1,1-Dimethylsilacyclobutane-Mediated Living Anionic Block Copolymerization of [1]Dimethylsilaferrocenophane and Methyl Methacrylate

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ABSTRACT: An efficient synthesis is described of diblock copolymers from [1]dimethylsilaferrocenophane (FS) and methyl methacrylate (MMA). First, living anionic polymerization of FS is carried out in THF. When the FS polymerization is complete, 1,1-dimethylsilacyclobutane (DMSB) and 1,1-diphenylethylene (DPE) are added in order to modify the living PFS chain ends in an appropriate way for the subsequent growth of the second block. This combination of an accelerator (DMSB) and an end-capping agent (DPE) is shown to be necessary to suppress side reactions which otherwise lead to significant quantities of PFS homopolymers. When all the PFS chain ends bear an anionic DPE end group, block copolymerization of MMA follows. Under optimum conditions, PFS-*b*-PMMA block copolymers can be obtained in >90% yield (in addition to <10% PFS homopolymer), having molar masses ranging from 27 000 to 85 000 and different PFS contents. Finally, the PFS homopolymers can be removed quantitatively by redissolving the raw product in THF followed by reprecipitation of the pure diblock copolymer using *n*-hexane. The obtained material has polydispersity indices clearly below 1.1.

Introduction

Block copolymers are key compounds in macromolecular science and engineering. They can be used as thermoplastic elastomers,[1,2] turn brittle polymers into high-impact materials,[3] or are useful phase compatibilizers,[4−6] turning incompatible polymer mixtures into blends with improved properties. In all these cases, advantage is taken of the specific phase behavior and the morphology[7] of block copolymers in order to either optimize or tailorize the technical thermoplastic's mechanical properties. In addition to these well-established applications, there are further technological fields where multiphase block copolymers could play a key role in the future.[8] It seems very attractive, for example, to combine the good processability and the excellent mechanical properties of a conventional thermoplastic with some special features such as electrical conductivity or magnetism in one single material. In such block copolymers, one block can be formed from a conventional thermoplastic while the other one represents a functional polymer which implements the desired special effect(s). To further examine the potential of this concept, appropriate target structures have to be initially selected, and synthetic strategies have to be developed which make the newly designed materials accessible. There is no doubt that the well-defined block copolymer architectures required are best available via living anionic polymerization techniques.[9−11] However, while many technical thermoplastics are readily accessible via anionic polymerization, there is a tremendous lack of monomers that could be used for the growth of the functional block via this process. Moreover, to be appropriate for efficient block copolymerization, such monomers (i) have to have pk_a values that are in harmony with those of their conventional counterparts,[10] (ii) must not undergo side reactions under the conditions of anionic polymerization, and (iii) have to guarantee a homogeneous and quantitative block formation.

PMMA is a transparent thermoplastic with excellent mechanical, thermal, and chemical properties. It could be very useful, therefore, to combine it—in terms of an AB block copolymer system—with an electrically conducting, high-refractive-index, or magnetic counterpart. Hence, we decided to develop synthetic access to functional block copolymers where PMMA plays the role of the technical thermoplastic. But what constitution might its functional counterpart have? Polyferrocenylsilanes (PFS) are very promising candidates in this respect:[12,13] This quite new class of organometallic polymers is thermally very stable, readily soluble in a variety of solvents, and—depending on their substituents attached to the silicon bridges—either amorphous or semicrystalline. Moreover, since the iron(II) centers are an integral part of the polymer main chains, PFS have interesting magnetic and redox properties.[14,15] Also, they can be converted into semiconducting materials by exposure to an oxidizing agent.[16,17] Consequently, PFS-based block copolymers might be very useful for preparing magnetic particles, semiconducting materials, electrochromic compounds, and antistatic coatings, for example. Among these examples, the utilization of PFS-based block copolymers as auxiliars in nanolithography applications is currently a topic of special interest.[18−22]

Therefore, it was a milestone in functional polymer synthesis when Manners et al. could show that PFS-based polymers are not only accessible via thermal ring-opening polymerization[23] or transition-metal-catalyzed polymerization[24−26] but also via living anionic polymerization of the strained [1]silaferrocenophane (FS) monomers.[27,28]

The anionic polymerization technique allows excellent control of the PFS molar masses and molar mass distribution (PDI) as well as the formation of special polymer architectures such as block and graft copoly-

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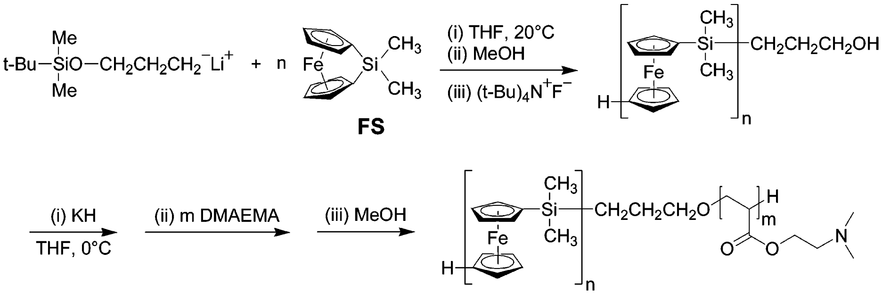
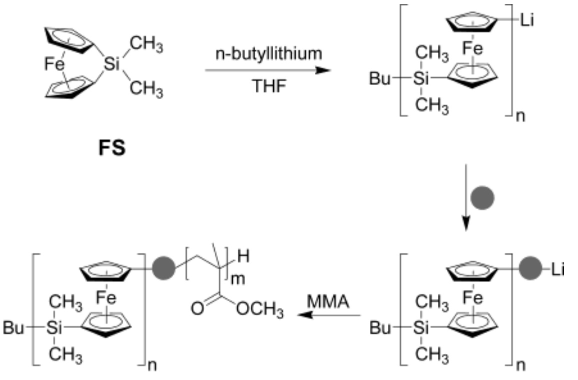
Scheme 1. Synthesis of Poly[ferrocenylsilane-*b*-2-(*N*,*N*-dimethylaminoethyl)methacrylate]



