Communications to the Editor

Template Synthesis of Organic Microtubules[†]

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Organic microtubules have recently caused a great deal of excitement in the physics, chemistry, and materials science communities.[1] Such tubules are inherently intriguing chemical systems and have myriad proposed technological applications;[1] they may also be useful as mimics of biological microtubules.[2] The only known synthetic route for preparing organic microtubules[3] involves extremely expensive reagents and produces tubules with a broad range of diameters and lengths. We have recently discovered a new method for synthesizing organic microtubules. This method uses a microporous membrane as a template during tubule synthesis. The most significant advantage of this template method is that it yields tubules with monodisperse diameters and lengths. We describe this template synthetic method in this paper.

The template method entails heterogeneous synthesis of an organic polymer across a microporous membrane. The simplest embodiment of this concept is shown schematically in Figure 1. The template membrane (a Nuclepore polycarbonate filter) contains linear, cylindrical pores of equivalent pore diameter.[4] This membrane separates a solution of a monomer from a solution of a polymerization reagent. We have used heterocyclic monomers (e.g., pyrrole) and ferric salts as the polymerization reagent.

The monomer and polymerization reagent diffuse toward each other, through the pores in the template membrane, and react to yield the polymer. We have discovered, however, that the nascent polymer chains adsorb to the pore walls yielding a thin polymer "skin".[5] This "skin" becomes thicker and thicker with time, until a solid fiber is produced.[4a] If polymerization is quenched before this point, polymeric tubules are obtained.[5]

A typical synthesis is as follows: Aqueous $FeCl_3$ (2 M) and aqueous pyrrole (0.3 M) were added to the outer and inner compartments, respectively, in Figure 1. The membrane used has 0.5-μm pores. Polymerization was allowed to proceed for 25 s. (The duration of the polymerization period determines the thickness of the wall of the microtubule.) Polymerization was then quenched by rinsing the membrane with water.

Template synthesis can also be conducted electrochemically by using membrane-modified electrodes similar to those described in refs 4b,c. A typical synthesis is as follows: A Nuclepore membrane (1.0-μm pores) was mounted onto the surface of a 0.5-cm^2 Pt disk electrode.[4b,c] This electrode was immersed into a CH_3CN solution 0.5 M in *N*-methylpyrrole and 0.2 M in Et_4NBF_4. Polymerization was accomplished galvanostatically at a current density of 1.0 mA cm^{-2};[4c] a total of 0.3 coulombs of charge was passed.

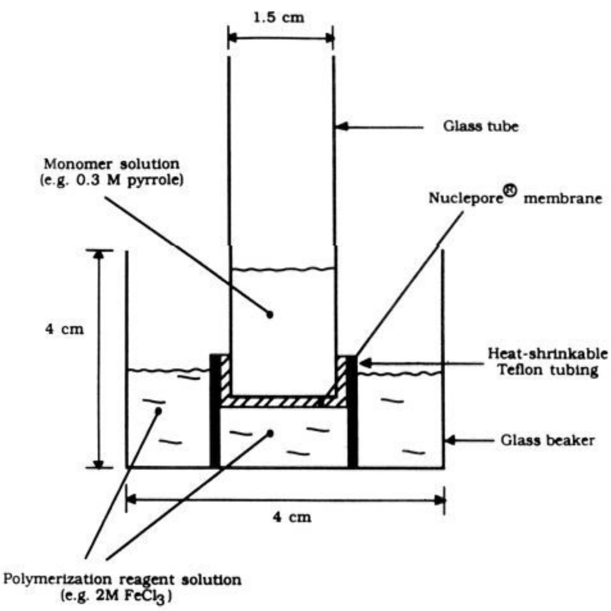

Figure 1. Schematic representation of apparatus used to conduct chemical template synthesis of organic microtubules.

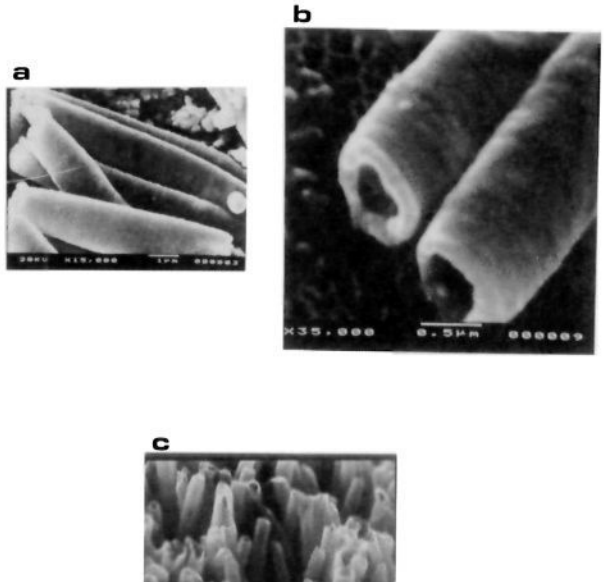

Figure 2. Scanning electron micrographs of chemically synthesized polypyrrole microtubules (a and b) and electrochemically synthesized poly(*N*-methylpyrrole) microtubules (c).

