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# Organic−Inorganic Hybrid Materials by Self-Gelation of Block Copolymer Assembly and Nanoobjects with Controlled Shapes Thereof

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ABSTRACT: Radical polymerization of a gelable monomer 3-(triethoxysilyl)propyl methacrylate (TEPM) mediated by a chain transfer agent (CTA), cumyl dithiobenzoate (CDB), i.e., reversible addition−fragmentation chain transfer (RAFT) polymerization, has been studied. A series of well-defined PTEPM-*block*-polystyrene (PTEPM-*b*-PS) diblock copolymers were synthesized via sequential RAFT polymerization of styrene mediated by the PTEPM macromolecular CTA. Both formations of PTEPM homopolymers and the PTEPM-*b*-PS diblock copolymers exhibited first-order kinetics, and the molecular weights increased linearly with monomer conversion. The bulk microphase separation behaviors of PTEPM-*b*-PS diblock copolymers were studied by a combination of small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). With change of the block composition, three different morphologies of microphase separation, i.e., lamellae, hexagonally packed cylinders, and spheres, were obtained. Afterward, self-gelation of the PTEPM phases was carried out in-situ to cross-link the PTEPM phase, and novel organic−inorganic hybrid bulk materials with ordered domain structures of three morphologies were obtained. Furthermore, when the gelated materials were dispersed in a good solvent for the PS matrix, the isolated organic−inorganic hybrid nanoobjects with controlled shapes including plates, cylinders, and spheres with PS hairs were prepared from the respective bulk materials. This self-gelation process of block copolymer aggregates in bulk can be universal and may be extended to prepare various ordered hybrid materials and isolated hybrid nanoobjects with tailored shapes and functionality.

## Introduction

Block copolymers comprised of chemically distinct polymers covalently joined together self-organize in bulk into well-defined nanoscopic morphologies such as body-centered-cubic (BCC) arrays of spheres, hexagonally packed cylinders, bicontinuous gyroids, and alternating lamellae simply by changing their molecular parameters.[1−3] In the past decade, block copolymers have been widely used in nanotechnologies in many different fields, such as preparation of nanoobjects[4] and nanocomposites,[5,6] patterned thin film,[7−9] and lithography[10,11] etc. Nanocomposites and nanoobjects with controlled shape, size, and composition based on block copolymer assembly are promising materials which may find considerable applications in areas such as drug delivery, catalysis, separation, photonics, energy generation and storage, electronics, etc. Cross-linking one domain of the preformed ordered structure of block copolymer in bulk is a very interesting approach to change the structure of block copolymer bulk materials. Furthermore, dispersing such bulk materials in a good solvent for the un-cross-linked domain may easily produce novel nanomaterials with a controlled morphology inherited from the bulk structure.

Until now, two approaches have been developed in this field. One is to fix the specific domains of the preformed assembly based on the block copolymers with a cross-linkable functional block. Many kinds of block copolymer have been used in this field, such as polystyrene-*block*-poly(2-cinnamoethyl methacrylate) (PS-*b*-PCEMA),[12,13] polystyrene-*block*-polyisoprene (PS-*b*-PI),[14,15] polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP),[16−19] poly(butyl methacrylate)-*block*-poly(2-cinnamoethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) (PBMA-*b*-PCEMA-*b*-P*t*BA),[20] polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(butyl methacrylate) (PS-*b*-P2VP-*b*-PBMA),[21] polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (PS-*b*-PB-*b*-PMMA),[22] etc. The most complete investigation focused on this way has been carried out by Liu et al. Using the block copolymers containing a photo-cross-linkable PCEMA block, they have prepared organic nanoobjects with controlled compositions, such as spheres,[23−25] fibers,[12−15,26,27] tubes,[20,28] and membranes with tunable nanochannels.[29−31] However, the block copolymers they used were purely organic polymers, which limited the application of nanoobjects in some aspects which need higher stability.

The other is to use the block copolymers as structure-directing agents for the metal oxide to prepare organic/inorganic hybrid materials and nanoobjects. This approach has been studied extensively by Wiesner et al. using the block copolymers such as polyisoprene-*block*-poly(ethylene oxide) (PI-*b*-PEO)[32] and poly(hexyl methacrylate)-*block*-poly(ethylene oxide) (PHMA-*b*-PEO).[33] The precursors of metal alkoxides selectively swelled the PEO phase of the block copolymers due to the hydrophilic nature of PEO. By changing the fraction between block copolymers and metal alkoxides, the organic/inorganic hybrid nanoobjects with controlled shape, size, and composition have been obtained.[4,33−38] These nanoobjects are robust due to the presence of inorganic components. However, the block copolymer used in their system has to meet the following criteria: first, the building blocks should show phase separation at ambient temperatures; second, the hydrolysis products of the metal alkoxides should preferentially swell the hydrophilic block; third, a low glass transition temperature of the hydrophobic block should introduce high mobility at ambient temperatures and

