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Organic/inorganic nanoobjects with controlled shapes from gelable triblock copolymers

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ABSTRACT

A functional gelable triblock copolymer, poly(2-vinylpyridine)-*block*-poly(3-(triethoxysilyl)propyl methacrylate)-*block*-polystyrene (P2VP-*b*-PTEPM-*b*-PS), was prepared by the combination of reversible addition-fragmentation chain transfer (RAFT) mediated radical polymerization and copper catalyzed click chemistry. Bulk microphase separation of P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ under different conditions was studied in order to prepare organic/inorganic nanoobjects by a procedure of crosslinking PTEPM phases and dispersing in a solvent. The conditions included using different annealing solvents and adding stearic acids to form supramolecular complexes with P2VP blocks respectively. Then the packed cylinders with P2VP cores and PTEPM shells dispersed in the PS matrix, lamella with alternating PS, PTEPM and P2VP layers, and the inverse cylindrical morphology with PS cores and PTEPM shells dispersed in the matrix of P2VP/stearic acid complex were obtained respectively just from the same triblock copolymer sample. After crosslinking PTEPM microdomains by sol-gel process and dispersing in solvents, a series of organic/inorganic polymeric nanoobjects, including two types of nanofibers with inverse internal structure and one novel kind of nanoplates, were produced. Further modification of the fibers with P2VP cores has been studied.

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1. Introduction

Block copolymers composed of incompatible chains can microphase separate to form a series of well-defined nanometersized structures in the bulk [1–3]. These fascinating nanostructures have endowed block copolymers with valuable applications in nanosciences and nanotechnologies, such as preparation of nanoobjects [4], nanocomposites [5,6], photonic band gap materials [7], and lithographic templates [8,9] etc. By selectively crosslinking the discontinuous domains in the preformed ordered structures of block copolymers in bulk and then dispersing materials in a good solvent of the continuous domains, a variety of nanoobjects may be generated and their shape, size and compositions can be easily manipulated [10-21]. These nanoobjects may find considerable applications in areas related with drug delivery, catalysis, and microfabrication etc. It is noteworthy that the non-crosslinked segments become the polymer hairs being densely grafted on the surface, which is important for stabilization and further functionalization.

Since their precursor block copolymers are normally organic polymers, the polymeric nanoobjects prepared by this approach are mainly pure organic structure, which will limit their applications in some aspects which need higher stability. Recently, based on a novel kind of self-gelable block copolymers containing inorganic precursors, we have developed a procedure to prepare a series of organic/inorganic nanoobjects with manipulated shape and composition [22-24]. Through the RAFT-mediated radical polymerization of 3-(triethoxysilyl)propyl methacrylate (TEPM), the well-defined block copolymers of PTEPM-b-PS [22], PTEPM-b-P2VP [23], and PTEPM-b-PS-b-P2VP [24] have been synthesized. By virtue of their microphase separation morphologies with PTEPM as discontinuous domains, and self-gelable property of PTEPM, a series of novel organic/inorganic hybrids with well-defined microstructure and changeable morphologies, such as spheres, fibers and plates, have been obtained. Furthermore, besides the introduced inorganic microdomains by covalent bonds, the densely attached functional polymer "hairs", such as P2VP, also endowed these hybrid nanoobjects with not only hydrophilicity and pH sensitivity, but also powerful ability for capturing the inorganic nanoparticles [23.24].

So far most of these researches were carried out by diblock copolymer systems because of their easy preparation. However, the





