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Poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) microsphere with shell thickness controllable structure prepared through self-assembly

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Abstract

A novel approach was applied to prepare shell thickness controllable magnetic microsphere precursor through the self-assembly of PDMS homopolymer with PFS-*b*-PDMS in selective solvent and adjusting the prepared conditions of samples such as temperature and aging time. The magnetic microsphere precursor provided with adjustable dimension of shell thickness 15, 40 and 90 nm, respectively, which made it possessing various potential applications in biomedical and separating engineering fields.

Keywords: Magnetic microsphere precursor; Self-assembly; Shell thickness controllable

1. Introduction

Magnetic microspheres, one kind of new functional material, are of considerable interest as they possess unique characteristics and potential appliance foreground in biomedical field and separating engineering field [1–4]. For example, magnetic microspheres possessing many functional groups can combine enzyme, cell, antibody, etc. and then they can quick move or separate through additionally magnetic field.

There are mainly two methods to prepare magnetic microspheres. One is to enwrap magnetic particles with natural polymers such as protein and polysaccharide [5]. Another is to polymerize monomers in the presence of magnetic particles through suspension polymerization or dispersion polymerization, etc. [6–9].

However, the magnetic microspheres used in biomedical field and separating engineering field need possess definite and controllable shell thickness because thinner shell of the magnetic microspheres is easily broken to make the magnetic core dissolved and as a result of losing magnetism in the condition of weak acidity, as well as the extraordinary thicker shell makes magnetism weaken. In addition, the shell of magnetic microsphere also need possess biology inertia lest the combined enzyme or cell were deactivated. Though magnetic microspheres are easily synthesized through the mentioned methods, usually the inert shell thickness of magnetic microspheres is hardy controllable.

Manners et al. [4] prepared magnetic microspheres through electrostatic self-assembly of oxidated polyferrocenylsilane with silica spheres to form composite core-shell particles. The dimension of magnetic core is so bigger that magnetic microspheres possess lasting magnetism when additionally magnetic field was stopped. Manners et al. [10–15] also reported that self-assembly of poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS) block copolymer in selective solvent, which provides a new powerful route to magnetic microspheres precursor with inert shell (shown in Fig. 1), but it is difficult to control the preparation of inert shell thickness.

For the self-assembly of PFS-*b*-PDMS, one of the noteworthy phenomena associated with the self-assembled aggregate systems is the existence of multiple morphologies, which includes sphere, rod and tube, etc. The sphere micelles, with the insoluble block PFS as the core and the soluble block PDMS as the shell, can be used as magnetic microsphere precursor [10–14]. The magnetic microsphere precursor can be oxidated to obtain a magnetic microsphere with core-shell structure [4]. It was also well

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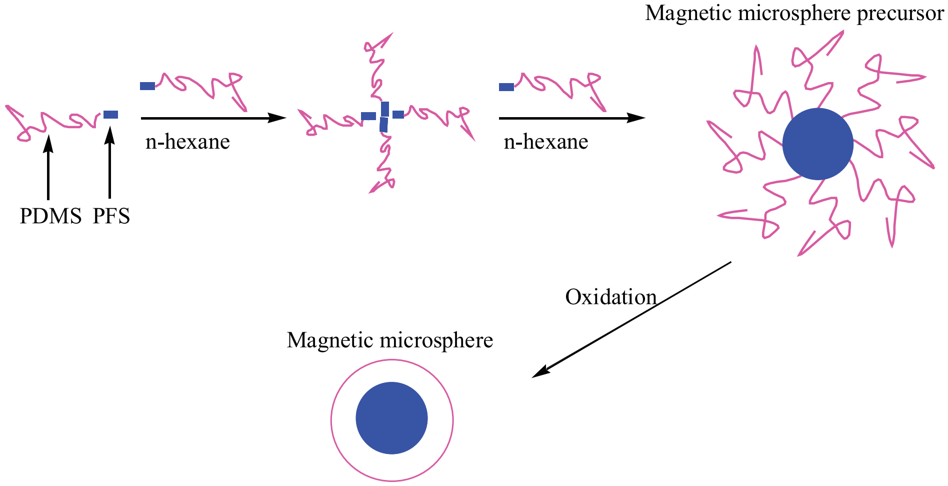

Fig. 1. Schematic illustration on the preparation of magnetic microsphere with shell-core structures from PFS-*b*-PDMS.

