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Atom-Transfer Radical Polymerization of a Reactive Monomer: 3-(Trimethoxysilyl)propyl Methacrylate

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ABSTRACT: Atom-transfer radical polymerizations (ATRPs) of a reactive monomer, 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), mediated by CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) in anisole have been studied using ethyl 2-bromoisobutyrate (2-EBiB) and poly(ethylene oxide) methyl ether 2-bromoisobutyrate (PEO-Br) as initiators. In general, the polymerizations of TMSPMA exhibited first-order kinetics, and molecular weights increased linearly with monomer conversion. Molecular weight distributions remained low throughout the polymerizations ($M_w/M_n = 1.20-1.40$). The overall rate of polymerization with PEO-Br as the initiator was enhanced compared to that with 2-EBiB as the initiator. A series of reactive diblock copolymers, poly(ethylene oxide)-*b*-poly[3-(trimethoxysilyl)propyl methacrylate] (PEO-*b*-PTMSPMA), were thus synthesized. By random copolymerization with methyl methacrylate (MMA), PEO-*b*-P(TMSPMA-*r*-MMA) copolymer was prepared at the same time. Organic/inorganic hybrid nanospheres were produced by the self-assembly of PEO-*b*-P(TMSPMA-*r*-MMA) in a selective solvent and further gelation of the trimethoxylsilyl groups within each individual sphere. Preparation of organic/inorganic nanocomposites was also explored preliminarily on the basis of the sol−gel process of PEO-*b*-PTMSPMA diblock copolymers and the tetraethyl orthosilicate.

1. Introduction

In recent years, atom-transfer radical polymerization (ATRP) has been developed as a versatile and powerful tool for the preparation of homopolymers and copolymers with predetermined molecular weights and narrow molecular weight distributions.[1−3] The polymerization is based on the combination of an organic halide initiator with a transition-metal/ligand catalytic system that enables fast initiation compared to propagation and then reversibly activates halogenated chain ends during polymerization. ATRP also works well with many monomers and initiators that carry functional groups. So far, many well-defined polymers carrying pendant- or end-functional groups have been prepared by ATRPs using functionalized monomers or by initiating with functional initiators.[1−3] Examples of ATRP of functional monomers include 2-hydroxyethyl (meth)acrylate,[4,5] 2-(dimethylamino)ethyl methacrylate,[6] (meth)acrylamides,[7] and glycidyl (meth)acrylate.[8]

3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) is a reactive monomer that is an important silane coupling agent widely used in the preparation of organic/inorganic hybrid nanomaterials.[9] The $-Si(OR)_3$ groups is readily hydrolyzed into the $-Si(OH)_3$ groups, which can subsequently be turned into the cross-linked polysilsesquioxane by polycondensation. If the polymer self-assemblies contain the $-Si(OR)_3$ groups, organic/inorganic hybrid materials may be produced after the gelation of the preformed self-assemblies.[10] Recently, an amphiphilic block copolymer containing a small amount of TMSPMA groups produced by ATRP was used to fabricate hybrid nanoparticles, without a detailed study of the ATRP of this monomer.[11] Therefore, the controlled polymerization of TMSPMA remained to be explored, and to our knowledge, there was only one example of the living anionic polymerization of TMSPMA reported in the literature.[12] Recently, we reported a novel organic/inorganic hybrid vesicle based on the self-assembly of an amphiphilic diblock copolymer, poly(ethylene oxide)-*b*-poly[3-(trimethoxysilyl)propyl methacrylate] (PEO-*b*-PTMSPMA).[13] Novel vesicular micelles were formed spontaneously in a selective solvent, i.e., a mixture of methanol and water. When a catalyst was added, the hydrolysis and cross-linking reaction occurred within the wall of each individual vesicle, which produced hybrid hollow particles with a cross-linked polysilsesquioxane wall. Given the above observations, we believe a detailed investigation on the ATRP of TMSPMA monomer is critical for preparing novel reactive block copolymers, which should subsequently stimulate further research to build well-defined organic/inorganic nanocomposites.

Hence, we report the kinetics of the TMSPMA polymerization using copper(I)-based ATRP in anisole solution. Some novel reactive diblock copolymers were synthesized using poly(ethylene oxide)-based macroinitiators as well. In addition, organic/inorganic hybrid nanospheres were made by gelation of the self-assembled block copolymers. Organic/inorganic nanocomposites with an ordered structure were also prepared on the basis of the sol−gel process of the block copolymers and the tetraethyl orthosilicate (TEOS).

2. Results and Discussion

2.1. ATRP of TMSPMA with 2-EBiB and PEO-Br as Initiators. ATRP of TMSPMA was studied using CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst. Ethyl 2-bromoisobutyrate (2-

