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Polyaniline nanotubes doped with polymeric acids

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Abstract

Self-assembled polyaniline (PANI) nanotubes were prepared in the presence of three different polymeric acids as dopants, namely poly(4-styrenesulfonic acid) (PSSA), poly(acrylic acid) (PAA) and poly(methyl vinyl ether-*alt*-maleic acid) (PMVEA) by oxidative polymerization using ammonium persulfate as the oxidant. The molecular structure of polymeric acids had a significant effect on the morphology and size of the polyaniline nanotubes as determined by SEM. The PANI nanotubes were also characterized by FTIR spectroscopy and electron paramagnetic resonance spectroscopy.

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Keywords: Polyaniline; Nanotubes; Polymeric acid

1. Introduction

Polyaniline (PANI) is one of the most widely investigated conducting polymers due to its desirable electrical, electrochemical and optical properties, as well as excellent environmental stability. PANI nanostructures have recently received much attention because the high surface area of these materials is of interest for the development of actuators, drug delivery systems, field emission displays, gas sensors, and biosensors [1–3]. A number of approaches have been used to synthesize PANI nanowires and nanotubes, and in this study we have adopted the self-assembly method because of its simplicity [4].

Polymeric acids have been shown to be easily incorporated as dopants in conducting polymers during synthesis, and examples include PANI doped with poly(2-acrylamido-2-methylpropane sulfonic acid) and poly(styrenesulfonic acid) [5,6]. The large size of macromolecular dopants ensures their permanent entrapment within the conducting polymer material. The presence of such macromolecules within conducting polymer nanostructures can bring further novel properties to the materials, as well as additional functionalities for building specific recognition sites or catalytic sites.

Different acids, including organic and inorganic acids, have been used as dopants in the preparation of PANI nanotubes by the self-assembly method [4]. We have recently shown that when poly(methyl vinyl ether-*alt*-maleic acid) (PMVEA) is used as a dopant the external diameter of the nanotubes can be controlled, to some extent, by the weight ratio of PMVEA to aniline in the reaction solution [7]. It was also found that PANI nanotubes doped with PMVEA can be used for covalent attachment of oligonucleotides through the carboxylic acid functionality and can act as DNA sensing elements [8].

Here we report the synthesis of self-assembled PANI nanotubes doped with a range of polymeric acids: poly(4-styrenesulfonic acid) (PSSA), poly(acrylic acid) (PAA) and PMVEA. The obtained nanostructured materials were characterized by means of scanning electron microscopy, transmission electron microscopy, FTIR spectroscopy and electron paramagnetic resonance.

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2. Experimental

2.1. Chemicals

Aniline, poly(4-styrenesulfonic acid) (PSSA, MW 75,000), poly(acrylic acid) (PAA, MW 100,000), poly(methyl vinyl ether-*alt*-maleic acid) (PMVEA, MW 216,000) and ammonium persulfate ($(NH_4)_2S_2O_8$, APS), were obtained from Aldrich Chem. Co. Aniline was distilled under reduced pressure before use. All solutions were prepared using Milli-Q grade water.

2.2. Synthesis and characterization of PANI nanotubes

Aniline 0.2 mol L^{-1} and 4 wt% of the polymeric acid in question (PSSA, PAA, or PMVEA, with structures given in Fig. 1) were dissolved in Milli-Q water at room temperature. The solution was cooled in a refrigerator at 3 °C for 30 min with the subsequent addition of an equal volume of a pre-cooled aqueous solution of 0.2 mol L^{-1} APS (making the concentrations of the reactants half of the values just given). The reaction continued for 16 h with the precipitation of a black–green PANI material. These were the optimium conditions in terms of obtaining the highest proportion of nanotubes. The product was then filtered and the precipitate washed several times with water, methanol and acetone. Finally, the product was dried in a vacuum oven at room temperature for 24 h.

