## Poly(ferrocenylsilane-*block*-methacrylates) via Sequential Anionic and Atom Transfer Radical Polymerization

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**Introduction.** The self-organization of block copolymers constitutes a versatile means of producing ordered periodic structures with phase-separated microdomain sizes on the order of tens of nanometers.<sup>1</sup> By varying the relative molar masses of the blocks and the total molar mass, control over morphology, microdomain size, and spacing is easily achieved in the bulk state. In thin films, asymmetric block copolymers can self-assemble to ordered monolayers, provided that, next to block copolymer composition, film thickness is controlled. Block copolymer thin films<sup>2</sup> are of significant interest as templates for the fabrication of a variety of nanoscale structures such as periodic dot arrays,<sup>3,4</sup> nanopores,<sup>5</sup> and nanowires.<sup>6,7</sup>

In a number of applications, the utility of the produced patterns, such as etch resistance or conductivity relies on the introduction of inorganic elements in separate loading steps. Poly(ferrocenylsilanes)<sup>8</sup> owe a number of useful characteristics such as redox activity and a very high resistance to reactive ion etching<sup>9</sup> to the presence of alkylsilane and ferrocene units in the main chain and combine these characteristics with the properties and processability of polymers.

We demonstrated the use of asymmetric organic– organometallic block copolymers featuring isoprene<sup>10</sup> or styrene<sup>11</sup> units as organic and ferrocenyldimethylsilane units as organometallic blocks in the formation of monolayer thin films of densely packed organometallic spheres in an organic matrix. Because of the very high resistance of poly(ferrocenylsilanes) to reactive ion etching,<sup>9</sup> these thin films could be used as nanolithographic templates, enabling a direct transfer of the nanoscale patterns into underlying silicon or silicon nitride substrates with high aspect ratios.<sup>12,13</sup> These hybrid block copolymers could even be used to pattern a variety of thin metal films into dot arrays for e.g. highdensity magnetic data storage.<sup>14</sup>

In block copolymer thin films, the presence of a substrate and surface can induce orientation of the microphase structure<sup>15</sup> and can result in changes in domain dimensions or phase transitions<sup>16,17</sup> due to substrate or surface preferences of one of the blocks. After having established the thin film morphology of PI-*b*-PFS and PS-*b*-PFS diblock copolymers, we were interested to have access to PFS block copolymers with more polar organic blocks, in particular poly(methyl methacrylate) which has a higher affinity for silicon substrates. In addition to organic–organometallic diblock copolymers featuring polar blocks, amphiphilic organometallic block copolymers are accessible when e.g.

trimethylsilyl or aminoalkyl methacrylate repeat units, which are readily transformed into ionic blocks by hydrolysis or quaternization, are employed. The only reported example of a poly(ferrocenylsilane-*block*-methacrylate) block copolymer, featuring a 2-(dimethylaminoethyl) methacrylate block,<sup>18</sup> was obtained in a route applicable for this specific monomer. Thus, poly(ferrocenylsilane)-poly(methacrylate) block copolymers have remained largely unexplored.

In this paper, we report the synthesis and characterization of poly(ferrocenylsilane-*block*-methyl methacrylate) block copolymers, in which the organometallic block is formed by anionic polymerization and the organic block by atom transfer radical polymerization (ATRP).<sup>19</sup> The latter technique allows the controlled polymerization of a much wider variety of vinyl monomers than anionic polymerization schemes and imposes less strict requirements on monomer purity.

