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Large-size bamboo-shape nanotube from self-assembly of poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) block copolymer

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Abstract

One kind of large-size bamboo-shape nanotube from self-assembly of poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS) block copolymer was obtained. It was found that firstly, PFS-*b*-PDMS formed sphere micelles and pearl-like cluster at room temperature, and then bamboo-shape nanotube formed when the solution was aged about 3 days. The formation mechanism of bamboo-shape nanotube was also discussed.

Keywords: Self-assembly; PFS-*b*-PDMS; Large-size

1. Introduction

Since the discovery of nanotube [1], its synthesis and properties is of considerable interest [2]. Recently, inorganic nanotubes with special structures such as bamboo-shape and Y-junctions have attracted much attention [3–7]. As the most common member of this family, bamboo-shape nanotube constructed by many separated hollow compartments and possessed analogous structures of some apparatus in organism, have been frequently investigated to explore their unique structure-associated properties and appliance in bionic field [4,5]. Thus, exploring the appropriate growth conditions of bamboo-shape nanotubes would also lead to their controllable synthesis and tune their structures selectively. Organic or organometallic nanotubes [8–15] would further remedy the available bamboo-shape nanotube structures and its bionic application. However, relatively few successes have been reported in this area for its difficulty of the synthesis and preparation [16].

Polyferrocenylsilanes are an interesting class of metal-containing polymers with a main chain consisting of alternating ferrocene units [17–21]. For the self-assembly of poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS), one of the noteworthy phenomena associated with the self-assembled aggregate systems is the existence of multiple morphologies [17,21,22]. As the chemical composition of the insoluble block and the lengths of the individual blocks can be varied, one can investigate systematically how these changes affect the size and structure of the resultant aggregate systems [21–25]. PFS-*b*-PDMS can self-assembly to form nanotube structure at appropriate condition [17].

Herein, we report the surprising and facile formation of the organometallic bamboo-shape nanotube using PFS-*b*-PDMS block copolymer in selective hexane solvent at room temperature (30 °C).

2. Experimental

2.1. Materials

n-Butyllium (*n*-BuLi, 1.6 M) in hexane, dimethyldichlorosilane (Me_2SiCl_2), hexamethylcyclotrisiloxane (D_3), tetramethylenedianine (TMEDA) were all purchased from

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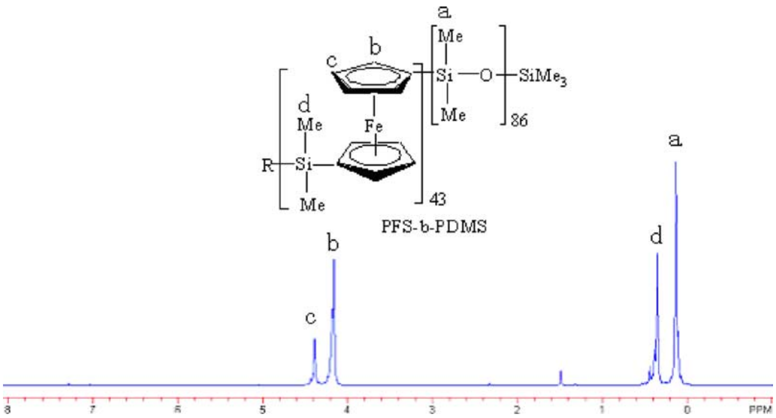
Acrocs [1]. Silaferrocenophane were synthesized according to previous methodology reported in the literature. Hexane and tetrahydrofuran was distilled from K/benzophenone. All reactions and manipulations were carried out under an atmosphere of pre-purified Ar using a standard Schlenk line.

2.2. Synthesis, characteristic and instrument

In a typical experiment, the PFS-*b*-PDMS (PFS:PDMS $\approx$ 1:2) was synthesized according to the literature with small modification [21].

^{1}H NMR spectra of polymers were recorded with a 500 MHz AVANCE NMR spectrometer (Model DMX500) in $CDCl_3$, using TMS as the standard. The ^{1}H NMR spectrum of PFS-*b*-PDMS showed peaks with following shift: 0.17(H, in $–CH_3$, $[Me_2SiO]$), 0.39(H, in $–CH_3$ $[(\eta–C_5H_4)_2FeSiMe_2]$), 4.19 and 4.41 (H in $–C_5H_4$). The NMR spectrum was shown as follows:



The molecular weight of these polymers was determined by gel permeation chromatography (GPC) with laser scattering detector, ultrastyragel column with pore sizes of 10^3–10^5 Å. The eluent was THF at a flow rate of 1.0 mL/min. A detection wavelength of 632.8 nm and the refraction index increment value of the polymer solutions d*n*/d*c* = 0.20 were used for laser scattering detection. The molecular characteristic and spectrum of PFS-*b*-PDMS was shown as follows (Table 1).

