The Flower-Like Hierarchical Architectures Assembled from Aniline Oligomers

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The flower-like hierarchical architectures assembled from aniline oligomers by a template-free method are reported. They are important because of their close relation to a conducting polymer, polyaniline. Their formation process is ascribed to the self-assembly of oligoanilines under non-covalent interactions, such as hydrogen bonding, hydrophobic forces, and π–π stacking. The model of directional growth is offered to explain the formation of petal-like objects and, subsequently, flowers. In order to investigate the chemical structure of the oligomers, a series of characterizations have been carried out, such as UV–visible, Fourier-transform infrared and Raman spectroscopies. Based on the results of characterization methods, a formation mechanism of the aniline oligomers and their self-assembly are proposed.

Keywords: Self-assembly, Aniline, Oligomers, Morphology, Flowers, Polyaniline.

1. INTRODUCTION

Polyaniline (PANI), the most studied conducting polymer, has been investigated not only because of its electrical conductivity but also for its ability to respond to various external stimuli by a change in electrical, optical or chemical properties. The variety of morphologies PANI adopts [1], such as nanofibers and nanotubes, is of additional interest. Aniline oligomers, formed during the first stage of aniline oxidation, have been proposed to guide the growth of conducting PANI nanorods and nanotubes during the second, polymerization stage. The analysis of aniline oligomers is thus crucial for the understanding of the evolution of PANI nano/microstructure. Self-assembly of aniline oligomers into supramolecular morphologies has recently attracted considerable attention. Yang et al. [2] have demonstrated the preparation of flower-like morphologies during the oxidation of aniline in the presence of *p*-toluenesulfonic acid in ethanol–water mixtures. The present study attempts to follow this synthetic procedure, and to extend the characterization of oxidation products. The formulation of the general concept of oligomers self-assembly is the main goal.

2. EXPERIMENTAL

2.1 Synthesis

Aniline monomer (Aldrich) was distilled under reduced pressure before use. Ammonium peroxydisulfate (APS), *p*-toluenesulfonic acid monohydrate (*p*-TSA) and ethanol (Aldrich) were of analytical grade and have been used without further purification. Aniline oligomers were prepared as follows: 100 mL of ethanol (40 vol.%)–water was used as a reaction medium. 2.23 mmol (0.425 g) *p*-TSA and 12.5 mmol (1.15 mL) aniline were dissolved in 50 mL of ethanol–water mixture at first. Then, 2.5 mmol APS (0.571 g) was dissolved also in 50 mL. Both solutions were precooled in ice-bath (≈ 0 ºC) for 30 min and then mixed to initiate the oxidation. APS to aniline mole ratio thus was 0.2, i.e. much lower than the stoichiometric ratio 1.25 currently used in the preparation of PANI. The reaction was allowed to proceed without agitation for 1 h under such conditions. Primary solids (product I) produced at the early stage of oxidation were separated after 1 h by filtration, and residual reactants in the filtrate were left to react in a refrigerator (≈ 4 °C) for 24 h, and then the precipitate (product II) was again collected. Both samples were rinsed with distilled water and dried in air overnight and then in a desiccator over silica gel.

2.2 Characterization

The morphologies of the resulting products were characterized by scanning electron microscope JEOL 6400 (Japan). Fourier-transform infrared (FTIR) spectra in the range 400–4000 cm^{-1} were recorded using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. UV–visible spectra in *N*-methypyrrolidone were recorded with a spectrometer Lambda 20 (Perkin Elmer, UK). In some cases, also the spectra of oligomeric films deposited on glass during the oxidation of aniline were also recorded.

