

Synthesis of Defined Polyhedral Oligosilsesquioxane-Containing Diblock and Triblock Methacrylate Copolymers by Atom Transfer Radical Polymerization

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ABSTRACT: Defined diblock and triblock copolymers composed of methyl methacrylate-*co*-glycidyl methacrylate block and 3-{3,5,7,9,11,13,15-hepta(2-methylpropyl)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxan-1-yl}propyl methacrylate block(s), i.e., P(MMA-*co*-GMA)-*b*-PiBuPOSSMA and PiBuPOSSMA-*b*-P(MMA-*co*-GMA)-*b*-PiBuPOSSMA, were synthesized by atom transfer radical polymerization (ATRP). First, monofunctional and bifunctional P(MMA-*co*-GMA) copolymers were synthesized by ATRP. Subsequently, these copolymers were successfully used as macroinitiators for ATRP of POSS-containing methacrylate monomer. The process showed high initiation efficiency of macroinitiators and led to products with low dispersity. The synthesized block copolymers were characterized by size exclusion chromatography, ¹H-NMR spectroscopy and their glass transition temperatures were determined by differential scanning calorimetry. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4294–4301, 2013

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INTRODUCTION

The preparation of new materials with specially designed chemical, mechanical, or physical properties is becoming increasingly important in many practical applications. In this respect, an increased demand for organic–inorganic hybrid polymer materials in recent years can be observed.^{1,2} Of these materials, polyhedral oligosilsesquioxane (POSS)-based hybrid (co)polymers attract much interest, both from the academic and industrial points of view. These (co)polymers contain POSS moieties covalently bonded to a polymer chain.

Polyhedral silsesquioxanes of typical formula $R_n(\text{SiO}_{1.5})_m$, where R is an organofunctional group and n is an even integer ≥ 4 , combine hybrid inorganic–organic composition with the nano-sized (1–3 nm) Si–O cage structure having dimensions comparable with those of most polymer segments or coils. POSS molecules may contain diverse organic substituents covalently bonded to the silicon atoms at the vertices of the cage, which makes the POSS nanostructure compatible with monomers, polymers, biological systems or surfaces. Moreover, when at least one of the substituents is a polymerizable or otherwise reactive group, the POSS moieties can be incorporated into a suit-

able polymer backbone by (co)polymerization or functionalization reactions (e.g., grafting, initiation, and termination), thus providing an opportunity to design and build materials that have a well-defined composition and dimensions and show nanophase behavior (nanocomposites).

The incorporation of POSS moieties into ordinary polymers can have a dramatic effect on the copolymer properties. It leads to increased glass transition and decomposition temperatures, increased oxygen permeability and resistance to oxidation, reduced flammability and heat evolution, enhanced miscibility, and modified mechanical properties.³ Furthermore, as a result of POSS high formula weights, incorporation of only a small molar percentage of a POSS reagent is necessary to attain a high weight percentage of POSS. For this reason, small amounts of a POSS reagent are often sufficient to achieve many property enhancements.

The synthesis of monomeric POSS reagents as well as the study of their physical properties are well documented in literature.^{3–7} Reports on synthesis of POSS-containing (co)polymers and their physical properties have been reviewed by Pyun and Matyjaszewski,⁸ Pittman and coworkers,⁵ Phillips et al.,⁹ Pielichowski et al.,³ Wu and Mather,¹⁰ and Kuo and Chang.⁷

Nowadays, an increased interest in the field of POSS-containing (co)polymers can be observed; various approaches are used to bind POSS moiety covalently to a polymer chain. Monomeric POSS reagents with reactive groups, such as halide,¹¹ thio,¹² azido,^{13,14} alkyne,¹⁵ or hydroxy¹⁶ groups, were synthesized and coupled with selected polymers containing in-chain hydroxy, epoxy, alkyne, azido, or isocyanato groups, respectively, to obtain (co)polymers randomly functionalized with the POSS moiety along the main chain. The POSS molecules can also be incorporated into initiators or chain transfer agents for the polymerization of various monomers to get end-functionalized (semitelechelic, “monochelic”) polymers. For instance, chloro-functionalized POSS,¹⁷ epoxy-functionalized POSS,¹⁸ and hydroxy-functionalized POSS^{19–22} were used as initiators for atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA), cationic polymerization of isobutylene, and ring-opening polymerization of lactones, respectively. A POSS-containing reversible addition-fragmentation transfer (RAFT) agent was used in the RAFT polymerization of *N*-isopropylacrylamide²³ or *tert*-butyl acrylate.²⁴ Alternatively, a POSS moiety can be incorporated into monomers for the synthesis of polymers with POSS group bonded to each monomeric unit of the polymer chain. Thus, appropriate POSS-containing monomers with polymerizable double bond have been polymerized by classical radical,^{25,26} atom transfer radical,^{27–30} reversible addition-fragmentation chain transfer,^{31,32} ring-opening metathesis,^{33,34} metallocene,³⁵ and anionic^{36–40} polymerization, to name but a few recent examples. From these approaches, the ATRP method appears to be especially attractive for synthesis of poly(POSS)-containing di-block or even multiblock architecture, particularly due to its robustness and relative experimental simplicity. In this approach, the retention of dormant initiation sites at the ends of preprepared polymeric chains generally allows their use as macroinitiators for polymerization of POSS monomers.²⁸ Nevertheless, the controlled polymerization of POSS monomers still remains a considerable challenge, mostly due to the POSS group bulkiness (in controlled radical polymerizations) and sensitivity to anionic attack (in anionic polymerizations). For these reasons, the reports using such an approach are still rather scarce.