Table 1
The molecular characteristic of PFS-*b*-PDMS

Block copolymer	M_n (g/mol)[a]	M_w/M_n[a]
PFS_{43}-*b*-$PDMS_{86}$[b]	1.7×10^4	1.96

[a] M_n determined by GPC.

[b] The number show the number average polymerization degrees of each block and determined by NMR and GPC.

Transmission electron micrographs were obtained on a JEOL model 1200EX instrument operated at an accelerating voltage at 160 kV.

2.3. Self-assembly of PFS-b-PDMS

The block copolymer was dissolved in *n*-hexane (the concentration of it is 2 mg/mL) at room temperature (30 °C). Then 20 μL of a dilute solution was aerosol sprayed onto the carbon films. The sample was air-dried before introduction into the transmission electron microscopy (TEM). Some of the above solution was aged to observe time dependence of micelles morphology. The morphology and structure of the prepared samples were examined with TEM.

3. Results and discussion

In hexane such the block ratio, 1:2 (PFS block vs. PDMS

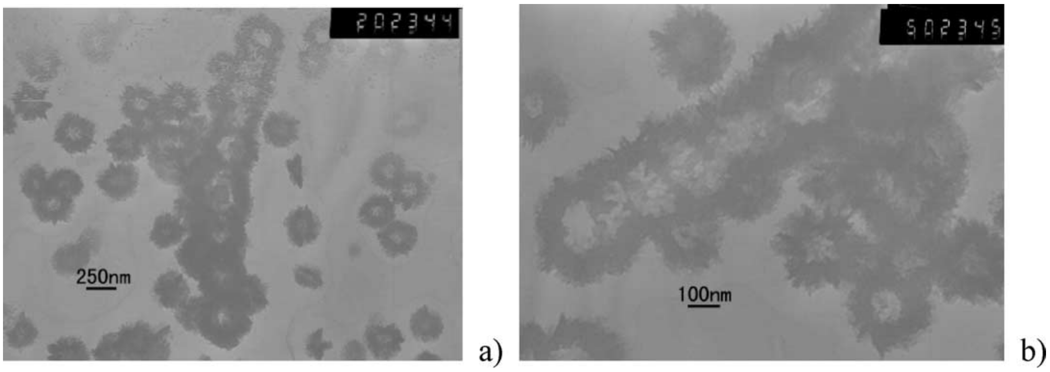


Fig. 1. (a) TEM image of typical sphere micelles. (b) Magnification of (a). Sample prepared of PFS-*b*-PDMS dissolved in *n*-hexane with 2 mg/mL prepared at room temperature (30 °C).