Experimental Section. a. Materials. Ferrocene (98%), N,N,N,N-tetramethylethylenediamine (TMEDA, 99.5+%), *n*-butyllithium (1.6 M in hexanes), chlorodimethylsilane (98%), dichlorodimethylsilane (99%), allyloxy-tert-butyldimethylsilane (97%), tetrabutylammonium fluoride (1.0 M in THF), diisobutylaluminum hydride (1.0 M in toluene), pyridine (anhydrous), methyl methacrylate (MMA, 99%), 2-bromo-2-methylpropionic acid (98%), 2-bromoisobutyryl bromide (98%), dichloro-(*p*-cymene)ruthenium(II) dimer, and tricyclohexylphosphine were obtained from Aldrich. Allyloxytrimethylsilane (>97%) and triethylamine (>99.5%) were obtained from Fluka. The platinum cyclovinylmethylsiloxane complex in cyclic methylvinylsiloxanes (3-3.5% Pt, CAS 68585-32-0) was obtained from ABCR, Karlsruhe. n-Heptane (for synthesis) and 4-(dimethylamino)pyridine (for synthesis) were purchased from Merck. Tetrahydrofuran (THF) for anionic polymerizations was distilled from sodium-benzophenone under argon, degassed in three freeze-pump-thaw cycles, and distilled by vacuum condensation from *n*-butyllithium. Toluene for ATRP was degassed on a high-vacuum line and distilled by condensation. 2-Bromoisobutyric anhydride was prepared according to a literature procedure.<sup>20</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.00 (CH<sub>3</sub>, s). The ATRP catalyst, (*p*-cymene)ruthenium(II) chloride-tricyclohexylphosphine, was synthesized as described earlier.<sup>21</sup>

**b.** Techniques. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a Varian Unity Inova (300 MHz) instrument at 300.3 MHz and on a Varian Unity 400 spectrometer at 399.9 MHz. A solvent chemical shift of  $\delta = 7.26$  ppm was used as a reference. GPC measurements were carried out in THF at 25 °C, using microstyragel columns (bead size 10  $\mu$ m) with pore sizes of 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, and 10<sup>6</sup> Å (Waters) and a dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502). Molar masses were determined relative to polystyrene standards.

**c. Monomer Purification.** [1]Dimethylsilaferrocenophane was prepared and purified as described earlier.<sup>22,23</sup> Methacrylate monomers were degassed on a high-vacuum line in three freeze–pump–thaw cycles and distilled under vacuum from calcium hydride immediately before use.

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**d. Anionic Polymerization.** [1]Dimethylsilaferrocenophane polymerizations were carried out in THF in a MBraun Labmaster 130 glovebox under an atmosphere of prepurified nitrogen (< 0.1 ppm of H<sub>2</sub>O), using *n*-butyllithium as initiator.

e. End-Capping Reagents. 3-(Trimethylsiloxy)propyldimethylchlorosilane (1). A two-necked 100 mL round-bottom flask fitted with a septum and connected to a Schlenk line was evacuated and filled with argon. Toluene (10 mL), allyloxytrimethylsilane (8.2 g, 63 mmol), chlorodimethylsilane (11.9 g, 126 mmol), and platinum catalyst (2–3 droplets,  $\sim 5 \times 10^{-6}$  mol of Pt) were added. After stirring the mixture under argon at room temperature for 4 days, complete conversion was achieved. The reaction mixture was degassed on a vacuum line in three freeze-pump-thaw cycles, and toluene and excess (CH<sub>3</sub>)<sub>2</sub>SiHCl were removed by vacuum condensation. The product was purified by vacuum distillation (bp 37-38 °C, 0.1 mm) and obtained as a colorless oil (isolated yield 12.7 g, 90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.56 (CH<sub>2</sub>O, t, 6.6 Hz, 2H); 1.62 (CH<sub>2</sub>, m, 2H); 0.81 (CH<sub>2</sub>Si, m, 2H); 0.42 (ClSi(CH<sub>3</sub>)<sub>2</sub>, s, 6H); 0.10 (OSi(CH<sub>3</sub>)<sub>3</sub>, s, 9H).

**3-(***Tert***-butyldimethylsiloxy)propyldimethylchlorosilane (2)** was prepared by a Pt-catalyzed hydrosilylation reaction of allyloxy-*tert*-butyldimethylsilane and chlorodimethylsilane in toluene, similar as described for **1**. The product was purified by vacuum distillation (bp 50-52 °C, 0.1 mm) and obtained as a colorless oil (isolated yield 13.5 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.60 (CH<sub>2</sub>O, t, 6.6 Hz, 2H); 1.62 (CH<sub>2</sub>, m, 2H); 0.90 (SiC-(CH<sub>3</sub>)<sub>3</sub>, s, 9H), 0.82 (CH<sub>2</sub>Si, m, 2H); 0.42 (ClSi(CH<sub>3</sub>)<sub>2</sub>, s, 6H); 0.06 (s, 6H, OSi(CH<sub>3</sub>)<sub>2</sub>).

