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Nanotube Formation through the Continuous One-Dimensional Fusion of Hollow Nanocapsules Composed of Layer-by-Layer Poly(lactic acid) Stereocomplex Films

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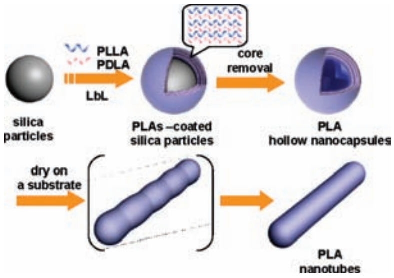
Considerable effort has been devoted to the construction of nanomaterials with well-defined morphologies.[1] In particular, nanotubes have attracted much attention in a wide variety of fields since they can be potentially applied as optoelectric nanodevices, chemical sensors, drug carriers, and so on.[2] Until now, in addition to carbon and inorganic nanotubes, various kinds of organic nanotubes have been reported because of their easy functionalization[3] among the nanotubes and their applicability as templates for fabricating inorganic materials[4] and drug carriers.[5] Most of the organic nanotubes have been prepared by the self-assembly of amphiphilic molecules including lipids,[6] macrocyclic molecules,[7] copolymers,[8] and peptides,[9] and by template methods such as endo-[10] and exotemplating.[11] It has also been reported that organic nanotubes can be formed by the covalent linkage of one-dimensionally arranged cyclodextrins.[12] However, the facile fabrication of organic nanotubes with controllable film thickness and diameters has remained a challenging subject.

Poly(lactic acid)s (PLAs) have been widely used as biomaterials due to their excellent biocompatibility, biodegradability, and mechanical strength.[13] The mixture of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) in polar organic solvents forms triclinic racemic crystals (β-form), called a stereocomplex, in which the left- and right-handed 3_1 helices pack side by side via van der Waals interactions.[14] The stereocomplex formation has been utilized as the driving force for the preparation of layer-by-layer (LbL) polymer thin films.[15] In the course of the fabrication of hollow nanocapsules composed of LbL stereocomplex films of PLLA and PDLA, we found that tubular nanostructures were formed by drying a water dispersion of the hollow nanocapsules on a substrate. Herein, we report a novel fabrication method for polymer nanotubes through the continuous one-dimensional fusion of PLLA/PDLA stereocomplex nanocapsules (Scheme 1).

The preparation of hollow nanocapsules composed of PLLA/PDLA stereocomplex multilayer shells was carried out by a combination of an alternate LbL assembly of PLLA and PDLA and the silica template method. Here, two different molecular weights of PLLAs (M_w = 30 000, M_w/M_n = 2.4 and M_w = 5500, M_w/M_n = 2.0) and PDLAs (M_w = 26 000, M_w/M_n = 2.0 and M_w = 5800, M_w/M_n = 2.3) were employed. Silica nanoparticles with a diameter of 300 nm were alternately immersed in acetonitrile solutions (5 mL) of PLLA and PDLA at 50 °C. The immersion process was continued for 10 cycles to afford 10 double layers of PLLA and PDLA. The resulting particles were then treated with 2.3% aqueous HF to remove the silica core. Figure 1 shows transmission electron microscopic (TEM) images of silica particles coated with a $(\text{PLLA/PDLA})_{10}$ film, where the combination of the higher molecular weights of PLLA (M_w = 30 000) and PDLA (M_w = 26 000) was used, and $(\text{PLLA/PDLA})_{10}$ hollow nanocapsules obtained after the HF treatment. These images clearly indicate that $(\text{PLLA/PDLA})_{10}$ hollow capsules were successfully fabricated by the removal of the silica core from the core−shell particles. The scanning electron microscopic (SEM) images of silica particles coated with a $(\text{PLLA/PDLA})_{10}$ film and hollow nanocapsules are shown in the Supporting Information (Figure S1). The TEM energy dispersive X-ray spectroscopy (TEM-EDX) and FT-IR/ATR spectra also confirmed the complete removal of the silica core (Figure S2 and S3). The $(\text{PLLA/PDLA})_{10}$ hollow capsules have a spherical shape with a diameter of 320 ± 20 nm, and their shell thickness is approximately 60 nm. In the electron diffraction (ED) pattern of these hollow particles, the crystalline patterns corresponding to (010) and (200) of the PLLA/PDLA stereocomplex were observed (Figure S4).[16] The Bragg spacing values of the diffraction spots d_{010} and d_{100} calculated by Au calibration were 0.339 and 0.424 nm, respectively. This result demonstrates that the hollow nanocapsules were composed of PLLA/PDLA stereocomplex films. Although a variety of hollow capsules were prepared by using electrostatic interactions and hydrogen-bonding interactions,[17] hollow capsules composed of nonionic multilayers constructed through van der Waals interactions are rare except for one example previously reported by our research group.[18]

Scheme 1. Schematic Illustration of Formation of Poly(lactic acid)s Hollow Nanocapsules and Nanotubes



The $(\text{PLLA/PDLA})_{10}$ hollow capsules showed unique fusion properties. When evaporating water at ambient temperature from a water dispersion of the hollow capsules composed of the lower molecular weights of PLAs ($M_{w\ \text{PLLA}}$ = 5500, $M_{w\ \text{PDLA}}$ = 5800) on a polyethylene terephthalate (PET) substrate, the formation of tubular assemblies was observed (Figure 2a). These tubular assemblies have an average diameter of 300 nm and lengths of 2−5 μm. On the other hand, tubular assemblies were not formed with hollow capsules composed of the higher molecular weights of PLLA (M_w = 30 000)

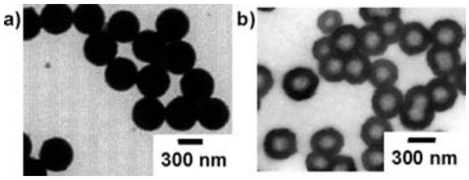


Figure 1. TEM images of (a) silica particles coated with $(\text{PLLA/PDLA})_{10}$ and (b) $(\text{PLLA/PDLA})_{10}$ hollow capsules obtained after HF etching.

