Notes

The Synthesis of Hybrid Polymers Using Atom Transfer Radical Polymerization: Homopolymers and Block Copolymers from Polyhedral Oligomeric Silsesquioxane Monomers

Jeffrey Pyun and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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Introduction

Recently, a novel class of hybrid polymers has been developed, based on polyhedral oligomeric silsesquioxanes (POSS). Interest in these hybrid polymers has arisen due to the enhanced thermal and potential reinforcing properties these materials possess.[1] The synthesis of linear polymers containing POSS has been reported using conventional radical techniques,[2,3] ring-opening metathesis,[4] and condensation polymerizations.[5,6] Applying POSS monomers to living and controlled polymerizations[3,7] is desirable, as novel materials of varying composition, topology, and well-defined molecular weights can be prepared. In particular, the synthesis of block copolymers and thermoplastic elastomers with POSS-based polymers as the hard segments may be of interest.

In this note, we report the atom transfer radical polymerization (ATRP) of methacrylate functional POSS monomers. Using this approach we have synthesized homopolymers and block copolymers containing POSS.

Results and Discussion

The synthesis of homopolymers from 3-(3,5,7,9,11,-13,15-heptacyclopentyl-pentacyclo[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]-octasiloxane-1-yl)propyl methacrylate (MA-POSS) was the first step taken in the preparation of well-defined hybrid polymers, using ATRP. In the ATRP of MA-POSS, 4-(methylphenyl) 2-bromoisobutyrate was used as the initiator, along with a copper(I) chloride/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) catalyst system at 50 °C.[8] Analysis by ^{1}H NMR revealed that monomer conversion reached 72% and polymers of p(MA-POSS) with $\mathrm{DP_n} = 14$ were synthesized. The molecular weight determined from ^{1}H NMR matched theoretically predicted degrees of polymerization ($\mathrm{DP_{n\ theoretical}} = 15$). Molecular weights determined from SEC were lower than theoretical predictions ($M_{\mathrm{n\ SEC}} = 9560$ vs $M_{\mathrm{n\ theoretical}} = 14\,440$), and low polydispersities ($M_\mathrm{w}/M_\mathrm{n} = 1.14$) were observed. The discrepancy between SEC molecular weights and theoretical values can be attributed to hydrodynamic differences between p(MA-POSS) with bulky POSS side groups and linear PS standards in a toluene mobile phase. SEC was done in toluene solutions due to the limited solubility of p(MA-POSS) in THF.

Hybrid triblock copolymers of MA-POSS and *n*-butyl acrylate were also synthesized. Previously, we reported the use of a difunctional macroinitiator of poly(*n*-butyl acrylate) (p(BA)) for chain extension with methyl methacrylate (MMA) to prepare p((MMA)-*b*-BA-*b*-(MMA)) triblock copolymers by ATRP.[9] Using this same approach, triblock copolymers of p((MA-POSS)-*b*-BA-*b*-(MA-POSS)) were prepared from a bromine terminated difunctional poly(*n*-butyl acrylate) macroinitiator and MA-POSS. Scheme 1 summarizes the synthesis of p((MA-POSS)-*b*-BA-*b*-(MA-POSS)).

The synthesis of p((MA-POSS)-*b*-BA-*b*-(MA-POSS)) was confirmed from ^{1}H NMR analysis. In the triblock copolymer synthesis, the macroinitiator was prepared by the ATRP of *n*-BA using dimethyl 2,6,-dibromoheptanedioate as the difunctional initiator. In the p(BA) macroinitiator, methyl protons from the difunctional initiator ($\delta = 3.6$ ppm, signal ***a***; Figure 1) were visible and enabled calculation of molar ratios of initiator fragments to p(BA) ($M_{\mathrm{n\ NMR}} = 14\,790$). Chain extension with MA-POSS from the p(BA) macroinitiator proceeded to high monomer conversion ($p > 0.95$), as evidenced by complete consumption of vinyl protons ($\delta = 6.10$, 5.50 ppm). Other resonances observed at $\delta = 0.60$, 1.00, 1.60, and 1.70 ppm were assigned to propyl and cyclopentyl protons (***1***) from p(MA-POSS) and overlapped with protons from the copolymer backbone and aliphatic protons from the *n*-butyl group. Additionally, resonances of methylene protons from p(MA-POSS) ($\delta = 3.95$ ppm, ***2***), methine protons from the p(BA) block ($\delta = 2.3$ ppm, ***3***) and methylene protons adjacent to the POSS cube ($\delta = 0.6$ ppm, ***6***) were clearly present.

