

Synthesis of luminescent nitrobenzene oligomers by aluminum chloride catalyzed dehydration of nitrobenzene



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This paper is dedicated to Malcolm Chisholm on the occasion of his 70th birthday; a mentor who taught us to look beyond the product to the mechanistic and structural chemistry responsible for its existence and properties.

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ABSTRACT

Under solvothermal reaction conditions, nitrobenzene is heated in the presence of aluminum chloride to yield a luminescent and paramagnetic low molecular weight polymeric material along with $\text{AlCl}_3 \cdot (\text{H}_2\text{O})_6$. MALDI mass spectral analysis demonstrates that the repeat unit consists of the biphenyl moiety ($-\text{ONC}_6\text{H}_3-\text{ONC}_6\text{H}_4-$). Four distinct fractions are isolated based on differential solubility characteristics. The primary differentiating features of these fractions appear to be their considerably different conjugation and branching characteristics. A radical mechanism, consistent with the formation of Wheland intermediates is proposed to account for the observed mass spec, IR, UV-Vis, EPR and size exclusion chromatographic data. Luminescence spectroscopy data is also provided demonstrating the white light emission exhibited by these polymers.

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1. Introduction

We and others have been interested in exploring the reactivity of Cu(I)Cl towards olefins, aromatics and carbonyls in the presence of strong Lewis acids such as AlCl_3 and ZrCl_4 [1–5]. Under such conditions, the d^{10} copper center reacts in a non-classical fashion acting as a σ -acid, bonding through its low-lying $4s/4p$ LUMO, as opposed to acting as a π -base with bonding through its $3d$ HOMO. It has already been demonstrated that benzene [4], and the more electron donating toluene [6], form stable adducts with CuAlCl_4 . We were curious to understand whether or not such non-classical Cu -aromatic bonding could also be observed for the electron deficient nitrobenzene. As demonstrated in this work, nitrobenzene does not form an adduct with the copper(I). Instead an oxygen of the nitro-group preferentially interacts with the aluminum which, in turn, initializes a dehydro-polymerization of the nitro-aromatic.

A search of the literature finds that a nitrobenzene/aluminum chloride adduct is known and has been crystallographically characterized [7]. In that compound, $(\text{C}_6\text{H}_5\text{NO}_2)\text{AlCl}_3$, an oxygen

from the nitro group is coordinated directly to the aluminum. There are additional reports of a two equivalent adduct phase, however, that compound has never been reliably isolated and characterized [8]. An early report notes an explosive reactivity of aluminum chloride and nitrobenzene, suggesting that a chlorinated nitrobenzene polymeric tar is the resultant product [9]. Under reaction conditions examined here no explosions occurred.

We find relatively few literature reports of the polymerization of nitrobenzene. Polymerization to yield a proposed nitro-substituted triarylamine is reported to be catalyzed by a cupric ferrocyanide gel [10]. Cavitation [11], and plasma [12] excitation induced polymerization of nitrobenzene are also reported. Nitration of polyanilines has successfully yielded better characterized nitroaromatic polymers that contain a polyphenylene backbone [13,14]. However with increasing interest in electronic modification of conjugated polymers for conducting and light emission applications, there is clearly value in developing such materials. The nitroaromatic polymers reported here exhibit broad emission across the visible spectrum and thus may be interesting candidates for organic light-emitting materials.

Here, we describe the synthesis of oligomers/polymers of nitrobenzene catalyzed by AlCl_3 under solvothermal reaction conditions. Three primary fractions are identified; readily differentiated

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by their color and solubility. The materials are characterized by, elemental and thermo gravimetric analysis, mass spectrometry, size exclusion chromatography, EPR, IR, UV–Vis and luminescence spectroscopy. A reaction mechanism proceeding through a Wheland intermediate, with AlCl_3 extracting water from the nitrobenzene is proposed, that accounts for conjugated and non-conjugated linkage of monomeric units. The extent of aromatic conjugation is proposed to account for the observed color and luminescence of the polymer fractions.

2. Results and discussion

2.1. Synthesis and purification

In an attempt to grow crystalline adducts of nitroaromatics with CuAlCl_4 , solvothermal reactions were employed since the CuAlCl_4 was not completely soluble in nitrobenzene at room temperature. CuAlCl_4 and dried nitrobenzene were placed into a thick walled (2 mm) fused silica tube under a N_2 atmosphere. The sample in the reaction tube was then frozen in liquid N_2 , evacuated, and sealed using a torch such that the reaction vessel was filled less than 50%. (*Caution: filling a solvothermal reaction vessel greater than 80% is dangerous and can lead to explosion upon heating. Even with lower fill volumes appropriate shielding should be in place around any solvothermal reaction as a precaution in the event of vessel rupture.*) Heating the reaction mixture at 180°C in an oven for 50 h yielded a blue gel-like material with a few colorless single crystals dispersed throughout. Upon further characterization based on independent reactions of nitrobenzene with CuCl and AlCl_3 , respectively, it was determined that CuCl was unnecessary for the reaction, and that the dark blue color was not a result of oxidized copper.

