

The Formation of Oligoaniline Microspheres in Alkaline Media

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(Received 11 June 2012; published online 25 August 2012)

Aniline oligomers are generally believed to be responsible for the self-assembly that guides the growth of polyaniline nanostructures. The oxidations of aniline with ammonium peroxydisulfate, which are started and finished above pH 2.5, produce aniline oligomers only. Under alkaline conditions, oligoaniline microspheres are formed as the dominating morphology. They will be potentially useful in applications that do not require conductivity, such as in electrorheology, corrosion protection, as ionic conductors or catalyst supports. Aniline oligomers prepared at alkaline conditions as microspheres have been studied by UV-Vis, infrared and Raman spectroscopies in the combination with optical and electron microscopic techniques.

Keywords: Conducting polymer, Polyaniline, Aniline oligomers, Infrared spectra, Raman spectra.

PACS numbers: 78.30.Am, 78.30.Fs

1. INTRODUCTION

Conducting polymers, such as polyaniline, are unique among polymers in their ability to produce a variety of nanostructures [1,2]. When oxidation of aniline with ammonium peroxydisulfate was started under alkaline conditions, microspheres of several micrometers in diameter were produced [3]. The oligomers are generated at the early stages of aniline oxidation at higher pH. Only at lower pH < 2, polymer is produced in addition to oligomers originated earlier (Fig. 1). The molecular structure of aniline oligomers prepared under alkaline conditions is discussed in the present study along with their supramolecular microspherical morphology in relation to polyaniline by using UV-Vis, infrared and Raman spectroscopies. Such oligomers have potentially useful redox and ion-exchange properties.

2. EXPERIMENTAL

2.1 Synthesis

Aniline (0.2 M; Aldrich) was oxidized with ammonium peroxydisulfate (0.2 M; Lach-Ner, Czech Republic) in the aqueous solutions of 0.1, 0.2, 0.5, and 1 M ammonium hydroxide or in water at room temperature. Solutions of a monomer and an oxidant in water were mixed at room temperature to start the oxidation. The reaction mixture was quickly poured over the silicon or gold supports placed in Petri dishes. After the end of polymerization, the windows were removed from the mixture, rinsed in water and dried in air. The solids were collected on a filter after 2 h, rinsed with water, dried in air and then over the silica gel in a desiccator. A part of products deposited on silicon windows or in solid state was converted to bases by overnight immersion in 1 M ammonium hydroxide, followed by separation and drying (Fig. 2).

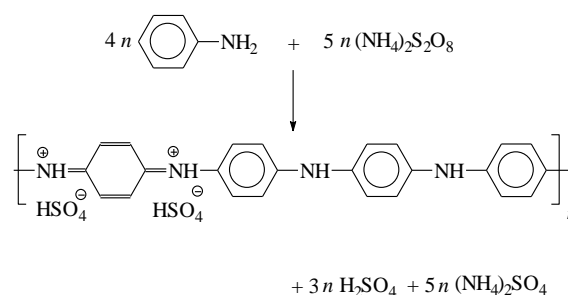


Fig. 1 – The oxidation of aniline with peroxydisulfate yields polyaniline hydrogen sulfate (or sulfate). Sulfuric acid and ammonium sulfate are by-products

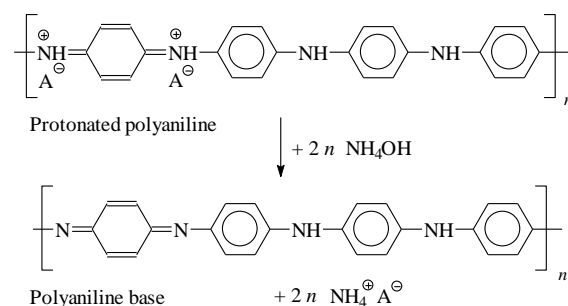


Fig. 2 – Polyaniline (emeraldine) salt is deprotonated in alkaline medium to polyaniline (emeraldine) base. A⁻ is an arbitrary anion, e.g., hydrogen sulfate

2.2 Characterization

The course of exothermic polymerization was monitored with a digital thermometer, and the acidity changes were recorded with a pH-meter. Scanning electron microscopy has been used to study the morphology of the samples. UV-Vis spectra of the oxidation products dissolved in *N*-methylpyrrolidone were recorded with a Lambda 20 spectrometer (Perkin Elmer, UK). Infrared spectra in the range of 400 – 4000 cm⁻¹ were recorded at 64 scans per spectrum at 2 cm⁻¹ resolution

