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ORIGINAL PAPER

# Synthesis and characterization of star-shaped block copolymers with polyhedral oligomeric silsesquioxane (POSS)core via ATRP

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**Abstract** Star-shaped PMMA-b-PS block copolymers with POSS core were prepared by atom transfer radical polymerization of St using star-shaped POSS/PMMA-Cl as a macroinitiator in presence of CuCl, 2,2,-bipyridine, toluene at 110 °C. The core-first method, which used an active multifunctional core to initiate the growth of polymer chains, was applicable to making star-shaped block copolymers with POSS core. The structure of hybrid star-shaped PMMA-b-PS block copolymers was characterized by GPC and $^1$H NMR, respectively.

**Keywords** Polyhedral oligomeric silsesquioxane (POSS) · Star-shaped · Block copolymers · Composites · Atom transfer radical polymerization (ATRP)

## Introduction

POSS-containing copolymers have received steadily increasing attention during the recent decade as a novel category of nanoscale-structured materials. These POSS-containing copolymers are attractive for their various applications in the areas such as liquid crystals [1, 2], nanocomposites [3, 4], photoresists in lithographic technologies [5], based on their high temperature, and oxidation resistance properties compared with these corresponding copolymers [6]. These properties may be attributed to the unique organic/inorganic hybrid structure of POSS. The typical POSS has a cubic inorganic $Si_8O_{12}$ core surrounded by eight organic corner groups. These eight organic corner groups can be functionalized by a variety of organic groups. Commonly, one of them is functionalized by a polymerizable or reactive group, while the others are nonreactive groups. In view of this unique structure, POSS molecule can be applied as

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polymerizable monomer or initiator to prepare a novel class of nanoscale structured hybrid copolymers modified by POSS. As a consequence of the emergence of the POSS, a variety of POSS-containing random copolymers have been prepared. Chang et al. [7] synthesized copolymers of Poly-(vinylpyrrolidone-co-isobutylstyryl-POSS) and poly-(acetoxystyrene-co-isobutylstyryl-POSS) using a conventional free radical polymerization technique. Kwon et al. [8] reported that the poly (NBECOOH-b-NBE POSS) block copolymers via ring-opening metathesis polymerization (ROMP). Organic/inorganic triblock copolymers of polystyrene-butadiene-polystyrene (SBS) containing polyhedral oligomeric silsesquioxane (POSS) molecules were prepared by Haddad et al. [9], through the hydrosilation between the block copolymers and POSS molecules. In order to yield ABA triblock copolymers, Mather et al. [10] used a commercially available difunctional PBA as a macroinitiator to initiate the ATRP of isobutyl MA-POSS. Although there are many reports on the synthesis and the properties of block copolymers containing POSS molecules, most investigations were focused on these linear polymers.

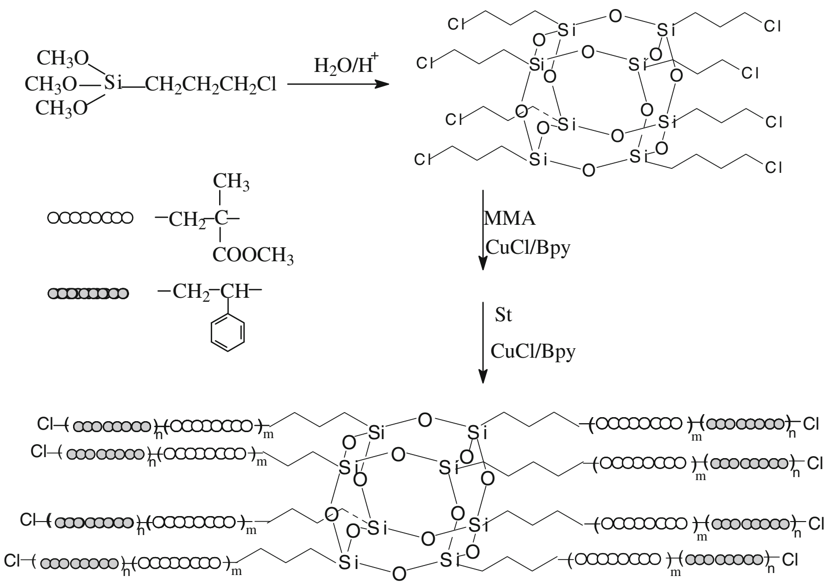
Star-shaped polymers constitute unique three-dimensional structures where a large number of arm chains radiating from the central core among the branched polymers since each molecule has only one branching point [11, 12]. Well-defined star-shaped polymers offer lower melt and solution viscosities compared with those of linear polymers. The synthesis of star-shaped polymers can generally be divided into two routes [13]. The first one is called arm-first approach that the pre-prepared macromolecular chains are coupled with multifunctional cores to afford hetero-armed or miktoarmed star-shaped polymers [14, 15]. The second one is core-first technique, in which multifunctional compounds are used to initiate the polymerization of monomers. Core-first approach has been proved to be efficient to prepare a series of well-defined star-shaped polymers with precise arm numbers and lengths. Zheng et al. [16] reported that star-shaped poly (3-caprolactone) with POSS core was synthesized using octa (3-hydroxypropyl) POSS as an initiator via ring-opening polymerization. Gnanou et al. [17] synthesized star-shaped polystyrene using octafunctional calixarene derivative in the presence of CuBr/2,2-bipyridyl by atom transfer radical polymerization (ATRP). Star-shaped Poly (methylmethacrylate) with four, six, and eight arm chains of controlled lengths were prepared by Sawamoto et al. [18] through ATRP.

