

Synthesis of tadpole-shaped POSS-containing hybrid polymers via “click chemistry”

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ABSTRACT

Copper-catalyzed alkyne-azide “click chemistry” is applied in the preparation of tadpole-shaped (“monochelic”) POSS-end functional hybrid polymers by combining with ATRP and RAFT polymerization. Alkyne-functionalized ATRP initiator and RAFT agent were respectively synthesized and applied in the preparation of alkyne-terminal poly(methyl methacrylate) and polystyrene. The tadpole-shaped POSS-containing hybrid polymers are easily obtained by the click reaction with an azido-functional POSS molecule. This presents a novel and effective method to prepare POSS-containing hybrid polymers.

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1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) have attracted great attention in materials science, since POSS, as unique nanosized agents, can be introduced into polymer matrices to effectively enhance polymeric properties such as thermal and oxidation resistance, and reduce flammability [1–8]. A typical POSS molecule (formula $[\text{RSiO}_{1.5}]_n$, where $n = 8, 10, 12$) has a cage-like inorganic core in the range of a nanometer, surrounded by organic corner groups, which endow the POSS molecule with a higher solubility in organic solvents and reactivity in the preparation of the POSS-containing hybrid materials [9,10]. In the past reports on the preparation of POSS-containing hybrid polymers, the POSS molecules were mostly used as an enhancing agent to be incorporated into the polymeric matrices by chemical copolymerization, crosslinking or physical blending [11–16].

Recently, more and more attention has focused on novel architectures of POSS-containing hybrid polymers using controlled/living radical polymerization technique such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. The POSS molecules can be modified into monomers, initiators, or chain transfer agents (CTAs) for the living polymerization. For example, POSS-containing homopolymers, linear and star-shaped block copolymers, have been synthesized

using a POSS-based methacrylate monomer via ATRP [17,18]. POSS-containing star-shaped hybrid polymers were prepared using the octa-bromo-functionalized POSS molecule as an ATRP initiator [19,20]. The mono-bromo-functionalized POSS molecule was also used as ATRP initiator to synthesize tadpole-shaped (“monochelic”, also named “hemi-telechelic” [21]) POSS-containing hybrid polymers [22,23]. RAFT polymerization, as a very useful living radical polymerization technique in polymer science, is widely used to design many novel polymeric materials with well-defined architectures [24–26]. We recently modified a RAFT chain transfer agent with a POSS molecule to prepare “tadpole-shaped” POSS-containing hybrid polymers via RAFT polymerization [27,28]. The polymerization can be well-controlled by the POSS-containing RAFT agent. Although a typical POSS molecule (molecular weight ~ 1000 g/mol) is small compared to the polymer it is attached to, its presence can cause important changes in the polymer properties. As an example, POSS-functional poly(acrylic acid) forms aggregates in water [27].

“Click chemistry” has been proven to be a fast and efficient approach to prepare polymers with novel architectures [29–31]. Currently, the copper-catalyzed Huisgen 1,3-dipolar cycloaddition between azides and alkynes is the most popular click reaction as it can be performed under mild reaction conditions and it has a good tolerance of functional groups [32,33]. When click chemistry is combined with the living/controlled polymerization technique, it becomes more powerful in constructing novel polymeric architectures [34–37].

So far, click chemistry has been mostly used to functionalize the end-group or pendant groups of polymers or to construct polymers

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with well-defined structures, and the click reaction occurred between a polymer chain and small organic molecules, or between two different polymer chains. We recently showed that the copper-catalyzed click reaction between alkyne-functional POSS molecules and mono-, di- and penta-functional azido-terminal polymers made by ATRP proceeds smoothly to form monochelic (tadpole-shaped), and di-telechelic (dumbbell-shaped) linear hybrid polymers as well as penta-telechelic, star-shaped hybrids [21].

Here, we show that an inversion of the procedure is possible. First, we synthesized an azido-terminal POSS molecule. This was then “clicked” to alkyne-terminal polymers, which were prepared using both an alkyne-terminal ATRP initiator and RAFT agent. We compare the efficiency between ATRP- and RAFT-synthesized polymers. Our results show that the click reaction is a useful alternative to using POSS-functional initiators or chain transfer agents.

2. Experimental section

2.1. Materials

Trisilanolheptaisobutyl polyhedral oligomeric silsesquioxane (POSS-(OH)₃) was purchased from Hybrid Plastics Company. Styrene and methyl methacrylate were kindly donated by BASF SE, and were passed through a silica column to remove the inhibitor. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. CuCl and CuBr were respectively purified by stirring with acetic acid overnight. After filtration, it was washed with ethanol and ether, and then dried in vacuum oven at room temperature overnight. Other reagents in analytical grade were all obtained from Aldrich. Tetrahydrofuran (THF) was distilled from a purple sodium ketyl solution.

2.1.1. Synthesis of (3-chloropropyl)heptaisobutyl polyhedral oligomeric silsesquioxane (POSS-Cl)

POSS-(OH)₃ (5.0 g, 6.3 mmol) was dissolved with 100 mL of absolute THF in two-neck flask with a magnetic stirring bar, and 1.76 mL of dry triethylamine was added. 3-Chloropropyltrichlorosilane (1.97 mL, 12.6 mmol) was quickly charged into the flask with ice-bath using an argon-purged syringe. The mixture was allowed to stir for 1 h at 0°C and 5 h at room temperature. After removing the salt byproduct by filtration, the solution was concentrated to about 20 mL by a rotary evaporator. The condensed solution was precipitated into 200 mL of acetonitrile twice, and the resulting product was dried under vacuum at 50°C for 24 h to give 4.80 g of POSS-Cl, 85.0% yield.

