

Synthesis and Characterization of Aniline and *o*-Toluidine Conducting Copolymer Microtubes with the Template-Synthesis Method

Ling-Yun Xin,¹ Xiao-Gang Zhang,¹ Guo-Qing Zhang,¹ Cheng-Min Shen²

¹Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, People's Republic of China

²Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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ABSTRACT: Copolymer microtubes composed of aniline and *o*-toluidine were prepared through the synthesis of the desired polymer within the pores of a microporous anodic aluminum oxide (AAO) template. Scanning electron microscopy and transmission electron microscopy revealed that the obtained copolymer microtubes had uniform and well-aligned arrays, and the aspect ratios of the AAO membranes could be controlled through their diameter and length. Infrared spectrometry and X-ray photoelectron spectroscopy supported the surface analysis for the microtubes and also

proved the formation of copolymers. Ultraviolet-visible/near-infrared spectra proved that the doping effect decreased with an increase of *o*-toluidine in the copolymers, but the solubility greatly improved (up to 3.83 g/L in *N,N*-dimethylformamide), and the conductivity was as high as approximately 17.4 S cm⁻¹. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1539–1543, 2005

Key words: conducting polymer; polyco-toluidine; templates; synthesis

INTRODUCTION

The study of special-morphology materials, in comparison with macroscopic samples of the same materials, is attracting increasing interest in modern chemical science.^{1–3} The transition between bulk and molecular scales often leads to dramatic changes in the properties of special-morphology materials. Therefore, much work has been done to improve the morphology.^{4,5} Among various special-morphology-material fabrication strategies, template synthesis has successfully played a crucial role. Different kinds of templates, such as anodic porous alumina, polymer, and nanochannel glass templates have been widely investigated. The anodic aluminum oxide (AAO) template, in comparison with other templates, has proved to be versatile and inexpensive. Furthermore, the AAO template can be used to control the sizes, shapes, and structural properties of synthesized materials.

As electronically conductive polymers have interesting and useful electronic, optical, and redox properties, many research groups have tried to apply templates to the synthesis of microstructures or nano-

structures of polymers, such as polypyrrole,⁶ poly(3-methyl thiophene),⁷ and polyacetylene.⁸ The electronic conductivity of polymers synthesized by the template-synthesized method is greater by an order of magnitude than that of bulk samples (e.g., powders and thin films) of the same polymers. Schultz's group⁹ also investigated the microstructures of conductive polymers. Li et al.¹⁰ prepared pyrrole/aniline copolymer nanofibrils.¹⁰ In this study, *o*-toluidine/aniline copolymer microtubes were fabricated with diameters of approximately 0.2 μm. The conductivity of this microtube was as high as 17.4 S cm⁻¹ due to the uniform orientation of poly(aniline-*co*-*o*-toluidine) (PANIOT) to the polaron migration; the increasing of activity and solubility of the copolymer was due to the appearance of —CH₃ in the branch chain.

EXPERIMENTAL

Preparation of the PANIOT copolymer microtubes

All the chemicals were analytical grade; *o*-toluidine and aniline were distilled under reduced pressure before use. All solutions were prepared with twice distilled water. A microporous AAO template with a pore diameter of 200 nm was purchased from Whatman International, Ltd. (Maidstone, England). The membranes had a pore density of approximately 10¹⁰ pores/cm². In this experiment, the template membrane was immersed in a precooled (5°C) solution that contained different ratios of aniline and *o*-toluidine in

Correspondence to: X.-G. Zhang (azhangxg@163.com).

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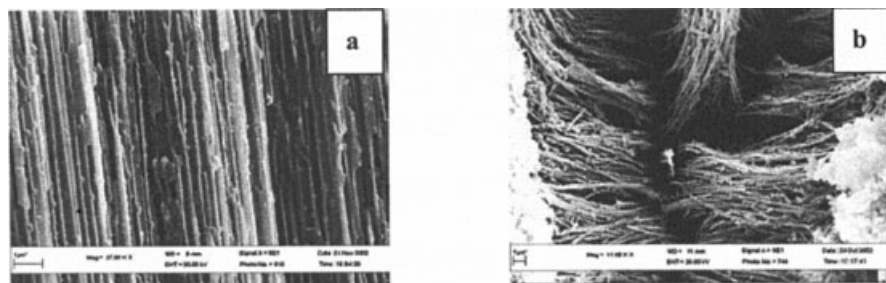


Figure 1 SEM images of (a) the AAO template in the cross section and (b) the PANIOT microtubes.