This article summarizes the synthesis and isolation of block copolymers with MMA, glycidyl methacrylate (GMA), and POSS monomeric units. To our best knowledge, this is the first example of ATRP synthesis of poly(POSS) block-containing block copolymers bearing reactive functional groups that can be used for preparation of more complex architectures. This report provides a basis for a follow-up study of nanocomposites composed of organic PMMA-based polymer network and inorganic POSS domains. In this forthcoming study, the micelle-like structure of the block copolymers will be fixed in the well-organized POSS-containing polymer network by a crosslinking reaction of the incorporated GMA units with diamines.

In the work reported here, we describe the synthesis and characterization of defined diblock and triblock copolymers composed of P(MMA-*co*-GMA) copolymer as the first or middle block and a polymer with POSS units as the second block or outer blocks, respectively. For the preparation of POSS-containing blocks, 3-{3,5,7,9,11,13,15-hepta(2-methylpropyl)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxan-1-yl}propyl methacrylate (iBuPOSSMA) was chosen as a monomer. ATRP was employed as a suitable method for the preparation of the requested P(MMA-*co*-GMA)-*b*-PiBuPOSSMA diblock and PiBuPOSSMA-*b*-P(MMA-*co*-GMA)-*b*-PiBuPOSSMA triblock copolymers.

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EXPERIMENTAL

Materials

Toluene-4-sulfonyl chloride (TsCl; Fluka, $\geq 99\%$), biphenyl-4,4'-disulfonyl chloride (BPDSC; Aldrich, 97%), 2,2'-bipyridine (BiPy; Aldrich, $\geq 99\%$), CuBr (Fluka, $\geq 98\%$), *N,N,N',N''*-pentamethyldiethylenetriamine (PMDETA; Aldrich, 99%), diphenylether (Aldrich; 99%), and 3-{3,5,7,9,11,13,15-hepta(2-methylpropyl)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxan-1-yl}propyl methacrylate (methacryl-isobutyl-POSS, iBuPOSSMA; Hybrid Plastics, molecular weight = 943.64) were used as received. Toluene was distilled with lithium aluminum hydride and from dibutylmagnesium prior to use. Tetrahydrofuran (THF) was distilled with lithium aluminum hydride and then from sodium anthracenide before use. MMA and GMA were distilled twice from calcium hydride before use and kept under argon.

The reaction components were deoxygenated before the polymerization reaction, and all syntheses were performed under argon.

Synthesis

P(MMA-*co*-GMA) Macroinitiators. Monofunctional macroinitiators MI-1, MI-2, and MI-3 as well as bifunctional macroinitiator MI-4 were prepared by ATRP of MMA and GMA, initiated by corresponding sulfonyl chlorides (see Table I), according to the following synthetic procedure. All reaction parameters are given in Table I.

Representative synthetic procedure (MI-2 synthesis): toluene-4-sulfonyl chloride (114.4 mg, 0.6 mmol), CuBr (86.1 mg, 0.6 mmol), and 2,2'-bipyridine (93.7 mg, 0.6 mmol) were mixed with degassed toluene (7 mL) and stirred for ca. 30 min under an inert atmosphere. Subsequently, MMA (3.21 mL, 30 mmol) and GMA (0.22 mL, 1.6 mmol) were added, and the suspension was stirred at 90°C for 5 h. Then, the reaction solution was diluted with THF (ca. 30 mL) and centrifuged. The supernatant was precipitated in hexane (400 mL); the precipitate was filtered, washed with hexane, thoroughly dispersed in methanol, filtered, washed with methanol, and dried *in vacuo* at room temperature (RT) for 48 h. The yield was 2.8 g (white powder). The product was stored under argon at ca. 5°C.

