

# Preparation and Characterization of Pyrrole/Aniline Copolymer Nanofibrils Using the Template-Synthesis Method

XIAOHONG LI, XIAOGANG ZHANG, HULIN LI

Chemistry department of Lanzhou University, Lanzhou 730000, People's Republic of China

Received 27 July 2000; accepted 29 November 2000

**ABSTRACT:** Copolymer nanofibrils composed of pyrrole and aniline had been prepared by synthesizing the desired polymer within the pores of microporous anodic aluminum oxide (AAO) template membrane. To analyze their structure and properties, FTIR spectra were taken and thermogravimetric analysis (TGA) was applied. Also, the copolymer nanofibrils were photographed under scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for microstructure analysis, and the conductivities were obtained by the four-probe method. The result of SEM and TEM revealed that the obtained copolymer nanofibrils had uniform and well-aligned array, and their diameter and length can be controlled by changing the aspect ratios of the AAO membrane. The result of IR spectrometry and TGA indicated that both polypyrrole and polyaniline were involved in the copolymer. The obtained nanofibrils were identified to be copolymer rather than composite. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3002–3007, 2001

**Key words:** copolymer; pyrrole; aniline; template-synthesis method; nanofibrils

## INTRODUCTION

Electronically conductive polymer nanostructures have recently caused a great deal of excitement in the physics, chemistry, and materials science communities.<sup>1–3</sup> Such nanostructures are inherently intriguing chemical systems, and have myriad proposed technological applications.<sup>4,5</sup> The general synthetic route for preparing electronically conductive polymer nanostructures involves the template-synthesis method. This method entails synthesis of a desired material within the pores of a microporous membrane. The membranes employed have cylindrical pores with monodisperse diameters. A tubule or fibril of the

desired material is obtained within each pore. The template-synthesis method has been used to prepare nanotubules or fibrils of electronically conductive polymers,<sup>6–9</sup> metals,<sup>10–12</sup> semiconductors,<sup>13,14</sup> and carbon.<sup>15</sup> Because the aspect ratios of the nanostructures prepared via this method can be controlled at will, this template approach is proving to be a versatile method for synthesizing nanomaterials.

Martin and coworkers have showed that template-synthesized electronic conductivity of over an order of magnitude when compared to bulk samples (e.g., powders, or thin films) of the same polymer. Such enhancements in conductivity were observed in template-synthesized nanocylinders composed of polyacetylene,<sup>6</sup> polypyrrole,<sup>7</sup> poly(3-methylthiophene),<sup>7</sup> and polyaniline.<sup>8,9</sup> This enhancement in electronic conductivity results from an enhancement in the supermolecular or-

---

Correspondence to: H. Li.

*Journal of Applied Polymer Science*, Vol. 81, 3002–3007 (2001)  
© 2001 John Wiley & Sons, Inc.

der within the template-synthesized polymer fibers. Specifically, the polymer chains within these fibers are highly aligned.<sup>7</sup>

Although a number of polymer have been prepared using the template-synthesis method, to our knowledge, there have been no reports on the production of copolymer. The formation of copolymers displaying electronic conductivity has been much less investigated. The main motivation for preparing copolymer composites lies in the possibility that these materials will display better properties and overcome the limitation of the rareness of new conjugated  $\pi$ -bond-containing monomers. In this work, we describe the template-synthesized electronically conductive copolymer nanofibrils derived from pyrrole and aniline, using uniform and straight channels of anodic aluminum oxide (AAO) film as a template. We have employed the chemical copolymerization technique for pyrrole and aniline loading, and investigated the structure and morphology of the copolymer fibers with Infrared spectrometry, thermogravimetric analysis (TGA), a scanning electron microscopy (SEM), and a transmission electron microscopy (TEM).

## EXPERIMENTAL

### Materials

The starting materials, pyrrole and aniline, were purchased from Acros Chemical Co., and distilled under reduced nitrogen prior to use. Ferric chloride hexahydrate was obtained from Jinshan Chemical Engineering Factory, Shanghai, China. Ammonium persulfate and *p*-toluenesulfonic acid were obtained from Xian Chemical Co., Xian, China. All the other ingredients were of analytical grade and used without further purification. All solutions were prepared with twice distilled water.