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using a Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. Raman spectra excited in the visible range with a HeNe 633 nm laser were collected on a Renishaw inVia Reflex Raman microspectrometer. A research-grade Leica DM LM Microscope equipped with a 50x Olympus objective has been used for optical microscopy and to focus the laser beam on the sample placed on an X-Y motorized sample stage. The scattered light was analyzed by the spectrograph with a holographic grating ($1800 \text{ lines mm}^{-1}$). A Peltier-cooled CCD detector ($578 \times 385 \text{ pixels}$) registered the dispersed light.

3. RESULTS AND DISCUSSION

3.1 Morphology

The oxidation of aniline in solutions of sulfuric acid leads to the granular morphology. Polyaniline prepared in the presence of weak acid or in water is produced mainly as nanotubes accompanied by a globular precipitate [1]. When the oxidation of aniline is carried out at alkaline conditions, microspheres are a typical product [3]. The morphology of the final films deposited on the silicon windows is shown in Fig. 3.

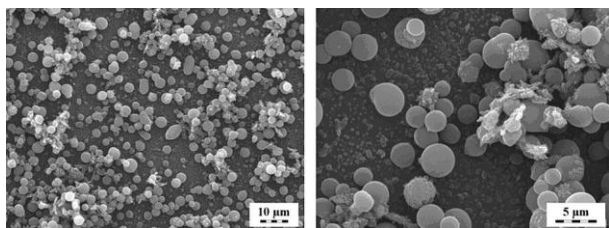


Fig. 3 – Scanning electron micrographs of the films obtained by the oxidation of aniline with ammonium peroxydisulfate in 1 M ammonium hydroxide on silicon support

Under alkaline conditions, aniline is present in the neutral form which has a limited solubility in water. For that reason, aniline microdroplets appear in the reaction mixture, and by oxidation at the aniline–water interface, oligomeric microspheres are produced [3].

3.2 Kinetics

The oxidation of aniline started in an alkaline medium is fast and exothermic and, consequently, the temperature increases during the reaction (Fig. 4a). Two hydrogen atoms are abstracted from each aniline molecule during their oxidative coupling, and they are released as protons; thus, the pH of the reaction mixture decreases (Fig. 4b) [3].

The oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate gradually generates 0.2 M sulfuric acid. The acid is partly neutralized by aniline or reaction intermediates containing primary amino groups, and especially with ammonium hydroxide which is the strongest base in the system (Fig. 4b). At its 0.1 M concentration, ammonium hydroxide becomes completely neutralized, and the pH drops to acidic values. The formation of polyaniline thus becomes possible in the advanced stages of oxidation. The 0.5 and 1 M ammonia was sufficient to maintain the reaction alkaline throughout the oxidation (Fig. 4b).

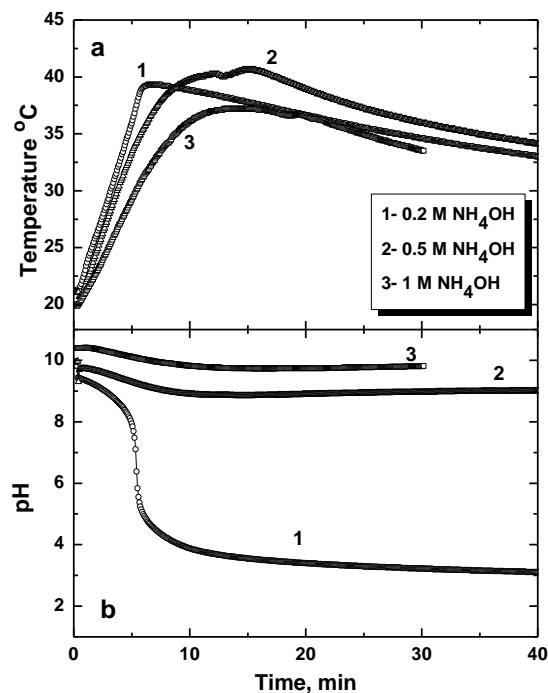


Fig. 4 – Temperature (a) and pH (b) profiles during the oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate in 0.2, 0.5, and 1.0 M ammonium hydroxide.