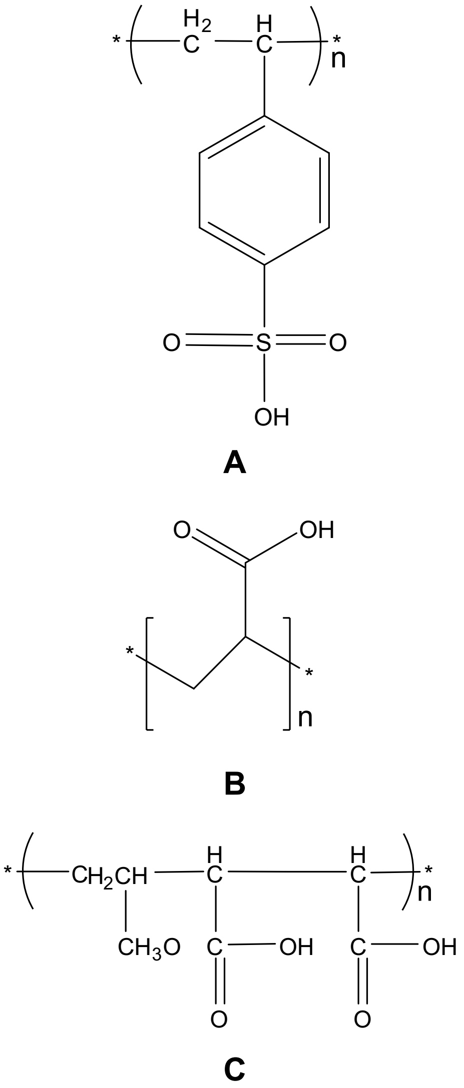

Fig. 1. Chemical structures of (A) PSSA, (B) PAA and (C) PMVEA.

The morphology of the reaction products was investigated using a Philips XL30S field emission scanning electron microscope (SEM) and a JEOL TEM-2010 transmission electron microscopy (TEM). The samples for SEM were mounted on aluminum studs using adhesive graphite tape and sputter-coated with platinum before analysis. Samples for TEM measurements were dispersed on copper coated micro-grids on a carbon support film. FTIR spectra in the range 400–4000 cm^{-1} were measured on PANI sample pellets made with KBr at a Perkin Elmer 1600 infrared spectrophotometer, using 10 scans at a resolution of 2 cm^{-1}. Electron paramagnetic resonance (EPR) spectra were recorded for samples in standard quartz EPR tubes using a JEOL JES-FA200 ESR spectrometer. The mass of all the PANI samples was fixed at 6.5 mg and the experiments were run under ambient conditions.

3. Results and discussion

3.1. Morphology of PANI nanotubes

SEM and TEM images of the PANI nanotubes obtained from the chemical oxidation of aniline in the presence of PSSA, PAA and PMVEA are shown in Fig. 2. The images reveal that the molecular structure of the polymeric acid had a significant effect on the morphology and size of the nanotubes that were formed. The outer diameter of PSSA-doped nanotubes (Fig. 2A) was larger than that of PAA or PMVEA-doped nanotubes. Based on a suggestion that the growth of PANI nanotubes is induced by formation of micelles between aniline and the dopant acid [9], the larger diameter of PANI–PSSA nanotubes may be due to differences in the structures of PSSA, PAA and PMVEA. Compared with PAA and PMVEA, PSSA has a bulky and stiff benzene ring in the each of the repeating units of the polymer. In addition PSSA bears sulfonic acid groups, and is a stronger acid than PAA or PMVEA which contain carboxylic acid groups. The average diameter (for $n = 20$) of the PANI–PSSA nanotubes was measured at 140 ± 20 nm, that of PANI–PAA at 100 ± 30 nm, and for PANI–PMVEA 85 ± 10 nm. The PANI–PAA nanotubes (Fig. 2B), obtained under the same conditions, showed a much denser packing than those obtained using PSSA and PMVEA. The length of these nanotubes was also much shorter and less regular than for the other two cases.

As mentioned above, a suggested mechanisms of formation of nanotubular structures in conducting polymers