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Enlarging the Toolbox: Epoxide Termination of Polyferrocenylsilane (PFS) as a Key Step for the Synthesis of Amphiphilic PFS–Polyether Block Copolymers

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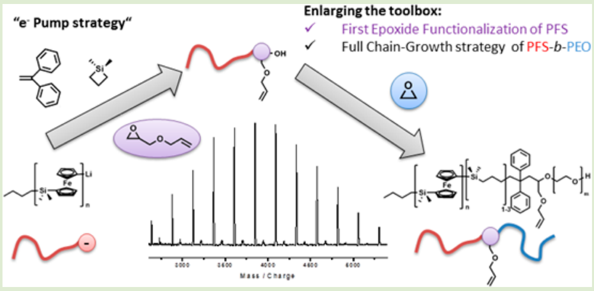
Supporting Information



ABSTRACT: Epoxide termination and functionalization of living poly(ferrocenyldimethylsilane) (PFDMS) is introduced by precapping the living PFDMS with a 4/2 molar mixture of 1,1-diphenylethylene and 1,1-dimethylsilacyclobutane acting as a "carbanion pump" system. Subsequent addition of allyl glycidyl ether (AGE) leads to quantitatively functionalized PFDMS–AGE polymers with molecular weights between 1500 and 15 400 g mol^{-1} and polydispersity indices ≤1.10, carrying one hydroxyl group and an additional allylic double bond. PFDMS–AGE was then applied as a macroinitiator for the living anionic ring-opening polymerization of ethylene oxide (EO) to generate amphiphilic and water-soluble poly(ferrocenyldimethylsilane-*b*-ethylene oxide) block copolymers with a low polydispersity index. All polymers have been characterized by ^{1}H NMR spectroscopy, DOSY ^{1}H NMR spectroscopy, size exclusion chromatography (SEC), and MALDI-ToF mass spectrometry. In addition, for the characterization of the morphology of the PFDMS-*b*-PEO block copolymers transmission electron microscopy (TEM) was performed in methanol, confirming the formation of cylindrical micelles with an organometallic core and polyether corona.

Metals are often the determining component of materials with magnetic, conductive, redox-active, and catalytic properties. Modern polymer science allows the precise synthesis of "soft materials" with metals incorporated in the structure. As early as 1955 at the DuPont company, poly(vinyl ferrocene) (PVfc) was synthesized to combine the advantages of polymers and inorganic solids. This opened the field of metal-containing polymers.[1] However, for a long time no well-defined polymers with high molecular weights could be achieved, due to low solubility, side reactions, or stability problems.[2−6] With the discovery of the ring-opening polymerization (ROP) of the ansa-metallocenophanes by Manners and co-workers, ferrocene-based (fc) polymers turned out to be no longer an academic curiosity.[7] Nowadays fc-containing polymers represent key materials in this research area, and fc-units can be incorporated in the polymer backbone or in the side chains for sensing, catalytic, or biomedical applications.[8−10]

Main-chain fc-containing polymers are of special interest due to their electrochemical properties and ability to control aggregation phenomena in bulk and solution.[11,12]

In 2007, Wang et al. discovered the first cylindrical block comicelles with narrow size distribution in analogy to a living chain growth polymerization mechanism by adding subsequently different poly(ferrocenyldimethylsilane) (PFDMS) block copolymers to a nonsolvent for PFDMS, leading to an epitaxial growth of the micelle due to crystallization of the PFDMS segment.[13] Recently, this modular system was expanded to the unidirectional growth of cylindrical micelles.[14] All these constructs, however, are currently only possible in organic (and mostly nonpolar) solvents.

To date, only few reports deal with the preparation of water-soluble fc-containing polymers. These approaches often rely on the introduction of hydrophilic segments or side chains.[15−17] The combination of fc-based polymers with epoxide-based monomers was not reported until recently. Our group introduced an fc-containing epoxide monomer, i.e., ferrocenyl glycidyl ether (fcGE), and copolymerized it with ethylene oxide (EO) to generate poly(ethylene oxide)s (PEO) carrying fc in the side chains. A variety of different molar ratios have been synthesized, leading to electroactive, thermoresponsive, and also water-soluble (up to 10 mol % incorporation of fcGE) polymers.[18] However, it has not been possible to combine PFDMS as a main-chain fc-containing polymer with the

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modular and well-established anionic ring-opening polymerization of epoxides.