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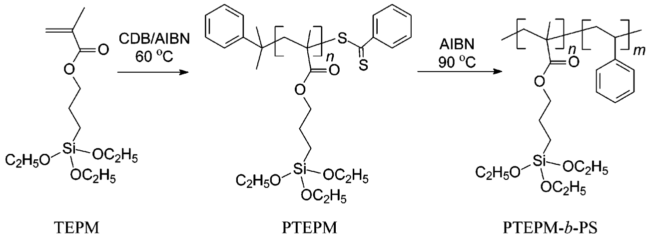
**Scheme 1. Synthesis of PTEPM and Its Block Copolymer Mediated by RAFT Polymerization**



should allow rapid formation of structures with long-range order even in the bulk.[33] Therefore, the suitable block copolymers used in this method were limited strictly. Also, Saito et al. have obtained organic−silica nanocomposites directed block copolymer assembly or phase separation of random copolymers.[39−41]

3-(Trialkyloxysilyl)propyl methacrylate is a kind of gelable monomer which is an important silane coupling agent widely used for the preparation of organic/inorganic hybrid materials. Recently, our group has studied the property of a kind of gelable block copolymers of poly(ethylene oxide)-*block*-poly(3-(trimethoxysilyl)propyl methacrylate) (PEO-*b*-PTMSPMA) obtained by the atom-transfer radical polymerization (ATRP) technique.[42] Through their self-assembly in solution, various organic/inorganic hybrid morphologies, including spheres,[43] vesicles[44,45] and compound vesicles,[46] with silica oxide network have been obtained by a gelation process occurred only in the PTMSPMA domains of the preformed aggregates. Through controlled radical polymerization like ATRP and RAFT,[47] different kinds of block copolymer containing PTMSPMA have been synthesized, with predetermined molecular weights and narrow molecular weight distributions. The well-defined organic/inorganic hybrid nanoobjects with controlled shapes could have been obtained by the microphase separation morphologies in bulk using such gelable block copolymers, whose structure could be similar to the nanoobjects prepared by Wiesner et al. It would be important if this self-gelation process could be extended to many different block copolymers, namely, various hybrid materials, and well-defined nanoobjects could be produced not only by the amphiphilic block copolymers with lower glass temperature hydrophobic block but also by the block copolymers containing higher glass transition temperature block, such as PS and PMMA, which are widely used polymers in application. Further, more functions like complexation to metal ions and stimulus-responsive could be endowed to these nanohybrids if the segment could be functionalized. Thomas et al. have reported an anisotropic nanoobjects via bulk self-assembly of poly(3-(triethoxysilyl)propyl isocyanate)-*block*-polystyrene (PIC-*b*-PS).[48] However, as far as we knew, this is the first report to prepare organic−inorganic hybrid nanoobjects based on the *self-gelation* process of block copolymers, and only one type of particle was obtained.

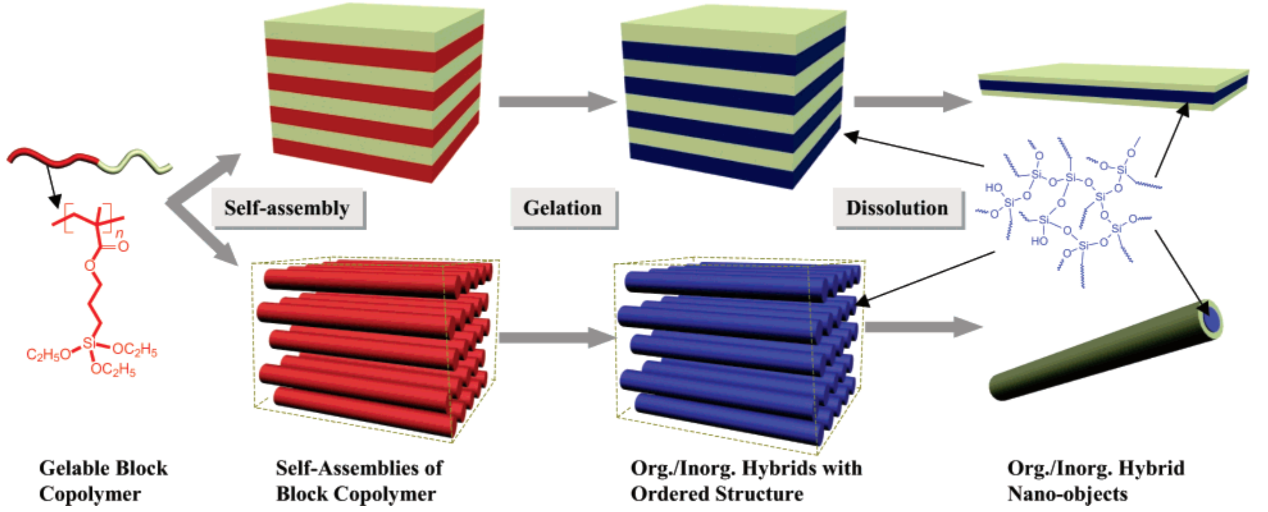
Herein, we report the preparation of hybrid bulk materials with organized domains from a new gelable block copolymer, poly(3-(triethoxysilyl)propyl methacrylate)-*block*-polystyrene (PTEPM-*b*-PS), which was synthesized by RAFT mediated radical polymerization. The self-gelation process of PTEPM phase in lamellar, cylindrical, and spherical structure was conducted with the preformed microphase structure. Moreover, the isolated organic−inorganic hybrid nanoobjects with controlled shape such as spheres, cylinders, and plates have been obtained by dispersing the bulk materials into a good solvent for PS. Scheme 1 shows the synthesis of the gelable block copolymer PTEPM-*b*-PS, and Scheme 2 presents the principle of the self-gelation process to generate novel hybrid materials.

