

Microtubes via Assembly of Imogolite with Polyelectrolyte

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Over the last few decades the fabrication of nanostructures via supramolecular chemistry has attracted a great deal of attention not only because they mimic certain biological systems but also because they show the potential to revolutionize novel technologies.¹ Many amphiphilic polymers can self-assemble to generate various morphologies, including micelles, rods, and vesicular aggregates.² Tube formation is less common because it generally requires highly ordered molecular packing and anisotropic intermolecular interactions,³ and the diameters of most of the tubular structures reported are in the range of several to tens of nanometers.⁴ Only very recently macroscopic tubes millimeters in diameter from self-assembly of an amphiphilic hyperbranched copolymer were reported,⁵ and other few examples of microtubes reported involve self-assembly of either bolaamphiphiles^{6,7} or lipid analogues.^{8–10} Here we report the self-assembly of polyelectrolyte homopolymers with imogolite by solution mixing to generate stable tubular structures several micrometers in diameter and thousands of micrometers in length. While the polymers used in assembly studies generally are amphiphilic or contain blocks of very different properties, the polymers used here are normal polyelectrolyte homopolymers such as poly(acrylic acid) (PAA), poly(allylamine hydrochloride) (PAH), poly(diallyldimethylammonium chloride) (PDDA), and poly(styrene sulfonate) (PSS).

Imogolite is a naturally occurring single-walled aluminosilicate nanotube with extremely high aspect ratios and composition of $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$. The external and internal diameters are approximately 2 and 1 nm, respectively, and the lengths range from several hundred nanometers to

micrometer scale.^{11,12} The nanotube walls consist of curved gibbsite-like sheets with Si–OH groups inside and Al–OH groups outside. The hydroxyl groups on walls and rims make the nanotube hydrophilic.¹³ First prepared by Farmer et al., the synthetic imogolite has properties similar to those of the natural ones.¹⁴ The nanotubes have positive charges in a wide pH range, and the stable dispersion in water can be envisaged as a mobile network of long fibers. Both natural and synthetic imogolites have been used to prepare imogolite/polymer hybrids.¹⁵ We prepared imogolite following the method reported by Farmer et al.¹⁶ and obtained nanotubes with an average length of ~ 100 nm. Detailed characterizations are provided in Supporting Information.

The imogolite solution was mixed with PAA aqueous solution at room temperature, and about 10 days later, some flocculent, fibrous material in the solution was observed with the naked eye. Figure 1 shows its optical micrograph. It can be seen that the flocs are composed of fairly uniform microtubes with diameters of approximately 1–3 μm and lengths ranging from hundreds of micrometers to millimeters with periodic bamboo-like structure with branches. The microtubes would collapse when the water is evaporated and then can resume the original shape and structure upon addition of water. For imogolite or PAA aged for up to 2 months under the same condition, the solutions remained clear and no microtube or any other structure was observed under the optical microscope.

The transmission electron microscopy (TEM) micrographs of the microtubes show that there are vesicular structures inside the bamboo-like tubes (Figure 2a), and the wall thickness of the microtubes is approximately 90 nm (Figure 2b). There is a network of imogolite nanotubes in the wall, with no ordered structure observed (Figure 2c,d), which is confirmed by the diffused rings in the electron diffraction (ED) pattern (Figure 2c, inset) corresponding to the scattering of individual tubes.¹⁴

Because synthetic imogolite and PAA have different thermal stabilities,^{14,17} thermogravimetric analysis (TGA) was used to assess the composition of the microtubes and shows an imogolite content of 23 wt % in the microtubes (for details see Supporting Information), indicating that imogolite acts as a framework in the microtubes, while PAA accounts for most of the mass.