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limited microphase separation morphologies of diblock copolymers restricted this approach to generate the polymeric nanoobjects with more shapes, fine structures and functionalities. It has already known that multiblock copolymers, such as triblock copolymers, may display much more morphologies by their microphase separation [25,26]. As a result, in principle various well-controlled nanoobjects with tunable shapes and functionalities can be generated by using multiblock copolymers. Moreover, it is especially amazing if the crosslinking segments are situated as the middle block of triblock copolymers. Liu et al have prepared novel polymer fibers with poly(acrylic acid) cores and poly(butyl methacrylate) coronas by photoinduced crosslinking the middle block of poly(butyl methacrylate)-*block*-poly(2-cinnamoethyl methacrylate)-block-poly(tert-butyl acrylate) [15]. Saito and Müller et al have prepared interesting Janus particles of different shapes with the crosslinked cores and two tethered polymer layers by crosslinking the middle blocks of polystyrene-block-poly(2-vinylpyridine)-blockpoly(butyl methacrylate) [16] and polystyrene-block-polybutadieneblock-polymethacrylates [27,28]. Janus polymeric hairy spheres [16,27,28], cylinders [29] and plates [30] thus have been prepared and they have displayed interesting properties in solution [31], on solid surface [28], and at interface [32,33]. In order to tune the fine structure of organic/inorganic nanohybrids, recently we have also synthesized the PTEPM-b-PS-b-P2VP triblock copolymers. For PTEPM₅₈-b-PS₂₆₅-b-P2VP₃₃₁, it can microphase separate to form a three-phase four-layer, alternating P2VP, PS, PTEPM and PS, lamellar morphology in the bulk. After in-situ self-gelation only in PTEPM microdomains and dispersing it in the good solvents of P2VP or P2VP-*b*-PS, we have obtained novel sandwich-like organic/ inorganic hybrid nanoplates with a crosslinked silica oxide layer sandwiched by PS-b-P2VP amphiphilic diblock copolymer layers [24].

Until now, in almost all of the publications, alternation morphology of the obtained nanoobjects was accomplished only by changing the copolymer composition. However, the synthesis of a well-defined multiblock copolymer is usually difficult and time consuming, which definitely limits the development in this field. Fortunately, the microphase separated morphologies of multiblock copolymers can also be altered simply by modifying microphase separation conditions, for example, the type of annealing solvents [34–39], and noncovalent modification of one block [40–43]. These properties make it possible that the nanoobjects with different morphologies would be prepared just from the same block copolymer sample, which is very important in practice because of

avoidance of the difficult and time consuming synthesis process. Herein, based on a new gelable poly(2-vinylpyridine)-*block*-poly(3-(triethoxysilyl)propyl methacrylate)-*block*-polystyrene (P2VP-*b*-PTEPM-*b*-PS) triblock copolymer, in which the gelable segment PTEPM is located in the middle of a triblock copolymer, we have shown these concepts by virtue of alternation annealing solvents and supramolecular modification of P2VP segments to generate different organic/inorganic hybrid polymeric nanoobjects. The main principle was presented in Scheme 1.

2. Experimental

2.1. Materials

2-Vinylpyridine (97%, Aldrich) was dried over calcium hydride overnight and distilled under a reduced pressure. 3-(Trimethoxysilyl)propyl methacrylate (>95%, Wuhan University Silicone New Material Co.) was used as received. 3-(Triethoxysilyl)propyl methacrylate (TEPM) was synthesized according to a literature from 3-(trimethoxysilyl)propyl methacrylate [44]. Styrene was dried over calcium hydride overnight and distilled under a reduced pressure. 2,2-Azoisobutyronitrile (AIBN) was recrystallized from methanol and stored at 4 °C. 4-(4-Cyanopentanoic acid) dithiobezoate [45], 4cyano-4-((thiobenzoyl)sulfanyl) pentanoic 3-azidopropyl ester (CTA 2) [46] and tris[2-(dimethylamino)ethyl]amine [47] were synthesized according to literature. Anhydrous ethanol (>99%, Beijing Chemical Reagent Co.) was refluxed over magnesium. Dichloromethane (DCM) was refluxed over calcium hydride. Propargyl alcohol, N,N'-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 3-chloro-1-propanol, stearic acid, 1bromohexane, 1-capric acid, chloroauric acid, anhydrous methanol, tetrahydrofuran (THF), chloroform, ethyl ether, hexane, and benzene were used as received.

2.2. Synthesis of 4-cyano-4-((thiobenzoyl)sulfanyl) pentanoic propargyl ester (CTA 1)

4-(4-Cyanopentanoic acid) dithiobenzoate (2.00 g, 7.16 mmol), propargyl alcohol (482.6 mg, 8.59 mmol) and DCC (1.76 g, 8.59 mmol) were dissolved in 15 mL of anhydrous DCM. DMAP (104.9 mg, 0.859 mmol) in 5 mL of anhydrous DCM was added dropwise. The reaction mixture was stirred at room temperature about 24 h. A white byproduct was filtrated out. The filtrate was concentrated and purified by a silica gel column with ethyl acetate: hexane (1:5, v/v) as