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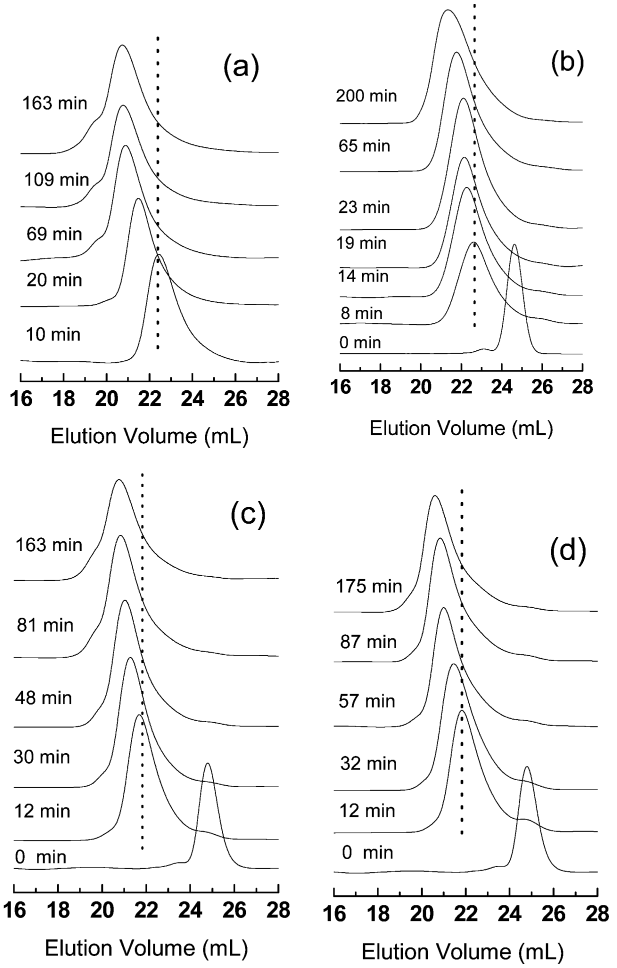

Figure 1. Size-exclusion chromatography (SEC) traces for the ATRP of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) in anisole (anisole/monomer = 1.3/1.0, v/v): (a) using ethyl 2-bromoisobutyrate (2-EBiB) as a initiator at 70 °C; (b−d) using poly(ethylene oxide) methyl ether 2-bromoisobutyrate (PEO-Br; number-average molecular weight 2000) as macroinitiator at 90, 70, and 50 °C, respectively. Conditions: $[\text{R-Br}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0/[\text{TMSPMA}]_0 = 1/1/1/50$.

EBiB) and poly(ethylene oxide) methyl ether 2-bromisobutyrate (PEO−Br) were used as initiators, respectively. Anisole was chosen as the solvent because it is a better solvent for PEO-based macroinitiators and copper(II) bromide/PMDETA complex than other nonpolar solvents.[3]

Polymerization of TMSPMA using 2-EBiB as an initiator in anisole at 70 °C was followed by size-exclusion chromatography (SEC). Figure 1a shows that the molecular weights of poly[3-(trimethoxysilyl)propyl methacrylate] (PTMSPMA) increase with reaction time. Monomodal peaks and low molecular weight distribution ($M_w/M_n < 1.2$) remain until ∼69 min. Then, a small shoulder in the high molecular weight region appears, indicating that the growing chains terminated by coupling. As shown in Figure 2a, the first-order kinetic plot, $\ln([M]_0/[M]_t)$ vs reaction time, is slightly curved. This result, together with the shoulder in the SEC traces, suggests that the radical concentration decreases due to partial termination of living free radicals. Both average molecular weights determined by SEC, $M_{n,SEC}$, and the theoretical molecular weights, $M_{n,th}$, calculated from monomer conversion[14] increased linearly, as shown in Figure 3a. This indicates that the ATRP of TMSPMA mediated by copper(I) bromide/PMDETA in anisole is a controlled process. The discrepancy between $M_{n,th}$ and $M_{n,SEC}$ is reasonable as the calibration of SEC was based on the polystyrene standards. The M_w/M_n's became high when conversion was over 80% (Figure 3a). Thus, it is necessary to keep a relatively low monomer conversion for better control of this polymerization process.

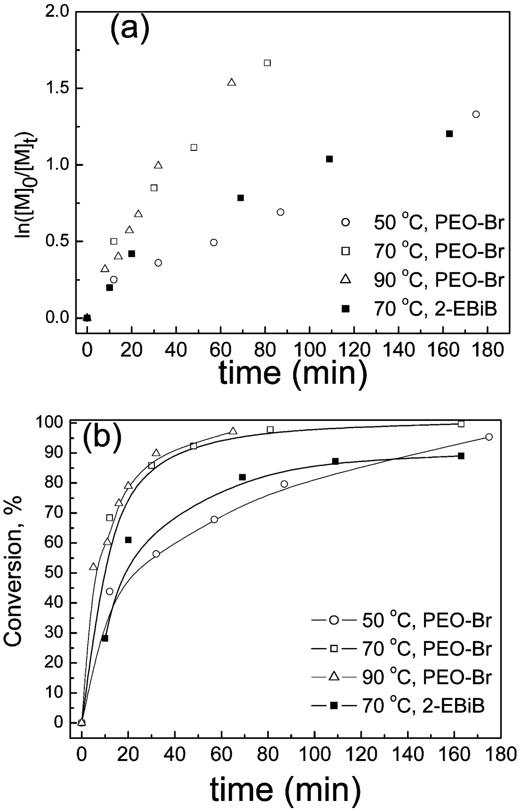

Figure 2. (a) Kinetic plots for the ATRP of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) in anisole initiated by ethyl 2-bromoisobutyrate (2-EBiB) and PEO-Br (number-average molecular weight M_n 2000), respectively. (b) Corresponding plots of monomer conversion vs time. For conditions, see the caption of Figure 1.

Polymerization of TMSPMA was also studied using PEO-Br as a macroinitiator in anisole. PEO-Br's were synthesized from the reaction of poly(ethylene oxide) methyl ether (M_n ca. 750, 2000, 5000) and 2-bromoisobutyryl bromide. The initiation efficiencies of these macroinitiators were confirmed by chain extension reactions through the ATRP of *tert*-butyl acrylate (*t*-BA) or *n*-butyl methacrylate (*n*-BMA) (Figure S1 in the Supporting Information).