¹H NMR (CDCl₃, ppm): 3.54 (t, 2H, –Si–CH₂CH₂CH₂Cl), 1.88 (m, 9H, –Si–CH₂CH(CH₃)₂, –Si–CH₂CH₂CH₂Cl), 0.98 (d, 42H, –Si–CH₂CH(CH₃)₂), 0.76 (m, 2H, –Si–CH₂CH₂CH₂Cl), 0.63 (q, 14H, –Si–CH₂CH(CH₃)₂). ¹³C NMR, δ (TMS, ppm): 47.65, 26.07, 24.25, 22.87, and 10.16. Elemental analysis calcd for C₃₁H₆₉ClO₁₂Si₈ (894): C, 41.65; H, 7.78. Found: C, 41.95; H, 7.65. Melting point: 266.3°C.

2.1.2. Synthesis of (3-azidopropyl)heptaisobutyl polyhedral oligomeric silsesquioxane (POSS-N₃)

POSS-Cl (3.0 g, 3.4 mmol) and sodium azide (2.2 g, 34 mmol) were reacted in 26.5 mL mixed solution of DMF/THF (v/v, 1/2) at 80°C for 48 h. The reaction mixture was cooled to room temperature, and the solvents were removed under pressure by heating evaporation. The product was dissolved in 50 mL dichloromethane, and washed with 250 mL of saturated NaCl aqueous solution twice. The organic layer was separated, dried over MgSO₄, and filtered. The solution was concentrated to obtain 2.8 g of POSS-N₃, 92% yield. ¹H NMR (CDCl₃, ppm): 3.26 (t, 2H, –Si–CH₂CH₂CH₂Cl), 1.88 (m, 7H, –Si–CH₂CH(CH₃)₂), 1.73 (t, 2H, –Si–CH₂CH₂CH₂Cl), 0.98 (d, 42H, –Si–CH₂CH(CH₃)₂), 0.71 (m, 2H, –Si–CH₂CH₂CH₂Cl), 0.63 (q, 14H, –Si–CH₂CH(CH₃)₂). ¹³C NMR, δ (TMS, ppm): 54.02, 26.06, 24.26, 22.84, and 9.70.

Elemental analysis calcd for C₃₁H₆₉N₃O₁₂Si₈ (901): C, 41.34; H, 7.72; N, 4.67. Found: C, 42.25; H, 6.44; N, 4.08. Melting point: 241°C.

2.1.3. Synthesis of propargyl 2-bromoisobutyrate (PBiB)

PBiB was prepared according to literature [38]. ¹H NMR (CDCl₃, ppm): 4.71 (m, 2H, CH≡CCH₂OOC(CH₃)₂Br), 2.50 (t, 1H, CH≡CCH₂OOC(CH₃)₂Br) and 1.89 (s, 6H, CH≡CCH₂OOC(CH₃)₂Br).

2.1.4. Preparation of alkyne-terminated poly(methyl methacrylate) via ATRP (alkyne-PMMA_{ATRP})

A round-bottom glass flask (20 mL) with a magnetic stirring bar was charged with methyl methacrylate (4.5 mL, 42.2 mmol), PMDETA (0.208 mL, 1.0 mmol), PBiB (0.205 g, 1.0 mmol), and anisole (4.5 mL) was purged with argon. After 20 min, CuCl (0.10 g, 1.0 mmol) was added under argon, and the flask was purged with argon for another 5 min. The polymerization was carried out at 40°C. Small samples (about 0.1 mL) were taken out from the reaction flask to check the conversion, which was measured by ¹H NMR. At the end of the polymerization reaction, the reaction solution obviously became viscous. Final conversion determined by ¹H NMR reached 57.5%. The reaction was stopped by opening to the air, and THF was added. After passing through a basic alumina column, the solution was concentrated by a rotary evaporator. Afterwards, it was precipitated into cold *n*-hexane to remove the residual monomer and other impurities. The polymer was dried under vacuum at 50°C for 24 h (*M*_{n, GPC} = 2770 g/mol, *M*_w/*M*_n = 1.25).

2.1.5. Preparation of tadpole-shaped POSS-containing hybrid poly(methyl methacrylate) via CuBr-catalyzed click coupling (POSS-PMMA_{ATRP})

A round-bottom glass flask (20 mL) with a magnetic stir bar was charged with alkyne-PMMA_{ATRP} (0.50 g, 0.18 mmol), POSS-N₃ (0.32 g, 0.36 mmol), PMDETA (0.075 mL, 0.36 mmol) and dioxane (10 mL) was purged with argon. After 20 min, CuBr (0.052 g, 0.36 mmol) was added under argon, and the flask was purged with argon for another 5 min. The reaction was carried out at 50°C. After 24 h, the flask was opened, and THF was added to quench the reaction. The solution was passed through a basic alumina column, and was concentrated by a rotary evaporator. Afterwards, it was precipitated into 500 mL of *n*-hexane to remove non-reactive POSS-N₃ and other impurities. The resulting product was dried under vacuum at 50°C for 24 h (*M*_{n, GPC} = 5290 g/mol, *M*_w/*M*_n = 1.21).