f. Macroinitiators. In a typical experiment, [1]dimethylsilaferrocenophane (600 mg, 2.48 mmol) in THF (5 mL) was polymerized by adding *n*-BuLi (0.25 mL of a 0.2 M solution in *n*-heptane,  $5 \times 10^{-5}$  mol) at room temperature. After 15 min, the solution was cooled to -70 °C, and end-capper 1 (56 mg,  $2.5 \times 10^{-4}$  mol) was added. After stirring for 2 h at -70 °C, the mixture was allowed to come to room temperature and added to MeOH (50 mL) to precipitate **3a**, which was dried under vacuum. The trimethylsilyl end group was cleaved in a mixture of THF (5 mL),  $H_2O$  (0.4 mL), and AcOH (2 droplets) by stirring at room temperature for 24 h, yielding hydroxypropyl-terminated PFS 4, which was precipitated in *n*-heptane and dried under vacuum. Alternatively, living PFS was end-capped with 2 at 20 °C to produce **3b**. Cleavage of the TBDMS ether, by stirring with *i*-Bu<sub>2</sub>AlH (0.5 mL,  $5 \times 10^{-4}$  mol) in CH<sub>2</sub>-Cl<sub>2</sub> (10 mL) at 20 °C for 24 h under argon, followed by precipitation in MeOH, stirring in  $CH_2Cl_2/H_2O$  (pH = 5), and precipitation in *n*-heptane gave **4**. Acylation of 4 (5  $\times$  10<sup>-5</sup> mol of OH) was carried out with 2-bromoisobutyric anhydride (0.16 g, 5  $\times$  10<sup>-4</sup> mol) in dry pyridine (5 mL) in the presence of 4-(dimethylamino)pyridine (20 mg, 1.6  $\times$  10<sup>-4</sup> mol). The mixture was stirred at room temperature under dry N<sub>2</sub> for 48 h. 2-Bromoisobutyryl end-functionalized PFS 5b was precipitated in MeOH and dried under vacuum.  $M_n =$  $1.20 \times 10^4$  g/mol,  $M_w = 1.26 \times 10^4$  g/mol,  $M_w/M_n = 1.05$ .

**g. Block Copolymer Synthesis.** A glass tube containing a magnetic stirring bar was charged with a PFS macroinitiator (60–210 mg), (*p*-cymene)ruthenium(II) chloride–tricyclohexylphosphine (5 mg), methyl methacrylate (0.80 g, 8.0 mmol), and degassed toluene (0.8– 1.5 mL) in the glovebox and sealed. The mixture was Scheme 1. Synthesis of End-Capping Reagents with Protected Hydroxyl Functionality



stirred in a thermostated oil bath (80 °C) for 14 h. After cooling, the mixture was diluted with THF and dropwise added to MeOH to precipitate the product. The block copolymers were dried under vacuum.

**Results and Discussion.** Our synthetic approach to PFS-*b*-PMMA block copolymers combines the living anionic ring-opening polymerization of [1]dimethylsila-ferrocenophane<sup>24</sup> with a living radical polymerization of methyl methacrylate by means of ATRP.<sup>25</sup> Anionic polymerization of [1]dimethylsilaferrocenophanes allows one to form well-defined organometallic blocks with controlled block lengths and low polydispersities.

In ATRP, free radicals are generated through a reversible redox process catalyzed by a transition metal complex. Uniform growth of chains is accomplished through fast initiation and a rapid reversible deactivation of free radicals.<sup>19</sup> An ATRP system consists of an initiator, a catalyst (transition metal complex), and monomer. For the synthesis of the methacrylate blocks, a ruthenium-based catalyst [RuCl<sub>2</sub>(*p*-cymene)(PR<sub>3</sub>)], with R = cyclohexyl, was chosen. Because of its high catalytic activity and control over the polymerization process, poly(methyl methacrylate) (PMMA) with polydispersities as low as  $M_w/M_n < 1.1$  can be obtained using this catalyst complex.<sup>26</sup>

Various  $\alpha$ -haloesters have been successfully employed as ATRP initiators. Among these, 2-bromoisobutyryl groups are particularly useful as initiator for the ATRP of methyl methacrylate,<sup>27</sup> as this initiator produces a radical that is structurally nearly identical to the propagating radical. Acrylates are polymerized successfully using 2-halopropionyl and 2-haloisobutyryl groups as initiator.<sup>19b,25</sup>