Scheme 1. Organic/inorganic hybrid nanoobjects generated by a procedure of (1) self-assembly P2VP-*b*-PTEPM-*b*-PS triblock copolymer in the bulk, (2) then gelation in PTEMPM phases and (3) dispersion in good solvents of non-crosslinked blocks. Condition: microphase separation (i) annealed from THF and Benzene, (ii) annealed from chloroform, and (iii) in presence of stearic acid. Nanoobjects A: cylinder with P2VP core and PS shell; B: plate with P2VP and PS tethered in two faces; C: cylinder with P2VP shell and PS core. Between P2VP and PS is crosslinked PTEPM phase (blue).

eluent. The red product (1.6 g) was obtained in a yield of 60%. ¹H NMR (CDCl₃) δ (ppm): 7.91-7.89 (2H, d), 7.58-7.54 (1H, t), 7.41-7.37 (2H, d), 4.72(2H, s), 2.72-2.59 (4H, m), 1.95 (3H, s).

2.3. Synthesis of PTEPM macromolecular chain transfer agent (Macro-CTA)

Bulk reversible addition-fragmentation chain transfer (RAFT) polymerization of TEPM was performed in a sealed ampule equipped with a stir bar under vacuum. The procedure was as follows: CTA1 (116.0 mg, 3.65×10^{-1} mmol), TEPM (11.67 g, 40.2 mmol) and AIBN (6.0 mg, 3.65×10^{-2} mmol) were added into a 50 mL glass ampule. The mixture was degassed through four freeze-evacuate-thaw cycles and then the ampule was sealed under vacuum. Polymerization was carried out in an oil bath at 60 °C for 18 h and was terminated by cooling with an ice bath. The resulted crude product was purified by precipitating into a large amount of methanol and water mixture (7:3 volume ratio) three times. Monomer conversion was determined by ¹H NMR spectrum. M_n NMR = 17300, M_n SEC = 13700, $M_w/M_n = 1.15$.

2.4. Synthesis of PTEPM-b-PS diblock copolymer

The polymerization was performed in a sealed ampule equipped with a stir bar under vacuum. PTEPM macro-CTA (3.18 g, 1.84×10^{-1} mmol) and styrene (57.50 g, 552.1 mmol) were charged into a 150 mL Schlenk flask. The mixture was degassed by four freeze-evacuate-thaw cycles and then flame-sealed under vacuum. Polymerization was carried out in an oil bath thermostated at 90 °C for 12 h. The reaction was terminated by cooling of the solution to room temperature and the mixture was exposed to air. The resulting product dispersed in THF was purified by precipitating into methanol three times. The composition was determined by ¹H NMR spectrum. $M_{n NMR} = 50800$, $M_{n SEC} = 49700$, $M_w/M_n = 1.15$.

2.5. Synthesis of P2VP homopolymer

The polymerization was also performed in a sealed ampule equipped with a stir bar under vacuum. CTA2 (66.80 g, 1.83×10^{-1} mmol), 2-vinylpyridine (13.70 g, 290.1 mmol) and AIBN (12.8 mg, 77.9 mmol) were charged into a 50 mL Schlenk flask. The mixture was degassed by four freeze-evacuate-thaw cycles and then flame-sealed under vacuum. Polymerization was carried out in an oil bath thermostated at 60 °C for 9 h. The crude product dispersed in THF was purified by precipitating into hexane three times. The block ratio was determined by ¹H NMR spectrum. *M*_n NMR = 33900, *M*_n SEC = 102500, *M*_w/*M*_n = 1.15.

2.6. Synthesis of P2VP-b-PTEPM-b-PS triblock copolymer

The PTEPM-b-PS-b-P2VP triblock copolymer was synthesized by click chemistry from PTEPM-b-PS diblock copolymer and P2VP homopolymer. PTEPM-*b*-PS diblock copolymer (1.93 g, $M_{\rm n}$ $C_{ONV} = 33900, M_w/M_n = 1.09), P2VP (6.26 g, M_n NMR = 50800, M_w/M_n = 1.09)$ $M_{\rm n} = 1.15$), tris[2-(dimethylamino)ethyl]amine (127.2 mg, $5.53\times10^{-1}\,mmol)$ and DMF (30 mL) were charged into a 100 mL Schlenk flask. The mixture was degassed by four freeze-evacuatethaw cycles and then CuBr (79.3 mg, 5.53×10^{-1} mmol) was added under the protection of N₂. After evacuating another 10 min, the flask was sealed under vacuum. The click chemistry was carried out at room temperature for 10 h. The crude product was diluted by THF and passed a basic alumina column to remove the catalyst. The polymer was firstly precipitated in hexane, methanol and finally ethyl ether to remove excessive P2VP. The overall yield of purified PTEPM-b-PS-b-P2VP triblock copolymer was ca. 50%. The composition was determined by ¹HNMR spectrum. M_n NMR = 79600, M_n SEC = 148900, M_w/M_n = 1.15.

