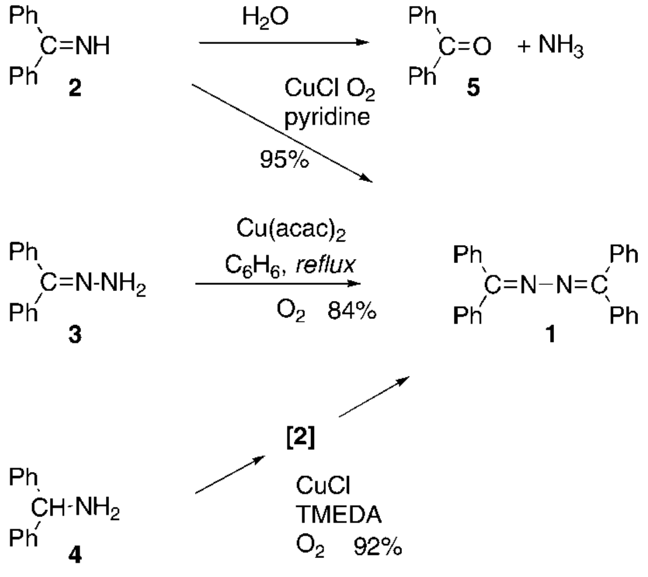
[c] Synthesized by oxidative coupling of bishydrazone **8b** at 50°C (Sch. 6).

[d] Polymer prepared from diimine hydrochloride salt (prior to polymerization **6e** hydrochloride was deprotected while stirring with Na_2CO_3 in chlorobenzene. The solution was dried over $MgSO_4$, filtered and directly introduced into the polymerization reactor).

[e] Reaction temperature 95°C.

Benzophenone azine formation from the imine was first disclosed in the work of Mayer[7] who obtained it from benzophenone imine **2** in 94.5% yield, via oxidative coupling with oxygen and a CuCl/pyridine catalyst at 20°C.

The byproduct was isolated and identified as benzophenone **5**, that results from base catalyzed hydrolysis of the imine **2** during the reaction with the water formed in the reaction (Sch. 1).



Scheme 1. Preparation of benzophenone azine.

Other monodentate amine ligands (γ-picoline, isoquinoline) showed similar reactivity to pyridine at 80°C but, at lower temperatures, which is desirable to avoid the side hydrolysis reactions, pyridine was the most effective.[5] A mechanism for catalysis was proposed in this work and in the cited literature. The copper-pyridine complex is easily converted to the copper-imine complex ($CuCl \cdot Ph_2C{=}NH$) by ligand exchange, which further undergoes the oxidation steps to form the final azine. The reaction proceeds at 120°C in an inert solvent over 7 h.

Bicycloamidines (1,8-diazabicyclo-[5.4.0]undecene-7(DBU), and 1,5-diazabicyclo-[4.3.0]nonene-5 (DBN), also promoted the oxidative coupling reaction and yielded up to 95% of azine at moderate temperatures whereas some bidentate ligands, such as ethylenediamine and monoethanolamine, inhibited the oxidative coupling.[6] The bidentate amine TMEDA is known to be an excellent ligand for acetylene oxidative coupling[21] and for the oxidative coupling reaction of 2,6-disubstituted phenols yielding the aromatic polyethers.[15] We have shown that this catalyst is very effective in azine bond formation from imines and we have utilized it for the oxidative polymerization of bisimines.

Benzophenone hydrazone **2** has been recently shown to form the azine **1** in 76–86% yield using $Cu(acac)_2/O_2$ catalyst (Sch. 1).[12] Here, also the major side reaction that occurred was the formation of a small amount of benzophenone by hydrolysis.

We have also demonstrated that **1** can be formed in high yield by oxidation of aminodiphenyl methane **4** (84–92%). The reaction probably goes through the intermediate step of imine formation (Sch. 1).

To optimize the oxidative coupling reaction conditions model studies were conducted. Three model compounds of different classes were examined; benzophenone imine **2**, benzophenone hydrazone **3**, and aminodiphenyl methane **4**. The reactions were monitored with HPLC and ^1H NMR. Various catalyst systems were examined in a temperature range of 25 to 90°C; CuCl/TMEDA, CuCl/DBU in THF, CuCl/butyronitrile (as ligand and solvent), and CuCl/pyridine in nitrobenzene. The most effective catalyst for benzophenone imine oxidation was CuCl/TMEDA using 0.1 equivalents vs the substrate, with a copper/ligand ratio: 1/2 and reaction temperature 80–85°C.