## Experimental Section

**Materials.** Styrene was dried over calcium hydride overnight and distilled under a reduced pressure. 3-(Trimethoxysilyl)propyl methacrylate (>95%, Wuhan University Silicone New Material Co.) was dried over $CaH_2$ overnight and distilled under a reduced pressure. 3-(Triethoxysilyl)propyl methacrylate (TEPM) was synthesized according to a literature from 3-(trimethoxysilyl)propyl methacrylate.[49] Cumyl dithiobenzoate (CDB) was synthesized according to the literature.[50] 2,2-Azoisobutyronitrile (AIBN) was recrystallized from methanol and stored at 4 °C. Anhydrous ethanol (>99%, Beijing Chemical Reagent Co.) was refluxed over magnesium. Anhydrous methanol, tetrahydrofuran (THF), toluene, and benzene (>99%, Beijing Chemical Reagent Co.) were used as received.

**Polymerization of TEPM and Synthesis of Poly(3-(triethoxysilyl)propyl methacrylate) (PTEPM) Macromolecular Chain Transfer Agent (Macro-CTA).** A general procedure: Bulk polymerization of TEPM was performed in a sealed ampule equipped with a stir bar under vacuum. A typical procedure was as follows: CDB (75.0 mg, $2.75 \times 10^{-1}$ mmol), TEPM (4.0 g, 13.8 mmol), and AIBN (4.5 mg, $2.74 \times 10^{-2}$ mmol) were added into a 10 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

**Scheme 2. Ordered Organic/Inorganic Hybrid Materials by Self-Assembly of Gelation Block Copolymer PTEPM-*b*-PS in Bulk and Isolated Hybrid Plate and Cylinder (Red: PEPM Chain; Yellow: PS Chain; Blue: Silica Oxide Network)**



30 h. The reaction 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 the $^1$H NMR spectrum.

**Synthesis of PTEPM-*b*-PS Diblock Copolymer.** The polymerization was performed in a sealed ampule equipped with a stir bar under vacuum. A general procedure: PTEPM macro-CTA (232 mg, $M_{n,NMR} = 11\,480$; $M_w/M_n = 1.15$) and styrene (6.34 g, 60.9 mmol) were charged into a 20 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 32 h. The reaction was stopped by cooling of the solution, and the mixture was exposed to air. The resulting product dispersed in THF was purified by precipitating into methanol three times. Monomer conversion was determined by the $^1$H NMR spectrum.

**Bulk Casting and Annealing of PTEPM-*b*-PS.** The casting and annealing of all PTEPM-*b*-PS diblock copolymers into bulk samples were conducted analogously. The representative procedure was described. A concentrated solution of PTEPM-*b*-PS diblock copolymer (50 mg/mL) in benzene was spread dropwise onto a clean Teflon plate and 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. Thermal annealing at 110 °C for 24 h under argon gave the diblock copolymer bulk sample with microphase separation.

**Self-Gelation in Microdomain Structure and Preparation of Nanoobjects.** PTEPM-*b*-PS bulk samples with microphase separation structure were immersed into 2 M HCl aqueous solutions for 24 h and then dried under vacuum at 60 °C for 12 h to carry out the sol−gel reaction of the PTEPM domain completely. After cross-linking, the samples were immersed in THF and stirred. The films became dispersed in around 1 day.

**Characterization.** Gel permeation chromatography (GPC) was performed by a set of a Waters 515 HPLC pump, a Waters 2414 refractive index detector, and the combination of Styragel HT-2, HT-4, and HT-5, the effective molecular weight range being 100−10 000, 5000−600 000, 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. Polystyrene standards were used for the calibration.

$^1$H NMR spectra were recorded on a Bruker DMX400 spectrometer with $CDCl_3$ 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.

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. No staining was performed for the microtomed sections. SAXS data were collected on a Rigaku RU300 copper rotating anode ($\lambda = 1.54$ Å) operated at 40 kV and 50 mA. X-rays were monochromized with a Ni filter and focused using orthogonal Franks mirrors. SAXS patterns were collected with a 1K × 1K pixel CCD detector.

## Results and Discussion

**Polymerization of TEPM Mediated by RAFT and Synthesis of PTEPM-*b*-PS Diblock Copolymers.** The polymerization kinetics was studied first. RAFT-mediated radical polymerizations of PTEPM were performed in bulk using CDB as RAFT agent and AIBN as initiator. The molar ratio between CDB and AIBN was fixed to 10/1. After being degassed by four freeze−evacuate−thaw cycles, the sealed ampule with mixture was thermostated to a certain temperature. Shown in Figure 1A is the semilogarithmic plot of $\ln([M]_0/[M])$ vs reaction time for the CDB-mediated polymerization of TEPM at 60 °C. Following an induction period (about 18 h) which could be caused by various factors discussed elsewhere,[51] a pseudo-first-order kinetic was observed. The monomer conversion reached 55% after 50 h. The evolution of molecular weight of polymerization determined by GPC traces is shown in Figure 1B. The peak position moves to the higher molecular weight direction gradually with increase of reaction time, and monomodal peaks with good symmetry are demonstrated.