Manners and co-workers devised different synthetic strategies to obtain PFDMS-*b*-PEO block copolymers. The first approach utilizes a Si−H end-functionalized methoxy-PEO as a macroinitiator for the Pt(0) (Karstedt's catalyst)-catalyzed ROP of dimethylsila[1]-ferrocenophane (FDMS), leading to—unlike most other PFDMS copolymers—spherical micelles in an aqueous solution.[19] By using a four-arm Si−H-functionalized PEO star polymer, Schacher et al. recently synthesized $[(\text{PEO-}b\text{-PFDMS})]_4$ star-block copolymers and studied their self-assembly behavior.[20] A different strategy relies on polymer coupling reaction, i.e., the combination of two functionalized homopolymers of PEO and PFDMS via a bis(terpyridine)-ruthenium(II) complex. In contrast to the previously observed spherical micelles, these authors found rod-like structures.[21] Very recently, Manners, Winnik, and co-workers enlarged the coupling methods by synthesizing terminal alkyne-functionalized PFDMS. Via copper-catalyzed "click" chemistry, a variety of block copolymers are accessible.[22]

Gallei and Frey et al. developed a strategy for the synthesis of PVFc-*b*-PEO block copolymers and PVFc-$(\text{PEO})_2$ miktoarm star polymers. Living anionic polymerization of VFc allowed quantitative termination functionalization with benzyl glycidyl ether (BGE), generating one free hydroxyl group and a second protected one. Subsequent ROP of EO leads to the block copolymer (prior to hydrogenolysis) or to miktoarm star polymers after hydrogenation.[23]

The current work describes the first quantitative end functionalization of PFDMS generated by living anionic polymerization with an epoxide, namely, allyl glycidyl ether (AGE). Direct epoxide termination of living PFDMS is not possible (Scheme 1, **3**) because the living PFDMS species is not capable of ring opening the epoxide. As detailed studies have shown, only protonated PFDMS is obtained after workup (see Supporting Information, Figure S 5). To overcome this problem and further activate the living PFDMS chain end, the so-called "carbanion pump" system was introduced prior to AGE termination.[24,25] 1,1-Dimethylsilacyclobutane (DMSB) can be easily attacked by molecules with limited nucleophilicity, such as living PFDMS, generating a very reactive terminal organolithium species. To prevent the living chain end from being proton terminated, the reactivity has to be adjusted by the introduction of 1,1-diphenyl ethylene (DPE). Furthermore, the living DPE-capped polymer chain cannot react with the remaining DMSB due to the sterical hindrance, but still with epoxide derivatives.

This termination strategy allows the introduction of two orthogonal functional groups at the PFDMS chain end and, more importantly, to combine carb- and oxyanionic polymerization to generate PFDMS−polyether block copolymers for the first time in a complete and living chain growth manner (Scheme 1).

A series of AGE-terminated PFDMS homopolymers have been prepared by living anionic polymerization of FDMS, using a subsequent "quenching" sequence (Scheme 1). All polymerizations of FDMS were carried out in THF at room temperature in a nitrogen-filled glovebox. After full conversion of FDMS was reached, the living PFDMS was reacted simultaneously with a mixture of DPE and DMSB (Scheme 1, **3**).[25] A change of color from light orange to deep red indicates complete formation of the precapped PFDMS. The subsequent addition of the epoxide changed the color of the reaction solution to orange, again indicative of the desired termination reaction. The end-functional series of homopolymers prepared exhibited molecular weights in the range of 1500−15 000 g mol^{-1}, with polydispersity indices (PDI) below 1.10 (see Table 1, further characterization data can be found in the Supporting Information).

