Living Radical Polymerization by Polyhedral Oligomeric Silsesquioxane-Holding Initiators: Precision Synthesis of Tadpole-Shaped Organic/Inorganic Hybrid Polymers

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ABSTRACT: Incompletely condensed polyhedral oligomeric silsesquioxane (POSS) with the highly reactive group of trisodium silanolate was used for the synthesis of two initiators for atom transfer radical polymerization, one with a 2-bromoisobutyl group and the other with a chlorosulfonyl group. These initiators were applied to solution polymerizations of styrene and methyl methacrylate in the presence of a copper complex. In both systems, polymerization proceeded in a living fashion, as indicated by the first-order kinetics of monomer consumption, the evolution of molecular weight in direct proportion to monomer conversion, the good agreement of molecular weight with the theoretical one, and the low polydispersity, thus providing tadpole-shaped polymers with an "inorganic head" of POSS and an "organic tail" of well-defined polymer. Thermogravimetric and differential scanning calorimetric studies showed that both thermal degradation and glass transition temperatures of the organic/inorganic hybrid polymers with molecular weights up to about 20 000 were enhanced as compared to those of model polymers without the POSS moiety.

Introduction

Polyhedral oligomeric silsesquioxanes (POSSs), cube-octameric molecules with Si−O−Si framework, have attracted much interest as a nanoscale building block for the construction of organic/inorganic hybrid materials.[1] Strategies have been made for the synthesis of hybrid materials by incorporating POSSs into polymers to improve their thermal and mechanical properties as a result of homogeneously dispersing inorganic substances into polymers at the nanometer level.[2,3] Vinyl monomers with a pendant group of POSSs were copolymerized with a variety of monomers.[4] POSSs functionalized with reactive groups such as epoxy, amine, isocyanate, and vinyl ones were used as a cross-linker to produce cross-linked hybrid polymers.[5,6] Poly(ethylene oxide) (PEG)-functionalized POSS was synthesized by the reaction of octahydrido-POSS with allyl-PEG in the presence of a Pt catalyst.[7] Hybrid polyoxazolines were synthesized by ring-opening polymerization of 2-methyl-2-oxazoline with an initiator-functionalized POSS.[8] Atom transfer radical polymerization (ATRP)[9,10] was also applied to the synthesis of POSS-based hybrid polymers.[11,12] Matyjaszewski et al. showed that a commercially available benzyl chloride-holding POSS served as an initiator for ATRP of styrene (S), yielding polystyrenes (PSs) having a POSS moiety at the end of polymer chain.[12] Laine et al. reported that a star polymer having a POSS core was synthesized by ATRP of methyl methacrylate (MMA) initiated by an octafunctional POSS initiator.[13]

Incompletely condensed POSS, which has a trisilanol moiety at one corner of the cubelike framework, is a fascinating compound because it undergoes corner-capping reaction with chlorosilanes, transition metal complexes, and metal alkyl complexes so as to produce a wide variety of functional POSSs.[14,15] Very recently, we developed an efficient method for the synthesis of incompletely condensed POSS with the highly reactive group of trisodium silanolate, heptaphenyltricycloheptasiloxane trisodium silanolate (7Ph-T_7-$(ONa)_3$, Scheme 1). The reaction of 7Ph-T_7-$(ONa)_3$ with varied types of trichlorosilanes proceeded much faster and more selectively than the conventional one using the trisilanol group, thus giving the desired products in a high yield.[16]

The goal of this study is to demonstrate that 7Ph-T_7-$(ONa)_3$ can be used to produce a more efficient and versatile initiator for copper-mediated ATRP for the synthesis of well-defined, tadpole-shaped polymeric hybrids with a POSS at the end of polymer chain. This will be illustrated by the synthesis of two types of initiators that will eventually yield POSS-carrying low-polydispersity polymers with a wide range of molecular weights. The thermal properties of the resultant hybrids will also be demonstrated in terms of glass transition and thermal degradation temperatures.