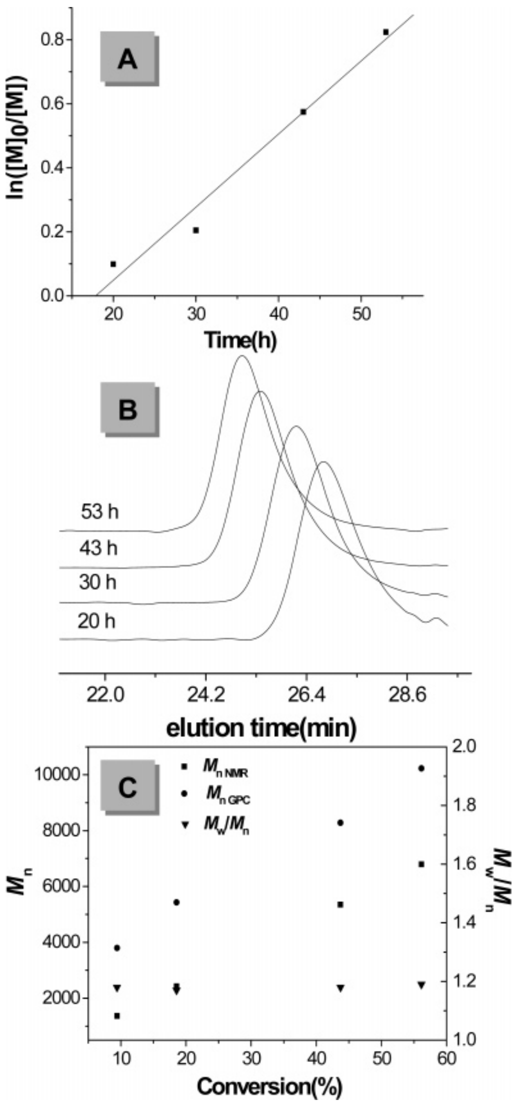


**Figure 1.** Polymerizations of TEPM mediated by CDB with AIBN as initiator: (A) dependence of $\ln([M]_0/[M])$ vs time, (B) GPC traces, and (C) evolution of the molecular weights and $M_w/M_n$ with monomer conversion. Reaction conditions: TEPM/CDB/AIBN = 40/1/0.1 (molar ratio), 60 °C.

The number molecular weight ($M_{n,NMR}$) of PTEPM homopolymers was calculated by the monomer conversion from the formula

$$M_n = M_{CTA} + M_{TEPM}\frac{[\mathrm{TEPM}]x_{TEPM}}{[\mathrm{CTA}]}$$

where $M_{CTA}$ and $M_{TEPM}$ were the molecular weights of RAFT agent and TEPM, respectively, and $x_{TEPM}$ was the monomer conversion. The contribution of the molecular weight of the chains initiated by AIBN was neglected. TEPM monomer conversion was determined by $^1$H NMR analysis, which was performed directly with the polymerization mixture in the

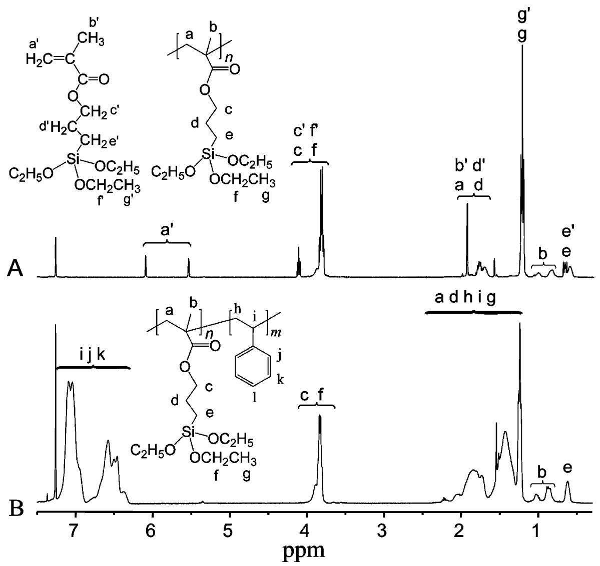


**Figure 2.** $^1$H NMR spectra of (A) TEPM polymerization mixture containing TEPM and PTEPM and (B) PTEPM-*b*-PS diblock copolymer.

deuterated choloroform. As shown in Figure 2A, $x_{TEPM}$ was obtained using

$$x_{TEPM} = \frac{A_{e'e} - A_{a'}}{A_{e'e}}$$

where $A_{e'e}$ and $A_{a'}$ were the areas of peaks e′e and a′, respectively.

Figure 1C shows the plots of $M_{n,GPC}$ (number-average molecular weight obtained by GPC), $M_{n,NMR}$, and $M_w/M_n$ values as a function of conversion. The molecular weights given by two ways increased linearly with the conversion. In addition, the molecular weight distribution, $M_w/M_n$, did not exceed 1.20 in all the cases. The discrepancy between $M_{n,GPC}$ and $M_{n,NMR}$ is reasonable as the calibration of GPC was based on the polystyrene standards. The above results demonstrate the RAFT of TEPM mediated by CDB in bulk is a controlled process.

Syntheses of PTEPM-*b*-PS diblock copolymers were performed in bulk using PTEPM as a macro-CTA. After degassed by freeze−evacuate−thaw cycles, the sealed ampule with mixtures was thermostated to 90 °C. Figure 3A shows the semilogarithmic plot of ln([M]$_0$/[M]) vs reaction time for synthesis of PTEPM-*b*-PS. A pseudo-first-order kinetics was observed after an induction period (about 4.8 h), indicating the radical concentration kept constant during this reaction.

