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Template Synthesis of Conducting Polymers - Enhanced Conductivity, Enhanced Supermolecular Order, Interesting Microstructures

by

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Template synthesis entails the synthesis of an electronically conductive polymer within the pores of a microporous membrane. The membranes employed have cylindrical pores of equivalent pre diameter. These pores spatially-confine the synthesis and act as templates for the resulting polymer. Conductive polymer fibrils are obtained, where the fibril diameter is determined by the pore diameter. We have shown that these fibrils can be orders of magnitude more conductive than conventional films of the analogous polymer. Conductive polymer tubules can also be obtained in certain membranes. Conductivity, supermolecular order, and tubule synthesis will be discussed.

INTRODUCTION

Template synthesis entails the synthesis of an electronically conductive polymer within the pores of a microporous membrane. The membranes employed have cylindrical pores of equivalent pore diameter (1-5). These pores spatially-confine the synthesis and act as templates for the resulting polymer. Conductive polymer fibrils (see Figure 1) and in some cases hollow fibrils (i.e., tubules, see Figure 2) (4) are obtained. We have used the template method to synthesize electronically conductive polymer fibrils and tubules with diameters ranging from 10 nm to 12 μm. This template synthesis is interesting from a variety of view points. First, this method allows for the production of polymeric micro and nanotubules with tobacco dimensions: this is particularly important for the case of tubules since there is currently only one other known method for synthesizing organic microtubules (6). We have also shown that the conductivities of nanoscopic conductive polymer fibrils can be orders of magnitude higher than conductivities of films of the analogous polymer (3). Finally, we have shown that the nanoscopic fibrils and tubules have enhanced supermolecular order. In this paper we will discuss various aspects of template synthesis and of the fibrils and tubules obtained.

EXPERIMENTAL

Polymer Syntheses. Nuclepore polycarbonate microporous membranes were obtained from the Nuclepore Corporation (Pleasanton, CA) (1,3). Anopore alumina microporous membranes were obtained from Anotech Ltd. (2,5). Polycetylene fibrils (Figure 3) were synthesized by polymerizing acetylene within the pores (dia = 200 nm) of an Anopore filtration membrane (5). The polymerization catalyst was Ti(OBu)₄/AlEt₃ (7). The Anopore membrane and catalyst solution were added to the polymerization vessel (a septum-sealed glass tube). The catalyst solution was impregnated into the pores of the host by evacuated vessel, heating to 70°C, and then back filling with Ar. Excess catalyst was removed with a syringe. The vessel was then evacuated again and acetylene was introduced. Polymerization proceeded for 2 hours, at 0°C. The membrane was then washed in methanol, and then dried in vacuo (5). Polypyrrole (PPy) and poly(3-methylthiophene) tubules and fibrils were template-synthesized using the apparatus shown in Figure 4 (3,4). The Nuclepore membrane separated the monomer solution from a solution of a chemical oxidant, which served as the polymerization agent. 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 that the nascent polymer chains absorb to the pore walls yielding a thin polymer "skin" (3,4). This "skin" becomes thicker and thicker with time, until a solid fiber is produced (3). If polymerization is quenched before this point, polystyrene tubules are obtained (4).

A typical synthesis is as follows: Aqueous FeCl₃ (2 M) and aqueous pyrrole (0.3 M) were added to the compartments, respectively, in Figure 4. The membrane used had 0.5 μm pores. Polymerization was allowed to proceed for the desired time. If tubules were desired, short polymerization times were employed (e.g., 25 sec). The duration of the polymerization period determines the thickness of the "skin" on the microtubule. If fibrils were desired, longer polymerization times (e.g., 30 min.) were used.

Conductivity Measurements. The conductivities of the PPy fibrils were obtained by measuring the bulk resistances of the fibril/Nuclepore composite membranes (3,5). Resistances were measured using a two-point method based on the apparatus shown in Figure 5. The upper electrode is a 0.5 μm dia. Pt wire sealed in glass. The lower electrode is a bed of 0.2 μm dia. Ag particles. A pressure of 1000 atm was applied between the upper and lower electrodes during the resistance measurements. This apparatus provides the bulk resistance of the composite membrane, R. If the composite membrane consists only of a distributed polymer fibril and intervening polycarbonate, then Rₚ is given by 1/Rₚ = 1/Rₚ + 1/Rₚ, where Rₚ is the parallel sum of the resistances of the conductive polymer fibrils and Rₚ is the resistance of the intervening polycarbonate. Because Rₚ >> Rₚ, the equation becomes 1/Rₚ = 1/Rₚ = n/Rₚ, where n is the number of fibrils in the composite membrane, and Rₚ is the resistance of an individual fibril. We know, from independent electron microscopic analysis (9) (the average size of the pores in all of the Nuclepore membranes used here), that Rₚ provides the conductivity of a single fibril (3).

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tubules with polydisperse diameters and lengths. As indicated in Figures 1 through 3, the template method yields fibrils and tubules with monodisperse dimensions. Plots of conductivity vs. diameter for PPy fibrils are shown in Figure 6; data for two different synthesis temperatures are shown. The smallest-diameter fibrils show conductivities which are an order of magnitude higher than the conductivity of conventional PPy film or powder (3). These are the highest conductivities ever achieved for PPy.

PIRAS data for the C-H stretching mode in the PA fibrils are shown in Figure 7 (11). In analogy to the stretch-oriented material (11), the fibrils preferentially absorb light polarized parallel to the fibril axis. An R value of 1.5 was obtained. R can be used to calculate the average orientation angle (θ) between the polymer chains and the fibril axis (11). This requires a value for the angle (α) between the transition moment of the vibration and the axis of the polymer chain (11); α = 18° for the C-H stretching mode in PA (11). A θ value of 22.5° is obtained for the PA fibrils, indicating a high degree of parallel orientation.

CONCLUSIONS

We have shown that template-synthesis yields enhanced supermolecular order and higher electronic conductivities in conductive polymers.

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Figure 1. Schematic of apparatus used to measure fibril conductivity.

Figure 2. PIRAS data for template-synthesized polyacetylene fibrils. $A_1$ and $A_2$ are absorbencies of beams polarized at 45° and perpendicularly (respectively) to the axes of the fibrils.

Figure 3. Plots of fibril conductivity vs. fibril diameter for typical polypyrrole fibrils.