Experimental Section

Materials. Ethyl 2-bromoisobutylate (98%, 2-(EiB)Br) was used as received from Nacalai Tesque Inc., Osaka, Japan. L-Sparteine (99%, Sp) was purchased from Aldrich and used without further purification. Methyl methacrylate (99%, MMA) and styrene (99%, S) were obtained from Nacalai Tesque Inc. and purified by distillation under reduced pressure over calcium hydride. 2-(4-Chlorosulfonylphenyl)ethyltrichlorosilane (50% in dichloromethane, CTS) was obtained from Gelest Inc. 7Ph-T_7-$(ONa)_3$ was prepared as described in the patent.[16] All other reagents were purchased from commercial sources and used as received.

Measurements. Gel permeation chromatographic (GPC) analysis was carried out at 40 °C on a high-speed liquid

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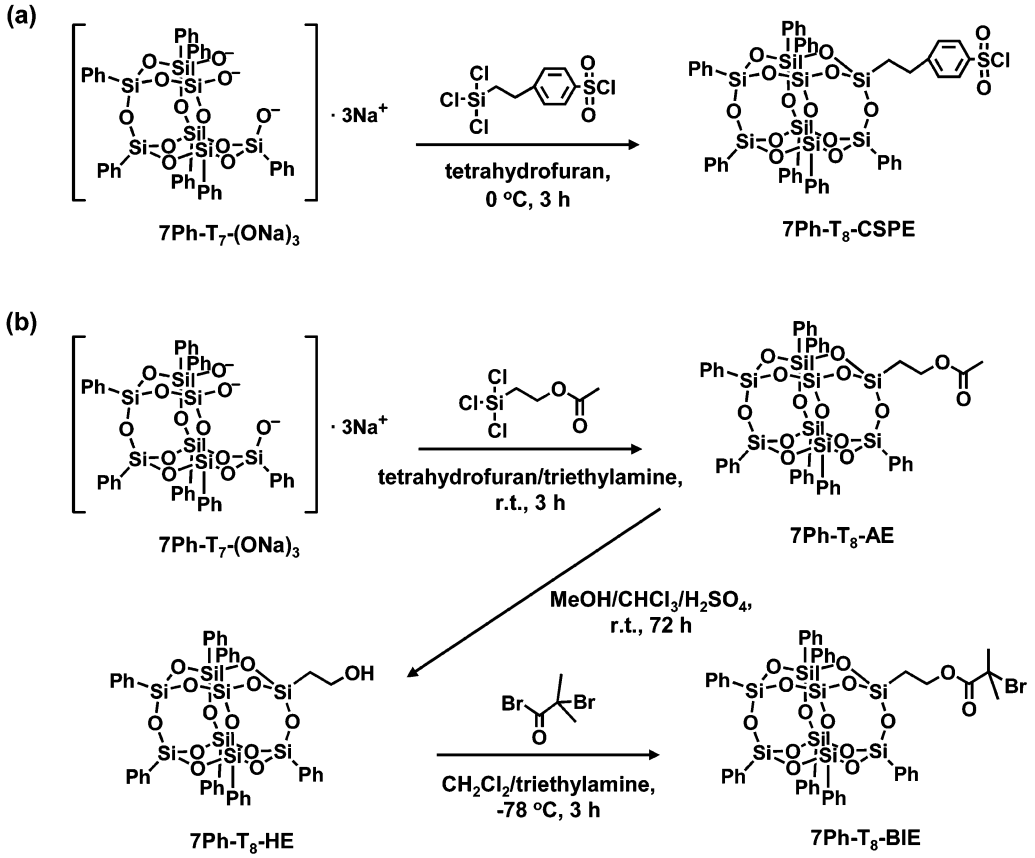
Scheme 1. Synthesis of (a) 7Ph-T_8-CSPE and (b) 7Ph-T_8-BIE



chromatography system (Shodex GPC-101) equipped with a guard column (Shodex GPC KF-G), two 30 cm mixed columns (Shodex GPC KF-804L, exclusion limit = 400 000), and a differential refractometer (Shodex RI-101). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.8 mL/min. Poly(methyl methacrylate) (PMMA) and polystyrene (PS) standards were used to calibrate the GPC system. Nuclear magnetic resonance (^{1}H, ^{13}C, and ^{29}Si NMR) spectra were obtained on a JEOL/AL400 400 MHz spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 thermogravimetric analyzer. Measurements were carried out under a continuous flow of He gas from 50 to 800 °C at the heating rate 20 °C/min. The degradation temperature T_{deg} was defined as the point of the maximum mass decrement rate. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 under a N_2 atmosphere. The instrument was calibrated with known standards: indium (T_m = 156.6 °C) and zinc (T_m = 419.5 °C). The sample was heated from 50 to 180 °C at the rate 200 °C/min and kept at 180 °C for 5 min and then cooled to 10 °C at the rate −200 °C/min. After the sample was kept at 10 °C for 3 min, measurement was carried out with the scan rate of 10 °C/min within the temperature range 10−150 °C. The glass transition temperature T_g was obtained at the midpoint of the specific heat increment.

