

Synthesis of High Molecular Weight Polymethacrylates with Polyhedral Oligomeric Silsesquioxane Moieties by Atom Transfer Radical Polymerization

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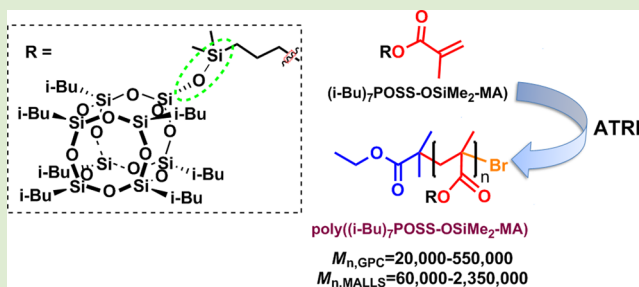
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Supporting Information

ABSTRACT: A new polyhedral oligomeric silsesquioxane (POSS) methacrylate monomer, 1-(3-(methacryloyloxy)propyl)dimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane ((i-Bu)₇POSS-OSiMe₂-MA, **1**), with a flexible spacer between the cubic POSS cage and methacrylate group was synthesized to reduce steric strain and thus achieve polymethacrylates (poly(POSS-MA)s) with high molecular weight (MW). Atom transfer radical polymerization (ATRP) of **1** at high monomer concentration (1 M, corresponding to ca. 85 wt % of **1**) led to polymers with the absolute number-average MW, determined by multiangle laser light scattering, $M_{n,MALLS} = 2\,350\,000$ (and apparent MW, measured by gel permeation chromatography with linear poly(methyl methacrylate) (PMMA) standards, $M_{n,GPC} = 550\,000$). Optimization of the reaction conditions, including the ATRP catalyst, targeted degrees of polymerization, monomer concentrations, as well as a monomer feeding, resulting in the first well-defined high MW polymers with POSS moieties.



Polyhedral oligomeric silsesquioxane (POSS)¹ with the empirical formula $R\text{SiO}_{1.5}$ is one of the most intriguing examples of well-defined, nanostructured moieties for the construction of high-performance, hybrid polymers.² Among various types of POSS monomers, the most promising one is the cubic-octameric framework with a single polymerizable vinyl group, leading to linear processable polymers via ionic or radical polymerization. POSS moieties can be treated as “giant atoms”³ and provide polymers with unique morphologies and thermomechanical properties.^{1–4}

The first POSS-based polymers described in the literature were polymethacrylates obtained by the conventional free radical polymerization (FRP) of $(c\text{-C}_5\text{H}_9)_7\text{POSS-MA}$ ($MW = 1027.71$) and $(c\text{-C}_6\text{H}_{11})_7\text{POSS-MA}$ ($MW = 1125.90$). The molecular weights of the resulted poly($(c\text{-C}_5\text{H}_9)_7\text{POSS-MA}$) and copolymer $(c\text{-C}_5\text{H}_9)_7\text{POSS-MA-co-(c-C}_6\text{H}_{11})_7\text{POSS-MA}$ reached $M_{n,GPC} = 117\,000$ ($M_w/M_n = 1.9$) and $M_{n,GPC} = 147\,000$ ($M_w/M_n = 2.55$), respectively, indicating that POSS-MA monomers can be readily polymerized.⁵ Due to their unique structures and high thermal stability (up to ca. 400 °C), the interest in such systems has arisen instantly; however, all further works employing FRP (in bulk⁶ or solution⁷) provided only oligomers. Subsequently, POSS monomers were successfully employed in controlled radical polymerization methods such as

atom transfer radical polymerization (ATRP).⁸ ATRP of $(c\text{-C}_5\text{H}_9)_7\text{POSS-MA}$ catalyzed by CuCl with N,N,N',N',N' -pentamethyldiethylenetriamine (PMDETA) in toluene (34 wt % relative to monomer) resulted in the formation of low MW polymers, $M_{n,GPC} = 9560$, and narrow molecular weight distribution (MWD) ($M_w/M_n = 1.14$).⁹ Similar results were obtained for isobutyl (i-Bu) or phenyl derivatives¹⁰ or when mono- or multifunctional macroinitiators were used.^{2d,11} The synthesis of poly(POSS-MA) by reversible addition–fragmentation chain transfer polymerization¹² and anionic polymerization¹³ was also reported, but again relatively low MWs were formed, always lower than by a free radical process.⁵ The reason for the formation of only oligomers by living systems was ascribed to the steric effect of the bulky POSS cage affecting both thermodynamics and kinetics of polymerization. Since high MW polymers with POSS moieties could strongly enhance their mechanical and thermal properties, or facilitate self-assembly of block copolymers,^{2d} we decided to use methacrylates with an extended linker to the POSS moiety under various conditions, including catalytic systems, targeted

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degrees of polymerization (DP), monomer concentrations, as well as monomer feeding.

