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Silacyclobutane-Mediated Re-Activation of "Sleeping" Polyvinylferrocene Macro-Anions: A Powerful Access to Novel Metalloblock Copolymers

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ABSTRACT: Little advantage has been taken so far of the manifold promising options provided by the living anionic polymerization of vinylferrocene. The major reason is that the propagating polyvinylferrocene (PVFc) chains suffer loss of reactivity in the oligomeric state already, and even can change into a "sleeping" mode prior to complete monomer consumption. Formation of broadly distributed and/or constitutionally inhomogeneous products is the consequence. Here we report on the efficient reactivation of the deactivated or sleeping PVFc macro-anions by their simultaneous treatment with 1,1-dimethylsilacyclobutane and 1,1-diphenylethylene. We demonstrate the efficiency of this procedure by synthesizing PVFc-based diblock copolymers with poly(methyl methacrylate) and poly(2-vinylpyridine), respectively, using sequential monomer addition protocols.

Introduction

Ferrocene-containing polymers attract much attention because of their unique mechanical, (electro)chemical, (opto)-electronic, and magnetic properties.[1−13] Plenty of synthetic strategies have been tested in order to provide broader access to polymeric metallocenes. However, there is still urgent need for more powerful living or controlled chain-propagation protocols, resulting in really well-defined and high-molecular weight products. Appropriate consideration of the complex reactivity profile of ferrocene-based monomers is one key to overcoming the highly persisting limitations. Manners' discovery of living ring-opening polymerization of *ansa*-metallocenophanes[14−16] and Pittman's[17−20] attempts in the field of anionic polymerization of ferrocenylmethyl (meth)acrylates—pioneering studies from the early 1970s which were further developed by us into a truly living methodology quite recently[21,22]—represent two of the still very scarce examples exhibiting success worth mentioning up to now. A third promising metallo-monomer, which is potentially highly useful in living polymerizations, is vinylferrocene (VFc). This is available in high yields and excellent purities by convenient syntheses, and was already proved to be polymerizable in the 1950s using free radical processes.[23] Moreover, random copolymers with e.g. styrene,[24] vinyl acetate,[24] *N*-vinylpyrrolidone,[25] *N*-vinylcarbazole,[26] methyl methacrylate,[24] maleic anhydride,[27] acrylonitrile,[24] and vinylanthracene[28] were prepared, and even TEMPO-mediated controlled radical VFc-polymerization has been shown to provide access to PVFc homopolymers and block copolymers.[29] In all these cases, however, average molar masses of above $M \approx 4000\ \mathrm{g \cdot mol^{-1}}$ are hardly accessible. ESR and Moesbauer spectroscopy indicate that the ferrocene moieties undergo redox reactions that affect the radical chain growth.[30−32] Moreover, further physical and chemical effects might limit proper radical chain growth in addition, and some of them might be similar to those discussed in the present paper.

Anionic VFc polymerization, on the other hand, was thought to be impossible for electronic reasons[33−35] until Burkhardt and Nuyken proved the feasibility even of that approach in the early 1990s. Narrowly distributed PVFc homopolymers as well as block copolymers with styrene, methyl methacrylate and propylene sulfide were described.[36,37] After that discovery, however, there was a break of 15 years in the literature on anionic PVFc synthesis. Balsara[38] and Faust[39−41] were the next who took advantage of that pioneering work: VFc block copolymers were synthesized with polyisoprene and polyisobutylene, respectively. Nevertheless, there are currently still fewer than ten serious papers in the open literature dealing with aspects of anionic VFc polymerization and characterization of the resulting products.

Careful reading of the published reports leads to the conclusion that hesitant application of anionic VFc polymerization is primarily because this reaction suffers from severe drawbacks and limitations: as long as the growing species are in the oligomeric state, for example, chain propagation proceeds rapidly and smoothly, with almost quantitative monomer conversion. However, the rate of chain propagation collapses as soon as the molar mass of the growing macro-anions exceeds values of around $M \approx 3000-5000\ \mathrm{g \cdot mol^{-1}}$. Finally, in the molar-mass regime above $M \approx 8000\ \mathrm{g \cdot mol^{-1}}$, chain propagation stops completely prior to quantitative monomer conversion—though the chains are unambiguously still "alive". In entries targeted to PVFc's of $M \approx 9000\ \mathrm{g \cdot mol^{-1}}$, for example, propagation already typically stops after a monomer consumption of 75%, but chain growth restarts instantaneously if additional VFc monomer is added to the reaction mixture.[36,37] Facing strange features like this, the lack of reports describing high-molecular-weight PVFc homopolymers or even well-defined block copolymers containing larger PVFc segments is hardly a surprise.

In the course of our studies dealing with anionic VFc polymerization, we have been able to reproduce all of the above characteristics. On the basis of careful analysis of the observed features, we have postulated a working hypothesis rationalizing why the initially rapidly growing PVFc oligomers change into less reactive states with increasing chain lengths and reaction times, and why they end in an essentially inactive—though still living—state, which we call "sleeping" in the following. On the basis of

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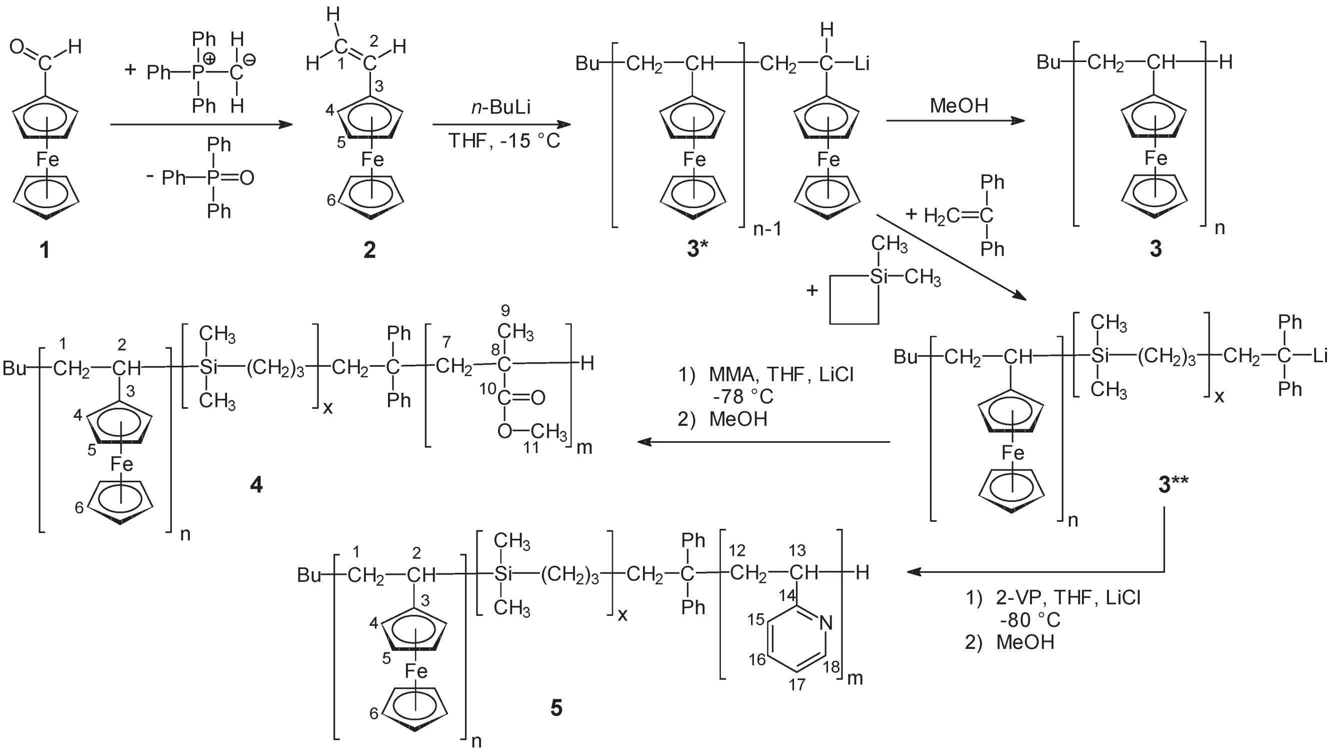
Scheme 1. Overview of the Syntheses Studied in This Work



this hypothesis, we have been trying to identify efficient measures allowing smooth and quantitative reactivation of the PVFc macro-anions for subsequent conversion in, e.g., block copolymer syntheses.

Recently, we demonstrated that the so-called "carbanion-pump" technique is a powerful tool for the preparation of well-defined block copolymers from polyferrocenylsilane (PFS) macro-anions, which also suffer from insufficient reactivity in some block copolymer syntheses:[42−48] mixtures of 1,1-dimethylsilacyclobutane (DMSB) as the activating species and 1,1-diphenylethylene (DPE) as the end-capping agent were added to the PFS macro-anions prior to the second monomer. Since exciting results were obtained for PFS, we decided to analyze whether similar improvements are also feasible for the "sleeping" PVFc macro-anions. In the present paper, we report on the benefits offered by that carbanion-pump technique when adapted to the synthesis of PVFc-based diblock copolymers with poly(methyl methacrylate) (PMMA) and poly(2-vinylpyridine) (P2VP) as the respective second blocks.

