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Template Synthesis of Polymeric and Metal Microtubules

by

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

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We describe in this report an elegant new method for the synthesis of organic microtubules This new method is based on the use of a microporous membrane as a template during tubule synthesis. This template method produces tubules with monodisperse lengths and diameters, and legth, diameter, and wall thickness can be varied at will. This type of precise control over tubule geometry is not possible with the existing synthetic method. The tubules obtained are composed of chemically and mechanically robust heterocyclic polymers.

We have recently described a "template" method for the synthesis of organic microtubules. This method entails the use of the pores in a microporous membrane as templates for tubule formation. The key to the tubule-formation procuess is the presence of "molecular anchors" on the pore walls. These anchors insure that the tuble-forming materials deposits as a thin skin which lines the pore wall. We describe in this paper an electrochemical template method for the synthesis of metal (Au) microtubules. We also present a general paradigm for the formatior of molecular anchors on the pore walls of alumina template membranes. We believe that this paradigm should allow for the synthesis of microtubules composed of any desired material.

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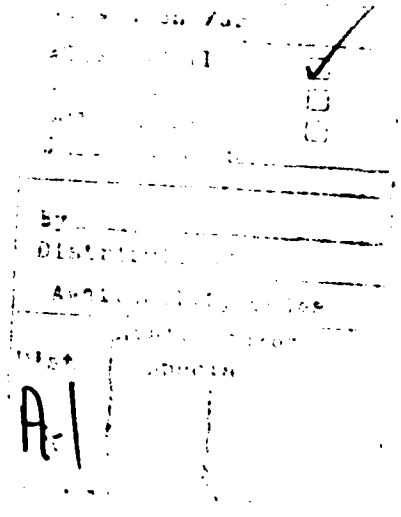
TEMPLATE SYNTHESIS OF POLYMERIC AND METAL MICROTUBULES

Charles R. Martin
Department of Chemistry
Colorado State University
Fort Collins, CO 80523



INTRODUCTION

In 1984 Yager and Schoen, of the U.S. Naval Research Laboratories (NRL), discovered a new type of microstructure - organic microtubules (1). These tubules resemble soda straws with diameters of approximately 0.5 μm and average length distributions ranging from one to several hundred microns (1). Yager and Schoen's microtubules are self-assembled from solutions of diacetylenic phospholipids (1).

While these microtubules are intriguing chemical systems, one could ask the question - what good are they? A panel of 30 physicists, chemists, materials scientists, and engineers was recently assembled to address this question (2,3). According to Joel Schnur (a member of the NRL team) after 3 days, this group had 600 suggestions, 100 of which were "reasonable enough to consider" (2). These proposed applications included use in drug delivery systems and (after coating with metal (1)) in microwave components and electronic and electro-optical devices (2).

One potential problem with the NRL method for preparing organic microtubules is expense. According to a recent review in Science, the lipids used to make these tubules currently cost ca. $6,800 per pound (2). However, the price for the raw material could go down if a large volume market were identified (2). A second potential problem is the polydispersity in tubule length and diameter obtained via the NRL method.

We have recently discovered a totally new procedure for preparing organic microtubules (4,5). This method entails using

the pores in a microporous membrane as templates for tubule synthesis. The most significant advantages of this "template synthesis" are that it yields tubules with monodisperse diameters and lengths and that length and diameter can be accurately controlled (4,5). Furthermore, the template method is a potentially inexpensive route for preparing microtubules. Finally, the template concept can be used to synthesize tubules composed of various materials. For example, we have recently used this method to prepare metal microtubules (5). The template synthetic method is reviewed in this article.

THE TEMPLATE METHOD

The key to this method is the microporous "template" membrane. An electron micrograph of the surface of a typical template membrane (a commercially-available Nuclepore polycarbonate filter) (4) is shown in Figure 1. These membranes are ca. 10 μm-thick, have linear, cylindrical pores of equivalent pore diameter, and are available with pore diameters ranging from 30 nm to 10 μm. The template method entails synthesis of a polymer within the pores of such membranes. For reasons which will be discussed below, the nascent polymer is preferentially deposited as thin skins which line the walls of the pores (4,6). Hence, hollow polymeric tubules are obtained.

Our work to data has focused on tubules composed of simple heterocyclic polymers (e.g. polypyrrole) (4). The easiest way to synthesize such tubules is to put a solution of the monomer (e.g. pyrrole) on one side of the template membrane and a solution of a

polymerization reagent (e.g. Fe^{3+}) on the other side (4). These two solutions flood the pores, the reactants meet, and polymer is formed. Because polypyrrole is insoluble in the solvent used (water) solid polymer is deposited within the pores (4,7).

There is no, a priori, reason to expect, however, that the polymer will preferentially precipitate on the pore wall to form a hollow tubule. Rather, it seems more likely that the polymer would just precipitate from the solution within the pore and eventually form a solid polymeric fiber. Indeed, this is what we anticipated when we began this work (7).

We believe that the key to tubule formation in the template method is the presence of "molecular anchors" on the pore walls (4,5). These putative anchors bind the nascent polymer to the wall and thus cause the wall to be coated with a thin film of the polymer. For the Nuclepore/polyheterocyclic system, the anchors might be anionic sites (8) on the pore wall. These anionic sites should allow for electrostatic interaction between the pore wall and the heterocyclic polycation (4,7). It is of interest to note that a similar surface adsorption phenomenon has been observed by Kuhn et al. (9). They have used this adsorption phenomenon to prepare polypyrrole-coated fabrics (9).