Scheme 2. General Strategy of the Transfer-Agent-Supported Synthesis of Poly(ferrocenylsilane-*b*-methyl methacrylate) Block Copolymers



mers.[29] Consequently, various diblock and triblock block copolymers containing segments of these organometallics have been prepared during recent years such as poly(ferrocenylsilane-*b*-ethylene oxide)s (via transition-metal-catalyzed block copolymerization),[30] poly(ferrocenylsilane-*b*-dimethylsiloxane)s,[28,31,32] poly(ferrocenylsilane-*b*-styrene)s,[33−35] and poly(ferrocenylsilane-*b*-isoprene)s.[18] Block copolymers from ferrocenylsilanes and MMA, however, have not yet been described to the best of our knowledge. The only known example of an FS−methacrylate block copolymer is poly[ferrocenylsilane-*b*-2-((*N*,*N*-dimethylamino)ethyl)methacrylate] (PFS-*b*-PDAEMA).[36] It was prepared via a multistep synthesis where in the first step the silaferrocenophane FS was polymerized using *tert*-butyldimethylsilyloxy-1-propyllithium as the initiator. Subsequently, the initiator fragment was deprotected, leading to hydroxy-terminated PFS chains. Deprotonation using potassium hydride gives the alkoxide which initiates the growth of the DAEMA block (Scheme 1).

However, even if DAEMA polymerizes in a living fashion when initiated by alkoxides, this is not a general method for polymerizing methacrylates: in most other cases, carbanionic species are the required initiators, and the polymerization has to be carried out at very low temperatures to prevent side reactions of the methacrylate's carbonyl groups. Hence, it was necessary to select alternative strategies for the preparation of well-defined PFS-*b*-PMMA block copolymers. The general strategy used in the present work is shown in Scheme 2. It was selected primarily because the different monomers in sequential anionic block copolymerizations have to be applied in an order where the nucleophilicity of the living chain end of block A is at least equal to—or higher than—the nucleophilicity of the new chain end which is created by the addition of the B-type monomer. The estimated pk_a of the carbanion's conjugated acid is approximately 39 in the case of PFS[37] while that of PMMA is 30−31.[10] Hence, block copolymerization should be possible when FS is first polymerized to give the A block, followed by MMA as the B-type monomer.

However, the shown procedure also has some risks to failure. This is particularly due to the well-known side reactions of the carbanionic chain ends with the MMA's carbonyl groups at elevated temperatures which are faced by the unknown reactivity of the living PFS chain ends at the very low temperatures to which the reaction mixtures have to be cooled prior to the addition of MMA. If problems arise here, appropriate measures have to be taken—such as the introduction of transfer agents—to ensure high block efficiency and narrow block-length distributions for the PMMA block as well. Hence, the goal of this work was to analyze under which conditions living anionic polymerization can be used to prepare PFS-*b*-PMMA block copolymers with both high block efficiency and narrow block length distribution. In the following, we first discuss some kinetic aspects of the FS homopolymerization and then present an elegant pathway to the desired functional copolymer systems.

Results and Discussion

Kinetics of FS Homopolymerization. Profound knowledge is required of the kinetics of the A-block formation if well-defined AB-type block copolymers are aimed at. While numerous kinetic studies exist for the anionic polymerization of MMA,[41] only very few data are available describing the kinetics of anionic FS homopolymerization. Therefore, we started our investigations by studying the anionic PFS synthesis to some more detail.

All the kinetic investigations described in the following were performed in THF at room temperature at constant initial monomer concentration. The concentration of *n*-BuLi as the initiator was varied from 1.68×10^{-5} to 4.80×10^{-5} mol/L. The resulting range of molar masses of the PFS homopolymer samples is exactly the same as that which will be realized for the A-block in the planned synthesis of block copolymers. After addition of the initiator to the monomer solution, samples were taken from the reaction mixture at regular intervals, terminated with degassed and water-free methanol, and analyzed using GC in order to determine the FS conversion as a function of time.[42] The monomer consumption was found to be quantitative in all cases. Exact experimental conditions and results of these kinetic studies are summarized in Table 1.

As confirmed by Figure 1, the reaction follows first-order kinetics. At higher initiator concentrations, the kinetics shows a linear dependency, and therefore the polymerization seems to be truly living. Only at lower

Table 1. Experimental Data Obtained from Kinetic Investigations of Anionic Homopolymerization of [1]Dimethylsilaferrocenophane[a]

run	$[I]_0$[b] (10^{-5} mol/L)	FS[c] (mg)	THF (mL)	$[M]_0$[d] (mol/L)	M_n (g/mol) calcd[e]	M_n (g/mol) found[f]	PDI[g]	$[P]_0$[h] (10^{-5} mol/L)	k_{app}[i] (10^{-3} s^{-1})
1	4.8	790	10	0.326	16 500	16 500	1.07	4.72	8.630
2	3.2	770	10	0.318	24 000	22 500	1.07	3.32	5.913
3	2.4	780	10	0.322	32 500	32 700	1.07	2.40	4.402
4	1.68	770	10	0.318	45 800	42 000	1.10	1.79	2.973