known that most important morphogenic factors are the block copolymer composition of PFS-*b*-PDMS such as block ratio (PDMS block length vs. PFS block length) or the prepared methods of micelles and the initial copolymer concentration in selective solvent [10–13]. For all of these cases we are aware, PFS-*b*-PDMS possessing the longer block ratio forms rod and tube structures, whereas the shorter block ratio forms the sphere micelles [14–16]. Thus, the inert shell thickness of magnetic microsphere precursor can be adjusting through changing the length of PDMS chain in PFS-*b*-PDMS at the condition of same molecular weight. However, the increasing of block ratio means the transition of micelles morphology from sphere micelle to rod or tube and magnetic microspheres precursor may be not obtained in a general way.

In this communication, we report the remarkable formation of magnetic microsphere precursor with controllable inert shell thickness through the self-assembly of PDMS homopolymer with PFS-*b*-PDMS block copolymer in hexane.

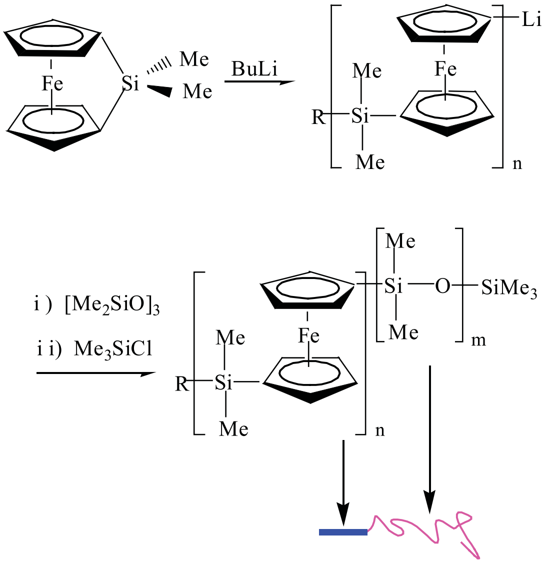

Fig. 2. Synthesis route of PFS-*b*-PDMS.

2. Experimental

PFS-*b*-PDMS was prepared using the method described previously [12]. The synthesis was accomplished by sequential anionic ring-opening polymerization in an atmosphere of pre-purified argon. The reaction involves the initiation by the reaction of the strained silicon-bridged [1] ferrocenophane with *n*-butyllithium, followed by addition of hexamethyltrisiloxane (D_3) (Fig. 2). Termination is achieved by adding chlorotrimethylsilane to the reactor. The block copolymer was precipitated into methanol in the presence of triethylamine. The block copolymer was passed through a size exclusion column in THF to eliminate any homopolymer present in the product. PDMS was prepared through anionic ring-opening polymerization in an atmosphere of pre-purified argon and termination is achieved by adding chlorotrimethylsilane to the reactor. ^{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.

^{1}H NMR data of PFS-*b*-PDMS is 0.07 (s, $[Me_2SiO]_{3y}$), 0.39 (s, $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_x$) and 4.35 (s, Cp), 4.10 (s, Cp), which correspond to the PDMS and PFS, respectively. ^{1}H NMR data of PDMS is 0.07 (s, $[Me_2SiO]_{3y}$).

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 weight of the PFDMS-*b*-PDMS and

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

Block copolymer	M_n (g/mol)^a	M_w/M_n^{a}
PFDMS$_{20}$-*b*-PDMS$_{200}$^{b}	1.9×10^4	1.06
PDMS	7.1×10^3	1.08

[a] M_n determined by GPC.

[b] The number show the number average polymerization degrees of each block.

PDMS was shown in Table 1. All micelles solutions described in this manuscript have a concentration of 1 mg/mL. Experiments in hexane examine the temperature and time dependence of micelles morphology. Solution of block copolymer micelles in hexane was prepared at 25 ± 0.5 °C by shaking the mixture until a homogeneous solution was obtained. Then 20 μL of a dilute hexane solution was aerosol sprayed onto the carbon films. The sample was air-dried before introduction into the electron microscope.

Some of the above solution was placed in a preheated water bath at 61 ± 0.5 °C for 3 h. Samples for TEM analysis were prepared at this temperature in two ways. The first, the micelles solution at 61 °C was rapidly sprayed onto the carbon films, and the second, then the mixture was cooled to room temperature over 7 days. Aliquots were then taken for TEM analysis.