Scheme 1. Synthetic Strategy for PFDMS−AGE and Amphiphilic PFDMS−PEO Block Copolymers

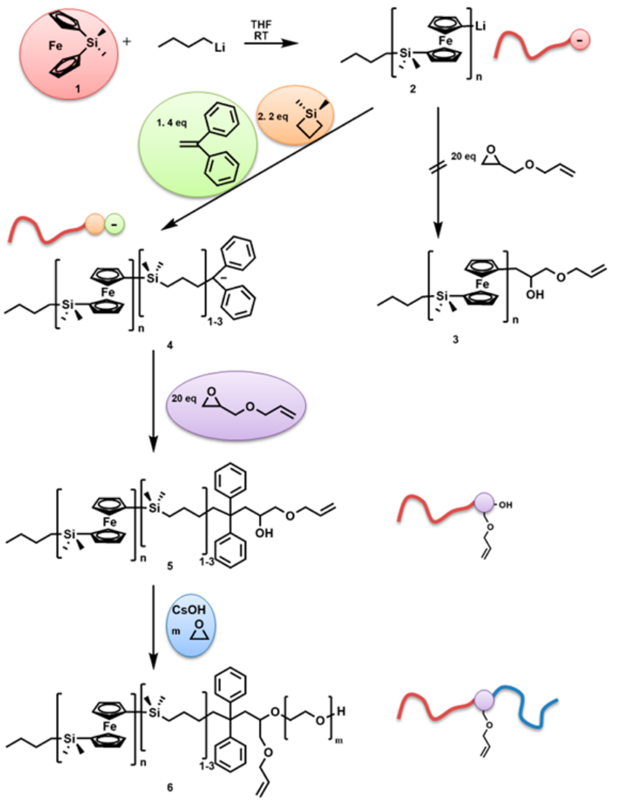

Table 1. Characterization Data for Homo- and Block Copolymers

no.	polymer[a]	M_n[a]	Mn[b]	PDI[b]
1	PFDMS_6−AGE	1500	1600	1.08
2	PFDMS_{14}−AGE	3400	3700	1.10
3	PFDMS_{28}−AGE	6800	9100	1.08
4	PFDMS_{64}−AGE	15400	16900	1.07
5	PFDMS_{14}−AGE-*b*-PEO_{186}	11600	6500[c]	1.10[c]

[a] Molecular weight in g mol^{-1}, calculated from ^{1}H NMR via end group analysis. [b] Number average and polydispersity index determined via size exclusion chromatography (SEC) in THF (vs PS standard). [c] Determined via SEC in DMF (vs PS standards).

To verify quantitative functionalization, different characterization methods were utilized. A very efficient tool for end group determination is high-resolution NMR spectroscopy, especially with a diffusion probe head. With this technique end group and polymer resonances can be distinguished with respect to the diffusion coefficient and integrated to calculate the degree of functionalization (Figure 1 shows the diffusion-ordered (DOSY) ^{1}H NMR spectrum). The horizontal axis displays the ^{1}H NMR spectrum (in benzene-d_6), while the vertical axis allows for determination of the diffusion coefficient. As a consequence of the terminal functionalization sequence

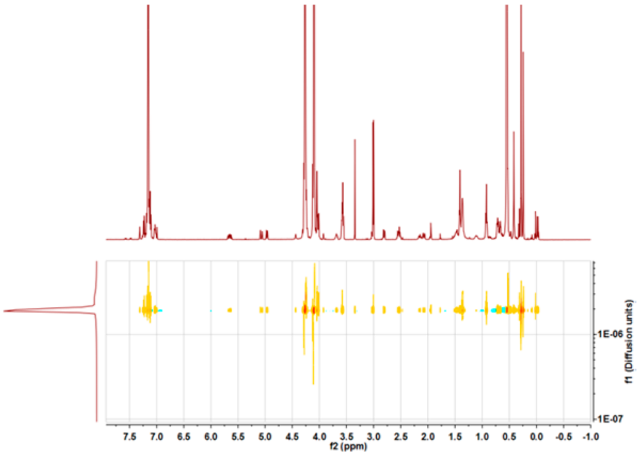

Figure 1. DOSY ^{1}H NMR spectrum (benzene-d_6, 700 MHz) of AGE-functionalized PFDMS (PFDMS−AGE #2), demonstrating that every signal belongs to the end-functional polymer.