The number molecular weights and composition of diblock copolymers were obtained from the $^1$H NMR analysis. As shown in Figure 2B, the composition was calculated by comparing the peak areas of the protons derived from two blocks, e.g., ijk ($-C_6H_5$) in PS block and e ($-CH_2Si(OC_2H_5)_3$) in PTEPM block. The molecular weight development of block copolymerization was traced by GPC as shown in Figure 3B. The peak moved to the higher molecular weight direction gradually with increase of reaction time, and no peak of macro-CTA was observed. From Figure 3C, the molecular weights estimated by GPC and $^1$H NMR analysis, $M_{n,GPC}$ and $M_{n,NMR}$, increased linearly with the conversion of St. In addition, molecular weight distribution, $M_w/M_n$, remained below 1.10 in all the cases. All the results demonstrate the RAFT of St mediated by PTEPM is a controlled reaction. As a result, a series of block copolymers for self-organization were prepared, and their properties are summarized in Table 1. The composition of PTEPM-*b*-PS diblock copolymers with different lengths of PTEPM and PS segments were synthesized by changing the macro-CTAs and the feed ratios of TEPM to macro-CTA.

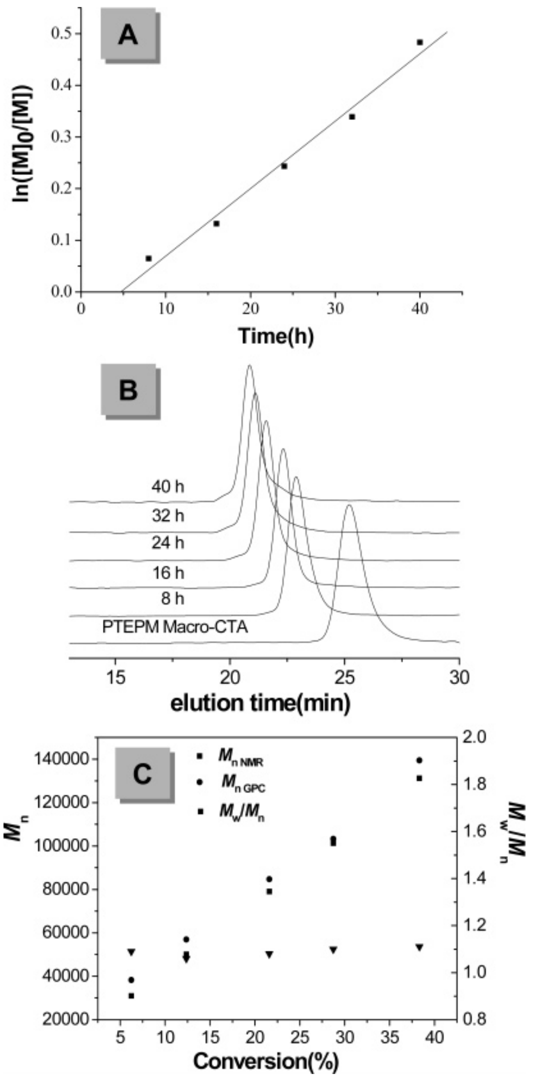


**Figure 3.** Formation of PTEPM-*b*-PS mediated by PTEPM macro-CAT: (A) dependence of ln([M]$_0$/[M]) vs time, (B) GPC traces, and (C) evolution of the molecular weights and $M_w/M_n$ with monomer conversion. Reaction conditions: St/PTEPM = 3000/1 (molar ratio), 90 °C.

**Morphologies of PTEPM-*b*-PS Diblock Copolymers in Bulk.** The bulk morphologies of all the block copolymers have been studied, and the results are listed in Table 1. In general, the phase structure developed from lamella to cylinder to sphere with increase the ratio of PS segment. The polymers of different composition, PTEPM$_{88}$-*b*-PS$_{408}$, PTEPM$_{66}$-*b*-PS$_{758}$, and PTEPM$_{46}$-*b*-PS$_{1009}$, were selected as representative examples to study their microphase separation morphologies in bulk by SAXS. The SAXS curves of the bulk films from these block copolymers are collected in Figure 4.

For polymer PTEPM$_{88}$-*b*-PS$_{408}$, whose molecular weight fraction of PTEPM block was 0.38, its bulk microphase separation formed a highly ordered lamellar morphology. Figure 4A (line a) shows the SAXS curve of this sample, and the peak position ratio is 1:2:3:4, consistent with a lamellar morphology. From the primary peak position value at low *q*, the average domain spacing was calculated to be 35.9 nm. This result of a lamellar structure was further confirmed by TEM analysis of a microtomed slice (Figure 5). The average periodic length of lamellae obtained by Figure 5 is 35.2 nm, which is similar to

