Synthesis and Self-Assembly of Stimuli-Responsive Amphiphilic Block Copolymers Based on Polyhedral Oligomeric Silsesquioxane

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ABSTRACT: A novel POSS-containing methacrylate monomer (HEMAPOSS) was fabricated by extending the side chain between polyhedral oligomeric silsesquioxane (POSS) unit and methacrylate group, which can efficiently decrease the steric hindrance in free-radical polymerization of POSS-methacrylate monomer. POSS-containing homopolymers (PHEMAPOSS) with a higher degree of polymerization (DP) can be prepared using HEMAPOSS monomer via reversible addition–fragmentation chain transfer (RAFT) polymerization. PHEMAPOSS was further used as the macro-RAFT agent to construct a series of amphiphilic POSS-containing poly(*N*, *N*-dimethylaminoethyl methacrylate) diblock copolymers, PHEMAPOSS-*b*-PDMAEMA. PHEMAPOSS-*b*-PDMAEMA block copolymers can selfassemble into a plethora of morphologies ranging from irregu-

INTRODUCTION The self-assembly of amphiphilic block copolymers has attracted extensive interests in the past several decades, since they can self-assemble into a rich variety of morphologies including spheres, rods, lamellae, vesicles, and others.¹⁻⁴ These assembled morphologies could endow them with the potential application in many fields such as nanoreactors, catalysis, and drug delivery systems.⁵⁻⁹ It is generally acknowledged that self-assembled morphologies of amphiphilic copolymers in selective solution are governed by three components: interfacial energy between the core and the solvent, the stretching of the core-forming block, and the repulsive interactions among coronal chains.^{1,10,11} Thus, the morphologies could be determined by the following parameters: the composition and concentration of the copolymer, the overall molecular weight, the nature of the common solvent, the solvent/nonsolvent ratio, the pH value, ions, etc.¹²⁻¹⁶

More recently, a growing number of stimuli-responsive polymers and their assemblies have been investigated due to the need to develop smart materials which have advantageous applications such as biotechnology, nanotechnology, catalysis, lar assembled aggregates to core-shell spheres and further from complex spheres (pearl-necklace-liked structure) to large compound vesicles. The thermo- and pH-responsive behaviors of the micelles were also investigated by dynamic laser scattering, UV spectroscopy, SEM, and TEM. The results reveal the reversible transition of the assembled morphologies from spherical micelles to complex micelles was realized through acid-base control. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2669–2683

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and drug delivery.^{7,8,17-19} These stimuli-responsive polymers also could form single, dual-, and multistimuli-responsive assemblies such as $pH_{,}^{20}$ temperature,²¹ $pH/temperature,^{22}$ pH/ions,²³ light/redox,²⁴ light/temperature,²⁵ and pH/temperature/ light^{26,27} responsive micelles. Among them, poly(*N*, N-dimethylaminoethyl methacrylate) (PDMAEMA), a typical dual-responsive polymer,^{28–30} is a weak polybase with pK_a of 7.0–7.8, and has a lower critical solution temperature (LCST) at the range of 25-95 °C in its aqueous solution depending on the pH, concentration, topological structure, and the molecular weight of PDMAEMA.31-33 Meanwhile, the LCST of PDMAEMA aqueous solution is also directly influenced by pH because the tertiary amine groups can be protonated or deprotonated at low or high pH, respectively. Thus PDMAEMA could be used for the preparation of drug- and gene-delivery systems by several groups.34-37 Nevertheless, there are few reports on the stimuli-responsive and assembly behavior of PDMAEMA containing inorganic components, especially for PDMAEMA block copolymers.

Polyhedral oligomeric silsesquioxane (POSS) molecules, with the general formula $(RSiO_{1.5})_n$ $(n \ge 6)$, have an inorganic

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cage-like core surrounded by organic corner groups which could be reactive or unreactive.³⁸⁻⁴⁰ POSS molecule and its derivatives have a diameter in the range 1-3 nm and could be thought of as the smallest existing silica nanoparticles.^{41,42} Recently, with the development of controlled/living radical polymerization, a variety of POSS-containing polymers with well-defined structures have also been synthesized.⁴³⁻⁴⁵ These POSS-containing hybrid polymers can be directly prepared using POSS-containing initiator or reversible addition-fragmentation chain transfer (RAFT) agent via living polymerization technique, and their self-assembly behavior was further studied. Li et al.²³ synthesized hemitelechelic amphiphilic POSS-containing hybrid PDMAEMA (HT-POSS-PDMAEMA) via atom transfer radical polymerization (ATRP), and found HT-POSS-PDMAEMA can selfassemble into a hierarchical structure in aqueous solution. Zheng et al.⁴⁵ have also synthesized POSS-capped $poly(\varepsilon-cap$ rolactone) (PCL) via ring-opening polymerization (ROP) of ε caprolactone with 3-hydroxypropylheptaphenyl POSS as the initiator, and the hemi-telechelic amphiphile can be used to incorporate into epoxy resin to prepare the nanostructured thermosets. Besides, Chang and coworkers⁴⁶ have synthesized a series of organic/inorganic hybrid star PCLs through coordinated ROP of ε -caprolactone using POSS as the initiator, and the star PCL can form inclusion complexes with α and γ -cyclodextrin. Li et al.³⁶ synthesized an amphiphilic star-shaped POSS-containing PDMAEMA via ATRP, and it is the first report of a cationic POSS-containing material for gene delivery. Additionally, hemitelechelic (tadpole-shaped), ditelechelic, and multitelechilic POSS-containing polymers could be easily constructed by a combination of living polymerization and coupling reaction such as click chemistry and hydrosilylation coupling. We have prepared POSS-containing telechelic hybrid poly(acrylic acid) by a combination of ATRP and click chemistry, and studied their self-assembly behaviour in water.47-49 Cheng et al.50,51 have reported a facile approach to prepare amphiphiles with POSS nanoparticle as the head group and a polymer chain as the tail via the combination of ROP and thiol-ene click chemistry. These functional POSS can serve as versatile nanobuilding blocks to be incorporated into other molecular structures for the bottomup construction of mesoscopic nanomaterials via selfassembly.