P(MMA-*co*-GMA)-*b*-PiBuPOSSMA Diblock and PiBuPOSSMA-*b*-P(MMA-*co*-GMA)-*b*-PiBuPOSSMA Triblock Copolymers. Diblock copolymers DB-1 and DB-2 as well as triblock copolymers TB-1 and TB-2 were synthesized from the corresponding macroinitiators MI-2, MI-3, and MI-4 (see Table I), and iBuPOSSMA monomer via ATRP polymerization according to the following procedure. All reaction parameters are given in Table I.

Representative synthetic procedure (TB-1 synthesis): the bifunctional macroinitiator MI-4 (1.4 g, ca. 0.1 mmol, ca. 0.2 mmol of initiating sites), iBuPOSSMA (940 mg, 1 mmol), and CuBr

Table I. Reaction Conditions for Preparation of Macroinitiators and Block Copolymers by ATRP in Toluene

Target copolymer ^a	Initiator	Monomer M1	Monomer M2 ^b	Ligand	[M1] : [I] ^c : [Cu ⁺] : [L]	Temp. (°C)
MI-1 ^d	TsCl	MMA	GMA	PMDETA	50 : 1 : 1 : 1	90
MI-2	TsCl	MMA	GMA	BiPy	50 : 1 : 1 : 1	90
MI-3	TsCl	MMA	GMA	BiPy	100 : 1 : 1 : 1	90
MI-4	BPDSC	MMA	GMA	BiPy	50 : 1 : 1 : 1	90
DB-1	MI-2	iBuPOSSMA	-	PMDETA	5 : 1 : 1 : 1	50
DB-2	MI-3	iBuPOSSMA	-	PMDETA	5 : 1 : 1 : 1	50
TB-1	MI-4	iBuPOSSMA	-	PMDETA	5 : 1 : 1 : 1	50
TB-2	MI-4	iBuPOSSMA	-	PMDETA	10 : 1 : 1 : 1	50

^aMI-1, MI-2, MI-3: monofunctional P(MMA-co-GMA); MI-4: bifunctional P(MMA-co-GMA); DB-1, DB-2: P(MMA-co-GMA)-*b*-PiBuPOSSMA; TB-1, TB-2: PiBuPOSSMA-*b*-P(MMA-co-GMA)-*b*-PiBuPOSSMA, ^b[Monomer 1] : [Monomer 2] = 19, ^cConcentration of initiation sites, ^dPolymerization performed in diphenylether as a solvent.

(32.1 mg, 0.22 mmol) were mixed with degassed toluene (10 mL) and stirred for ca. 30 min under an inert atmosphere. Subsequently, PMDETA (0.05 mL, 0.24 mmol) was added; the mixture was stirred for 5 min at RT and then for 24 h at 50°C. Then, the reaction solution was diluted with toluene (ca. 20 mL) and centrifuged. The supernatant was precipitated in methanol (300 mL); the precipitate was filtered (filter paper KA 2M; basis weight 80 g/m², filtration rate 32 s; Fisher Scientific, Czech Republic), thoroughly washed with methanol, and dried *in vacuo* at RT for 48 h. The yield was 1.7 g (white powder). The product was stored under argon at ca. 5°C.

Measurements

Size exclusion chromatography (SEC) of the isolated copolymers was performed at 25°C with two PLgel MIXED-C columns (300 × 7.5 mm, SDV gel with particle size 5 μm; Polymer Laboratories, Amherst, USA) and with UV (UVD 250; Watrex, Prague, Czech Republic) and RI (RI-101; Shodex, Tokyo, Japan) detectors. THF was used as a mobile phase at a flow rate of 1 mL/min. The M_n values (g/mol) were calculated using Clarity software (Data-Apex, Prague, Czech Republic). Calibration with PMMA standards (PSS, Mainz, Germany) was used; for this reason, the molecular weights determined by SEC analysis are only approximate.

Differential scanning calorimetry (DSC) measurements were performed with a Perkin-Elmer Pyris 1 DSC calorimeter. Samples of about 5 mg were closed in aluminum sample pans, and the system was flushed with dry helium during the DSC scan. The temperature scale was calibrated according to the melting points of cyclohexane and indium. The power output scale was calibrated with indium. The samples were scanned in the 0°C–160°C temperature interval in the standard DSC mode with constant heating rate 10°C/min in heating and cooling runs. The DSC curves were evaluated by standard Perkin Elmer software.

The ¹H-NMR spectra were measured in deuteriochloroform (CDCl₃) at 57°C on a Bruker DPX 300 spectrometer at 300.1 MHz. Hexamethyldisiloxane was used as an internal standard.