1M HCl, and then an equal volume was added of a precooled (5°C) oxidant solution containing 0.5M ammonium persulfate and 0.5M D-(+)-10-camphorsulfonic acid as the dopant in 1M HCl. The mixture was left for polymerization for 4 h at about 5°C. During this period, the copolymer was produced from the monomers and deposited within the pores of the AAO membrane. The template-synthesis method yielded either tubes or fibers of the desired copolymer within the pores of the AAO membrane according to the polymerization time and temperature.

Electron microscopy

Scanning electron microscopy (SEM) photomicrographs were recorded with a Leo 1430VP microscope (Oberkochen, Germany). The samples were obtained as follows. After thin films of the copolymer were deposited on both faces of the membrane, the AAO-template-deposited PANIOT microtubes were polished with 0.05 μm alumina powder and ultrasonicated in 1M HCl to remove the alumina powder; the resulting membrane was immersed in a 1M NaOH solution for 1 h to dissolve the AAO template. A soft membrane, losing the AAO template, was obtained, and it was vertically glued (with epoxy) to a piece of glass. This sample was attached to an SEM sample stub with conductive carbon paint. Subsequently, 10 nm of Au was sputtered onto the surface before SEM imaging.

Transmission electron microscopy (TEM) images of the samples were obtained as follows. PANIOT microtubes with the AAO template were directly immersed in 1M NaOH for 1 h to dissolve the membrane and were ground into a powder; then, the sample was imaged with a Hitachi 600 electron microscope (Tokyo, Japan).

Infrared (IR) spectrometry and ultraviolet-visible (UV-vis)/near-infrared (NIR) absorption spectroscopy

All IR spectra were obtained with a Bruker Equinox 55 Fourier transform infrared (FTIR) spectrometer (Billerica, MA) (frequency range = 4000–400 cm^{-1}).

The UV-vis/NIR absorption spectra of the copolymer were recorded on a Hitachi-U-3010 spectrophotometer (Tokyo, Japan). The samples were obtained as follows. PANIOT copolymers (25 mg) with different ratios were moderately dissolved [in N,N-dimethylformamide (DMF)] and then were filtered. The filtrate was transparent and light green and was diluted before it was measured.

X-ray photoelectron spectroscopy (XPS) and conductivity measurements

XPS was recorded on an Escalab 5 X-ray photoelectron spectrometer (East Grinstead, UK) with monochromator Al X-rays. Before the measurements, each sample was bombarded 4 min with argon ions to get rid of the PANIOT copolymer on the surface of AAO. The conductivities of the prepared polymers were measured with the four-probe method with Bio-Rad Microscience HL5500 Hall system (Bend, OR).

RESULTS AND DISCUSSION

Morphology of the copolymer microtubes

Figure 1(a) shows an SEM image of a porous AAO template with a pore diameter of approximately 0.2 μm . The pores were parallel to each other and perpendicular to the surface of the AAO template. Figure 1(b) shows an image of PANIOT microtubes after the template was removed. Although the microtubes arrays that lost the AAO support membrane toppled, the PANIOT microtubes still had highly ordered arrays. The microtubes dissolving the AAO template were dispersed and independent of one another and still maintained the original pore arrays of the AAO template. Furthermore, the microtubes had a uniform diameter and were connected to the membrane of the AAO template, like the bristles of a brush. PANIOT was deposited not only along the porous wall of the AAO template but also on both surfaces of the AAO template.

