Supplementary Material

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

James N. Wilson, Carlito G. Bangcuyo, Belma Erdogan, Michael L. Myrick, and Uwe H. F. Bunz*

USC NanoCenter, Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208 (USA), Fax: (+1) 803-929-0267, Email: bunz@mail.chem.sc.edu

Experimental.

Synthesis of the polymers 1-5 has been described.1 Solutions of the polymers were prepared in chloroform or THF by heating the respective polymer. Dilute solutions were approximately 1 mg polymer/mL solvent and concentrated solutions were 10-15 mg polymer/mL solvent. Films were drop-cast from chloroform onto the commercially available anodiscs (Whatman Anodisc 47; 0.2 µm pore size); approximately 0.5 mL of the solution were utilized per film. After allowing the solvent to evaporate for 1 h, the discs were affixed onto a stationary phase (3M clear packing tape), and placed in a 1 mol/L NaOH solution for 1 h to allow the template to dissolve completely. The films were rinsed three times with deionized water, and dried briefly in a vacuum oven at 90-100 °C. The samples were cut into small portions (pie pieces, 1 cm length) to fit as many as possible samples on the sample holder. The samples were then placed into a sputterer (Denton Vacuum Inc., Desk II) and 0.4 nm of Au was sputtered onto the films. The samples were then placed in a scanning electron microscope (Hitachi 2500 Delta), and the pictures were obtained digitally.

Reference
Table 1. Properties of Nanostructures Formed by Poly(aryleneethynylene)s 1-5 Utilizing Whatman Filter Anodiscs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sample Geometry</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed structure, pristine</td>
<td>Only tubules</td>
<td>Tubules and towes</td>
<td>Towers</td>
<td>Towers</td>
<td>Towers, with cauliflower tops</td>
<td>Towers and tubules</td>
</tr>
<tr>
<td>Length</td>
<td>Thin films 2.5 µm</td>
<td>Thick films &gt; 9.5 µm</td>
<td>Thin films 7 µm</td>
<td>Thick Films 43 µm</td>
<td>Thick film 30 µm</td>
<td>Thick films tower 12 µm tubule 3 µm</td>
</tr>
<tr>
<td>Width</td>
<td>Thin films D₁ 250 nm D₉ 350 nm</td>
<td>Thick films 300 nm</td>
<td>Thin films 300 nm</td>
<td>Thick films 200 – 300 nm</td>
<td>Thick film 350 nm</td>
<td>Thick films D₁ 270 nm D₉ 340 nm</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>7</td>
<td>&gt; 32</td>
<td>23</td>
<td>Up to 140</td>
<td>86</td>
<td>Towers 34 Tubules 8.6</td>
</tr>
<tr>
<td>Pₙ</td>
<td>55</td>
<td>512</td>
<td>316</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDI</td>
<td>2.8</td>
<td>3.2</td>
<td>2.4</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comment</td>
<td>Thin films give fragile tubules.</td>
<td>High density of fibers prevented accurate measurement of length of towers.</td>
<td>Predominantly rigid towers randomly spaced. Geometry I did not give useful structures.</td>
<td>Thick films show highly textured fibers. Geometry I did not give useful structures.</td>
<td>Dense well developed towers, and some tubules observed at base for thick films.</td>
<td>Dense well developed towers, and some tubules observed on top of film.</td>
</tr>
</tbody>
</table>

The utilized filters have pore width of 340 nm, Anodisc 47, 0.2 µm.
Figure 1. Polymer 1. Picture dimensions are 6x6 µm (left) and 4.5 x 4.5 µm (right). Drop-cast films. On the left picture the junction of hollow and solid tubules is shown. The right picture shows a perfect fill of the mesopores.
Figure 2. Polymer 4. Picture dimensions are 18 x 18 μm in both cases. Well visible is the wire-like characteristic of the polymer preparation. The aspect ratio of the wires is in excess of 50. Especially remarkable is that the nanostructures are almost defect-free. On the left side the cauliflower geometry of the top is visible. This geometry mirrors the geometry of the utilized Whatman mask.

Figure 3. PPE 3. The picture dimensions are 9 x 9 μm (left) and 6x6 μm (right). Particularly interesting is the horizontal striation of 140 nm in these blunted wires. The aspect ratio of 3 is approx. 30.
**Figure 4.** 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 x 6 µm. On the right hand a picture of the cauliflower geometry of the didodecyl-PPE 2. The picture dimensions are 9 x 9 µm. The splitting into the narrow base-wires is well visible and represents the topology of the Whatman filter anodisc.