RESULTS AND DISCUSSION

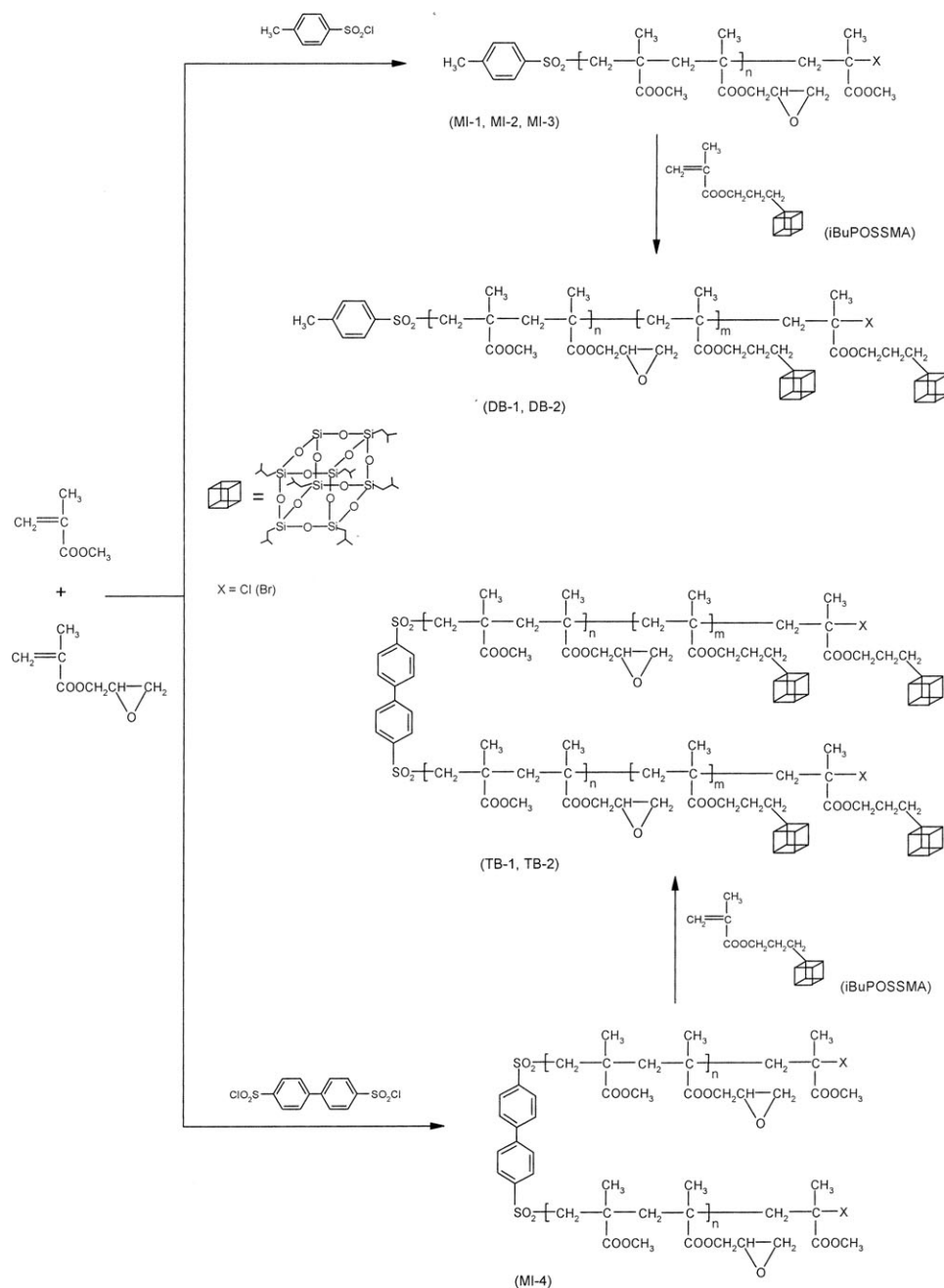
Scheme 1 provides an overview of the synthetic pathway leading to the target diblock and triblock copolymers. First, monofunc-

tional and bifunctional halogen-ended MI-1, MI-2, MI-3, and MI-4 macroinitiators were prepared by ATRP of MMA and GMA monomers using monofunctional and bifunctional ATRP initiators. Then, diblock (DB-1, DB-2) and triblock (TB-1, TB-2) copolymers with target content of ca. 5 mol % of GMA and various amount of iBuPOSSMA were prepared from MI-2, MI-3, and MI-4 macroinitiators and iBuPOSSMA monomer by ATRP. In the following part, the synthesis and product isolation will be discussed in detail.