Here, PFS homopolymers end-capped with a 2-bromoisobutyryl moiety serve as macroinitiators for methacrylate polymerization. This group is easily introduced by reacting hydroxyl-terminated PFS with e.g. 2-bromoisobutyryl bromide or 2-bromoisobutyric anhydride. We attempted to prepare hydroxyalkyl-terminated PFS by treating living PFS anions with styrene oxide, but incomplete end-functionalizations were found. Similar results were reported for the end-capping of living polystyrene with this reagent.<sup>25</sup>

We then explored the use of 3-(trimethylsiloxy)propyldimethylchlorosilane (**1**) and 3-(*tert*-butyldimethylsiloxy)propyldimethylchlorosilane (**2**) (Scheme 1) as end-capping reagents for living anionic PFS. Chlorosilanes in general are particularly successful end-capping reagents in anionic polymerization due to their high reactivity and lack of side reactions,<sup>28</sup> and their utility can be increased further by incorporating protected functional groups. Nevertheless, only a few accounts have appeared in the literature on the use of such reagents in the end-functionalization of living polymer anions.<sup>29,30</sup> Chlorosilanes **1** and **2** were synthesized by the hydrosilylation of allyloxyalkylsilanes with chlorodimethylsilane in toluene (Scheme 1).





Table 1. Degrees of Polymerization DPn of Various PFS Macroinitiators 5 Based on GPC and <sup>1</sup>H NMR Analysis

	$M_{n,GPC}^{a}$ (g/mol)	$M_{ m w}/M_{ m n}$	$\mathrm{DP}_{\mathrm{n,GPC}}^{b}$	$DP_{n,NMR}^{c}$ -CH <sub>3</sub> ( <i>n</i> -Bu)	${{\operatorname{DP}}_{{\operatorname{n}},{\operatorname{NMR}}}}^d -{\operatorname{C}}({\operatorname{CH}}_3)_2{\operatorname{Br}}$	${{\operatorname{DP}}_{{\operatorname{n,NMR}}}}^{e} -{\operatorname{Si}}({\operatorname{CH}}_{3})_{2}$
PFS-Br <b>5a</b>	8 000	1.02	33	34	49	46
PFS-Br <b>5b</b>	12 000	1.05	50	44	64	72
PFS-Br 5c <sup>f</sup>	12 000	1.07	50	46	60	52

<sup>*a*</sup> Measured by GPC, relative to polystyrene standards. <sup>*b*</sup> Calculated from  $M_n$  determined by GPC. <sup>*c*</sup> Calculated from ferrocenyl and initiator integrals (CH<sub>3</sub>). <sup>*d*</sup> Calculated from ferrocenyl and 2-bromoisobutyryl integrals. <sup>*e*</sup> Calculated from backbone Si(CH<sub>3</sub>)<sub>2</sub> and end-capper Si(CH<sub>3</sub>)<sub>2</sub> integrals. <sup>*f*</sup> Obtained via **3b**, deprotected using *i*-Bu<sub>2</sub>AlH.

The hydroxyl-protecting group should be stable in the presence of the PFS carbanion and cleave quantitatively under conditions that do not deteriorate the PFS chain. Trimethylsilyl ethers are cleaved under very mild conditions but are also prone to nucleophilic attack by organolithium compounds.<sup>31</sup> To prevent reaction of living PFS anions with the trimethylsilyl ether moiety of **1**, end-capping reactions were carried out at -70 °C. Hydrolysis of the trimethylsilyl ether in a mixture of THF, water, and acetic acid produced the hydroxypropyl-terminated PFS **4**, which was then acylated with 2-bromoisobutyric anhydride in pyridine with 4-(dimethylamino)pyridine as a catalyst<sup>22,32</sup> to macroinitiator **5** (Scheme 2).