Initially, we synthesized POSS-monomer with an O-SiMe₂ linker between the 3-methacryloyloxypropyl group and a hybrid core (i-Bu)₇POSS-OSiMe₂-MA (Figure 1). This modification

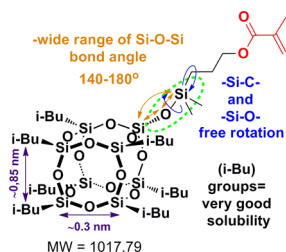


Figure 1. Structure of (i-Bu)₇POSS-OSiMe₂-MA (1).

relaxes the strain caused by a sterically bulky cage through longer Si–O–Si bonds with increased bond angles. The longer spacer should also provide better arrangement of the octameric cage in polymer chains and make the end group more accessible for the monomer and the catalyst in the ATRP process. Moreover, a very good solubility of the i-Bu derivative in spite of high mass (MW = 1017.79) should enhance the solubility of the resulting polymers and thermodynamic polymerizability.

First, polymerizations of **1** were carried out with the PMDETA/CuBr/CuBr₂ catalytic system with EBiB as an initiator in toluene at 50 °C (Scheme 1). At 0.37 M initial monomer concentration (C_m) (32 wt % of **1**) the polymer with $M_{n,GPC} = 24\,000$ ($M_w/M_n = 1.16$) (**2**) was obtained at 51% conversion. After 69 h, no further increase of MW was observed. The limited conversion could be due to either termination/transfer or limited thermodynamic polymerizability (i.e., equilibrium between monomer and polymer) resulting from a steric hindrance.

When the C_m was increased to 0.57 and 0.77 M and at the same target degree DP ($[1]_0/[EBiB]_0 = 100$), the conversion increased from 51% to above 90%, yielding polymers with low dispersity $M_w/M_n = 1.25$ and $M_{n,GPC} = 47\,000$ and 48 600, respectively. Polymerization was faster at higher C_m . A polymer isolated at lower conversion had MW determined by multiangle laser light scattering (MALLS) in a good agreement with theoretical value (indicating quantitative initiation) and about double compared to that determined by GPC using linear PMMA standards (Table 1, polymers 5 and 7).

Kinetics and evolution of MW with conversion are illustrated in Figure 2, and reaction conditions are reported in Table 1. These results indicate that the monomer conversion as well as polymer MW are affected by C_m in the reaction mixture. The influence of POSS-MA concentration on the thickness of a polymer layer (could be correlated with MW and DP) grafted from the flat silicon wafers by surface-initiated ATRP was already reported.¹⁴

Polymerizations at higher targeted DP = 200 (**7**), 1000 (**8**), and 10 000 (**9**) were conducted by reducing the amount of initiator in the reaction mixtures, and the molar amounts of the catalyst remained unchanged for **7** and **8** and was doubled for **9**. At $C_m = 0.77$ M, 85% conversion was achieved, and the polymer **7** with $M_{n,GPC} = 80\,000$ and $M_w/M_n = 1.2$ was formed. The polymerization in a more concentrated solution yielded a poly((i-Bu)₇POSS-OSiMe₂-MA) **8** with $M_{n,GPC} = 181\,500$ and relatively narrow MWD. The reaction proceeded faster, reaching 50% monomer consumption within 1 h, and was stopped due to an ineffective stirring caused by the high solution viscosity. For polymerization with higher targeted DP = 10 000, the same C_m as in the polymerization of **8** was used; however, the total concentration of Cu catalyst was doubled (**9**, Table 1). The polymer **9** formed after 1 h had $M_{n,GPC} = 353\,000$; however, the control over the polymerization was limited, $M_w/M_n \sim 2.8$. The larger-scale polymerization of **1** (10 g) at $C_m = 1$ M and a 10-fold excess of the PMDETA resulted in a uniform growth of poly((i-Bu)₇POSS-OSiMe₂-MA) **10** with narrow MWD (<1.2). Finally, poly((i-Bu)₇POSS-OSiMe₂-MA) with $M_{n,GPC} = 403\,000$ and $M_w/M_n = 1.45$ was formed after 42 h (Figure 3).

To solve problems related to high viscosity, a semibatch polymerization with the feeding of monomer solution was applied. This enabled maintenance of a high monomer concentration in the solution throughout the entire process, while keeping the polymer fully dissolved and providing a lower viscosity of the polymerization mixture.