The microtubes are quite stable even under harsh conditions, such as sonication for 75 min or in aqueous sodium

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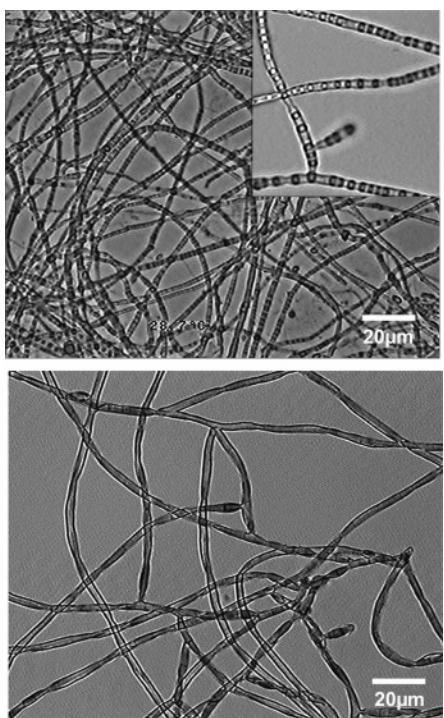


Figure 1. Optical micrographs of the microtubes in water (top) and dried (bottom). The magnified image (inset) shows the bamboo-like structure and the branches.

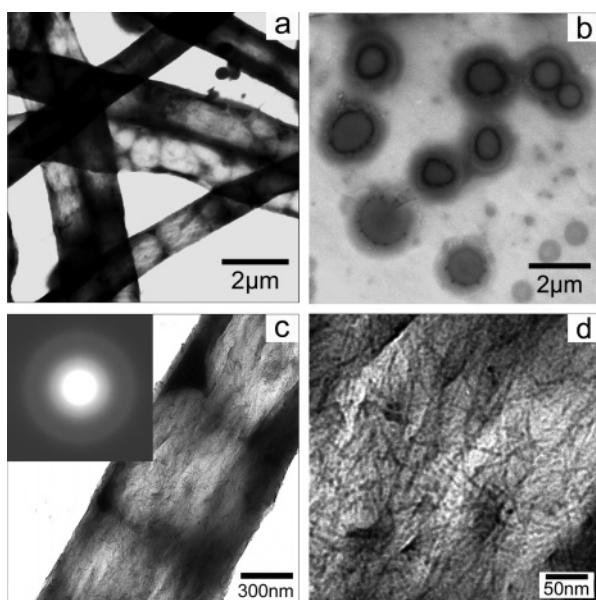


Figure 2. TEM micrographs of the microtubes display the vesicular-like structures inside (a) and the cross-section of the microtubes embedded in epoxy (b). Images at high magnifications (c and d) and the ED pattern (inset) show a network of imogolite in the wall with no ordered structure.

hydroxide (1 M) at 75 °C for 15 min, which implies strong interactions between imogolite and PAA in the microtubes. It has been reported that PAA can interact with alumina via hydrogen bonding and ionic interaction.^{18,19} The interactions between the components of the microtubes were assessed by Fourier transform infrared spectroscopy, and Figure 3 compares the spectra of pure PAA, imogolite, and the

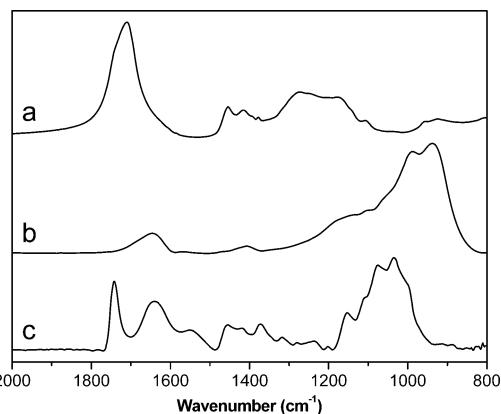


Figure 3. IR spectra of PAA (a), imogolite (b), and the microtubes (c).

