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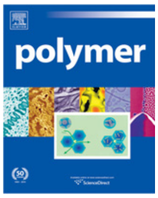

Synthesis of tadpole-shaped POSS-containing hybrid polymers via “click chemistry”

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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.

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 $[RSiO_{1.5}]_n$, 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 regents 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.

^{1}H NMR ($CDCl_3$, ppm): 3.54 (t, $2H$, $-Si-CH_2CH_2CH_2Cl$), 1.88 (m, $9H$, $-Si-CH_2CH(CH_3)_2$, $-Si-CH_2CH_2CH_2Cl$), 0.98 (d, $42H$, $-Si-CH_2CH(CH_3)_2$), 0.76 (m, $2H$, $-Si-CH_2CH_2CH_2Cl$), 0.63 (q, $14H$, $-Si-CH_2CH(CH_3)_2$). ^{13}C NMR, δ (TMS, ppm): 47.65, 26.07, 24.25, 22.87, and 10.16. Elemental analysis calcd for $C_{31}H_{69}ClO_{12}Si_8$ (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-N_3)

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 $MgSO_4$, and filtered. The solution was concentrated to obtain 2.8 g of POSS-N_3, 92% yield. ^{1}H NMR ($CDCl_3$, ppm): 3.26 (t, $2H$, $-Si-CH_2CH_2CH_2Cl$), 1.88 (m, $7H$, $-Si-CH_2CH(CH_3)_2$) 1.73 (t, $2H$, $-Si-CH_2CH_2CH_2Cl$), 0.98 (d, $42H$, $-Si-CH_2CH(CH_3)_2$), 0.71 (m, $2H$, $-Si-CH_2CH_2CH_2Cl$), 0.63 (q, $14H$, $-Si-CH_2CH(CH_3)_2$). ^{13}C NMR, δ (TMS, ppm): 54.02, 26.06, 24.26, 22.84, and 9.70. Elemental analysis calcd for $C_{31}H_{69}N_3O_{12}Si_8$ (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]. ^{1}H NMR ($CDCl_3$, ppm): 4.71 (m, $2H$, $CH{\equiv}CCH_2OOC(CH_3)_2Br$), 2.50 (t, $1H$, $CH{\equiv}CCH_2OOC(CH_3)_2Br$) and 1.89 (s, $6H$, $CH{\equiv}CCH_2OOC(CH_3)_2Br$).

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 ^{1}H NMR. At the end of the polymerization reaction, the reaction solution obviously became viscous. Final conversion determined by ^{1}H 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-N_3 (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-N_3 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/$CuBr_2$ 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]. ^{1}H NMR ($CDCl_3$, ppm): 0.90 (*t*, $3H$, $-(CH_2)_{11}CH_3$); 1.20–1.48 (m, $18H$, $-(CH_2)_9CH_3$); 1.64–1.83 (m, $8H$, $-SC(CH_3)_2COOH$ and $-CH_2(CH_2)_9CH_3$), and 3.30 (t, $2H$, $-CH_2(CH_2)_{10}CH_3$).

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]. ^{1}H NMR ($CDCl_3$, ppm): 0.87 (t, $3H$, $-(CH_2)_{11}CH_3$); 1.14–1.46