3.3 UV-Vis Spectra

UV-Vis spectrum of aniline oligomers prepared in 0.5 and 1 M ammonium hydroxide displays a local maximum at 348 nm and a characteristic long tail extending to longer wavelengths (Fig. 5). The absorption band of polyaniline (emeraldine) base having the maximum above 600 nm is absent in aniline oligomers.

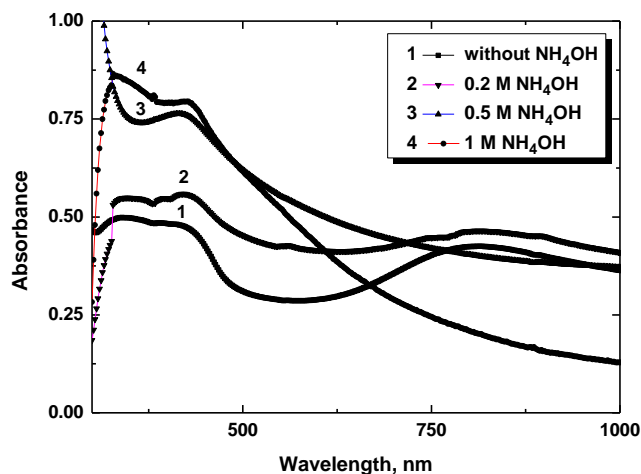


Fig. 5 – UV-Vis spectra of the powders obtained by the oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate in 0.2, 0.5, and 1.0 M ammonium hydroxide and in water

The absorption maximum appears in the case of oxidation in 0.2 M ammonium hydroxide and in water, when the pH drops to acidic values and the formation of polyaniline (emeraldine) becomes possible (Fig. 4b).

3.4 FTIR Spectra

In the infrared spectra of samples prepared in 0.2, 0.5, and 1 M ammonium hydroxide, the bands due to quinonoid and benzenoid ring-stretching vibrations are situated at 1581 and 1503 cm^{-1} . A shoulder observed at about 1630 cm^{-1} corresponds most probably to N–H scissoring vibrations of aromatic amines or to the presence of phenazine units. The contribution of benzoquinones is possible. The sharp band at 1445 cm^{-1} is attributed to the skeletal C–C stretching vibrations of the substituted aromatic ring [3]. The broad band in the 1300 – 1230 cm^{-1} region indicates the presence of the C–N stretching vibration of a primary aromatic amine, which confirms the oligomeric nature of the oxidation products. The band at about 1035 cm^{-1} is assigned to the symmetric stretching vibrations in sulfonic groups linked by covalent bonds to the benzene ring. A prominent band at 824 cm^{-1} in the substitution region 900 – 650 cm^{-1} in the spectrum of the PANI base is due to the C–H out-of-plane bending vibrations of dominating *para*-coupled constitutional units. The bands at 746 and 691 cm^{-1} correspond to the C–H out-of-plane bending and out-of-plane ring deformations of a mono-substituted phenylene ring, respectively [3,4].

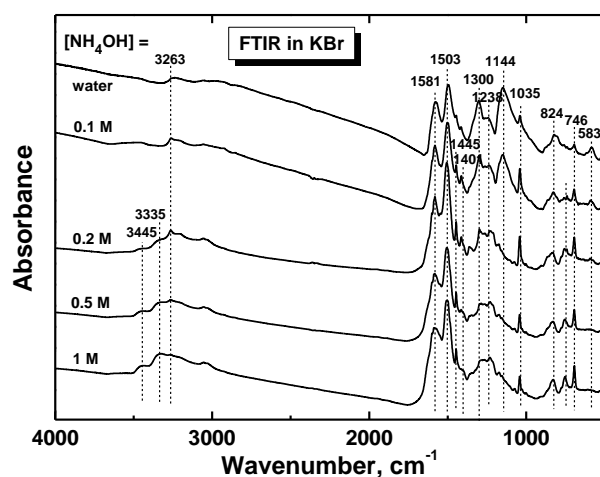


Fig. 6 – Infrared spectra of the powders obtained by the oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate in 0.1, 0.2, 0.5, and 1 M ammonium hydroxide and in water

The spectrum of the oligomers displays bands at 3440 and 3324 cm^{-1} of asymmetric and symmetric free N–H stretching vibrations, supporting the contribution of the N–H scissoring vibration. The peaks at 3266 and 3195 cm^{-1} corresponding to the hydrogen-bonded N–H vibrations are detected in the spectrum of aniline oligomers. They are connected with hydrogen bonding of N–H groups with sulfonic or carbonyl groups [3].