Experimental Section

Materials. All chemicals and solvents were purchased from Acros, Aldrich and Strem chemical companies. Ferrocene carbaldehyde (p.a. grade) was purchased from Sigma-Aldrich chemical company and used as received. Methyl methacrylate (MMA) and 2-vinylpyridine (2 VP) were purified by 2-fold distillation over calcium hydride. In the case of MMA, triethyl aluminum (25 wt % in hexane) was subsequently added dropwise until a permanent yellowish color appeared. Prior to use, the monomers were freshly distilled from those solutions. 1,1-Diphenylethylene (DPE) was distilled after titration with *n*-BuLi from the deeply red solution. 1,1-Dimethylsilacyclobutane (DMSB) was stirred over CaH_2, distilled, and stored in a glovebox at −15 °C. THF and lithium chloride were dried and deoxygenated following standard procedures. Deuterated solvents were purchased from Deutero GmbH, Kastellaun, Germany.

Methods. All syntheses were carried out under an atmosphere of purified nitrogen or argon, using Schlenk technique or a glovebox equipped with a Coldwell apparatus. NMR spectra were recorded using a Bruker ARX 300 NMR spectrometer working at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR), and on a Bruker DRX 500 NMR spectrometer working at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). NMR chemical shifts are given relative to tetramethylsilane, the signal assignment was carried out according to the numbering of protons and carbons as specified in Scheme 1. Standard SEC was performed with THF as the mobile phase (flow rate 1 mL·min^{-1}) on a Mixed Gel column set from PL (PL Mixed Gel B, PL Mixed Gel C, PL Mixed Gel D) or an SDV column set from PSS (SDV 1000, SDV 100000, SDV 1000000) at 30 °C. Calibration was carried out using polystyrene (PS; from Polymer Standard Service (PSS), Mainz) and PVFc (self-made) calibration standards. For the SEC−MALLS experiments, a system composed of a Waters 515 pump (Waters, Milford, CT), a TSP AS100 autosampler, a Waters column oven, a Waters 486 UV detector operating at 254 nm, a Waters 410 RI-detector, and a DAWN DSP light scattering detector (Wyatt Technology, Santa Barbara, CA) was used. For data acquisition and evaluation of the light-scattering experiments, Astra version 4.73 (Wyatt Technology, Santa Barbara, CA) was used. The light-scattering instrument was calibrated using pure toluene, assuming a Rayleigh ratio of 9.78×10^{-6} cm^{-1} at 690 nm. An injection volume of 118 μL, a sample concentration of 1−2 g·L^{-1}, a column temperature of 35 °C, and a THF flow rate of 1 mL·min^{-1} was used, and SEC analysis was performed on a high resolution column set from PSS (SDV 5 μm 10^6 Å, SDV 5 μm 10^5 Å, SDV 5 μm 1000 Å). DSC measurements were carried out using a Mettler-Toledo DSC822^e equipped with a TSO801R0 autosampler. A scan rate of 5 K·min^{-1} was employed. T_g values were determined from the inflection points of the change in heat capacity. TEM experiments were carried out using a Zeiss CEM 902 electron microscope operating at 80 kV. All shown images were recorded with a slow-scan CCD camera obtained from ProScan Inc. in bright field mode. Camera control was computer-aided using the Vario Vision software 3.2 from LEO. The sample preparation was carried out as described in the Results and Discussion. No staining was required.

Table 1. Comparison of M_n Values of PVFc Determined Using SEC in THF, Once Calculated Using PS Calibration Standards and Once Determined Using MALLS Detection[a]

PVFc molar mass (in g·mol^{-1}) determined using PS standards	1000	1550	3200	5100	6800
PVFc molar masses (in g·mol^{-1}) determined using MALLS	1000	4150	7500	9600	9900

[a] A value of dn/dc = 0.186 was determined for the PVFc homopolymers and used for MALLS evaluation. PVFc does not absorb at a wavelength of λ = 658 nm, which was used for MALLS detection, but absorbs at $\lambda \leq 550$ nm only.

Vinylferrocene (VFc), 2. In a dry 1 L Schlenk flask equipped with a rubber septum and a stirring bar, a suspension of 12.3 g (31.6 mmol, 1.35 equiv) methyltriphenylphosphonium iodide (crystallized from isopropanol) and dry THF (350 mL) is cooled at −60 °C. A solution of *n*-butyl lithium (*n*-BuLi) in hexane (1.6 *M*, 57.3 mL, 35.8 mmol, 1.53 equiv) is added dropwise over a period of 10 min. The orange solution is allowed to warm up to room temperature and stirred further for approximately 15 min. When all solid material is dissolved, the solution is cooled at −60 °C again. Ferrocene carbaldehyde **1** (5.01 g, 23.4 mmol, 1 equiv), dissolved in dry THF (20 mL), is added slowly. The resulting solution is allowed to warm up to room temperature and stirred overnight. Diethyl ether (200 mL) is added, the mixture is washed with distilled water (5 × 200 mL) and dried (Na_2SO_4). After filtration, the solvent is removed, and the solid orange residue is dissolved in hexane and filtered over a pad of silica gel. After removal of the solvent, the obtained solid is sublimed (1×10^{-3} mbar, oil-bath temperature: 40 °C). Quite pure VFc (**2**) is obtained in 96% yield (4.77 g, 22.5 mmol). Prior to its polymerization, further purification is indicated: **2** is dissolved in dry hexane and stirred over CaH_2 at room temperature for 8 h. After removal of the solvent, the solid is sublimed (1×10^{-3} mbar, oil-bath temperature: 40 °C). The yield of highly pure monomer **2** is 89% (4.41 g, 20.8 mmol); ^{1}H NMR ($CDCl_3$): δ = 4.11 (s, 5H, H^6), 4.23 (t, 2H, H^5, J^3 = 1.73 Hz), 4.39 (t, 2H, H^4, J^3 = 1.73 Hz), 5.04 (d, 1H, H^{1a}, ^3J = 10.72 Hz), 5.35 (d, 1H, H^{1b}, ^3J = 17.52 Hz), 6.42 (dd, 1H, H^2, J^3 = 10.72 Hz (cis), J^3 = 17.52 Hz (trans)). ^{13}C NMR ($CDCl_3$): δ = 66.70 (C^4), 67.95 (C^3), 68.69 (C^5), 69.24 (C^6), 111.09 (C^1), 134.69 (C^2).

Polyvinylferrocene (PVFc), 3. In an ampule equipped with a stirring bar, pure VFc (**2**) is dissolved in dry THF. The solution is cooled to −15 °C, and the indicated volume of a solution of *n*-BuLi in hexane (1.6 M) is added quickly. After complete chain growth (see Table 1), the PVFc chains are terminated using degassed methanol, and the mixture is allowed to warm up to room temperature. The entry is poured into a 10-fold excess of methanol. The formed PVFc precipitates nearly quantitatively (yield depends on the targeted molar mass, see Table 1 for example), is collected by filtration, washed with methanol, and dried in vacuo. ^{1}H NMR ($CDCl_3$): δ = 0.80−2.70 (H^{1,2}), 3.65−4.55 (H$^{4-6}$). ^{13}C NMR ($CDCl_3$): δ = 33 (C^1), 43 (C^2), 67 (C^{4,5}), 68.5 (C^6), 95.5 (C^3).

DMSB-Mediated DPE-End-Capping of Living PVFc Anions. At −15 °C, DPE (2 equiv with respect to the living chains **3***) is added to the PVFc macro-anions, immediately followed by 1 equiv of DMSB. The resulting deeply red solution is stirred at −15 °C for 2 min and then allowed to warm up to room temperature. Now, it is ready to be used as macroinitiator for monomers like MMA or 2 VP.

Starting Materials Used for the Preparation of a DPE-End-Capped PVFc of $M_n \approx 3000$ g·mol^{-1}. VFc (**2**) (600 mg, 2.83 mmol), THF (15 mL), *n*-BuLi (1.6 *M* in hexane, 125 μL, 200 μmol, 1 equiv), DPE (71 μL, 400 μmol, 2 equiv), and DMSB (26 μL, 200 μmol, 1 equiv) were used.

Poly(vinylferrocene-*b*-methyl methacrylate) (PVFc-*b*-PMMA), 4. The solution of the DPE-end-capped PVFc macroinitiator is diluted with THF (20 mL) and cooled to −78 °C. A solution of LiCl in dry THF (0.142 *M*) is added (10 equiv. with respect to the living chain ends), followed by a precooled (−78 °C) solution of MMA in THF (1:1 v/v; to be added quickly). The reaction mixture is stirred at −78 °C for 2 h in order to ensure complete conversion. The active chains are terminated by degassed methanol, the mixture is allowed to warm up to room temperature and then poured into a 10-fold excess of *n*-hexane. The formed diblock copolymer precipitates quantitatively, is collected by filtration, washed with *n*-hexane, and dried in vacuo.