The kinetics using PEO_{45}-Br (M_n = 2000) as the macroinitiator were studied in anisole over a range of temperatures (90, 70, and 50 °C). As illustrated in Figure 1b−d, all SEC traces of PEO-*b*-PTMSPMA formation obtained at different temperatures show monomodal peaks. In contrast to the results in Figure 1a, there are no shoulders even though the monomer conversion of polymerization reached nearly 100% at 90 or 50 °C, although a slight shoulder appears when monomer conversion was more than 90% after ∼48 min at 70 °C. As demonstrated by the plots of $\ln([M]_0/[M]_t)$ vs time in Figure 2a, ATRPs of TMSPMA with PEO-Br as initiator are consistent with first-order kinetics with respect to the TMSPMA at different temperatures.

The slopes of the kinetic plots increase with increasing temperature, indicating faster reaction rates at higher temperatures. In addition, the polymerization rate with

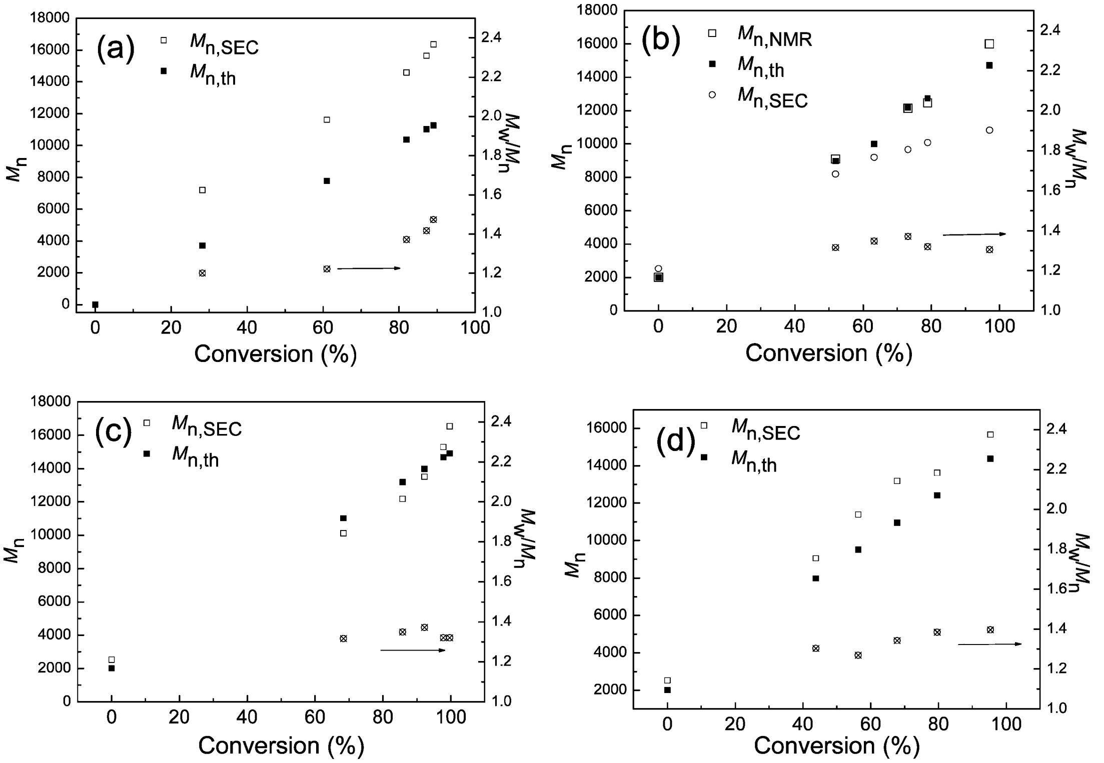

Figure 3. Evolution of the molecular weights and polydispersities with monomer conversion for the ATRP of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA): (a) using ethyl 2-bromoisobutyrate (2-EBiB) as initiator at 70 °C; (b−d) using PEO-Br (number-average molecular weight 2000) as macroinitiator at 90, 70, and 50 °C, respectively. For conditions, see the caption of Figure 1.

PEO-Br as the initiator was greater than that with 2-EBiB as the initiator under similar conditions. As shown in Figure 2b, the monomer conversion was over 60% after 10 min at 90 and 70 °C using PEO_{45}-Br as the initiator whereas the conversion was less than 30% using 2-EBiB as the initiator at 70 °C. The apparent rate constants, k_{app}'s, evaluated from the slopes of the semilogarithmic plots were 3.65×10^{-4}, 2.78×10^{-4}, and 1.12×10^{-4} s^{-1} for PEO-Br at 90, 70, and 50 °C, respectively, and 1.07×10^{-4} s^{-1} for 2-EBiB at 70 °C. Haddleton et al. have also found such rate enhancements in the ATRP in the presence of oxyethylene groups which were from either monomers, initiators, or 1,2-diethoxyethane as a cosolvent.[15] They ascribed such phenomena to a more active catalyst as a result of complexation of the oxyethylene groups at the copper in a dynamic state with the pyridylmethanime ligand complexation. The plot of $\ln(k_{app})$ vs $1/T$ (Figure S2 in the Supporting Information) corresponds to an apparent activation energy of $\Delta E_{app} = 29$ kJ/mol for the ATRP of TMSPMA with PEO-Br as the initiator.