2.7. Bulk casting and annealing of P2VP-b-PTEPM-b-PS

A solution of P2VP-*b*-PTEPM-*b*-PS triblock copolymer (50 mg/ mL) in THF, CHCl₃ or benzene was spread onto a clean Teflon plate and the solvent was allowed to evaporate in a vacuum desiccator over 5 days. The resulting bulk sample (ca. 0.5 mm in thickness) was then dried for 12 h under vacuum at 60 °C.

2.8. Self-assembly of P2VP-b-PTEPM-b-PS with stearic acid

A solution of P2VP-*b*-PTEPM-*b*-PS triblock copolymer (50 mg/ mL, 2 mL) and stearic acid (0.36 mg) in CHCl₃, where the molar ratio between 2VP unit and stearic acid was fixed to 1:1, was spread onto a clean Teflon plate and the solvent was allowed to evaporate in a vacuum desiccator over 5 days. The resulting bulk sample (ca. 0.5 mm in thickness) was then dried for 12 h under vacuum at 60 °C.

2.9. Gelation in microdomain structure and preparation of nanoobjects

Bulk samples with microphase separation structure were exposed to HCl atmosphere for about 8 h and then dried under vacuum at temperature of 60 °C for 12 h to carry out the sol-gel reaction of the PTEPM domain completely. The nanoobjects were prepared by dispersing the gelated bulk samples in THF or CHCl₃ three days.

2.10. Supporting gold nanoparticles into nanofibers

After dispersing gelated hybrid bulk materials (5 mg) from THF annealing solvent in THF (2 mL) and stirred three days, a water solution of NaAuCl₄ (ca. 1 mg/mL) was added slowly, where the molar ratio between 2VP and NaAuCl₄ was fixed to 1:0.2. When the mixture solution was stirred ca. 24 h, a freshly prepared aqueous solution of sodium borohydride (10 mg/mL) (ca. 0.1 mL) was added dropwise under vigorously stirring. After the addition was finished, the stirring was kept about 10 h.

2.11. Loading 1-bromohexane into nanofibers by quaternization

To load 1-bromohexane into the core of nanofibers from THF annealing solvent by quaternization, the dispersed nanofibers were collected from THF by centrifugation and then put into 1-bromohexane (1 mL). The reaction mixture was sealed and stirred for 48 h at 70 °C. At last, the quaternized nanofibers were thoroughly rinsed by THF no less than 5 times to remove the unreacted 1-bromohexane completely, and then dispersed in chloroform.

2.12. Loading 1-capric acid into nanofibers by hydrogen-bonding

To load 1-capric acid into the core of nanofibers from THF annealing solvent by hydrogen-bonding, the dispersed hybrid nanofibers with deprotonated P2VP microdomain (5 mg) and 1-capric acid were mixed together in chloroform (2 mL), where the molar ration between the 1-capric acid and pyridine group was about 1.1:1. After the mixtures were stirred for 12 h, the chloroform was slowly removed by evaporation at room temperature.

2.13. Characterization

Gel permeation chromatography (GPC) was performed by a set of a Waters 515 HPLC pump, a Waters 2414 refractive index



Scheme 2. Synthesis of P2VP-b-PTEPM-b-PS triblock copolymer by RAFT-mediated radical polymerization combined with click chemistry coupling.

detector, and the combination of Styragel HT-2, HT-4, and HT-5, the effective molecular weight range being 100-10,000, 5,000-600,000, and 50,000-4,000,000, respectively. THF was used as an eluent at a flow rate of 1.0 mL/min at 35 °C, or DMF with 1 g/L LiBr was used as eluent at flow rate of 1.0 mL/min at 50 °C. Polystyrene standards were used for the calibration.

¹H NMR spectra were recorded on a Bruker DMX400 spectrometer with CDCl₃ as solvent at room temperature.

Fourier-Transform Infrared (FT-IR) spectroscopy was recorded by a deuterate triglycine sulfate (DTGS) detector on a Bruker EQUINOX 55 spectrometer and processed by the Bruker OPUS program. Samples were prepared by milled with potassium bromide (KBr) to form a very fine powder and then compressed into a thin pellet or by dropped from chloroform/THF solution onto KBr plate.