tert-Butyldimethylsilyl (TBDMS) ethers are stable toward organometallic reagents, allowing one to endcap living polymers with 2 at room temperature. TB-DMS ethers are usually cleaved either under acidic conditions or by treatment with tetra-n-butylammonium fluoride (TBAF) in THF.33 Acidic hydrolysis is not an option for cleaving a *tert*-butyldimethylsilyl protecting group as acidic conditions (pH < 4) are not tolerated by PFS chains. TBAF cleaves tert-butyldimethylsilyl ethers quantitatively, but it also is a powerful desilylation reagent.34 We observed a significant broadening and tailing to lower molar mass values of PFS in GPC traces upon deprotection of **3b** by TBAF. Clearly, TBAF causes chain scission in PFS. By treating 3b with diisobutylaluminum hydride,<sup>35</sup> however, a clean deprotection of the TBDMS ether was achieved, yielding 4 without any molar mass decline (Scheme 2).

Hydroxypropyl-terminated PFS **4** and corresponding macroinitiators **5** of varying molar mass were obtained and characterized using GPC and <sup>1</sup>H NMR. GPC showed **4** and **5** to be well-defined polymers, with polydispersities  $M_{\rm w}/M_{\rm n} < 1.1$ , indicating that the end-capping and deprotection steps did not cause any molar

mass decline of the PFS chains. A diagnostic end group signal clearly observed in the <sup>1</sup>H NMR spectra of **4** was a triplet at  $\delta = 3.56$  ppm, belonging to the methylene protons adjacent to the hydroxyl group. This methylene signal was no longer visible in the <sup>1</sup>H NMR spectra of 5, nor was the signal of the acyloxymethylene group due to overlap with the ferrocenyl signals of the PFS chain. Clearly present, however, was the characteristic singlet at  $\delta = 1.93$  ppm due to the 2-bromoisobutyryl moiety. Also, the signal due to the CH<sub>3</sub> group of the *n*-butyl initiator moiety was observed at  $\delta = 0.90$  ppm. Endgroup analysis of 5 was performed on the basis of the ratio of the initiator and end-capper integrals to the ferrocenyl integral at  $\delta = 4.01$  and 4.22 ppm. Similarly, the dimethylsilyl signal of the end-capper moiety was compared with the dimethylsilyl signal of the polymer backbone. In Table 1, the number-average degrees of polymerization (DP<sub>n</sub>) obtained by GPC and by <sup>1</sup>H NMR are summarized. The values correlate reasonably well.

Comparison of the dimethylsilyl signals of the initiator (s,  $\delta = 0.21$  ppm) and end-capper (s,  $\delta = 0.24$  ppm) moieties of **4** and of the corresponding signals of **5** seems to be the most accurate way to gauge the degree of end-functionalization. End-capping with **2** followed by reductive cleavage of the TBDMS ether by *i*-Bu<sub>2</sub>AlH and acylation gave 90–95% end-functionalization. GPC measurements following the formation of the second block should provide further information on end-capping efficiency.

The 2-bromoisobutyryl end-capped poly(ferrocenylsilane) **5** was then used as initiator in the rutheniummediated living polymerization of methyl methacrylate (Scheme 3). In a typical experiment, macroinitiator **5a** (60 mg), ruthenium complex (5 mg), methyl methacrylate (0.80 g, 8.0 mmol), and toluene (0.8 mL) were placed in a glass tube under a nitrogen atmosphere. The tube was sealed, and the reaction mixture was stirred at

Scheme 3. Synthesis of Poly(ferrocenyldimethylsilane-block-methyl methacrylate) Block Copolymers



Table 2. Molar Mass Characteristics of PFS-b-PMMA Block Copolymers 6

	M <sub>n,GPC</sub> <sup>a</sup> (g/mol) PFS-Br	M <sub>n,NMR</sub> <sup>b</sup> (g/mol) PMMA	M <sub>n,NMR</sub> (g/mol) PFS- <i>b</i> -PMMA	M <sub>n,GPC</sub> <sup>a</sup> (g/mol) PFS-b-PMMA	M <sub>w</sub> /M <sub>n</sub> PFS- <i>b</i> -PMMA	wt % PFS <sup>c</sup>
PFS-b-PMMA 6a <sup>d</sup>	8 000 ( <b>5a</b> )	114 000	122 000	95 700	1.06	7
PFS- <i>b</i> -PMMA <b>6b</b> 1 <sup>d</sup>	12 000 ( <b>5b</b> )	116 300	128 300	101 700	1.10	9
PFS- <i>b</i> -PMMA <b>6b</b> <sub>2</sub> <sup>d</sup>	12 000 ( <b>5b</b> )	53 200	65 200	66 900	1.06	18
PFS-b-PMMA 6cd	12 000 ( <b>5c</b> )	33 600	45 600	40 500	1.18	26