As shown in Figure 3b, the molecular weights estimated from ^{1}H NMR spectroscopy, $M_{n,NMR}$'s, agree well with $M_{n,th}$'s, as expected during the polymerization at 90 °C. In each cases, $M_{n,NMR}$, $M_{n,th}$, and $M_{n,SEC}$ increase linearly with monomer conversion. For the block copolymers prepared at 70 and 50 °C, $M_{n,SEC}$ and $M_{n,th}$ also increase linearly with monomer conversion (Figure 3c,d). The values of M_w/M_n's remained over a range of 1.2−1.4. These results further demonstrated the controlled nature for the ATRP of TMSPMA.

2.2. Block Copolymer Preparation. PEO-*b*-PTMSPMA diblock copolymers with different lengths of PEO and PTMSPMA segments were synthesized by changing the macroinitiators and the feed ratios of TMSPMA to PEO-Br, as shown in Table 1 (runs 1−7). The compositions of these block copolymers calculated from their ^{1}H NMR spectra and the monomer conversions were consistent. SEC traces of these copolymers (Figure 4) exhibit monomodal peaks with narrow molecular weight distributions.

Poly(ethylene oxide)-*block*-poly[3-(trimethoxysilyl)propyl methacrylate-*random*-methyl methacrylate], PEO-*b*-P($TMSPMA_y$-*r*-MMA_x), were synthesized by random copolymerization of TMSPMA with different monomers such as methyl methacrylate (MMA), as listed in Table 1 (runs 8−10). The copolymer compositions were consistent with the targeted values. However, as shown in Figure 4, SEC traces of these copolymers (runs 9 and 10) obviously tail in the low molecular weigh region and the corresponding M_w/M_n's are much higher when compared to PEO-*b*-PTMSPMA in every cases that was generally less than 1.4. This behavior is unexpected since the ATRPs of both MMA and TMSPMA are well controlled compared to the TMSPMA/MMA random copolymerization (for ATRP of MMA, $M_w/M_n < 1.2.$[16]). However, the solution chemistry of ATRP of two different monomers might be far more complicated than the homopolymerization of one monomer.[17] Different side groups of MMA and TMSPMA may lead to different cross-propagation rates and different reactivity of the dormant carbon−halogen terminals, which may broaden the molecular weight distribution. Such broadening phenomenon during the random copolymerization has also been observed by Uegaki et al.[18]

2.3. ^{1}H NMR Characterization. The ^{1}H NMR spectrum in Figure 5a clearly demonstrates the formation of PTMSPMA homopolymer. Figure 5b shows the ^{1}H NMR spectrum of the PEO-*b*-PTMSPMA diblock copolymer in $CDCl_3$. There are resonances attributable to both blocks. Considering the remarkable increase in the molecular weight and the monomodal SEC peak

Table 1. Syntheses of Block Copolymers by Atom-Transfer Radical Polymerization (ATRP) of 3-(Trimethoxysilyl)propyl Methacrylate (TMSPMA) Using Poly(ethylene oxide) Methyl Ether 2-Bromoisobutyrate (PEO-Br) as Macroinitiators in Anisole and the Properties of Polymers

run[a]	feed ratio[b]	T (°C)	conv (%)	M_n[c]	M_w/M_n[c]	ratio by ^{1}H NMR[d]	ratio by conv[e]	tacticity[f] (rr/mr)
1[g]	45/40	90	99			45/49	45/40	1.16/1
2	45/50	90	80	11 600	1.34	45/42	45/40	1.60/1
3	45/50	90	100	13 500	1.39	45/54	45/50	1.55/1
4	45/200	70	88	45 000	1.10	45/180	45/176	1.77/1
5	113/200	70	91	28 600	1.25	113/206	113/182	1.77/1
6[g]	113/35	90	91			113/46	113/32	1.30/1
7	17/200	70	91	40 200	1.16	17/178	17/182	2.18/1
8[g]	45/30/15	90	73[h]			45/25/14		1.20/1
9	45/35/35	70	76[h]	13 600	1.58	45/42/39		1.96/1
10	45/15/60	70	73[h]	12 700	1.78	45/19/67		1.68/1

[a] Conditions: [PEO-Br]$_0$/[CuBr]$_0$/[PMDETA]$_0$/[TMSPMA]$_0$ = 1/1/1/x (x = 40, 50, 50, 200, 200, 35, and 200, corresponding to runs 1–7, respectively); for runs 8–10, [TMSPMA]$_0$ was replaced by [TMSPMA]$_0$/[MMA]$_0$. [b] EO/TMSPMA (feed) for runs 1–7, EO/TMSPMA/MMA (feed) for runs 8–10; the figures of 17, 45, and 113 refer to the degree of polymerizations (DP) of different PEO-Br's (number-average molecular weights are 750, 2000, and 5000). [c] Obtained from SEC relative to polystyrene standards. [d] EO/TMSPMA or EO/TMSPMA/MMA. [e] EO/TMSPMA, estimated by equation DP$_{EO}$/([TMSPMA]$_0$ × conv %). [f] Obtained from ^{1}H NMR spectra. [g] In toluene. [h] Yields of polymers after purification.