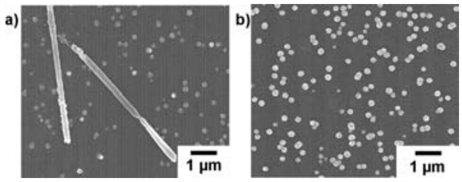


Figure 2. SEM images of nanostructures obtained after evaporation of water from the water dispersion of PLA hollow nanocapsules on a PET substrate: (a) $M_{\mathrm{w\ PLLA}} = 5500$, $M_{\mathrm{w\ PDLA}} = 5800$; (b) $M_{\mathrm{w\ PLLA}} = 30\,000$, $M_{\mathrm{w\ PDLA}} = 26\,000$.

and PDLA ($M_w = 26\,000$) (Figure 2b). It is well-known that the stability of stereocomplex polymer films increases with an increase in the molecular weight of the polymer components.[19] These results suggest that the formation of nanotubes is related to the stability of the PLAs stereocomplex films comprising the hollow capsule shell. Figure S5 shows TEM images of PLA nanotubes and hollow capsules composed of lower molecular weights of PLAs ($M_{\mathrm{w\ PLLA}} = 5500$, $M_{\mathrm{w\ PDLA}} = 5800$). The hollow feature of these tubular structures was confirmed by the TEM image (Figure S5d). Figure S5a−c clearly indicates that two or more hollow nanocapsules one-dimensionally fused with each other. These observations reveal that the PLA nanotubes were formed through the continuous one-dimensional fusion of PLA hollow nanocapsules.

To fabricate nanotubes more efficiently from hollow nanocapsules, silica nanoparticles coated with $(\mathrm{PLLA/PDLA})_{10}$ films were densely deposited onto the PET substrate by a vertical deposition technique[20] in advance, and then the nanoparticles deposited on the PET substrate were immersed into 2.3% aqueous HF to remove the silica core. SEM images of silica nanoparticles coated with $(\mathrm{PLLA/PDLA})_{10}$ ($M_{\mathrm{w\ PLLA}} = 5500$, $M_{\mathrm{w\ PDLA}} = 5800$) deposited on the PET substrate and the nanostructures obtained after the HF treatment are shown in Figure 3a and 3b, respectively. These images clearly show that efficient formation of nanotubes was achieved by the dense deposition of hollow capsules onto the substrate. The diameters and lengths of the formed nanotubes were 400 ± 70 nm and $3.0 \pm 2.0\ \mu$m, respectively. On the other hand, when silica particles coated with the higher molecular weights of PLAs ($M_{\mathrm{w\ PLLA}} = 30\,000$, $M_{\mathrm{w\ PDLA}} = 26\,000$) were treated with the same procedure, nanotube formation was not observed (Figure 3d and e). Taken together these findings with the above-mentioned tendency for tube formation suggest that the formation of nanotubes is closely related to the stability of the PLA stereocomplex film; less stable PLA hollow capsules would lead to a more efficient transformation into PLA nanotubes.

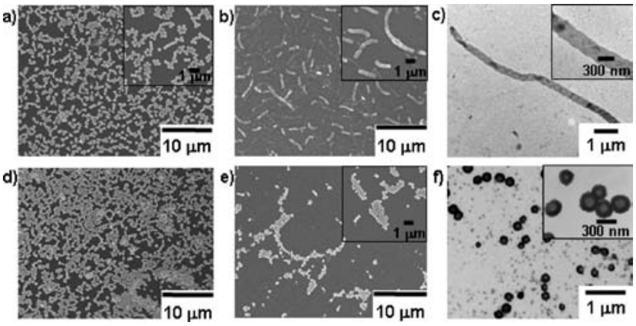


Figure 3. SEM images of (a, d) silica particles coated with $(\mathrm{PLLA/PDLA})_{10}$ and (b, e) nanotubes and hollow capsules obtained after HF etching. TEM images of (c) nanotube and (f) hollow capsules. Molecular weights of PLAs are (a, b, c) $M_{\mathrm{w\ PLLA}} = 5500$, $M_{\mathrm{w\ PDLA}} = 5800$; (d, e, f) $M_{\mathrm{w\ PLLA}} = 30\,000$, $M_{\mathrm{w\ PDLA}} = 26\,000$.

In conclusion, we have demonstrated that hollow capsules composed of layer-by-layer stereocomplex films of PLLA and PDLA one-dimensionally fuse together to generate novel PLA nanotubes. The formation of these nanotubes was affected by the molecular weights of the PLAs comprising the hollow capsules. However, the detailed mechanisms responsible for nanotube formation, including the driving force of the one-dimensional fusion of the hollow capsules, remain unclear. We believe that nanotube formation through the one-dimensional fusion of layer-by-layer hollow capsules may provide a new strategy for creating nanotubes with a defined diameter.

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Supporting Information Available: Experimental procedures and additional EDX, FT-IR/ATR, ED, SEM, and TEM data. Fluorescent microscopic image of the dye-encapsulated microtubes. SEM and TEM images of nanotubes prepared using a smaller silica template. This material is available free of charge via the Internet at http://pubs.acs.org.

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