The size distribution of micelles is measured by zeta potential and laser dispersion particle size analyzer (Zetasizer 3000HS Advanced, Malvern Instruments Ltd). The above aging sample for TEM analysis was adopted in the testing of size distribution.

3. Results and discussion

Fig. 3 shows a set of TEM pictures demonstrating the morphologies of magnetic microsphere precursor made by dissolution of 70% PDMS homopolymer and 30% PFS$_{20}$-*b*-PDMS$_{200}$ in hexane. The inert shell thickness of magnetic microsphere precursor can be controlled through changing the prepared methods of sample, such as temperature or aging time. Adjusting temperature is an effective method to control the shell thickness of magnetic microsphere precursor. The size of precursor is about 50 nm at 25 °C (Fig. 3, left). If the samples was heated to 61 °C (Fig. 3, middle), the size would be reached 100 nm. From previous reports [12–17], usually, it is known that the size of PFS core possesses 20 nm in any condition of prepared magnetic microsphere precursor. The factors that impact self-assembled behavior may change the morphologies or subtle size [18]. Obviously, herein the increasing cosmically of precursor dimension could not be primary precursor from PFS-*b*-PDMS block copolymers, and their forming must be related to the presence of the PDMS homopolymer. In addition, it has been reported that the dimension of magnetic microsphere precursor is 20–30 nm and tubes in diameter is 11–30 nm in the absence of PDMS homopolymer [14–16]. Thus, the increased size of magnetic microsphere precursor attributes to existing PDMS homopolymer and also indicated from Fig. 3 (left) that the inter shell thickness is about 15 nm, and from Fig. 3 (middle) that the inter shell thickness is about 40 nm.

Aging time is another effective approach to affect the shell thickness of magnetic microsphere precursor. Magnetic microsphere precursor possessed 200 nm can also be obtained when the samples were prepared after immersed 61 °C about 3 h and then was allowed to age 7 days at 25 °C (Fig. 3, right). It is indicated from Fig. 3 (right) that the inter shell thickness is about 90 nm. Further, the size distribution of micelles at this condition was also examined and listed in Fig. 4. Result indicated that the average size is 280 nm, which was bigger than micelles size in TEM on an experimentally accessible time scale.

So one simple method is applied to prepare controllable inert shell thickness of magnetic microsphere precursor. The inert shell thickness of the precursor, 15, 40 and 90 nm is obtained.

In general, the principles for morphological transitions in selective solvent of pure block copolymers appear to be also applicable to solution of the blends [19–22]. However, the difference in solubilities of the PFS-*b*-PDMS and PDMS homopolymer is also an important factor. Herein the existing PDMS homopolymer makes longer block ratio copolymer self-assembly to form spheres micelles but nanotube. We speculate that plenty of PDMS homopolymer in the self-assembled systems easily dissolving than PFS-*b*-PDMS in hexane and existing in solvent and in the PDMS corona, which means increasing the concentration of PDMS

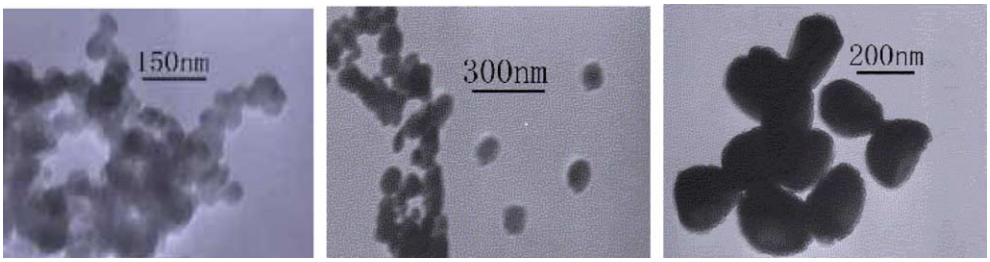

Fig. 3. TEM micrographs of PFS$_{20}$-*b*-PDMS$_{200}$ and PDMS self-assemblies prepared in *n*-hexane, (left) the samples was prepared at 25 °C, (middle) the samples was prepared after immersed 61 °C about 3 h, (right) the samples was prepared after immersed 61 °C about 3 h and then was allowed to age 7 days at 25 °C.