<sup>*a*</sup> Measured by GPC, relative to polystyrene standards. <sup>*b*</sup> Calculated from ferrocenyl and CH<sub>3</sub>O integrals, based on  $M_{n,GPC}$  of the PFS block. <sup>*c*</sup> Calculated from ferrocenyl and CH<sub>3</sub>O integrals. <sup>*d*</sup> **6a**: MMA = 8.0 × 10<sup>-3</sup> mol, PFS-Br = 7.5 × 10<sup>-6</sup> mol, toluene 0.8 mL, Ru catalyst 5 mg, MMA conversion 45%. **6b**<sub>1</sub>: MMA = 7.3 × 10<sup>-3</sup> mol, PFS-Br = 8.5 × 10<sup>-6</sup> mol, toluene 1.0 mL, Ru catalyst 5 mg, MMA conversion 60%. **6b**<sub>2</sub>: MMA = 4.0 × 10<sup>-3</sup> mol, PFS-Br = 8.8 × 10<sup>-6</sup> mol, toluene 1.0 mL, Ru catalyst 5 mg, MMA conversion 58%. **6c**: MMA = 7.2 × 10<sup>-3</sup> mol, PFS-Br = 1.8 × 10<sup>-5</sup> mol, toluene 1.5 mL, Ru catalyst 5 mg, MMA conversion 60%.



Figure 1. GPC traces of PFS macroinitiator 5a and its corresponding PFS-*b*-PMMA block copolymer 6a.

80 °C for 14 h. After precipitation in methanol and drying under vacuum, PFS-*b*-PMMA block copolymer **6a** was obtained. Figure 1 shows the GPC traces of macroinitiator **5a** and PFS-*b*-PMMA block copolymer **6a**. Essentially all of the PFS macroinitiator was converted into block copolymer, indicating that the end-capping strategy (Scheme 2) enabled a near-quantitative incorporation of 2-bromoisobutyryl groups.

Control over block copolymer composition and molar mass was achieved by varying the initiator concentration  $[I]_0$  with respect to monomer concentration  $[M]_0$ . Alternatively, the molar mass of the PFS macroinitiator can be tuned, while keeping the monomer-to-initiator ratio [M]<sub>0</sub>/[I]<sub>0</sub> constant. Characteristic GPC traces of obtained PFS-b-PMMA block copolymers are shown in Figure 2. For block copolymers **6a**, **6b**<sub>1</sub>, **6b**<sub>2</sub>, and **6c**, MMA conversions of 45%, 60%, 58%, and 60% were reached, respectively, in 14 h. Block copolymer compositions were determined using <sup>1</sup>H NMR by relating the integral of the CH<sub>3</sub>O signal at  $\delta$  = 3.59 ppm belonging to the methacrylate repeat units to the ferrocenyl signal integral at  $\delta$  = 4.01 and 4.22 ppm. Combined with  $M_{\rm n}$ values of the PFS block obtained by GPC, total block copolymer molar masses  $M_{\rm n}$  were calculated and compared with values obtained by GPC. The results, summarized in Table 2, are in good agreement. The block copolymers described here are asymmetric, with PFS weight fractions ranging from 7 to 26%.

In summary, a route to 2-bromoisobutyryl end-functionalized poly(ferrocenyldimethylsilane), allowing essentially quantitative end-capping, is described. Fol-



**Figure 2.** GPC traces of representative PFS-*b*-PMMA block copolymers.

lowing the formation of the organometallic block by anionic polymerization, a ruthenium-mediated controlled radical polymerization of methyl methacrylate was employed to grow the second block. Well-defined PFS-*b*-PMMA block copolymers with low polydispersities ( $M_w/M_n < 1.1$ ) and controlled compositions were obtained. The use of ATRP to form the second block implies that a wide variety of (meth)acrylic and other vinyl monomers can be used, thus opening up the way to novel hybrid organic–organometallic block copolymers and amphiphilic organometallic block copolymers.

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