Transmission electron microscopy (TEM) images were obtained using a Hitachi H-800 instrument operated at an accelerating voltage of 100 kV. The images were recorded by a digital camera. Samples were embedded in epoxy and cured at 40 °C overnight. Thin sections (50–100 nm) were obtained using Leica Ultracut UCT ultramicrotome and a diamond knife at room temperature. The microtomed sections were stained by I₂ vapor 30 min before observation.

3. Results and discussion

3.1. Synthesis and characterization of P2VP₃₁₀-b-PTEPM₅₈-b-PS₃₂₂ triblock copolymers

The present P2VP-*b*-PTEPM-*b*-PS triblock copolymer could not be polymerized by a step sequent RAFT procedure due to the problem of the efficiency for chain extension. We have applied a procedure of RAFT-mediated radical polymerizations combined with click chemistry for preparing this kind of triblock copolymer (Scheme 2). Firstly, PTEPM-*b*-PS diblock copolymer and P2VP were synthesized by using 4-cyano-4-((thiobenzoyl)sulfanyl) pentanoic propargyl ester (CTA1) and 4-cyano-4-((thiobenzoyl) sulfanyl) pentanoic 3-azidopropyl ester (CTA2) as functional RAFT agents respectively. Secondly, P2VP-*b*-PTEPM-*b*-PS triblock copolymer was obtained by azide—alkyne 1,3-dipolar click cycloaddition.

Polymerization of TEPM was performed according to a previous reported procedure [22,23]. Shown in Fig. 1 A (line a) is the SEC curve of PTEPM₅₈ homopolymer (Run 1 in Table 1) in THF using standard polystyrene as calibration, giving a monomodal peak. Synthesis of PTEPM-*b*-PS diblock copolymer was performed in bulk using PTEPM as a macro-CTA, where the block composition and actual number molecular weight were determined by ¹H NMR spectrum [22]. Fig. 1 A (line b) is the SEC curve of PTEPM₅₈-*b*-PS₃₂₂ diblock copolymer (Run 2 in Table 1). Compared with its macro-CTA (line a in Fig. 1 A), the peak with a polydispersity of 1.15 at the higher molecular weight direction was displayed and no peak of



Fig. 1. SEC curves of (A line a) PTEPM₅₈ macro-CTA (Run 1 in Table 1) and (A line b) the corresponding PTEPM₅₈-*b*-PS₃₂₂ diblock copolymer (Run 2 in Table 1), THF used as the eluent. (B) SEC curve of $P2VP_{310}$ (Run 3 in Table 1), DMF with 1 g/L LiBr as solvent.

Table 1

Polymerization and characteristics of P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ triblock copolymer and its precursors.

Run ^a	Feed ratio ^b	Conv. (%) ^c	M_n^{c}	$M_{n GPC}^{d}$	M_w/M_n^d	2VP/TEPM/St ^c
1	110:1	52.8	17300	13700	1.15	0/58/0
2	3000:1	10.7	50800	49700	1.15	0/58/322
3	700:1	44.8	33900	102500	1.09	310/0/0
4	3:1	-	79600	148900	1.13	310/58/322

^a Run 1, 2, 3 and 4 show the PTEPM₅₈ homopolymer, PTEPM₅₈-*b*-PS₃₂₂ diblock copolymer, P2VP₃₁₀ homopolymer and P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ triblock copolymer respectively.

^b Molar ratio of TEPM/CTA 1 for Run 1, St/PTEPM macro-CTA for Run 2, 2VP/CTA 2 for Run 3 and P2VP/PTEPM-*b*-PS for Run 4.

^c Calculated by weight for Run 3 and the others calculated by ¹HNMR spectrum. ^d THF used as the eluent for Run 1, 2 and DMF with 1 g/L LiBr used as the eluent for Run 3, 4.

macro-CTA was observed. Fig. 1 B shows the SEC curve of $P2VP_{310}$ homopolymer (Run 3 in Table 1) in DMF using standard polystyrene as calibration, giving a monomodal peak with a polydispersity of 1.09.