As an important kind of well-defined polymers, POSScontaining hybrid block copolymers also have been explored using POSS-based monomers. Pyun and Matyjaszewski^{52,53} first reported the synthesis of homopolymers, triblock copolymers, and star-block copolymers of hybrid polymers from a POSS methacrylate monomer via ATRP. He's group^{54-⁵⁶ synthesized well-defined amphiphilic diblock and triblock copolymers of poly(ethylene glycol) as a hydrophilic block and poly(methacrylisobutyl POSS) (PMAPOSS) as a hydrophobic block, and the micelle formation, gelation, and rheological performance were further studied. Although POSScontaining block copolymers have been developed by several groups, even if Hayakawa and coworkers⁵⁷ recently synthesized diblock copolymers of PS-*b*-PMAPOSS and PMMA-*b*-} PMAPOSS with a relatively high degree of polymerization (DP) of POSS unit via the living anionic polymerization, the synthesis and self-assembly of POSS-containing block copolymers still have not been well studied, especially in solution. This is because the POSS-containing monomers used in previous researches are the commercial monomers, which has a great steric hindrance in radical polymerization, especially for living radical polymerization such as ATRP^{58,59} and RAFT polymerization.^{60,61}

In this contribution, we extended the length of the side chain between POSS unit and methacrylate group to prepare a novel POSS-containing methacrylate monomer (HEMAPOSS), which could efficiently overcome the steric hindrance of POSS unit in free-radical polymerization, and obtained a high DP of POSS-containing hybrid polymers. The kinetic process of HEMAPOSS RAFT polymerization was evaluated by Gel Permeation Chromatography (GPC) and ¹H NMR. PHEMA-POSS was further used as the macro-RAFT agent to construct a series of POSS-containing amphiphilic PDMAEMA diblock copolymers, PHEMAPOSS-b-PDMAEMA. The self-assembly behavior of amphiphilic PHEMAPOSS-b-PDMAEMA block copolymers was investigated by transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning electron microscopy (SEM), and dynamic light scattering (DLS). Finally, the dual stimuli-responsiveness of assembled aggregates was also studied by varying pH and temperature.

EXPERIMENTAL

Materials

Aminoisobutyl POSS was purchased from Hybrid Plastics Company. *N*, *N*-dimethylaminoethyl methacrylate (DMAEMA, Aladdin, 99%) was passed through a column of basic aluminum oxide to remove inhibitors shortly before polymerization. The RAFT agent cumyl dithiobenzoate (CDB) was synthesized according to the literature.⁶² Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Tetrahydrofuran (THF) and toluene were distilled from a purple sodium ketyl solution, respectively. Dichloromethane (DCM) and triethylamine (TEA) were separately dried over calcium hydride and distilled before use. Other regents and solvents in analytical grade were obtained from Aladdin and used as received unless otherwise noted.

CHARACTERIZATION

Nuclear Magnetic Resonance Spectroscopy (NMR)

A Bruker 400 MHz NMR spectrometer instrument was used to acquire the proton NMR spectra. The samples were dissolved with deuterated $CDCl_3$ and measured with tetramethylsilane (TMS) as an internal reference.

Gel Permeation Chromatography

The molecular weight and molecular weight distribution of PHEMAPOSS homopolymers and PHEMAPOSS-*b*-PDMAEMA diblock copolymers were determined with a GPC (Waters 1515). A series of monodisperse polystyrene standards were

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used for calibration, and THF was used as the eluent at a flow rate of 1 mL/min.

Critical Micelle Concentration (CMC)

CMC measurements were estimated by fluorescence spectroscopy on Hitachi FL-4500 using pyrene as a probe.

Transmission Electron Microscopy

TEM images were taken on a JEOL JEM1400 instrument operated at an accelerating voltage of 100 KV. The samples were made by directly dropping a drop of PHEMAPOSS-*b*-PDMAEMA aqueous solution (0.25 mg/mL) onto a copper grid (300 mesh) coated with a carbon film, and the sample was allowed to dry at room temperature.

Atomic Force Microscopy

AFM observation was carried out on a Veeco's NanoScope IV of Digital Instruments using Tapping Mode. The measurements were prepared by spin-coating the aggregate solutions (0.25 mg/mL) onto freshly cleaved mica surfaces and then dried naturally at room temperature for 24 h.

Scanning Electron Microscopy

SEM was performed using a Hitachi S4800 electron microscope at an acceleration voltage of 1 kV. The aggregate solution (0.25 mg/mL) was directly dropped onto a freshly cleaved mica and then dried at room temperature. Before the measurement, the sample was sputtered by gold.

Turbidity Measurement

Transmittance experiments were carried out with a UV-visible spectrophotometer (UV-2450, Shimadzu, Japan). Transmittance at 500 nm was monitored. Heating scans were performed between 30 and 80 $^\circ\text{C}$ at a scanning rate of 0.1 $^\circ\text{C/min}.$

Dynamic Light Scattering

DLS measurements were performed by using a BECKMAN COULTER Delasa Nano C particle analyzer at a fixed angle of 165°. All measurements were repeated at least three times and the average result was accepted as the final hydrodynamic diameter ($D_{\rm h}$).

