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Linear nano-templates of styrene and maleic anhydride alternating copolymers

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ABSTRACT

Poly(styrene-alt-maleic anhydride) (SMA) self-assembles in aqueous solution to form nanotube structures. These can be used as templates to linearly guide the growth of a secondary polymeric or inorganic material. Templates are made starting from a basic SMA solution, followed by slow pH decrease by dialysis against deionized water, until a 50% degree of protonation is reached. The nanotube structure is composed of multiple polymer chains, associating sideways by π-stacking to form the nanotube walls. The SMA templates were used to grow linear composites, which shows the applicability of the template properties and also confirms the nanotube association mechanism. Linear polymer composites were formed using this SMA template: pyrrole was polymerized, silver nitrate was reduced to silver and silver cyanide nanowires were grown.

1. Introduction

A nanotube can be described as a hollow curved macromolecular chemical structure, or assembly, with a diameter in the nanometer range of any length [1–5]. Organic nanotubes are of interest for their versatility as templates, and because they can be chemically modified to create new functional materials. A wide variety of inorganic [6–9], organic [10–12] and hybrid organic/inorganic [5,13,14] nanotubes and nanorods have been fabricated through molecularly self-assembled and template-assisted methods [15,16]. Template techniques to fabricate nanoscale structures, such as nanorods, are useful because they offer possibilities not achievable with lithographic techniques.

We have recently successfully used an organic template of poly(styrene-alt-maleic anhydride) (SMA) to grow silver cyanide nanowires with diameters ranging from 5 to 100 nm, and lengths varying from hundreds of nanometers to several microns. AgCN growth is templated by the presence of hydrolyzed SMA at 50% degree of protonation [17]. Hydrolyzed SMA is a copolymer with alternating hydrophilic succinic acids and hydrophobic styrenes. This polymer has three different protonation states, with two pKa values [18]: pH 4.4 and pH 10.3. AgCN-polymer nanowires are shown in Fig. 1. The preparation and characterization of these AgCN structures, as well as their conversion to metallic silver, is described elsewhere [17]. AgCN nanowires were synthesized using different M_w SMA: 1.6, 12 and 50 kDa. In all cases, the smallest rod diameter is about 5 nm, and the nanowires are 1–3 orders in magnitude longer than a single polymer contour length. Larger AgCN–SMA nanowires have an underlying structure composed of multiple smaller rods of comparable diameter stacked side-by-side (inset Fig. 1(a)). When the sample is sonicated during AgCN growth, larger fibers are broken into shorter ones, and bundles range from 1 to 5 nanowires.

Conformational and energy calculations are presented, supporting the nanotube formation mechanism proposed by Malardier-Jugroot et al. [19]: the polymer nanotube walls are formed from multiple SMA polymers associating

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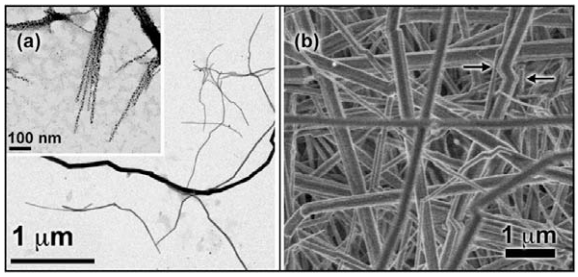

Fig. 1. (a) TEM image of linear AgCN–SMA nanowires (M_w 1.6 kDa). Inset: enlarged view of sonicated fibers, showing underlying structure of stacked nanorods. (b) SEM image of the AgCN–SMA stacks of nanowires without sonication. In (a) and (b), kinks (arrows) indicate 45° folds.

sideways through π-stacking. Nanotubes grow in length by additional polymer associations at the open ends. Additionally, sideways aggregation forms nanotube bundles. Molecular modeling and experimental studies has helped understand the required conditions to form and use this nanotube template in aqueous solution. In this paper, we focus on a novel preparation method to produce these SMA templates in improved yields. We also focus on the dimensions of the structural features obtained from different templating experiments.