The PTEPM-b-PS-b-P2VP was then obtained by the click chemistry between PTEPM-b-PS diblock copolymer with propargyl end group and P2VP homopolymer with azide end group, where CuBr and tris[2-(dimethylamino)ethyl]amine were used as catalyst and ligand respectively. In order to facilitate the subsequent purification, the mole ratio between P2VP and PTEPM-b-PS was kept to 3:1. Fig. 2 A is the SEC curve of the mixture of PTEPM₅₈-b-PS₃₂₂ and P2VP₃₁₀ before click reaction, where two distinct peaks were ascribed to P2VP₃₁₀ (lower elution time) and PTEPM₅₈-b-PS₃₂₂ (higher elution time) respectively. After reaction, the PTEPM₅₈-b-PS₃₂₂ peak was disappeared completely (Fig. 2 B). Since the trace of triblock copolymer product was covered by that of two folds of excessive P2VP, it cannot be observed obviously in Fig. 2 B. When the excess of P2VP₃₁₀ was readily removed just by fractionation in methanol, there was no the excessive P2VP₃₁₀ remained (Fig. 2 C) and a new peak of the product was recovered. However, from Fig. 2 C, except the main peak of P2VP₃₁₀-b-PTEPM₅₈-b-PS₃₂₂, a small shoulder peak on the higher molecular weight was also observed, which formed by the unknown reason. Shown in Fig. 3 is the ¹H NMR spectrum of P2VP₃₁₀-b-PTEPM₅₈-b-PS₃₂₂ with the corresponding peak



Fig. 2. SEC curves of (A) the mixture of PTEPM₅₈-*b*-PS₃₂₂ and P2VP₃₁₀ before click reaction, (B) the corresponding mixture after click reaction and (C) the purified P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ triblock copolymer (Run 4 in Table 1). DMF with 1 g/L LiBr used as the eluent.



Fig. 3. ¹H NMR spectrum of P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ triblock copolymer in CDCl₃ (Run 4 in Table 1).

assignments, where the proton peaks of P2VP, PTEPM and PS can be observed clearly, indicating the successful synthesis of the expected triblock copolymer. As a result, the P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ triblock copolymer was prepared and its property was summarized in Table 1. Theoretically, the composition of triblock copolymers can be controlled simply by changing the compositions of P2VP homopolymer and PTEPM-*b*-PS diblock copolymer.

3.2. Self-assembly of P2VP₃₁₀-b-PTEPM₅₈-b-PS₃₂₂ triblock copolymer in different annealing solvents and nanoobjects obtained thereof

The microphase separation morphologies of triblock copolymers can be changed by the annealing solvents by virtue of the different polymer/solvent interaction parameter. In case of preferential solvent, as the solution becomes more concentrated during annealing process, the less solvated block will phase separate from the solution then followed by the microphase separation of the other two blocks [34]. For P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂, THF, benzene and chloroform are all good solvents but have different solubility parameter which is 18.6, 18.8 and 19.0 at the room temperature. As a result, they were used as three different annealing solvents to study the bulk microphase separated morphologies of the present triblock copolymer. For TEM analysis, the microtomed slices embedded in epoxy resin were treated with I₂ vapor to stain the P2VP domains.

Fig. 4 A is a representative TEM image of a microtomed slice of bulk samples annealed from THF, where the white and the dark phases were the PS and stained P2VP microdomains respectively. It demonstrated that, when THF was used as annealing solvent, the P2VP cylinders were orderly packed in PS matrix with the period of 56 nm. Based on the macromolecular structure, the PTEPM domain should be located between P2VP and PS microdomain, although it cannot be observed from Fig. 4 A. When using benzene as annealing solvent, the similar cylindrical morphology was obtained. As shown in Fig. 4 B, the dark stained P2VP cylinders were dispersed regularly in the white PS matrix, where the period was also ca. 56 nm. Fig. 4 C shows the TEM image of a microtomed slice of bulk samples annealed from chloroform, in which the lamellar morphology with an alternation of dark P2VP and white PS layers was observed. Similarly, the PTEPM phase should be located between the P2VP and PS phases and the average domain spacing was estimated to be



Fig. 4. TEM images of microtomed slices of the P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ bulk samples annealed from (A) THF, (B) benzene, and (C) chloroform (these three samples were stained with I₂). (D) TEM image of microtomed slice of the crosslinked P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ bulk samples annealed from chloroform without staining.

of ca. 52 nm. As a result, the microphase morphologies of P2VP₃₁₀*b*-PTEPM₅₈-*b*-PS₃₂₂ triblock copolymers can be controlled simply by changing the annealing solvents.