TEM images of copolymer microtubes at different magnifications were shown in Figure 2. The images show the presence of uniform copolymer microtubes

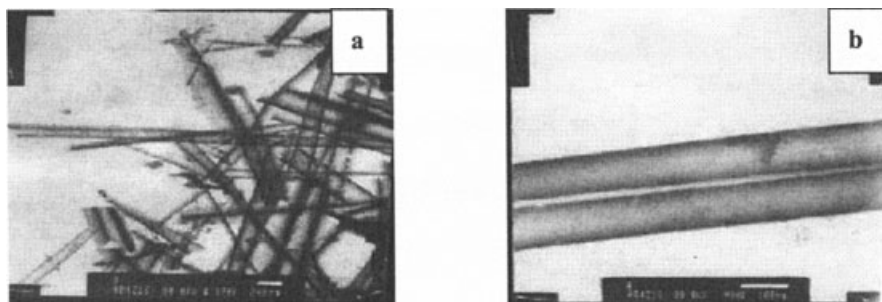



Figure 2 TEM photographs of PANIOT microtubes: (a) low magnification and (b) high magnification.

with a diameter of 0.2 μm . Some microtubes are crowded together. Furthermore, both sides of the microtubes were darker than the middle, and this indicates that the tube wall was thicker and that the electron beam had difficulty penetrating it. These results suggest that PANIOT was tubular and preferentially adsorbed and grew on the pore wall of the AAO template.

IR spectroscopy

FTIR spectroscopy was used to identify the structure of the copolymer. The FTIR spectra of the PANIOT copolymer microtubes, pure polyaniline (PANI) and poly(*o*-toluidine) (POT) are shown in Figure 3. Characteristic bands appeared at 1565–1580 and 1485–1493 cm^{-1} because of benzenoid and quinoid ring C—C stretching frequencies^{11,12} and were found in all the polymers; with an increasing of molar portion of *o*-toluidine, the two character peaks happened to red-shift. This was probably due to the electron-donating character of the —Me groups increasing the electron density on the phenyl ring and thus enhancing the dipole moment. Likewise, the band at 1280–1324 cm^{-1} was thought to be due to benzenoid and quinoid ring >C—N— asymmetric stretching vibrations;^{13,14} the band separated into three small peaks as a result of an increase in the asymmetric group —Me in the benze-

noid ring. A strong absorption at 1155–1100 cm^{-1} was assigned to an aromatic C—N stretching vibration. A C—H out-of-plane vibration (strong) appeared at 878–882 and 797–810 cm^{-1} in the copolymer for 1,2,4-trisubstituted benzene rings ( group).

Furthermore, Figure 3(a–c) shows two strong peaks gradually appearing at about 3000 and 1380 cm^{-1} . They were attributed to a $\nu_{\text{C—H}}$ stretching vibration and a characteristic $\delta_{\text{C—H}}$ absorption in the —Me group, respectively. It was proved that —Me in the copolymer increased accordingly. On the other hand, with an increase in *o*-toluidine, the two characteristic peaks appeared at approximately 1320 and 1024 cm^{-1} . They were due to the new bonds between aniline and *o*-toluidine.

XPS

Figure 4 shows the XPS survey scan from 0 to 1000 eV for PANIOT/AAO composites. PANIOT was deposited not only on the surface of AAO but also in the pores of AAO according to the peaks appearing in the chart; the appearance of Al_{2p} and O_{1s} peaks indicates that the X-ray photoelectrons reached the inner part of the PANIOT/AAO composite. During the examination, we found the binding energies of C, N, O, and Al,

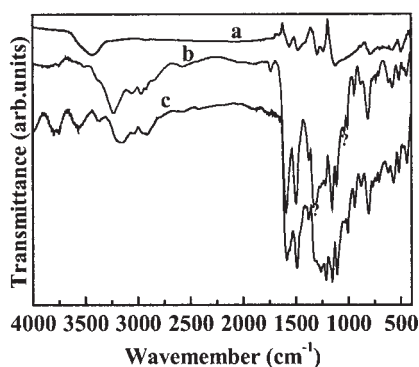


Figure 3 IR spectra of (a) PANI, (b) PANIOT (1:1 aniline/*o*-toluidine), and (c) POT.