*Starting Materials Used for a Diblock Copolymer **4** of an Overall $M_n \approx 12000$ g·mol^{-1}, Composed of a 2500 g·mol^{-1} PVFc Block and a 9500 g·mol^{-1} PMMA Block.* VFc (**2**) (300 mg, 1.41 mmol), THF (10 mL), *n*-BuLi (1.6 M in hexane, 75 μL, 120 μmol); DPE (42 μL, 240 μmol, 2 equiv); DMSB (16 μL, 120 μmol,1 equiv); MMA (1.49 g, 14.89 mmol), THF (20 mL), and LiCl in THF (0.142 *M* in THF, 1.2 mmol, 5.2 mL, 5.9 equiv) were used.

Poly(vinylferrocene-*b*-(2-vinylpyridine)) (PVFc-*b*-P2VP), 5. The solution of the DPE-end-capped PVFc macroinitiator is diluted with THF (20 mL) and cooled to −80 °C. A solution of LiCl in THF (0.142 *M*) is added (10 equiv. with respect to living chain ends, followed by a precooled (−80 °C) solution of 2 VP in THF (1:1; to be added quickly). The reaction mixture is stirred at −80 °C for 2 h. Afterward, the active chain termini are terminated by degassed methanol, the mixture is allowed to warm up to room temperature and then poured into a 10-fold excess of *n*-hexane. The formed diblock copolymer precipitates quantitatively, is collected by filtration, washed with *n*-hexane, and dried in vacuo.

*Starting Materials Used for a Polymer **5** of an Overall $M_n \approx 10000$ g·mol^{-1}, Composed of a 1500 g·mol^{-1} PVFc Block and a 8500 g·mol^{-1} P2VP Block.* VFc (**2**) (290 mg, 1.37 mmol), THF (10 mL), *n*-BuLi (1.6 *M* in hexane, 121 μL, 193 μmol); DPE (68 μL, 386 μmol, 2 equiv); DMSB (25 μL, 193 μmol, 1 equiv); 2 VP (1.55 g, 14.74 mmol), THF (20 mL), and LiCl in THF (0.307 *M* in THF, 5.0 mL, 1.54 mmol, 7.98 equiv) were used.

*Starting Materials Used for a Polymer **5** of an Overall $M_n \approx 36000$ g·mol^{-1}, Composed of a 5000 g·mol^{-1} PVFc Block and a 31000 g·mol^{-1} P2VP Block.* VFc (**2**) (500 mg, 2.36 mmol), THF (15 mL), *n*-BuLi (1.6 M in hexane, 63 μL, 100 μmol); DPE (35 μL, 200 μmol, 2 equiv); DMSB (13 μL, 100 μmol, 1 equiv); 2 VP (3.10 g, 29.48 mmol), THF (35 mL), and LiCl in THF (0.307 *M* in THF, 3.2 mL, 0.982 mmol, 9.82 equiv) were used.

Results and Discussion

Monomer Synthesis. Two efficient pathways are known for the synthesis of VFc (**2**). One of them proceeds via dehydration of 1-ferrocenylethanol using aluminum oxide,[23] the other one starts from ferrocene carbaldehyde **1** and involves a Wittig reaction:[49] first, methyltriphenylphosphonium iodide is treated with *n*-BuLi, and the resulting ylide is then converted with ferrocene carbaldehyde **1** (Scheme 1). The latter approach was selected for our studies because it promised higher yields. Indeed, fairly pure vinylferrocene **2** was obtained in 96% yield using the standard recipe. However, additional purification proved to be indicated for successful anionic polymerization: hence, **2** was stirred in dry hexane with an excess of CaH_2. After removal of hexane, the residue was sublimed under reduced pressure. Highly pure monomer **2** was isolated in 89% yield.

PVFc Homopolymer Synthesis. Following basically the original procedure described by Burkhardt and Nuyken,[36,37] we studied the progress of the living anionic VFc polymerization by treating the pure monomer **2** in dry THF at different temperatures, with different monomer concentrations, and with different amounts of initiator (*n*-BuLi). After

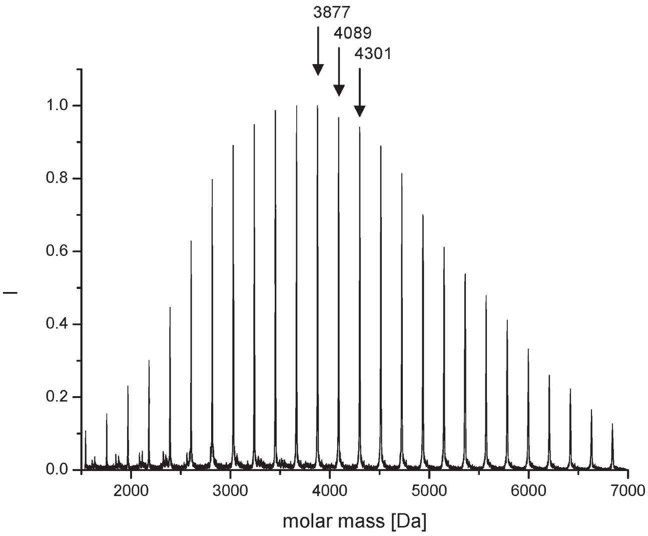


Figure 1. MALDI TOF mass spectrum of a PVFc (**3**) sample having an average molar mass $M_n \approx 3900$ g·mol^{-1} ($P_n \approx 18$) and an SEC polydispersity index PDI = 1.03; the mass of an *n*-butyl fragment (C_4H_9) is 57 and that of a VFc repeating unit is 212.

termination and precipitation in methanol, the formed PVFc's (**3**) were characterized using NMR spectroscopy, MALDI−TOF mass spectrometry, and size-exclusion chromatography (SEC). In the NMR spectra, we observed broad and unstructured absorptions in the correct intensity ratios at the expected chemical shifts. The development of the molar masses over reaction time, as monitored using SEC and MALDI, also reconfirmed the published reaction conditions as being highly appropriate.

Excellent agreement with the reported kinetic data was found in particular for entries carried out at temperatures from −25 to 0 °C, for monomer concentrations of 0.1−0.2 mol·L^{-1}, and for PVFc molar masses below $M \approx$ 5000 g·mol^{-1}.[51] Moreover, we proved polystyrene (PS) standards to give exhaustively misleading values of the PVFc molar masses when used for SEC calibration. Therefore, we analyzed selected PVFc samples using an SEC instrument equipped with a multiple-angle laser light-scattering (MALLS) detector, and took advantage of those samples as additional calibration standards in subsequent studies. Table 1 compares some values of M_n determined by SEC using PS standards with those obtained using MALLS detection.

The data shown in Table 1 disclose the PVFc chains to feature considerably smaller hydrodynamic volumes compared to e.g. PS chains of identical contour length. In other words, PVFc is rather weakly solvated even in powerful solvents like THF—which is the usually applied solvent for SEC analysis and polymer synthesis—and assumes a quite compact coil conformation even therein. Compact coil conformation in combination with limited segmental dynamics—as is also reflected by the rather high PVFc glass-transition temperatures[52]—also provides a reasonable explanation for the unusually broad and ill-resolved ^{1}H and ^{13}C NMR absorptions obtained for all PVFc's exceeding molar masses of $M \approx 1500$ g·mol^{-1}. Finally, MALDI mass spectrometry also proved the anionic chain growth to proceed very homogeneously for PVFc samples of moderate molar masses: there is just one sequence of mass peaks observable, representing the polymer-homologous series of Bu−[VFc]$_n$−H chains **3** bearing an *n*-butyl (Bu) initiator fragment at one end and hydrogen at the other. As an example, Figure 1 shows the MALDI mass spectrum of a PVFc (**3**) having an average molar mass $M_n \approx 3900$ g·mol^{-1} ($P_n \approx 18$) and a polydispersity index PDI = 1.03.

Table 2. Results of Representative Entries Leading to PVFc (3) of Different Molar Masses[a]

reaction temperature (°C)	−10	−10	−10
conversion of monomer VFc (%)[b]	97	94	91
reaction time (h)	7	12	48
M_n [g·mol^{-1}][c]	4166	7542	29 710
PDI[c]	1.10	1.12	1.49

[a] $[\text{VFc}]_0$ = 40 g·L^{-1} = 0.189 mol·L^{-1} [b] Gravimetric determination of the yields; the given data include all solid material obtained after pouring the reaction mixture into an excess of methanol (where only monomeric VFc (**2**) remains dissolved). [c] GPC−MALLS.

All in all, the above investigations verified the results published in the literature. Even monomer conversion of above 97% could be reproduced—*provided that* the targeted PVFc molar masses were below $M \approx 5000$ g·mol^{-1}. If the intended PVFc molar mass rose above the mentioned limit, on the other hand, quantitative monomer conversion proved to be impossible: in fact, the higher the aspired molar mass, the higher the amount of monomer left unconverted even after very long reaction times under the best known reaction conditions (approximately 5% for PVFc (**3**) with $M \approx$ 5000−10000 g·mol^{-1} and approximately 10% for PVFc (**3**) with $M >$ 10000 g·mol^{-1}; see Table 2). Keeping in mind this strange feature, it is neither a surprise that the PVFc (**3**) with the highest molecular weight we could realize so far had an M_n of 29700 g·mol^{-1} and an M_w of 44600 g·mol^{-1}, nor the fact that its PDI is around 1.50, which is significantly larger than those of shorter PVFc chains, where values of 1.03−1.10 are typically observed.

