Nanostructuring of Poly(aryleneethynylene)s: Formation of Nanotowers, Nanowires, and Nanotubules by Templated Self-Assembly

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We report novel, nanoscale polyaryleneethynylene (PAE) morphologies that are created by a solution molding process utilizing nanostructured anodiscs (Whatman filter disks, alumina wafers). Depending upon the molecular structure of the utilized PAE, different self-assembled nanostructures are formed during templating.

Nanostructuring of conjugated polymers is an important process that modifies their electronic and electron transport properties.[1−3] Nanostructuring plays a crucial role in device applications, for example in the fabrication of photovoltaic cells, where self-assembly of an interpenetrating network of a conjugated polymer and an *n*-semiconductor is the critical factor for success.[4] Nanostructuring is of interest in photonic band gap materials[5] and fabrication of heterojunction devices in which two different conjugated polymers have to interact intimately to increase their interface.[4] In many cases, conjugated polymers show self-assembly into nanoscopic structures; however, their self-assembly modes are difficult to control and not always predictable.[6] Thus, it is of interest to develop processes that furnish conjugated polymers with an engineered nanoshape. A potent and elegant solution for this problem was developed by Martin for organic, inorganic, and metallic nanostructures utilizing templating procedures.[3] This approach utilizes filter anodiscs that are commercially available, are inexpensive, and display pores of defined size and diameter. The material of choice is deposited into these pores, and the anodisc is dissolved in dilute base or acid to give nanotubes of excellent quality. While metallic and insulator nanostructures have been made by this method, only very few examples of conjugated polymers have been structured by this method.[3] Polyaniline, polythiophene, and polypyrrole are examples of polymers that form electrochemically *in* the preformed pores of the filter disk.[3] However, there is a large number of conjugated polymers available that do *not* form by electropolymerization. As a result, these materials have to be nanostructured in a different way. In this paper, we describe the fabrication of semiconducting nanotowers, nanowires, and nanotubules by solution-phase self-assembly of poly(aryleneethynylene)s **1**−**5**.[7]

In the first experiment, a dilute solution of polymer **1** was drop cast (Figure 1, geometry II) onto a Whatman filter anodisc[8] and allowed to dry. Subsequent dissolution of the alumina mask led to products that had formed nanotubes of poor quality (by SEM). Utilizing dilute solutions of **1** led to fragile nanostructures that were washed away when dissolving the anodisc. In subsequent experiments, we utilized more concentrated solutions (10 mg/mL, see experimental details in the Supporting Information). These solutions were utilized mostly in geometry II, and gave more robust products that were examined by SEM. Polymer **1** forms both

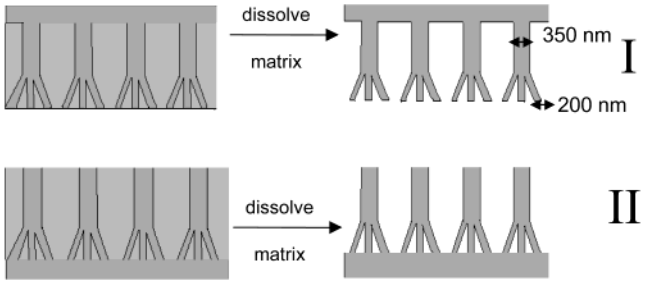
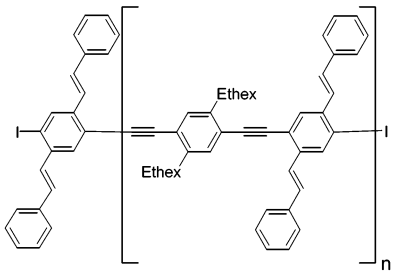


Figure 1. Schematic of the formation of PAE nanotowers and nanotubes.



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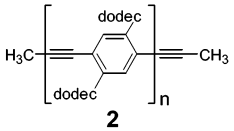

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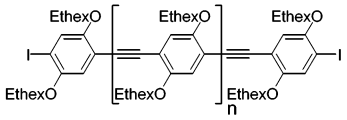

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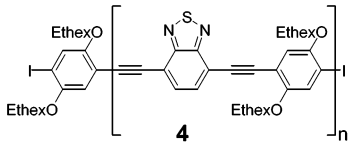

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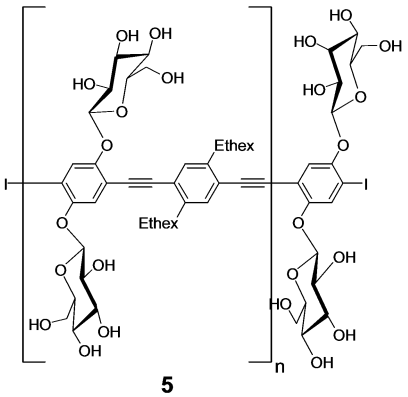

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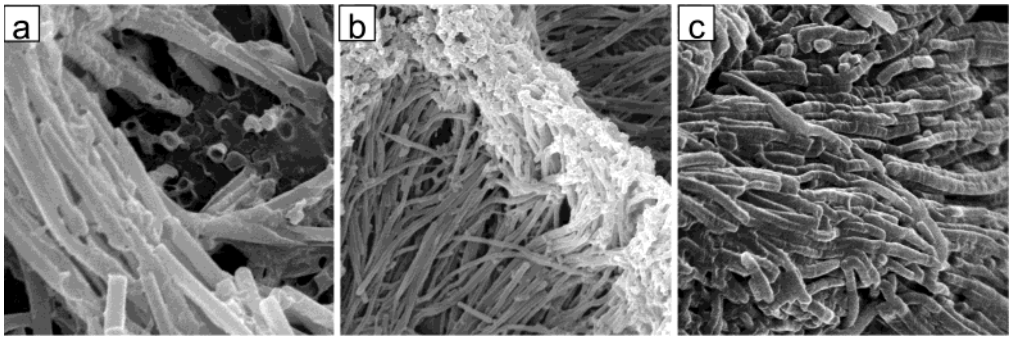

