

Novel Metallopolymer Architectures via Living Anionic Polymerization Methodologies

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Introduction

I. Manners' discovery of the ring-opening polymerization of silaferrocenophanes in the 1990s reawaked research on polymeric ferrocenes,^{1,2,3,4} and there are good reasons why such macromolecules will gain technical relevance in future. In order to broaden the materials' basis, it is worthwhile to search for further metallocene-based monomers accessible to living anionic polymerization, which can be obtained in high purity and without laborious work-up procedures. In this respect, vinylferrocene (VFc) and various ferrocene-containing (meth)acrylates seem promising candidates: ferrocenylmethyl methacrylate (FMMA), for example, has been known for quite a long time, and its synthesis and purification procedures seem rather convenient. Rather surprisingly, however, searching in the literature resulted in the conclusion that advantage of these monomers has not been taken so far: certainly, some papers published in the 1970s report both free radical and living anionic polymerization of ferrocene-containing (meth)acrylates, and first block copolymers were described as well.^{5,6,7,8} Success of these attempts was limited, however.

Since we are convinced that substantial improvement of the living anionic polymerization of VFc, FMMA, and related monomers is not a matter of illusion, we started to reinvestigate the potential of this approach systematically. In the present contribution, we describe efficient access to the highly pure monomers VFc and FMMA as well as appropriate conditions for their truly living anionic polymerization leading to polyvinylferrocene (PVFc) and poly(ferrocenylmethyl methacrylate) (PFMMA) homopolymers and AB-type diblock copolymers with e.g. polystyrene (PS-*b*-PFMMA). Moreover, we describe powerful procedures for living grafting-from processes using ferrocene-containing monomers.

Experimental

Materials. All chemicals and solvents were purchased from Acros, Aldrich and Strem chemical companies. Starting materials were used as received, solvents were dried and de-oxygenated following standard procedures. All syntheses were carried out under an inert atmosphere of nitrogen.

Instrumentation. NMR spectra were recorded using a Bruker AM 300 NMR spectrometer). SEC chromatograms were measured in THF as the mobile phase at a flow rate of 1 mL·min⁻¹. Measurements were carried out on a Mixed Gel column set from PL (PL Mixed Gel B, PL Mixed Gel C, PL Mixed Gel D) at 30 °C with UV-vis detection at 254 nm. 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.

Poly(ferrocenylmethyl methacrylate) (PFMMA). FMMA is dissolved in dry THF. A solution of LiCl in THF is added, and the resulting mixture is cooled down to -78 °C. In a second reaction flask, a solution of *n*-butyllithium in hexane (1.6 M) is added to the solution of diphenylethylene in dry THF at room temperature. The resulting dark red solution of the formed 1,1-diphenylhexyllithium initiator is added quickly to the monomer solution using a syringe. In order to ensure complete conversion, the reaction mixture is stirred at -78 °C for 2 h. The chains which are still active are terminated by adding degassed methanol. The whole reaction mixture is poured into a tenfold excess of methanol. The polymer precipitates quantitatively.

Poly(styrene-*b*-ferrocenylmethyl methacrylate) (PS-*b*-PFMMA). Styrene is dissolved in dry cyclohexane, and *sec*-BuLi is added at room temperature. In a glove box, the mixture is stirred at room temperature for 2 h. DPE is added using a syringe, and stirring at room temperature is continued for a further 7 h. After nearly quantitative removal of the solvent, the living PS chains are dissolved in a solution of LiCl in THF at -20 °C. The resulting solution is cooled down to -78 °C and then added quickly to the stirred and cooled solution of FMMA in THF. After 2 h stirring, the active chains are terminated by adding methanol. The mixture is poured into an excess of methanol. The polymer precipitates quantitatively.

Vinylferrocene (VFc). In a dry 1 L Schlenk flask, 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 approx. 15 min. When all solid material is dissolved, the solution is cooled at -60 °C again. Ferrocene carbaldehyde (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 (Na₂SO₄). 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). Pure VFc is obtained in 89% yield (4.41 g, 20.8 mmol).

Polyvinylferrocene (PVFc). In an ampoule equipped with a stirring bar, pure VFc 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, 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 tenfold excess of methanol. The formed PVFc precipitates nearly quantitatively, is collected by filtration, washed with methanol, and dried in vacuo

Results and Discussion

Vinylferrocene (VFc) was synthesized and polymerized as described in the experimental part, ferrocenylmethyl methacrylate (FMMA) was prepared in analogy to the literature (Figure 1):

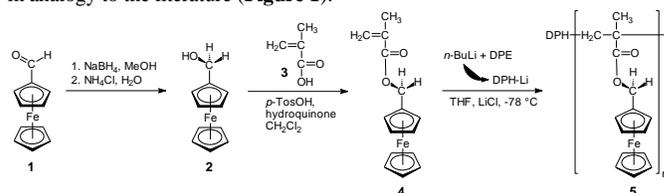


Figure 1. Synthesis and living anionic homopolymerization of FMMA 4.