2. Experimental

2.1. Materials

Poly(styrene-alt-maleic anhydride) (SMA) of different molecular weights (M_w) were used. High M_w SMA, 50 kDa, was purchased from SP^2 Scientific Polymer Source. Intermediate M_w SMA, 12 kDa was synthesized using a UV-controlled RAFT polymerization, Wu et al. [20]. The polymer had a 50.1% styrene and 49.9% maleic anhydride content from HNMR. The molecular weight was determined by GPC using polystyrene standards as references. pK_a values from 12 kDa SMA titrations agreed with reported values [18].

2.2. Instruments

The pH was measured using an Accumet Basic AB15 (Fisher Scientific). AFM images were acquired in intermittent mode on a Digital Instruments NanoScope IIIA, using SiN tips (Veeco). NanoScope version 6.13r software was used for image analysis. TEM measurements were performed on a JEOL JEM-2000FX 80 kV. TEM size analysis was performed using SigmaScan Pro (version 4).

2.3. Computational methods

All calculations were performed using Gaussian 03 program [21]. The structure of hydrolyzed SMA, 50% protonated, was investigated by Semi-Empirical PM3 calculations. Optimizations were performed with Li metal atoms and without, by postulating a negative charge for each succinic acid. The conformations obtained using a Li atom bound to the succinic acids were not significantly different. The metal atoms balanced the negative charges on the oxygens at a 50% protonation, and localizing the charges. Using the metal atoms required fewer iterations and the calculations converged faster. This method was used to compute different chirality polymers. Terminal monomers exhibited edge effects, which distorted their spatial arrangement with respect to the inner monomers of the polymer chain, and therefore did not represent the overall polymer structure. Because only short oligomers could be studied and because the centre block is representative of a long polymer chain, the terminal monomers were removed for geometry comparisons. PM3 energies for π-stacking interactions overestimate electrostatic contributions and were corrected by an *ab-initio* Hartree–Fock MP2 energy calculation. MP2 closely predicts experimental energies of π-stacking aromatics [22–23]. Gas phase calculations were performed because water solvation shells added to SMA were shown not to significantly alter the polymer conformation, compared to gas phase conformation [24].

2.4. SMA nanotube preparation

The maleic anhydrides of SMA were hydrolyzed: excess NaOH was added, to obtain a pH > pKa_2 = 10.3 [18]. Three mole equivalents of NaOH was added (SMA monomer = (styrene–maleic anhydride)). The base was dissolved in deionized water, the polymer, 0.1 wt.%, was added and stirred until it dissolved (overnight). 50% degree of protonation was achieved by dialyzing the basic solution against 2 L of deionized water, using 1000 Da cut-off regenerated cellulose membrane (SpectraPore). The solution was changed twice daily and the pH inside the dialysis bag recorded after every water change, over 2–3 days. Dialysis was stopped at pH 7.5–8. SMA concentrations were 2–5 mg/ml. The concentration was determined by UV–vis absorbance (258 nm), and a Beer's law calibration curve. The wt.% concentration was related to the absorbance: [SMA] (mg/ml) = $(A - 2.42)/1288$. SMA nanotubes were prepared in a buffer solution with the 12 kDa SMA. 1.5 mole equivalents of NaOH was added. One liter of pH 6.5 buffer was prepared using K_2PO_4 and 1 N NaOH standard solution (Riel-de-Hägen). The basic solution was dialyzed against buffer for 3 days, 1000 Da cut-off membrane, without changing the solution. The final pH inside and outside the dialysis bag was pH 6.8.

2.5. Linear composites and sample preparation for imaging

Pyrrole polymerization: pyrrole (Aldrich) was used as *marking agent* to increase the stability and allow imaging of the nanostructures [10,25,26]. One hundred microliters of pyrrole per milliliter of dialyzed SMA solution, was added. The mixture was stirred for 12 h and kept in the dark; the solution was homogeneous and light brown. The solution in a quartz vial, was exposed for 48 h to four UV lamps (150 W), ~50 rpm stirring. The solution turned dark green and remained homogeneous with time, with precipitates from free pyrrole polymerization. The green color is characteristic of pyrrole oligomers. *$AgNO_3$ reduction*: 20 mole equivalents of silver nitrate was dissolved