Estimation of the relative compositions of p(MA-POSS) to p(BA) was conducted by integration of methylene protons from (MA-POSS) (***2***) and p(BA) ($\delta = 4.10$ ppm, ***4***). Because of the poor resolution between the two kinds of methylene protons, direct integration of the individual resonances could not be done to determine the relative composition. Thus, integration of methyl protons (***a***) from the initiator fragment of p(BA) was utilized to correct the integration of methylene protons ***2*** and ***4***. Since the ratio of protons ***a*** and ***4*** was previously ascertained in the ^{1}H NMR characterization of the p(BA) macroinitiator, the incorporated amount of p(MA-POSS) was quantified.

From the integration of p(BA) to p(MA-POSS), the mole percent of each component was calculated (85% p(BA) and 15% p(MA-POSS)), as well as the molecular weight of the triblock copolymer. The molecular weight of the p((MA-POSS)-*b*-BA-*b*-(MA-POSS)) triblock copolymer was estimated by factoring in the weight percentages of each block and dividing the molecular weight of the p(BA) macroinitiator by the p(BA) weight percentage. The molecular weight of the triblock copolymer was slightly lower than predicted ($M_{\mathrm{n\ NMR}} =$

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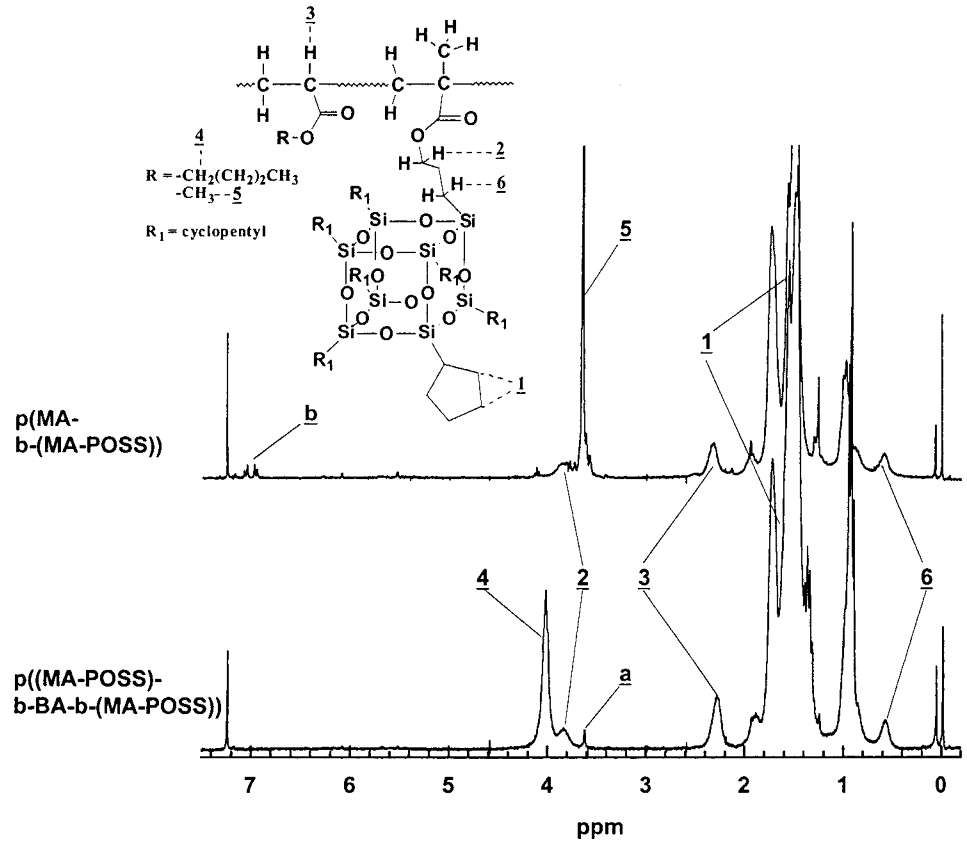
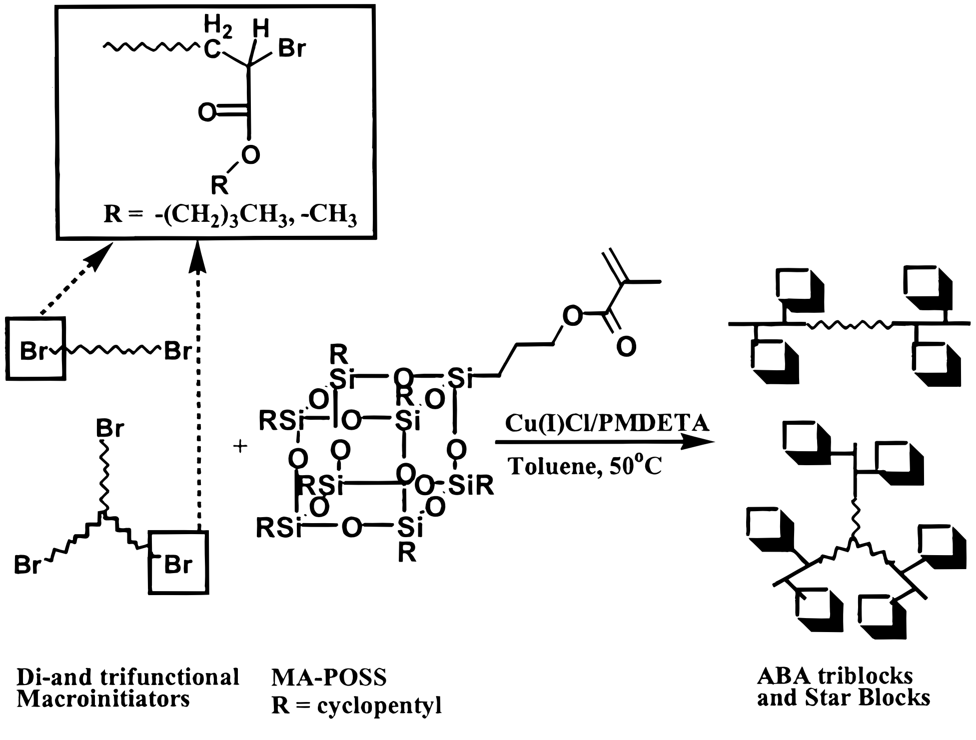


Figure 1. ^{1}H NMR spectra of a p((MA-POSS)-*b*-BA-*b*-(MA-POSS)) triblock copolymer ($M_{\mathrm{n\ NMR}} = 36\ 070$) chain extended from a p(BA) macroinitiator ($M_{\mathrm{n\ NMR}} = 14\ 790$) and a p(MA-*b*-(MA-POSS)) star–block copolymer ($M_{\mathrm{n\ NMR}} = 30\ 270$) chain extended from a p(MA) star polymer ($M_{\mathrm{n\ NMR}} = 7780$).

Scheme 1. Synthesis of p((MA-POSS)-*b*-BA-*b*-(MA-POSS)) Triblock and p(MA-*b*-(MA-POSS)) Star–Block Copolymers



36 070 vs $M_{\mathrm{n\ theoretical}} = 41\ 510$).[10] This small deviation may be caused by the difficulty in measuring high conversions of MA-POSS monomer by ^{1}H NMR. Because of the high molar mass of MA-POSS (1027.7 g/mol), a low initial monomer concentration (0.43 M) was used, making determinations of high conversions difficult to ascertain and potentially causing $M_{\mathrm{n\ theoretical}}$ values to be slightly inflated.