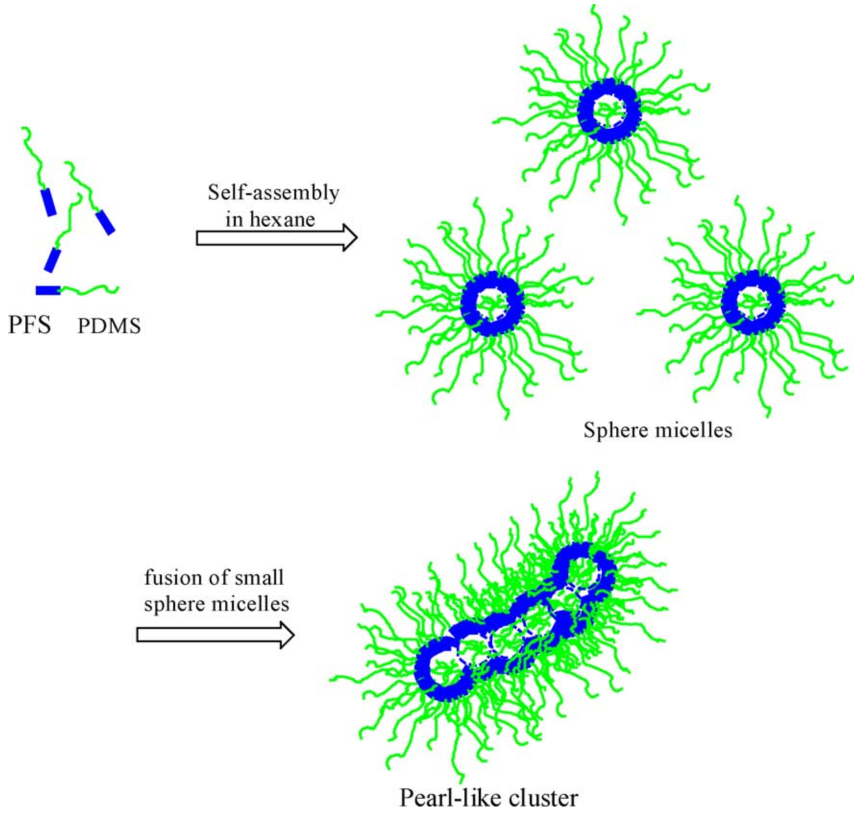


Fig. 2. Schematic models of the pearl-like cluster aggregates derived from the fusion of sphere micelles.

block) would be expected to promote the formation of spherical micelles with a PFS core. However, a remarkable self-assembly process to form large-size bamboo-shape nanotubes morphology induced through a change in aging for sample **1** dissolved in hexane with concentration (2 mg/mL) at 30 °C. This sample forms sphere micelles and pearl-like cluster mixture at room temperature, and bamboo-shape nanotube formed when the solution is aged for 3 days.

Fig. 1 shows TEM images of a typical sample of sphere micelles, which has diameters ranging from 200 to 400 nm, width of the PFS shell is about 50–100 nm, and thus leaves a cavity width of 100–200 nm. It was also found from Fig. 1 that many sphere micelles abut upon to form pearl-like cluster and the length of it reaches several micrometers.

From the pearl-like cluster, we can conclude that their formation may arise from the fusion of small sphere micelles and the schematic model was shown in Fig. 2.

Previous study on this PFS-*b*-PDMS system with close block ratio indicated it self-assembled in hexane to form crew-cut sphere micelles only [17,21]. Here, the coexisting of sphere micelles and pearl-like cluster may bring another possible mechanism and may attribute to the high polydispersity index (PDI) of polymer. High PDI may induce to exist some high block ratio polymer in the sample,

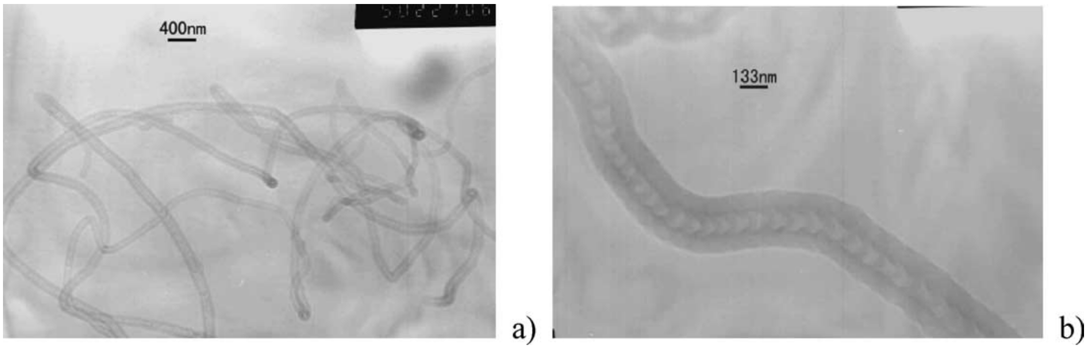


Fig. 3. (a) TEM image of bamboo-shape nanotube. (b) Magnification of (a). Sample prepared of PFS-*b*-PDMS dissolved in *n*-hexane with 2 mg/mL prepared at room temperature and was aged for 3 days.

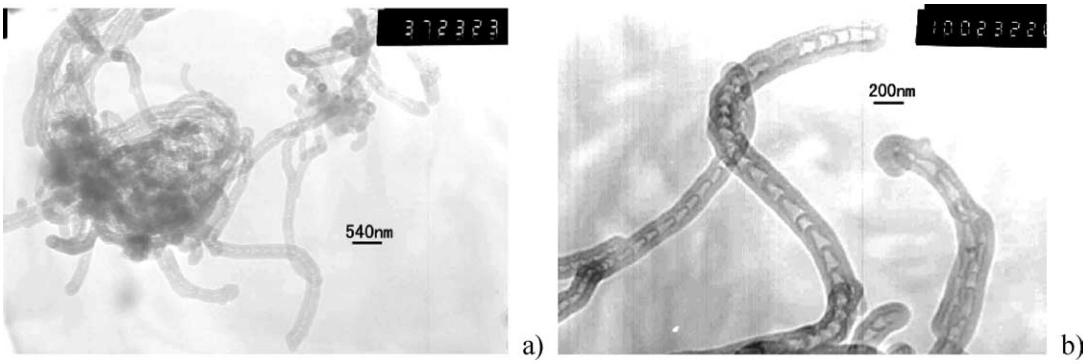


Fig. 4. (a) TEM image of bamboo-shape nanotube. (b) Magnification of (a). Sample prepared of PFS-*b*-PDMS dissolved in n-hexane with 2 mg/mL prepared at room temperature and was aged for 14 days.

which makes some block copolymer with upper block ratio self-assembly in hexane to form pearl-like cluster [26].