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3. RESULTS AND DISCUSSION

3.1 Morphology

Early-stage oxidation product I consists of large quantity of regular and uniform flower-like oligoaniline hierarchical architectures which are composed of leaf-like or petal-like sheets (Fig. 1A). The average length of a single nanosheet is estimated to be 2.5 μm, the width is 1.5 μm, and the thickness is about 100 nm. In addition, monodisperse nanospheres with an average diameter of 300 nm are also observed at closer inspection and they produce a bed on which flowers grow. When the early oxidation products have been separated from the reaction mixture and oxidation was left to proceed, the morphology of solids became granular (Fig. 1B).
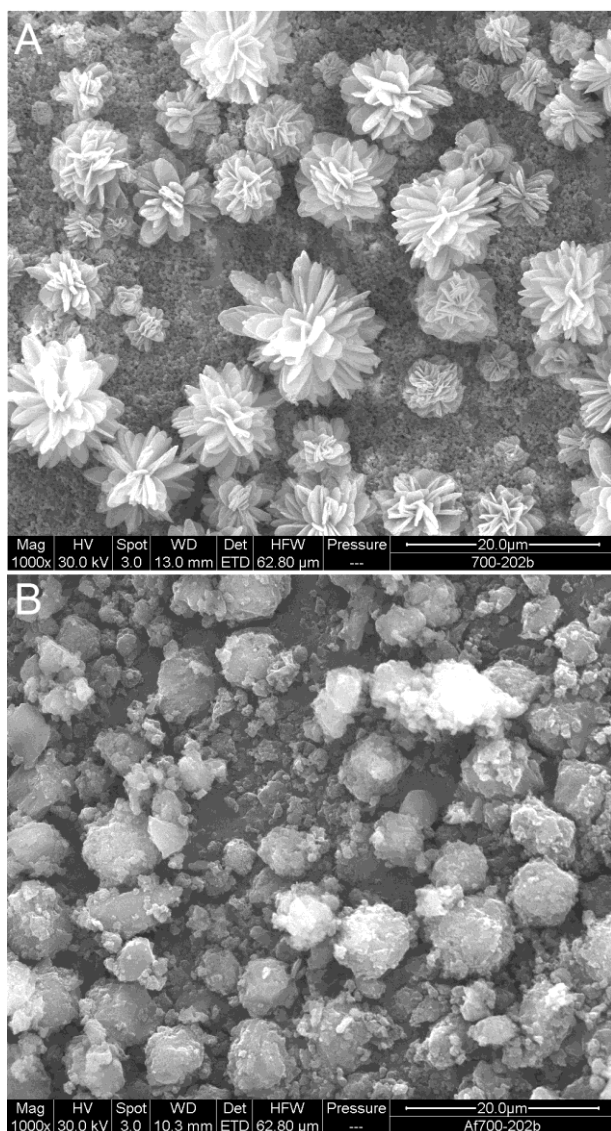

Fig. 1 – Scanning-electron micrographs of flower-like oligoaniline hierarchical architectures collected (A) after 1 h (product I) and (B) after 24 h (product II) of aniline oxidation

We therefore assume that aniline oligomers in the former case are structurally uniform and able to crystallize to defined morphologies, while in the latter the molecular polydispersity restricts such organization. This hypothesis is tested below.

3.2 Chemistry of Aniline Oxidation

It is generally agreed that the oxidation of aniline at neutral or mildly acidic media leads to an aniline dimer, *p*-semidine (= *p*-aminodiphenylamine, *N*-phenyl-*p*-phe-nylenediamine) as a dominating species (Fig. 2). The formation of *o*-semidine has also been considered in the literature. Other aniline dimers, such as benzidine, azobenzene, diphenyline, or phenazine, are other possible oxidation products. In the next step, aniline molecule can be added to form an aniline trimer and, similarly, a tetramer. An aniline tetramer can be produced directly by the dimerization of semidine (Fig. 2). Many authors assume the exclusive formation of linear chains by *para*-linking of aniline molecules, others admit also the intramolecular cyclization to phenazine heterocycles. Higher aniline oligomers can subsequently be produced.
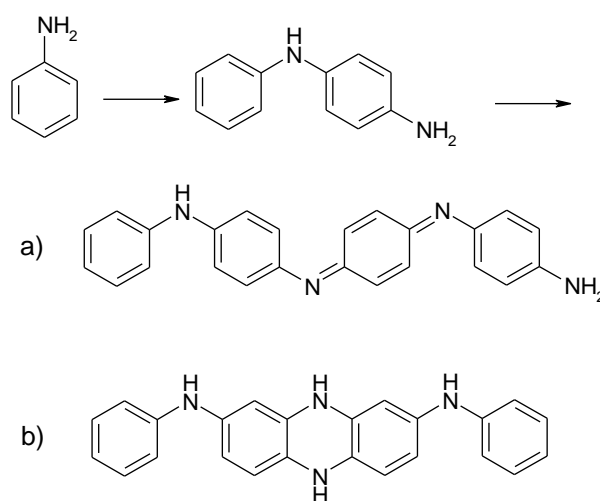
Fig. 2 – The oxidation of aniline yields an aniline dimer, *p*-semidine, and later tetramers, such as (a) linear form or (b) phenazine-containing structure