Synthesis of 2-(4-Chlorosulfonylphenyl)ethylheptaphenyl-T_8-silsesquioxane (7Ph-T_8-CSPE, Scheme 1). 50 wt % of CTS in dichloromethane (10.17 g, 15 mmol of CTS) was quickly added to a cold solution of 7Ph-T_7-$(ONa)_3$ (10 g, 10 mmol) in dry THF (200 mL) at 0 °C. The mixture was magnetically stirred for 1 h at 0 °C. The resultant precipitate was removed by filtration, and the filtrate was concentrated by a rotary evaporator to obtain a slightly yellow oil. The residue was diluted with ethyl acetate (100 mL), and the mixture was again concentrated by a rotary evaporator until a slightly cloudy solution was obtained. The system was cooled in a refrigerator to obtain a white solid, which was recrystallized from ethyl acetate (4.88 g, 42%). IR (KBr, cm^{-1}): 1430 and 1135−1090 (Si−Ph), 1380 and 1190 (−SO_2Cl), and 1090−1020 (Si−O−Si). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.23 (t, 2H, Si−CH_2−), 2.91 (t, 2H, −CH_2−C_6H_4), 7.30−7.79 (m, 39 H, Si−C_6H_5 and −C_6H_4−SO_2Cl). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.0 (Si−CH$_2$−), 29.0 (−CH$_2$−C_6H_4), 128.1, 130.2, 131.1, and 134.3 (Si−C_6H_5), 127.2, 129.3, 142.0, 152.3 (−C_6H$_4$−SO_2Cl). ^{29}Si NMR ($CDCl_3$, 79 MHz): δ −66.69 (−CH_2−SiO$_{1.5}$), −78.35, −78.41, and −78.67 (C_6H_5−SiO$_{1.5}$). Anal. Calcd for $C_{50}H_{43}O_{14}SClSi_8$: C, 51.77; H, 3.74. Found: C, 52.08; H, 3.74.

Synthesis of 2-Bromoisobutyryloxyethylheptaphenyl-T_8-silsesquioxane (7Ph-T_8-BIE, Scheme 1). 7Ph-T_8-BIE was synthesized via the three step reactions described below. First, 7Ph-T_7-$(ONa)_3$ (10 g, 10 mmol), triethylamine (1.5 g, 14.8 mmol), and dry THF (200 mL) were charged into a round-bottom flask, to which acetoxyethyltrichlorosilane (3.3 g, 14.8 mmol) was quickly added at room temperature. The mixture was magnetically stirred for 2 h at room temperature and then poured into *n*-hexane (1 L) to obtain a crude product. The resultant solid was redissolved in toluene (100 mL) and washed three times with water (3 × 330 mL). The organic layer was collected and dried over anhydrous $MgSO_4$. After filtration, ethanol (100 mL) was added into the filtrate to yield acetoxyethylheptaphenyl-T_8-silsesquioxane (7Ph-T_8-AE) as a white solid (6.88 g, 66%). IR (KBr, cm^{-1}): 1740 (C=O), 1430 and 1135−1090 (Si−Ph), 1240 (C−O), 1090−1000 (Si−O−Si). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33−1.37 (t, 2H, Si−CH_2−), 1.84 (s, 3H, CH_3−C=O), 4.28−4.32 (t, 2H, −O−CH_2−), 7.31−7.46 and 7.72−7.82 (m, 35 H, Si−C_6H_5). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.2 (Si−CH$_2$−), 20.8 (CH$_3$−C=O), 60.6 (−O−CH$_2$−), 128.1, 130.2, 131.0−130.1, and 134.3−130.4 (Si−C_6H_5), 171.2 (C=O). ^{29}Si NMR ($CDCl_3$, 79 MHz): δ −67.97 (−CH_2−SiO$_{1.5}$), −78.36 and −78.67 (C_6H_5−SiO$_{1.5}$).

