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Spectroscopic study of the highly homogeneous polyaniline film formation on gold support

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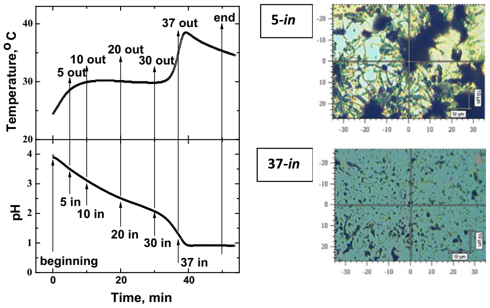
HIGHLIGHTS

- Experimental evidence of highly homogeneous polyaniline film formation.
- Spectroscopic monitoring of the self-assembly and film formation.
- Unique series of experiments consisting in the immersion of gold supports in the reaction mixture.
- The mechanism of the film formation and surface interaction of aniline oligomers with gold support.

GRAPHICAL ABSTRACT



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ABSTRACT

The oxidation of aniline with ammonium peroxydisulfate in the aqueous solution of acetic acid has two subsequent phases: the oxidation of the neutral aniline molecules at low acidity, which was followed by the oxidation of the anilinium cations after the acidity became higher. The final polyaniline film deposited on immersed surfaces is usually contaminated with semi-crystalline oligomers which precipitated during induction period from the reaction medium. To obtain a homogeneous film, which is important in the fabrication of many molecular electronic devices, we have studied the course of aniline oxidation in a view of new experimental evidence. In the unique series of experiments, the silicon or gold supports have been immersed in the reaction mixture at crucial stages of oxidation reaction, and the deposits at the end of the reaction were analyzed. The growth of a highly homogenous film on the gold-coated glass substrate immersed in the reaction mixture at the end of the polymerization period has been observed. The molecular structure of the products was monitored with UV–visible, infrared, and Raman spectroscopies. The possible mechanism of the film formation and the molecular mechanism of the surface interaction of chemisorbed aniline oligomers with gold support are proposed.

1. Introduction

Depending on the acidity conditions during the chemical oxidation of aniline with ammonium peroxydisulfate, different types of products can be identified: globular polyaniline (PANI) is formed when the oxidation of aniline is started in acidic media, PANI nanotubes in mildly acidic or neutral media and oligoaniline microspheres in alkaline media [1–8]. The pH decreases during the reaction due to the formation of sulfuric acid from peroxydisulfate, the changes in acidity define three aniline oxidation regimes. The oxidation of aniline started at mildly acidic conditions goes through all of them [9–11]. In the first exothermic step, the aniline dimers, semidines, are the first oxidation products [12–14]. Induction period follows; the formation of aniline trimers and tetramers containing a *N*-phenylphenazine moiety, so-called

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nucleates, was proposed at this step [9]. When the acidity is sufficiently high, pH < 2.5, nucleates were supposed to convert to initiation centers that start the subsequent exothermic propagation of PANI chains [9–11].

The model of nucleates assembly was offered to explain various supramolecular structures produced by PANI [9]. It was proposed that the hydrophobic nucleates randomly aggregate in the aqueous phase or become organized to form one-dimensional stacks stabilized by π–π interactions during the second phase of aniline oxidation. The random agglomeration of nucleates gives rise to PANI globules and regular self-assembly into stacks subsequently leads to PANI nanofibers. Nucleates were supposed to adsorb and self-assemble along various interfaces giving subsequently rise to additional conducting polymer morphologies. The adsorption of nucleates at solid surfaces immersed in the reaction mixture leads to PANI films or coatings of various substrates. This model was based on the *ex-situ* characterization of the reaction intermediates during the course of oxidation of aniline [12,15]. The reaction was terminated at various times and the intermediates deposited *in situ* on silicon supports have been studied. The presence of oligomers produced at the first stage of the oxidation was found to be necessary for the later occurrence of PANI nanotubes [9]. On the other hand, the presence of short oligomers during film deposition leads to the formation of inhomogeneous films.