Synthesis of P(MMA-co-GMA) Macroinitiators MI-1, MI-2, MI-3, and MI-4

For the synthesis of monofunctional and bifunctional macroinitiators, we used aromatic sulfonyl chlorides as ATRP initiators in conjunction with CuBr as a catalyst and a tertiary amine as an organic ligand. It was previously shown that sulfonyl radicals possess certain advantages over other initiator options; for instance, sulfonyl chlorides allow quantitative initiation, facilitate a higher rate of initiation than propagation, and thus, enable better control of polymerization process of various kinds of monomers.^{41–45} Moreover, the initiator fragment that gets build into the polymer chains bears benzene ring hydrogens that can be advantageously used for the ¹H-NMR-based calculation of molecular weights and molar compositions of the synthesized copolymers. For the above reasons, toluene-4-sulfonyl chloride and biphenyl-4,4'-disulfonyl chloride were chosen as initiators for the preparation of the ω-telechelic, monofunctional macroinitiators MI-1, MI-2, MI-3 and the α,ω-telechelic, bifunctional macroinitiator MI-4, respectively. Biphenyl-4,4'-disulfonyl chloride was preferred over other commercially available bifunctional initiator, benzene-1,3-disulfonyl chloride, as it provides better control of the polymerization process. As shown in literature,⁴⁴ sulfonyl chloride groups attached to the same benzene ring influence each other and do not behave as independent initiating sites in the ATRP process.

A mixed halide initiating system consisting of a sulfonyl chloride-type initiator and the CuBr catalyst was used here. As was previously reported, such an arrangement generally gives better control of the polymerization of methacrylates, compared with R-Cl/CuCl systems.^{45,46}



Scheme 1. Preparation of macroinitiators and block copolymers.

It is known that the GMA oxirane ring can undergo a nucleophilic attack by tertiary amine ligands.^{47–49} To avoid these unwanted side reactions, we performed all polymerizations in nonpolar solvent at moderate temperatures. Indeed, neither viscosity increase nor precipitate formation was observed, which indicated a smooth, side-reaction free polymerization process.

Monofunctional Macroinitiators MI-1, MI-2, and MI-3. Initially, we used the toluene-4-sulfonyl chloride/CuBr/PMDETA/diphenylether system for synthesis of the MI-1 macroinitiator. Molecular weights of the copolymer product, measured by SEC and determined from the ¹H-NMR spectrum were in a fair agreement (Table II). However, they were much higher than the

theoretical value calculated from the monomer/initiator molar ratio and monomer conversion. This undesirable result probably stems from initiator consumption caused by the fast side reaction of sulfonyl chloride initiator with PMDETA. This conclusion is supported by literature reports.⁵⁰ For this reason, PMDETA was replaced with 2,2'-bipyridine in the synthesis of macroinitiators MI-2 and MI-3 as this ligand does not react with sulfonyl chlorides. Moreover, diphenylether (m.p. = 25°C–27°C) was replaced with more convenient toluene. As illustrated in Table II, the MI-2 and MI-3 molecular weights, measured by SEC and calculated from ¹H-NMR spectra, were in a very good agreement with the theoretical values.

Table II. Composition, Molecular Weights, and T_g of Synthesized Macroinitiators and Block Copolymers

Product	Composition (mol %) ^a			Conversion (%)	Molecular weights				T_g (°C)
	MMA	GMA	iBuPOSSMA		M_n (theor.) ^b	M_n (NMR)	M_n (SEC)	M_w/M_n	
MI-1	95	5	–	100	5400	12,500	15,500	1.18	–
MI-2	93	7	–	100	5400	6300	5500	1.49	94.8
MI-3	95	5	–	100	10,800	12,300	10,800	1.47	–
MI-4	94	6	–	100	10,800	11,500	14,100	1.26	103.3
DB-1	85	6	9	~100	11,000	11,900	9000	1.28	120.5
DB-2	91	5	4	84	17,000	16,800	14,100	1.42	111.4
TB-1	89	6	5	77	20,900	17,400	22,200	1.30	114.9
TB-2	81	6	13	~100	30,400	27,000	26,500	1.31	–

^aDetermined from ^1H NMR spectra, ^bFor macroinitiators calculated from monomer/initiator molar ratio; for block copolymers calculated from macroinitiator $M_{n(\text{NMR})}$ and monomer/macroinitiator molar ratio (100% conversion assumed).

In general, the synthesized MI-1, MI-2, and MI-3 macroinitiators can be isolated by precipitation of the reaction mixture either in hexane or in methanol. Nevertheless, as the precipitate in methanol forms difficult-to-isolate milky suspension, precipitation in hexane was preferred. The catalytic complex was then efficiently removed from the isolated discolored product by thorough methanol washing.