3.3 FTIR Spectra

Infrared spectra of the product I and product II are very close to each other (spectra *a* and *b* in Fig. 3). Only small differences may be found in the product II which suffers of small oxidative degradation during long-time oxidation. They are practically identical with the spectra of the aniline oligomers obtained at the early stages of the oxidation of aniline with APS in aqueous medium (spectrum *c* in Fig. 3) [3]. An orchid-like morphology for [*p*-TSA]/[aniline] mole ratio of 1/5 [2] displaying the same FTIR spectra have also been reported. In that case, the prepared aniline oligomeric products were incorrectly called as "polyaniline".

3.4 UV–Visible Spectra

The proof that we are dealing aniline oligomers and not PANI is provided by UV–visible spectra that display the absorption bands located at 276 nm and 370 nm (Fig. 4). Both of these two peaks confirm the formation of aniline oligomers. Weak n–π* shoulder at ~ 520 nm corresponds in the product II may be as-

signed to phenazine-like structures. Absorption bands at longer wavelength typical of PANI, such as 630 nm for blue PANI base and 810 nm for green PANI salt, are missing. In this case, results from UV–visible spectra are in agreement with our conclusion that the products are composed of oligomers.

3.5 The Structure of Aniline Oligomers

The detailed molecular structure of aniline oligomers is still open to discussion and seems to depend on reaction condition in general and on acidity in particular [4]. Phenazine-like constitutional units (Fig. 5a) seem to dominate in the product prepared under acidic conditions, while the incorporation of oxygen-containing units (Fig. 5b,c) seems to be the realm of neutral and alkaline oxidation media.
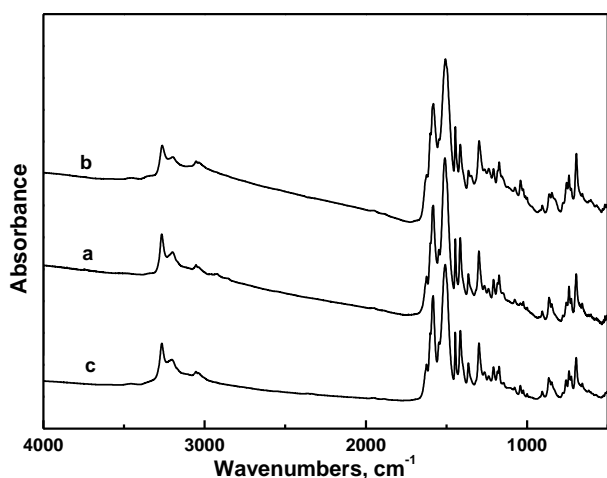

Fig. 3 – FTIR spectra of (a) early-stage product I and (b) product II compared with (c) the sample collected at the beginning of aniline oxidation in water [3]
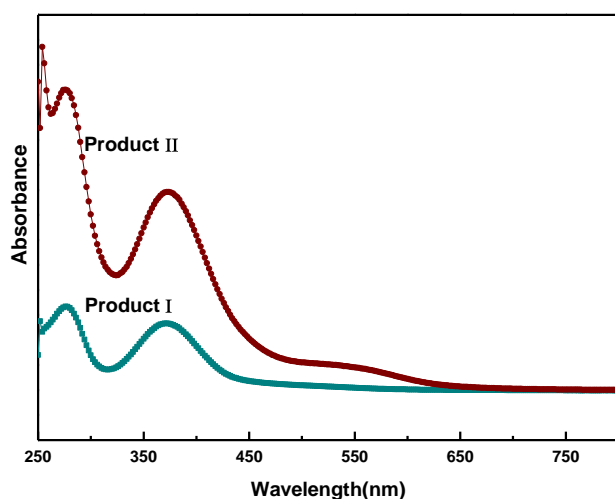

