(2)

OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

R&T CODE: 4133032

TECHNICAL REPORT NO. 82

Template Synthesis of Electronically Conductive Polymers - A New Route for Achieving Higher Electronic Conductivities

by

C. R. Martin, R. Parthasarathy and V. Menon

Prepared for publication

in

Synthetic Metals

Department of Chemistry
Colorado State University
Ft. Collins, CO 80523

February 22, 1993

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	Feb 1992	Interim

4. TITLE AND SUBTITLE
Template Synthesis of Electronically Conductive Polymers - A New Route for Achieving Higher Electronic Conductivities

5. FUNDING NUMBERS
Contract
N00014-82K-0612

6. AUTHOR(S)
C. R. Martin, R. Parthasarathy and V. Menon

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Dr. Charles R. Martin
Department of Chemistry
Colorado State University
Fort Collins, CO 80523

8. PERFORMING ORGANIZATION REPORT NUMBER
ONR TECHNICAL REPORT # 82

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
We have recently developed a method for synthesizing microscopic fibers and tubules of electronically conductive polymers. This method entails synthesis of the polymer within the pores of a microporous host membrane. Conductivities in the narrowest of these "template-synthesized" tubules and fibers can be significantly higher than in conventional forms (e.g. powders or thin films) of the analogous polymer. These previous conductivity data were based on a two-point measurement of the resistance of the host membrane after synthesis of the conductive polymer fibers within this membrane. In this paper we will show results of conductivity measurements on thin films composed of the template-synthesized tubules and fibers. A four-point conductivity measurement was used on these thin films. These four-point measurements corroborate the earlier two-point conductivity data and, again, show that the template-synthesized materials are significantly more conductive.

14. SUBJECT TERMS
Nanochemistry, Electronically conductive polymers

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
		UNCLASSIFIED	

TEMPLATE SYNTHESIS OF ELECTRONICALLY CONDUCTIVE POLYMERS - A NEW ROUTE FOR ACHIEVING HIGHER ELECTRONIC CONDUCTIVITIES

C.R. MARTIN, R. PARTHASARATHY, AND V. MENON
Department of Chemistry, Colorado State University, Fort Collins, CO 80523

ABSTRACT

We have recently developed a method for synthesizing microscopic fibers and tubules of electronically conductive polymers. This method entails synthesis of the polymer within the pores of a microporous host membrane. Conductivities in the narrowest of these "template-synthesized" tubules and fibers can be significantly higher than in conventional forms (e.g. powders or thin films) of the analogous polymer. These previous conductivity data were based on a two-point measurement of the resistance of the host membrane after synthesis of the conductive polymer fibers within this membrane. In this paper we will show results of conductivity measurements on thin films composed of the template-synthesized tubules and fibers. A four-point conductivity measurement was used on these thin films. These four-point measurements corroborate the earlier two-point conductivity data and, again, show that the template-synthesized materials are significantly more conductive.

INTRODUCTION

We have been exploring the idea of synthesizing electronically conductive polymers within the pores of microporous host membranes (1-7). The membranes employed have linear, cylindrical pores of equivalent diameter. We call this method "template synthesis" because the pores in the host membrane act as templates for the nascent electronically conductive polymer. Because of this templating effect, electronically conductive polymer fibers and hollow fibers (i.e. tubules) are obtained when the polymer is synthesized within the pores of the host membrane. Figure 1 shows an electron micrograph of some typical conductive polymer tubules obtained via the template synthetic method.