Figure 2 shows electron micrographs of typical polyheterocyclic tubules obtained via the template method (4). These tubules have monodisperse lengths, diameters and wall thicknesses. The isolated tubules in Figures 2A and B were obtained by dissolving the template membrane and filtering the

resulting solution. The upright array of tubules shown in Figure 2C was obtained via an electrochemical version of the template method (4). These tubules are composed of poly(N-methylpyrrole) and are connected at their bases to a thin film of this polymer (4). The ability to produce a parallel array of tubules is an interesting (and perhaps useful) feature of the template method.

Finally, we have recently shown that the template method can be used to produce metal microtubules (5). An electron micrograph of an array of Au tubules is shown in Figure 3. These tubules were synthesized electrochemically within the pores of a microporous alumina (Anopore) membrane (5). It is important to point out however, that tubules were only obtained when a molecular anchor (an organocyanide) was attached to the pore walls in these alumina template membranes (5). Solid Au fibers were obtained in the absence of this molecular anchor. This reinforces the notion that a molecular anchor is essential to the tubule formation process.

Metal microtubules are potentially important because several of the proposed applications of these microstructures require electronic conductivity (2,3). In this regard, it is important to point out that polyheterocyclics are electronically conductive polymers (7). Hence, our plastic tubules are also electronic conductors.

THE FUTURE

We are currently attempting to expand the template method to other materials. We are using conventional silanization chemistry (5) to attach specific molecular anchors to the pore walls of the

Anopore alumina membranes. We are then synthesizing polymers (and other materials), which can bond to these molecular anchors, within the pores of these membranes. We believe that this should function as a general paradigm for the synthesis of microtubules composed of any desired material.

Finally, there is another advantage to using the microporous alumina membranes for template synthesis. These membranes are ca. 65 % porous as opposed to, at most, ca. 10 % porosity for the Nuclepore membranes. Hence, more tubules per unit raw material (the membrane) can be prepared from the alumina membranes. This could be important if commercial applications are to be realized.

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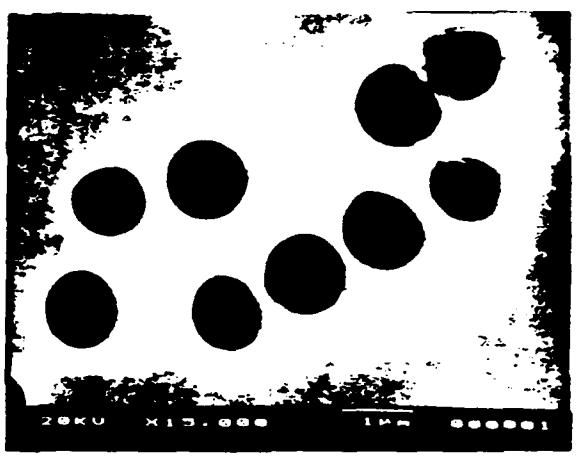
FIGURE CAPTIONS

Figure 1. Scanning electron micrograph of the surface of a typical template membrane.

Figure 2. Scanning electron micrographs of typical template-synthesized polyheterocyclic microtubules.

Figure 3. Scanning electron micrograph of template-synthesized Au microtubules.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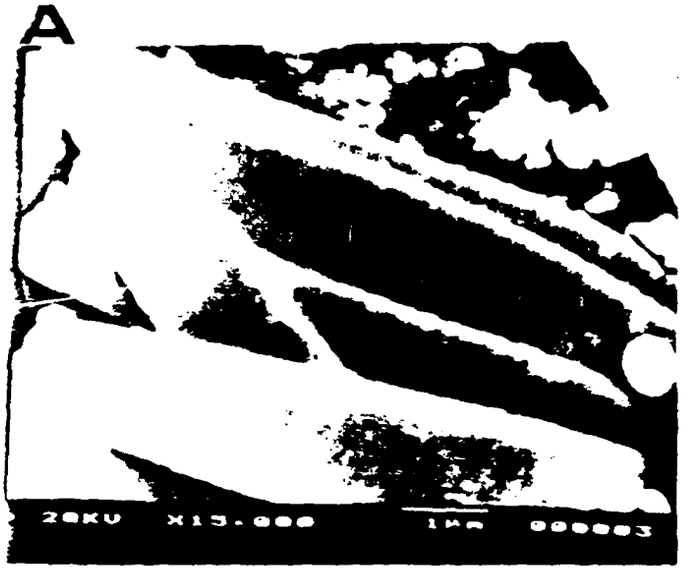
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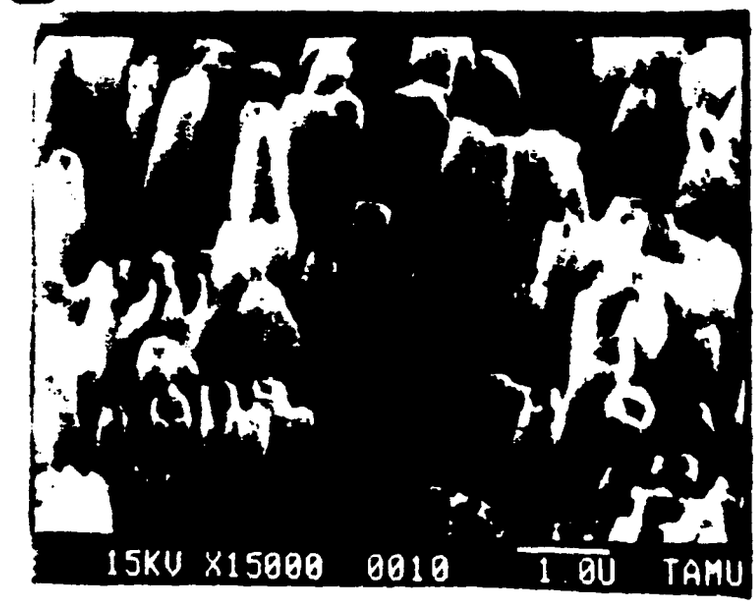
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