In this article, a POSS core was used as an initiator to polymerize methyl methacrylate for the preparation of a star-shaped POSS/PMMA-Cl via ATRP. Star-shaped POSS/PMMA-Cl was then used as macroinitiator for the ATRP of Styrene.The AB block copolymers based on POSS were prepared, forming star-shaped structure with a “core” of POSS and an “arms” of polymer (Scheme 1).

## Experimental section

### Materials

3-Chloropropyltrimethoxysilane was purchased from Hybrid Co Ltd. Methyl methacrylate (MMA) and Styrene (St) were obtained from Shanghai Sinopharm



**Scheme 1** Synthetic route of star-shaped POSS/PMMA-b-PS with POSS core

Chemical Reagents Co Ltd. MMA and St were washed with an aqueous solution of sodium hydroxide (5 wt%) three times and then with distilled water until neutralization. After being dried with anhydrous magnesium sulfate, MMA, and St were distilled under reduced pressure [19]. CuCl was obtained from Shanghai First Chemical Work. 2,2'-bipyridine (Bpy) and other reagents were used as received.

## Characterization

$^1$H NMR and $^{29}$Si NMR spectra were recorded on Bruker AVAN300 CE instrument with CDCl3 as the solvent and tetramethylsilane (TMS) as an internal standard. FTIR spectra were measured on a Bruker VECTOR-22 FTIR spectrometer. The molecular weight and polydispersity indexes were determined on a Waters 150 °C gel permeation chromatograph (GPC) equipped with ultrastyragel columns (500,$10_3$,$10_4$ Å) and Waters RI detector at 30 °C. Monodispersed polystyrene standards were used in the calibration of molecular weights and THF was used as eluent at a flow rate of 1.0 mL/min.

## Synthesis of octa (3-chloropropyl) POSS [$(ClC_3H_6)_8Si_8O_{12}$]

Octa (3-chloropropyl) POSS [$(ClCH_2CH_2CH_2)_8Si_8O_{12}$] was synthesized by the following method described by Dittmar et al. [20]. Methanol (90 mL), 3-chloropropyltrimetho xysilane(3.975 g, 0.02 mol), concentrated hydrochloric acid (4.5 mL) were mixed and the hydrolysis and rearrangement reactions were allowed to carry out for 5 days, and then colorless crystals (20%) were obtained after dried in vacuo vacuum at 60 °C.

### Synthesis of star-shaped POSS/PMMA-Cl

All the polymerization reactions were carried out under nitrogen atmosphere using a vacuum-line system. The polymerization of MMA was accomplished according to a typical ATRP method [21]. Octa (3-chloropropyl) POSS (100 mg), CuCl (76 mg), Bpy (360 mg), MMA (10 mL), and toluene (20 mL) were added to the glass tube equipped with a magnetic stir. The tube was degassed by means of three freeze–pump–thaw cycles, filled with nitrogen, and immersed in an oil bath. The reaction was stirred at 110 °C for 12 h, and then quenched with ice at −15 °C. The reaction mixture was dissolved in THF and passed through a short neutral alumina column to remove the catalyst. The solution was concentrated under reduced pressure, then precipitated into methanol and filtered. The collected polymer (star-shaped POSS/PMMA-Cl) was dried in vacuum oven at 50 °C.