Bifunctional Macroinitiator MI-4. The biphenyl-4,4'-disulfonyl chloride/CuBr/2,2'-bipyridine/toluene system was used for the synthesis of the macroinitiator MI-4. The isolation of MI-4 was easier, compared with the previously mentioned macroinitiators, because it precipitated readily in methanol. To verify that both the initiator's sulfonyl chloride groups participated in the initiation, a detailed analysis of the ^1H -NMR spectrum (aromatic region) of the isolated copolymer was performed. From literature, it is known that resonance of aromatic protons in aromatic sulfonyl compounds is sensitive to the substituent bonded to SO_2 group.^{42–44} Indeed, replacement of the chlorine atom in SO_2Cl with methylene group of the first monomeric unit resulted in the upfield shift of the relevant aromatic protons. Thus, the chemical shift of *ortho* protons from 7.82–7.90 (biphenyl-4,4'-disulfonyl chloride) to 7.75–7.82 ppm (MI-4) as well as the shift of *meta* protons from 8.15–8.23 (biphenyl-4,4'-disulfonyl chloride) to 7.95–8.05 ppm (MI-4) were observed in the corresponding ^1H -NMR spectra (not shown here). This indicated participation of both the sulfonyl chloride groups in initiation and formation of the corresponding bifunctional macroinitiator.

Molecular weights of the product measured by SEC and calculated from the ^1H -NMR spectrum were in a good agreement. Also, they agreed very well with the theoretical values (Table II), which indicated high initiation efficiency. The GMA content (5–7 mol %) in all the synthesized macroinitiators, calculated from ^1H -NMR spectra, was in excellent agreement with the target value (5 mol %).

Synthesis of P(MMA-*co*-GMA)-*b*-PiBuPOSSMA Diblock Copolymers DB-1 and DB-2

Target diblock copolymers were prepared by ATRP of iBuPOSSMA initiated by MI-2 or MI-3 macroinitiators. Polymerization was performed in toluene and catalyzed by the CuBr/PMDETA system.

Incorporation of iBuPOSSMA into the copolymer complicated the isolation. It was already mentioned that the macroinitiators are insoluble in both methanol and hexane. On the other hand, iBuPOSSMA is hexane soluble and methanol insoluble. Consequently, DB-1 and DB-2 precipitated on reaction mixture addition to methanol while clear solution was observed on addition to hexane. This observation also means that the contamination of the product with unreacted macroinitiator was negligible. Nevertheless, the product still could contain unreacted iBuPOSSMA monomer. Therefore, special separation techniques must be used to isolate the requested product. Several methods have been reported in the literature,²⁸ such as ultrafiltration or trituration in nonane. We partly succeeded with simple filtration of the precipitated solids on the filter paper for qualitative analysis (see Experimental section). In this way, most of the well-coagulated diblock copolymer was retained on the filter while the very fine suspension of iBuPOSSMA precipitate went through the filter. Thus, diblock copolymers free of the unreacted iBuPOSSMA monomer were isolated; no residual peak of iBuPOSSMA was detected by SEC (Figure 1).

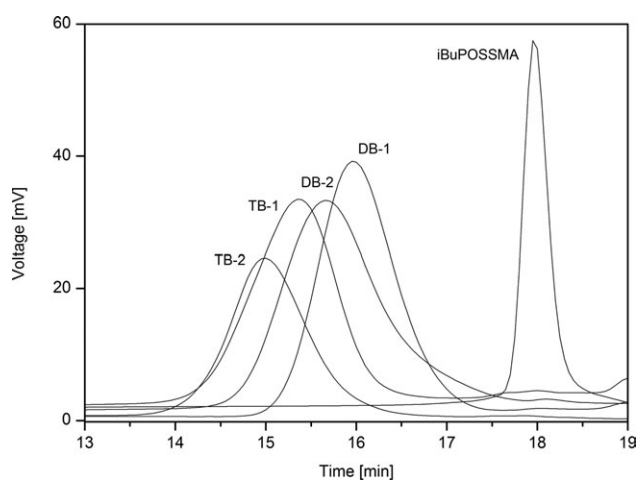


Figure 1. SEC curves of diblock copolymers DB-1 and DB-2, triblock copolymers TB-1 and TB-2, and iBuPOSSMA monomer.