The infrared spectra of samples prepared in 0.1 M ammonium hydroxide and in water display a broad absorption band at wavenumbers higher than 2000 cm^{-1} , an increased absorption of the bands at 1300 and 1238 cm^{-1} , and a broad band centred at 1144 cm^{-1} , which are characteristic of the conducting protonated form of polyaniline [4].

3.5 Raman Spectra of the Final Films

The Raman spectra of the products of *in-situ* oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate in 0.1, 0.2, 0.5, and 1 M ammonium hydroxide and in water deposited *on silicon supports* are shown in Fig. 7. Raman spectra of oligoanilines, precipitated at low acidity in the first stages of the oxidative polymerization of aniline in water have been interpreted in [5]. Vibrations originating from oxidized quinonoid units are in resonance with 633 nm laser excitation wavelengths and a strong fluorescence appears. The strong peak of the C=C stretching vibration in the quinonoid ring is observed at 1594 cm^{-1} . The C–C vibration in quinonoid ring of pernigraniline- and pseudomauveine base-like units can possibly contribute to the band at 1564 cm^{-1} . The band at 1480 cm^{-1} corresponds to the C=N stretching vibration in quinonoid units. A sharp band at 1378 cm^{-1} is due to the C–N⁺ ring-stretching vibrations of substituted *N*-phenylphenazines together with the peak at 1412 cm^{-1} . The band observed at 1367 cm^{-1} corresponds to the C–N⁺ stretching vibration of the developing still localized polaronic structures in the samples prepared in 0.2, 0.1 M ammonium hydroxide and in water [5].

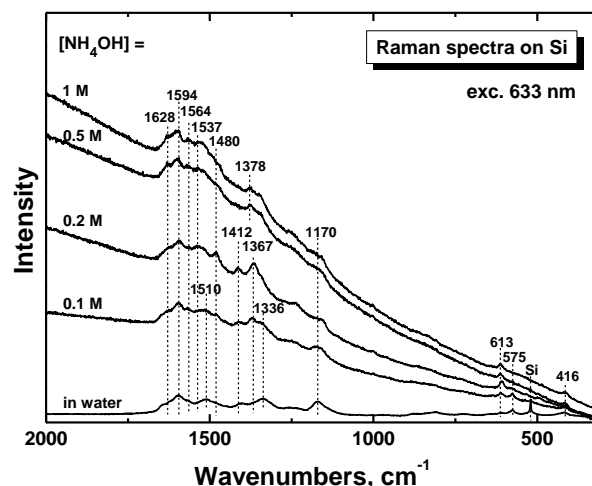


Fig. 7 – Raman spectra of the products of *in-situ* oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate in 0.1, 0.2, 0.5, and 1 M ammonium hydroxide and in water on silicon supports

The band at 1170 cm^{-1} corresponds to the C–H bending vibration of the semi-quinonoid rings. The band which can be connected with the ring sulfonation appeared at 613 cm^{-1} in all spectra. The band at 576 cm^{-1} can be attributed to phenoxazine-type units. The phenazine spectrum contains a band at 416 cm^{-1} . We have observed the band at 416 cm^{-1} in the Raman spectra of all samples. The Raman spectrum of the sample prepared in water is very close to the spectrum of emeraldine [5].

The Raman spectra of the products of *in-situ* oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate in 0.1, 0.2, 0.5, and 1 M ammonium hydroxide and in water deposited *on gold supports* are shown in Fig. 8. The spectra of the samples prepared in more alkaline media in 0.2, 0.5, and 1 M on gold support display a strong fluorescence and the peaks at 1632, 1594,

1568, 1530, 1378, 608, and 575 cm^{-1} , which are very close to the bands observed in the case of silicon support.