Second step: 7Ph-T_8-AE (2.58 g, 2.47 mmol), methanol (175 mL), and chloroform (175 mL) were charged in a round-bottomed flask, to which concentrated H_2SO_4 (0.7 mL) was added at room temperature. The mixture was magnetically stirred for 72 h at room temperature and concentrated by a rotary evaporator. The oily residue was redissolved in ethyl acetate (500 mL) and washed twice with water (2 × 500 mL). Drying over anhydrous $MgSO_4$, filtration, and evaporation of

the solvent produced a white solid, which was recrystallized from toluene to obtain hydroxyethylheptaphenyl-T_8-silsesquioxane (7Ph-T_8-HE) (2.3 g, 91%). IR (KBr, cm^{-1}): 3600−3200 (OH), 1420 and 1135−1090 (Si−Ph), 1090−1000 (Si−O−Si). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.26−1.31 (t, 2H, Si−CH_2−), 1.42−1.62 (br, 1H, −OH), 3.85−3.87 (t, 2H, −O−CH_2−), 7.31−7.46 and 7.72−7.82 (m, 35 H, Si−C_6H_5). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.5 (Si−*C*H_2−), 58.6 (−O−*C*H_2−), 127.9−128.1, 130.3, 131.0−130.1, and 134.1−134.5 (Si−*C*$_6H_5$). ^{29}Si NMR ($CDCl_3$, 79 MHz): δ −67.31 (−CH_2−*Si*$O_{1.5}$), −78.42 and −78.79 (C_6H_5−*Si*$O_{1.5}$).

Third step: 2-Bromoisobutyryl bromide (0.3 g, 1.3 mmol) was added to a cold solution of 7Ph-T_8-HE (1.21 g, 1.2 mmol) in dry dichloromethane (5 mL) with triethylamine (0.12 g, 1.19 mmol) at −78 °C. The mixture was magnetically stirred for 1 h at −78 °C and then another 2 h at room temperature. After filtration, the filtrate was diluted with dichloromethane (100 mL) and washed with water (300 mL), twice with 1 wt % of aqueous $NaHCO_3$ solution (2 × 300 mL), and again twice with water (2 × 300 mL). After drying over $MgSO_4$ and filtration, the filtrate was concentrated by a rotary evaporator. Methanol (400 mL) was added into the resultant residue, and the mixture was kept in a freezer to yield the final product 7Ph-T_8-BIE as a white solid (1.13 g, 81.4%). IR (KBr, cm^{-1}): 1740 (C=O), 1430 and 1135−1090 (Si−Ph), 1270 (C−O), 1090−1000 (Si−O−Si). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.39−1.43 (t, 2H, Si−CH_2−), 1.79 (s, 6H, −BrC(CH_3)$_2$), 4.37−4.41 (t, 2H, −O−CH_2−), 7.31−7.46 and 7.72−7.82 (m, 35 H, Si−C_6H_5). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.9 (Si−*C*H_2−), 30.6 (−BrC(*C*H_3)$_2$), 55.8 (−Br*C*$(CH_3)_2$), 62.5 (−O−*C*H_2−), 128.0−128.1, 130.1−130.2, 131.1, and 134.3 (Si−*C*$_6H_5$), 171.7 (*C*=O). ^{29}Si NMR ($CDCl_3$, 79 MHz): δ −68.27 (−CH_2−*Si*$O_{1.5}$), −78.4 and −78.7 (C_6H_5−*Si*$O_{1.5}$). Anal. Calcd for $C_{48}H_{45}O_{14}BrSi_8$: C, 50.11; H, 3.94. Found: C, 50.11; H, 4.01.

ATRP of MMA by 7Ph-T_8-CSPE. A Y-shaped glass tube with two compartments was charged in one side with a predetermined amount of Cu(I)Br, Sp, and anisole and in the other side with a mixture of MMA, the rest of anisole, and 7Ph-T_8-CSPE. The glass tube was attached to a vacuum line and subjected to three freeze−pump−thaw cycles. The reactants were mixed by pouring the solutions into each compartment and then collected in one side. The mixture was degassed again by one freeze−pump−thaw cycle and subsequently sealed off under vacuum. The polymerization was carried out in a shaking oil bath (TAITEC Corp., Saitama, Japan, Personal H-10) thermostated at 70 °C and, after a prescribed time t, quenched to room temperature. An aliquot of the solution was taken out for NMR measurement to estimate monomer conversion and for GPC measurement to determine molar mass and molecular weight distribution. The rest of the reaction mixture was diluted by THF and precipitated in an excess of *n*-hexane to obtain a polymer POSS−PMMA as a white powder.