Synthesis of HEMA-COOH

2-Hydroxyethyl methacrylate (HEMA; 6.1 mL, 0.05 mol) was dissolved in anhydrous THF in a schlenk flask (250 mL) with a magnetic stirring bar at room temperature under nitrogen. Succinic anhydride (6 g, 0.06 mol), 12 mL of pyridine, and 4-dimethylamiopryidine (0.49 g, 0.004 mol) were added, and then the reaction mixture was stirred for 24 h at 40 °C under nitrogen. After cooling to room temperature, the solvent was evaporated under vacuum and the residue was dissolved in DCM followed by washing it three times with 0.1 M HCl solution. The organic phase was dried over anhydrous magnesium sulfate overnight and filtered. After evaporation of the solvent, the remaining HEMA-COOH product was dried under vacuum at room temperature. A viscous liquid was obtained (10.9 g, yield 95%) and confirmed by ¹H NMR. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 6.13 (s, 1H,

HCH=C(CH₃)-), 5.61 (s, 1H, HCH=C(CH₃)-), 4.36 (t, 4H, $-00C(CH_2)_20CO$ -), 2.68 (t, 4H, HOOC(CH₂)₂COO-), and 1.95 (s, 3H, $H_3CC(COO-)CH_2$).

Synthesis of HEMA-COCl

A Schlenk flask (250 mL) with a magnetic stirring bar was connected to a standard Schlenk line system and was degassed and then refilled with highly pure nitrogen three times. Four gram of HEMA-COOH and 30 mL of anhydrous DCM were introduced into the flask. Freshly distilled thionyl chloride (25 mL) was added dropwise into the mixture solution over 30 min under nitrogen atmosphere. Then the reaction mixture was heated to 40 °C at reflux for about 1 h. The solvent was removed by distilling at atmospheric pressure and then under vacuum to produce HEMA-COCl, which was directly used in next step.

Synthesis of HEMAPOSS Monomer

Aminoisobutyl-POSS (7.6 g, 8.7 mmol) was dissolved in 50 mL of anhydrous THF and 2.4 mL of anhydrous TEA was added. The fresh HEMA-COCl was dissolved in 30 mL of anhydrous THF and was added slowly (about 1 h) into the above POSS solution at 0 °C under nitrogen atmosphere, and the mixture was stirred for 12 h at room temperature. A white precipitate (triethylamine hydrochloride) was removed by filtration and the resulting solution was concentrated under vacuum at room temperature. The residue was purified by a silica gel chromatography with ethylacetate/petroleum ether (1:2, v/v) as the eluent. A white solid was obtained (7.6 g, yield 80.5%). ¹H NMR analysis: ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 6.13 (s, 1H, HCH=C(CH₃)-), 5.60 (s, 1H, HCH=C(CH₃)-), 4.35 (s, 4H, -OCO(CH₂)₂OCO-), 3.26-3.20 (m, 2H, -CH₂-NHCO-), 2.72-2.69 (m, 2H, --NHCO--CH2--), 2.50-2.44 (m, 2H, -CH₂CH₂COO-), 1.95 (s, 3H, H₃CC(COO-)CH₂), 1.88-1.82 (m, 7H, $-Si-H_2CCH(CH_3)_2),$ 1.61 (m, 2H. -Si-CH₂CH₂CH₂-NH-), 0.96 (d, 42H, -Si-CH₂CH(CH₃)₂), 0.61 (d, 16H, -Si*CH*₂CH(CH₃)₂, -Si*CH*₂CH₂CH₂-NH-).

Preparation PHEMAPOSS Homopolymer

In a typical experiment, HEMAPOSS monomer (1 g, 0.92 mmol), CDB (250.2 μ L, 20 mg/mL CDB toluene solution, 0.0184 mmol) and AIBN (98.5 μ L, 10 mg/mL AIBN toluene solution, 0.006 mmol) and 0.6 mL toluene were placed in a dry glass tube equipped with a magnetic stirring bar. The mixture was degassed by at least three freeze-pump-thaw cycles. After the tube was flame-sealed under vacuum, it was stirred in an oil bath at 65 °C for 48 h. The reaction was stopped by plunging the tube into liquid nitrogen. After precipitating into a solvent mixture (methanol/acetic ether = 6/1, volume ratio) three times, the product was dried under vacuum at 30 °C for 24 h to afford PHMEAPOSS. $M_n = 25,400$ g/mol, $M_w/M_n = 1.12$.

Synthesis of PHEMAPOSS-b-PDMAEMA Block Copolymers

A representative example of the synthesis of the PHEMA-POSS-*b*-PDMAEMA block copolymers is as follows: PHEMA-POSS (0.3 g, 0.0061 mmol), DMAEMA (0.8 g, 5.1 mmol), and AIBN (33 μ L, 10 mg/mL AIBN THF solution, 0.006 mmol)





SCHEME 1 Synthesis of POSS-containing HEMAPOSS monomer.

and 2 mL THF were placed in a dry glass tube equipped with a magnetic stirring bar. The mixture was degassed by at least three freeze-pump-thaw cycles. After the tube was flame-sealed under vacuum, it was stirred in an oil bath at 65 °C for 12 h. The reaction was stopped by plunging the tube into liquid nitrogen. The solution was diluted into 10 mL by using THF and dialyzed in water at least three times to completely remove the DMAEMA monomer. To obtain the pure block copolymers, stepwise precipitation was further carried out to remove the dead polymer, PHE-MAPOSS macro-RAFT agent. The final product was dried by freeze-drying for two days. $M_n = 59,100$ g/mol, $M_w/M_n = 1.20$.

Self-Assembly of PHEMAPOSS-*b*-PDMAEMA in Aqueous Solution

In a typical process, PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆ (10 mg) block copolymer was first dissolved in 10 mL of dioxane (common solvent). The solution was stirred overnight and gradually dialyzed against the mixture solvent of dioxane with ultrapure water (selective solvent) for 3 days. The self-assembly solution was dialyzed at least three times using ultrapure water to make sure to remove dioxane completely. The pH in the experiment was adjusted by using hydrochloric acid and sodium hydroxide solution.