The semibatch polymerization **11** was performed with the initial molar ratios: 800/1/3/3 of the monomer, initiator, CuBr, and PMDETA, respectively. The initial monomer concentration was set to 1 M, and reaction was run at 50 °C. A monomer solution with 0.82 M concentration was added dropwise during the period of 30 min, targeting the final DP = 900 (**11**, Table 1). After 1 h the polymerization was stopped due to the high viscosity. A polymer with $M_{n,GPC} = 190\,000$ and $M_w/M_n = 1.34$ was formed.

When the $[1]_0/[EBiB]_0$ ratio was increased to 2000 and the reaction mixture was fed with an additional 1333 mol equiv of the monomer, poly(POSS-methacrylate) with $M_{n,GPC} = 550\,000$ was obtained after 15 h (**12**, Table 1). The polymerization results for **11** and **12** showed that the feeding provides even high MW polymers, but the issues with the high viscosity persisted, leading to the nonuniform growth of polymer chains and broader MWD.

As mentioned before, the number-average MW of poly-(POSS-MA) determined by GPC with refractive index detectors provides underestimated values, which is due to the fact that the hydrodynamic volume of POSS-based polymer is significantly smaller than linear PMMA standards.^{13a} Therefore, the absolute MWs of selected polymers were measured using MALLS technique and are summarized in Table 1. The $M_{n,MALLS}$ corresponds well with $M_{n,theor}$ for polymers with DP up to 160 and is over two times higher than M_n determined by GPC. These results are comparable to those reported by Hirai

Scheme 1. ATRP of (i-Bu)₇POSS-OSiMe₂-MA (1)

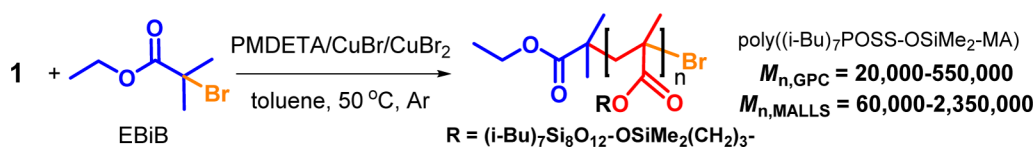


Table 1. Polymerization Conditions and Molecular Weights of Polymers 2–12

polymer	reagents ratio ^a	monomer (1)				$M_{n,theor.} \times 10^3$	$M_{n,GPC} \times 10^3$	$M_w/M_n(GPC)$	$M_{n,MALLS} \times 10^3$	$M_w/M_n(MALLS)$
		C_m (M)	mol %	wt %	conv. (%)					
2	100/1/2.66/0.66/3.32	0.37	4.1	32	51	51.9	24.1	1.16	-	-
3	100/1/2.66/0.66/3.32	0.57	7.9	49	90	91.6	47.0	1.25	-	-
4	100/1/2.66/0.66/3.32	0.77	14.6	65	94	95.7	48.6	1.26	-	-
5 ^b	100/1/2.66/0.66/3.32	0.77	14.6	65	60	61.0	29.5	1.14	60.3	1.16
6	200/1/5.32/1.32/6.64	0.77	14.6	65	85	173.0	80.0	1.20	-	-
7 ^b	200/1/5.32/1.32/6.64	0.77	14.6	65	80	163.4	72.7	1.13	175	1.20
8	1000/1/26.6/6.6/33.2	0.83	17.6	70	50	508.8	181.5	1.44	-	-
9	10000/1/532/132/664	0.83	17.6	70	35	3562	352.7	2.80	-	-
10 ^c	3333/1/2.6/0.66/33	1.00	34.8	85	45	1526	403.0	1.45	1060	1.40
11 ^{b,d}	900/1/3/0/3	0.92	24.0	78	90	732.8	190.0	1.34	576	1.33
12 ^{c,d}	3333/1/3/0/3	0.92	24.0	78	94	3189	550.0	2.35	2350	1.97

^a $[1]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$. Reaction conditions: 0.3 g of **1**, toluene, 50 °C, Ar. ^b2.4 g of **1**, toluene, 50 °C, Ar. ^c10 g of **1**, toluene, 50 °C, Ar. ^dSemibatch polymerization: $[1]_0/[EBiB]_0$ ratio increased from 800/1 to 900/1 for polymer 11 and from 2000/1 to 3333/1 for polymer 12, respectively.