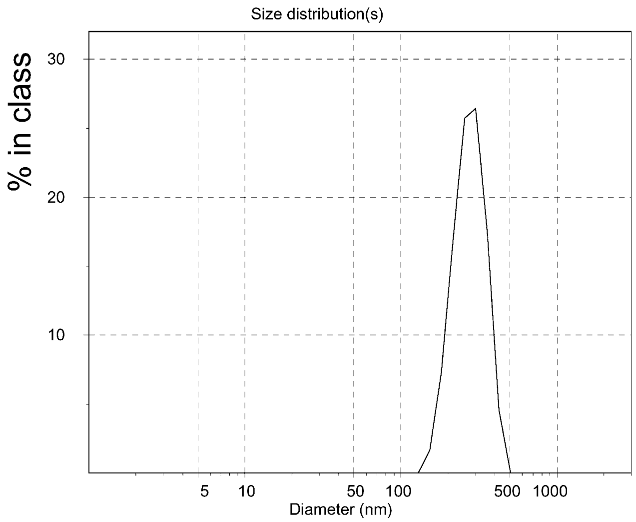

Fig. 4. The size distribution of micelles derived from PFS_{20}-*b*-$PDMS_{200}$. The micelles samples was prepared after immersed 61 °C about 3 h and then was allowed to age 7 days at 25 °C.

in local region, extension of PDMS block becomes difficult at those local region and a new phase forms but transits to nanotubes. The new sphere phase should include mainly PFS-*b*-PDMS block copolymer, which is as the substrate of the sphere micelles. PDMS homopolymer is absorbed on the surface of PFS-*b*-PDMS self-assembled sphere micelle, and the more of absorption, the bigger of dimension of sphere micelle, and the possible process is shown in Fig. 5. At higher temperature, the PDMS corona chains are more swollen. Steric repulsion among corona chains promotes curvature at the core-corona interface to increase the volume accessible to each corona chain, which induced more PDMS homopolymer to exist in the PDMS corona of sphere micelles. When the self-assembled system temperature is lowered, the PDMS chains contract, but much PDMS homopolymer exist among PDMS chains of sphere micelles and prevent PDMS chains contracting. In order to obtain the balance and steric repulsion decrease, the dimension of the micelles must be enlarged than pure block copolymer in self-assembled system. Aging time also benefits the absorption of PDMS homopolymer to micelles substrate, and aging sample makes PDMS homopolymer and PFS-*b*-PDMS block copolymer balance in this absorption process, as a result the dimension of micelles became bigger.

More finer dimension control of shell can be done through designing the composition of block copolymer, for example, increasing block ratio at the same molecular weight or blending different content of PDMS homopolymer, adjusting the sample preparation temperature also can change the micelles dimension. More detail studies are undertaken.

4. Conclusions

In summary, we have presented that a novel approach to prepare shell thickness controllable magnetic microsphere precursor through the self-assembly of PDMS homopolymer with PFS-*b*-PDMS in selective solvent and adjusting the prepared conditions of samples such as temperature and aging time. The magnetic microsphere precursor provided with adjustable dimension of shell thickness made it possessing various potential applications in biomedical and separating engineering fields.

Acknowledgements

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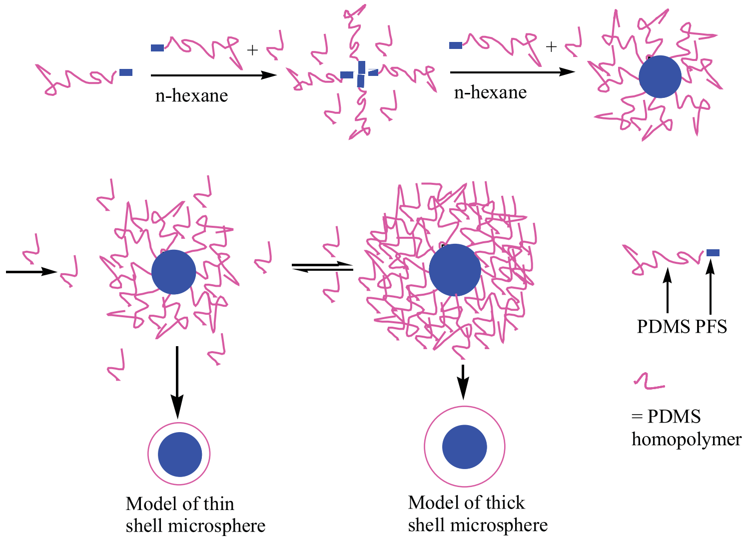

Fig. 5. Model of self-assembly of PDMS homopolymer with PFS-*b*-PDMS in *n*-hexane and the variety of shell thickness.

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