RESULTS AND DISCUSSION

Synthesis of HEMAPOSS Monomer

Although some POSS-containing hybrid polymers with advantageous properties have been reported, there are still many challenges in the development of well-defined POSS-containing hybrid polymers. This is because POSS monomers used in previous research are commercial, which has a high steric hindrance in free radical polymerization of POSS-based monomers. Here, we fabricated a novel POSS-containing methacrylate monomer (HEMAPOSS) by extending the side chain between POSS unit and methacrylate group, which would efficiently decrease the steric hindrance of POSS unit in free-radical polymerization of POSS-based monomers, and the POSS-containing homopolymer (PHEMAPOSS) with a higher DP could be achieved.

The synthetic procedure for the single long-armed POSSbased monomer, namely HEMAPOSS is illustrated in Scheme 1. We selected HEMA to synthesize the POSS-containing methacrylate monomer, since the hydroxyl group of HEMA is easily converted to other functional groups. Here, the hydroxyl group of HEMA was converted into a carboxylic acid to produce HEMA-COOH using succinic anhydride, which is also helpful for the extension of the side chain of POSS-based monomer (¹H NMR spectrum of HEMA-COOH is shown in Supporting Information Fig. S1). To improve the reaction efficiency between HEMA-COOH and POSS-NH₂, the carboxyl group of HEMA-COOH was converted into acyl chloride to prepare HEMA-COCl via the acylation reaction between HEMA-COOH and SOCl₂. Finally, the POSScontaining methacrylate monomer (HEMAPOSS) was successfully synthesized via the amide reaction between POSS-NH₂ and freshly prepared HEMA-COCl, which is confirmed by ¹H NMR (Supporting Information Fig. S2).

Preparation of PHEMAPOSS Homopolymer

In recent years, RAFT polymerization was found and widely used in construction of well-defined polymers.⁴⁴ Here, RAFT polymerization of HEMAPOSS was carried out in toluene



SCHEME 2 Synthesis of PHEMAPOSS and PHEMAPOSS-b-PDMAEMA successively via RAFT Polymerization.

using the CDB as a transfer agent, AIBN as the initiator, and the molar feed ratio of HEMAPOSS/CDB/AIBN is 50/1/0.33 (see Scheme 2). The polymerization conversion at intervals was measured by ¹H NMR.

Figure 1 shows the evolution of GPC curves with reaction time. With increasing reaction times, the curves shift to lower elution time whereas the PDI keeps <1.12. The kinetic plot of the RAFT polymerization of HEMAPOSS is shown in Figure 2. A very satisfactory linear relationship exists between $\ln[1/(1-x)]$ and reaction time even up to high conversions (around 60%), indicating a constant concentration of propagating chains during the RAFT polymerization of HEMAPOSS is in

a living manner and followed pseudo-first-order kinetics. The relationships of number-average molecular weights, PDI and the molecule weight calculated by ¹H NMR versus the monomer conversion are shown in Figure 3. It can be seen that the molecular weights calculated by ¹H NMR linearly increases with the conversion, but it differs from the number-average molecular weights determined by GPC (see also Table 1). This should be noted that the molar masses evaluated by GPC with PS standards are underestimated owing to the relatively compact cage structure of HEMA-POSS, which has a very different solution behavior with PS standard in THF.^{63,64}

Figure 4 shows the ¹H NMR spectrum of PHEMAPOSS₄₅, the peaks at $\delta = 0.97$ ppm (o) and 0.62 ppm (m, g) are ascribed



FIGURE 1 Evolution of GPC curves for the RAFT polymerization of HEMAPOSS at 65 °C in toluene with different reaction times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 2 Pseudo-first-order kinetic plot for the RAFT polymerization of HEMAPOSS using CDB as a RAFT agent at 65 $^{\circ}$ C in toluene.



FIGURE 3 Evolution of molecular weight and polydispersity with conversion for the RAFT polymerization of HEMAPOSS at 65 °C in toluene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the methyl protons and methylene protons of POSS units, respectively. The signals of the phenyl protons of the RAFT agent still can be identified in the insert enlarged spectrum. We also can calculate the molecular weight from ¹H NMR spectrum by comparing the peaks at 0.62 and 7.81 ppm (aromatic protons of CDB). The average degrees of polymerization (\overline{DP}) on of PHEMAPOSS and the molecular weight were calculated as $\overline{DP} = I_{0.6} / (8^* I_{7.81})$ and $M_{n,PHEMAPOSS,NMR} = I_{0.6}/(8*I_{7.81}) \times M_{HMEAPOSS} + M_{CDB}$, where the M_{HEMAPOSS} and M_{CDB} are the molecular weights of HEMA-POSS monomer and CDB, respectively. Here "I" represents the area of a peak, and we first set $I_{0.6}$ to 16.00. The result shows the well-defined homopolymer PHEMAPOSS has a DP of 45, and $M_{n,PHEMAPOSS,NMR}$ of 48,900 g/mol. Based on the above GPC and NMR results, we have successfully synthesized the PHEMAPOSS with a higher DP by extending the side chain of the POSS-based monomer, moreover, the poly-

TABLE 1 Conditions and Results of the RAFT Polymerization of HEMAPOSS Using CDB as RAFT Agent

Samples ^a	Time (h)	Conversion (%)	10 ⁻³ М _{n,} ммв ^b	10-3M _{n,} GPC ^c	PDI ^c
1	1	0.38	0.48	\	\
2	2	6.3	3.7	١	١
3	4	17.1	9.6	7.52	1.05
4	7	32.1	17.7	9.84	1.11
5	11	48.4	26.5	10.7	1.12
6	17	61.4	33.7	12.3	1.12
7	22	68.8	37.7	13.3	1.12

^a In toluene, [*M*]₀ = 0.3 mol/L; [CTA]/[AIBN] = 3.

