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Synthesis of Polyaniline in Carbonated Water in the Form of Nanofibre

Abstract

The polymerisation of aniline was conducted in carbonated water in the presence of ammonium persulphate (APS) as an oxidizer. Infrared (IR) absorption spectroscopy was used to confirm the chemical structure of polyaniline (PANI) thus prepared in carbonated water, and scanning electron microscopy (SEM) confirmed that PANI possessed nanofibrous morphology. It is believed that the environment provided by carbonated water for the polymerisation of aniline resulted in the formation of nano-fibres. The electrical conductivity of PANIs thus prepared was in the range of $10^{-4}$ S/m.

Key words: carbon dioxide, electrical conductivity, nanofibre, polyaniline, synthesis polymerisation.

Introduction

Since polyacetylene films prepared with doping [1] display a high electrical conductivity comparable to that of metals [2], electrically conductive polymers have attracted considerable attention from both basic research and industrial perspectives. Polyaniline (PANI) is one of the most promising conductive polymers. The synthesis of PANI is different from the more general methods used for the production of other conductive polymers [3, 4]. Aromatic polymers, such as polythiophenes and polyphenylene vinylenes are synthesised in an organic solvent with the aid of metal complex catalysts. On the other hand, PANI is generally synthesised in water with an oxidiser, such as ammonium persulphate (APS), in an ambient atmosphere.

Conductive polymers have found use in various industrial applications, for example as buffer layers in organic electroluminescent devices, organic electrodes, and conductors. Progress has also been made in the preparation and processing of polymer textiles [5 - 8]. In the synthesis of PANI by chemical polymerisation, the ionisation of the N-position of the monomer with H$_2$SO$_4$ or HCl in water is required in the first step. APS is subsequently added to the reaction solution to initiate polymerisation. Recently, the application of CO$_2$ for the preparation of plastic materials has been reported. CO$_2$ has good solubility in water, and the resultant carbonated water is acidic. In the field of conductive polymer research, the electrochemical preparation of PANI in supercritical carbonated water has been performed [9, 10].

In the present study, saturated carbonated water was employed instead of H$_2$SO$_4$ for the preparation of PANI. The optical absorption, infrared (IR) absorption spectroscopy, electron spin resonance (ESR) and electrical conductivity of the PANI prepared in carbonated water were examined.

Experimental

Materials

The aniline (Tokyo Kasei, TCI) and water were distilled prior to use. Ammonium persulphate (APS; Kanto Chemicals, Japan) was used as received. Saturated carbonated water was prepared for the present research by the injection of high pressure CO$_2$ gas into distilled water in a small stainless steel jar.

In the present study, saturated carbonated water was employed instead of H$_2$SO$_4$ for the preparation of PANI. The optical absorption, infrared (IR) absorption spectroscopy, electron spin resonance (ESR) and electrical conductivity of the PANI prepared in carbonated water were examined.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>APS, g</th>
<th>ESR results</th>
<th>Conductivity</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>g-value</td>
<td>$\Delta H_{pp}^0$, mT</td>
</tr>
<tr>
<td>PANI-1</td>
<td>1.2</td>
<td>2.00346</td>
<td>0.317</td>
</tr>
<tr>
<td>PANI-2</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI-3</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI-4</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Synthesis of polyaniline.
Synthesis

Aniline (1.0 g) was added to 100 mL of saturated carbonated water (pH = 4.66) in an Erlenmeyer flask at 278K, and then the mixture was stirred for 30 min. Carbon dioxide dissolved in water provided acidity [11] for the polymerisation of the aniline monomer. Pre-cooled solutions containing various quantities of APS (1.2 – 3.6 g, see Table 1) in carbonated water (20 mL) were then slowly added to the aniline mixtures at 278 K to initiate polymerisation (Figure 1). After 6 h, the mixture was filtered, washed with a large volume of water for 12 h at room temperature, filtered again, and then washed with a large volume of methanol for 12 h. After filtration, the PANI was dried to yield a dark emerald green powder.

The synthesis yields of the polymerisation products are summarised in Table 1 (see page 15), showing that the quantity of APS in the reaction increases the PANI yield (PANI-1 to PANI-4, Table 1).