microtubes. The IR spectrum of the imogolite exhibits the characteristic Si—O and Si—O—Al stretching vibrations at around 1080 and 960 cm⁻¹,^{20,21} while the predominant feature in the PAA spectrum is the broad and asymmetric band of C=O stretching at ~1710 cm⁻¹ contributed by various carboxyl species.^{22–24} In the spectrum of the microtubes, this band disappears, and three new bands appear in the 1480–1780 cm⁻¹ region. The band at 1743 cm⁻¹ indicates the COOH...HO—Al hydrogen bonding between the PAA with the imogolite.²² In addition, the 1640 and 1549 cm⁻¹ bands, assignable to the asymmetric stretching of COO⁻, suggest the presence of ionic interaction between the PAA and the imogolite.^{19,22,25} Furthermore, the Si—O—Al bands of the imogolite shift from ~960 to ~1050 cm⁻¹, indicating the conversion of tetrahedral Al from octahedral Al.²¹ These observations reveal that the interactions between the PAA and the imogolite involve both hydrogen bonding and ionic interaction. These interactions prompt PAA to glue the imogolite nanotubes and form the microtubes.

The formation process of the microtube structure was characterized by optical micrographs collected for solutions sampled at different times. As shown in Figure 4a, after 1 day isolated microscopic elliptical vesicles are observed dispersing in the solution. The number of the vesicles in solution increases with time (Figure 4b–c), and in the solution aged for 1 week the vesicles start to join together along the long axis of the ellipsoid (Figure 4d), eventually forming microtubes (Figure 4e,f). Thus it is clear that the formation of the microtubes consists of multi-staged assemblies by imogolite and PAA, which result in structure changes spanning from nanoscale to microscale.

It has been known that imogolite can adsorb either cations or anions.¹⁴ Under similar conditions we mixed imogolite with other polyelectrolytes, including PSS, a strong polyanion, PAH, a polycation capable of both hydrogen bonding

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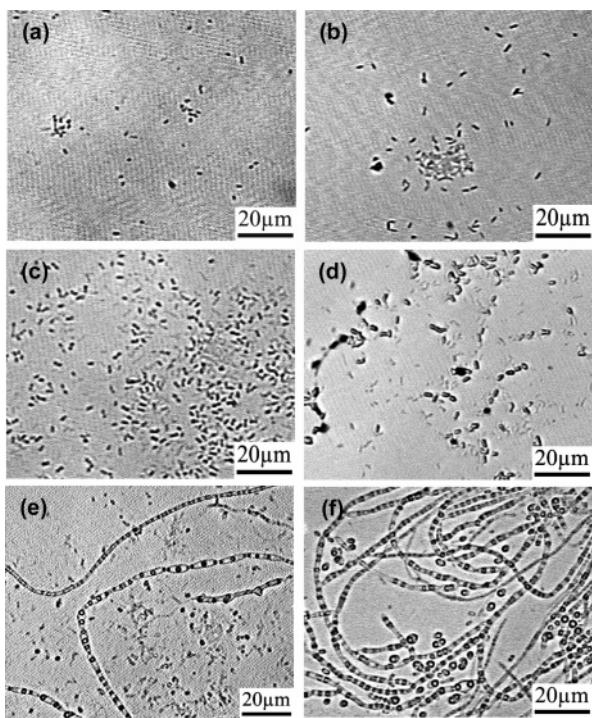


Figure 4. Structure formation of the microtubes observed by optical microscopy. The aging time for the solution is 1 day (a), 3 days (b), 5 days (c), 7 days (d), 10 days (e), and 12 days (f), respectively.

and ionic association, and PDDA, where hydrogen bonding is absent, and in all cases similar microtubes were observed

(optical micrographs are included in Supporting Information).

In summary, imogolite can assemble with PAA to form elliptical vesicles, which then connect and lead to supramolecular microtubes. Hydrogen bonding and ionic interactions between imogolite and PAA both contribute to the construction of the microtubes. Similar assembly behavior was observed with other polyelectrolytes independent of the type of the charge and the presence of hydrogen bonding interaction. No special polymer architecture or interaction seems required. The spontaneous assembly evolving from randomly dispersed nanotubes to one-dimensional ordered microtubes with no local order may provide new inspiration in the area of supramolecular assembly.

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Supporting Information Available: XRD and TEM data for the synthetic imogolite and TGA results and optical micrographs of microtubes assembled by mixing imogolite with other polyelectrolytes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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