 $^{\rm b}$ Calculated as $\it M_{n,NMR}\,{=}\,[\it M]_0/[{\rm CTA}]_0\,{\times}\,M_{\rm HEMAPOSS}\,{\times}\,x+M_{\rm CDB}$, $[\it M]_0$ and $[CTA]_0$ are, respectively, the initial concentrations of the HEMAPOSS and CDB agent; $M_{\rm HEMAPOSS}$ is the molecular weight of HEMAPOSS, M_{CDB} is the molecular weight of RAFT agent and x is the conversion.

^c Measured by GPC calibrated with PS standards.



FIGURE 4 ¹H NMR spectrum of PHEMAPOSS₄₅. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

merization process of HEMAPOSS follows pseudo-first-order kinetics at the conversion <60%.

Preparation of Amphiphilic PHEMAPOSS-b-PDMAEMA **Diblock Copolymers**

PHEMAPOSS-b-PDMAEMA amphiphilic diblock copolymers (ABCPs) with different PDMAEMA block length were synthesized using $PHEMAPOSS_{45}$ as a macro-RAFT agent, and the polymerization results were listed in Table 2. Their GPC curves are shown in Figure 5, and the eluograms shift to lower elution volume with increasing the length of PDMAEMA chain. The ¹H NMR spectrum of PHEMAPOSS₄₅-b-PDMAEMA₂₈₆ is shown in Figure 6. Besides the signals from the main chain of block copolymers, the peaks at 2.30 ppm are assigned to methyl protons of PDMAEMA block, which also can be used to estimate the molecular weight of PDMAEMA block. The average polymerization degree of PDMAEMA ($\overline{DP}_{PDMAEMA}$) and the molecule weight of diblock copolymers ($M_{n,PHEMAPOSS-b-PDMAEMA,NMR}$) can be calculated according to the peaks at 0.6 ppm of methylene protons next to silicon ($-Si-CH_2CH_2CH_2-$) with the peaks at 2.3 ppm of the dimethyl protons as follows: The $\overline{DP}_{PDMAEMA}$ is determined as $\overline{DP}_{PDMAEMA} = (16*I_{2.3})/(6*I_{0.6}) \times \overline{DP}_{PHEMAPOSS}$, and the $M_{n,PHEMAPOSS-b-PDMAEMA,NMR}$ is determined as $M_{n,PHEMA-}$ $POSS-b-PDMAEMA,NMR = DP_{PDMAEMA} \times M_{n,DMAEMA} + M_{n,PHEMAPOSS}$ $_{\rm NMR}$, where the $M_{\rm n,PHEMAPOSS, NMR}$ is the molecular weight of PHEMAPOSS.

Self-Assembly of PHEMAPOSS-b-PDMAEMA in Aqueous Solution

The self-assembly behaviors of hybrid polymers based on POSS have attracted considerable interest in recent years, and some interesting self-assembly morphologies have been obtained, which is obviously different with the pure organic amphiphilic polymers.^{40,65,66} However, the self-assembly of POSS-containing amphiphilic block copolymers in selective solution have not been well studied, due to the absence of the suitable POSS-containing block polymers. Here, to well investigated the self-assembly behavior of POSS-containing

TABLE 2 PHEMAPOSS- <i>b</i> -PDMAEMA ABCPs S	Synthesized Successively	^v via RAFT Polymerization
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Samples ^a	[HEMAPOSS]:[CDB] ^b or [<i>M</i>]/[Macro-CTA] ^b	10 ⁻³ <i>M</i> _{n, NMR} ^a	10 ⁻³ <i>M</i> _{n, GPC} ^c	PDI ^d	f _{HEMAPOSS} (wt %) ^a
PHEMAPOSS ₄₅	50:1	48.9	25.4	1.12	100.0%
PHEMAPOSS ₄₅ - <i>b</i> -PDMAEMA ₃₄	61:1	54.3	28.5	1.15	90.0%
PHEMAPOSS ₄₅ - <i>b</i> -PDMAEMA ₆₈	133:1	59.7	30.4	1.16	82.0%
PHEMAPOSS ₄₅ - <i>b</i> -PDMAEMA ₁₀₆	206:1	65.7	35.2	1.21	74.6%
PHEMAPOSS ₄₅ - <i>b</i> -PDMAEMA ₁₄₅	332:1	71.7	43.2	1.21	68.2%
PHEMAPOSS ₄₅ - <i>b</i> -PDMAEMA ₂₈₆	830:1	93.8	59.1	1.20	52.1%
PHEMAPOSS ₄₅ - <i>b</i> -PDMAEMA ₆₉₉	1784:1	158.7	104.4	1.22	30.8%

^a The final composition (DP and the mass fraction of PHEMAPOSS in the block copolymer) and $M_{n,NMR}$ were determined from the integration of ¹H NMR spectra.

^b The feed molar ratio between the chain transfer agent and the initiator AIBN was maintained at 1:0.33.

amphiphilic block copolymers in solution, we synthesized a series of amphiphilic PHEMAPOSS-b-PDMAEMA block copolymers with different PDMAEMA block lengths. According to previous researches,^{1,10,67} the assembled morphology of amphiphilic block copolymers is mainly dependent on the ratio of hydrophilic and hydrophobic blocks. In this case, we mainly studied the influence of the ratio of hydrophilic and hydrophobic blocks on the self-assembled behavior of amphiphilic PHEMAPOSS-b-PDMAEMA block copolymers. First, we studied the self-assembled morphologies formed from PHE-MAPOSS-b-PDMAEMA with the molar ratio of hydrophobic/ hydrophilic block (PHEMAPOSS/PDMAEMA) of around 1/ 15.5, 1/6.4, and 1/3.2 (System I). To further explore the assembled morphologies with shorter hydrophilic chain, we decreased the chain length of hydrophilic PDMAEMA block in ABCPs, and the molar ratio of hydrophobic/hydrophilic block (PHEMAPOSS/PDMAEMA) is around 1/2.4, 1/1.5, and 1/0.8 (System II).