**Table 1. Radical Polymerizations of the PTEPM Mediated by CDB and Properties of PTEPM-*b*-PS**

| run[a] | feed ratio[b] | conv (%)[c] | $M_{n,NMR}$ | $M_{n,GPC}$ | $M_w/M_n$ | TEPM/St[c] | $W_{PTEPM}$ (%) | structure[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | 50:1 | 76.3 | 11 480 | 14 570 | 1.15 | 38/0 | | |
| 2 | 120:1 | 73.0 | 25 980 | 29 860 | 1.17 | 88/0 | | |
| 3 | 100:1 | 66.1 | 19 520 | 22 640 | 1.13 | 66/0 | | |
| 4 | 55:1 | 83.6 | 13 780 | 16 770 | 1.12 | 46/0 | | |
| 5 | 3000:1 | 6.2 | 30 970 | 38 230 | 1.09 | 38/187 | 36 | lam |
| 6 | 3000:1 | 12.3 | 50 130 | 56 960 | 1.06 | 38/371 | 22 | hex |
| 7 | 3000:1 | 28.7 | 101 240 | 103 260 | 1.10 | 38/826 | 11 | sphere |
| 8 | 3000:1 | 38.3 | 131 230 | 139 450 | 1.11 | 38/1150 | 8 | sphere |
| 9 | 1000:1 | 40.8 | 68 050 | 69 190 | 1.20 | 88/408 | 38 | lam |
| 10 | 2112:1 | 35.9 | 98 110 | 100 250 | 1.09 | 66/758 | 20 | hex |
| 11 | 6000:1 | 16.8 | 118 450 | 120 130 | 1.10 | 46/1009 | 11 | sphere |

[a] Runs 1−4 show the PTEPM homopolymers mediated by CDB at 60 °C. The molar ratio between CDB and initiator AIBN was 10/1. Runs 5−12 show the synthesis and characteristics of the PTEPM-*b*-PS diblock copolymers mediated by corresponding PTEPM macro-CTA at 90 °C. [b] TEPM/CDB (molar ratio) for runs 1−4; St/macro-CTA (molar ratio) for runs 5−12. [c] Calculated by $^1$H NMR spectrum. [d] Microphase separation morphologies of PTEPM-*b*-PS diblock copolymers: lam means alternating PTEPM and PS lamellae, hex means hexagonally packed PTEPM cylinders in PS matrix, and sphere means PTEPM spheres in PS matrix.

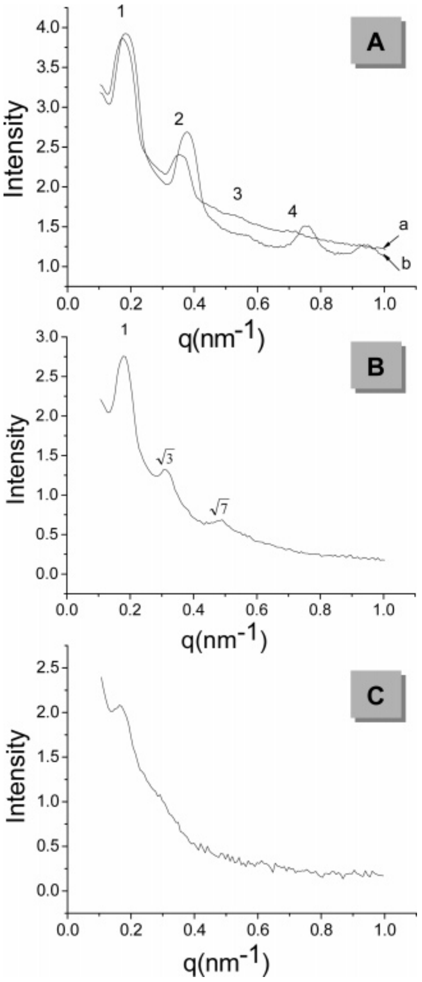


**Figure 4.** Small-angle X-ray scattering curves of the bulk samples from (A) PTEPM$_{88}$-*b*-PS$_{408}$ before (a) and after cross-linking (b), (B) PTEPM$_{66}$-*b*-PS$_{758}$, and (C) PTEPM$_{46}$-*b*-PS$_{1009}$.

the result of SAXS. The polymer PTEPM$_{66}$-*b*-PS$_{758}$, whose weight fraction of PTEPM block was 0.20, formed a highly ordered cylindrical morphology. As demonstrated in the SAXS curve in Figure 4B, the reflection pattern of a ratio $1:\sqrt{3}:\sqrt{7}$ supported a hexagonally packed cylinder morphology. From the main peak position value, the average periodicity was calculated to be 35.4 nm. The polymer PTEPM$_{46}$-*b*-PS$_{1009}$, with smallest weight fraction of 0.11, generated a liquidlike spherical micelle morphology, a state between BCC and disordered phase.[3] Figure 4C is the SAXS curve of this sample, whose feature is consistent with a liquid spherical micelle morphology since no periodic pattern was observed.

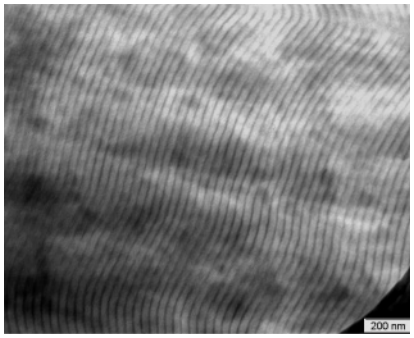


**Figure 5.** TEM image of the alternating lamellae formed by PTEPM$_{88}$-*b*-PS$_{408}$ microphase separated in the bulk at equilibrium.