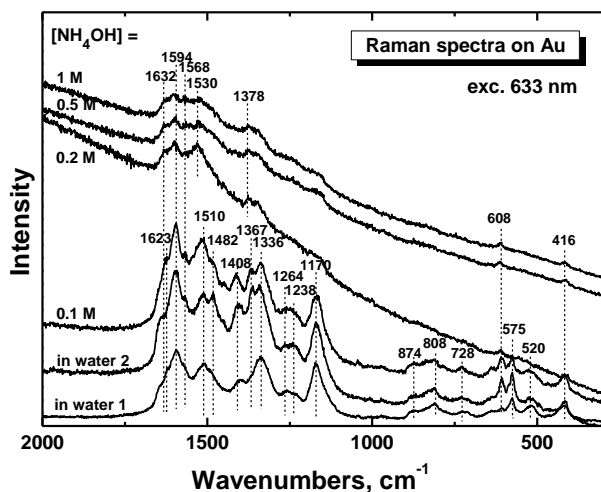


Fig. 8 – Raman spectra of the products of *in-situ* oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate in 0.1, 0.2, 0.5, and 1 M ammonium hydroxide and in water on gold supports

The spectra of the samples prepared in 0.1 M ammonium hydroxide or in water, when the pH drops to acidic values, on gold support strongly differs from the spectra of samples deposited on silicon windows (Fig. 8). The intense fluorescence no more appears and the intensity of the spectra is strongly enhanced. The spectra exhibit the main bands corresponding to the protonated emeraldine form of polyaniline films deposited on gold support in [6]. The weak but sharp peak at 1623 cm^{-1} assigned to the C–C stretching of the benzenoid ring, and the strong band at 1594 cm^{-1} linked to C=C stretching vibration in the quinonoid ring are observed in the spectra. The strong band at 1336 cm^{-1} provides the information on the C–N⁺ vibration of delocalized polaronic structures. The C–N stretching vibrations and benzene-ring deformations are connected with the bands at 1264 and 1238 cm^{-1} . The band at 1170 cm^{-1} corresponds to the C–H bending vibration of the semi-quinonoid rings in cation-radical segments. The maximum at 874 cm^{-1} is linked to C–N–C wag and/or benzene-ring deformation in the polaronic or bipolaronic form of emeraldine salt. The band at 808 cm^{-1} corresponds to benzene ring deformations and the peak at 725 cm^{-1} may be assigned to the amine deformation reported for the bipolaronic form of emeraldine salt.

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In comparison with the spectrum of the sample prepared in water on silicon window the intensity of Raman spectra of the samples prepared in 0.1 M and also in water strongly increased (see Fig. 8), and some new peaks appeared: a shoulder at 1632 cm^{-1} (belongs to phenazine-like structures or N–H deformations), the peak at 1568 cm^{-1} (N–H deformation vibrations associated with semi-quinonoid structures), 1482 cm^{-1} (C=N stretching vibration in quinonoid units), 1408 cm^{-1} (vibrations of phenazine-like structures), 1367 cm^{-1} (C–N⁺ vibration of delocalized polaronic structures), 608 cm^{-1} (vibrations of the ring sulfonation or sulfate anion), and 575 cm^{-1} (vibrations of phenoxazine-type and cross-linked units). The bands at 520 and 416 cm^{-1} correspond to out-of-plane ring-deformations. All these peaks belong to the first oligoanilines, precipitated at low acidity in the first stages of the oxidative polymerization of aniline which have been interpreted in [5]. The Raman spectra of the films deposited on gold support exhibit the surface enhanced Raman scattering (SERS) of the molecules or constitutional units which are present on the interface of the oxidation products and the metallic surface. These products correspond to the short oligomers constituting the first molecular layer adsorbed on gold support.

4. CONCLUSIONS

Oligoaniline microspheres were prepared by oxidation of 0.2 M aniline with 0.2 M ammonium peroxydisulfate in 0.1, 0.2, 0.5, and 1 M ammonium hydroxide and in water. Their formation on silicon and gold supports has been studied by infrared and Raman spectroscopies in combination with optical and electron microscopic techniques, and UV–Vis spectroscopy.

Raman spectra of the products prepared in 0.1 M ammonium hydroxide or in water when the pH drops to acidic values are strongly enhanced in case of gold support. The oligomers are expected to be adsorbed due to the interaction between the molecule and an optically-excited electron at the gold surface, and SERS of the first products of oxidation is observed. The protonation plays a crucial role in this process.

ACKNOWLEDGEMENTS

The authors thank the Grant Agency of the Academy of Sciences of the Czech Republic (IAA100500902) and the Czech Grant Agency (P205/12/0911 and 108/11/P763).

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