

Polymerization of aniline in ice

Elena N. Konyushenko*, Jaroslav Stejskal, Miroslava Trchová,
Natalia V. Blinova, Petr Holler

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

ARTICLE INFO

Article history:

Received 13 June 2007

Received in revised form 21 April 2008

Accepted 20 June 2008

Available online 12 August 2008

Keywords:

Aniline

Polyaniline

Conducting polymer

Redox reaction

Nanotube

Nanowire

Electron transfer

Ice

Solid-state polymerization

ABSTRACT

It was observed that the oxidative polymerization of aniline proceeded well not only in the liquid mixtures at 20 °C or –5 °C but also in ice at –24 °C. The oxidative polymerization took place in the solutions of strong acid (0.1 M sulfuric acid) or weak acid (0.4 M acetic acid). It is proposed that the initially generated polyaniline participates in the further redox process, leading to new polyaniline formation. The molecules of the monomer (aniline) and oxidant (peroxydisulfate) thus react by transferring electrons through the conducting polyaniline, without the need to be in direct contact. The polymerization in the liquid phase or in the solid frozen state changes the morphology of the polyaniline. Polyaniline nanogranules or nanotubes are produced in the liquid state, while thin nanowires of 20 nm diameter connecting the submicrometre polyaniline particles have been observed when the polymerization took place in ice.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Polyaniline (PANI), the most common conducting polymer [1,2], is typically prepared by the oxidation of aniline in an acidic aqueous medium [3]. It has been observed that the polymerization carried out at reduced temperature yielded PANI with a higher molecular weight [4] and higher degree of crystallinity [5], although the improvement of conductivity was marginal [5]. The higher molecular weight is of benefit when the mechanical properties of PANI are important, e.g., when the solutions of PANI base in *N*-methylpyrrolidone are used to cast PANI membranes [6] or are spun to produce PANI fibres [7] or nanofibres [8].

The freezing point of the reaction mixture containing 0.2 M aniline hydrochloride and 0.25 M ammonium peroxydisulfate is –12 °C. In order to prevent freezing at lower temperatures in similar experiments, copious amounts of lithium chloride have been added into reaction mixture [4,9–14], which stayed liquid even at –40 °C. It has been observed, however, that the polymerization of aniline proceeds well, and to a high yield, even at –50 °C when the reaction mixture was frozen [5,15]. Although the polymerizations of monomers in crystals or solid monomer solutions are well known,

and have been reviewed [16], this behavior in the present system of aniline oxidation is still rather unexpected.

Besides the polymerization in ice, solid-state reactions involving PANI have been described in the literature. The protonation reactions between PANI base and solid organic acids have been established [7,17–22]. The same approach, the mixing of the components in the solid state, has been successfully used for the preparation of PANI complexes with fullerene [23]. The mechanochemical polymerization of aniline, an oxidation of aniline in the solid state, has only recently been reported [24–26]. In this case, the aniline monomer and an oxidant produce a polymer as a result of the joint mechanical grinding of the components. One would expect that, when the oxidation of aniline takes place in the solid state, like in the frozen medium, the process would be slow, if feasible at all, due to the restricted diffusion of reactants in the solids and the reduced probability of their contact. Yet, for reasons discussed below, the polymerization takes place easily even under such conditions.

Kocherginsky et al. [6,27] have demonstrated that the molecule of an oxidant and a reductant separated by a PANI membrane may undergo a redox reaction. This was achieved without any direct contact between the reacting molecules, by simply transporting an electron from the oxidant to the reductant through conducting PANI; the redox reaction between iron(III) chloride and ascorbic acid has been used as an example. This concept has been extended to the preparation of PANI by the oxidation of aniline

* Corresponding author.

E-mail address: elenak@imc.cas.cz (E.N. Konyushenko).

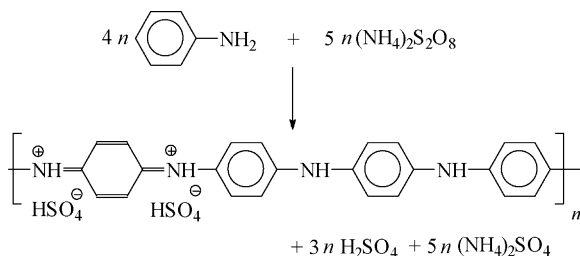


Fig. 1. Aniline is oxidized with ammonium peroxydisulfate to PANI hydrogen sulfate. Sulfuric acid and ammonium sulfate are by-products.

with ammonium peroxydisulfate, solutions of the two components being separated by a PANI membrane [28]. It is elaborated in the present study to provide an understanding of the oxidative polymerization of aniline, which is a typical redox reaction, in a frozen aqueous reaction medium, *i.e.*, in ice.

2. Experimental

2.1. Oxidation of aniline

For the polymerizations in liquid state, aniline (0.2 M) was oxidized with ammonium peroxydisulfate (0.25 M) in 0.1 M sulfuric acid or in 0.4 M acetic acid (Fig. 1). Solutions of a monomer and an oxidant were mixed at 20 °C or after pre-cooling at 0 °C or –5 °C to start the oxidation.

For the polymerizations in ice, the solutions of reactants were mixed at –5 °C in polyethylene containers and immediately cooled to –190 °C in liquid nitrogen. The solid frozen samples were then placed into a freezer at –24 °C. After 20 days, the green solid content was melted and the PANI was isolated on a filter, rinsed with the corresponding acid, and acetone, and dried in air.