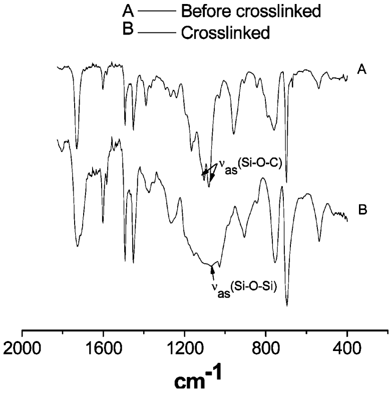


**Figure 6.** FT-IR spectra of the bulk sample of PTEPM$_{88}$-*b*-PS$_{408}$ of lamellar morphology (A) before and (A) after gelation occurred in PTEPM microphase.

**Organic−Inorganic Hybrid Bulk Materials by Self-Gelation Process and Nanoobjects Thereof.** When the microphase separation of dibolock copolymers was finished, the PTEPM phase was distributed in the PS phase as lamellae, cylinders, and spheres. The PTEPM-*b*-PS diblock copolymers synthesized in this article contained a gelable PTEPM block, which may occur sol−gel reaction under acid or basic conditions. To carry out the sol−gel reaction of the PTEPM block, the materials having tailored microphase separation morphologies were immerged into an acidic water solution for 24 h and then dried under vacuum at temperature of 60 °C for another 24 h. The reactions were completely carried out as confirmed by FT-IR spectroscopy (Figure 6). Before gelation, the absorption peaks at 1103 and 1079 cm$^{-1}$ were assigned to the asymmetric Si−O−C stretch and the peaks at 1167 and 960 cm$^{-1}$ were the characteristics of the ethoxy group. After the reaction, the characteristic peaks disappeared, whereas a strong

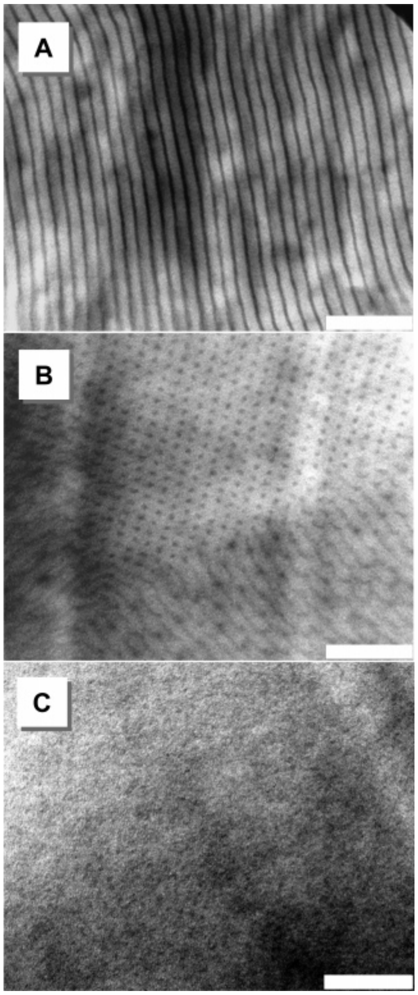


**Figure 7.** TEM images of gelated bulk materials from (A) PTEPM$_{88}$-*b*-PS$_{408}$, (B) PTEPM$_{66}$-*b*-PS$_{758}$, and (C) PTEPM$_{46}$-*b*-PS$_{1009}$. Scale bar: 200 nm.

broad peak in the range of 1000−1140 cm$^{-1}$ appeared, which could be ascribed to the asymmetric Si−O−Si stretching vibration, indicating that the sol−gel reaction was carried out completely. At this stage, the PTEMP-rich phases in above three structures were transformed into silica oxide networks confined in the preformed microdomains.

Figure 4A (line b) is the SAXS curve of the microphase separated by PTEPM$_{88}$-*b*-PS$_{408}$ after sol−gel reaction. The lamellar morphology, with a *d*-spacing of 33.8 nm, remained, but a little shrinkage of the periodic length was observed. Shown in Figure 7A is the corresponding microtomed TEM photograph, where an ordered array of alternating PTEPM and PS lamellae with an average domain spacing of 33.2 nm is demonstrated. The shrinkage is reasonable since the small molecules are lost during gelation. Therefore, the lamellar morphology microphase separated by PTEPM$_{88}$-*b*-PS$_{408}$ did not change during the gelation process. This is because the glassy PS domains had frozen the structure, and the acidic water molecules penetrated into PTEPM domains to trigger the gelation.

As indicated by the TEM image in Figure 7B, an ordered array of PTEPM cylinders in the PS matrix was observed from the gelated sample of PTEPM$_{66}$-*b*-PS$_{758}$. The periodic length, 34.1 nm measured from TEM photograph, agreed with the data obtained from SAXS curve. Also, Figure 7C shows the TEM photograph of a thin slice of the gelated polymer PTEPM$_{46}$-*b*-PS$_{1009}$, which displayed a liquidlike packing of PTEPM spheres in the PS matrix. Therefore, the self-gelation process did not alter the phase structure of these two block copolymers preformed.