### Preparation of AAO Films

AAO films were prepared by anodic oxidation of electropolished aluminum plate at a cell voltage of 80 V in 0.5 M phosphoric acid at 25°C for 1.5 h. The details of this method were described elsewhere.<sup>16</sup> The porosity of the anodic membrane consisted of an array of parallel and straight channels with a diameter of about 80 nm, and the film diameter and its thickness were 15 mm and ~20  $\mu$ m, respectively.

### Preparation of Copolymer Nanofibrils

Gregory et al.<sup>17</sup> have developed a method for coating textiles with conductive polymers. We have used a similar procedure for chemically synthesizing copolymer of pyrrole and aniline within the pores of AAO membranes. In this method, the template membrane is immersed in a precooled (5°C) solution that contained 0.325 M aniline in 1 M HCl and 0.3 M pyrrole. An equal volume of precooled (5°C) oxidant solution containing 2 M ferric chloride hexahydrate, 0.125 M ammonium persulfate, and 0.5 M *p*-toluenesulfonic acid in 1 M HCl was then added. The mixture was left for polymerization for 2 h at ca. 5°C. During this period, copolymer was produced from the monomers and deposited within the pores of AAO membrane.

The template-synthesis method yielded either tubules or fibers of the desired copolymer within the pores of AAO membrane by controlling the polymerization time and temperature. In addition, thin films of the copolymer were deposited on both faces of the membrane. One or both of these surface films were removed prior to characterization. This was accomplished by simply polishing the surface films of the membrane with 1  $\mu$ m alumina powder. The membrane was then ultrasonicated in 1 M HCl to remove the alumina powder.

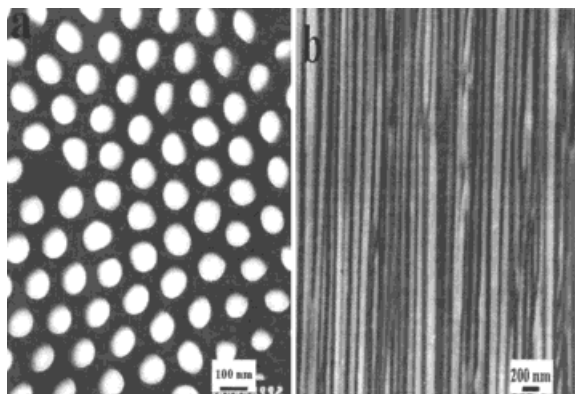
### Electron Microscopy

SEM images of the copolymer nanofibrils were obtained as follows: One surface layer was removed, and the membrane was glued (using epoxy) to a piece of glass with the polished face up. The resulting membrane was immersed into 6 M NaOH solution for 2 min to dissolve the AAO membrane. A JSM-5600LV electron microscope was used. The copolymer nanofibrils were sputtered with a thin film of gold prior to imaging.

TEM images of the samples were obtained as follows: both surface layer were removed, and a piece of the resulting membrane was placed onto a carbon film-coated TEM grid. The 6 M NaOH solution was then applied to the membrane to dissolve the alumina. The freed copolymer nanofibrils were imaged using a HATACHI-600 electron microscope. The accelerating voltage of the electron beam was 100 kV.

### Infrared Spectrometry

All IR spectra were obtained by using a Nicolet AVATAR-360 fourier transform infrared (FTIR)



**Figure 1** TEM image of top surface structure (a) and SEM image of cross-section (b) of AAO template membrane.

spectrometer. Both surface layer of the copolymer membrane were removed. Because the alumina had no absorption above  $600\text{ cm}^{-1}$ ,<sup>18</sup> the FTIR spectra showed the absorption of the copolymer.

#### Thermogravimetric Analysis

A general Du Pont model 1090B instrument was used for thermogravimetric analysis. The samples were heated up to  $800^\circ\text{C}$  with a rate of  $10^\circ\text{C min}^{-1}$  under nitrogen atmosphere.

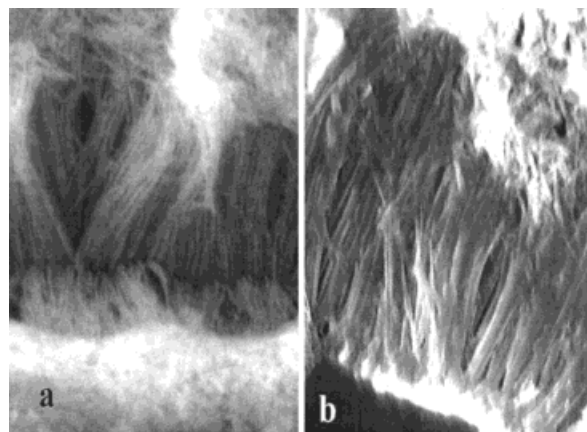
Conductivities of the prepared polymers were measured employing the four-probe method.