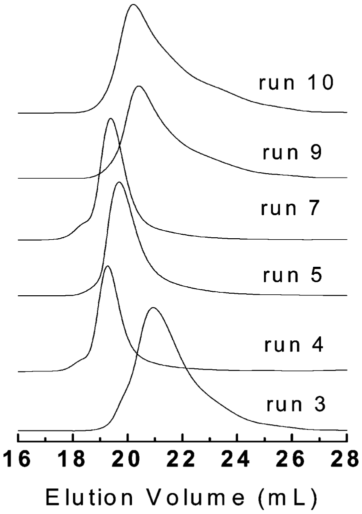

Figure 4. Typical SEC traces of poly(ethylene oxide)-*block*-poly[3-(trimethoxysilyl)propyl methacrylate] (runs 3–5 and 7 in Table 1) and poly(ethylene oxide)-*block*-poly[3-(trimethoxysilyl)propyl methacrylate-*random*-methyl methacrylate] (runs 9 and 10 in Table 1) prepared by the ATRP using PEO-Br as macroinitiator.

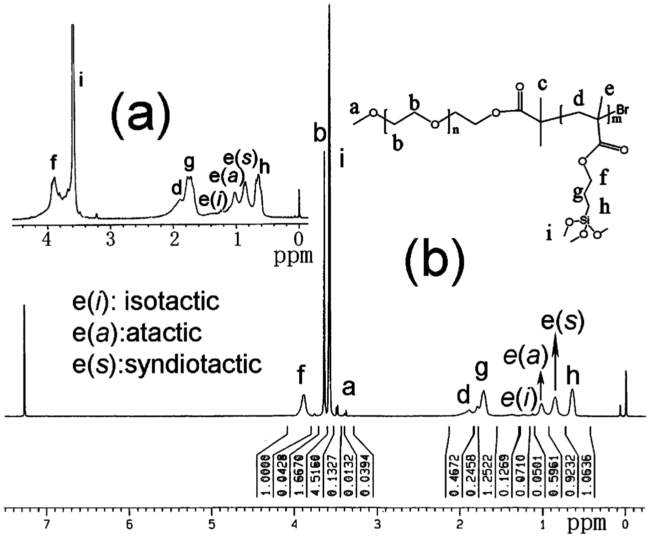

Figure 5. ^{1}H NMR spectra of (a) poly[3-(trimethoxysilyl)-propyl methacrylate] homopolymer and (b) poly(ethylene oxide)-*block*-poly[3-(trimethoxysilyl)propyl methacrylate] diblock copolymer (run 3).

after the polymerization of TMSPMA, the ^{1}H NMR results are consistent with formation of a block copolymer. The compositions of the block copolymers were estimated by comparing the peak areas of the protons derived from two blocks, e.g. b ($-OCH_2CH_2-$) in PEO block and h ($-SiCH_2-$), i [$-Si(OCH_3)_3$], or f ($-COOCH_2-$) in the PTMSPMA block.

The ^{1}H NMR spectrum of PEO-*b*-P(TMSPMA$_y$-*r*-MMA$_x$) copolymer is shown in Figure S3 (in the Supporting Information). Though the peaks assigned to the $-OCH_3$ groups in MMA overlapped with the one assigned to the $-Si(OCH_3)_3$ groups in TMSPMA, the copolymer composition could be determined by comparing the area of the corresponding peaks. (For detailed calculation procedure, see the Supporting Information.) The compositions estimated by ^{1}H NMR were roughly consistent with the targeted ones, as shown in Table 1 (runs 8–10).

There was no evidence of hydrolysis of the $-Si(OCH_3)_3$ groups, which was confirmed by the expected peak areas of h, i, and f in Figure 5b. The ^{29}Si NMR spectrum of this PEO-*b*-PTMSPMA diblock copolymer gave a monomodal peak at −40.9 ppm, which was assigned to the $-Si(OCH_3)_3$ group.

Relatively high syndiotacticity was noticed from ^{1}H NMR spectra of PTMSPMA homopolymers and PEO-*b*-PTMSPMA diblock copolymers (e.g. proton resonance at 0.8 ppm in Figure 5). The ratio of syndiotacticity to atacticity was independent of initiator but appeared to be influenced by the reaction temperature and the polarity of solvent. As demonstrated in Table 1, a lower temperature, e.g. 70 °C, or a polar solvent, e.g. anisole, led to higher syndiotacticity than at higher temperature, e.g. 90 °C, or the nonpolar toluene.

2.4. Preliminary Preparation of Hybrid Nanospheres. Self-assembly of the block copolymer, PEO-*b*-PTMSPMA, in a binary solvent mixture of methanol and water may produce polymer vesicles with PEO as the corona and the hydrophobic block as the core. The vesicles gelled in the presence of catalyst and novel hybrid nanocapsules were produced.[13] Herein, hybrid nanospheres were obtained on the basis of the self-assembly of PEO$_{45}$-*b*-P(TMSPMA$_{19}$-*r*-MMA$_{67}$) copolymer (run 10) in solution and followed by the gelation process. The copolymer was first dissolved in dimethyl formamide (DMF), and then water was added slowly until its content reached 51.4 wt %. A blue tint solution was

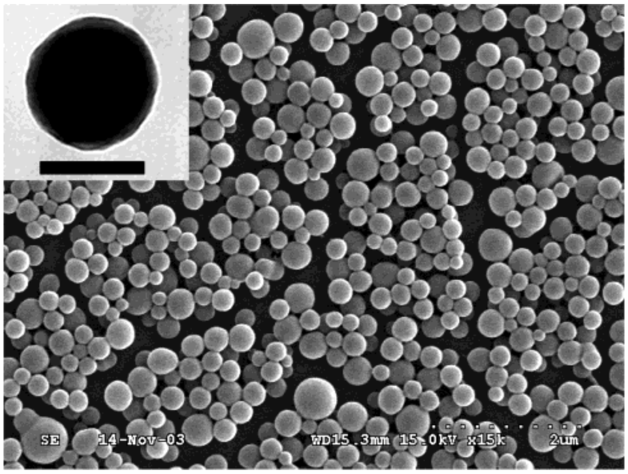

Figure 6. Scanning electron microscope (SEM) image of hybrid nanospheres based on the self-assembly and gelation of poly(ethylene oxide)-*block*-poly[3-(trimethoxysilyl)propyl methacrylate-*random*-methyl methacrylate], PEO_{45}-*b*-P($TMSPMA_{19}$-*r*-MMA_{67}), copolymers in DMF/water (51.4 wt % of water). The initial polymer concentration in DMF is 10.0 mg/mL; the inset at the top left corner is the transmission electron microscope image of one nanosphere, and the scale bar represents 250 nm.