In a typical run, the solution polymerization of MMA with the starting materials of MMA (2.88 g, 28.7 mmol), 7Ph-T_8-CSPE (67 mg, 0.057 mmol), Cu(I)Br (16 mg, 0.115 mmol), Sp (54 mg, 0.23 mmol), and anisole (2.74 g) carried out at 70 °C for 18 h gave a monomer conversion of 46% and a POSS−PMMA product with M_n = 27 800 and M_w/M_n = 1.17.

ATRP of S by 7Ph-T_8-BIE. A Pyrex glass tube was charged with a predetermined amount of Cu(I)Br, to which was quickly added a mixture of S and diphenyl ether containing a prescribed concentration of 7Ph-T_8-BIE and Sp. The system was immediately degassed by three freeze−pump−thaw cycles and subsequently sealed off under vacuum. The polymerization was carried out in a shaking oil bath thermostated at 110 °C and, after a prescribed time t, quenched to room temperature. The characterization of the resultant polymer was carried out in a similar way as the ATRP of MMA. Methanol was used as a nonsolvent for the purification of the polymer POSS−PS.

In a typical run, the solution polymerization of S with the starting materials of S (4.53 g, 43.5 mmol), 7Ph-T_8-BIE (100 mg, 0.869 mmol), Cu(I)Br (12 mg, 0.869 mmol), Sp (41 mg, 1.74 mmol), and diphenyl ether (4.37 g) carried out at 110 °C for 9 h gave a monomer conversion of 46% and a POSS−PS product with M_n = 25 600 and M_w/M_n = 1.28.

Results and Discussion

Synthesis of POSS−Holding Initiators. Matyjaszewski et al. showed that a commercially available benzyl chloride (BzCl)-functionalized POSS, which contains seven cyclopentyl groups for providing increased solubility in organic solvents and one BzCl moiety for initiation site for ATRP, was useful for the synthesis of well-defined PS with one bulky POSS moiety at the end of polymer chain.[12] BzCl, however, is not a particularly good ATRP initiator, for the dissociation rate constant of the C−Cl bond of benzyl chloride is smaller than those of the carbon−halogen bonds of most other common initiators when compared in the same conditions.[17] A fast initiation is an important requisite for obtaining low-polydispersity polymers. To introduce a better initiation site into one corner of POSS, we exploited the chemistry that involves the corner-capping reaction of 7Ph-T_7-$(ONa)_3$ by trichlorosilanes.

We first tried to introduce a chlorosulfonylphenyl moiety, a precursor of which 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane (CTS) is easily available from a commercial source. The chlorosulfonylphenyl moiety provides a good initiation site for ATRP, in particular, of methacrylates.[18] The corner-capping reaction of 7Ph-T_7-$(ONa)_3$ with CTS was carried out in THF at 0 °C. The crude product before purification was analyzed by liquid chromatography and thin-layer chromatography, which apparently showed the presence of byproducts, presumably tosylates arising from the reaction of sulfonyl chloride group of CTS with sodium silanolates. The byproducts and unreacted starting materials were easily removed by repeated recrystallization to give 7Ph-T_8-CSPE in about 40% yield. Its high purity was confirmed by ^1H, ^{13}C, and ^{29}Si NMR and elemental analysis.

The 2-bromoisobutyryl group is among the most common initiation sites for ATRP. It has wide applicability to ATRP of various monomers including styrenes and (meth)acrylates and is easily introduced to many types of materials with a hydroxyl group by reaction with commercially available 2-bromoisobutyryl bromide.[10] Therefore, we next tried to introduce the 2-bromoisobutyryl group into one corner of POSS. First, we synthesized acetoxyethyl group-carrying POSS, 7Ph-T_8-AE, by the corner-capping reaction of 7Ph-$T_7(ONa)_3$ with acetoxyethyltrichlorosilane. 7Ph-T_8-AE was then treated with acid to deprotect the acetoxy group to obtain hydroxyl group-carrying POSS (7Ph-T_8-HE). A *dilute* acidic condition must be used for the deprotection to prevent the decomposition of the Si−O−Si framework of POSS. Finally, the acylation of 7Ph-T_8-HE with 2-bromoisobutyryl bromide and the subsequent purification by repeated recrystallization gave the desired product 7Ph-T_8-BIE in a moderate overall yield of 50%.