[a] *n*-Butyllithium was the initiator, THF was the solvent, and the reactions were carried out at room temperature. [b] $[I]_0$ = initial initiator concentration. [c] FS = [1]dimethylsilaferrocenophane. [d] $[M]_0$ = initial monomer concentration. [e] $M_{n,calcd} = [M]_0/[I]_0 \times m(FS)$. [f] Determined using SEC in THF at room temperature vs PMMA standards. [g] PDI = polydispersity index; determined from the slope of the corresponding P_n vs x_P plot in Figure 1. [h] $[P]_0$ = initial concentration of living polymer chains. [i] k_{app} = apparent rate constant of propagation; determined from the slopes of the first-order time vs conversion plots in Figure 2. For run 3 and run 4 only the initial slopes were considered.

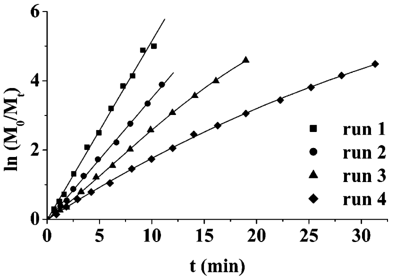


Figure 1. First-order reaction plot obtained from the kinetic investigation of the [1]dimethylsilaferrocenophane homopolymerization (THF, room temperature, initiated with *n*-BuLi; four different initiator concentrations, ranging from 1.68 × 10^{-5} to 4.80 × 10^{-5} mol/L).

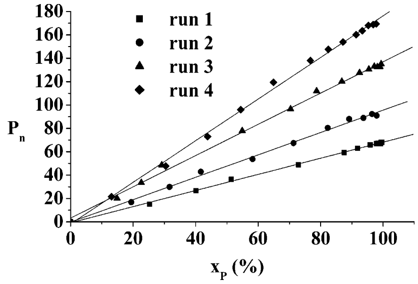


Figure 2. Conversion (x_P) dependence of the experimentally determined degrees of polymerization P_n (SEC, PMMA calibration) for the anionic polymerization of [1]dimethylsilaferrocenophane in THF at room temperature, initiated with *n*-BuLi (four different initiator concentrations ranging from 1.68 × 10^{-5} to 4.80 × 10^{-5} mol).

Table 2. Reaction Conditions Applied to the Polymerization of [1]Dimethylsilaferrocenophanes Obtained via Two Different Purification Procedures[a]

run	*n*-BuLi (10^{-5} mol)	FS[b] (mg)	hexane (mL)	THF (mL)	M_n (g/mol) calcd	M_n (g/mol) found[c]	PDI[c]
5	7.2	510	6	6	6800	18500	1.04
6	6.9	500	6	6	7800	9800	1.05

[a] For details, see text. [b] FS = [1]dimethylsilaferrocenophane. [c] M_n was determined using SEC (PMMA calibration) from samples isolated immediately after complete monomer consumption; PDI = polydispersity index.

initiator concentrations do the plots get slightly curved. This indicates a certain extent of chain termination as the chain growth proceeds to higher conversions. In full agreement with this statement, it can be seen from Table 1 that the obtained polymers exhibit narrow molar mass distributions and molecular weights in excellent agreement with the values expected from the reaction stoichiometry.

The excellent control of FS homopolymerization is also evident from the plot of P_n vs x_P shown in Figure 2. Here as well, no deviation from linearity is observed. This demonstrates that chain transfer reactions are virtually absent during the polymerization process. All together, the collected data clearly show excellent control of the FS homopolymerization. Moreover, the rate constant of propagation, k_P, could be calculated on the basis of these data to be 1.9 (mol s)$^{-1}$ for FS homopolymerization under the applied reaction conditions.

Long-Term Stability of Living PFS Chains. All kinetic experiments discussed so far were carried out using [1]dimethylsilaferrocenophanes of very high purity (for best purification procedure, see Experimental Section). Nevertheless, in some cases PFS samples of bimodal molecular weight distributions were obtained. This was in particular the case when the monomer was not purified exactly according to the optimum procedure. To demonstrate this tremendous sensitivity toward impurities, a sample of crude FS was sublimed, recrystallized from hexane at −60 °C, and finally sublimed once again. A second FS sample was purified in the same way but finally sublimed twice. The obtained samples were dissolved in hexane, *n*-BuLi was added, and the mixtures were stirred overnight (runs 5 and 6, respectively). While no FS polymerization occurs under these conditions in the nonpolar solvent hexane, all impurities potentially present even after the above purification procedures should be destroyed during that time. Then, FS polymerization was started by adding some THF to the solutions. The experimental data obtained from these experiments are summarized in Table 2.

Comparison of calculated and found values of M_n shows that for run 5 approximately two-thirds of the added *n*-BuLi was exhausted by impurities still present in the monomeric FS while for run 6 where FS was once more sublimed the loss of initiator was rather negligible. Moreover, for both runs monomodal molar mass distribution and thus quite low PDIs were observed. However, this latter situation changed when the living reaction mixtures were allowed to stay for some more time. This was shown by taking further samples from the living polymer solutions at regular intervals after complete monomer consumption. The samples were quenched by carefully degassed methanol and analyzed using GPC. Now, the appearance of a second, high-molecular-weight polymer fraction was detected. Its amount grew at the expense of the original monomodal PFS peak. More profound analysis of this second peak revealed that it exhibits almost twice the molecular weight of the original fraction. This probably indicates a coupling process of two active PFS chains. Figure 3a shows the evolution of the coupled fractions with respect to time.

