

CHEMISTRY

Polymer Nanotubes by Wetting of Ordered Porous Templates

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We have developed a simple technique for the fabrication of polymer nanotubes with a monodisperse size distribution and uniform orientation. When either a polymer melt or solution is placed on a substrate with high surface energy, it will spread to form a thin film, known as a precursor film, similar to the behavior of low molar mass liquids (1, 2).

Similar wetting phenomena occur if porous templates are brought into contact with polymer solutions or melts: A thin surface film will cover the pore walls in the initial stages of wetting. This is because the cohesive driving forces for complete filling are much weaker than the adhesive forces. Wall wetting and complete filling of the pores thus take place on different time scales. The latter is prevented by thermal quenching in the case of melts or by solvent evaporation in the case of solutions, thus preserving a nanotube structure. If the template is of monodisperse size distribution, aligned or ordered, so are the nanotubes, and ordered polymer nanotube arrays can be obtained if the template is removed. Any melt-processible polymer, such as polytetrafluoroethylene (PTFE), blends, or multi-component solutions can be formed into nanotubes with a wall thickness of a few tens of nanometers. Owing to its versatility, this approach should be a promising route toward functionalized polymer nanotubes.

We used ordered porous alumina and oxidized macroporous silicon templates with narrow pore size distribution (3). Extended regular pore arrays were prepared by lithography. The pores are well-defined, straight, with a smooth inner surface and with diameters D_p between 300 and 900 nm. To process melts, we placed the polymer on a pore array at a temperature well above its glass transition temperature, in

the case of amorphous polymers, or its melting point, in the case of partially crystalline polymers. The liquid polymer forms a thin wetting film covering the entire pore surface on a time scale ranging from a few minutes to half an hour. Polymer solutions were dropped on the

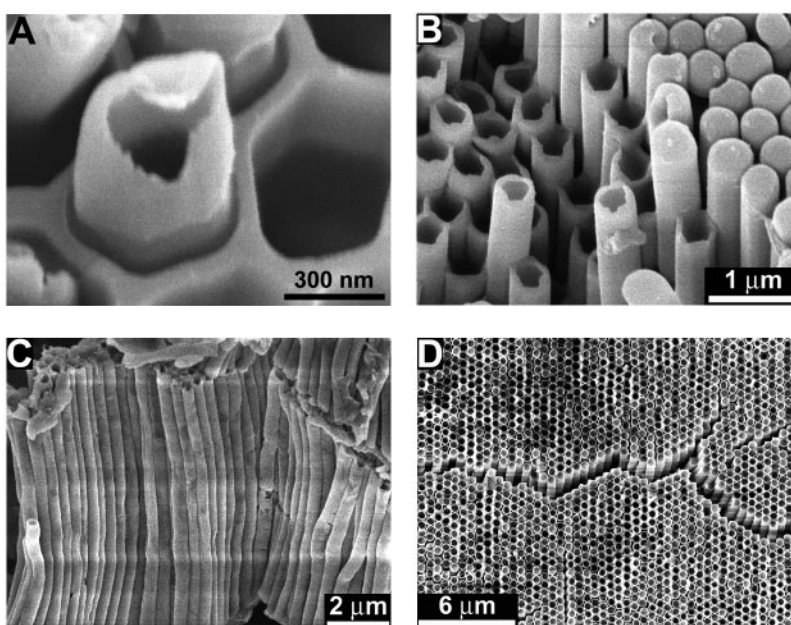


Fig. 1. Scanning electron micrographs of nanotubes obtained by melt-wetting. (A) Damaged tip of a PS nanotube ($M_n \sim 850,000$ g/mol) protruding from a porous alumina membrane. The substrate, on which the pore array was located, has been removed to uncover the tube tips. (B) Ordered array of tubes from the same PS sample after complete removal of the template. (C) Array of aligned PTFE tubes. (D) PMMA tubes with long-range hexagonal order obtained by wetting of a macroporous silicon pore array after complete removal of the template.

templates at ambient conditions (fig. S1A) (4). The resulting nanotubes obtained from either method had wall thicknesses between 20 and 50 nm and lengths of up to 100 μm . Oligomers as well as polymers with molecular masses M_n up to several hundreds of thousands of grams per mol were processed. Figure 1 depicts nanotubes formed from several polymers by melt-wetting. The tip of a polystyrene (PS) nanotube ($M_n \sim 850,000$ g/mol) formed in an alumina template was uncovered by etching the alumina substrate with aqueous potassium hydroxide (Fig. 1A) (4). Figure 1B shows the same sample after the complete removal of the template. Figure 1C depicts an array of aligned PTFE nanotubes obtained by wetting an alumina template and Fig. 1D a highly

ordered array of polymethyl methacrylate (PMMA; $M_n \sim 80,000$ g/mol) nanotubes prepared by wetting a macroporous silicon template. After selectively dissolving the template, the remaining nanotube array still exhibits its hexagonal long-range order.

The wetting technique can be easily extended to prepare functionalized nanotubes, for example, palladium/polymer composite nanotubes. We first wetted the porous templates with a solution containing poly-L-lactide (PLLA) and palladium(II)acetate under ambient conditions. After evaporation of the solvent dichloromethane, a PLLA/palladium(II)acetate film covered the pore walls. The template was subsequently annealed in vacuum at temperatures of up to 300°C to degrade PLLA (5) and to reduce Pd. In a second wetting step, molten PS was added, so that Pd/PS composite tubes were formed (fig. S1B). Energy-dispersive x-ray microanalysis verified the presence of Pd (fig. S1C), and selected area electron diffraction of single composite tubes revealed that it was metallic with a typical crystallite size of 2 to 3 nm (fig. S1D). As demonstrated by this example, template-wetting should have an outstanding potential in providing customized nanotubes for a broad range of applications in nanoscience.

References and Notes

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6. Support from the Deutsche Forschungsgemeinschaft (WE 2637/1-1 and WE 496/19-1) and transmission electron microscopy investigations by C. Dietzsch are gratefully acknowledged.

Supporting Online Material

www.sciencemag.org/cgi/content/full/296/5575/1997/DC1
Materials and Methods
Fig. S1

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