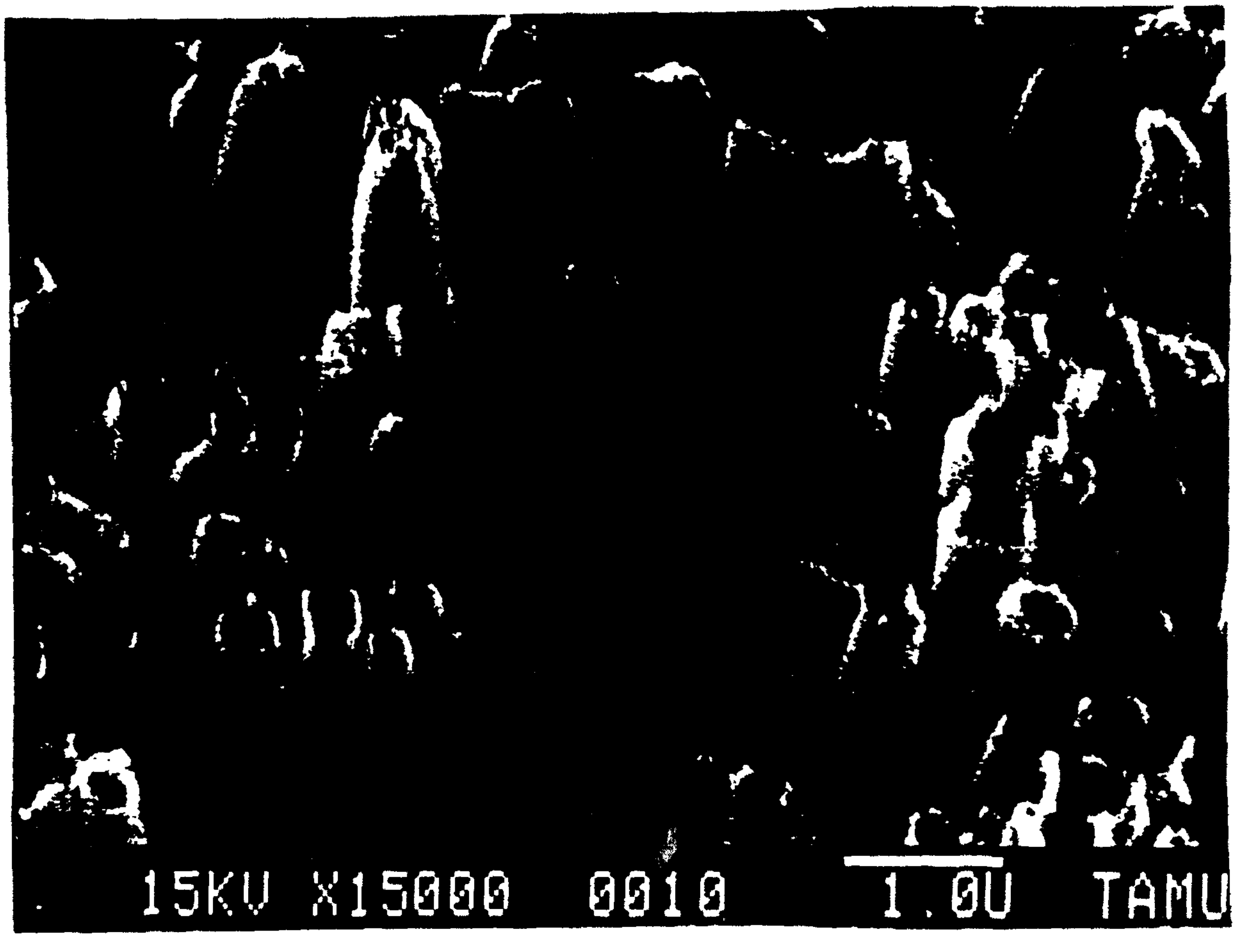

Fig 1. Scanning electron micrograph of poly(N-methylpyrrole) tubules obtained via the template synthetic method.

We have shown that the narrowest template-synthesized fibers and tubules (i.e. fibers and tubules synthesized in host membranes with the smallest-diameter pores) can have conductivities that are over an order of magnitude higher than conventional versions (i.e. powders or thin films) of the analogous polymer (3,5,6). We have demonstrated this enhancement in electronic conductivity for fibers composed of polypyrrole (3,5), poly(3-methylthiophene) (3), polyacetylene (6), and polyaniline. This enhancement in electronic conductivity results from an enhancement in the supermolecular order within the template-synthesized fibers (relative to a powder or film sample) (5). Specifically, we have shown that the polymer chains within these fibers are highly aligned (5).

Our previous conductivity data for the template-synthesized materials were based on two-point measurements of the resistance of pressure of $6x10^{4}$ psi. Four-point conductivity measurements were made on these compacted thin films.

RESULTS AND DISCUSSION

An electron micrograph of a typical thin film composed of the template-synthesized polyaniline tubules is shown in Figure 2. Note that the tubular structure can not be seen in this cross-sectional image. This means that the tubules were crushed under the high pressures used to compact the film. We have obtained analogous thin films from polypyrrole tubules; however, for this polymer, the tubule structure is retained in the compacted thin film. This suggests that polypyrrole has better mechanical properties than polyaniline.