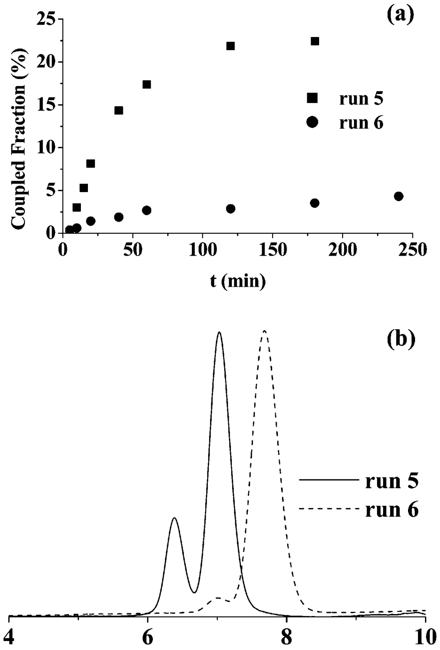


Figure 3. (a) Evolution of the high-molecular-weight fractions formed in runs 5 and 6 after full monomer conversion. The values are determined by integrating the peak area in the SEC elugramms (for polymerization conditions, see Table 2). (b) Representative SEC traces from runs 5 and 6; polymer samples were isolated from the living polymer solutions 3 h after full monomer consumption.

In addition, representative GPC elugramms of samples isolated from both solutions 3 h after complete monomer consumption are shown in Figure 3b.

From these data it is evident that the proposed coupling process is slow with respect to the FS homopolymerization but might become significant in combination with a slow B-block formation process during block copolymer synthesis. Also, the slowly formed high-molecular-weight PFS fraction is much less significant when very pure FS monomer is used. This may suggest a bifunctional impurity which ties together two living PFS chains. The appearance of products having twice the expected molar mass in anionically synthesized polymers often involves oxygen introduced by nondegassed quenching agents.[43] However, this mechanism was excluded by the experimental conditions applied here, and moreover the very low rate of the coupling process also indicates a reaction different from oxidative coupling. Analysis of the isolated material using MALDI–TOF mass spectrometry and NMR did not reveal reproducible results that could help to identify the species responsible for the coupling process. Therefore, we are unable so far to give a final explanation for the observed homocoupling.

Block Copolymerization of FS and MMA. In some first trial experiments the question should be answered whether the living PFS chain ends can be used without modifications to initiate the MMA block copolymerization. This procedure would be the most convenient way to prepare the desired block copolymers (Scheme 3).

Hence, homopolymerization of FS was first carried out at room temperature, as described above. As soon as this conversion was complete, the reaction mixture was cooled to −78 °C. Then MMA was added. The reaction was carried out in the presence of a 10-fold excess of LiCl to ensure a readily controlled synthesis of the

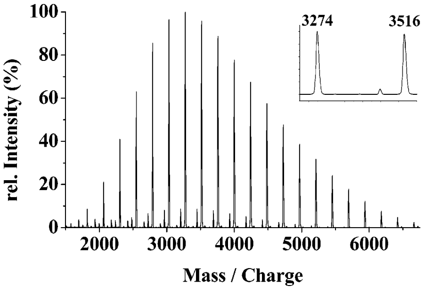
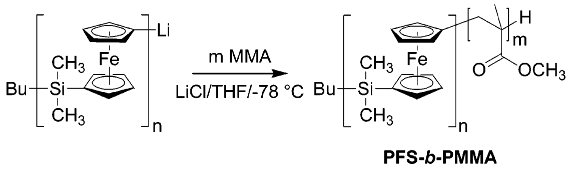


Figure 4. Analysis of MMA-terminated polyferrocenylsilanes using MALDI–TOF mass spectrometry; $m_{\text{peaks}} = m(n\text{-butyl}) + n \times m(\text{FS}) + m(\text{vinyl ketone}) = 57.11$ g/mol $+ n \times 242.17$ g/mol $+ 69.6$ g/mol

Scheme 3. Direct Synthesis of Poly(ferrocenylsilane-*b*-methyl methacrylate) Block Copolymers



PMMA block. Unfortunately, the reactivity of the living PFS chain end proved to be too high even at low temperatures, resulting in quantitative chain termination via reaction with MMA's carbonyl group and the formation of vinyl ketone functionalized PFS chains. This is a commonly observed termination reaction in the anionic polymerization of MMA, when initiated with highly reactive reagents, too nucleophilic for selective addition at the double bond.[41] In the case of living PFS chains as an initiator for the MMA polymerization, this termination mechanism was confirmed by analyzing PFS oligomers with MALDI–TOF spectrometry.

On the basis of these observations, measures had to be taken to lower the reactivity of the living PFS chain ends toward the MMA carbonyl groups at low temperatures. A well established method to achieve this goal is to end-cap the living chain ends of the first block using 1,1-diphenylethylene (DPE): DPE living chain termini do not attack carbonyl groups but readily start MMA polymerization even at −78 °C.[44] Moreover, the chain terminus formed by a single attack of a DPE molecule will not add further DPE molecules even at room temperature because of its appreciable steric load. Thus, there is always exactly one DPE moiety between blocks A and B in the final copolymer.

In practice, after polymerization of FS under the above standard conditions, a small quantity of DPE was added to the reaction mixture at room temperature (1.2 equiv. DPE were typically applied per PFS chain end equivalent). Unfortunately, the results obtained were again very disappointing: the conversion of the living PFS chain ends with DPE proved to be very incomplete (~80%) even after reaction at room temperature for 1.5 days (Figure 5).