Triggered by the obvious limitations associated with the standard reaction procedure developed so far, we varied the reaction temperature and the solvent systematically, and we added coordinating species such as crown ethers or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) to the reaction mixtures. However, all these measures failed: when VFc polymerization was attempted in THF at room temperature, for example, no polymer formation was observed, but unchanged monomer was isolated after work-up. We assume that the *n*-BuLi deprotonates the ferrocene moieties under these conditions, leading to anionic species which are unable to induce PVFc chain growth. When reaction temperature was below room temperature but above 0 °C, some PVFc could be obtained, but it showed a rather broad PDI. The PDIs decreased with decreasing reaction temperature, which was interpreted as a further hint toward side reactions being in operation at ambient temperature. At very low temperatures, finally, side reactions proved to be suppressed, but the rate of PVFc chain growth drops down tremendously as well. All in all, reaction temperatures in the range from −15 to −25 °C seem indeed the best choice for PVFc formation in THF as the solvent. Addition of crown ethers or TMEDA neither accelerated the chain growth nor caused more complete monomer conversion in THF, in agreement with expectations.[50] On the contrary, broadening of the PDI was found. On the other hand, no PVFc was formed in weakly coordinating and less polar solvent systems such as diethyl ether, *n*-hexane/THF (∼1:1) or *n*-hexane/cyclohexane (∼1:1), but addition of crown ethers or TMEDA can induce anionic PVFc chain growth in these solvents. Nevertheless, the drawbacks and limitations associated with these latter solvent systems proved to be more pronounced than those of the original standard procedure. Therefore, we carried out all subsequent PVFc syntheses in THF as the solvent at −15 °C.

Incomplete monomer conversion in spite of unambiguously continued existence of living chain ends, and progressive broadening of the molar-mass distributions with increasing PVFc chain lengths and reaction times indicate that side reactions come into play, which first lower the reactivity of the macro-anions **3*** progressively and finally convert them into an apparently sleeping state. In addition to this, there might be further side reactions in operation causing irreversible termination of the living chain-ends of **3***.

So far, there is no final statement possible concerning the chemical and physical backgrounds of the side processes leading to the less reactive, sleeping, and/or irreversibly terminated PVFc macro-anions **3***. However, aggregation seems to play a crucial role—maybe similar to what was proposed for the radical pathway years ago:[30−32] for example, aggregation appears as the driving factor behind the observations that (*i*) essentially all entries of anionic PVFc synthesis turn turbid after a maximum reaction time of 1 h[53] and that (*ii*) continued stirring under the reaction conditions results in increasing amounts of powdery orange particles in the still intensively red and thus "living" solution. Profound SEC characterization of representative samples of the finally obtained product mixtures—that include the mentioned solid fractions formed under *in situ* conditions—resulted in molar-mass distribution curves showing, in addition to the expected intense peak representing the regular PVFc material **3**, a second broad distribution at huge molar masses, corresponding to apparent values $M \approx 10^6-10^8$ g·mol^{-1}.[53] It is reasonable to assume that this fraction has its primary origin in the aggregation of multiple PVFc chains, but it is unlikely that the material which precipitates during the PVFc growth is just an aggregate. Instead, there is evidence that the primary aggregates formed by the living PVFc chains **3*** undergo consecutive reactions during or after their appearance as solid particles, leading to chemically cross-linked polymeric micronetworks: if the mysterious solid was isolated prior to precipitation of the regular PVFc chains after complete PVFc synthesis, dispersed in THF, and analyzed using SEC, elugrams resulted that showed a rather weak peak at retention times corresponding to the molecular-dispersely dissolved PVFc single chains **3**, and a much more intensive second peak corresponding to the $M_{\mathrm{app}} \approx 10^6-10^8$ g·mol^{-1} species. Obviously, a few regular PVFc chains **3** could be extracted out of this powdery solid during SEC sample preparation, but the major amount of the material remained an apparently unswollen, solid-like micropowder. In fact, it proved to be impossible to redissolve detectable amounts of the latter material in any tested solvent even if elevated temperatures were applied, or when reactive agents were added to the living polymerization mixtures that should undergo immediate conversion with any type of carbanionic species.

Two further observations seem worth mentioning in this respect: first, the dominant parameter determining the relative amounts of insoluble material formed in an entry is the reaction time. Second, insoluble material is also formed in entries targeting very low-molecular-weight PVFc's. That means that there is no significant contribution of the chain length to the unknown side reaction. Instead, it seems mainly driven by the anionic entities themselves—independent of what else is connected to them. In order to demonstrate this feature explicitly, we carried out a VFc polymerization designed (and verified) to give essentially quantitative monomer conversion after stirring at −15 °C for 10 h, and a PVFc of $M \approx 2500$ g·mol^{-1}. In this particular experiment, however, stirring at −15 °C was extended to 54 days under the highly inert conditions of a well-performing glovebox. After this time, the overwhelming majority of the PVFc macromonomers **3*** was still alive, leading to 91% yield of regular, readily soluble PVFc (**3**) after termination and isolation. Additionally, however, a 9 wt % quantity of the mysterious insoluble orange solid had formed—despite the distinctly oligomeric nature of the primary macro-anions **3***. The latter experiment also disproved all speculation concerning physical cross-links by persistent chain entanglements or partial crystallization as the origin of the insoluble products.[54] Instead, it underlines our understanding that it is a slow side reaction which produces chemically cross-linked and thus irreversibly insoluble side-products. Nevertheless, the process remains somehow mysterious, for example because it is not accompanied by a simultaneous increase in polydispersity of the regularly soluble PVFc material: if the assumed chemical cross-linking reaction proceeded at random between living macro-anions **3***, starting with regularly dissolved species and ending with the mentioned insoluble solids, SEC should indicate the appearance of additional peaks with increasing reaction times centered at double, triple, 4-fold,..., molar masses of the primary PVFc chains **3**. However, no one SEC run gave hints pointing toward such additional coupling products. Therefore, preaggregation of a minimum number of living chains **3*** to larger clusters seems to be the prerequirement of subsequent cross-linking resulting in the intractable solid. Summarizing, there is a slow side reaction in operation during anionic growth of PVFc **3*** which results in apparently chemically cross-linked insoluble micropowders.

The above side reaction, however, is definitively not the reason why the propagating macro-anions **3*** loose their reactivity in a progressive fashion during anionic PVFc synthesis, and finally end in a sleeping state despite incomplete monomer consumption, where they can survive for weeks, and from which they can restart continued PVFc chain growth if additional VFc (**2**) is added. Again, aggregation of the anionic centers of **3*** is very likely to play a key role in the progressive loss of reactivity, but in contrast to the irreversible side reaction discussed before, the PVFc chains already formed seem to additionally contribute to the latter process: the sleeping state is especially observed in those cases where high-molecular-weight PVFc chains were targeted. Facing the facts that (*i*) PVFc macro-anions **3*** having molar masses $M > 3000-5000$ g·mol^{-1} fall asleep as soon as the remaining amount of VFc monomer reaches a critical minimum value (approximately 5−10% of $[\mathrm{M}]_0$), (*ii*) this critical value is the higher the larger the molar mass of the PVFc chains already formed, but (*iii*) the sleeping chains **3*** can continue their growth even after weeks if further VFc monomer **2** is added, the crucial question to be asked is: why is a minimum amount of monomeric VFc (**2**) essential to maintain reactivity of the PVFc macro-anions **3***? Let us speculate that this excess of VFc monomer **2** acts as a cosolvent for the otherwise weakly solvated PVFc chains, and/or as a coligand in the anion aggregates formed by the reactive chain termini of **3***. If **2** is playing the role of a coligand, it might perturb the structure of the otherwise too closed and/or too static macro-anion clusters, thereby maintaining sufficient reactivity for continued monomer addition steps. On the other hand, there is strong evidence from SEC and T_g that the PVFc chains attached to the aggregating macro-anions **3*** tend to form an only weakly solvated, and hence rather compact, immobile and impenetrable "shell" around their anion cluster, which is thicker and more impassable the longer the PVFc chains already formed are. Here, the excess of VFc (**2**) might act as a cosolvating species for the PVFc segments, which maintains a minimum mobility and penetrability of this shell, and thus supports other monomer molecules to approach the anionic centers. On the basis of the evidence available, it seems that the synergistic combination of progressively perfect macro-anion aggregates surrounded by decreasingly penetrable shells of collapsed PVFc, which slow down the rate of PVFc chain growth until finally an apparently sleeping system results, and only sufficient excess of monomeric VFc in the reaction mixture are able to guarantee reactivity and accessibility of the aggregated macro-anions **3*** after extended reaction times and especially for PVFc's **3*** of higher chain lengths.