### Synthesis of star-shaped POSS/PMMA-b-PS

The synthesis of star-shaped POSS/PMMA-b-PS was carried out in a similar way except that the octa(3-chloropropyl)POSS was replaced by star-shaped POSS/PMMA-Cl as macroinitiator. Star-shaped POSS/PMMA-Cl (79.12 mg), CuCl(38 mg), Bpy (180 mg), St (10 mL), and toluene (20 mL) were added to the glass tube equipped with a magnetic stirring. The tube was degassed by means of three freeze–pump–thaw cycles, filled with nitrogen, and immersed in an oil bath. The reaction was stirred at 110 °C for 24 h, and then quenched with ice at −15 °C. The reaction mixture was dissolved in THF and passed through a short neutral alumina column to remove the catalyst. The solution was concentrated under reduced pressure, then precipitated into methanol and filtered. The collected polymer (star-shaped POSS/PMMA-b-PS.) was dried in vacuum oven at 50 °C.

## Results and discussion

### Synthesis of octa (3-chloropropyl)POSS

Octa (3-chloropropyl) POSS was synthesized via the hydrolytic condensation of 3-chloropropyltrimethoxysilane as the method described by Dittmar et al. [20]. The typical $^{1}$H NMR spectrum of octa (3-chloropropyl) POSS is shown in Fig. 1. There are three peaks (0.78, 1.86, 3.52 ppm) corresponding to the proton peaks of SiC*H*2,CH2C*H*2CH2, C*H*2Cl, respectively. In addition, $^{29}$Si NMR spectrum of octa (3-chloropropyl) POSS is present in Fig. 2. There is only one single resonance at −67.0 ppm, which indicates that the eight silicon atoms are magnetically equivalent. Therefore, the octa (3-chloropropyl) POSS was successfully prepared.

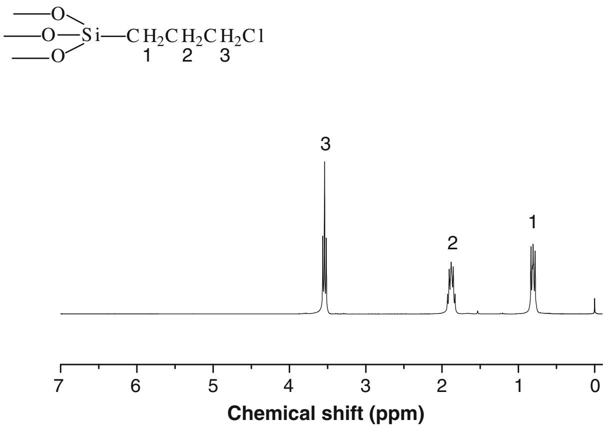


**Fig. 1** $^1$H NMR spectra of the octa (3-chloropropyl) POSS

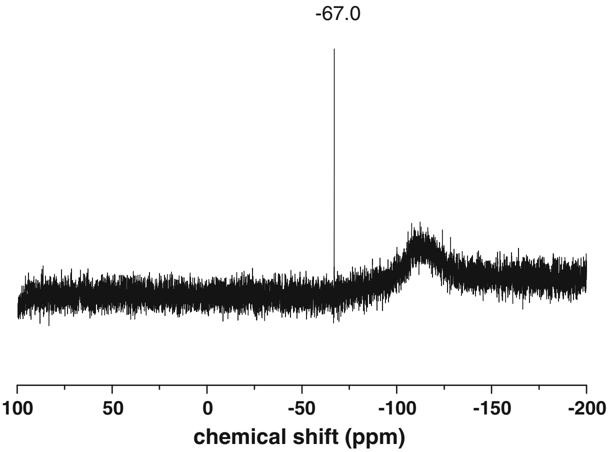


**Fig. 2** $^{29}$Si NMR spectra of octa(3-chloropropyl) POSS

## Synthesis of star-shaped POSS/PMMA-Cl via ATRP

Atom transfer radical polymerization was used to synthesize star-shaped POSS/PMMA-Cl homopolymer with controlled Mn and polydispersity (Table 1). The conversion of octa (3-chloropropyl) POSS to star-shaped POSS/PMMA-Cl was analyzed using FTIR and $^1$H NMR. In the FTIR spectrum of octa (3-chloropropyl) POSS (Fig. 3a), there are two distinct bands (1109, 689 cm$^{-1}$) corresponding to the stretching vibration of Si–O–Si, C–Cl [16]. After the reaction of octa (3-chloropropyl) POSS with MMA, the FTIR spectrum in Fig. 3b shows the appearance of the two new peaks at 1,730 and 1,147 cm$^{-1}$ which are consistent with stretching vibration of C=O and C–O–C in the PMMA chain [22]. In addition, the proton signals of octa (3-chloropropyl) POSS are also seen in the $^1$H NMR spectrum of star-shaped