Shechter has demonstrated the oxidation of benzhydrylamine **4** with potassium permanganate and demonstrated that the first intermediate was the imine.[33] Using a CuCl/TMEDA catalyst, oxidation of **4** takes place in 1.5–2 h to give benzophenone azine in 84–92% yield. Decreasing the temperature to 60°C extended the reaction time around twice, but no significant changes were observed in the ratios of the product mixtures. A small amount of benzophenone was always identified. In the copper/TMEDA system, benzophenone imine **2** in ca. 15 min was converted to benzophenone azine **1** in 92–97% yield (^1H-NMR). To reach the higher yields with this catalyst system was not possible-probably due to side reactions causing monomer hydrolysis. Even an increase of copper/ligand feed ratio to 1 : 3 and introduction of $MgSO_4$ as drying agent in the reaction mixture, did not significantly improve the final azine yield.

Oxidation of benzophenone hydrazone **3** was extremely fast under similar conditions. In about 3 min. the formation of azine was practically complete (HPLC). The azine was detected along with benzophenone in an estimated ratio of 60 : 40. Decreasing the reaction temperature to 25°C increased the target compound content to $\sim$90% and the reaction was finished in 15 min.

Encouraged by the excellent yields in imine oxidation using CuCl/TMEDA as catalyst, we set out to synthesize aromatic polyazines form aromatic diimines. It should be noted that Smets[28] has previously synthesized polyazine structures of this type with molecular weights of about 4000 by acid catalyzed condensation of hydrazones.

Monomer Synthesis

Synthesis of bisimines was carried out in two steps from aromatic dinitriles that were converted to bisimines by reaction with phenyllithium.

Six bisnitriles (**6a–f**) were utilized in his work. 1,4-Dicyanobenzene (**6a**) is a commercially available product and was used after recrystallization. Other dinitriles **6b–e** have been reported in the literature and were prepared by the following routes. (Sch. 2).

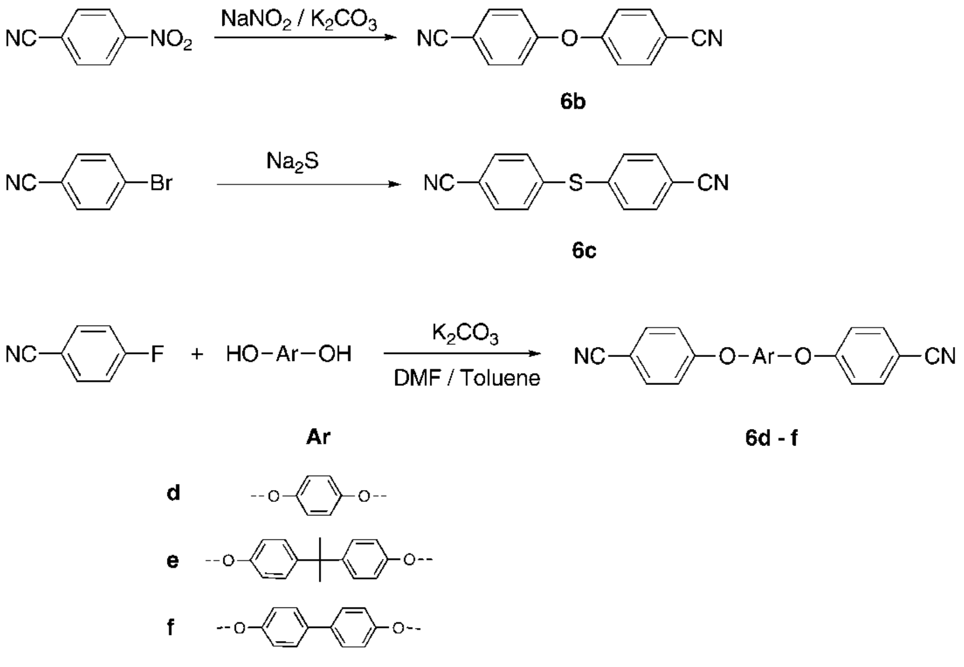
4,4′-Oxybis(benzonitrile) **6b** was synthesized by the self-condenstion of p-nitrobenzonitrile in the presence of a KNO_2/Na_2CO_3 catalyst system in an aprotic polar solvent. The formation of the diphenyl ether linkage is depicted in Sch. 2. Pale yellow crystals of **6b** were obtained in 66% yield, with m.p. 177–178°C after recrystallization from 85% ethanol, and treatment with charcoal. (m.p. lit.[25] 179–180°C).