observed immediately if the initial polymer concentration (C_{ini}) was 2.0 mg/mL. In general, this phenomenon indicates micelle formation. Then, the hybrid nanospheres were created in the presence of a small amount of a catalyst, triethylamine, which was added to accelerate the hydrolysis and polycondensation of the $-Si(OCH_3)_3$ groups within individual sphere. A scanning electron microscope (SEM) image of the hybrid nanospheres after 1 week is shown in Figure 6. The transmission electron microscope (TEM) image of a nanosphere is shown in the inset of Figure 6; the spheres appear to be a solid structure. These particles are not originated from the star micelles because their sizes are too large. They are likely from the so-called large compound micelles (LCMs) as described by Eisenberg et al.[19] The surface of the sphere consists of hydrophilic PEO chains while the internal structure should be the reverted micelles. No vesicles such as those prepared from PEO_{45}-*b*-$PTMSPMA_{59}$ in methanol/water were found in the current study.[13] The size distributions were low as shown in Figure S4 (in the Supporting Information). In fact, the solid nanospheres could also be prepared in DMF/water under different C_{ini}'s and their diameters increase with the C_{ini}.[20] For example, when the C_{ini} was 2.0, 10.0, and 20.0 mg/mL with the water content kept at 51.4 wt %, the corresponding diameters averaged over 100 spheres from SEM images were 221 ± 42, 280 ± 48, and 609 ± 166 nm, respectively. The higher C_{ini} led to the broader size distribution.

2.5. Preparation of Hybrid Nanocomposites. Organic/inorganic hybrid nanocomposites were prepared using the above block copolymers for potential applications of polymer/silica nanocomposites in the structural materials for aerospace application, electronics, and sensors.[21−24] Three methods were usually employed to prepare nanocomposites: (a) mixing polymer with silica particles or silica precursors (e.g. TEOS) directly;[21] (b) direct mixing polymeric monomer with silica particles followed by the polymerization of monomer;[22] (c) mixing both silica precursors and polymer monomers followed by an in situ polymerization of the precursors and monomers.[23] Nevertheless, there are no reports on how to prepare hybrid nanocomposites by applying the above reactive block copolymers, which may induce the formation of well-defined nanostructures in the composites. As a preliminary test, nanocomposites were prepared by a sol−gel method on the basis of PEO_{45}-*b*-$PTMSPMA_{42}$ (run 2) and TEOS. The products were transparent solid materials with a slightly blue color. SEM images of the resulting hybrid organic/ inorganic materials are illustrated in Figure 7. Panels a and b represent surface- and cross-sectional morphology, respectively. From which we could find spheres with a diameter of ~50 nm were adhered together. Panel c is the SEM image of cross-section of this material after calcination at 450 °C for 7 h in air. Spheres were fused further than previously. No obvious distortion was found after calcination.

3. Conclusion

In summary, polymerization kinetics of TMSPMA were studied by ATRP mediated by CuBr/PMDETA using 2-EBiB and PEO-Br as initiators, respectively. The molecular weight distributions of the homopolymers and the block copolymers were kept relatively low as a result of controlled polymerizations. PEO-Br macroinitiator enhanced the overall polymerization rate relative to 2-EBiB. A series of novel amphiphilic reactive block copolymers and block-random copolymers, PEO-*b*-PTMSPMA and PEO-*b*-P($TMSPMA_y$-*r*-MMA_x), were synthesized by ATRP of TMSPMA using PEO-Br as initia-

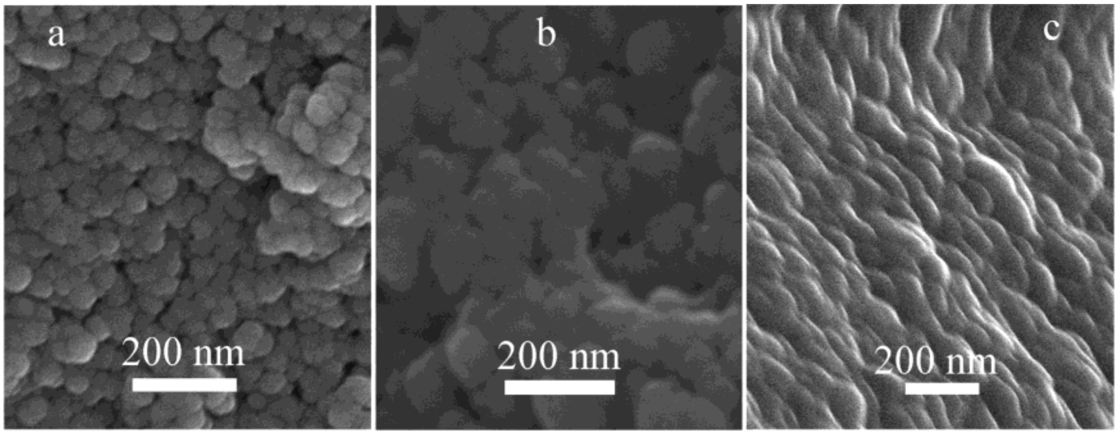

Figure 7. SEM images of hybrid organic/inorganic materials based on sol−gel reaction of poly(ethylene oxide)-*block*-poly[3-(trimethoxysilyl)propyl methacrylate] diblock copolymer (run 2) and tetraethyl orthosilicate: (a) surface section; (b) cross-section; (c) cross-section of materials after calcination at 450 °C for 7 h.