2.1.6. Preparation of alkyne-terminated polystyrene via ATRP (alkyne-PS_{ATRP})

The preparation of alkyne-PS_{ATRP} is similar to that of alkyne-PMMA_{ATRP} (*M*_{n, GPC} = 8350 g/mol, *M*_w/*M*_n = 1.16). Here, PMDETA/CuBr/CuBr₂ was used as catalyst at a ratio of 1.0:0.9:0.05.

2.1.7. Preparation of tadpole-shaped POSS-containing hybrid polystyrene via CuBr-catalyzed click coupling (POSS-PS_{ATRP})

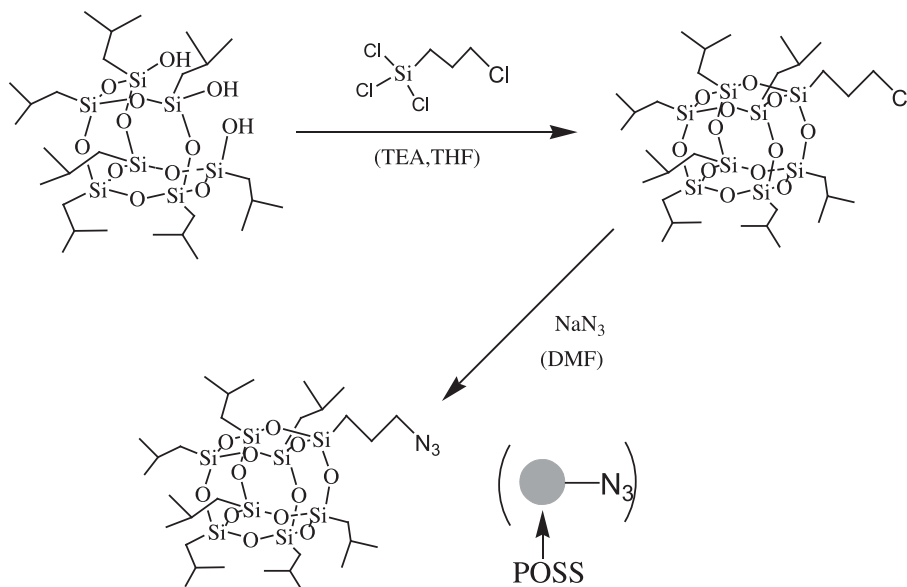
The preparation of POSS-PS_{ATRP} is similar to that of POSS-PMMA_{ATRP} (*M*_{n, GPC} = 10,210 g/mol, *M*_w/*M*_n = 1.15).

2.1.8. Preparation of S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (DDAT)

DDAT was prepared according to the literature [39]. ¹H NMR (CDCl₃, ppm): 0.90 (t, 3H, –(CH₂)₁₁CH₃); 1.20–1.48 (m, 18H, –(CH₂)₉CH₃); 1.64–1.83 (m, 8H, –SC(CH₃)₂COOH and –CH₂(CH₂)₉CH₃), and 3.30 (t, 2H, –CH₂(CH₂)₁₀CH₃).

2.1.9. Preparation of alkyne-terminated S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic ester chloride) trithiocarbonate (alkyne-DDAT)

The preparation of alkyne-DDAT has reported by Brittain et al. [40]. ¹H NMR (CDCl₃, ppm): 0.87 (t, 3H, –(CH₂)₁₁CH₃); 1.14–1.46



Scheme 1. Synthesis of (3-azidopropyl)heptaisobutyl polyhedral oligomeric silsesquioxane (POSS-N₃).

(m, 18H, $-(CH_2)_9CH_3$); 1.55–1.80 (m, 8H, $-SC(CH_3)_2COOH$ and $-CH_2(CH_2)_9CH_3$); 2.46 (t, 1H, $-OCH_2C\equiv CH$), 3.26 (t, 2H, $-CH_2(CH_2)_{10}CH_3$), 4.69 (m, 2H, $-OCH_2C\equiv CH$).

2.1.10. Preparation of alkyne-terminated poly(methyl methacrylate) using DDAT-alkyne via RAFT polymerization(alkyne-PMMA_{RAFT})

A round-bottom glass flask (20 mL) with a magnetic stir bar was charged with MMA (3.20 mL, 30 mmol), DDAT-alkyne (0.10 g, 0.26 mmol), AIBN (0.014 g, 0.085 mmol) and 6.0 mL of toluene. The mixture solution was purged with argon for 30 min, and then the glass tube was sealed under argon. The polymerization was carried out in a thermostated oil bath at 70°C. Small samples (about 0.1 mL) were taken out from the reaction flask at intervals to check the conversion measured by ¹H NMR. At the end of the polymerization reaction, the polymerization was stopped by plunging the tube into ice water. The polymerization flask was opened, and THF was

added. The solution was precipitated into 250 mL of hexane. The polymer was filtered and dried under vacuum at 50°C for 24 h ($M_{n, GPC}$ = 6860 g/mol, M_w/M_n = 1.52).

2.1.11. Preparation of tadpole-shaped POSS-containing hybrid poly(methyl methacrylate) via CuBr-catalyzed click coupling (POSS-PMMA_{RAFT})

A round-bottom glass flask (20 mL) with a magnetic stir bar was charged with alkyne-PMMA_{RAFT} (0.5 g, 0.073 mmol), POSS-N₃ (0.13 g, 0.14 mmol), PMDETA (0.030 mL, 0.14 mmol) and dioxane (10 mL) was purged with argon. After 20 min, CuBr (0.021 g, 0.14 mmol) was added under argon, and the flask was purged with argon for another 5 min. The reaction was carried out at 50°C. After 24 h, the flask was opened, and THF was added to quench the reaction. The solution was passed through a basic alumina column, and was concentrated by a rotary evaporator. Afterwards, then precipitated into 500 mL *n*-hexane. The precipitated solution was kept in cooling-room (4°C) overnight, and was centrifuged at 3000 rpm for 10 min. The resulting product was dried under vacuum at 50°C for 24 h ($M_{n, GPC}$ = 9080 g/mol, M_w/M_n = 1.46).