Fig. 4 – The comparison of UV–visible spectra of early-stage oxidation product I and product II

Sulfur has been identified in all aniline oligomers and may be a result of ring-substitution reactions (Fig. 5d, e). Sulfur may be also be present as a part of sulfate counter-ions that balance the eventual positively charged nitrogen atoms.
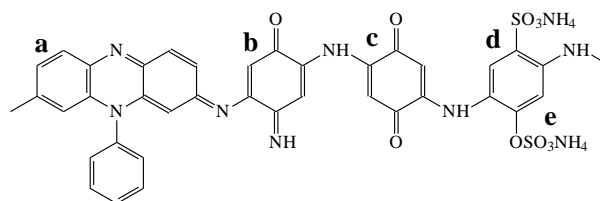

Fig. 5 – The structure of aniline oligomers should consider the presence of (a) phenazine-like heterocycles, (b) quinoneiminoid and (c) quinonoid constitutional units, as well as (d) sulfonate or (e) sulfate groups [4]

3.6 The Model of Directional Growth

In order to explain the leaf-like morphology constituting petals in flowers, the following scenario is offered. Let us approximate an aniline oligomer molecule with a box (Fig. 6). The fronts of the box, marked by red, blue and white colors, reflect their different ability to interact with each other and with the molecules of constituting the environment. Intermolecular interactions between the fronts are represented by, e.g., π–π stacking, hydrogen bonding, ionic bonding, hydrophobic contacts, etc. If the interaction between blue fronts is preferred on the basis of particular interactions, their association will tend to produce extended aggregates (Fig. 6). When the proliferation in the perpendicular direction controlled by aggregation of white fronts proceeds as well, but more slowly, and contact between red fronts are restricted, the leaf-like (petal-like) morphology will start to develop.
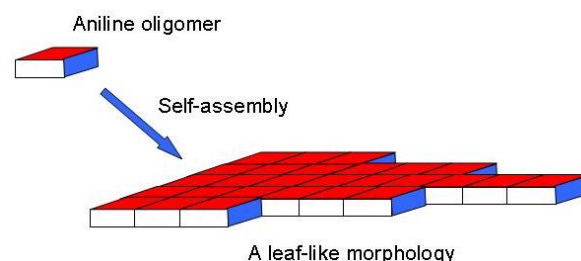

Fig. 6 – Directional self-assembly of aniline oligomers into a leaf (petal)-like object

The primary leaf-like structure can produce more complex hierarchical objects, such as four-arm stars or micromats [3] composed by perpendicularly crossed leaves, or hierarchical flower-like morphology represented by many such objects (Fig. 1A). The interactions between the individual parts of oligomer molecules can be affected by the environment. For example, when the intermolecular contacts are based on hydrophobic interactions, the addition of an organic solvent to aqueous medium will reduce them. Consequently, other contacts may become important and more preferred, and the oligomer molecules will arrange in different manner, thus producing another type of morphology. Similarly, the ionic interactions may be reduced by introduction of electrolytes, the increase in acidity may promote them as primary amine groups become protonated, etc. We propose that the morphology of aniline oligomers is thus controlled by the balance of molecular interactions between oligomer molecules themselves and molecules that form the environment.

4. CONCLUSIONS

Aniline oligomers have been produced by the oxidation of aniline in mildly acidic media. The oxidation products are composed especially of aniline tetramers to hexamers. Due to good structural homogeneity at the early stages of oxidation, i.e. at low reaction conversion, they are crystalline. Aniline oligomers are insoluble and crystallize to produce micrometre-sized flower-like objects. The model of directional growth is offered to explain the formation of leaf-like morphology. It assumes that aniline oligomer molecules self-assemble preferentially in various directions, the preference being dependent on the molecular structure and the balance between interactions, such as π–π stacking, hydrogen bonding, ionic bonding, hydrophobic interactions, etc. The oxidations products obtained at higher conversions are molecularly polydisperse and, consequently, they do not form well-defined supramolecular assemblies.

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