To induce gelation in the PTEPM microdomains, the bulk samples with performed structures were exposed to an atmosphere of hydrochloric acid for about 8 h and further treated at 60 °C under vacuum. As shown previously, this self-gelation process could be carried out completely and did not alter the preformed morphology as well. At this stage, the silica oxide networks formed within the PTEPM microdomains and the microphase separated organic/inorganic hybrid bulk materials were obtained. Fig. 4 D shows the TEM image of one microtomed slice of the crosslinked P2VP310-b-PTEPM58-b-PS322 bulk samples annealed from chloroform without staining and the lamellar morphology was remained. Due to the higher electron density of silica, the black thin domains in Fig. 4 D were attributed the gelated PTEPM layers. By comparing Fig. 4 C and D, it is apparently that the PTEPM layers were located between PS and P2VP layers and, as a result, dispersing the gelated materials in good solvent would give individual polymeric nanoobjects with PS and P2VP tethered onto two sides of the gelated PTEPM microdomains respectively. These hybrid materials with different structures were dispersed in THF for 3 days and the dispersions were characterized by TEM. Shown in Fig. 5 A and B are representative TEM images of nanofibers with a diameter of ca. 61 nm obtained from the hybrid materials annealed by THF and benzene respectively, where the black "backbones" were composed by iodine stained P2VP cores surrounded by crosslinked PTEPM cyclic layers. The periphery PS corona kept the nanofibers from congregation. Shown in Fig. 5 C is the TEM image of the unstained nanofibers dispersed from the hybrid materials annealed by THF, where the tubular nanoobjects were observed because the silica-rich crosslinked PTEPM domain scattered more electron beam. This also demonstrated that the PTEPM microdomains were laid between PS and P2VP phases clearly. Note that, instead of hollow, the inside of the "tube" was actually filled with P2VP blocks tethered inwards. Fig. 5 D shows

the TEM picture of nanoplates dispersed from the hybrid materials annealed by chloroform, where the isolated sheets with irregular periphery were obtained. Based on the block sequence of P2VP₃₁₀*b*-PTEPM₅₈-*b*-PS₃₂₂ as well as the TEM images being stained and unstained (Fig. 4 C and D), the nanoplates obtained here should have a "Janus" structure, where the isolated PS and P2VP hairs scattered in each side of the crosslinked PTEPM planar backbone (the properties and self-assembly behavior of this "Janus" hybrid nanoplate will be reported elsewhere).

3.3. Supramolecular self-assembly of P2VP₃₁₀-b-PTEPM₅₈-b-PS₃₂₂ triblock copolymer with stearic acid and nanoobjects obtained thereof

It is known that the noncovalent complexation between polyvinylpyridine blocks and small organic molecules may change the packing parameters of the block copolymers and, as a result, to alter the microphase separated morphology [40–43]. Herein, we demonstrated this concept in this system by using hydrogen-bonding interaction between P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ and stearic acid.

Fig. 6 A shows the TEM image of microtomed samples formed by P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ hydrogen-bonded with stearic acid, where the molar ratio between 2VP and stearic acid was fixed to 1:1 and CHCl₃ was used as annealing solvent. As shown in Fig. 6 A, the morphology of isolated white PS cylinders scattered in the black stained P2VP matrix was observed and the period of 58 nm was measured. Compared with Fig. 4 C, the bulk lamellar morphology formed in chloroform without stearic acid was changed to a cylindrical morphology successfully by the hydrogen-bonding interaction. It was noteworthy that the cylindrical structure also differed to those from the THF and benzene annealing solvents shown in Fig. 4A and B. The PS domains became the cores while the P2VP complexed with stearic acids became the coronas of the fibrillar nanoobjects. The reason of the reversed structure can be explained by increase of the volume fraction of P2VP domains via complexation with stearic acids.



Fig. 5. TEM images of the dispersed nanoobjects in THF from P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ annealed by different solvents. (A): Nanofibers annealed from THF, stained by I₂; (B): Nanofibers annealed from benzene, stained by I₂; (C): Unstained nanofibers annealed from THF and (D) "Janus" nanoplates annealed form chloroform.

After gelation in PTEPM microdomains and then dispersion in chloroform, isolated nanofibers with a diameter of ca. 62 nm were obtained (Fig. 6 B). Their internal structure was composed of a PS core and external coronas were P2VPs complexed by stearic acid. Therefore, hairy fibrils with reversed internal and external polymers have been obtained from the sample block copolymers being treated by different means.