**Table 1** Results of ATRP of star-shaped POSS/PMMA-Cl macroinitiator and star-shaped POSS/PMMA-b-PS composite

| | DP | Conv[g] (%) | $M_n^a$ | $M_w^b$ | PDI[c] | POSS content[d] (%) |
|---|---|---|---|---|---|---|
| Star-shaped PMMA[e] | 173 (*m*) | 6 | 140,000 | 230,000 | 1.61 | 0.74 |
| Star-shaped PMMA-b-PS[f] | 84 (*n*) | 17 | 210,000 | 350,000 | 1.66 | 0.49 |

[a] $M_n$, [b] $M_w$ and [c] $M_w/M_n$ were measured by GPC

[d] Octa(3-chloropropyl) POSS content was calculated according to eq ($M_n$poss/$^aM_n$)

[e] Star-shaped POSS/PMMA-Cl was synthesized via ATRP at 110 °C with the molar ratio in feed: MMA: octa(3-chloropropyl) POSS: CuCl:bpy = 1,048:1:8:24

[f] Star-shaped POSS/PMMA-b-PS was synthesized via ATRP using Star-shaped POSS/PMMA-Cl as macroinitiator at 110 °C with the molar ratio in feed: St: Star-shaped POSS/PMMA-Cl: CuCl: bpy = 967:1:8:24

[g] Conversion was measured with gravimetric method

$m = (M2 - M1)/M4$, $n = (M3 - W2)/M5$

M1: the molar mass of octa (3-chloropropyl) POSS; M2: the Mn of star-shaped POSS/PMMA-Cl; M3: the Mn of star-shaped POSS/PMMA-b-PS; M4: the molecule of MMA; M5:the molar mass of St

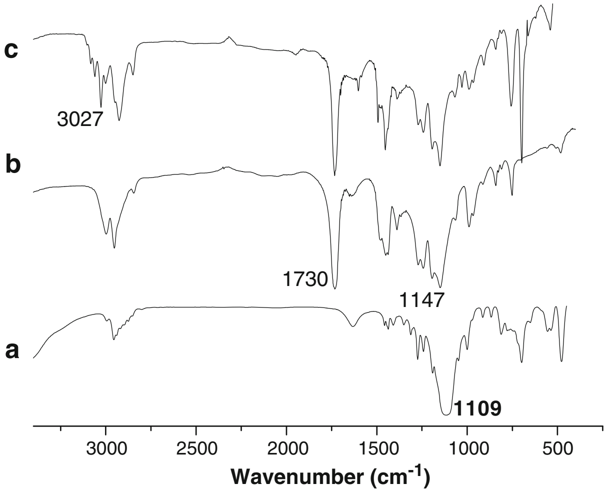


**Fig. 3** FTIR Spectra of the Octa (3-chloropropyl) POSS (*a*), the star-shaped POSS/MMA-Cl (*b*) and the star-shaped POSS/PMMA-b-PS composite (*c*)

POSS/PMMA-Cl after the reaction, along with the simultaneous appearance of the methyl proton peak (3.6 ppm) of the ester unit, the methene proton peak (1.0–2.8 ppm) in backbone of the grafted PMMA chain, and the substituted methyl groups' proton peak (0.77, 0.95 ppm), as shown in Fig. 4. These spectral changes are consistent with the polymerization of MMA [23]. Therefore, the conversion of octa (3-chloropropyl) POSS to star-shaped POSS/PMMA-Cl was confirmed by FTIR and $^1$H NMR.