FIGURE 5 GPC curves of PHEMAPOSS₄₅ and PHEMAPOSS-*b*-PDMAEMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

^c Calculated as $M_{n,PHEMAPOSS-b-PDMAEMA, NMR} = \overline{DP}_{PDMAEMA} \times M_{n,DMAE-MA} + M_{n,PHEMAPOSS, NMR}$, where the $M_{n,PHEMAPOSS, NMR}$ is the molecular weight of PHEMAPOSS.

^d Measured by GPC against polystyrene standards.

In this study, dioxane is chosen as the common solvent and water as selective solvent in which PHEMAPOSS block is insoluble. The CMC of ABCPs in water at pH = 7 was measured using pyrene as a probe by fluorescence spectrophotometry. Supporting Information Figure S3 shows three CMC values of ABCPs in aqueous solution. Obviously, with the increase of the length of PDMAEMA segment, the CMC value increased remarkably, since water is a good solvent for PDMAEMA chains. The self-assembly morphology of PHEMA-POSS-*b*-PDMAEMA ABCPs was investigated by TEM, AFM, SEM, and DLS.

System I

Self-assembled morphologies from ABCPs with the molar ratio of hydrophobic/hydrophilic block (PHEMAPOSS/ PDMAEMA) of around 1/15.5, 1/6.4, and 1/3.2.

First, we synthesized three ABCPs of PHEMAPOSS₄₅-*b*-PDMAEMA₆₉₉, PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆, and





FIGURE 7 TEM images [scale bar, 500 nm (a), 200 nm (b)] of PHEMAPOSS₄₅-b-PDMAEMA₆₉₉ self-assembled aggregates in aqueous solution.

PHEMAPOSS₄₅-*b*-PDMAEMA₁₄₅, and the molar ratio of hydrophobic/hydrophilic block (PHEMAPOSS/PDMAEMA) is around 1/15.5, 1/6.4, and 1/3.2, respectively.

Figure 7 presents the TEM images of $PHEMAPOSS_{45}$ -b-PDMAEMA₆₉₉. From Figure 7(a,b), we can find that there are some irregular assembled aggregates formed, and the density of these aggregates are not uniform, where the dark domains formed by the POSS units. The dimension of the little dots in assembled aggregates is about 8.5 nm. Apparently, the hydrophilic group dimension becomes so large that the aggregates of PHEMAPOSS are embedded in the PDMAEMA matrix, which is very different from the typical core-shell micelles with a hydrophobic block as the core and a hydrophilic block as the shell in the ABCPs. The morphology of these aggregates characterized by AFM (shown in Supporting Information Fig. S4) is relatively in good agreement with that shown in TEM images. It is mentionable that the height of the micelles (the height is 8.8 nm shown in Supporting Information Fig. S4c) exported from Supporting Information Fig. S4a is in accordance with the dimension of the dark dots observed in the TEM images. This further suggests the aggregates are the loose structure, where POSS domain mixed with PDMAEMA chains. This result is similar to that of our group's previous study⁵⁰ in self-assembly of hemitelechelic poly(acrylic acid) (POSS-PAA), where the chain of hydrophilic PAA is also very longer compared to the hydrophobic POSS moiety. Their self-assembly morphologies are not the typical core-shell micelles, and the density is nonuniform in a single aggregate.

For PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆ and PHEMAPOSS₄₅-*b*-PDMAEMA₁₄₅, we can find they have a similar selfassembled morphology, although the chain length of hydrophilic PDMAEMA of PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆ is about 2 times to that of PHEMAPOSS₄₅-*b*-PDMAEMA₁₄₅. The morphologies shown in the Figures 8 and 9 are both typical core-shell spherical micelles, which both possess a diameter at the range 33-48 nm in their TEM image [Figs. 8(a,b) and 9(a,b)]. The spherical micelles were further confirmed by AFM (Supporting Information Figs. S5 and S6), where diameter of the micelles is at the range 65-116 nm, which is quite larger than that observed in the TEM images. We can attribute this phenomenon to the following reason: because of the high repeat units of the hydrophilic chain, the micelles have a relatively long corona in the aqueous solution, and the shell resulting from the shrinkage of the corona is taken into consideration in the AFM measurement, while the TEM images only exhibit the PHEMAPOSS core. Additionally, it is worth to mention that the height (about 45 nm) exhibited in Supporting Information Figs. S5c and S6c, respectively, exported from Supporting Information Figs. S5a and S6a is in good agreement with the diameter observed in TEM images. This also confirms the assembled morphology is a typical core-shell structure.

System II

Self-assembled morphologies from ABCPs with the molar ratio of hydrophobic/hydrophilic block (PHEMAPOSS/PDMAEMA) of around 1/2.4, 1/1.5, and 1/0.8. To further explore the effect of the molar ratio of hydrophobic/hydrophilic block morphologies, we decreased the chain length of PDMAEMA block, and we designed the molar ratio of the hydrophobic/hydrophilic block (PHEMAPOSS/PDMAEMA) of around 1/2.4, 1/1.5, and 1/0.8.

From the TEM images of PHEMAPOSS₄₅-*b*-PDMAEMA₁₀₆ assembled aggregates in water in Figure 10(a,b), we found not only spherical core-shell micelles (30–55 nm), but also the pearl-necklace-like morphology formed from the linked spherical aggregates. This observation was also confirmed by AFM image (Supporting Information Fig. S7). With further decreasing the chain length of PDMAEMA, PHEMAPOSS₄₅-*b*-PDMAEMA₆₈ has a much clearer pearl-necklace-like morphology shown in Figure 11 and Supporting Information Figure S8, but we found PHEMAPOSS₄₅-*b*-PDMAEMA₆₈ has a



FIGURE 8 TEM images [scale bar, 200 nm (a), 50 nm (b)] of PHEMAPOSS₄₅-b-PDMAEMA₂₈₆ self-assembled aggregates in aqueous solution.