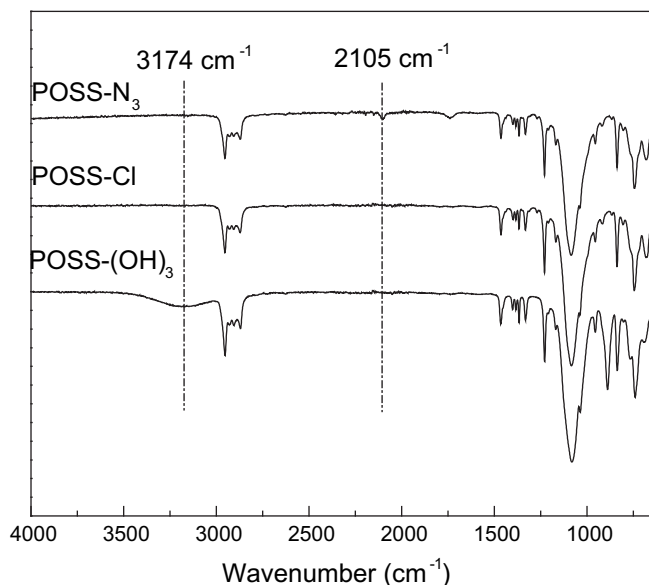


Fig. 1. FT-IR of POSS-(OH)₃, POSS-Cl and POSS-N₃.

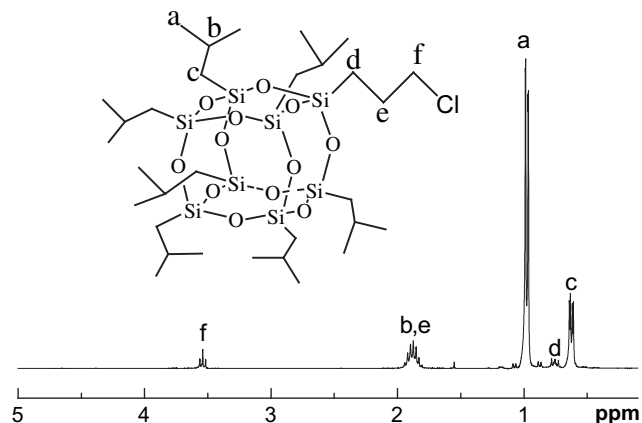
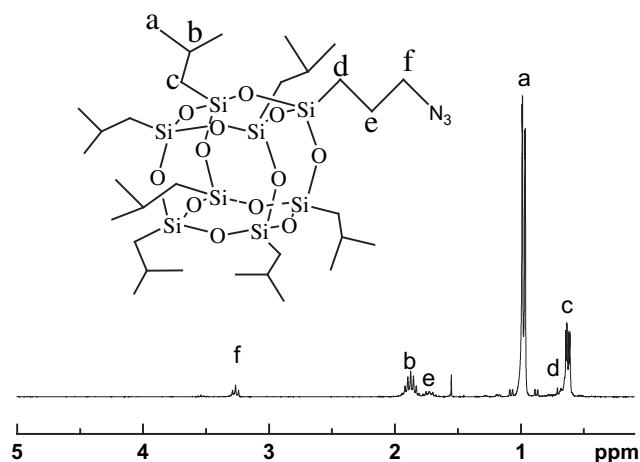


Fig. 2. ¹H NMR of POSS-Cl oligomeric silsesquioxane (POSS-Cl).

Fig. 3. ^1H NMR of POSS- N_3 .

2.1.12. Preparation of alkyne-terminated polystyrene via RAFT polymerization (alkyne- PS_{RAFT})

The preparation of alkyne- PS_{RAFT} is similar to that of alkyne- $\text{PMMA}_{\text{RAFT}}$ ($M_{n,\text{GPC}} = 3470$ g/mol, $M_w/M_n = 1.10$).

2.1.13. Preparation of tadpole-shaped POSS-containing hybrid polystyrene via CuBr-catalyzed click coupling (POSS- PS_{RAFT})

The preparation of POSS- PS_{RAFT} is similar to that of POSS- $\text{PMMA}_{\text{RAFT}}$ ($M_{n,\text{GPC}} = 4550$ g/mol, $M_w/M_n = 1.11$).