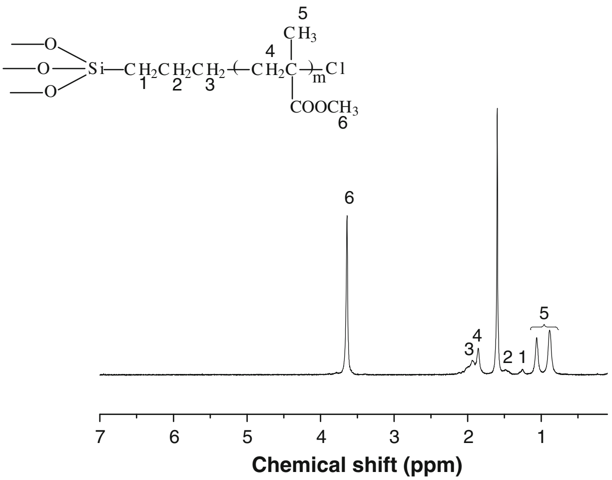


**Fig. 4** $^1$H NMR spectrum of the star-shaped POSS/PMMA-Cl

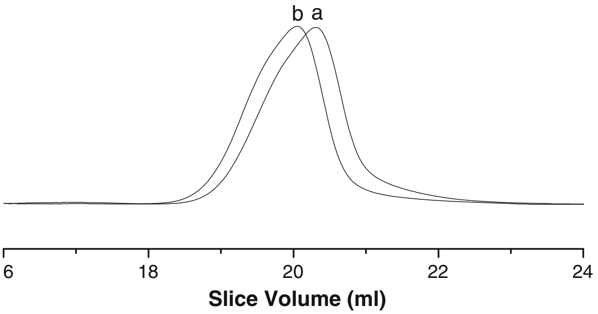


**Fig. 5** GPC traces of the star-shaped POSS/PMMA-Cl (*a*) and Star-shaped POSS/PMMA-b-PS composite (*b*)

For further clarifying whether the star-shaped POSS/PMMA-Cl was prepared.The typical GPC curve of star-shaped POSS/PMMA-Cl is shown in Fig. 5a. The chromatograms indicate a unimodal molecular weight distribution, but an increase in the molecular weight as a result of the ATRP.

## Synthesis of star-shaped POSS/PMMA-b-PS through ATRP

Using star-shaped POSS/PMMA-Cl as macroinitiator, the polymerization of St was carried out at 110 °C for 24 h. The typical FTIR spectrum of star-shaped PMMA-b-PS is shown in Fig. 3c. Compared with FTIR spectrum of star-shaped POSS/PMMA-Cl shown in Fig. 3b, the following characteristic absorption bands of PS can be clearly seen in Fig. 3c: the out-of-plane bending band of C–H in the benzene ring at 693 cm$^{-1}$; the skeletal vibration bands of benzene ring at 1,604 and 1,493 cm$^{-1}$;

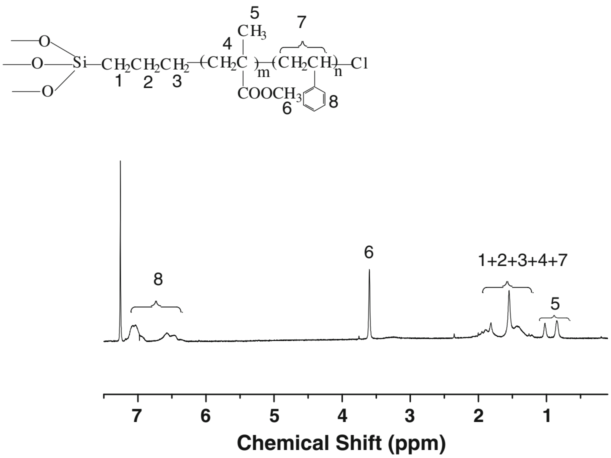


**Fig. 6** $^1$H NMR spectrum of star-shaped POSS/PMMA-b-PS composite

the weak overtone and successive bands at 1,731–1,944 cm$^{-1}$; and aromatic C–H stretching bands at 3,027 cm$^{-1}$ [24]. The FTIR peaks of PS obviously indicate the existence of St in the copolymer. To further verify that the reaction was carried out, the $^1$H NMR spectrum of block copolymer was measured, which indicates the presence of protons from PS (Fig. 6). Resonances at 2.12–0.77 ppm are poorly resolved due to the abundance of protons from methene and methine protons of the PS backbone, with the exception of methene protons from star-shaped POSS/PMMA-Cl. At higher chemical shift, methyl proton of the ester unit (3.6 ppm) and the phenyl proton of St (6.3–7.2 ppm) [25] are observed, indicating that successful chain extension had occurred.

Meanwhile, GPC trace of the block copolymer confirms the incorporation of PS. Clear increase in molar mass relative to the macroinitiator is observed (Fig. 5a). Importantly, unimodal molecular weight distribution means that no evident star-shaped POSS/PMMA-Cl exists.

With the two steps ATRP, star-shaped PMMA-b-PS block copolymers with polyhedral oligomeric silsesquioxane (POSS) core were synthesized.

## Conclusion

In this study, we reported the synthesis of the octaarmed star-shaped PMMA-b-PS block copolymers which grown from the octa (3-chloropropyl) POSS by ATRP. On the basic analysis results of $^1$H NMR, FTIR, and GPC, the PMMA-b-PS chains were grown from the POSS core. The octaarmed star-shaped block copolymers with POSS core were successfully synthesized.

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