ATRP by POSS-Holding Initiators. 7Ph-T_8-CSPE was employed for polymerization of MMA mediated by a copper complex in anisole at 70 °C. Figure 1a shows the first-order plot of monomer concentration for the polymerization. The plot can be approximated by a straight line passing through the origin, thus giving first-order kinetics with respect to monomer conversion. This means that the concentration of propagating species is constant throughout the course of polymerization. Figure 1b shows the number-average molecular weight

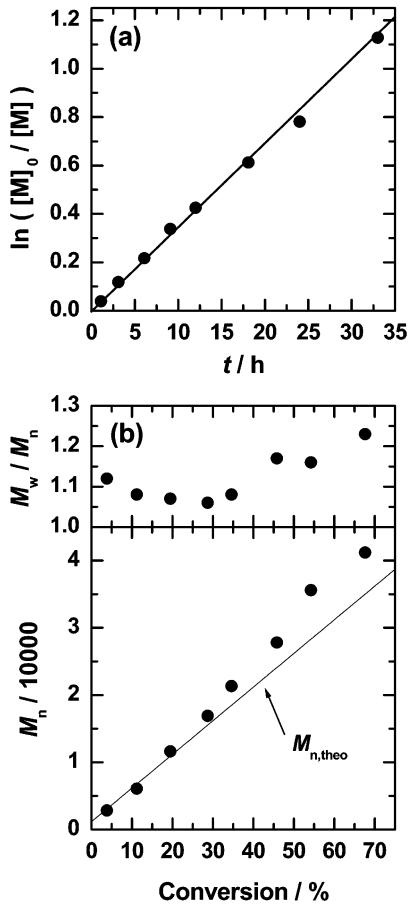


Figure 1. (a) Plot of $\ln([M]_0/[M])$ vs t for the polymerization of methyl methacrylate (MMA) and (b) evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of POSS−PMMAs as a function of monomer conversion. Solution polymerization of MMA (50 wt %) in anisole at 70 °C with 7Ph-T_8-CSPE: $[MMA]_0/[7Ph\text{-}T_8\text{-}CSPE]_0/[Cu(I)Br]_0/[Sp]_0$ = 500/1/2/4. The full line in (b) represents the theoretical prediction.

M_n and the polydispersity index M_w/M_n of the produced polymer, both estimated by PMMA-calibrated GPC, as a function of monomer conversion. The M_n increases linearly with conversion, remaining close to the theoretical value $M_{n,theo}$ calculated as the molar ratio of polymerized monomer to the initiator. To check the validity of the GPC analysis, ^{1}H NMR measurement of one sample with M_n (GPC) = 3500 was carried out. The estimated M_n value was 3450, in good agreement with the GPC value. These results indicate that the initiation efficiency of 7Ph-T_8-CSPE is approximately 100%. The M_w/M_n ratio gradually decreases with increasing monomer conversion, approaching less than 1.1 at about 50% of monomer conversion, and after this conversion, it gradually increases with monomer conversions but still stays lower than 1.3. This system could be successfully applied to the synthesis of PMMA with a higher molecular weight by simply changing the molar ratio of starting materials. For instance, the bulk polymerization of MMA with the initial molar ratio of $[MMA]_0/[7Ph\text{-}T_8\text{-}CSPE]_0/[CuBr/2Sp]_0$ = 1000/1/4 carried out at 70 °C for 12 h gave a POSS−PMMA product of M_n = 108 000 and M_w/M_n = 1.2. These results show that the chlorosulfonylphenyl moiety attached to the bulky POSS works as an efficient initiation site for ATRP like the low molar mass initiator, *p*-toluenesulfonyl chloride, for example.