## RESULTS AND DISCUSSION

#### Morphology of Copolymer Nanofibrils

Figure 1(a) shows the TEM photographs (top view) of porous AAO template with a pore diameter of about 80 nm and a pore density of about  $10^{10}\text{--}10^{11}\text{ cm}^{-2}$ . Perfect hexagonal pore arrays can be observed within domains of microsize, which are separated from neighboring alumina domains with a different orientation of the pore lattice by grain boundaries. Figure 1(b) depicts the cross-section of the AAO template with pores parallel to each other and perpendicular to the surface of the membrane.

Figure 2 shows the SEM images of copolymer nanofibrils composed of polypyrrole and polyaniline with low (a) and high (b) magnification. The AAO membrane has been dissolved to expose the copolymer fibers prepared in the pores. This yields an ensemble of copolymer nanofibrils that protruded from the epoxy surface like the bristles



**Figure 2** SEM images of copolymer nanofibrils: (a) low and (b) high magnification images.

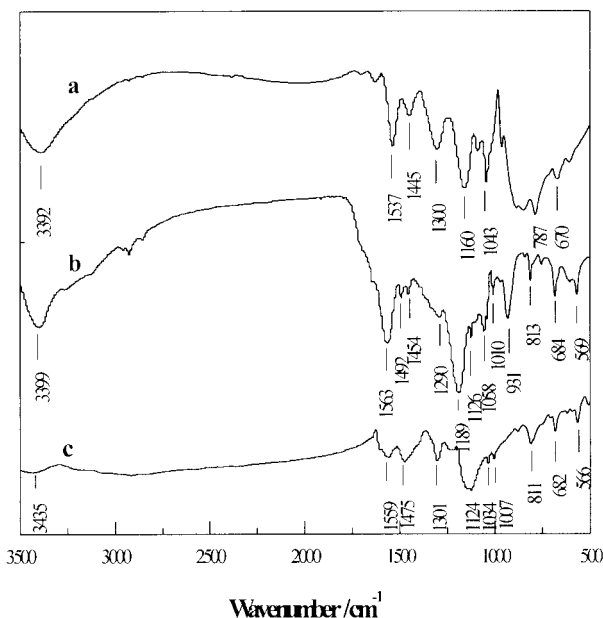
of a brush. Some residual copolymer surface layer is observed at the tops of these fibers. Note the high density of fibrils; this reflects the very high porosity of the AAO template membrane. As would be expected, the fibrils diameter is equivalent to the pore diameter (80 nm) of the template membrane. The lengths of these fibrils show that they span the complete thickness ( $20\ \mu\text{m}$ ) of the template. Figure 3 shows the TEM image of copolymer fibrils. The image exhibits the presence of uniform copolymer nanofibrils with diameter and length of 80 nm and  $20\ \mu\text{m}$ , respectively. Some fibrils crowd together with each other due to physical adsorption on the surface of the fibrils.

#### Characterization of Copolymer Nanofibrils

The FTIR spectroscopy was used to identify the structure of the copolymer. The FTIR spectra of



**Figure 3** TEM image of copolymer nanofibrils.



**Figure 4** Infrared spectra of (a) pure polypyrrole, (b) copolymer nanofibrils, and (c) pure polyaniline.

copolymer together with that of pure polypyrrole and polyaniline are shown in Figure 4. The most impressive characterization is the evolution of the absorption bands located around  $1460\text{ cm}^{-1}$ . In the spectrum of pure polypyrrole, the single peak located at  $1445\text{ cm}^{-1}$  is assigned to a combination of C=C stretch, C—N stretch, and the deformation of the five-membered ring which contains the C=C—N, C=C—C deformation.<sup>19,20</sup> In the spectrum of polyaniline, the single peak located at  $1475\text{ cm}^{-1}$  is assigned to the C=C, N—N, and C—N stretch mode. In the spectrum of copolymer, this peak is split into two isolated peaks located at  $1454$  and  $1492\text{ cm}^{-1}$ . Another similar characterization is that the bands of the copolymer in  $1189\text{ cm}^{-1}$  and  $1126\text{ cm}^{-1}$ , which are assigned to the C=C stretch, C—C in-ring stretch, and C—N stretch of polypyrrole and polyaniline, respectively. This indicated that the monomers of pyrrole and aniline are, indeed, incorporated into the copolymer.

