POLYANILINE VIA SCHIFF BASE CHEMISTRY

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ABSTRACT

We have attempted a total unambiguous synthesis of polyaniline via Schiff base chemistry and suggest this synthetic approach will allow wide flexibility in preparing polyaniline (PANI) derivatives.

In an attempt to establish a correlation between the base unit to quinone imine ratio and conductivity, three polymers were synthesized. Polymers, B_2Q -2HCl and BQ-2HCl, show conductivities of 4 X 10⁻⁴ and 4 X 10⁻⁸ S respectively. The reflectance spectra are discussed. A sample of PANI prepared in our labs gave a conductivity of 2 ($\Omega \cdot cm$)⁻¹ and is discussed for comparison. Only an impure sample of B_3Q -2HCl was available.

A rationale for the maximum conductivity of the B_3Q -2HCl system and declining conductivity of the B_2Q -2HCl and BQ-2HCl systems may be offered on the basis of simple coulombic repulsion of charged centers.

INTRODUCTION

In the continuing quest for an environmentally stable conducting polymer, much recent work has been done on the protonated form of polyaniline (PANI)¹. At least two major problems exist in current research efforts: an unambiguous structure proof and an improvement of physical properties, ie., processability.

This conductive polymer in its various forms has been widely studied; however, because of its rather limited solubility, its structure remains one of conjecture 2 .

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We have undertaken a direct and unambiguous approach to the synthesis of PANI and variations thereof via standard Schiff base chemistry and suggest this approach will allow wide flexibility in preparing polyaniline derivatives.

In the current literature, it is suggested that the conducting form of polyaniline consists of a repetition of three p-phenylene units interconnected by a quinone imine unit³. This polymer subunit is herein designated B_3^0 .



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When protonated it is suggested this becomes the highly resonance stabilized conducting form of PANI: B_2Q -2HCl.



8-301-2HC1

In this study, we also synthesized the lower homologs of the conductive form of PANI; namely the BQ and the B_2Q polymers in their protonated forms and compared their conductivities with that of PANI.

SYNTHESIS AND RESULTS

Preparation of the 1:1 base to quinone (BQ) condensation product was a straightforward literature preparation 4 which was repeated in our laboratory.

The resultant blue-black powder was stirred in 1N aq. HCl for 24 hours, filtered, thoroughly dried <u>in vacuo</u>, pressed into a pellet and gave a conductivity of 4 X 10⁻⁸ S. See also Figure 1a.



Preparation of the B_2Q polymer proceeded via condensation of 4,4-diaminodiphenylamine sulfate with 1,4-cyclohexanedione in DMSO. Oxidation of the resultant polymer was attempted with various oxidants but best results were obtained using dichlorodicyanoquinone (DDQ) in DMSO. The precipitate was rigorously washed with methanol, ethanol, and acetone prior to suspension in 1N HCl and stirred over the weekend. The dried powder in pellet form gave a conductivity of 7 X 10⁻⁴ S. See also Figure 1b.



Synthesis of the B_3Q condensate proved much more difficult in that it was necessary to synthesize the base trimer itself prior to its reaction with 1,4-cyclohexanedione. Two approaches were attempted in the synthesis of the triphenylenetetraamine precursor. A double nucleophilic aromatic substitution reaction of p-phenylenediamine with two equivalents of p-fluoronitrobenzene in water at elevated temperatures; a process which gave the desired product of dubious guality and in poor yield.

$$H = N + \frac{1}{4} + \frac{1}{4} + 2 F + \frac{1}{4} + 2 F + \frac{1}{200 \text{ eC}}$$

$$O_2 N - \bigvee_{H} \bigvee_{H} \bigvee_{H} \bigvee_{H} NO_2 - \frac{Fe}{HC1} > H - N - \bigvee_{H} \bigvee_{H} \bigvee_{H} \bigvee_{H} - \bigvee_{H} \bigvee_$$

A much better approach was the single nucleophilic aromatic substitution of commercially available 4,4-diaminodiphenylamine sulfate and p-fluoronitrobenzene in refluxing DMF which yielded the p-nitrotriphenylenetriamine product in good yield as a deep red-brown solid. The purification of this material is difficult and a method is still being sought to produce it uncontaminated with starting material.

$$H - N - \bigvee_{H} - \bigvee_{H} - \bigvee_{H} + H_{2}SO_{4} + F - \bigvee_{H} - NO_{2} - NO_{2} - NO_{2}$$

$$H - N - \bigvee_{H} -$$

Reduction of the crude nitro derivative with iron and HCl in ethanol proceeded smoothly and the triphenyltetraamine product was precipitated as its air stable sulfate salt from anhydrous ether.



In the final step of this synthesis the triphenylenetetraamine sulfate salt was reacted with an equimolar amount of 1,4-cyclohexanedione in dry nitrogen swept m-cresol at 110° C. overnight. During this time a tan precipitate formed. After cooling to room temperature, ether was added and the precipitate filtered and washed thoroughly with ethanol. The resultant polymer was suspended in 1N HCl and allowed to react with 4 equivalents of ammonium persulfate for 56 hours, filtered, and dried in vacuo. The pressed pellet conductivity of the deep green powder was 6 X 10^{-2} S. See Figure 1c. The FTIR spectrum was identical to published spectra for PANI^{5,6}. See Figure 2.



A sample of PANI prepared in our labs via the ammonium persulfate oxidation of aniline gave a conductivity of 2 S. The slightly lower conductivity value we obtained for our sample of PANI synthesized via the Schiff base condensation is no doubt due to contamination of the triphenylenetetraamine starting material with some of its diphenylenetriamine precursor thus producing a B_3Q polymer contaminated by some B_2Q material. Work is in progress to correct this deficiency.



FIGURE 2.



A rationale for the maximized conductivity of the $B_3Q-2HCl$ system and the declining conductivities of the $B_2Q-1HCl$ and BQ-2HCl systems may be offered on the basis of simple coulombic repulsion of the charged centers.



In B_3Q -2HCl there are alternate charged centers whereas in the other cases of necessity there are charged centers adjacent to each other, thus increasing the conduction band gap.

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