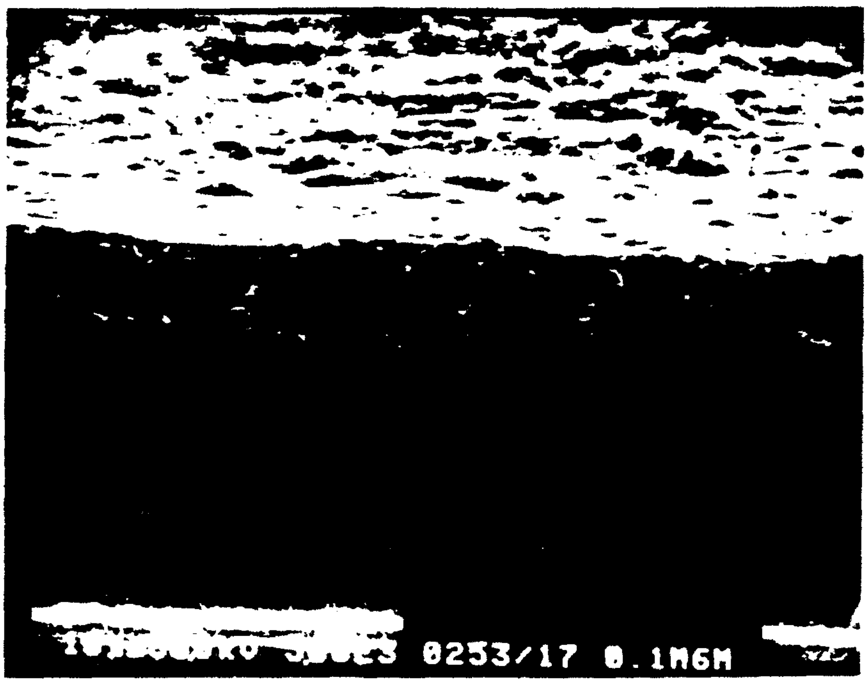

Fig. 2. Scanning electron micrograph of a thin film prepared form 0.1 μm-diameter polyaniline tubules.

Conductivity data obtained from thin films prepared from polyaniline tubules of various diameters are shown in Table 1. There are several interesting points to note from Table 1. First, in agreement with our 2-point conductivity data reported previously (1-5), the conductivities obtained on these thin films, prepared from template-synthesized tubules, increase as the diameter of tubule used to prepare the thin film decreases. We have shown that this increase in conductivity occurs because the smallest-diameter the host membrane after synthesis of the electronically conductive polymer fibers within this membrane. Four-point conductivity measurements are always preferable to two-point measurements. Furthermore, the two-point method used previously required that the pore density and pore size in the host membrane be accurately known. We have recently developed a method for forming thin films of template-synthesized conductive polymer tubules and fibers and we have conducted four-point conductivity measurements on these thin films. These more reliable four-point measurements corroborate the earlier two-point conductivity data. That, is the four-point conductivity measurements also show that the template-synthesized polymers are significantly more conductive.

EXPERIMENTAL

Nuclepore polycarbonate filters were used as the host membranes (1-7). These membranes have cylindrical pores with highly-monodisperse diameters. Membranes with pore diameters ranging from 100 nm to 400 nm were used in these investigations. In our previous investigations (3-5), tubule and fibril polymerizations were carried out by allowing the membrane to separate an aqueous solution of the monomer from an aqueous solution of the oxidizing agent. We have since developed an easier method for conducting these template syntheses. In this method, the host membrane is simply immersed into a solution containing both the monomer and the oxidizing agent. This method is based on the work of Kuhn et al. (8). Conductive polymer tubules are obtained within the host membrane.

We will present data for polyaniline tubules synthesized within these membranes. The monomer solution was 0.325 M in aniline and 1 M in HCl. The oxidant solution was 0.125 M in sodium vanadate, 1 M in HCl, and 0.5 M in p-toluenesulfonate. The template membrane was immersed in the monomer solution and an equal volume of the oxidant solution was added. Polymerization was allowed to proceed for two hours. After polymerization, the tubule-impregnated membrane was rinsed with 1 M HCl and the polyaniline surface membranes were removed by polishing the faces of the membrane with alumina powder.

The template membrane (Nuclepore polycarbonate) was then dissolved in methylene chloride and the polyaniline tubules were collected on an Anopore filter. A film of polyaniline tubules was obtained on the filter surface. This film was compacted using a tubules have highly-ordered polymer chains (5). Second, note that the conductivities obtained for the film prepared from the smallest-diameter tubules is higher than the conductivity of bulk samples of polyaniline. Bulk samples of polyaniline prepared under the same conditions gave conductivities of 9 S cm^{-1}.

TABLE 1

Four-point conductivity data form polyaniline films prepared from template-synthesized tubules of various diameters.

Diameter of Tubules Used to Prepare the Film (nm)	Conductivity (S cm^{-1})
100	50
200	17
400	14

CONCLUSIONS

We have shown that template-synthesized polyaniline tubules can be processed into highly-conductive thin films. While not reported on here, we have also processed template-synthesized polypyrrole tubules into thin films. We have also shown that a more reliable four-point conductivity measurement confirms our early two-point measurements which showed that these nanoscopic template-synthesized fibers and tubules have enhanced electronic conductivities.

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research and the Air Force Office of Scientific Research.

REFERENCES

1 R.M. Penner and C.R. Martin, J. Electrochem. Soc. 133 (1986) 2206.

2 L.S. Van Dyke and C.R. Martin, Langmuir 6 (1990) 1118.

3 Z. Cai and C.R. Martin, J. Am. Chem. Soc. 111 (1989) 960.

4 C.R. Martin, L.S. Van Dyke, Z. Cai, and W. Liang, J. Am. Chem. Soc. 112 (1990) 8976.

5 Z. Cai, J. Lei, W. Liang, V. Menon, and C.R. Martin, Chem. Materials 3 (1990) 960.

6 W. Liang and C.R. Martin, J. Am. Chem. Soc. 112 (1990) 9666.

7 C.R. Martin, Advan. Materials 3, (1990) 457.

8 R.V. Gregory, W.C. Kimbrel, and H.H. Kuhn, Synth. Met. 28 (1989) C823.