On the basis of the observed behavior and the unsafe long-term stability of the PFS precursor discovered in the homoplymerization experiments, both of which can dramatically lower the blocking efficiency, we decided to further optimize the DPE end-capping reaction.

Accelerated Introduction of 1,1-Diphenylethylene. The idea which was followed next was to take advantage of a highly reactive auxiliar for improving the efficiency of the DPE attachment to the PFS chain

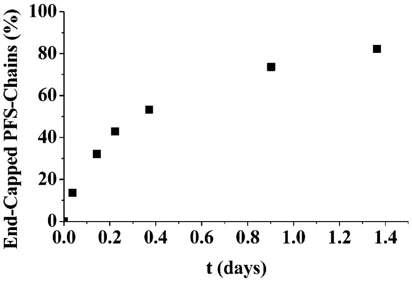
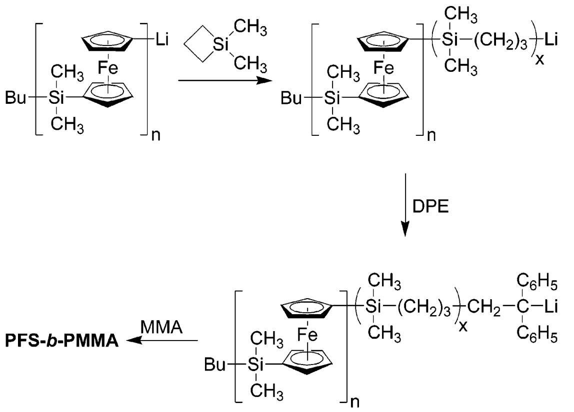


Figure 5. Percentage of DPE end-capped PFS precursors as a function of time (determined by measuring the DPE content in the reaction mixture using GC). The end-capping reaction was performed in THF at room temperature starting from living PFS oligomers (M_n: 4000 g/mol) with a 1.2 M excess of DPE with respect to the living PFS chain ends.

Scheme 4. 1,1-Dimethylsilacyclobutane-Mediated Living Anionic Synthesis of Poly(ferrocenylsilane-*b*-methyl methacrylate) Block Copolymers



ends. This auxiliar should guarantee faster conversion of the PFS chain termini—by preventing side reactions, such as PFS homocoupling—as well as accelerated subsequent addition of DPE. A very interesting potential candidate for solving this problem was reported first by Zundel et al., who used strained disilacyclopentane derivatives to convert potassium silanolate into a silyl anion.[45] This chain terminus was reported to be reactive enough to polymerize monomers like styrene or MMA in a living fashion. Unfortunately, the initiation efficiency of this system for the polymerization of MMA was fairly low. A similar approach was reported by Sheikh et al., who used 1,1-dimethylsilacylobutane as a “carbanion pump”, forming a carbanionic species from potassium *tert*-butyl alcoholate.[46] The resulting carbanion could be trapped efficiently with 1,1-diphenylethylene (88%).[47] Encouraged by this promising literature data, the latter activation method was tested to achieve more efficient end-capping of the PFS chains with DPE.

Again, FS was polymerized until complete conversion was achieved, followed by simultaneous addition of DMSB and DPE in a 2/4 ratio related to the living chains (Scheme 4). A change in color to deep red was now observed within only a few minutes, indicating a very fast end-capping reaction. Then, a solution of MMA and LiCl in THF was added to the resulting deep red solution at −78 °C. After 75 min reaction time, the reaction mixture was quenched by adding methanol, and the whole polymer was precipitated in methanol and subsequently analyzed using NMR and SEC. Figure 6 shows the SEC trace of a PFS precursor, end-capped with DMSB and DPE, as well as the corresponding trace of the obtained FS−MMA block copolymer. It is evident that approximately 90% block efficiency could be achieved in this manner when optimum reaction conditions were adhered to.

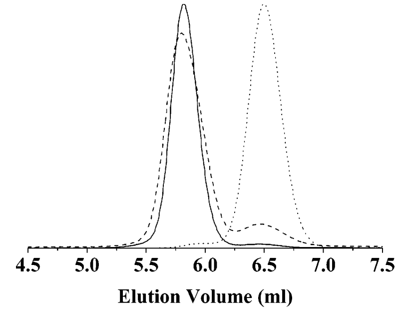


Figure 6. SEC traces obtained from a representative block copolymer synthesis according to Scheme 4 using 1,1-dimethylsilacylobutane as blocking accelerator (dashed line). The dotted line corresponds to the polyferrocenylsilane precursor and the solid line to the PFS-*b*-PMMA block copolymer finally obtained after selective precipitation from THF/hexane.

Table 3. Experimental Data for Poly(ferrocenylsilane-*b*-methyl methacrylate) Block Copolymers

sample[a]	w(PFS)	M_n(g/mol)[b]	PDI
PFS$_{27}$PMMA$_{73}^{68}$	0.27	68 300	1.05
PFS$_{39}$PMMA$_{61}^{85}$	0.39	84 500	1.03
PFS$_{42}$PMMA$_{58}^{41}$	0.42	41 000	1.08
PFS$_{47}$PMMA$_{53}^{27}$	0.47	27 100	1.08

[a] The subscript denotes the weight-fractions w of each component in %; the superscript denotes the overall molecular weight in kg/mol [b] Determined using SEC in THF vs PMMA standards.