Further support of the proposed nature of the "sleeping" PVFc chains **3***, and of the role of excess monomer **2**, was expected from complementary studies where the PVFc macro-anions **3*** are used as macroinitiators in block copolymer syntheses. The next challenging question, therefore, was: under which conditions and to what extent the still active PVFc macro-anions **3*** on the one hand, and the sleeping PVFc macro-anions **3*** on the other, can be converted into well-defined block copolymer architectures. For synthetic and mechanistic reasons, but also because we were expecting fascinating properties of the resulting materials, we decided to test methyl methacrylate (MMA) and 2-vinylpyridine (2 VP) as the monomers for the second block.

Modification of the PVFc Macro-Anions for Block Copolymer Synthesis. If it is intended to polymerize monomers like MMA or 2 VP in a well-defined fashion by living anionic polymerization, it is necessary to adjust the reactivity of the initiating species appropriately. Instantaneous initiation of block growth has to be ensured as well as reliable suppression of undesired side reactions leading to premature termination. A highly advantageous initiating species for MMA and 2 VP chain growth is obtained for example when the original (macro-)carbanions are terminally modified using 1,1-diphenylethylene (DPE). Thus, it was the next task to end-cap the reactive termini of macro-anions **3*** quantitatively with a reagent like DPE, leading to modified macroinitiators like **3**** ($x = 0$ in Scheme 1). So we had to find out whether the active and/or sleeping PVFc macro-anions **3*** do react with DPE in a homogeneous fashion and how they can be activated appropriately if this is not the case.

In a first series of experiments, we tested whether end-capping of **3*** is possible just by adding DPE to the living PVFs chains as obtained from the anionic chain growth. Stirring for up to 24 h at different temperatures, termination using degassed methanol, and characterization of the isolated products using NMR spectroscopy and MALDI mass spectrometry resulted in the disappointing conclusion that only a minor fraction of the PVFc chains was end-capped by DPE, i.e., was represented by the general formula $\mathrm{Bu{-}[VFc]_n{-}DPE{-}H}$ [mass peaks at $m/e = 4057 \pm x(212)$ in the MALDI spectrum shown in Figure 2]. The overwhelming majority of the PVFc chains, typically approximately 90%, had the constitution $\mathrm{Bu{-}[VFc]_n{-}H}$ (mass peaks at $m/e = 3877 \pm x(212)$ in Figure 2) instead, meaning that no conversion had occurred with DPE under these conditions. Results like this were not only obtained for PVFc macro-anions **3*** of higher molar masses but—*nota bene*—for small oligomers **3*** as well! This either implies that 90% of the PVFc macro-anions **3*** were already dead when DPE was added, or they were still alive but insufficiently reactive and/or accessible at that time. If we remember that identical PVFc macro-anions **3*** continue the chain growth immediately and without a significant increase in the PDIs if further VFc (**2**) is added, the former explanation is not viable.

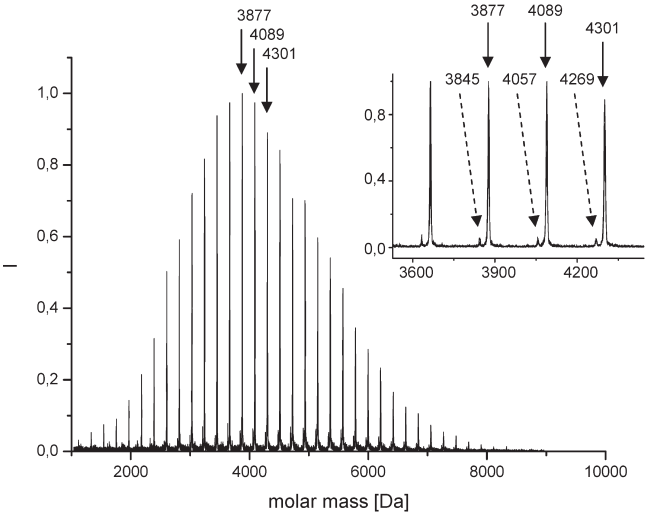


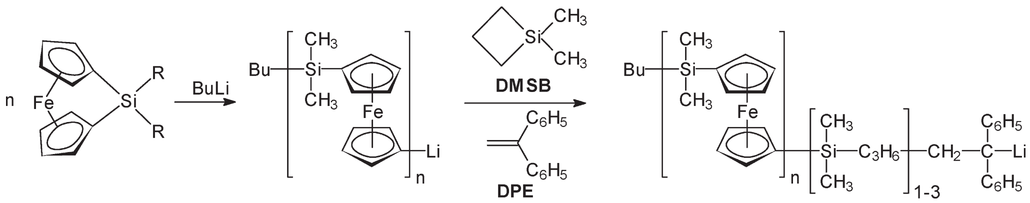
Figure 2. PVFc homopolymers obtained after treatment of **3*** with 2 equiv of DPE and termination with degassed methanol; the desired chains $\mathrm{Bu{-}[VFc]_n{-}DPE{-}H}$ are represented by the mass peak series $m/e = 4057 \pm x(212)$, the unmodified chains $\mathrm{Bu{-}[VFc]_n{-}H}$ by the mass peak series $m/e = 3877 \pm x(212)$; the average degree of polymerization of the PVFc chains under investigation was $P_n = 18$.

Formation of 10% DPE end-capped chains **3**** demonstrates on the other hand that macro-anions **3*** are basically able to add DPE. A reasonable interpretation which takes into consideration all experimental data, and which is in harmony with the observations during PVFc homopolymer synthesis as well, is based on the assumption that the approximately 90% PVFc macro-anions—the fraction which does not react with DPE—just suffer from insufficient reactivity and/or accessibility. Very importantly, moreover, these studies underline that loss of reactivity of the PVFc macro-anions **3*** already starts at a very early stage of VFc polymerization.

Let us remember our initial working hypothesis, which assumes progressive aggregation and shielding of the anionic centers of **3*** to be the cooperative reason for the macroscopically observed loss of reactivity. On the basis of this, the next idea was to first treat the PVFc macro-anions **3*** with a small-sized but highly reactive auxiliary agent, i.e., prior to the addition of DPE. Once a modified chain terminus is formed, basically changed aggregation behavior and accessibilities should result. Recently, we succeeded in solving related problems associated with insufficient macro-anion reactivity using the so-called carbanion-pump technique: when living polyferrocenylsilane was treated with a mixture of 1,1-dimethylsilacyclobutane (DMSB) and DPE, nearly 100% DPE end-capping was achieved after 1−3 DMSB addition steps (Scheme 2).

Therefore, an analogous procedure was tested for the reactivation of the PVFc macro-anions **3***: different amounts and ratios of DPE and DMSB were added to the reaction mixtures after complete VFc chain growth, the mixtures were stirred for different times at different temperatures, and finally the anions were terminated using degassed methanol (Scheme 1). Figure 3 shows a representative MALDI mass spectrum obtained after treating a sample of **3*** with DMSB/DPE at room temperature for 10 min. The fact that mass peaks corresponding to the $\mathrm{Bu{-}[VFc]_n{-}H}$ series (mass peak series at around $m/e = 3877 \pm x(212)$ in Figure 2) are completely missing now allows the immediate conclusion that essentially all PVFc chains possess a modified end-group: we observe an intensive series of mass peaks

Scheme 2. DMSB Carbanion Pump Procedure Applied for DPE End-Capping of Living PFS Macro-Anions



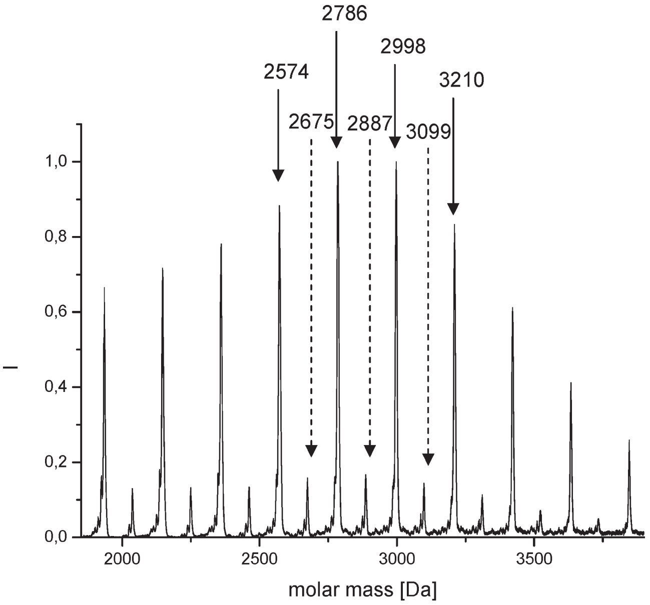


Figure 3. PVFc homopolymer obtained after treatment of the living macro-anions **3*** with a mixture of DMSB and DPE. Chains of general structure Bu−[VFc]$_n$−DPE−H are represented by the mass peak series m/e = 2786 ± x(212), those having the general structure Bu−[VFc]$_n$−DMSB−DPE−H by the mass peak series m/e = 2887 ± x(212); the mass of a DPE unit is 180, that of a DMSB unit is 100, and the P_n of the PVFc was 12.

at m/e = 2786 ± x(212), and another homologous series with lower intensity at m/e = 2887 ± x(212). Detailed analysis of these mass peaks, however, resulted in a further surprise: it is the minority fraction (approximately 10% of the material) which has the expected constitution Bu−[VFc]$_n$−DMSB−DPE−H (m/e = 2887 ± x(212)) bearing a DMSB unit between the PVFc chain and the terminal DPE moiety. It was our understanding of the carbanion-pump operating mode so far that at least one DMSB molecule must add to a macro-anion prior to the terminal addition of a DPE moiety. Contrary to this expectation, the overwhelming majority of the PVFc chains is end-capped by a DPE moiety, but has no DMSB fragment in its penultimate position, i.e. is represented by the general formula Bu−[VFc]$_n$−DPE−H.