more compacted structure, where the single spherical aggregate has merged with the adjacent one and the edge almost could not be discerned. For the PHEMAPOSS-*b*-PDMAEMA block copolymers with a shorter PDMAEMA hydrophilic chain, the slow kinetics in dilute solution hinder assembled nanostructures from reaching global equilibrium state to form pearl-necklace-like aggregates, due to the slow chain exchange between micelles. The similar assembled aggregates were also observed by other groups.^{68–72}

Additionally, some single spheres coexist in these two selfassembled morphologies, which indicating the spheres formed in the self-assemble process first, and then they further involve adhesive collisions, resulting in the formation of a pearl-necklace-liked structure.^{73,74}

We further decreased the length of the soluble PDMAEMA block to prepare PHEMAPOSS₄₅-b-PDMAEMA₃₄, where the molar ratio of hydrophobic/hydrophilic reaches to about

1/0.8. Surprisingly, the morphology of the micelles changed dramatically and large compound vesicles (LCVs) which have both inner and outer hydrophilic surfaces were obtained in Figure 12. The size of the LCVs is in the range of 297-372 nm in TEM image [Fig. 12(a,b)], but it is about 450 nm in AFM image (Supporting Information Fig. S9a). Here, the size of LCVs in AFM image is not much larger than that in TEM image compared with that in the core-shell spherical or pearl-necklace-like structure, which means the difference may be attributed to the tip convolution effects. Additionally, the height of the LCVs observed in AFM (Supporting Information Fig. S9c) is 296.5 nm, which is smaller than the size in TEM images. We can attribute this to the hollow structure among the LCVs that collapsed on the mica, which also confirms that LCVs were obtained successfully. Additionally, the assembled LCVs of PHEMAPOSS₄₅-b-PDMAEMA₃₄ in aqueous solution were further revealed by SEM images (Supporting Information Fig. S10), which is consistent with the TEM and AFM results.



FIGURE 9 TEM images [scale bar, 200 nm (a), 50 nm (b)] of PHEMAPOSS₄₅-*b*-PDMAEMA₁₄₅ self-assembled aggregates in aqueous solution.



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FIGURE 10 TEM images [scale bar, 200 nm (a), 50 nm (b)] of PHEMAPOSS₄₅-b-PDMAEMA₁₀₆ self-assembled aggregates in aqueous solution.

In our previous studies of hemi-telechelic and telechelic amphiphilic POSS-containing hybrid PAAs, the POSS moieties are only located at the end of polymer chains, moreover, the POSS content is quite lower in these hybrid polyelectrolytes, thus the self-assembly of POSS-containing hybrid polyelectrolytes could not be well studied. However, in this work, we constructed a series of amphiphilic POSS-containing hybrid block copolymers, and systematically studied the influence of the content of POSS on the assembled morphologies. Based on above AFM and TEM results, we found there are mainly four assembled morphologies formed from PHEMAPOSS-b-PDMAEMA block copolymers in water, which are dependent on the molar ratio of hydrophobic/hydrophilic block (Scheme 3). For PHEMAPOSS₄₅-b-PDMAEMA₆₉₉ with the longest hydrophilic PDAEMA chain ($f_{PHEMAPOSS} = 30.8\%$), it self-assembled into some irregular aggregates with some dark dots. This structure is similar to that of our previous study in hemitelechelic POSS-PAA, which is rarely found from the selfassembly of the pure organic amphiphilic block copolymers.

With decreasing PDMAEMA chain length, PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆ ($f_{\rm PHEMAPOSS} = 52.1\%$) and PHEMAPOSS₄₅-*b*-PDMAEMA₁₄₅ ($f_{\rm PHEMAPOSS} = 68.2\%$) can form typical coreshell spherical micelles where the hydrophobic PHEMAPOSS block as the core and hydrophilic PDMAEMA block as the shell. With further decreasing PDMAEMA chain length, PHE-MAPOSS₄₅-*b*-PDMAEMA₁₀₆ ($f_{\rm PHEMAPOSS} = 74.6\%$) and PHEMAPOSS₄₅-*b*-PDMAEMA₆₈ ($f_{\rm PHEMAPOSS} = 82.0\%$) self-assembled into pearl-necklace-like aggregates from the single core-shell micelles. Finally, PHEMAPOSS₄₅-*b*-PDMAEMA₃₄ ($f_{\rm PHEMAPOSS} = 90.0\%$), formed a LCV and this is rarely reported from the self-assembly of hybrid block copolymers.

The self-assembled aggregates of PHEMAPOSS-*b*-PDMAEMA in aqueous solution (0.25 mg/mL) were also studied by DLS. Figure 13 shows the intensity-weighted hydrodynamic diameter distributions and hydrodynamic diameter of PHEMA-POSS-*b*-PDMAEMA ABCPs self-assembly aggregates in aqueous solution at pH = 7. In system I, the diameter of the



FIGURE 11 TEM images [scale bar, 200 nm (a), 50 nm (b)] of PHEMAPOSS₄₅-*b*-PDMAEMA₆₈ self-assembled aggregates in aqueous solution.



FIGURE 12 TEM images [scale bar, 200 nm (a), 50 nm (b)] of PHEMAPOSS₄₅-*b*-PDMAEMA₃₄ self-assembled aggregates in aqueous solution.

three block copolymers measured by DLS are all larger than those in AFM or TEM images, which can be explained by the highly stretched conformation of the PDMAEMA chains at pH = 7 in aqueous solution, and the DLS data directly reflects the dimension of micelles in solution. Whereas, in system II, with the decreasing of the length of the hydrophilic chain, the diameter observed in DLS is more close to the diameter of the AFM images. It can be seen that the hydrodynamic diameter (176.6 nm) of PHEMAPOSS₄₅-b-PDMAEMA₆₈ has a broad distribution, which attributed to the pearl-necklace-like structure and a small number of spheres. Additionally, the hydrodynamic diameter (436.4 nm) of PHEMAPOSS₄₅-b-PDMAEMA₃₄ with the shortest soluble block chain is in good agreement with that in

AFM images, because the very short soluble chain contributes little to the hydrodynamic diameter.