7Ph-T_8-BIE was used for solution polymerization of styrene with a copper complex in diphenyl ether at 110 °C. As Figure 2a,b shows, the polymerization proceeded in a living manner, as indicated by the first-order kinetics of monomer consumption, the evolution of M_n in direct proportion to monomer conversion, the good consistency of M_n with the theoretical value, and the low polydispersity. Thus, no influence of the bulky POSS on the initiation efficiency of 7Ph-T_8-BIE was observed, as in the case of 7Ph-T_8-CSPE. The versatility of 7Ph-T_8-BIE was also confirmed by the successful control of ATRP of MMA. For instance, the solution polymerization of MMA (50 wt %) with the initial molar ratio of $[MMA]_0/[7Ph\text{-}T_8\text{-}BIE]_0/[CuBr/2Sp]_0$ = 500/1/1 carried out in anisole at 70 °C for 3 h gave a monomer conversion of 44% and a POSS−PMMA product with M_n = 27 700 and M_w/M_n = 1.16.

Thermal Analysis of POSS-Carrying Polymers. Interesting thermal properties, such as improved thermal oxidative stability and increased glass transition temperature, have been reported for a variety of POSS-carrying polymers prepared by different techniques.[3,6,19] In the following we will describe some of our preliminary results for the thermal properties of POSS−PMMAs prepared in this work.

DSC analysis was carried out to estimate the glass transition temperature, T_g, of POSS−PMMAs with different molecular weights and a series of PMMA control samples synthesized by ATRP with *p*-toluenesulfonyl chloride as an initiator (Ts-PMMA). Figure 3 shows the T_gs of POSS−PMMA and Ts−PMMA as a function of M_n. For both samples, T_g increases with increasing M_n, leveling off at around 125 °C. This is a well-known behavior of PMMA.[20] Importantly, the T_g value of POSS−PMMA is higher than that of the corresponding Ts−PMMA, in particular, in the lower molar mass region. Assuming that T_g of the POSS segment is very large, the increased T_g of POSS−PMMA is reasonably explainable by the Gordon−Taylor theory[21] of the composition dependence of the T_g of random copolymers. This theory simply states that the T_g of a copolymer or a mixture forming one phase is given by a composition average of those of the components. Namely, the observed T_g enhancement may be attributed to the high T_g or the low mobility of the POSS segment.

Thermogravimetric analysis was carried out to estimate the thermal degradation temperature, T_{deg}, of POSS−PMMA and Ts−PMMA. Chen et al. previously showed that the vinylidene-terminated PMMAs produced by the conventional free radical polymerization with disproportionation termination thermally degrade at lower temperature than the saturated PMMAs prepared by the technique using the combination of lactams and thiols.[22] They explained this result in terms of the difference in initiation mechanism of degradation: namely, the degradation of the vinylidene-terminated PMMA is initiated by scissions at the weak bond of the unsaturated end of the polymer chain, while the degradation of the saturated PMMA is initiated mainly by the random scission on the polymer main chain.[22,23] PMMA prepared here by ATRP is expected to have a very small fraction of such an unsaturated chain end due to the living character of the polymerization process. In fact, the T_{deg}s of Ts−PMMAs are higher than that of the vinylidene-terminated PMMA and are as high as that of the saturated PMMA prepared by Chen et al. Figure 4 compares the T_{deg}s of

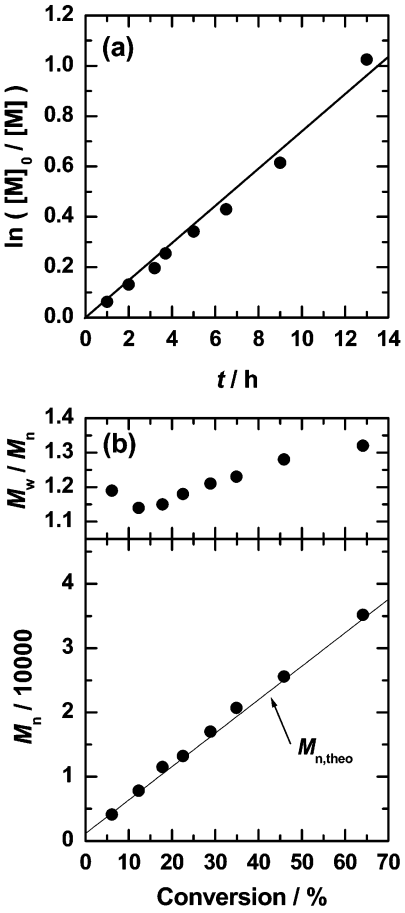


Figure 2. (a) Plot of $\ln([M]_0/[M])$ vs t for the polymerization of styrene (S) and (b) evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of POSS−PSs as a function of monomer conversion. Solution polymerization of S (50 wt %) in diphenyl ether at 110 °C with 7Ph-T_8-BIE: $[S]_0/[7Ph\text{-}T_8\text{-}BIE]_0/[Cu(I)Br]_0/[Sp]_0 = 500/1/1/2$. The full line in (b) represents the theoretical prediction.