Bis(4-cyanophenyl)sulfide **6c** was prepared from 4-chlorobenzonitrile and anhydrous sodium sulfide by nucleophilic aromatic substitution in 68% yield, m.p. 135–136°C (Sch. 2).

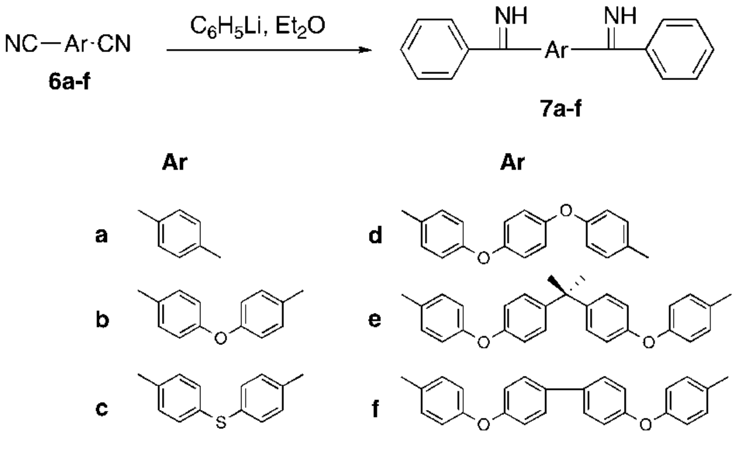
The other three dinitriles **6d–f** were synthesized by nucleophilic displacement of halogen of p-fluoronitrile in a two step addition-elimination reaction (S_NAr) to form the aryl ether linkage with hydroquinone, 4,4′-isopropylidenediphenol (bisphenol A), and 4,4′-biphenol (Sch. 2). The melting points and ^{1}H-NMR, and FT-IR spectrum of each of the preceding compounds was recorded and compared with published data. MALDI-TOF mass spectroscopy of compound **1e**, described for the first time, and for the others confirmed the structures of the prepared materials.

Synthesis of Bisketoimines 7a–f

The bisketoimines syntheses were carried out according to Sch. 3.

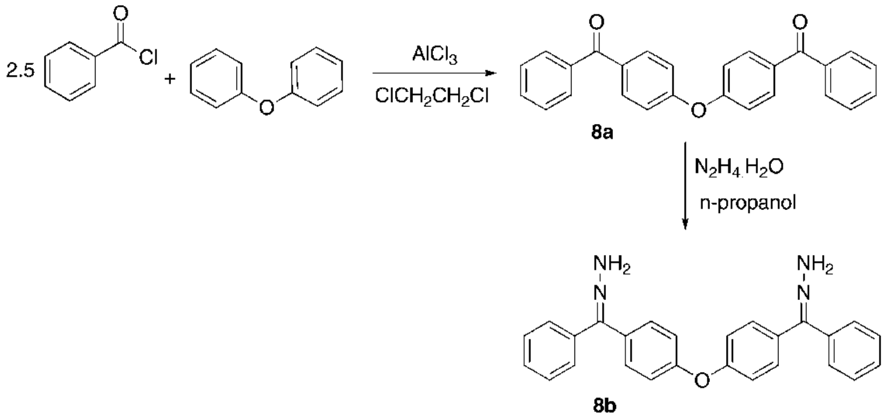


Scheme 2. Synthesis of dinitriles **6b–f**.

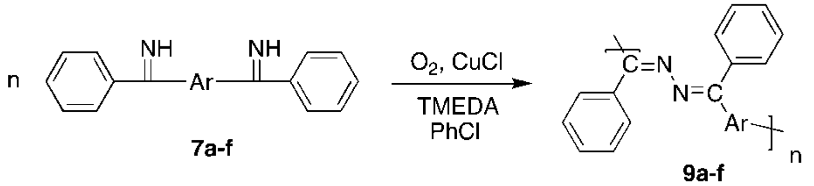


Scheme 3. Synthesis of bisimines **7b–f**.