tors. Organic/inorganic hybrid nanospheres were reported preliminarily on the basis of the self-assembly of PEO-*b*-P(TMSPMA$_y$-*r*-MMA$_x$) and the gelation in DMF/water solvent mixture. Organic/inorganic hybrid nanocomposites were also prepared by a sol−gel approach using the PEO-*b*-PTMSPMA diblock copolymer and TEOS as precursors. These examples can be extended to the generation of a series of structurally controllable hybrid nanomaterials in which only simple variation of preparative conditions will be needed. This work will enable the synthesis of a wide range of reactive block copolymers, which will become a new scaffold to construct a variety of organic/ inorganic hybrid nanomaterials.

4. Experimental Section

4.1. Materials. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA; >99%, Aldrich), TMSPMA (>95%, Wuhan University Silicone New Material Co.), and ethyl 2-bromoisobutyrate (2-EBiB; >99%, Aldrich) were dried over CaH_2 overnight and distilled under reduced pressure. Anisole (>98%, Beijing Donghuan United Chemical Co.) was washed with 5% aqueous NaOH three times, washed with water until the aqueous phase became neutral, and then dried over anhydrous Na_2SO_4 and CaH_2 overnight and distilled under reduced pressure. CuBr was synthesized according to a literature procedure.[25] Anhydrous methanol (>99%, Beijing Chemical Reagent Co.) was refluxed over magnesium. Anhydrous tetrahydrofuran (THF; Beijing Chemical Reagent Co.) was dried by refluxing in the presence of sodium flake and distilled prior to use. $CDCl_3$ and petroleum ether (60−90 °C) were dried over CaH_2, distilled prior to use. Poly(ethylene oxide) methyl ethers (MeO-PEO; M_n ca. 5000, 2000, and 750, purchased from Alfa, Aldrich, and Acros, respectively) were dried azeotropically with anhydrous toluene to remove water. 2-Bromoisobutyryl bromide (>98%, Aldrich), triethylamine (>99%, Beijing Chemical Reagent Co.), tetraethyl orthosilicate (Beijing Xizhong Chemical Reagent Co.), and other reagents were used as received.

4.2. Polymer Characterization. M_n and M_w/M_n of polymers were obtained at 35 °C by SEC equipped with a Waters 515 pump, a Waters 2414 refractive index detector, and a combination of Styragel HT-2, HT-3, and HT-4; the effective molecular weight ranges were 100−10 000, 500−30 000, and 5 000−600 000 Da, respectively. Linear polystyrene standards were applied as the calibration. The eluent was THF at a rate of 1.0 mL/min. ^1H NMR (300 and 400 MHz) and ^{29}Si NMR (60 MHz) spectra were recorded on a Bruker DMX400 and a DMX300 spectrometer, respectively, with dried $CDCl_3$ as solvent at room temperature.

TEM images were obtained using a JEM 100 instrument operated at 100 kV. To prepare TEM samples, 0.010 mL of micelle solution was dropped onto a carbon-coated copper grid, with the water droplet evaporating in air. Scanning electron microscope (SEM) was used to view surface morphologies of hybrid nanospheres and nanocomposites. To obtain an SEM image of nanospheres, a drop of solution was spread on a silica wafer and was left until dryness. The nanocomposite sample was broken to obtain the cross-sectional morphology. All samples were coated with platinum and viewed by a Hitachi S-4300 electron microscope operated at 15 kV. The images were recorded by a digital camera.

4.3. Syntheses of PEO-Br Macroinitiators. PEO-Br macroinitiators were prepared by the reaction of MeO-PEO with 2-bromoisobutyryl bromide in the presence of triethylamine according to a modified literature procedure.[26] For example, triethylamine (2.20 mL, 0.016 mol) was added to a solution of MeO-PEO (M_n ca. 5000, 40.0 g, 0.008 mol) dissolved in anhydrous methylene chloride (100 mL) at room temperature. 2-Bromoisobutyryl bromide (2.00 mL, 0.016 mol) was dissolved in anhydrous methylene chloride (30 mL) and added dropwise over 2 h to the cooled MeO-PEO solution in an ice bath. The solution was then allowed to warm to room temperature and was stirred for 2 days. Precipitated byproducts were removed by filtration. The filtrate was poured into water, and the mixture was stirred vigorously for 1 h. The organic phase was collected, and the water phase was extracted with methylene chloride three times. The combined organic solution was further washed with 1.0 M HCl and 1.0 M NaOH aqueous solution successively and dried over anhydrous $MgSO_4$, and the solvent was then removed using a rotary evaporator. The crude product was dissolved in 10 mL of methylene chloride and then precipitated in 500 mL of diethyl ether twice. Yield: 95%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.93 (s, 6H, $BrC(CH_3)_2$), 3.38 (s, 3H, OCH_3), 3.64 (s, 4*n*H, OCH_2CH_2). Yields for other PEO-Br's (M_n ca. 2000 and 750) were around 80 and 90%.