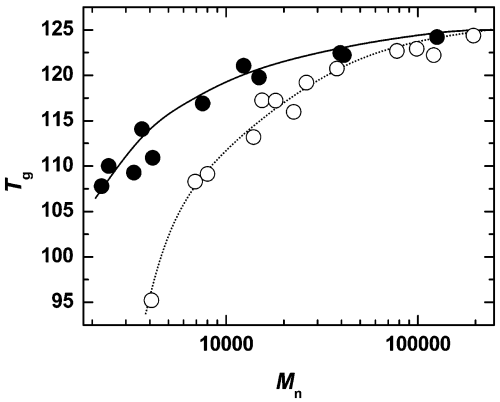


Figure 3. Glass transition temperatures T_gs of POSS−PMMA (●) and Ts−PMMA (○) as a function of number-average molecular weight (M_n). The data are the mean of the three individual experiments.

POSS−PMMAs and Ts−PMMAs as a function of M_n. In both cases, T_{deg} increases with decreasing M_n. This is a well-known behavior of PMMA with a saturated chain end. Namely, once a bond on the main chain undergoes thermal homolysis (random scission) to produce polymer radicals, degradation by the depropagation mechanism would proceed to the chain end(s). In this mechanism, a longer chain would be more easily degraded than a shorter chain, since the probability of bond scission should be independent of chain length.[24]

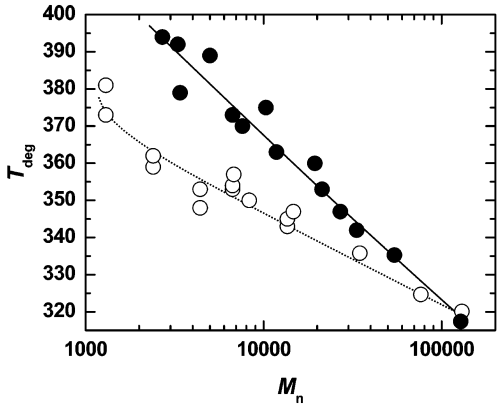


Figure 4. Thermal degradation temperatures T_{deg}s of POSS−PMMA (●) and Ts−PMMA (○) as a function of number-average molecular weight (M_n). The data are the mean of the two individual experiments.

More interestingly, in the studied range of M_n, the T_{deg} value of POSS−PMMA is higher than that of the corresponding Ts−PMMA by a maximum of 30 °C. Clearly, the POSS moiety has a marked effect on the thermal stability of PMMA. Even though we cannot provide a definite explanation for this phenomenon at present, we would consider that it has something to do with the low mobility of the POSS segment. If the polymer radical mediating degradation should chain transfer to other polymer to produce a new degradation point there, this process would be correlated with the mobility of the chains or the system as a whole. In this regard, POSS−PMMA and Ts−PMMA can be different, as suggested by the above-noted T_g experiments.

Although we do not present the data, the POSS−PS hybrids showed qualitatively similar thermal behavior to POSS−PMMA.

Conclusions

Two types of ATRP initiators, one with a 2-bromoisobutyl group and the other with a chlorosulfonyl group, were synthesized by the reaction of incompletely condensed POSS and trichlorosilanes. The solution polymerization of S or MMA using these initiators mediated by a copper complex proceeded in a living fashion, thus providing tadpole-shaped polymers with an "inorganic head" of POSS and an "organic tail" of well-defined polymer. TGA and DSC studies showed that both T_{deg} and T_g of the organic/inorganic hybrid polymers were more and more enhanced compared to those of the model polymers without a POSS moiety, as the polymer tail became shorter or the weight fraction of the POSS moiety became larger.

References and Notes

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