To conclude, approximately 90−95% of the living PFS precursor chains lead to the desired PFS-*b*-PMMA block copolymers under optimum conditions, while the remaining 5−10% die either due to spontaneous chain termination or homocoupling. Despite much effort, no further reduction of this latter fraction could be achieved so far. Hence, last traces of PFS homopolymer have to be removed afterward by selective precipitation of the block polymers. Advantage can be taken here of the fact that the solubility of PMMA is quite different from that of PFS: while PMMA readily dissolves in polar solvents like THF, acetone, or ethyl acetate, PFS is additionally soluble in less polar solvents like cyclohexane or mixtures of THF and hexane. Hence, selective precipitation of the block copolymers was achieved by redissolving the material in THF, followed by slow addition of *n*-hexane, which is not a solvent for PMMA. As proved by SEC (Figure 6), the PFS precursor efficiently can be removed from the block copolymer by this way. Applying this method, a series of very pure and really high-molecular-weight PFS-*b*-PMMA block copolymers could be obtained for the first time. Data of representative samples of these materials are given in Table 3.

Details of DMSB-Mediated End-Capping. When it became clear that the DMSB-mediated end-capping reaction is the method of choice for the preparation of PFS-*b*-PMMA block copolymers (and maybe for many further PFS-based block copolymers), we studied the characteristics of this process in more detail. Some key results will be outlined in the following.

First of all, we were interested in learning more about the reactivity and the stability—as well as about potential side reactions—of the DMSB/DPE-end-capped PFS chains prior to MMA addition. Therefore, we tried to

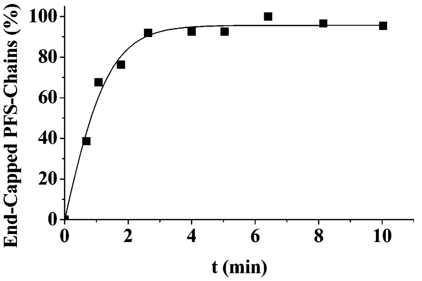
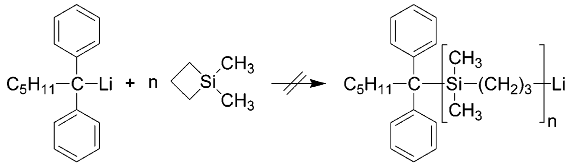


Figure 7. Percentage of DPE end-capped PFS precursors as a function of time for DMSB-mediated end-capping in THF and room temperature; [n-BuLi]/[DMSB]/[DPE] = 1/2/4; for details, see text. The values were determined by following the unreacted DPE content in the living polymer solution with GC.

Scheme 5. Potential Homopolymerization of 1,1-Dimethylsilacylobutane, Initiated by 1,1-Diphenylhexyllithium



homopolymerize DMSB in THF, using 1,1-diphenylhexyllithium (DPHLi) as a model initiator instead of the living DPE end-capped PFS (Scheme 5).

In agreement with our expectations it was found that no polymerization occurs according to Scheme 5. This allows the conclusion that also in the case of the living PFS chains no further addition of DMSB can occur as soon as a first anionic DPE end group is formed. This is of considerable importance for the homogeneity of block copolymer formation because otherwise DMSB chain termini could be present in the reaction mixture after completed end-capping. Such strongly nucleophilic chain termini would presumably decompose in the presence of THF and will definitely undergo nucleophilic attack on the MMA's carbonyl group—both leading to irreversible termination of the precursor.

The kinetics of DMSB-mediated end-capping was also investigated. As an example, Figure 7 shows the percentage of end-capped PFS precursor chains plotted vs time. The experimental data required for this plot were obtained by monitoring the concentration of DPE in the reaction mixture as a function of time using GC. This information is sufficient to calculate the respective part of end-capped PFS chains because DPE adds exactly once to a living PFS chain—as we could prove in the foregoing experiment. From Figure 7 it is obvious that end-capping is dramatically accelerated by DMSB, and more than 95% of the PFS chains bear living DPE termini after 5 min already.

To prove the exact constitution of the terminated end-capped PFS chains, a PFS oligomer ($M_n \approx 3000$ g/mol) was end-capped as described above for the kinetic studies. Subsequently, it was analyzed using MALDI–TOF mass spectrometry (Figure 8).

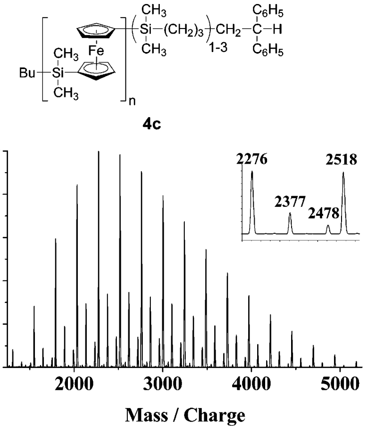


Figure 8. Analysis of PFS chain-end structure after DMSB-mediated DPE end-capping in THF and room temperature ([n-BuLi]/[DMSB]/[DPE] = 1/2/4) using MALDI–TOF mass spectrometry; $m_{\text{peak}} = m(n\text{-butyl}) + n \times m(\text{FS}) + (1, ..., 3) \times (\text{DMSB}) + m(\text{DPE}) + m(\text{H}) = 57.11$ g/mol $+ n \times 242.17$ g/mol $+ (1, ..., 3) \times 100.23$ g/mol $+ 180.25$ g/mol $+ 1$ g/mol.