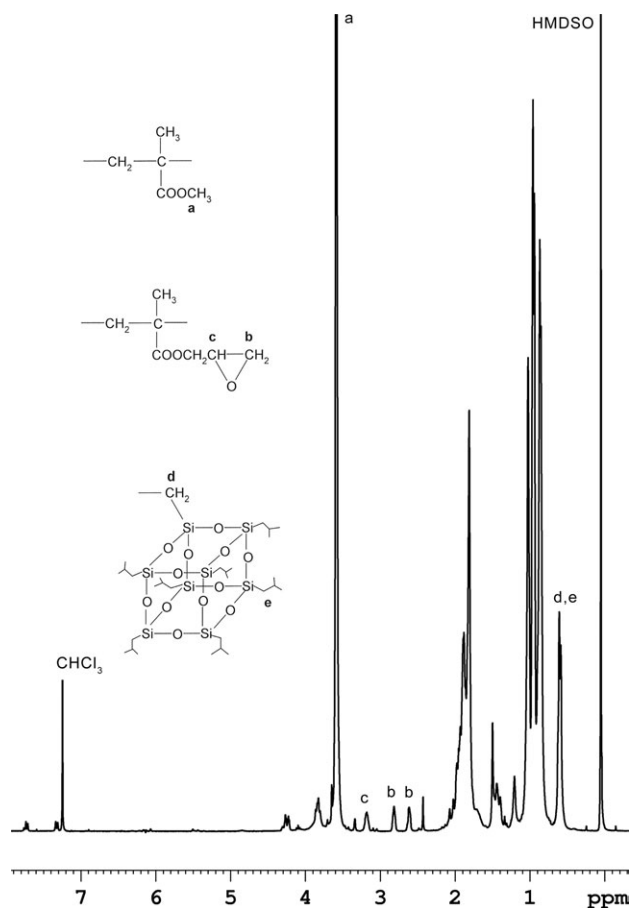


Figure 2. $^1\text{H-NMR}$ spectrum of diblock copolymer DB-1.

The incorporation of iBuPOSSMA in the diblock copolymers was evidenced by characteristic signal of SiCH_2 groups at ca. 0.6 ppm in the $^1\text{H-NMR}$ spectra (Figure 2). The molar composition of diblock copolymers (Table II) was calculated from the characteristic signals of OCH_3 protons in MMA units (ca. 3.6 ppm), CH and CH_2 protons of oxirane ring in GMA units (ca. 2.6, 2.8, and 3.2 ppm), and SiCH_2 protons in iBuPOSSMA units (ca. 0.6 ppm). For the calculation of number-average molecular weights (M_n ($^1\text{H-NMR}$)), signals of the initiator aromatic protons (ca. 7.7–8.1 ppm) were used.

Molecular weights of the synthesized diblock copolymers measured by SEC, calculated from their $^1\text{H-NMR}$ spectra, and estimated from the monomer/macoinitiator molar ratio were in a fair agreement (Table II). This observation indicates high initiation efficiency of the used macroinitiators (92% and 85% for DB-1 and DB-2, respectively) and together with low dispersity values support the assumption that the ATRP process could proceed in a well-controlled fashion.

Synthesis of PiBuPOSSMA-*b*-P(MMA-*co*-GMA)-*b*-PiBuPOSSMA Triblock Copolymers TB-1 and TB-2

Triblock copolymers were synthesized by ATRP initiated with the MI-4 macroinitiator and catalyzed by the CuBr/PMDETA system. Experiments were performed in toluene. The experimental setup and copolymer isolation were similar to diblock

copolymers DB-1 and DB-2. Triblock copolymers free of the unreacted macroinitiator and iBuPOSSMA monomer have been isolated—no residual peak of iBuPOSSMA can be seen in SEC eluograms of the products (Figure 1).

It is generally accepted that polymer growth proceeds at both the initiating groups of a bifunctional macroinitiator, which results in the formation of a triblock copolymer. Nevertheless, the direct evidence (similar to the NMR proof of the biphenyl-4,4'-disulfonyl chloride bi-initiator behavior; see above) is hardly feasible in the case of the triblocks TB-1 and TB-2. The incorporation of iBuPOSSMA into the copolymers is clearly seen in the $^1\text{H-NMR}$ spectra as a characteristic signal of SiCH_2 groups at 0.6 ppm (not shown here).

The molar composition and number-average molecular weights (Table II) of both the triblocks were calculated from the $^1\text{H-NMR}$ spectra in the same way as in the case of the DB-1 and DB-2 diblocks. Molecular weights of the synthesized triblock copolymers measured by SEC, calculated from their $^1\text{H-NMR}$ spectra, and estimated from the monomer/macoinitiator molar ratio agreed well. The initiation efficiency was again very high (92% and $\sim 100\%$ for TB-1 and TB-2, respectively). The achieved molecular weights of PiBuPOSSMA blocks were in a good agreement with the values reported previously by Matyjaszewski and coworkers²⁸ who observed limited reactivity of iBuPOSSMA in ATRP polymerization.

DSC Characterization of the Synthesized Copolymers

It is known that incorporation of POSS moiety into polymeric chains can result in both an increase and decrease of T_g .³ Table II provides T_g values for the synthesized block copolymers as well as selected macroinitiators; the corresponding DSC traces are given in Figure 3. Glass transition temperatures of macroinitiators MI-2 (94.8°C) and MI-4 (103.3°C) were slightly lower than T_g of PMMA homopolymer (105°C⁵¹; Figure 3). Higher T_g of MI-4 in comparison with that of MI-2 is probably caused by its higher molecular weight.