SEC analysis of the triblock copolymer synthesis also confirmed efficient chain extension of MA-POSS from

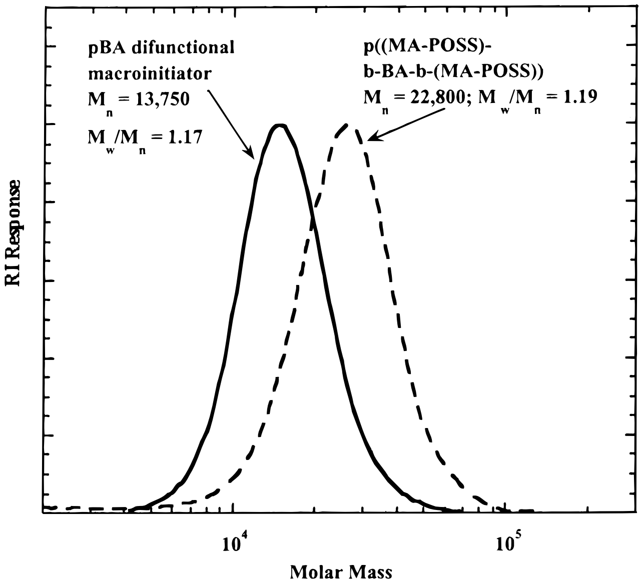


Figure 2. SEC chromatogram of p((MA-POSS)-*b*-BA-*b*-(MA-POSS)) triblock copolymer with relative weight compositions 37–63% of p(BA) to p(MA-POSS).

a p(BA) macroinitiator. Starting from a difunctional macroinitiator of p(BA) ($M_{\mathrm{n\ SEC}} = 13\,750$; $M_w/M_n = 1.17$), the incorporation of p(MA-POSS) produced an ABA triblock copolymer ($M_n = 22\,800$; $M_w/M_n = 1.19$) (Figure 2). While a well-defined polymer was prepared, a 45% difference in the SEC determined versus theoretical molecular weights was observed ($M_{\mathrm{n\ SEC}} = 22\,800$ vs $M_{\mathrm{n\ theoretical}} = 41\,510$). This disparity may be caused by hydrodynamic differences between p(MA-POSS) polymers and linear PMMA standards in THF solutions.

Star–block copolymers of poly(methyl acrylate) (p(MA)) and p(MA-POSS) were also prepared, using ATRP. A similar synthetic approach as described for the triblock copolymers was used where a star polymer[11] was prepared by the ATRP of MA using a trifunctional initiator (1,1,1-tris(4-(2-bromoisobutyryloxy)phenyl)-ethane). In the ^{1}H NMR of the p(MA) star polymer, aromatic protons from the initiator ($\delta = 7.0$ ppm, ***b***) were observed and molecular weights were ascertained ($M_{\mathrm{n\ NMR}} = 7780$). The p(MA) star polymer was then used as a macroinitiator in the ATRP of MA-POSS, and the ^{1}H NMR spectrum of the product confirmed the presence of both p(MA) and p(MA-POSS) resonances (Figure 1). A high monomer conversion for the chain extension reaction was achieved ($p = 0.91$), as evidenced by consumption of vinyl protons. Peak assignments of resonances from the p(MA-*b*-(MA-POSS)) copolymer (i.e., POSS cyclopentyl protons, ***1***; methine backbone protons from pMA, $\delta = 2.25$ ppm, ***3***; methylene protons adjacent to POSS group, $\delta = 0.6$ ppm, ***6***; Figure 1) were similar to those described for the p((MA-POSS)-*b*-BA-*b*-(MA-POSS)) copolymer. Methylene ($\delta = 4.1$) and vinyl ($\delta = 5.5$ and 6.1) proton resonances from residual MA-POSS monomer were also observed. Resonances at $\delta = 7.0$ ppm were assigned to aromatic protons (***b***) from the trifunctional initiator used in the synthesis of the p(MA) macroinitiator.

Compositions of the star–block copolymer were estimated by integration of p(MA-POSS) methylene ($\delta = 3.8$ ppm, ***2***) and p(MA) methyl ($\delta = 3.60$ ppm, ***5***) protons. As in the case of the triblock copolymer, calculation of the composition was complicated by poor resolution between methylene (***2***) and methoxy (***5***) protons. Thus, integration of the aromatic protons (***b***) from the initiator of the p(MA) block was done to determine a corrected integration of methoxy protons (***5***).