When estimating the rate of oxidation, the containers were removed after a specified time, their frozen content was transferred to excess of 1 M ammonium hydroxide, and left to melt there. The combination of the alkaline medium and the accompanying dilution stopped the conversion of aniline to PANI in 0.4 M acetic acid. The precipitated oxidation product was quickly collected on the filter, and thus separated from the residual oxidant and aniline, and dried. For polymerizations in 0.1 M sulfuric acid this approach was not successful, because the ice, if white after removal from the freezer, turned green before it completely melted.

2.2. Characterization

Scanning electron micrographs were taken with a JEOL 6400 microscope (Japan). Molecular-weight distributions (MWD) were assessed by gel-permeation chromatography using a 8 mm × 600 mm PLMixedB column (Polymer Laboratories, UK) operating with *N*-methylpyrrolidone and calibrated with polystyrene standards, with spectrophotometric detection. The samples were dissolved in *N*-methylpyrrolidone containing 0.025 g cm⁻³ triethanolamine for deprotonation of PANI, and 0.005 g cm⁻³ lithium bromide to prevent aggregation. Infrared spectra were recorded with a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. The spectra of the samples dispersed in potassium bromide were recorded in the transmission mode and corrected for the presence of carbon dioxide and water vapour in the optical path. The conductivity was measured with a four-point van der Pauw method, on pellets compressed at 700 MPa with a manual hydraulic press, using as the SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter with a 2000 SCAN 10-channel scanner card.

3. Results

3.1. The course of aniline polymerization: liquid aqueous medium and ice

The fact that the oxidation of aniline in an acidic aqueous medium yields PANI and the conversion of aniline to PANI is practically complete has been well established [2,3]. It is, however, implicitly assumed that the reaction medium is liquid. Nevertheless, it has been demonstrated that, even if the medium becomes frozen, the polymerization of aniline takes place [5]. The polymerization of 0.2 M aniline with 0.25 M ammonium peroxydisulfate (Fig. 1) at 20 °C takes 15 min to complete in 0.1 M sulfuric acid or 40 min in 0.4 M acetic acid [29]. At –24 °C in ice, the process takes place in the solid state, the reaction is slower, yet still feasible. The originally white ice becomes gradually dark green. In 0.4 M acetic acid, the full conversion of aniline to PANI was achieved after 4 h (Fig. 2). The similar oxidation of aniline in 0.1 M sulfuric acid was faster. When trying to estimate the rate of oxidation in this case, we have not been able to stop efficiently this process during the melting of ice.

3.2. Morphology

Polyaniline is known to exhibit a variety of supramolecular morphologies, such as thin films on various substrates [30,31], colloidal particles [32–36], nanotubes [29,37–40], nanowires [41–43], sometimes referred to as nanofibres [44,45], and hollow PANI microspheres [37,45,46]. It is likely that PANI morphology, based on the self-assembly of PANI chains, will also be affected by the

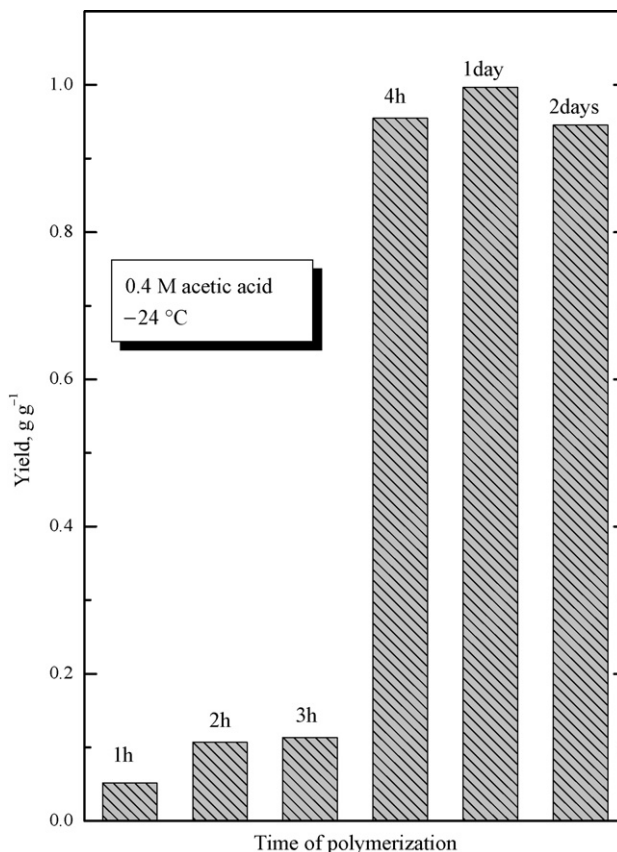


Fig. 2. The time-dependence of the yield of PANI (a polymer obtained from 0.2 M aniline monomer) in the oxidation of 0.2 M aniline with 0.25 M ammonium peroxydisulfate in 0.4 M acetic acid in ice at –24 °C.

Download English Version:

<https://daneshyari.com/en/article/1443774>

Download Persian Version:

<https://daneshyari.com/article/1443774>

[Daneshyari.com](https://daneshyari.com)