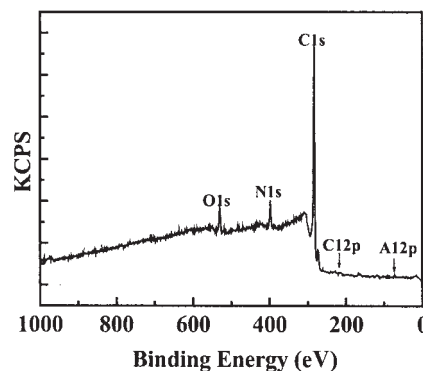


Figure 4 XPS survey scan of a PANIOT/AAO composite membrane. KCPS = the intensity of peaks.

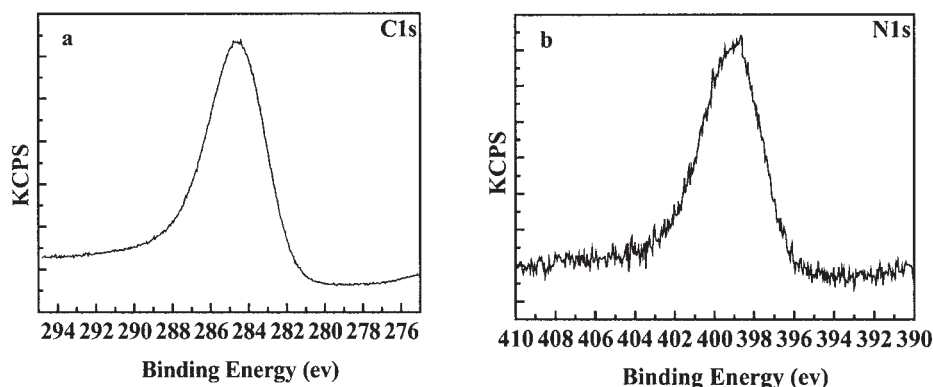


Figure 5 XPS (a) C_{1s} and (b) N_{1s} spectra of a PANIOT/AAO composite membrane.

which were in good agreement with the reported results from standard XPS, and charge emendation did not to be conducted. This result revealed the conductive characteristics of the copolymers on the surface.

For the further study of the elaborate situation of C and N in the copolymers, Figure 5 shows the C_{1s} and N_{1s} regions of a typical XPS spectrum. The peaks of the C_{1s} (284.8 eV) and N_{1s} (399.0 eV) regions were strong and expressed the characteristic regions of PANIOT. According to ref. 15, there was a small difference between the experimental and reference binding energies of C_{1s} and N_{1s} . It was probably caused by the different chemical circumstances of the copolymers. According to the atomic percentage, we could also calculate the ratio of C/N to be 15:1.

UV-vis/NIR absorption spectra analysis

The UV-vis/NIR absorption spectra of the copolymer were shown in Figure 6. The peaks gradually blue-shifted as the *o*-toluidine ratio increased. This was due to the induction and conjugative effect of the —Me group being small, but the steric effect occupied a

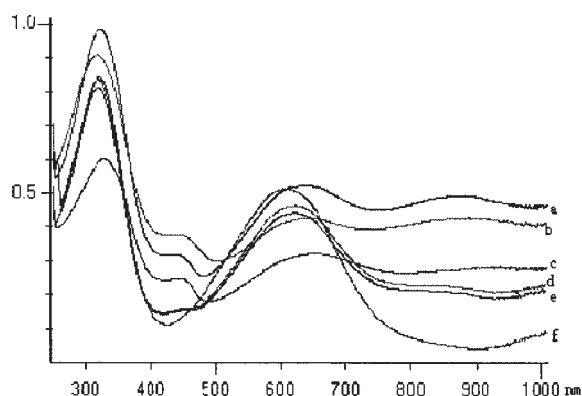


Figure 6 UV-vis/NIR spectra of (a) 5:1, (b) 3:1, (c) 1:1, (d) 1:3, and (e) 1:5 aniline/*o*-toluidine copolymers and (f) dedoped copolymer of 1:1.