The bisketoimines **7a–f** were crystalline yellow solids, with the exception of **7e** that was a viscous liquid and did not crystallize even after long time storage at room temperature. To simplify the handling of **7e**, the compound was converted to the hydrochloride salt by passing dry HCl gas into an ether solution of the bisimine. The hydrochloride collected as a white crystalline powder with melting point of 171–174°C. Compound **7f** is a highly crystalline material, which has very low solubility in chlorobenzene at the optimized polymerization temperature (85°C). In this case, the polymerization temperature was increased to 95°C. Diketoimines were crystallized from cyclohexane or cyclohexane–toluene mixtures. For further purification, diketoimine **7a** was distilled at 170–175°C under vacuum. Attempts to distill **7b** and **7c** failed. Formation of imine groups was confirmed by ^{13}C NMR spectroscopy. All prepared imines gave a ^{13}C NMR peak at 177.6 ± 0.1 ppm, that was assigned to the imine carbon. IR measurements also detected relatively weak signals corresponding to N–H (ca. $3220\,\mathrm{cm}^{-1}$) and C=N ($1650 \pm 10\,\mathrm{cm}^{-1}$) stretching in conjugation with aromatic C=C peaks ($1600\,\mathrm{cm}^{-1}$).



Scheme 4. Synthesis of bishydrazone **8b**.



Scheme 5. Oxidative polymerization of bisimines **7a–f**.

To examine the polymer formation from dihydrazones, and compare this with the imine polymerization, dihydrazone monomer **8b** was also prepared (Sch. 4). The method involved two sequential synthesis steps. Preparation of 1,1′-bis(4-benzoylphenyl) ether (**8a**) was carried out by Friedel-Crafts acylation of phenyl ether with benzoyl chloride in 1,2-dichloroethane solution and gave **8a** in 74% yield. **8a** was further converted to 4,4′-dibenzoyldiphenyl ether dihydrazone by refluxing of bisketone with excess of hydrazine hydrate in n-propanol as described previously.[28] Acetic acid was employed as catalyst in this case. Recrystallization from n-propanol gave **8b** as white crystals with a mp 170–172°C in a 55% yield (Sch. 6). During the recrystallization, it was necessary to add a few drops of hydrazine monohydrate to avoid the disproportionation reaction.

Polymerization Study

Several runs were conducted to optimize the polymerization reaction parameters. Compound **7d** was employed as a model monomer. Polymerizations were carried out in chlorobenzene at preselected temperatures, with various monomer/copper ratios (Table 1) (Sch. 5). The copper/TMEDA ratio (1 : 2) was kept constant. Table 1 summarizes the various reaction conditions that were tried. Gel-permeation chromatography (GPC) showed that only oligomers were formed. A maximum molecular weight $M_n = 6200$ which corresponds to ca. 13 repeat units in the polymer chain was achieved at copper/monomer ratio of 1/10. Increasing the catalyst ratio to 1/4 did not improve the molecular weight. No polymer was formed when copper/monomer ratio was less than 1/50.

In Table 1, the reported product yields were taken after a second reprecipitation, since the isolated polymers still contained some copper salts as impurities.

The polymers were readily soluble in common organic solvents. Aromatic polyazines reported previously, prepared by condensation of aldehydes or ketones with hydrazine, have been described as insoluble, intractable materials.[34–36] However, the polymers synthesized by Smets, which are more similar in structure, were soluble.[28] Yellow colored flexible films were cast from chloroform solution of polymer #4, Table1.