Thermoresponsive Behavior of PHEMAPOSS-*b*-PDMAEMA Block Copolymers

It is well known that thermoresponsive polymers can undergo a solubility transition by varying the temperature in water due to the reversible disruption of hydrogen bonds between the polymer and water. Thermoresponsive micelles containing PDMAEMA that involve a coil-to-globule transition have been reported by many groups.^{26,28,31} Here, the representative block copolymer of PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆ in the systems was chosen to study the dual stimuliresponsive behaviors, since the mass fraction of



SCHEME 3 Self-assembly of PHEMAPOSS-*b*-PDMAEMA in water with the decreasing length of hydrophilic PDMAEMA chain.



FIGURE 13 Intensity-weighted hydrodynamic diameter distributions of PHEMAPOSS-*b*-PDMAEMA self-assembled aggregates in aqueous solution at pH = 7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PHEMAPOSS/PDMAEMA in PHEMAPOSS₄₅-b-PDMAEMA₂₈₆ is roughly equal to 1/1 (the mass fraction of PDMAEMA is 52.1%). DLS and UV spectroscopy were performed to study the thermal behavior of the micelles formed by PHEMA-POSS₄₅-*b*-PDMAEMA₂₈₆. As seen from Figure 14, the solutions (0.25 mg/mL) at pH = 7 and pH = 9 (deprotonation) were conducted in the experiments, respectively. There is no abrupt change of the hydrodynamic diameter in both conditions, but a broaden collapse transition appears under heating the solution from 25 to 85 °C, which is attributed to the shrinkage of the corona of the micelles upon heating. The temperature dependence of transmittance was also studied by UV and was shown in Supporting Information Figure S11. It can be seen that the transmittance of solution almost does not change with the increasing temperature, which is agreeable with DLS results. Furthermore, TEM was also used to characterize the self-assembled morphology of PHEMA-POSS₄₅-*b*-PDMAEMA₂₈₆ at 60 °C in aqueous solution (pH = 7), as shown in Supporting Information Figure S12. There is no apparent change in the morphology, compared with that of the self-assembly at room temperature [Fig. 8(a)], and they are still typical core-shell spherical micelles, which is in accordance with DLS and UV results.

pH-Responsive Behavior of PHEMAPOSS-*b*-PDMAEMA Block Copolymers

PDMAEMA is a pH-responsive polymer and the tertiary amine groups along its main chain can be charged or uncharged at low or high pH, respectively. DLS was used to study the pH-responsive behavior of PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆, and the result was shown in Figure 15. It can be seen that with increasing the pH of the micelles solution, the diameter of the micelles goes through three stages: sharply decrease, keep constant and sharply increase. In the first stage, when the pH increased, the amino groups of PDMAEMA were deprotonated and the corona shrunk dra-



FIGURE 14 Temperature dependence of the hydrodynamic diameter of PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆ solution at different pH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

matically, resulting in the abrupt decrease of the hydrodynamic diameter. In the second stage, with the increase of the pH, the diameter of the micelles almost does not change in solution. However, in the third stage, the bimodal distribution can clearly see in Supporting Information Figure S13, which indicates the micelles aggregated into complex micelles.

To further confirm the structural change of the micelles due to the stimuli-responsive behavior of PDMAEMA, the self-assembled morphology of PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆ under high pH was characterized by TEM and SEM, respectively [Fig. 16(b) and Supporting Information Fig. S14]. The results showed the assembled micelles obviously shrunk and aggregated into a complex micelles under high pH (pH = 12.5), compared with that of the original assembled morphology at pH = 7 [Figs. 8(a) and 16(a)], which means



FIGURE 15 Hydrodynamic diameter of PHEMAPOSS₄₅-*b*-PDMAEMA₂₈₆ in aqueous solution at different pH.



FIGURE 16 SEM image [scale bar 500 nm, pH = 7 (a)] and TEM images [scale bar 200 nm; pH = 12.5 (b), pH = 7 (c)] of PHEMA-POSS₄₅-*b*-PDMAEMA₂₈₆ self-assembled aggregates in aqueous solution. Schematic illustration of the reversible assembly morphology transition of the micelles through acid-base control (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PDMAEMA segment is fully deprotonated and the shell has collapsed under high pH. Surprisingly, when we adjusted the alkaline self-assembled solution to pH = 7, the complex micelles can transfer back to the original spherical morphology [Fig. 16(c)]. Thus, the reversible assembly morphology transition of the micelles was realized through acid-base control.

CONCLUSIONS

In summary, a novel POSS-containing methacrylate monomer (HEMAPOSS) with a long side chain was fabricated, and further used to prepare well-defined PHEMAPOSS homopolymer with a high DP of POSS unit via RAFT polymerization. The kinetics study shows the RAFT polymerization of HEMAPOSS is in a controlled way and followed pseudo-first-order kinetics. Then, a series of PHEMAPOSS-b-PDMAEMA ABCPs with different length of PDMAEMA chain were synthesized by using PHEMAPOSS as the macro-RAFT agent. The PHEMA-POSS-b-PDMAEMA ABCPs can self-assemble into a variety of morphologies in aqueous solution. The morphologies can be tuned from irregular assembled aggregates to spherical coreshell micelle and further from pearl-necklace-liked structure to LCVs by varying the length of hydrophilic PDMAEMA block chain. Furthermore, the thermoresponsive behavior of PHEMAPOSS-b-PDMAEMA ABCPs revealed that the PDA-MEMA corona of the aggregates exhibits a broaden collapse transition from 25 to 85 °C. Additionally, SEM and TEM results clearly showed the reversible transition of the assembled morphologies from spherical micelles to complex micelles was realized through acid-base control.

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