several additional resonances can be distinguished in the ^{1}H NMR spectra in comparison to a proton-terminated PFDMS homopolymer (fc signals at 4.1 and 4.3 ppm)—most importantly, the signals of the terminal allyl group at 5.0 and 5.7 ppm. All ^{1}H NMR resonances can be assigned to the same diffusion signal at 1.93×10^{-6} m^2/s proving that the end group is attached to the PFDMS with the same molecular weight. Full signal assignment was achieved by the combination of the ^{1}H with the ^{13}C-HSQC NMR spectrum (Figure S 3, Supporting Information).

Conclusive evidence for quantitative termination of the functionalized PFDMS−AGE polymer samples (#1−4, Table 1) is gained by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS). Each signal of the resulting spectrum can be assigned to AGE-terminated polymer chains.

Figure 2 shows the MALDI-ToF mass spectrum of polymer sample #2. The main distribution marked in red can be attributed to the quantitatively functionalized polymer with 14 repeating units of the FDMS monomer (respective mass 3843 Da). The peaks of the small subdistribution have an increased molecular weight compared to the main distribution of 100 Da, which can be assigned to the AGE-functionalized polymer with two DMSB repeating units.

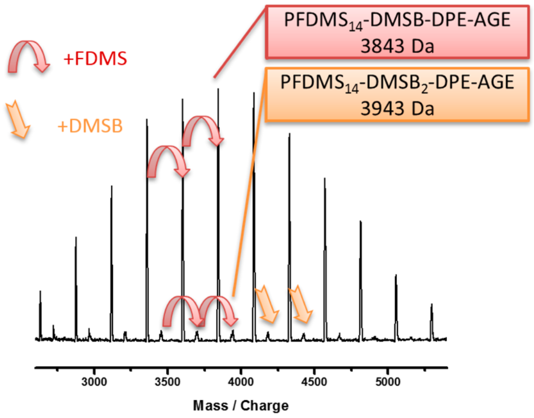

Figure 2. MALDI ToF MS spectrum of quantitative functionalized PFDMS−AGE (#2).

The quantitative end functionalization of PFDMS opens a new field for PFDMS chemistry in general. First of all, termination with any epoxide leads inevitably to a terminal hydroxyl group. Earlier, deprotection steps were necessary to generate terminal hydroxyl groups, which could be harmful to the PFDMS backbone, as reported before.[26] The generated hydroxyl group can be used for subsequent post modification or initiation of anionic or other, e.g., controlled radical polymerizations to generate PFDMS-based copolymers in a subsequent polymerization step. Furthermore, the use of functionalized glycidyl ethers offers a new access to multi- and heterofunctional PFDMS polymers, as demonstrated by the functionalization with AGE. As mentioned before, to demonstrate one possible application, the AGE-functionalized PFDMS has been used as a macroinitiator for the anionic ROP of EO. The hydroxyl group of PFDMS−AGE (#2, Table 1) was deprotonated with cesium hydroxide, and subsequent addition of EO leads to the formation of water-soluble, redox-active PFDMS−AGE-*b*-PEO block copolymer (#5, Table 1), still carrying an additional double bond at the block junction. The PFDMS−AGE-*b*-PEO block copolymer has been characterized by ^{1}H NMR, DOSY ^{1}H NMR, SEC, and transmission electron microscopy (TEM).

The increase in molecular weight detected by SEC and the appearance of the polyether resonances in the ^{1}H NMR spectrum (at 3.5 ppm) indicate successful formation of the targeted block copolymer. Conclusive evidence is gained from the DOSY ^{1}H NMR spectrum (shown in Figure 3). Clearly, the resonances of the fc groups at 4.3 and 4.1 ppm as well as the signals of the PEO backbone at 3.5 ppm can be detected at the same diffusion coefficient at 1.30×10^{-6} m^2/s, verifying complete block copolymer formation and the absence of any homopolymer (note that the second signal on the vertical axis belongs to the NMR solvent, benzene-d_6).