In case of DMSB-supported DPE end-capping of PFS macro-anions following Scheme 2, we had never observed evidence of direct linkage of DPE and PFS macro-anions. Instead, up to three DMSB moieties added to the PFS macro-anions prior to final DPE addition. These contradictory observations underline once more that the reason for slow conversion of DPE with living PFS and PVFc macro-anions, respectively, is basically different: whereas the highly flexible and readily soluble PFS macro-anions suffer intrinsically from insufficient reactivity, the PVFc macro-anions **3*** can basically provide sufficient reactivity for DPE addition, but aggregation and/or shielding effects nevertheless result in unsatisfactory end-capping efficiencies. Luckily, penetration of very few DMSB moieties into the partially deactivated or sleeping PVFc aggregates followed by their reaction with possibly one single macro-anion **3*** already seems sufficient to trigger decay of the whole aggregate, and thus also changes all other macro-anions **3*** participating at the respective aggregate to reactive.[55] In conclusion, the investigations dealing with DMSB-triggered reactivation of PVFc macro-anions **3*** provided valuable further support for our initial hypothesis, describing the unusual reactivity profile observed for anionic VFc polymerization to be the result of the pronounced aggregation tendency of the anionic chain termini of **3*** in combination with shielding effects induced by the weakly solvated, collapsed and rather inflexible PVFc chains that form an outer shell around their anion aggregates. Also, the end-capping studies showed that deceleration of chain growth already starts at a very early stage of VFc polymerization but is manifested only after longer reaction times and with higher PVFc chain lengths in the case of VFc homopolymerizations.

At this point, one might ask whether addition of DMSB, either in combination or without DPE, is able to push incomplete VFc conversion during the synthesis of high-molecular-weight PVFc to completeness by adding to the "sleeping" PVFc macro-anions **3*** and thus formation of a more reactive DMSB (or DPE) anionic chain terminus. With the help of various model reactions and MALDI mass spectrometry we could demonstrate that neither the anionic DMSB chain termini nor their DPE analogues are able to add VFc monomer. Thus, both types of end-capped PVFc macro-anions are not reactive enough for inducing continued PVFc chain growth.

Diblock Copolymer Syntheses. The next task in the present study was syntheses of AB diblock copolymers using the DPE-terminated PVFc macro-anions **3**** as an initiator, i.e., following sequential monomer addition protocols. An optimized DMSB/DPE end-capping procedure was developed for that purpose, which is treatment of **3*** with 2 equiv of DPE and 1 equiv of DMSB for 2 min at −15 °C, followed by allowing the reaction mixture to warm up to room temperature. The deep red solutions of **3**** obtained can be stored for several days at room temperature without any deactivation or termination and were used to synthesize the desired diblock copolymers.

*PVFc-b-PMMA Diblock Copolymers **4**.* For the synthesis of PVFc-*b*-PMMA diblock copolymers **4**, the THF solution of DPE end-capped PVFc macro-anions **3**** having molar masses in the range of $1500 \leq M \leq 20000$ g·mol^{-1} were cooled to −78 °C. LiCl was added followed by the indicated amounts of MMA. After stirring at −78 °C for 2 h, the conversions were complete and the living chains were terminated. Back at room temperature, the polymeric materials were precipitated as orange solids in *n*-hexane in essentially quantitative yields. The remaining hexane solutions were colorless for shorter PVFc segments and slightly orange for longer PVFc segments, due to monomeric VFc (**2**) that remained unconverted in the synthesis of the A-block.[56] NMR spectroscopy confirmed both the homogeneous

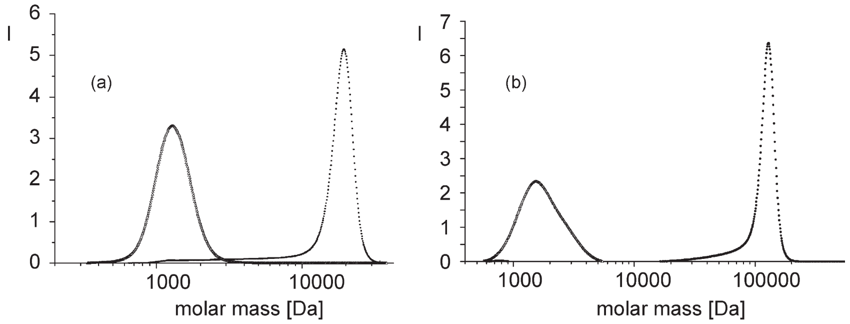


Figure 4. SEC traces (vs PS standards) of PVFc-*b*-PMMA diblock copolymers **4** with (a) an $M \approx 2200$ g·mol^{-1} PVFc block and an $M \approx 10000$ g·mol^{-1} PMMA block (•) and (b) an $M \approx 5100$ g·mol^{-1} PVFc block and an $M \approx 107600$ g·mol^{-1} PMMA block (•), both together with the SEC trace of the precursor PVFc block (Δ).

constitution and the expected composition of the PVFc-*b*-PMMA block copolymers **4** obtained (the PMMA block was shown to be predominantly syndiotactic). Moreover, NMR spectroscopy allowed identification of the absorptions of both the butyl initiator fragment and the (DMSB)/DPE linker moiety in the case of rather low-molecular-weight block copolymers **4**.

Although NMR spectroscopy delivers valuable information about the constitution, configuration, and overall composition of the formed materials, it cannot provide ultimate proof of block formation nor quantification of the blocking efficiency. SEC is the method of choice for gaining these key data as well. Figure 4a shows the SEC traces of a diblock copolymer **4** composed of a PVFc block having $M \approx 2200$ g·mol^{-1} ($M_{\mathrm{app}} \approx 1200$ g·mol^{-1} vs PS standards) and a PMMA block with $M \approx 10000$ g·mol^{-1}, and of its PVFc precursor **3** (again with calibration vs PS standards). Figure 4b shows the analogous curves for a sample **4** having a PVFc block of $M \approx 5100$ g·mol^{-1} (PVFc calibration; PDI 1.12) and a PMMA block molar mass of $M \approx 107600$ g·mol^{-1} (PS calibration; PDI 1.07).[57] It is important to note that the copolymer samples were not purified prior to SEC analysis but reflect the representative product mixture formed in the respective entry.

In both cases, there is almost no evidence of PVFc homopolymers in the SEC traces of the diblock copolymers, proving that a nearly quantitative blocking efficiency was reached. This means that in fact quantitative reactivation of the precursor chains **3*** → **3**** as well as highly efficient initiation of subsequent MMA chain growth can be realized! Moreover, conversion of the second monomer, MMA, proved to be quantitative in all cases, and resulted in B-blocks of very narrow molar-mass distributions ($\mathrm{PDI}_{\mathrm{PMMA}} < 1.05$). Thus, the PVFc chains representing the A-block in the copolymer do not affect subsequent growth of the B-block once reactivated and started in an appropriate fashion. Identical results were obtained from many further entries leading to diblock copolymers **4**, which covered PVFc block molar masses from 1500 to 20000 g·mol^{-1} and PMMA block molar masses from 12000 to 113000 g·mol^{-1}. To summarize, the developed method of PVFc macro-anion activation and DPE end-capping as well as subsequent growth of the PMMA block are highly efficient processes. It was the question whether the same also applies to 2 VP as the second monomer.

PVFc-b-P2VP Block Copolymers **5**. Using essentially the identical procedure as described for the synthesis of **4**, we tried to obtain PVFc-*b*-P2VP diblock copolymers **5**: after addition of some LiCl and cooling the THF solutions of end-capped PVFc precursors **3**** to −80 °C, the respective amounts of 2 VP were injected. After a reaction time of 2 h, the active chains were terminated and the orange polymers were isolated by precipitation in hexane. NMR investigations verified quantitative conversion of 2 VP as well as the constitution of the P2VP block.

All absorptions observed in the ^{1}H and ^{13}C NMR spectra could be assigned unambiguously to the respective hydrogens and carbons of polymer **5**. As an example, Figure 5 shows the ^{1}H and ^{13}C NMR spectra of a PVFc-*b*-P2VP diblock copolymer **5** having an overall molar mass $M \approx 10200$ g·mol^{-1} (PDI 1.04), a PVFc block of $M \approx 1500$ g·mol^{-1} (PDI 1.05), and a P2VP block of $M \approx 8700$ g·mol^{-1}. In addition to the rather well-resolved absorptions of the P2VP block, one can see the clearly broader and less structured absorptions of the PVFc block, pointing toward the already mentioned weak solvation and limited chain mobility of the latter. Moreover, the NMR spectra allow reliable exclusion of significant amounts of Fe(III) centers in these copolymers, which are often postulated to form spontaneously in PVFc systems and to affect both the synthesis and final properties of the resulting materials. If only traces of paramagnetic ferrocenium centers were present in the samples under investigation, it would not be possible to obtain such nicely resolved NMR spectra.