Thermal properties of polymers #3 and #5, Table 1, were measured by DSC. Both polymers showed the same glass transition temperature at 127°C.

$$\mathbf{8b} \xrightarrow[\text{TMEDA, PhCl}]{\text{O}_2\text{, CuCl}} \mathbf{9b}$$

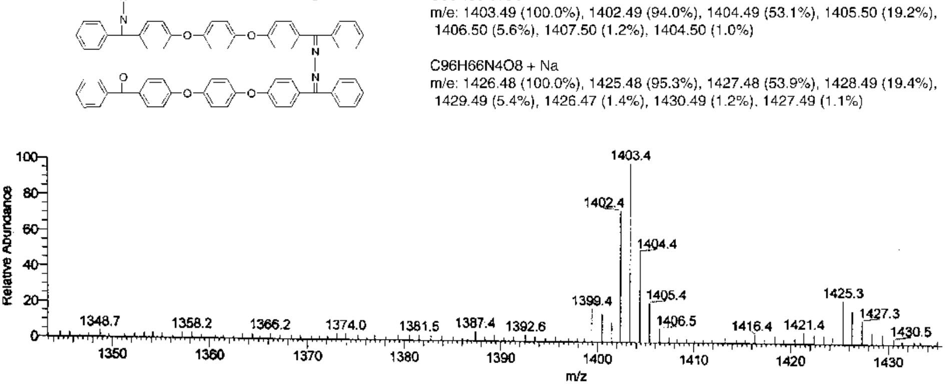
Scheme 6. Oxidative polymerization of bishydrazone **8b**.

The chemical structures of the polyazines were identified by IR and Electrospray Ionization MS (ESI MS). The IR spectra contain distinctive sharp signals, indicating that no conjugation between double bonds along the polymer chain occurred. Signals characteristic of the imine N–H bond vibrations at 3200 cm^{-1} were not detectable. Instead, a signal at 1600 cm^{-1} increased, corresponding to the C=N linkage[37,38] in conjugation with the aromatic C=C signal which generally occurs at 1590 cm^{-1}. A small peak at 1660 cm^{-1} can be assigned as a C=O end-group that formed after hydrolysis. The ESI MS spectrum for the trimer region (Fig. 1) shows only the linear trimer (and trimer with Na^{+} attachment) with C=O end groups with no cyclomer present. We have previously been successful in using MALDI-TOF mass spectrometry for distinguishing between linear and cyclic oligomers in poly(aryl ether)s and poly(aryl thioether)s.[39] The MALDI spectra of the azines showed a regular progression of masses but we were unable to definitely assign all the peaks. There appeared to be multiple attachments of lithium from the cationization reagent LiCl and MALDI on the model compound 1,2-bis(diphenylmethylene)hydrazine **10** indicates fragmentation by N–N cleavage reactions.

The most successful reaction conditions—entry #4 from Table 1 were then applied to the synthesis of a series of polymers from other diimines **2a–c, e, f** (Sch. 7). The results are summarized in Table 2.

The polyazines have good solubility in organic solvents. GPC measurements in THF indicated that the polymers have lower molecular weights, than the **9d** polyazine from Table 1, #4. Despite this fact, polymers **9b**, **e**, and **f** still form flexible yellow colored films upon casting from chloroform.

It is interesting that **9b** polyazine, prepared from dihydrazone **8b**, achieved a number average molecular weight of 2500 Daltons. The reaction proceeded extremely fast, even at 50°C. Upon exposure to O$_2$ the pink solution of the catalyst-dihydrazone complex became greenish-yellow in a few seconds, which indicated completion of the reaction.



9d trimer calculated isotopic distribution
C96H66N4O8
m/e: 1403.49 (100.0%), 1402.49 (94.0%), 1404.49 (53.1%), 1405.50 (19.2%), 1406.50 (5.6%), 1407.50 (1.2%), 1404.50 (1.0%)

C96H66N4O8 + Na
m/e: 1426.48 (100.0%), 1425.48 (95.3%), 1427.48 (53.9%), 1428.49 (19.4%), 1429.49 (5.4%), 1426.47 (1.4%), 1430.49 (1.2%), 1427.49 (1.1%)

Figure 1. Electrospray ionization MS of **9d** (#6) in trimer region.

Conclusions

The results of present work demonstrate that it is possible to synthesize soluble aromatic polyazines by the oxidative coupling reaction from diimines and dihydrazones. As catalyst a CuCl/TMEDA complex was employed. The maximum molecular weights obtained using this catalyst were $M_n = 6200$ and $M_w = 10{,}000$ Da. The principal termination reaction was the hydrolysis of the imines by the water formed in the reaction.

Acknowledgments

This research was funded by the Natural Sciences and Engineering Research Council of Canada. We thank Antisar R. Hlil for the MALDI-TOF MS spectra and Nadim Saadeh for the ESI MS spectra.

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