Aging time is another effective approach to affect aggregate morphology and a detailed time-dependence study is desirable [21]. Previous studies indicated that longer aging benefit self-assembled system to reach the thermodynamic balance. Fig. 3 indicated bamboo-shape nanotube was formed when the solution is aged for 3 days. Nanotube can be observed from the Fig. 3(a). Furthermore, we may clearly observe bamboo-shape nanotubes from Fig. 3(b) of the magnification of Fig. 3(a). It is found from Fig. 3(a) and (b) that bamboo-shape nanotubes possess diameters ranging from 80 nm to about 300 nm and lengths ranging from hundreds of nanometers to several micrometers. From Fig. 3(b), which indicated that bamboo-shape nanotubes possess those nanotubes structure. In the process of self-assembly, some PDMS form the outer corona, some PDMS exist in interior and PFS self-assembled to inner tube.

A further investigation on the self-assembled morphology by TEM when the sample was aged for 14 days reveals that bamboo-shape nanotube existed still (as shown in Fig. 4). And the diameter and lengths have not change almost.

The possible mechanisms of the morphological transition from spheres to nanotubes can be summarized as follows: The mechanism involves a continual fusion of small spherical micelles and form pearl-like cluster micelles, the precursor of bamboo-shape nanotube [27]. When the sample was aged, every sphere micelles in the pearl-like cluster would be transited to rod-like for high micelles concentration in local. Eventually the micelles change the structure from pearl-like cluster to nanotubes when the core diameter of pearl-like cluster micelles has reached some critical value. The schematic model of morphology transition as follow (Fig. 5).

In conclusion, we have successfully obtained bamboo-shaped nanotubes with large-size through the self-assembly of PFS-*b*-PDMS in hexane at room temperature. These bamboo-shaped nanotubes possess diameters hundreds of

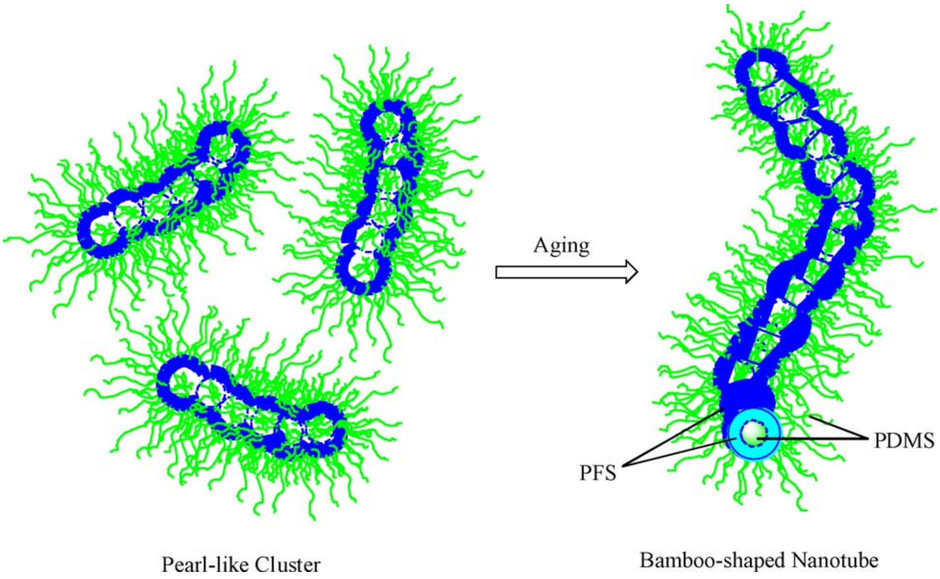


Fig. 5. Schematic model of morphology transition from pearl-like cluster aggregates to bamboo-shape nanotube and potential application as transmission tube.

nanometers and lengths ranging from hundreds of nanometers to several micrometers. Furthermore, bamboo-shaped nanotubes obtained from our experiment can be used as potential in the building blocks of nanoelectronics and bionic field.

Acknowledgements

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