SEC, on the other hand, was the method of choice to provide the final proof of block formation, and to quantify the blocking efficiency of the activated precursors **3**** for P2VP chain growth. Various samples of the synthesized PVFc-*b*-P2VP diblock copolymers **5** were analyzed by SEC. Figure 6 shows the SEC results obtained for the specific copolymer **5** which was already documented by the NMR spectra shown in Figure 5.

Quantitative activation of the PVFc precursor as well as nearly 100% blocking efficiency are immediately evident. Moreover, the block molar masses and PDIs determined in this manner were also in harmony with a very smooth and homogeneous block formation process. Without exception, the NMR and SEC studies reconfirmed almost quantitative blocking efficiencies and very low polydispersities (PDI ≈ 1.04−1.07) for all PVFc-*b*-P2VP diblock copolymers **5** prepared so far, which covered PVFc block molar masses from 1500 to 6000 g·mol^{-1} and P2VP block molar masses from 7000 to 50800 g·mol^{-1}. Thus, once again, the developed method of PVFc reactivation and terminal DPE functionalization proved to be a highly powerful tool for block copolymer synthesis.

Block Copolymer Morphology. It was not the main intention of this synthetically oriented study to provide deeper insights into the thermal properties and morphological characteristics of the presented diblock copolymers. Some preliminary results shall be mentioned nevertheless. Film samples of the PVFc-*b*-PMMA diblock copolymers **4** were

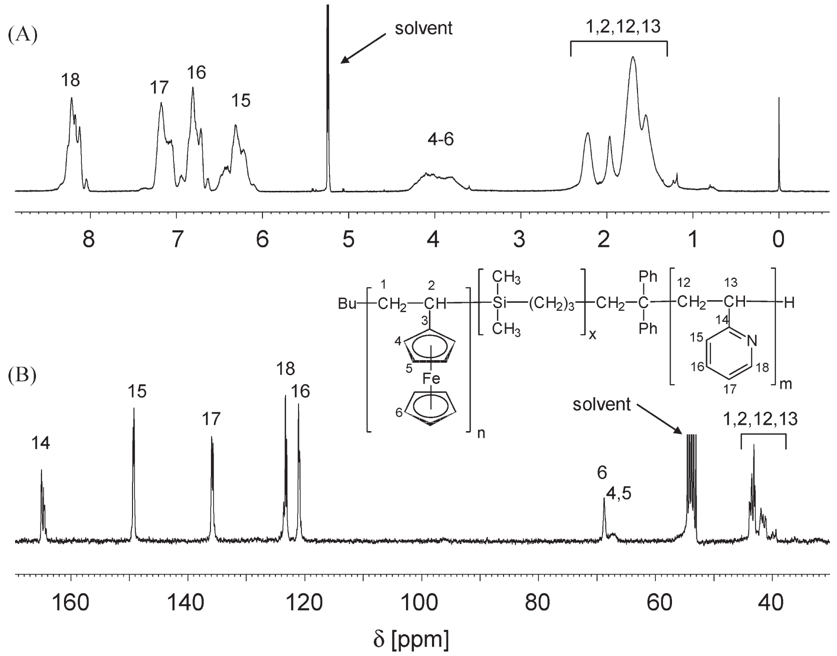


Figure 5. ^{1}H (A) and ^{13}C (B) NMR spectra of a PVFc-*b*-P2VP diblock copolymer **5**, having an overall molar mass $M \approx 10200$ g·mol^{-1} (PDI 1.04), a PVFc block of $M \approx 1500$ g·mol^{-1} (PDI 1.05), and a P2VP block of $M \approx 8700$ g·mol^{-1}; for the ^{13}C NMR spectrum, the measuring time was 12 h, and the number of scans was 25000.

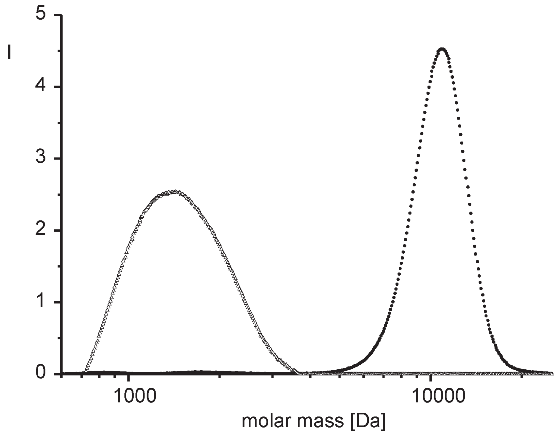


Figure 6. SEC traces (vs PS standards) of a PVFc-*b*-P2VP diblock copolymer **4** with an $M \approx 1500$ g·mol^{-1} PVFc block and an $M \approx 8700$ g·mol^{-1} P2VP block (•), together with the SEC trace of the precursor PVFc A-block (Δ).

prepared from methylene chloride solution. The samples were stored in the solvent vapor at room temperature for up to 8 weeks in order to facilitate phase separation and ripening of the micromorphologies in these high-T_g materials. Finally, the films were heated (100−150 °C) in high vacuum for several hours to remove last traces of solvent. Despite this time-consuming procedure, it was found to be extremely difficult to obtain TEM pictures showing properly phase-separated micromorphologies. This was especially the case for all samples of moderate overall molar masses and shorter PVFc block lengths. The best pictures we could obtain so far were from a highly pure (essentially no PVFc homopolymer impurity) and very narrowly distributed (PDI 1.02) PVFc-*b*-PMMA material, having an $M \approx 20416$ g·mol^{-1} PVFc block and an $M \approx 81000$ g·mol^{-1} PMMA block (Figure 7).[58]

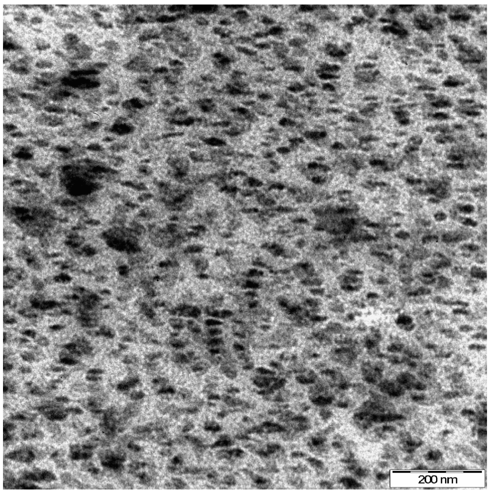


Figure 7. TEM picture of a highly pure and narrowly distributed (PDI = 1.02) PVFc-*b*-PMMA diblock copolymer, having an $M \approx 20416$ g·mol^{-1} PVFc block and an $M \approx 81000$ g·mol^{-1} PMMA block. The film sample was prepared from methylene chloride solution, stored in the solvent vapor at room temperature for 8 weeks, and finally heated (150 °C) in high vacuum to remove the last traces of solvent.

On the basis of the volume fractions of the PVFc and PMMA blocks, respectively, the PVFc should appear as dispersed spheres in the PMMA matrix. There is no doubt evidence of phase separation leading to such morphology, but the system still seems away from the equilibrium state. DSC investigations as well provided convincing evidence of rather complete phase separation: two glass transitions were observed for the above film samples, one at $T_g \approx 130$ °C, which is characteristic of syndiotactic PMMA, and a second one at $T_g \approx 200$ °C, which corresponds to the PVFc segment. One might argue that T_g(PMMA) is slightly higher than expected and, *vice versa*, the T_g(PVFc) seems slightly too low. Indeed, incomplete phase separation and/or partial miscibility of PMMA and PVFc have both to be taken into account at the present time, and future studies will show to what extent PVFc and PMMA are thermodynamically

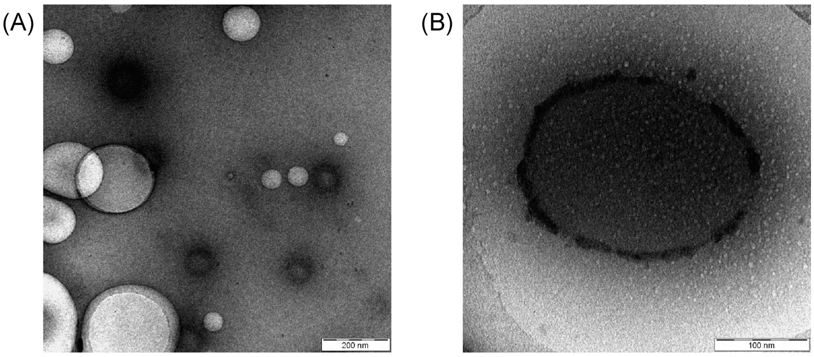


Figure 8. TEM pictures of a highly pure sample of the PVFc-*b*-P2VP diblock copolymer **5**, having a PVFc block of $M \approx 1500$ g·mol^{-1} and a P2VP block of M ≈ 8500 g·mol^{-1}, prepared from aqueous dispersion using the drop-casting method.

compatible. Another promising feature of the PVFc-*b*-PMMA diblock copolymers **4** was identified by TGA studies: the block copolymers do not suffer weight loss up to 380 °C, which is a very high temperature especially for systems containing PMMA that are known to undergo depolymerization above approximately 250 °C.