4.4. Polymerization of TMSPMA by ATRP. In a general ATRP procedure, a Schlenk flask with a magnetic stir bar and a rubber septum was charged with CuBr (72.0 mg, 0.500 mmol), PEO-Br macroinitiator (1.00 g, 0.500 mmol), TMSPMA (6.00 mL, 25.0 mmol), and anisole (8.0 mL). The flask was degassed by three freeze−pump−thaw cycles. PMDETA (105 μL, 0.500 mmol) was deoxygenated by bubbling N_2 for 0.5 h before injection into the reaction system. The flask was then immersed in an oil bath thermostated at 70 °C. After 7.5 h, the flask was taken away from the bath and the reaction mixture was cooled to slow the polymerization, and then anhydrous THF was added to dilute the polymer solution. The solution of crude product was transferred into a basic alumina column by a syringe to remove the catalyst, and then the polymer was precipitated in anhydrous petroleum ether three times to remove the unreacted monomer and anisole. The characteristics of the polymer are shown in run 3 in Table 1.

For kinetic studies, aliquots of the solution were withdrawn at timed intervals. Monomer conversion was obtained by gravimetry. To avoid polymer loss during the period of precipitation, anhydrous petroleum ether was added into sample vial slowly and then shaken vigorously for 20 min. The vial was rested for 1 h, and then the liquid phase was drawn out carefully by syringe. Finally, the samples were dried at 50 °C in reduced pressure for 48 h. For SEC analysis, samples were diluted with anhydrous THF and then filtrated. These polymers were very moisture sensitive and should be kept carefully in an absolutely dry container or sealed glass tubes.

4.5. Copolymerization of TMSPMA and MMA by ATRP. In a typical procedure (run 10), a Schlenk flask with a magnetic stir bar and a rubber septum was charged with CuBr (72.0 mg, 0.500 mmol), PEO-Br macroinitiator (1.00 g, 0.500 mmol), TMSPMA (1.80 mL, 7.50 mmol), MMA (3.08 mL, 30.0 mmol), and anisole (6.4 mL). The flask was degassed by three freeze−pump−thaw cycles. PMDETA (105 μL, 0.500 mmol) was deoxygenated by bubbling N_2 for 0.5 h just before injection into the reaction system. The flask was then immersed in an oil bath thermostated at 70 °C. After 3 h, the flask was taken away from the bath and the reaction mixture was cooled to slow the polymerization; then anhydrous THF was added to dilute the polymer solution. The solution of crude product was transferred into a basic alumina column by a syringe to remove the catalyst, and then the polymer was precipitated in anhydrous petroleum ether three times to remove the unreacted monomer and anisole. Yield: 73%. The ^1H NMR spectrum is shown in Figure S3 (in the Supporting Information).

4.6. Preparation of Hybrid Nanospheres. To prepare the hybrid nanospheres, water (2.0 mL) was added dropwise into PEO$_{45}$-*b*-P(TMSPMA$_{19}$-*r*-MMA$_{67}$) solution in DMF (2.0 mL; the initial polymer concentrations were 2.0, 10.0, and 20.0 mg/mL; i.e., 0.15, 0.74, and 1.49 μmol/mL) within 10 min by a syringe, accompanying by vigorous stirring in the sample vial. The color of the micelle solution turned opalescence from blue, the Tyndall effect of colloids, when C_{ini} increased. After 5 h, TEA (0.02 mL, 0.14 mmol) was dropped into solution to accelerate the hydrolysis and polycondensation within the aggregates. The solution was stirred at room temperature for 1 week before the TEM and the SEM analysis.

4.7. Preparation of Nanocomposites. A typical sol−gel method was utilized. The PEO$_{45}$-*b*-PTMSPMA$_{42}$ diblock copolymer (0.200 g, 0.016 mmol) was dissolved in methanol (2.00 mL) in a 5 mL of weighing bottle, and then tetraethyl orthosilicate (TEOS, 0.40 g, 1.9 mmol), water (50.0 μL, 2.78 mmol), and $NH_3 \cdot H_2O$ (40.0 μL, 0.56 mmol) were added sequentially with vigorous stirring in the bottle. After ca. 5 min, the solution became slightly blue tint and the color became deeper gradually. The stirring was stopped after 0.5 h, and the magnetic stir bar was removed. A gel appeared at ∼1 h, and the bottle was sealed by Parafilm. After 1 month, three tiny holes were poked to let the solvent and the produced small molecules evaporated slowly. After 3 months, the resulting transparent film was further dried under vacuum for several days at the ambient temperature. If all the alkoxyorganosilane groups and TEOS were hydrolyzed and cross-linked, the final mass of nanocomposites should be 0.27 g. The actual mass of nanocomposites was 0.21 g. For calcination, the sample was placed in a tubular temperature-programming electric resistance furnace (Beijing Electric Furnace Plant). The temperature in tube was increased at a rate of 5 °C/min and kept at 450 °C for 7 h.

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Supporting Information Available: Figures S1−S4 and a description of the calculation of the molecular weight of polymers by ^{1}H NMR (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) $M_{\mathrm{n,th}} = M_{\mathrm{n,PEO-Br}} + [\mathrm{TMSPMA}]_0/[\mathrm{PEO\text{-}Br}]_0 \times \mathrm{conversion} \times M_{\mathrm{TMSPMA}}$, where $[\mathrm{TMSPMA}]_0/[\mathrm{PEO\text{-}Br}]_0$ is the feed ratio and M_{TMSPMA} is molar mass of TMSPMA.

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