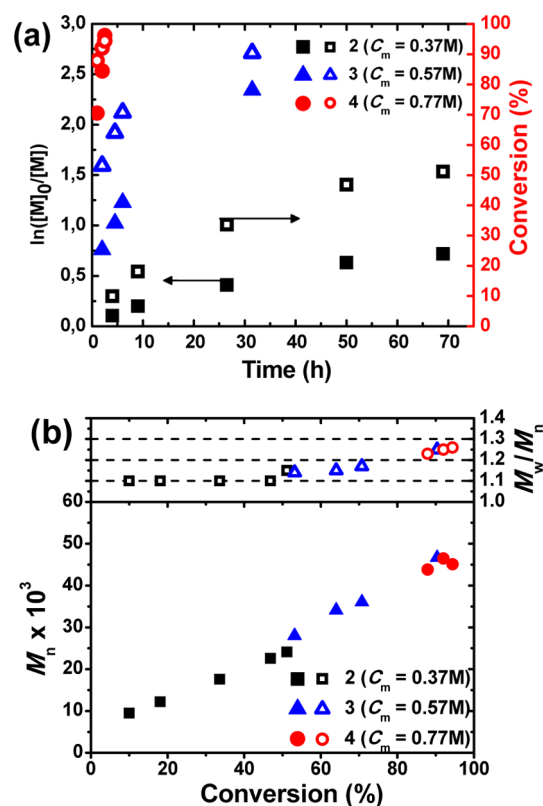


Figure 2. (a) Plot of $\ln([M]_0/[M])$ vs time and conversion vs time. (b) Plot of M_n vs conversion and M_n vs M_w/M_n for polymerizations 2–4.

et al. for poly((i-Bu)₇POSS-MA) with DP < 100, prepared by anionic polymerization.^{13a} However, with the increase of MW, the difference of M_n determined by GPC and MALLS techniques is more significant, and for polymer 12 $M_{n,MALLS} = 2\,350\,000$ is over four times higher than $M_{n,GPC}$ (Figure 4). Values of $M_{n,MALLS}$ smaller than theoretical MWs at very high targeted DP could be related to a small contribution of chain transfer and side reactions during the polymerization.

Summarizing, methacrylates with an extended linker to a bulky, nanoscale “giant atom” POSS cage, (i-Bu)₇POSS-OSiMe₂-MA, can be readily polymerized by ATRP at high monomer concentrations to form well-defined high MW

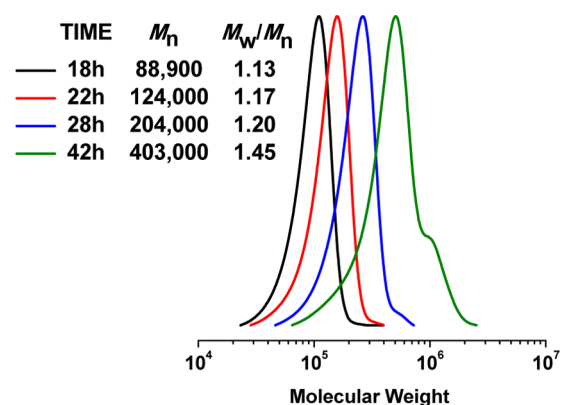


Figure 3. GPC traces of polymer 10.

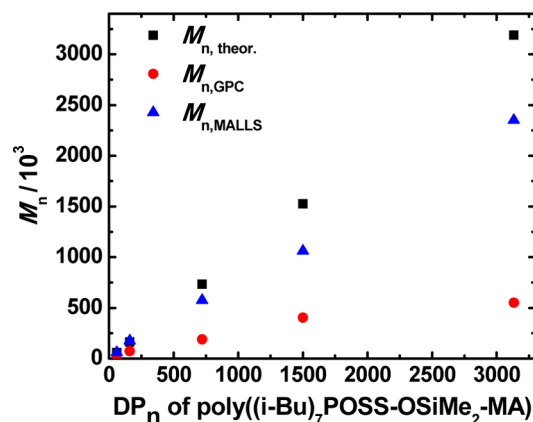


Figure 4. $M_{n,theor}$, $M_{n,GPC}$, and $M_{n,MALLS}$ of poly((i-Bu)₇POSS-OSiMe₂-MA)s as a function of targeted DP.

polymers. Poly((i-Bu)₇POSS-OSiMe₂-MA)s with a wide range of MWs, up to $M_{n,GPC} = 550\,000$, and the absolute MW determined by MALLS as high as $M_{n,MALLS} = 2\,350\,000$ and relatively narrow MWD, $M_w/M_n = 1.13$ –2.00, were obtained for the first time. This new approach gives a great opportunity for the synthesis of a wide spectrum of novel POSS-based systems with complex composition and architecture and will be the subject of our forthcoming reports.

■ ASSOCIATED CONTENT**■ Supporting Information**

Synthetic experimental details and additional polymerization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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