3.4. Properties of organic/inorganic hybrid nanofibers with P2VP cores

Because functional P2VPs can be easily modified by quaternized reaction or by supramolecular interaction such as hydrogenbonding or coordination, these nanoobjects with different internal structures can be used as universal templates for making novel nanoobjects with more delicate structures and multi-functionality. Herein we showed this concept by using P2VP core of the nanofibers formed by P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ annealed in THF as an example.

3.4.1. Nanofibers loaded with gold nanoparticles

When HAuCl₄ was added slowly into the nanofibers dispersed in THF with vigorously stirring, the color of the white dispersion turned pale yellow after separation by centrifugation from THF, indicating that the Au ions had been captured by the nanofibers. After a freshly prepared aqueous solution of sodium borohydride was added, the color of the solution immediately turned from pale yellow to red, indicating the formation of Au nanoparticles. Fig. 7 A shows the TEM micrograph of the corresponding nanofibers loaded with gold nanoparticles and demonstrates that the gold particles had been located in the core of fibers. Furthermore, a magnification was also inserted in Fig. 7A, where the Au nanoparticles were observed clearly.

3.4.2. Modification of P2VP cores of nanofibers by quaternization and hydrogen-bonding

Since P2VP can be easily modified by quaternization and hydrogen-bonding, it allowed us to load functional molecules into the core-shell nanofibers. Herein, we used 1-bromohexane and 1-capric acid as model molecules to demonstrate these concepts respectively.



Fig. 6. TEM images of microtomed slices of (A) the P2VP₃₁₀-b-PTEPM₅₈-b-PS₃₂₂ hydrogen-bonded with stearic acid and (B) the corresponding nanofibers dispersed in chloroform. Samples were stained with I₂.



Fig. 7. TEM micrographs of the modified hybrid nanofibers from $P2VP_{310}$ -*b*-PTEPM₅₈-*b*-PS₃₂₂ annealed and dispersing in THF being (A) loaded with gold nanoparticles, (B) quaternized by 1-bromohexane and (C) hydrogen-bonded with 1-capric acid. These samples were not stained.



Fig. 8. (A) FT-IR spectra of the nanofibers by P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ annealed in THF. (a) Hydrid nanofibers, (b) quaternized by 1-bromohexane, and (c) hydrogenbonded with 1-capric acid. (B) is a magnification of A.

FT-IR analysis was chosen to characterize the successful quaternization and hydrogen-bonding, and the related results were shown in Fig. 8, where B is a magnification of A from 900 cm^{-1} to 1100 cm⁻¹. The curves a in Fig. 8 A and B show FT-IR spectra of hybrid nanofibers by P2VP₃₁₀-b-PTEPM₅₈-b-PS₃₂₂ annealed in THF. After quaternizing with 1-bromohexane, the FT-IR spectra, the curves b in Fig. 8 A and B. showed that the bands corresponding to the carbon-nitrogen stretching in free pyridine rings at 1590 $\rm cm^{-1}$ were greatly decreased whereas a new bond of pyridinium rings was observed at 1618 cm⁻¹. Moreover, the distortion vibration of the pyridine rings at 993 cm^{-1} also disappeared due to the quaternization. Fig. 7 B gave the TEM image of modified nanofibers, where the cylindrical morphology was remained. Similarly, the P2VP cores were modified with 1-capric acid via hydrogen-bond. As shown in the curves c in Fig. 8 A and B, the characteristic absorption peaks of free pyridine rings at 1590 cm⁻¹ and 993 cm⁻¹ were shifted to 1601 cm⁻¹ and 1012 cm⁻¹ respectively because of hydrogen-bonding. The fibrillar morphology after modification remained unchanged as shown by TEM micrograph in Fig. 7 C.

4. Conclusion

By combining RAFT-mediated radical polymerizations with click chemistry, we have prepared triblock copolymer P2VP₃₁₀-*b*-PTEPM₅₈-*b*-PS₃₂₂ whose middle blocks were macromolecular silanes. By changing different annealing solvent, this block copolymer self-assembled in the bulk into the ordered packed cylinders and lamella respectively. Also by introducing stearic acid to form complexes with the P2VP blocks, the cylinders with reversed structure have been obtained. The morphologies of these materials were further fixed by inducing gelation crosslinking in the PTEPM phases. Followed by dispersing in solvent, two hairy polymer nanofibers with reversed structure and one "Janus" nanoplates have been obtained. These results indicated that one triblock copolymer sample bearing PTEPM as a middle block formed the polymeric nanoobjects of different shape and different structure.

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