The model of nucleates assumes that they are hydrophobic and adsorb at available interfaces. The PANI chains grow from pre-organized nucleates, which convert to initiation centers at sufficiently high acidity, at pH < 2.5. One of the consequences is, that it is not expected the film will grow on a support inserted in the reaction mixture in this last period. To test this hypothesis, we provided a new modified experiment:

(1) As nanotubes are typically produced in mildly acidic aqueous media, when the induction period is long enough, the course of aniline oxidation with ammonium peroxydisulfate in acetic acid aqueous solutions has been investigated [1,2,5].
(2) To test an interaction of nucleates with the surface, beside the silicon also gold supports have been used in the new experiment.
(3) The most original modification of previous experiment [5,15], in which reaction intermediates produced on various supports were removed from the reaction mixture, where they have been placed from the beginning of the reaction after various times specified by the course of oxidation, in the new second complementary experiment various supports were immersed in the reaction media at crucial times from the beginning of the reaction and left there till the end of the polymerization.

We have concentrated our attention on the decisive moments of the reaction (Fig. 1): (1) the end of the fast exothermic *oligomerization of neutral aniline* molecules, (2) the end of the intermediate *induction period*, and (3) the time during the fast *polymerization of anilinium cations*. One of the most surprising results of the newly designed experiment was the growth of the polyaniline films of high quality on the gold substrates introduced into the reaction mixture at the end of the reaction.

Preparation of thin PANI films of high quality is important in the fabrication of many molecular electronic devices [11]. The fabrication of thin PANI film at the air/liquid interface during aniline oxidation using the falling pH approach in the presence of hydrochloric acid has been recently reported in [16,17]. Highly crystalline PANI film obtained after the standard synthesis, upon simple drying of the reaction suspension, has been recently described [18]. In the present report, conditions for the formation of highly homogeneous polyaniline film on the basis of several spectroscopic methods, including UV–visible, infrared and Raman spectra excited with 514, 633, and 785 nm lasers, have been analyzed. The possible formation mechanism of the film on silicon and gold surfaces, and the nature of the interaction of PANI film with various supports was proposed.

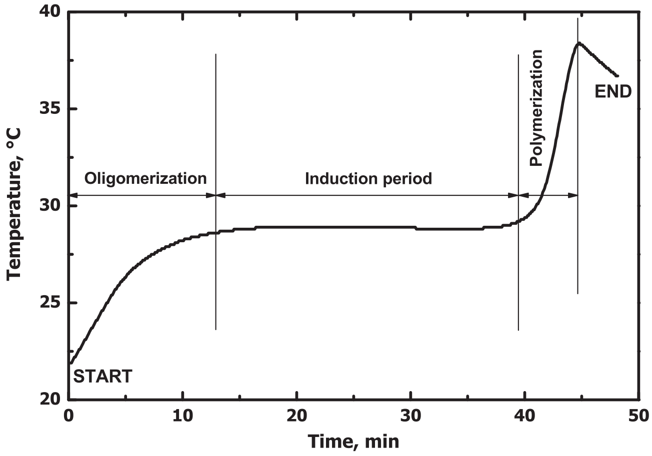

Fig. 1. Temperature profile of aniline oxidation under mildly acidic conditions: oligomerization of neutral aniline molecules is followed by induction period and then by fast exothermic polymerization of anilinium cations. Adapted from Ref. [2].

2. Experimental section

2.1. Sample preparation

Aniline (0.2 M) was oxidized with ammonium peroxydisulfate (0.25 M) in aqueous solution of acetic acid (0.4 M) [1,2,9]. Solutions of a monomer and an oxidant in water were mixed at room temperature to start the polymerization. Depending on the type of spectroscopic characterization, three types of supports have been used: silicon, quartz glass, and gold-coated glass.

The oxidation products were deposited on various supports in two different experiments. (1) In the so called "*out*-analysis", the supports were placed in the reaction media at the beginning of the reaction and removed after time intervals, selected on the basis of the course of polymerization [1,2,5,19]: 5, 10, 20, 30 and 37 min (the samples are denoted as 5-*out*, 10-*out*, 20-*out*, 30-*out* and 37-*out*). (2) In the so-called "*in*-analysis", the supports were introduced into the reaction media at the same times listed above and left there till the end of the polymerization (the samples are denoted as 5-*in*, 10-*in*, 20-*in*, 30-*in* and 37-*in*). The sample introduced at the beginning and left there till the end is labeled as 0-*in*. In all cases, the supports were subsequently rinsed with water, and dried in air.

2.2. Spectroscopic characterization

UV–visible spectra of the original films *in-situ* polymerized on quartz-glass supports 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 using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. The spectra of the thin films on silicon substrate were measured in transmission mode. Raman spectra excited with an argon-ion 514 nm, HeNe 633 nm, and near-infrared diode 785 nm lasers were collected on a Renishaw inVia Reflex Raman spectrometer. A research-grade Leica DM LM microscope with an objective magnification ×50