Three distinct distributions can be clearly identified. They can all be assigned to readily DPE end-capped PFS chains, having one, two, and three opened DMSB units between the last FS moiety of the precursor chain and the DPE terminus. Virtually no other distributions that for example would point toward a spontaneous termination reaction of the living PFS chains during the functionalization reaction could be detected in this analysis. Consequently, these results support the picture of the DMSB-mediated DPE end-capping of living PFS chains as a nearly quantitative reaction.

Conclusions

Very pure FS monomers and DMSB-mediated DPE end-capping allow the production of living PFS precursors readily activated for block copolymerization with PMMA. Really high-molecular-weight PFS-*b*-PMMA block copolymers are thus available (molar masses from 30 000 to 85 000 g/mol in this work) with PDIs < 1.1 and different PFS contents. The thermal properties and the phase behavior of the new polymers are presently under investigation and will be reported in a subsequent paper.

Experimental Section

Equipment. Unless otherwise noted, all manipulations were carried out using either a MBraun glovebox equipped with a refrigerator or an all-glass high-vacuum line equipped with Teflon valves and a removable four inlet glass reactor. Both were operated with prepurified nitrogen. The preparation of polymeric precursors and other reagents and solutions involved the use of ampules, also equipped with Teflon valves, which can be directly attached to the reactor.

Materials. n-Butyllithium (n-BuLi) (Aldrich, 1.6 and 2.5 M solution in hexane) was used as received. Tetrahydrofuran (THF) and diethyl ether were purified by distillation from deep purple sodium benzophenone. Hexane was distilled from sodium metal. While THF and hexane were stored over red 1,1-diphenylhexyllithium (DPHLi), diethyl ether was used directly. Dichlorodimethylsilane (Aldrich, 99%) was distilled and carefully degassed in order to remove dissolved HCl. Ferrocene (Aldrich, 98%) was purified by recrystallization from hexane. *N*,*N*,*N*′,*N*′-Tetramethyethylenediamine (TMEDA) (Aldrich, 99.5%) was distilled over CaH_2 (Fluka, ≥95%). Methyl methacrylate (MMA) (Aldrich, 99%) was first dried by stirring over CaH_2. After distillation it was titrated further with a small amount of triethylaluminum (Aldrich, 1.0 M solution in hexane) until a slight yellowish color appeared and then stored in the glovebox refrigerator at −20 °C. Just prior to use it was condensed in vacuo and kept in liquid nitrogen in order to avoid autopolymerization. Lithium chloride (LiCl) (Aldrich, 99%) was dissolved in a small amount of purified THF and placed into an ampule. After removing the THF in vacuo, the ampule was carefully heated out under high vacuum and then stored in the glovebox. For purification of the 1,1-diphenylethylene (DPE) (Acros, 99%), a small amount of n-BuLi was added until a deep red color appeared and distilled via a short-path distillation apparatus under high vacuum. The DPE purified and degassed in this manner was divided into small portions and stored in the glovebox refrigerator until used. 1,1-Dimethylsilacyclobutane (DMSB) (Fluka) was stirred over CaH_2, degassed, distilled, and stored in the glovebox. Methanol was dried by refluxing over magnesium metal in an atmosphere of N_2, distilled, and carefully degassed by repeated freeze−pump−thaw cycles.

Methods. Quantitative SEC analysis was performed with THF as the mobile phase at a flow rate of 1 mL/min on a modular setup consisting of a Waters model 515 pump, a Waters model 410 refractive index (RI) detector, and a three-column set (PSS−SDV−gel; 5 μm, 10^6, 10^5, 10^4 Å). Molecular weight determination was carried out with respect to PMMA standards (purchased from PSS Polymer Standards Service GmbH, Mainz, Germany). The reliability of applying PMMA standards as calibrants for PFS homopolymers as well as for PFS-*b*-PMMA block copolymers was tested in advance. For this purpose a series of narrowly distributed PFS homopolymers (PDI: < 1.1, molecular weight range: 10 000−30 000 g/mol) were synthesized and subsequently analyzed by multiple laser-light-scattering (MALLS). The detector used was a Wyatt Technologies DAWN EOS light-scattering detector integrated in the modular SEC setup described above. The detector was calibrated using pure toluene assuming a Rayleigh ratio of 9,-78 $\times 10^{-6}$ at 690 nm. The d*n*/d*c* for PFS was taken from literature[38] as 0.196 mL/g (for 23 °C in THF at 633 nm), neglecting the wavelength dependency of the scattering intensity. The thus-measured absolute weights (M_w) were compared with the corresponding data obtained by RI detection using PMMA standards. The deviation was found to be less than 10% in the whole molecular weight range tested. Qualitative SEC reaction tracing as well as the determination of the amount of coupled byproduct were performed using an SDV-linear-S column (5 μm, PSS).

Gas chromatography (GC) experiments were performed on a Fisons Instruments GC 8160, equipped with a Supelco SPB-5 column and an AS 800 autosampler. *n*-Decane was used as the internal standard.

MALDI−TOF MS spectra were recorded on a Kratos Kompact MALDI 3 instrument operating with a 20 kV acceleration voltage in linear mode. The irradiation source was a pulsed nitrogen laser delivering 3 ns pulses at a wavelength of 337 nm. The instrument was calibrated with PEO standards. For sample preparation 4 mg of the polymer were dissolved together with 10 mg dithranol in 1 mL THF. 1 μL of this solution was placed on the sample holder and allowed to evaporate in air. All measurements were performed without addition of salt. ^{1}H NMR spectra were recorded on a Bruker AC300 operating at 300 MHz.

Synthesis and Purification of [1]Dimethylsilaferrocenophane (FS). The two-step synthesis of the monomer was carried out with some modification with respect to the literature procedures.[28,39,40] This particularly concerns the purification of the final product.