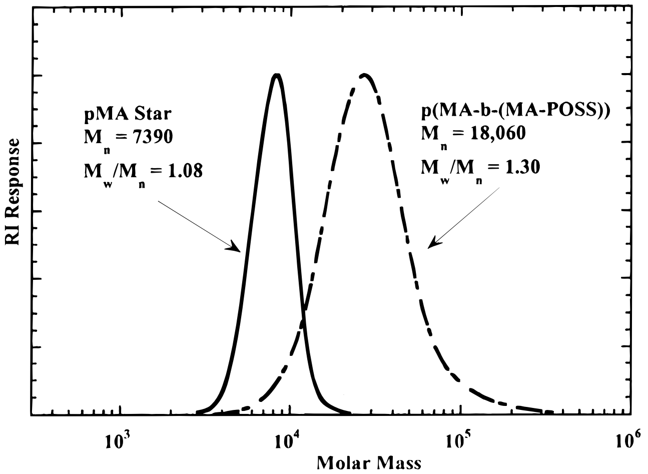


Figure 3. SEC chromatogram of p(MA-*b*-(MA-POSS)) star–block copolymer with relative weight compositions 25–75% of p(MA) to p(MA-POSS).

From the integration of p(MA-POSS) to p(MA), the mole percentages of each component was calculated (25% p(MA-POSS) and 75% p(MA)), along with molecular weights of the copolymer. The molecular weight of the star–block copolymer was then estimated by dividing the molecular weight of the p(MA) macroinitiator by the p(MA) weight percentage. Molecular weights of the p(MA-*b*-(MA-POSS)) block copolymers obtained from ^{1}H NMR analysis were slightly lower than theoretical predictions ($M_{\mathrm{n\ NMR}} = 30\,270$ vs $M_{\mathrm{n\ theoretical}} = 34\,730$), for reasons previously discussed.

From SEC of the star–block copolymer, efficient chain extension from a p(MA) macroinitiator ($M_{\mathrm{n\ SEC}} = 7390$; $M_w/M_n = 1.08$) with p(MA-POSS) was observed, yielding a star–block copolymer ($M_n = 18\,060$; $M_w/M_n = 1.30$) (Figure 3). SEC of these polymers was conducted using THF as the mobile phase, against linear PMMA standards. The molecular weight of the star–block copolymer based on linear standards did not correlate with the theoretical molecular weight for the product ($M_{\mathrm{n\ SEC}} = 18\,060$ vs $M_{\mathrm{n\ theoretical}} = 34\,730$), presumably due to both branching and hydrodynamic volume effects.

Conclusion

We have synthesized novel hybrid polymers from a POSS-based methacrylate monomer using ATRP. From this approach, homopolymers, triblock copolymers, and star–block copolymers of p(MA-POSS) have been prepared. While polymers containing POSS were made by other methods, using ATRP, hybrid-POSS polymers with previously unattainable compositions and drastically lower polydispersities have been synthesized.

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(8) General synthesis of MA-POSS homo-, block copolymers. To a 4 mL glass vial with magnetic stir bar was added MA-POSS (1.0 g, 0.973 mmol) and $\mathrm{Cu^{I}Cl}$ (2.3 mg, 0.024 mmol). The vial was fitted with a rubber septum and was evacuated and backfilled with argon for three cycles. Argon bubbled toluene (60 wt % relative to monomer) was then added to the vial to dissolve the monomer, followed by the addition of PMDETA (5.0 mL, 0.024 mmol). 4-Methylphenyl 2-bromoisobutyrate (12.4 mg, 0.048 mmol) was dissolved in argon-bubbled toluene (0.5 mL) and added via syringe after the copper complex was allowed to form. The vial was then placed in an oil bath at 50 °C for an appropriate reaction time. The polymer solution was then filtered through neutral alumina and precipitated into methanol (10-fold excess). From precipitation into methanol, residual monomer could not be separated from the polymer. In the preparation of block copolymers the same procedure was used, except poly(methyl acrylate) star and poly(*n*-butyl acrylate) macroinitiators were weighed into the reaction vial along with the other solids, prior to the addition of solvent.

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