Furthermore, another noticeable feature in the spectra is that the absorption bands around  $3399$ ,  $1560$ , and  $684\text{ cm}^{-1}$ , which correspond to the N—H stretch, C=C stretch, and C—H ring out-of-plane bending, respectively, appear both in the copolymer and in pure polypyrrole and polyaniline. The intensity of these bands in the copolymer are relatively strong compared to that of pure polymers. These observation demonstrate that each polymer are involved in the copolymer.

As it can be seen in Table I, the copolymer has the highest conductivity with a conductivity value of  $1.2 \times 10^{-2}\text{ S cm}^{-1}$ ; whereas the polypyrrole has the lowest conductivity with a value of  $1.6 \times 10^{-3}\text{ S cm}^{-1}$ . The important difference between the conductivities of these polymers can be elucidated as counterion effects.<sup>21,22</sup> The conductivities of the polymers tend to change according to the preparation medium.

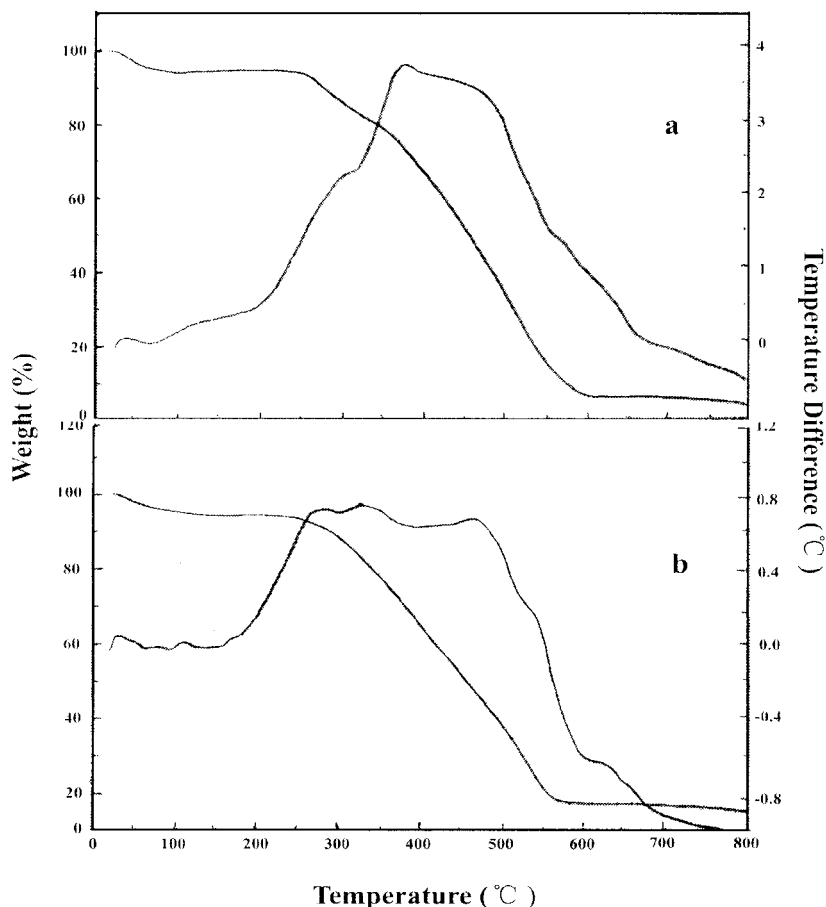
However, neither conductivity measurements nor spectrum results reveal whether the samples were copolymer or composite. The curves of thermogravimetric analysis (TGA) of copolymer and mechanical mixture of polypyrrole and polyaniline are given in Figure 5. The results are also tabulated in Table II. As seen from Table II, the three decomposition temperatures ( $T_i$ ,  $T_{\max}$ , and  $T_p$ ) of the polymers are different from each other. The mixture decomposition temperature of the copolymer is higher than that of the mixture of polypyrrole and polyaniline. This proof could support the idea that the obtained polymer are copolymers.<sup>23</sup> Moreover, from the decomposition temperatures it was observed that the copolymer was thermally stable.