Ferrocene (13 g, 70 mmol) was initially placed in a Schlenck flask which was sealed with a rubber septum and then carefully evacuated and purged with nitrogen. After complete dissolution, *n*-BuLi (62 mL, 0.155 mmol, 2.5 M in hexane) was added at room temperature via syringe, followed by the addition of TMEDA (23 mL, 152 mmol) over a period of 15 min. The resulting red solution was stirred at room temperature for 24 h while an orange precipitate of the highly pyrophoric 1,1′-dilithioferrocene−TMEDA complex was formed which was filtered using a nitrogen-flushed glass-sintered crucible. After washing with two portions of hexane and drying in vacuo, 16.4 g (75%) of product was obtained.

In a glovebox, the 1,1′-dilithoferrocene·TMEDA complex (16 g, 48 mmol) was transferred into a Schlenck flask. After sealing it with a rubber septum it was brought outside, and 450 mL of dry diethyl ether was added. Under constant purging with nitrogen, the suspension was cooled to −78 °C, and freshly purified dichlorodimethylsilane (7.6 mL, 63 mmol) was added dropwise with a syringe over a period of 10 min. The reaction mixture was allowed to reach room temperature overnight, while at about −60 °C the color of the solution started changing to red due to the formation of the bridged ferrocene and a white precipitate of LiCl. The ether was evaporated in vacuo, and the resulting residue was dried under vacuo for 1 day in order to remove TMEDA and excess dichlorodimethylsilane. The residue was redissolved in hexane to remove the LiCl. After filtering this suspension under nitrogen and evaporating the hexane at room temperature, the remaining red [1]dimethylsilaferrocenophane was dried again under vacuum for 1 day. The isolated material still contained some impurities, mainly oligomers. Therefore, it was sublimed at 10^{-3} mbar in a 40 °C oil bath. The yield was 10.4 g (84%).

To obtain highly pure monomers suitable for anionic polymerization, the material needed to be purified further. The procedure involved recrystallization from hexane at −60 °C under an atmosphere of nitrogen, followed by dissolving in THF and stirring this solution over CaH_2 for 1 day. After evaporating the THF and a final sublimation from the dried residue the complete purification cycle was repeated once again. Highly pure monomers (4.5−5 g, 36 to 40%) were isolated by this way. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.48$ (s, 6H, Me), 4.06 (m, 4H, Cp), 4.53 (m, 4H, Cp).

Optimized Procedure for PFS Homopolymer Formation. All FS homopolymerizations were performed in the glovebox at room temperature using ampules. In a typical polymerization experiment highly pure FS (1.5 g, 6.19 mmol), dissolved in THF (20 mL), was initiated by fast addition of *n*-BuLi (1.6 M in hexane, 47 μL, 0.075 mmol). A change in color from red to amber was observed during the polymerization, indicating consumption of the monomer. After 30 min the living PFS chains were terminated with a few drops of degassed methanol and precipitated in methanol. The yield was quantitative. SEC (RI detection, PMMA-calibration): M_n: 21 000 g/mol; PDI: 1.06. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 0.47$ (s, 6H, CH_3) 4.02 (m, 4H, Cp) 4.23 (m, 4H, Cp).

Optimized Procedure for the Synthesis of PFS-*b*-PMMA Block Copolymers. In a representative example FS (1.5 g, 6.19 mmol) was polymerized in 20 mL of THF by addition of *n*-BuLi (50 μL, 0.08 mmol, 1.6 M in hexane) to give a living PFS precursor with $M_n = 18\,000$ g/mol and PDI = 1.08. After complete conversion of the monomer DPE (56 μL, 0.32 mmol) was added immediately, followed by DMSB (21 μL, 0.16 mmol; [*n*-BuLi]/[DMSB]/[DPE] = 1/2/4). A change in color from amber to deep red within 5 min indicated a fast end-capping reaction. In a second ampule dry LiCl (34 mg, 0.8 mmol) was dissolved in THF (30 mL). Both ampules were attached to the polymerization reactor, and after combining the solutions the reactor was immersed into a liquid nitrogen/2-propanol bath at −78 °C. For the polymerization of the second block, MMA (1.8 g, 18 mmol) was rapidly introduced from a syringe into the reactor through a Teflon-coated silicon septum under vigorous stirring. The deep red color of the living end-capped PFS precursor disappeared immediately, indicating a fast initiation of the MMA block polymerization. The polymerization was finally terminated after stirring the solution for 75 min at −78 °C by adding degassed methanol. After precipitating in methanol and drying under vacuum, 3.3 g (98.5%) of crude PFS-*b*-PMMA was isolated. As this material still contained about 10% of PFS homopolymer, the pure diblock copolymer was selectively precipitated. Therefore, the crude product was dissolved in THF (200 mL). After complete dissolution, hexane (200 mL) was added dropwise until the pure diblock started to precipitate. The precipitate was isolated by ultracentrifuging for 7 min at 4000 U/min. This procedure allows nearly quantitative separation of the pure diblock copolymer from the PFS homopolymer. SEC (RI detection, PMMA calibrants): M_n: 41 000 g/mol; PDI: 1.08. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 0.47$ (s, 6H, CH_3), 0.7−1.05 (2m, 3H, CH_3, PMMA), 1,7−1,95 (m, CH_2 and CH, PMMA), 3.58 (s, 3H, OCH_3, PMMA), 4.02 (m, 4H, Cp), 4.23 (m, 4H, Cp).

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