Figure 2. (a) Polymer **1.** Picture dimensions are 6 × 6 μm. Drop-cast films are observed. The junction of hollow and solid tubules is shown. (b) Polymer **4**. Picture dimension is 18 × 18 μm. Well visible is the wirelike characteristic of the polymer preparation. The aspect ratio of the wires is in excess of 50. The nanostructures are almost defect-free. The cauliflower geometry of the top is visible. (c) PPE **3.** The picture dimension is 6 × 6 μm (right). Particularly interesting is the horizontal striation of 140 nm in these blunted wires. The aspect ratio of tubes **3** is approximately 140.

filled and hollow nanotubes with an aspect ratio of approximately 32 (Figure 2a). The width of the tubes ranges from 300 to 350 nm, which is in good agreement with the specifications of the filter pores. The length of the tubes ranges from 2 to 10 μm. The aspect ratio is quite low (7−32). Even though the length of the channels in the Whatman filters is 60 μm, the pores of the disk are only slightly penetrated by the viscous polymer solution. Annealing of the anodisc/polymer hybrid structure did not lead to better penetration of the polymer into the inorganic pores. Similarly dimensioned nanostructures were observed after dissolution of the anodisc.

We wanted to explore the influence of PAE structure on the process of the nanowire formation. As a consequence, we investigated PAEs **2**−**5.** The heterocyclic polymer **4** (Figure 2b) formed well-developed wires that seemed to penetrate the pores almost completely. The dimension of these wirelike structures is 350 nm × 30 μm, and the aspect ratio of these solid wires is approximately 90. The wires are well developed over the entire area of the film. Visible is the splicing of the template that is preserved in the top part of the wires. This splicing leads to a cauliflowerlike topology that is typical for a geometry II (Figure 1) preparation. The heterocyclic polymer **4**, an excellent film-former, is almost ideal for the generation of tubules and wires of great length.

The more polar, sugar-substituted, and methanol-soluble PPE **5** forms a different nanoscale morphology altogether. For **5**, short "macaroni" tubules are formed (Figure 3a). Their outer diameter is 330 nm, while the diameter of the "eye" is 210 nm. The tubules are 2 μm long, and their aspect ratio is only slightly above 6. Concentrated solutions give isolable macaroni structures, while dilute solutions give materials that fragment upon dissolution of the anodisc. In the case of **5,** the hollowness of the tubes is visible via defects that lead to some holes in the walls of the tubes. The highly hydrophobic didodecyl−PPE **2** forms short nanotubes that show the cauliflower geometry of the spliced matrix (Figure 3b).

We examined as well a moderately polar PPE, bis-ethylhexyloxy−PPE **3**. This PPE furnished long, well-developed wire-type structures that seem to be solid, completely filled, 200−300 nm thick, and up to 43 μm long. Aspect ratios of 140−215 result. These materials seem to penetrate the membrane almost completely. Additionally, these tubules show (Figure 2c) horizontal striations that are slightly irregular but have an average

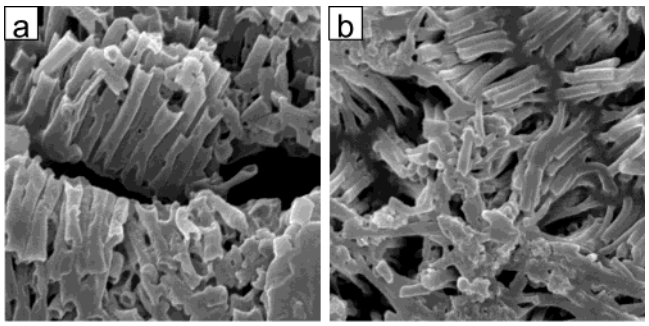

Figure 3. Sugar−PPE **5** forms thick macaroni-type structures. The thickness of the wall in these tubes is 60 nm and the picture dimensions are 6 × 6 μm. On the right-hand a picture of the cauliflower geometry of the didodecyl−PPE **2.** The picture dimensions are 9 × 9 μm. The splitting into the narrow base-wires is well visible and represents the topology of the Whatman filter anodisc.

width of 140 nm. In all of the examined cases, we obtain nanostructures which are covered by the bulk material in the form of a thin film on the bottom. An interesting observation is that the formation of the nanostructures (see Supporting Information) is not visibly correlated with the molecular weights[9] of the examined PAEs.

In conclusion, we have extended Martin's nanostructuring process to PAE's. Up to now, conjugated polymers have been *formed* inside the pores of anodiscs. We have demonstrated that PAE's can be *cast* into the mesopores of anodiscs to give free-standing, high aspect ratio nanostructures of excellent quality after the removal of the template. The nanostructuring of conjugated materials may lead to advancement in semiconductor applications by increasing the surface area of the polymer under consideration. At the moment, we are attempting to process the nanostructrures into thin films of homogeneous thickness by spin casting, and our future work in this area will focus on the construction of photovoltaic and light emitting devices in collaboration with electrical engineers.

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Supporting Information Available: Text giving experimental details of preparation of the nanotowers, a table describing their properties, and figures showing more SEM pictures. This material is available free of charge via the Internet at http://pubs.acs.org.

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