Both the chemical and electrochemical syntheses yield a collection of polyheterocyclic tubules dispersed within the pores of the template membrane. This configuration would be ideal for some of the proposed applications of organic microtubules.[1] The ability to obtain such a parallel array of tubules is a unique advantage of the template method. However, it might also be desirable to free and then collect the tubules. This can be ac-

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[†] Part of this work was conducted at Texas A&M University.

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[5] In addition thin polyheterocyclic skins being formed on the pore walls, thin (ca. 0.2 μm) polyheterocyclic layers are formed on both membrane faces. These layers must be removed before dissolution of the template membrane. This can be accomplished by rubbing with a Kim-Wipe.

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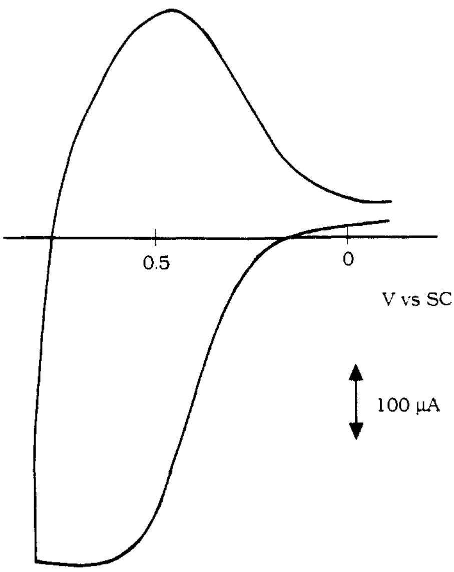

Figure 3. Cyclic voltammogram of an array of poly(*N*-methylpyrrole) microtubules (see Figure 2c). Tubule diameter was 1.0 μm. The substrate electrode was a 0.5-cm^2 Pt disk. The supporting electrolyte was 0.2 M Et_4NBF_4 in CH_3CN. The scan rate was 10 mV s^{-1}. Anodic currents are down and cathodic currents are up in this figure.

complished by dissolving the membrane in CH_2Cl_2 and collecting the tubules by filtration.[4c,6]

Figure 2a shows an electron micrograph of typical template-synthesized polypyrrole microtubules, Because the Nuclepore membrane used was 8 μm thick, these tubules are 8 μm long. This ability to produce tubules with monodisperse lengths is a unique and important feature of the template method. Furthermore, because Nuclepore membranes have monodisperse pore diameters,[4b] monodisperse tubule diameters are also obtained (Figure 2b). Finally, tubule diameter and length can be varied, at will, by varying the characteristics of the template membrane.[4b]

Figure 2c shows an electron micrograph of electrochemically synthesized poly(*N*-methylpyrrole) tubules. Note that while the template membrane has been dissolved away, the tubules are still arranged in an upright array. This is because electrochemically synthesized tubules are connected at their bases to a thin contiguous film of the heterocyclic polymer. This ability to produce an upright array of tubules, connected by a common base-layer film, is another unique, and perhaps useful, feature of the template method.

The polyheterocyclic tubules show redox reactions typical of the parent polymer[7] (Figure 3). Thus, like the parent polymer, these tubules can be reversibly switched between electronically insulating and electronically conductive states.[7] Furthermore, we have recently shown that template synthesis dramatically enhances the electronic conductivities of such polymers.[4a] The redox chemistry in Figure 3 also raises the interesting possibility of making tubule-based electroreleasing systems.[8] We are currently pursuing this possibility.

Finally, it is interesting to speculate on the mechanism responsible for tubule formation in the template process. The key to this process is the adsorption of the nascent polyheterocyclic chain to the pore wall. Heterocyclic polymers are synthesized via oxidation of the monomer and subsequent coupling of the radial cations obtained;[7] a cationic polymer is produced. The pore walls in Nuclepore membrane are anionic,[9] Thus, electrostatic attraction undoubtedly contributes to the adsorptive interaction between the pore wall and the nascent polyheterocyclic chain. We are using this hypothesis to identify other polymers and membranes which can be used for template syntheses of organic microtubules.

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Alkali Metal Recognition Induced Isomerization of Spiropyrans

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A new class of host molecules whose optical properties are markedly perturbed by the presence of cations are of current interest.[1] These "recognition and signaling" molecules may stimulate the investigation of molecular sensors for biologically important alkali-metal ions. Thus, numerous fluoroionophores[2] and chromoionophores[3] have been synthesized.

We report herein the preliminary results obtained for spiropyrans[4] bearing a monoaza-crown ring (**1**) as a recognition site,[5] of which isomerization to the colored merocyanines (**2**) is induced by recognition of alkali-metal cations (Scheme I). This new type of chromoionophore is conceptually different from the crown ether dyes so far synthesized, because in the latter cases, the absorption bands of chromophores are merely shifted by the complexation of cations.

The new spiropyrans **1** were prepared in three steps from *N*-chloroacetyl monoaza-crown ethers **7**[6] in 28–32% overall yields (Scheme II).

The spiropyrans **1** thus prepared showed no absorption bands above 450 nm in nonhydroxylic solvents (CH_3CN, acetone, etc.). However, addition of alkali-metal iodides to these solutions gave rise to changes in their absorption spectra. When a 5-fold molar

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