For the PVFc-*b*-P2VP diblock copolymers **5**, on the other hand, much clearer evidence was obtained for block incompatibility and pronounced phase segregation tendency. DSC investigations carried out on film samples prepared from methylene chloride solution allow clear identification of two glass transitions, one for the P2VP block at around 110 °C, and a second one for the PVFc at around 210 °C. Nevertheless, sample preparation for complementary TEM studies proved to be tricky because **5** is highly hydrophilic and hygroscopic, which complicates proper cutting of ultrathin slices using standard procedures. Moreover, the PVFc-*b*-P2VP diblock copolymers readily dissolve in many solvents including methanol, even in the presence of a small amount of water, especially for PVFc block molar masses below $M_{\mathrm{PVFc}} \approx 2000$ g·mol^{-1}. Slightly turbid dispersions of presumably micelle-like or vesicular species are only formed for larger PVFc blocks, with larger amounts of water in the methanol solution, or if solid copolymers **5** are treated with pure neutral water. Formation of complex aggregates in an aqueous dispersion and in dispersions containing smaller amounts of methanol could be supported by TEM studies using the drop-casting procedure for sample preparation: the polymer is dissolved in water, methanol, or mixtures thereof (polymer concentration $c_{\mathrm{P}} \approx 1-3$ g·L^{-1}), and one drop of these solutions is positioned on top of a cellulose-nitrate recovered TEM grid. In the case of water as the solvent, the drop is carefully frozen with liquid nitrogen and subsequently freeze-dried at high vacuum (10 min). In the case of methanol-containing solutions, the solvent is allowed to evaporate under ambient conditions. The block copolymer thus deposited on top of the grid is analyzed using TEM.

TEM pictures taken from samples of **5** prepared by drop-casting from pure methanol, or from clear solutions of **5** in mixtures of methanol and water, did not show meaningful morphologies so far. When the TEM samples were prepared from the turbid solutions of **5** in methanol/water mixtures containing larger amounts of water, or from dispersions of **5** in pure neutral water, nicely reproducible TEM pictures were obtained that point toward the formation of ring-like or spherical micelles or vesicles. Figure 8 shows two representative TEM pictures of these unusual specimens as obtained from dispersions in pure water. Identical sample preparation using dispersions containing additional small amounts of methanol result in qualitatively very similar pictures, but the observed spherical specimens grow in diameter along with increasing amounts of added methanol.

It is our current understanding of these pictures that the P2VP blocks are readily dissolved in the dispersions of **5** in methanol/water or pure water, but the PVFc blocks agglomerate to give compact (primary) particles. Some of these more or less spherical PVFc-aggregates, which have a diameter of approximately 10 nm and are covered and stabilized by their coronae of readily dissolved P2VP chains, seem nicely resolved in picture B of Figure 8 as isolated black dots. These core–shell micellar block copolymer aggregates, however, seem unstable under the applied conditions and aggregate further to give the observed ring-like or spherical specimens as their secondary structures having characteristic diameters in the 100–200 nm range when prepared from pure water. Currently, systematic studies are under way to develop a more profound understanding of what the mechanism might be that leads to the formation of such unusual superstructures.

Conclusions and Outlook

The studies described in this paper lead to the conclusion that during living anionic VFc polymerization the originally highly reactive chain termini suffer progressive loss of their initially high reactivity. Simultaneously, tiny amounts of insoluble, presumably cross-linked material are formed. Finally, the PVFc macroanions end in an essentially sleeping state prior to complete monomer conversion. Nevertheless, the anionic centers are still alive even in that sleeping state, as could be demonstrated by the addition of further amounts of VFc monomer: continued chain growth without significant broadening of the PDIs is the result. Progressive loss of reactivity seems the synergistic result of aggregation of the macro-anions **3*** to provide increasingly perfect and static ion clusters and, correlated with that, the formation of a hardly penetrable shell of collapsed and inflexible PVFc chains growing around these aggregated macro-anions. Thus, aggregation-induced lowering of macro-anion reactivity seems additionally intensified by complicated accessibility of the "hot spots" in the reaction mixture, which could rationalize the quite special reactivity profile observed for anionic VFc polymerization.

Luckily, deactivated as well as sleeping macro-anions **3*** can be reactivated essentially quantitatively in an appropriate fashion for subsequent conversions: treatment with DMSB and DPE leads to modified PVFc macroinitiators **3**** which act highly efficiently in block copolymer syntheses following sequential monomer addition approaches. PVFc-*b*-PMMA and PVFc-*b*-P2VP diblock copolymers having PVFc block molar masses of up to $M \approx$ 20000 g·mol^{-1} and PMMA/P2VP block molar masses of above $M \approx 100000$ g·mol^{-1} could be realized using this approach.

First studies dealing with thermal behavior and morphology of these diblock copolymers showed both systems to tend to phase separation. Moreover, the PVFc-*b*-PMMA systems **4** proved to exhibit a very high thermal stability, while fascinating micromorphologies were obtained for the PVFc-*b*-P2VP diblock copolymers **5** by sample preparation from aqueous solutions using the drop-casting method. Currently, we are broadening the scope of the presented synthetic route further, and are analyzing the thermal and phase behaviors of the obtained materials in more detail.

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References and Notes

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(51) Burkhardt and Nuyken analyzed the kinetics of PVFc chain propagation in the temperature range from −40 to 0 °C in THF solution, using *n*-BuLi as the initiator. The apparent rate constant, k_{app}, of the polymerization reaction was determined assuming the chain growth to follow first-order kinetics with respect to monomer concentration. For an initial monomer concentration $[\mathrm{VFc}]_0 = 0.173\ \mathrm{mol\cdot L^{-1}}$ and an initiator concentration $[n\text{-BuLi}]_0 = 0.015\ \mathrm{mol\cdot L^{-1}}$, evaluation following the Arrhenius approach gave an activation energy for chain propagation, E_{A}, of $40\ \mathrm{kJ\cdot mol^{-1}}$. This is in agreement with what we observed, and allows precise prediction of the reaction time needed to obtain PVFc's of the desired molar masses. For example, a reaction time of 2 h is needed to produce a PVFc with $M_{\mathrm{n}} \approx 2400\ \mathrm{g\cdot mol^{-1}}$ for $[\mathrm{VFc}]_0 = 0.173\ \mathrm{mol\cdot L^{-1}}$ and $[n\text{-BuLi}]_0 = 0.015\ \mathrm{mol\cdot L^{-1}}$ at −25 °C, and a reaction time of 1 h is indicated to end with an $M_{\mathrm{n}} \approx 4000\ \mathrm{g\cdot mol^{-1}}$ PVFc for $[\mathrm{VFc}]_0 = 0.217\ \mathrm{mol\cdot L^{-1}}$ and $[n\text{-BuLi}]_0 = 0.009\ \mathrm{mol\cdot L^{-1}}$ at 0 °C.
(52) In the literature,[36,37] the T_{g} of PVFc was reported to vary from 180 to 220 °C; in our studies, we found strong dependency of T_{g} on the molar mass of the PVFc: short oligomers, having less than 5−7 repeating units per chain, gave a $T_{\mathrm{g}} \approx 190$ °C, whereas a PVFc with $M_{\mathrm{n}} \approx 10000\ \mathrm{g\cdot mol^{-1}}$ showed its T_{g} at 239 °C.
(53) Bimodal SEC traces were also reported by Faust,[39] who correlated the high-molecular-weight fractions with aggregation processes, in agreement with our interpretation.
(54) Involvement of ionic interactions induced by Fe(III) centers—which might be formed by oxidation of some Fe(II) centers—analogous to the aggregation/clustering in ionomers can also be ruled out considering the presence of carbanionic centers and the lack of oxidizing agents in the reaction mixture.
(55) Maybe a similar mechanism is also in operation when fresh VFc (**2**) is added to the sleeping macro-anions **3***.
(56) VFc monomer **2** present during the synthesis of the B block behaves completely inert during anionic growth of MMA or 2 VP. No evidence was found pointing toward random copolymerization of VFc and MMA/2 VP, or formation of tapered segments.
(57) The SEC plots of the block copolymers **4** and **5** were calibrated vs PS standards because the B-block is the dominant block. In order to allow direct comparison with the PVFc precursor chains of the A-block, the PVFc homopolymers are also plotted in the PS calibration mode. Nevertheless, the values given in the text for *M*(PVFc) are determined with calibration vs PVFc standards.
(58) Nuyken et al.[36] report just a single glass transition for their PVFc-*b*-PMMA systems, and thus assume compatibility of the two involved blocks. The reason for this contradictory observation might be sample pretreatment or insufficient block lengths for proper phase separation in these previous studies.