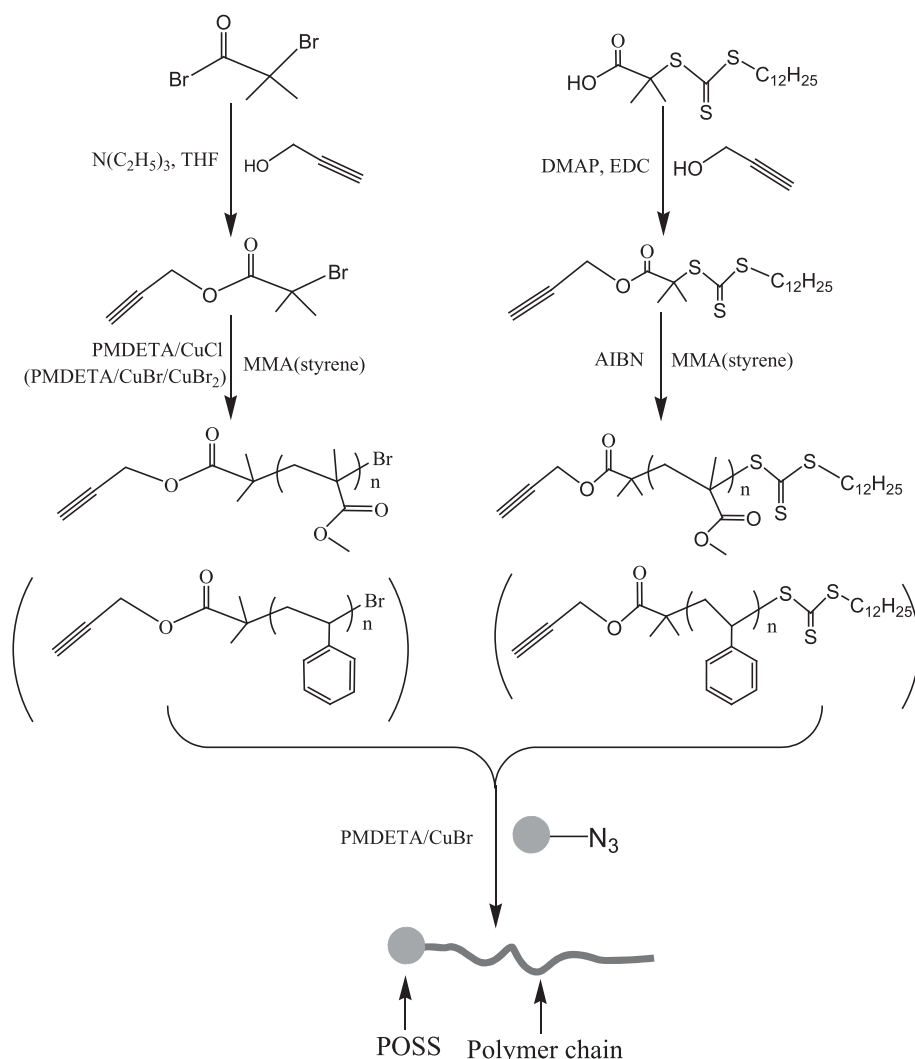
2.2. Methods

^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) measurements were carried out on a Bruker AC-250 instrument with tetramethylsilane (TMS) as an internal reference.

Fourier transform infrared spectroscopy (FT-IR) measurements were conducted on a PERKIN-ELMER Spectrum One FT-IR spectrophotometer equipped with an ATR sampling unit (25°C).

Elemental analyses were performed on a Vario Elementar EL III.

Gel permeation chromatography (GPC). The molecular weights and molecular weight distribution were measured by conventional GPC. Column set: $5\ \mu\text{m}$ SDV gel, 10^2 , 10^3 , 10^4 , and 10^5 Å, 30 cm each (PSS, Mainz). Detectors used are RI and UV operated at 254 nm. Polystyrene and PMMA standards, respectively (PSS, Mainz), with narrow molecular weight distribution were used for the calibration of the column set, and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min.



Scheme 2. Synthesis of tadpole-shaped PMMA and polystyrene, respectively, via click chemistry.

Table 1
GPC characterization of PMMA and polystyrenes before and after click reaction.

	Conv., x (%)	$10^3 M_{n,th}$ g/mol	$10^3 M_{n,GPC}^c$ g/mol	M_w/M_n^c
Alkyne-PMMA _{ATRP}	57.5	2.64 ^a	2.8	1.25
POSS-PMMA _{ATRP}	—	3.54 ^b	5.3	1.21
Alkyne-PS _{ATRP}	34.0	8.38 ^a	8.4	1.16
POSS-PS _{ATRP}	—	9.28 ^b	10.2	1.15
Alkyne-PMMA _{RAFT}	42.7	5.37 ^a	6.9	1.52
POSS-PMMA _{RAFT}	—	6.27 ^b	9.1	1.46
Alkyne-PS _{RAFT}	32.5	3.05 ^a	3.5	1.10
POSS-PS _{RAFT}	—	3.95 ^b	4.6	1.11

^a $M_{n,th} = [M]_0 x / [I]_0 \times M_{monomer} + M_{initiator}$, where x is the monomer conversion.

^b Estimated as $M_{n,th} = M_{n,th}(\text{alkyne-Polymer}) + M_{azido-POSS}$.

^c Measured by GPC calibrated with linear PMMA and PS standards, respectively.

3. Results and discussion

3.1. Synthesis of Azido-POSS

To prepare the azido-functionalized POSS molecule, (3-chloropropyl)heptaisobutyl polyhedral oligomeric silsesquioxane (POSS-Cl) was first synthesized as a precursor (Scheme 1). Trisilanolheptaisobutyl polyhedral oligomeric silsesquioxane (POSS-(OH)₃) was corner-capped with 3-chloropropyltrichlorosilane to afford POSS-Cl. The chlorine group of POSS-Cl was converted to the azido group using sodium azide in a mixture solution of DMF/THF (v/v, 1/2) at 80°C for 24 h, which was confirmed by FT-IR and ¹H NMR, respectively. The broad peak at about 3174 cm⁻¹, corresponding to the stretching vibration of three silica-hydroxyl groups, completely disappeared, and a new peak appeared at 2105 cm⁻¹, which is ascribed to the asymmetric stretching of the azido group (Fig. 1). The ¹H NMR also clearly reveals that POSS-Cl was successfully prepared (Fig. 2). The characteristic signals at $\delta = 3.54$ and 0.98 ppm are respectively assigned to the resonance of the methylene protons (–Si–CH₂CH₂CH₂Cl) and methyl protons (–SiCH₂CH(CH₃)₂) of POSS-Cl. Compared to the ¹H NMR spectrum of POSS-Cl and POSS-N₃ (Fig. 3), it can be seen that the peak of the methylene protons shifts from 3.54 ppm in the spectrum of POSS-Cl to 3.26 ppm in that of POSS-N₃.