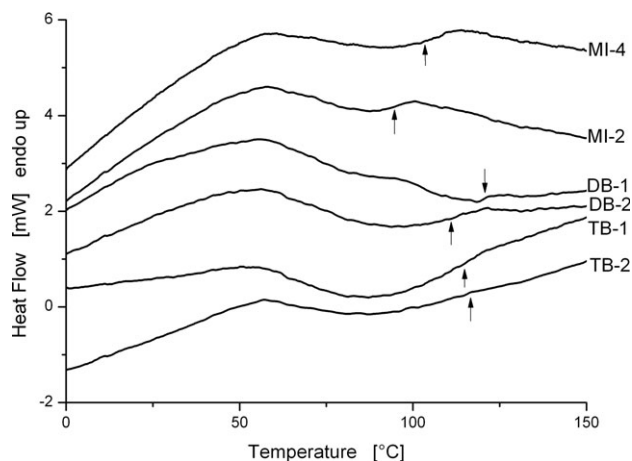


Figure 3. DSC traces (the second heating) of macroinitiators MI-2 and MI-4, diblock copolymers DB-1 and DB-2, and triblock copolymers TB-1 and TB-2 (glass transition temperatures marked with arrows).

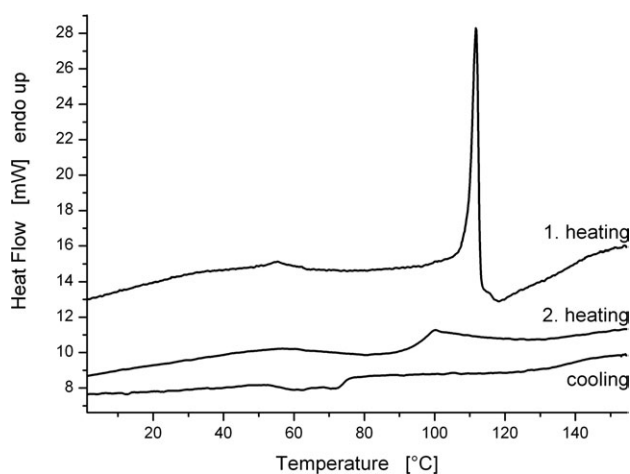


Figure 4. DSC traces of iBuPOSSMA monomer.

Williams and coworkers⁵² have found two melting endotherms at 112°C and 132°C for neat POSS compound containing one epoxy group and seven isobutyl groups per molecule. Interestingly, we identified only one endothermic peak at 111.7°C in the first heating run of the iBuPOSSMA monomer (Figure 4). This observation indicates preservation of some crystalline structure in the thermally untreated sample. After sample melting and cooling, weak exothermic (cooling curve, Figure 4) and weak endothermic (second heating curve, Figure 4) peaks can be detected. Thermal treatment of iBuPOSSMA eliminates crystalline structure; only poorly organized structure is preserved. T_g of the methacrylate unit in iBuPOSSMA monomer was not observed.

Incorporation of iBuPOSSMA units into the diblock (DB-1, DB-2) and triblock (TB-1, TB-2) copolymers caused an increase in their glass transition temperatures in comparison with the macroinitiators (Table II, Figure 3). In the case of copolymer TB-2, the DSC trace did not show clear glass transition; therefore, a T_g value is not included in Table II. In general, the higher content of iBuPOSSMA in the copolymer, the higher T_g , which could be explained by retardation of chain segmental motion caused by bulky POSS moieties.⁵³

CONCLUSIONS

Well-defined monofunctional and bifunctional P(MMA-co-GMA) macroinitiators were prepared by ATRP initiated by monofunctional and bifunctional sulfonyl chlorides, respectively. ¹H-NMR method was used to confirm that both the initiation sites of the bifunctional biphenyl-4,4'-disulfonyl chloride initiator were active during the initiation stage. Subsequently, the prepared macroinitiators were used for ATRP synthesis of P(MMA-co-GMA)-*b*-PiBuPOSSMA diblock and PiBuPOSSMA-*b*-P(MMA-co-GMA)-*b*-PiBuPOSSMA triblock copolymers. Polymerizations showed low dispersity of the products and high initiation efficiency of the macroinitiators. Monomer-free products were obtained by filtration of the precipitated reaction mixture through suitable filter paper. Composition of the copolymers was determined by SEC and ¹H-NMR spectroscopy; the obtained molecular weights were in a very good agreement with theoretical values. The highest achieved degree of polymeriza-

tion of PiBuPOSSMA blocks was relatively low (~ 8), which was probably caused by steric reasons arising from the bulkiness of the POSS moiety. DSC analysis revealed an increase in T_g of the block copolymers, compared with the starting macroinitiators.

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