Upon addition of AlCl_3 , nitrobenzene's pale yellow color changes to a brighter yellow. Monitoring the progress of this reaction we observed that the bright yellow solution began to darken to a brownish color after about 30 min at 180°C . The reaction mixture had turned a deep red after 2 h, and a dark blue color was observed within 24 h. After about 50 h the reaction was cooled to room temperature at 5 deg/min with the product being a dark blue gel along with a few colorless crystals. As previously stated, the MSDS and literature reports indicate the combination of AlCl_3 and nitrobenzene is explosive at elevated temperatures [9]. However, those reports do not indicate inert reaction conditions were employed. Though precaution was taken, in over twenty reactions we have had no explosion. We presume that the closed system and inert atmosphere of the solvothermal reaction preclude explosion. Instead these reaction conditions induce dehydro-polymerization. Analogous reactions with nitrotoluene as the solvent/reactant resulted in the formation of a similar, dark blue polymer, and reaction with nitromethane resulted in the formation of a colorless solid product. The products of the nitrotoluene and nitromethane reactions have not yet been significantly characterized.

To obtain a sufficient quantity of product from the polymerization of nitrobenzene for characterization studies, the reaction was scaled up using a Teflon lined stainless steel autoclave. Anhydrous AlCl_3 and dried nitrobenzene were combined and sealed in the autoclave in a nitrogen filled glove box and reacted at 180°C for 50 h. The product gel is not air sensitive and can be handled on the bench-top. After drying the gel under vacuum or by evaporation in a hood to remove the unreacted nitrobenzene, the resulting isolated product from reactions of a 6:1 nitrobenzene: AlCl_3 mixture was consistent with about 25% of the nitrobenzene being converted to the solid. No significant efforts to optimize the yield of this reaction have yet been pursued.

Elemental analysis (EA) and thermal gravimetric analysis (TGA) of the polymeric products indicate the presence of inorganic component(s), however, the mass spectra described below, showed no evidence of the inorganic aluminum or chloride. The EA of the dried blue fraction exhibits an elemental distribution of 29.2% C, 3.0% H, 5.5% N and 18.5% O, whereas that material subsequently washed with water exhibits an elemental distribution of 49.7% C, 2.1% H and 8.4% N. These are consistent with the empirical formula $\text{C}_{12}\text{H}_7\text{N}_2\text{O}_2$, the primary ion observed in the mass spectrum of all fractions, along with an equimolar amount of AlCl_3 and 2/3 of an equivalent of $[\text{Al}(\text{OH})_2]_2\text{Cl}_3$ for the former (EA Calc: 28.5% C, 3.0% H, 5.5%N, 19.0% O), and 2/3 of an equivalent of AlCl_3 for the latter water washed fraction (EA Calc: 48.0% C, 2.4% H, 9.3%N). TGA analysis of the bulk polymer is shown in Fig. 1a. Under a flow of nitrogen, the sample lost 48% of its mass by heating to 500°C . After 10 min at 500°C , the purge gas was changed to O_2 to combust the organic component of the polymer leaving an ash of 30.9% of the original sample. This is consistent with both AlCl_3 and $[\text{Al}(\text{OH})_2]_2\text{Cl}_3$ inorganic components decomposing to $\text{Al}(\text{OH})_2\text{Cl}$ (Calc. 31.8%) with loss of HCl , analogous to a previous report of the thermal decomposition of $[\text{Al}(\text{OH})_2]_2\text{Cl}_3$ that indicates $\text{Al}(\text{OH})_2\text{Cl}$ is the primary ash when heated to 500°C [15,16]. To remove all inorganic by-products from the material, the water washed material was subsequently washed with 6 M HCl . TGA measurement of the acid washed bulk, shown in Fig. 1b, demonstrates a 33% weight loss upon heating to 500°C under a nitrogen stream. But when the purge gas was shifted to oxygen after 15 min at 500°C essentially no residue remained (2.5%) after thermal oxidation confirming the removal of the inorganic component.

While acid washing successfully separates residual inorganic components from the nitrobenzene polymer, further solubility studies indicate that the material can be separated into at least four fractions. Attempts to dissolve the material in acetone in order to obtain NMR spectra resulted in the extraction of a red/purple solution from the dark blue solid. No meaningful NMR

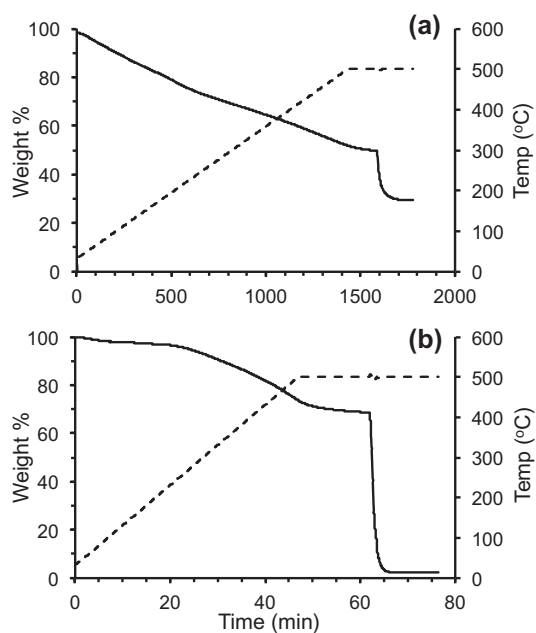


Fig. 1. TGA analysis of the (a) as synthesized and (b) acid-washed nitrobenzene polymer. Weight% is represented as the solid line and left axis, temperature as the dashed line and right axis. After 10 (a) or 15 (b) min at 500°C , the purge gas was switched from N_2 to O_2 to combust organic material. 30.9 weight% inorganic ash remained in the as synthesized sample, whereas 2.5 weight% ash remained in the acid-washed sample.

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