3.2. ATRP using an alkyne-functional initiator

The alkyne-terminated polymers were prepared using an alkyne-functionalized ATRP initiator and a RAFT chain transfer agent,

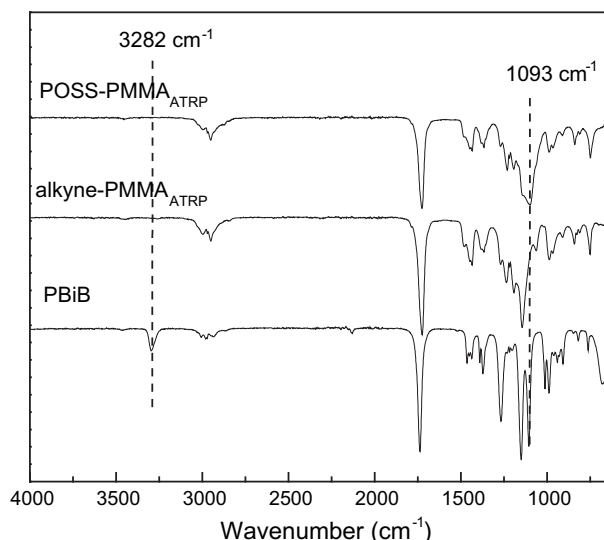


Fig. 4. FT-IR of PBiB ATRP initiator, alkyne-PMMA_{ATRP} and POSS-PMMA_{ATRP}.

respectively (Scheme 2). The alkyne-functionalized typical ATRP initiator propargyl 2-bromoisobutyrate (PBiB) was synthesized according to Tsvarevski et al. [38], and it was respectively applied to synthesize alkyne-terminated PMMA and PS via ATRP in presence of Cu(I)/PMDETA as catalyst (Figure S1, Supporting Information). In this case, we attempt to prepare alkyne-terminal PMMA with a lower molecular weight, so that the cycloaddition reaction can be easily detected. As we expected, alkyne-terminal PMMA with a short chain was obtained (see Table 1). Although the stretching peak of alkyne group is very weak in the FT-IR spectrum of alkyne-PMMA (Fig. 4), the ¹H NMR clearly showed the signals of alkyne protons at 4.68 and 2.50 ppm (Fig. 5a).

The click cycloaddition of azide/alkyne was performed at 50°C for 24 h using CuBr/PMDETA as catalyst and dioxane as solvent. To complete the coupling reaction, the initial molar ratio of POSS-N₃ to alkyne-PMMA was 2:1. The unreactive POSS-N₃ is removed by precipitating the resulting product into *n*-hexane, since POSS-N₃ is well soluble in *n*-hexane. The click reaction was confirmed by ¹H NMR and FT-IR. Since the molecular weight of the PMMA block is very low, the proton signals of the POSS-containing PMMA (POSS-PMMA_{ATRP}) are clearly displayed in Fig. 5b. Except for the overlapping region of the proton signals about from 0.68 to 2.2 ppm, the other signal peaks are easily to be identified. The signals at $\delta = 3.61$ ppm (k) and 0.62 ppm (c) are respectively assigned to the methyl

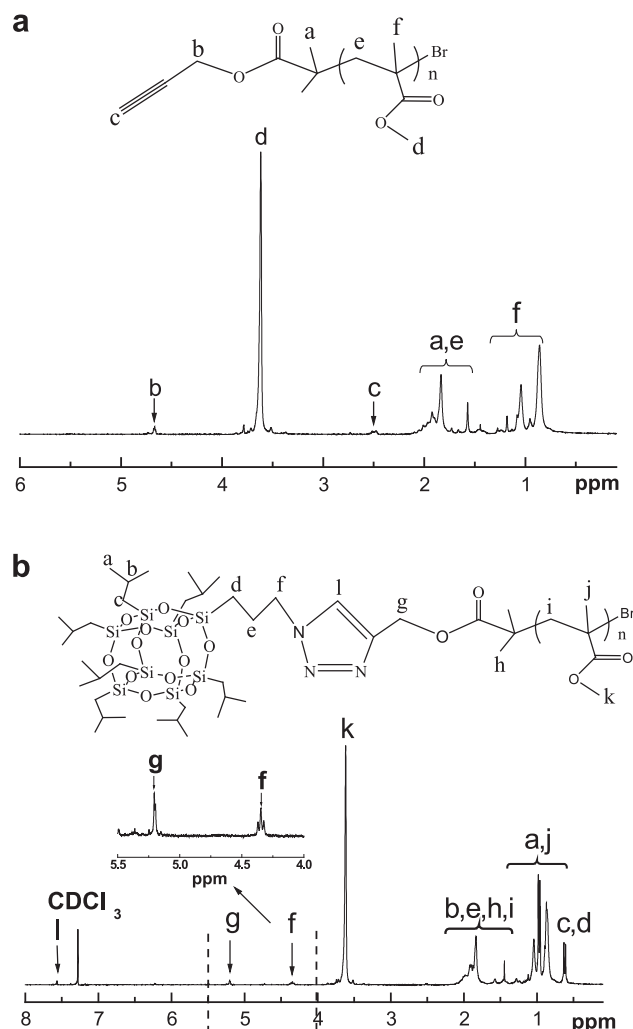


Fig. 5. ¹H NMR of alkyne-PMMA_{ATRP} (a) and POSS-PMMA_{ATRP} (b).