## CONCLUSION

Copolymer nanofibrils was synthesized in the pores of a microporous AAO membrane. Electron microscopy results showed that the template technique using the AAO membrane can control the length, diameter, and thickness of copolymer

**Table I** Conductivity of Copolymers, Polyaniline, and Polypyrrole

Polymer	Medium (Oxidant)	Conductivity ( $\times 10^{-3}\text{ S cm}^{-1}$ )
Copolymer	$0.125\text{M } (\text{NH}_4)_2\text{S}_2\text{O}_8/0.5\text{M } p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}/1\text{M HCl} + 2\text{M FeCl}_3$	12
Polyaniline	$0.125\text{M } (\text{NH}_4)_2\text{S}_2\text{O}_8/0.5\text{M } p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}/1\text{M HCl}$	3.5
Polypyrrole	$2\text{M FeCl}_3$	1.6



**Figure 5** TGA of (a) copolymer, (b) polypyrrole + polyaniline mixture in a 1 : 1 ratio.

nanofibrils and produce uniform and monodisperse copolymer nanofibrils. From IR spectra studies, it was revealed that the copolymer nanofibrils were composed of polypyrrole and polyaniline. The study of thermogravimetric analysis (TGA) of the copolymer nanofibrils demonstrated that the obtained polymer was copolymer rather

than composite. In addition, we found out that the copolymer was thermally stable.

**Table II** TGA of Copolymer and Polypyrrole + Polyaniline Mixture in a 1 : 1 Ratio

Polymer	Decomposition Temperature (°C)		
	$T_i^a$	$T_{max}^b$	$T_f^c$
Copolymer	263	385	575
Polypyrrole + Polyaniline (mixture in 1 : 1 ratio)	258	325	545

<sup>a</sup>  $T_i$ : initial temperature.

<sup>b</sup>  $T_{max}$ : maximum decomposition temperature.

<sup>c</sup>  $T_f$ : final temperature.

## REFERENCES

1. Kuwabata, S.; Ito, S.; Yoneyama, H. *J Electrochem Soc* 1988, 135, 1691.
2. Peters, E. M.; Van Dyke, J. D. *J Polym Sci Part A Polym Chem* 1992, 30, 1891.
3. Parthasarathy, R. V.; Martin, C. R. *Nature* 1994, 369, 298.
4. Cha, S. K. *J Polym Sci Part B Polym Phys* 1997, 35, 165.
5. Zotti, G.; Musiani, M.; Schiavon, G. *Chem Mater* 1998, 10, 480.
6. Liang, W.; Martin, C. R. *J Am Chem Soc* 1990, 112, 9667.
7. Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. R. *Chem Mater* 1991, 3, 960.
8. Martin, C. R.; Parthasarathy, R.; Menon, V. *Synth Met* 1993, 55, 1165.
9. Parthasarathy, R. V.; Martin, C. R. *Chem Mater* 1994, 6, 1627.

10. Tierney, M. J.; Martin, C. R. *J Phys Chem* 1989, 93, 2878.
11. Foss, C. A.; Tierney, M. J.; Martin, C. R. *J Phys Chem* 1992, 96, 9001.
12. Foss, C. A.; Hornyak, G. L.; Stockert, J. A.; Martin, C. R. *Adv Mater* 1993, 5, 135.
13. Lakshmi, B. B.; Dorhout, P. K.; Martin, C. R. *Chem Mater* 1997, 9, 857.
14. Lakshmi, B. B.; Patrissi, C. J.; Martin, C. R. *Chem Mater* 1997, 9, 2544.
15. Kyotani, T.; Pradhan, B. K.; Tomita, A. *Bull Chem Soc Jpn* 1999, 72, 1957.
16. Peng, Y.; Zhang, H. L.; Pan, S. L.; Li, H. L. *J Appl Phys* 2000, 87, 1.
17. Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. *Synth Met* 1989, 28, C823.
18. *Inorganics IR Grating Spectra*, vols. 1–2, Y1K-Y600K.
19. Kofranek, M.; Kovar, T.; Karpfen, A.; Lischka, H. *J Chem Phys* 1992, 96, 4464.
20. Kostic, R.; Eakovic, D.; Stepanyan, S. A.; Davidova, I. E.; Gribov, L. A. *J Chem Phys* 1995, 102, 3104.
21. Talu, M.; Kabasakaloglu, M.; Oskoui, H. R. *J Polym Sci Part A Polym Chem* 1996, 34, 2981.
22. Sari, B.; Talu, M. *Synth Met* 1998, 94, 221.
23. Geissler, U.; Hallensleben, M. L.; Toppare, L. *Synth Met* 1991, 40, 239.