dominant position and warped the copolymer chains; therefore, the effective conjugation lengths were short because of a nonplane effect. During the PANIOT-based dedoping, two characteristic transitions were monitored [Fig. 6(f)]. The bands appeared at 325 nm for the $\pi-\pi^*$ transition and at 624 nm for the exciton transition.¹⁶ Upon protonation by doping (as-synthesized copolymer), the intensity of the exciton transition gradually diminished as the ratio of aniline increased. Concomitantly, two or more new absorption bands appeared at approximately 440 and 890 nm. These bands were assigned to the polaron transition in the doped form.⁸ It was also proved that an increase in the —Me group in the copolymer could reduce the doping effect. The lowering of the doping extent may have been caused by steric repulsion between —Me and SO_3H groups (in D-(+)-10-camphorsulfonic acid (D-CSA)) and adjacent phenyl ring hydrogens;⁹ even in Figure 6(e), the copolymer hardly shows doping character. In DMF, the copolymers with different molar ratios almost exhibited only pristine polymer characteristic absorption. This was due to the solubility of D-CSA in DMF being far greater than that in water. Therefore, the absorption in the electronic spectra depended on the level of doping, the nature of the polymer, the polymer-solvent interaction, and the nature of the solvent. Although the increase in —Me was not due to doping, the solubility of the copolymer improved more with an increased in the —Me group. As a result, the solubility of the copolymers (1:1 aniline/*o*-toluidine) in DMF was approximately 80 times greater than that of PANI.

Conductivity and solubility

Generally, the conducting polymers with substituents in their frameworks had lower conductivities than that of the original PANI. The room-temperature conductivity of the copolymers was approximately $10^{-1} S cm^{-1}$ (Table I). The conductivities of the doped copol-

TABLE I
Conductivity and Solubility of the Copolymers with Different Ratios

Copolymer	Ratio	Morphology	Conductivity (S/cm)	Solubility (g/L)
PANIOT	5:1	Particle (template absent)	0.270	1.72
PANIOT	3:1	Particle (template absent)	0.113	2.45
PANIOT	1:1	Particle (template absent)	9.62×10^{-2}	3.49
PANIOT	1:1	Microtubes in AAO	17.4	3.83
PANI		Particle (template absent)		5.20×10^{-2}

ymers decreased as the molar ratio of *o*-toluidine increased. Although $-\text{SO}_3\text{H}$ (in D-CSA) had strong doping-inducing features, the deactivating effect due to the strong electron-withdrawing character of the $-\text{SO}_3\text{H}$ group could nullify the doping effect. Likewise, the steric repulsion between the $-\text{Me}$ and $-\text{SO}_3\text{H}$ groups could lower the doping extent. Therefore, the steric and electronic effects of the $-\text{SO}_3\text{H}$ and $-\text{Me}$ groups essentially reduced the conductivity. However, when PANIOT formed nanotubes in AAO, the conductivity greatly increased, up to 17.4 S cm^{-1} , because of the uniform orientation of PANIOT to the polaron migration; this made up for the flaw caused by the $-\text{CH}_3$ group. Consequently, the copolymer nanotubes had two orders of magnitude in comparison with the copolymer particles with the same ratio. The results show that the morphology had an important effect on the conductivity.

Although the conductivity of the copolymers slightly decreased as *o*-toluidine increased, their solubility greatly increased. Table I shows that the solubility of the copolymer in DMF was approximately 80 times that of the PANI homopolymer when the ratio of aniline to *o*-toluidine was 1:1.

CONCLUSIONS

The aniline/*o*-toluidine copolymer microtubes were fabricated with the AAO template. SEM and TEM showed that the copolymer microtubes had a uniform diameter (ca. $0.2 \mu\text{m}$) that depended on the AAO template. The IR and XPS spectra demonstrated that the products were copolymers. Furthermore, the UV-vis/NIR spectra of copolymers with different molar

ratios proved that the doping effect decreased as *o*-toluidine increased in the copolymers. Accordingly, the conductivity was lower than that of PANI, but the solubility was greatly improved. However, the formation of copolymer microtubes in AAO sharply improved the conductivity to 17.4 S cm^{-1} , which was two orders of magnitude higher than that of the copolymer particles (0.0962 S cm^{-1}) with the same ratio. Therefore, it made up for the flaw caused by the $-\text{CH}_3$ group.

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