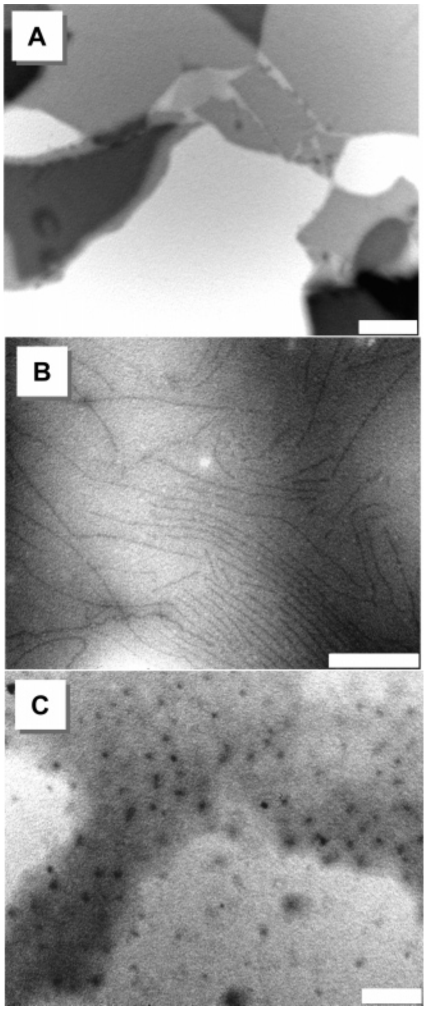


**Figure 8.** TEM micrographs of the hybrid nanoobjects obtained through dispersing the bulk samples in THF after gelation: (A) PTEPM$_{88}$-*b*-PS$_{408}$, (B) PTEPM$_{66}$-*b*-PS$_{758}$, and (C) PTEPM$_{46}$-*b*-PS$_{1009}$. Scale bar: (A) 1000, (B) 500, and (C) 200 nm.

When the sol−gel reaction in PTEPM microdomains was completed, the organic−inorganic hybrid materials with different microphase morphologies could be obtained; namely, the hard inorganic structure hybridized with the soft organic polymers in an ordered packing. Dispersing these materials in the solvent of PS matrix, well-defined nanoobjects with different shapes could be obtained according to the structure of microphase separation.

To prepare well-defined isolated organic−inorganic hybrid nanoobjects, the hybrid bulk materials were dispersed in THF, a good solvent for the PS matrix for about 3 days with stirring. Figure 8 shows the TEM photographs of three kinds of hybrid nanoobjects with different shapes obtained by this process. By dispersing the hybrid materials prepared by PTEPM$_{88}$-*b*-PS$_{408}$, isolated organic−inorganic hybrid plates bearing PS hairs were obtained. When the same procedure was applied to the hybrid materials prepared by PTEPM$_{66}$-*b*-PS$_{758}$ and PTEPM$_{46}$-*b*-PS$_{1009}$, well-defined organic−inorganic hybrid nanofibers and nanospheres were also obtained, respectively. Since the cores of these objects were derived from the corresponding PTEPM phases, the thickness of plates and the diameter of cylinders are rather uniform and should be the same to the values of PTEPM phases in bulk. For examples, the core diameter of the fibers in Figure 8B was measured to be 13 nm, which agrees with that of cylinders measured from Figure 7B. It is noteworthy that PS hairs are tethered onto the surfaces of plates, cylinders, and spheres by covalent bonding, which are different than the physically embedded structure previously.[4]

The above results demonstrate that the self-gelation of preformed block copolymer assembly in bulk have successfully produced several organic−inorganic nanohybrids of different shapes. These materials were prepared by spontaneous self-assembling the block copolymers bearing a gelable block, and therefore, this process is rather facile compared with those template approaches. It should be mentioned that the soluble PS hairs are tethered along the surface of plates, cylinders, and spheres, which are very important for dissolving the objects in solvents and other polymer matrix.[52,53] Theoretically, through controlled polymerization, different kinds of block copolymers containing the gelable PTEPM or PTMSPMA block, such as poly(3-(triethoxysilyl)propyl methacrylate)-*block*-poly(vinylpyridine), poly(3-(triethoxysilyl)propyl methacrylate)-*block*- poly(*tert*-butyl acrylate), etc., can be obtained easily using controlled radical polymerization. So, various isolated organic−inorganic hybrid nanoobjects not only with controlled shapes but also with different functional hairs can be prepared by the approach developed in this article, which may stimulate various researches and find potential applications in the nanomaterials and technology.

## Conclusion

We have demonstrated that the CDB-mediated RAFT method can be used to polymerize the gelable monomer TEPM with controlled molecular weights and narrow molecular weight distributions. By a sequential RAFT polymerization of St mediated by PTEPM macro-CTA, we have also successfully synthesized a series of well-defined PTEPM-*b*-PS diblock copolymers. With changing the molecular weight fraction of PTEPM block in the diblock copolymer from 0.38 to 0.20 to 0.11, three different microphase separation morphologies, i.e., lamella, hexagonally packed cylinders, and liquidlike spheres, were obtained. An in-situ sol−gel reaction of triethoxylsilyl groups limited in the PTEPM microphase was conducted with the aid of acidic water, and novel hybrid bulk materials with an organized microstructure have been obtained. Furthermore, individual and dispersible organic−inorganic hybrid nanoobjects of lamellar, cylindrical, and spherical shape were prepared by dispersing the gelated materials into THF. We are going to expand the types of polymer architecture and morphology in order to prepare various hybrid nanoobjects with different shapes and functionalities. In addition, this new gelable block copolymer may be also used to generate patterned thin films that can be hybridized by silica oxide and even transformed into inorganic patterns.

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