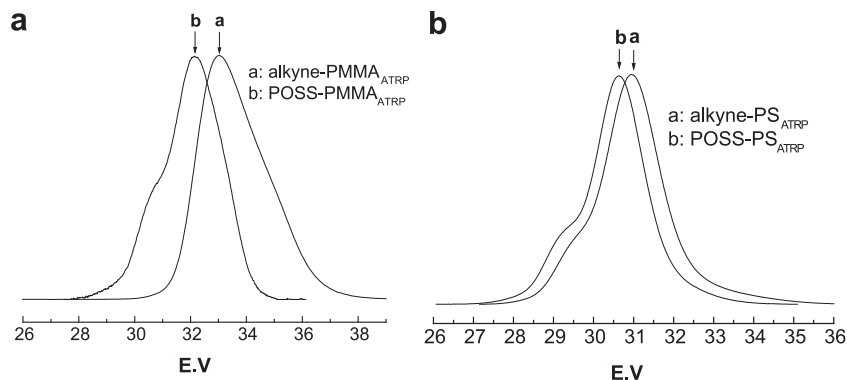


Fig. 6. Evolution of GPC chromatograms for alkyne-PMMA_{ATRP} and POSS-PMMA_{ATRP} (a); alkyne-PS_{ATRP} and POSS-PS_{ATRP} (b).

protons ($-\text{COOCH}_3$) and methylene protons ($-\text{SiCH}_2\text{CH}(\text{CH}_3)_2$, $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$). The integral ratio of these two peaks is well equal to the theoretical value, which confirms the click reaction is complete. Moreover, the signals at $\delta = 5.20$ ppm (g) and 4.35 ppm (f) of methylene protons adjacent to the triazole ring can be clearly discerned in the enlarged inset. FT-IR also confirmed that POSS-PMMA_{ATRP} was successfully prepared. Compared to the FT-IR spectrum of alkyne-PMMA_{ATRP}, a new band appears at 1093 cm^{-1} in the spectrum of POSS-PMMA_{ATRP}, which is assigned to the stretching vibration of Si–O–Si (Fig. 4).

The preparation procedure of “tadpole-shaped” POSS-containing hybrid polystyrene using ATRP (POSS-PS_{ATRP}) is similar to that of the above POSS-PMMA_{ATRP}. The alkyne-functionalized polystyrene (alkyne-PS_{ATRP}) was prepared using propargyl 2-bromoisobutyrate (PBiB) as initiator and PMDETA/CuBr/CuBr₂ as catalyst. The synthetic steps were characterized by FT-IR and ^1H NMR, which are respectively shown in Figures S2 and S3 (Supporting Information). In the FT-IR spectrum of POSS-PS_{ATRP}, it is also seen that a new peak appears at 1110 cm^{-1} , which corresponds to the stretching vibration of Si–O–Si. In the ^1H NMR spectrum of POSS-PS_{ATRP}, the signals of the characteristic protons derived from POSS are shown at $\delta = 0.98$ ppm and 0.62 ppm.

The GPC traces of the alkyne- and POSS-functional polymers are shown in Fig. 6. In both cases the eluograms of the POSS-functional polymers shift to a lower elution volume, which indicates an increased molecular weight. However, in contrast to the GPC curve of alkyne-PMMA_{ATRP}, the curve of POSS-PMMA_{ATRP} is not perfectly symmetrical, showing a small shoulder towards lower elution volumes. In the case of PS, the same shoulder appears in both traces. This shoulder is assumed to stem from the radical–radical coupling of polymer chains during polymerization. However, we cannot exclude that the alkyne group undergoes a coupling reaction with a radical chain end. A similar shoulder was observed by Tsarevsky et al. and Laurent and Grayson [38,41], when using an alkyne-functional ATRP initiator.

In the case of PMMA one might argue that the shoulder in the POSS-functional polymers is due to a side reaction in the click reaction. In fact, adding CuBr/PMDETA as the catalyst for the alkyne-azide cycloaddition will also form radicals at the chlorine-terminated chain end. These chain ends might undergo coupling. For that reason we removed the chlorine by using dodecylthiol as a chain transfer agent (for details, see Supporting Information). This did not lead to any improvement (Figure S4). Thus, coupling of the chlorine-terminal chain ends during the click reaction is not the reason for the shoulder. We prepared the silyl-protected ATRP initiator, 3-(trimethylsilyl)propargyl 2-bromoisobutyrate (TMS-PBiB), according to Grayson’s work [42] (see ^1H NMR in Figure S5). Again, this did not lead to an improvement (Figure S6).

Table 1 shows that the molecular weight of the POSS-functional polymer measured by GPC is always higher than the theoretical value. We believe that the POSS-functional polymers have a different hydrodynamic volume as compared to their corresponding precursors. A similar observation was made in our previous work and Mather’s work [4,27].