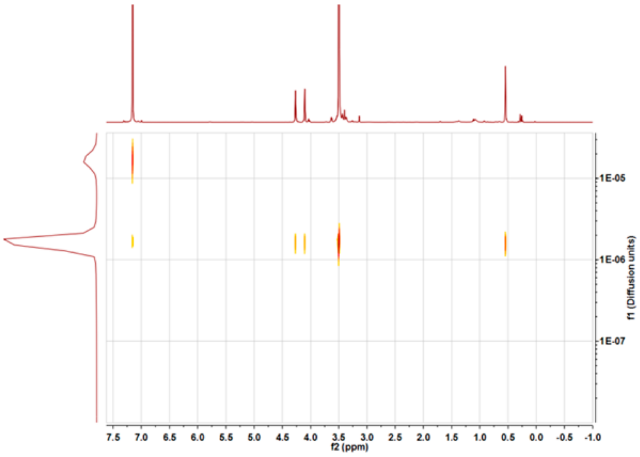

Figure 3. DOSY ^{1}H NMR spectrum (benzene-d_6, 500 MHz) of the PFDMS$_{14}$−AGE-*b*-PEO$_{186}$ block copolymer, verifying block formation.

Furthermore, preliminary studies on the self-assembly of the amphiphilic PFDMS−AGE-*b*-PEO block copolymers were accomplished via TEM (by drop-cast from an aqueous or a methanol solution). To this end, the respective block copolymer was directly dissolved in water or methanol ($c \approx 1$ g L^{-1}), and one drop of the solution was deposited on a carbon-coated copper TEM grid. The prepared TEM grid was dried under high vacuum overnight before recording the TEM images. Typical TEM images are shown in Figure 4. With the highly crystalline PFDMS-block forming the inner part of the aggregates, exclusively cylindrical micelles are obtained with a length in the range of approximately 400 nm for the aggregates from methanol and longer aggregates from water which are currently under further investigation.

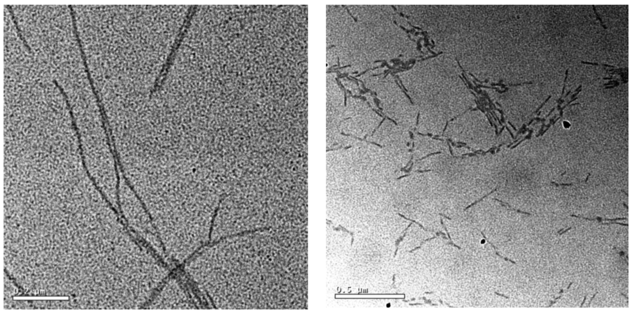

Figure 4. TEM images of the amphiphilic PFDMS-*b*-PEO block copolymer (#5, Table 1), prepared by drop-casting of an aqueous solution (left, $c \approx 1$ g L^{-1}) and of a methanol solution (right, $c \approx 1$ g L^{-1}); scale bar: 0.5 μm.

In summary, epoxide termination of PFDMS has been established as a key step for the preparation of well-defined and orthogonally functionalized PFDMS with low PDI by living carbanionic polymerization. Compared to the well-studied terminal functionalization of conventional vinyl monomers with different epoxide derivatives, direct termination is not possible for living PFDMS and leads to the coexistence of living PFDMS and unreacted epoxide.[27,28] To transfer the epoxide termination chemistry to living PFDMS the "electron pump" system established by Rehahn et al.[6,25] had to be introduced prior to termination, leading to quantitative end functionalization. Use of AGE as the termination agent introduces two different terminal functionalities, an allylic double bond and a hydroxyl group. This robust synthetic protocol allows for a large variety of further post modifications, some of which are currently under investigation. In addition, the AGE-functionalized PFDMS has been used as a macroinitiator for the living anionic ROP of ethylene oxide to generate a well-defined, water-soluble PFDMS-*b*-PEO block copolymer. Further studies on other functionalization sequences as well as the aggregation behavior of PFDMS-*b*-PEO with different block ratios in combination with other PFDMS block copolymers are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures as well as analytical and spectral characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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