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The azanes: A class of material incorporating nano/micro self-assembled hollow spheres obtained by aqueous oxidative polymerization of aniline

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Abstract

The nature of the product of the "conventional" aqueous oxidative polymerization of aniline by ammonium peroxydisulfate and HCl is extremely sensitive to the pH of the polymerization system. This is observed when the concentrations of reagents are sufficiently dilute (at a pH of 3–4) to isolate the first-formed product of the reaction which we believe is a member of the class of azanes, polymeric or oligomeric species containing a N—N backbone in which each N atom is forming three covalent single bonds. The brown solid isolated has been characterized by its elemental analysis, UV–vis, FTIR, and ^{1}H NMR spectra. We believe, in the simplest case, it may be an organic-substituted hexa-azane. It is completely different in every way from any known form of "polyaniline", in any oxidation state, of any degree of protonation. It is isolated as hollow microspheres (diameter, ~1.5–6 μm), which have an essentially identical SEM appearance to hollow microspheres previously ascribed to conventional polyaniline. As the pH of the reactant system falls during the polymerization, polyaniline in its conventional forms begins to be formed; however, especially if the pH is held constant by a buffer solution, the pure azane can be isolated. We believe the azanes open up a new field of self-assembled nano/micro particles of very considerable potential applicability to the emerging field of nanoscience.

Keywords: Aniline; Azanes; Self-assembly; Nano/micro hollow spheres

1. Introduction

In view of the increasing activity in nano/micro science/technology during the past few years, it is of interest to re-examine and build upon earlier observations of organic polymers, which were of much of interest in the past primarily because of their unusual electronic properties [1,2]. The sensitivity of the type of nano/micro morphology on the synthetic method employed including variation in pH [3] opens up a vast unexplored potential field, which has not as yet been tapped. For example, chemical and/or electrochemical synthesis of an electroactive polymer, such as polyaniline, alone yields a wide variety of materials depending on the pH of the system [4] and morphologies ranging from the first reported synthesis of nanofibers of polyaniline [5] to the dependency of the nucleation step and resulting morphology on the nature of the counter ion [6], to the chemical synthesis of polypyrrole which can yield a matte-like film [7,8] or nanospheres (diameter 25–125 nm) [7,8]. Indeed it is not unlikely that the nucleation step may well dictate the subsequent nanoscience, and may be dependent on the presence of dust and related nucleation-inducing suspended particulate matter [9], as for example, in "seeding" to produce nanofibers of polyaniline, polypyrrole [10]. The present study reported here involves only one small step involving particles of self-assembled nano/micro spheres derived from the oxidative polymerization of aniline. We believe the spheres are composed of members of the class of polyazanes, little studied material containing –N–N– single bonds in the polymer backbone [11].

During the past 20 years much excellent research has been carried out world-wide on "polyaniline"—its chemical and electrochemical synthesis, characterization and electronic, magnetic, optical, and related properties [12]. Polyaniline and its derivatives have attained considerable world-wide importance principally because of their unique set of electronic properties. From the present study it seems highly likely that in the future new products of the oxidative polymerization of aniline

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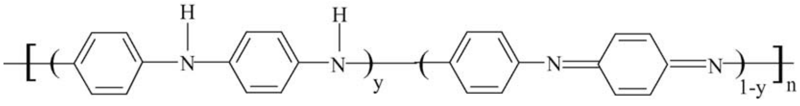
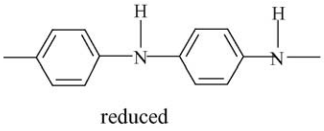
may claim considerable importance not because of their electronic properties but because of their contribution to the field of nano/micro science and potential future technology.

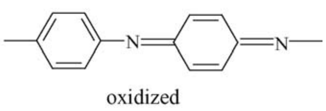
To understand the importance of aniline in the field of azanes it is highly desirable to appreciate some of the key aspects of the “polyanilines”—the most highly studied material obtained by the oxidative polymerization of aniline. The base forms of the polyanilines contain only N–C and C–C (covalent) aromatic bonds as shown below.

The base form of polyaniline, which has the generalized composition [12]



consists of alternating reduced and oxidized repeated units



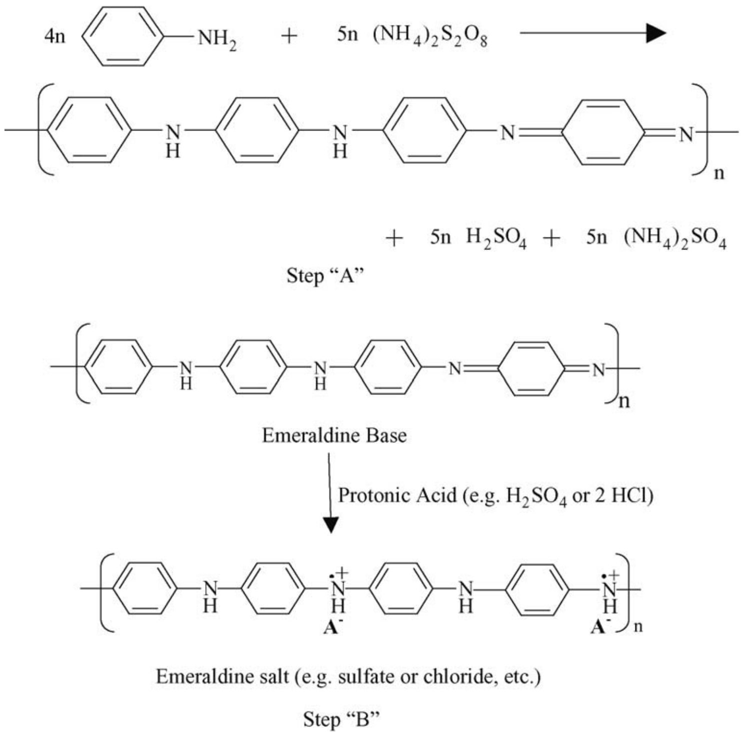


The terms “leucoemeraldine”, “emeraldine” and “pernigraniline” refer to the different oxidation states of the polymer where $y = 1$, 0.5, and 0, respectively, either in the base form, for example, emeraldine base, or in the protonated “salt” form, for example, emeraldine hydrochloride. In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depending on its oxidation state and on the pH of the aqueous acid. Complete protonation of the imine nitrogen atoms in the emeraldine base by aqueous HCl, for example, results in the formation of the hydrochloride “salt” accompanied by an increase in conductivity of about 10^{10} [13,14].

Polyaniline of the above emeraldine type of structure is easily synthesized by the chemical (or electrochemical) oxidative polymerization of aniline in aqueous solution, the most common method, based with many modifications on our original method [5,15], employs ammonium peroxydisulfate as the oxidizing agent.

Sulfuric acid is produced during the reaction as shown by Scheme 1 below and hence the polymerization system becomes more acidic during the course of the polymerization [12,16].

For simplicity the process in Scheme 1 is divided into two hypothetical parts—Part A: polymerization; Part B: protonation by the H_2SO_4 produced or by any other acid that has been added to the polymerization system. It should be noted that the quantity of acid formed during the polymerization step significantly exceeds the amount of acid required in the protonation step—hence, a net increase in acid concentration during poly-



Scheme 1. Release of acid during polymerization of aniline by $(NH_4)_2S_2O_8$ (A^- is an anion of appropriate charge).