Results and discussion

The molecular structure of the monomer and polymer (PANI) was confirmed by the IR measurements. A ν\textsubscript{NH} stretching vibration was observed for aniline at 3397 cm\(^{-1}\) in the IR absorption spectra, whereas the PANI species exhibited no absorption bands related to the ν\textsubscript{NH} stretching \textit{(Figure 2.a)}. An absorption band associated with a quinoid (Q) structure was observed at 1580 cm\(^{-1}\), and an absorption band appeared at 1510 cm\(^{-1}\) due to the benzenoid (B) structure. These absorption bands are characteristic of PANI. PANI-2, PANI-3, and PANI-4, which exhibited the same absorption bands in their respective IR spectra \textit{(Figures 2.a - 2.d)}.

UV-Vis optical absorption spectra of the polymers in NMP were also examined \textit{(Figure 3)}. The absorption band at 340 nm was assigned to the π–π* transition of the benzene ring in the main chain. The absorption band at around 630 nm was due to the polarons acting as charge carriers, which are typical optical absorption features for PANI. The absorption intensity at 630 nm increased with the quantity of APS employed as an oxidiser during the polymerisation. Since PANI-1 is a relatively short oligomer, it showed no distinct absorption band due to polarons, because of the short π-conjugation length. In this case, a small amount of APS as an oxidiser restricts polymerisation activity in the carbonated water.

Synthesised pristine PANI is in a half-protonated state, as is evident from the UV-vis absorption. All the PANI prepared in this study have charge carriers, i.e., radical cations (polarons) and dication (bipolarons), and display electrical conductivity. ESR measurements were employed to detect the presence of radicals as charge carriers in PANI, the results of which are summarised in Table 1. The line shape of the ESR signals corresponds to an almost symmetric Lorentz pattern. In the case of graphite, an asymmetric Disonian line shape is observed in the ESR measurements. However, the present ESR results indicate the intrusion of microwaves into the bulk polymer sample. The g-value for the polymers is \(\sim 2.003\). All the polymers have a constant \(\Delta H_{pp}\) (the peak-to-peak width) value of \(~0.32\) mT. The spin numbers of the polymers increase with the amount of APS employed during polymerisation, as shown in Table 1, because APS functions as a dopant for the polymers. The electrical conductivity of the PANI was examined using the four-probe method. Sample pellets were prepared for the electrical conductivity measurements by uniaxial pressing (13.7 MPa, diameter = \(10^{-4}\) m). The electrical conductivity of the polymer pellets was in the range of \(5.76\times10^{-5} - 1.37\times10^{-4}\) S/m \textit{(Table 1)}. Such conductivities of polymers prepared in carbonated water are considered to be moderate for a conductive polymer. The conductivity of PANI-1 is very low...
(<10<sup>-9</sup> S/m), because PANI-1 is an oligomer.

Scanning electron microscopy (SEM) observation revealed a nano-fibrous structure of PANI-4 (Figure 4, left). Furthermore, its doughnut-like texture consists of twisted fine nano-fibres (Figure 4, right). These results indicate that PANI nanofibres can be conveniently prepared in carbonated water.

Conclusions

PANI was prepared by oxidative polymerisation in saturated carbonated water. Although an appropriate acid condition is required for producing PANI nanofibres in general, the present results demonstrate that the mild conditions provided by carbonated water also lead to the formation of PANI nanofibres. This result is an example of the production of PANI nanofibres without the use of a strong acid, such as H<sub>2</sub>SO<sub>4</sub> or HCl.

Acknowledgment

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References


INSTITUTE OF BIOPOLYMERS AND CHEMICAL FIBRES

LABORATORY OF BIODEGRADATION

The Laboratory of Biodegradation operates within the structure of the Institute of Biopolymers and Chemical Fibres. It is a modern laboratory with a certificate of accreditation according to Standard PN-EN ISO/IEC-17025: 2005 (a quality system) bestowed by the Polish Accreditation Centre (PCA). The laboratory works at a global level and can cooperate with many institutions that produce, process and investigate polymeric materials. Thanks to its modern equipment, the Laboratory of Biodegradation can maintain cooperation with Polish and foreign research centers as well as manufacturers and be helpful in assessing the biodegradability of polymeric materials and textiles.

The Laboratory of Biodegradation assesses the susceptibility of polymeric and textile materials to biological degradation caused by microorganisms occurring in the natural environment (soil, compost and water medium). The testing of biodegradation is carried out in oxygen using innovative methods like respirometric testing with the continuous reading of the CO<sub>2</sub> delivered. The laboratory’s modern MICRO-OXYMAX RESPIROMETER is used for carrying out tests in accordance with International Standards.

The methodology of biodegradability testing has been prepared on the basis of the following standards:


The following methods are applied in the assessment of biodegradation: gel chromatography (GPC), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

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