3.3. RAFT polymerization using an alkyne-functional chain transfer agent

Alkyne-terminal polymers were also prepared using an alkyne-functionalized RAFT agent (Scheme 2). We chose S-1-dodecyl-S’-(α , α' -dimethyl- α' -acetic acid) trithiocarbonate (DDAT), as the precursor for this RAFT agent (alkyne-DDAT), since DDAT has a high chain transfer efficiency and has been used in many RAFT polymerization systems [43,44]. In addition, it contains a carboxylic group, which can be easily functionalized into other novel RAFT agents [45]. Alkyne-DDAT was synthesized from DDAT and propargyl alcohol [40]. ^1H NMR and FT-IR verified that alkyne-DDAT with high purity was successfully synthesized (Figures S7 and S8). The signals at $\delta = 4.69$ ppm (b) and 2.45 ppm (c) are respectively ascribed to the resonance of the alkyne group protons. The stretching vibration peak at 3306 cm^{-1} of the alkyne group clearly shows in the FT-IR spectrum.

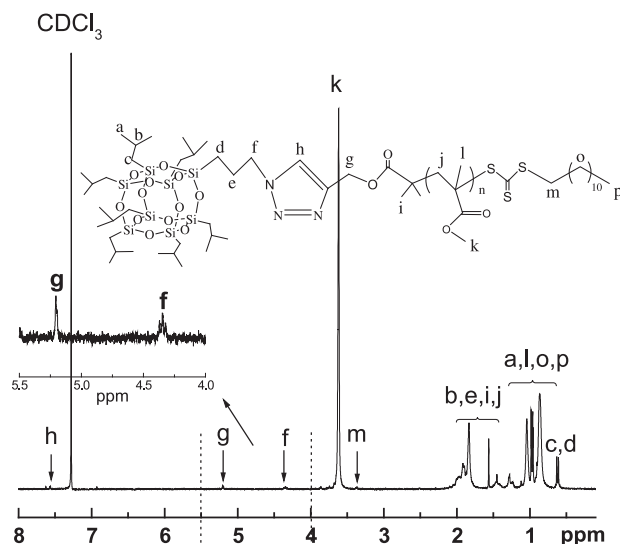


Fig. 7. ^1H NMR of POSS-PMMA_{RAFT}.

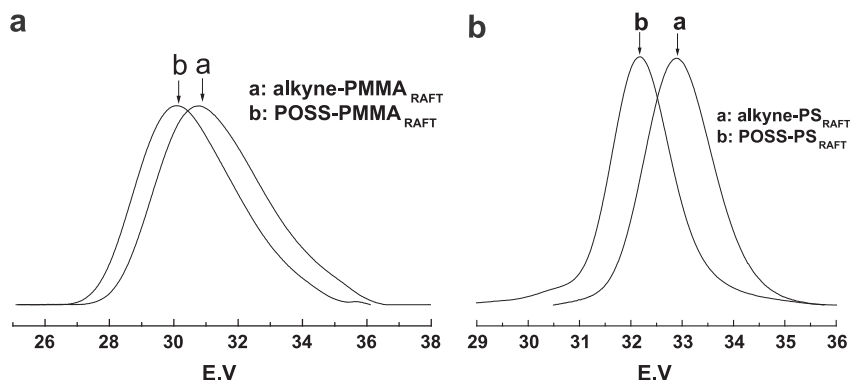


Fig. 8. Evolution of GPC chromatograms for alkyne-PMMA_{RAFT} and POSS-PMMA_{RAFT} (a); alkyne-PS_{RAFT} and POSS-PS_{RAFT} (b).

The RAFT polymerizations of MMA and styrene were carried out in toluene at 70°C. The procedure of the click reaction is similar as shown above for the polymers made by ATRP. The reaction was also performed in dioxane, and the feed ratio of POSS-N₃ to alkyne-PMMA_{RAFT} or alkyne-PS_{RAFT} was 2/1. After the reaction, the reaction solution filtered through an alumina column, and was then precipitated in excess *n*-hexane. Then precipitated solution was kept at 4°C overnight, and was centrifuged to afford the resulting product. The click reaction was also verified by FT-IR and ¹H NMR. The peak of the Si–O–Si stretching vibration respectively appears at 1140 cm^{−1} and 1107 cm^{−1} in the FT-IR spectra of POSS-PMMA_{RAFT} and POSS-PS_{RAFT} (Figures S8 and S9). The click coupling was also confirmed by ¹H NMR (Fig. 7 and Figure S10). Fig. 7 shows the signals of the methylene protons originating from POSS ((−Si−CH₂CH(CH₃)₂), −Si−CH₂CH₂CH₂−) at 0.62 ppm (c, d). The signals of the methylene protons adjacent to the triazole ring still can be identified in the enlarged graph.

The GPC traces of POSS-PMMA_{RAFT} and POSS-PS_{RAFT} are shown in Fig. 8. We again find that the curves of the POSS-functional polymers are shifted to lower elution volume relative to the alkyne-functional ones. No shoulders are observed in these spectra, indicating the absence of coupling reactions of polymer chains both during polymerization and click reaction.

4. Conclusions

Tadpole-shaped (“monochelic”) POSS-PMMA and POSS-PS were successfully synthesized by the combination of “click chemistry” with ATRP and RAFT polymerization, respectively. In principle, both ATRP and RAFT polymerization can be applied in this system. However, GPC results show that RAFT polymerization is better suited than ATRP in the presence of alkyne functions. In summary, “click chemistry” using azide-functional POSS and an alkyne-functional RAFT agent is an effective method to synthesize POSS-containing hybrid polymers.

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Appendix. Supplementary information

Supplementary information associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2010.03.028.

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