Living anionic polymerization of FMMA was performed using diphenylhexyl lithium (DPH-Li) as the initiator. Small quantities of LiCl in THF were added to the solution of the monomer in THF in order to break up the lithium clusters. Monomer and initiator solutions were combined after cooling down the former to -78 °C. The mixture was stirred at -78 °C for 2 h to ensure completed conversion. Finally, the active chains were terminated at -78 °C using degassed methanol, and the formed polymers were precipitated in an excess of methanol.

The yellowish-orange homopolymers were characterized using NMR, SEC and MALDI mass spectrometry. The absorptions found in the ¹H and ¹³C NMR spectra were in full agreement with the expected constitution of the products. MALDI mass spectrometry as well reconfirmed formation of constitutionally regular polymers, bearing one DPH and one hydrogen chain terminus per chain. SEC characterization proved monomodal molar-mass distribution for all PFMMA samples. Calculated and experimentally determined molar masses were found to be in excellent agreement as well. Variation of the applied molar ratio of DPH-Li initiator and FMMA monomer provided access to a series of polymer samples, covering the molar-mass range from 5.000 up to 100.000 Da, without any problem. Throughout, polydispersity indices were in the range from 1.03 - 1.05.

Next we prepared a broad variety of different PVFc- and PFMMA-based di- and -triblock copolymers. Poly(styrene-*b*-ferrocenylmethyl methacrylate) (PS-*b*-PFMMA) diblock copolymer, for example, was obtained by the following procedure: in the first step, living polystyrene macro-initiators were prepared, followed by the grafting-onto procedure using FMMA (Figure 2). Screening a variety of procedures finally led to the conclusion that the best diblock copolymers are available using the following technique: styrene is polymerized at room temperature, using *sec*-BuLi as the initiator and cyclohexane as the solvent. After complete conversion (approx. 2 h), DPE is added in order to convert the living polystyryl anions into chain termini of lower nucleophilicity, and thus appropriate reactivity for controlled initiation of the FMMA grafting-onto process. Quantitative formation of the DPE-

terminated polystyrene macro-initiator was ensured by stirring the mixture at room temperature for 7 h. The resulting dark red solution was freeze-dried, and the resulting red, foamy material was redissolved in a solution of LiCl in THF, cooled down to -78 °C, and added quickly to the cooled (-78 °C) solution of FMMA in THF. The dark red color of the DPE-terminated PS macro-initiators disappeared instantaneously, and full conversion of the living chains was achieved after approx. 2 h. De-activation of the living chains using degassed methanol followed by precipitation of the polymer in an excess of methanol resulted in essentially quantitative yields of orange solids.

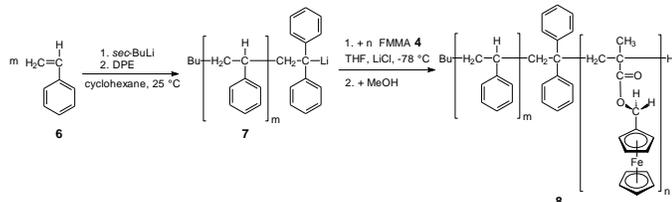


Figure 2. Synthesis of poly(styrene-*b*-ferrocenylmethyl methacrylate) via sequential living anionic polymerization.

NMR spectroscopy reconfirmed the expected constitution and composition of the products, and SEC provided deeper insights into the block structure of the products. It became evident that grafting of FMMA onto the PS macroinitiator was successful: only a very small amount of polystyrene homopolymer, formed by premature termination, is present in the raw diblock copolymer material. Such minor amounts of PS homopolymer can be completely removed by a selective precipitation step. Using this procedure, a variety of PS-*b*-PFMMA materials was prepared. Overall molar masses ranged from 15.000 to 110.000 Da, and block compositions (M_{PS}/M_{PFMMA} mass ratio) could be realized in the range from 10/1 to 1/10 so far.

In order to gain first insights into their microphase behavior, DSC and TEM investigations were performed. In the course of earlier TEM studies on silaferrocenylene-based block copolymers,^{9,10,11,12,13} we had learned that methylene chloride is an appropriate solvent for casting films of ferrocene-containing macromolecules. Therefore, we prepared a series of film samples of the new PS-*b*-PFMMA materials from the same solvent. In contrast to what we had found for the mentioned silaferrocenylene-based block copolymers, however, marginal microphase separation was observed for all PS-*b*-PFMMA systems after film-casting followed by annealing at 190 °C for 7 d. A further increase in annealing temperature to > 200 °C did not improve the results. Storage of the films in saturated methylene chloride atmosphere was considered to be a worthwhile alternative procedure. Consequently, PS-*b*-PFMMA copolymer films were prepared from methylene chloride solution and subsequently exposed to methylene chloride vapor at room temperature over up to 8 weeks. The recorded TEM pictures supported our assumption that insufficient chain mobility in the bulk state is the main reason for retarded or even prevented formation of defined microphase morphologies: when swollen in the solvent vapor for 8 weeks, the films showed essentially more completed microphase separation, and quite nicely developed morphologies.

We assume that in many cases the observed morphologies do not represent the thermodynamic equilibria but “frustrated” states. Even though a final explanation cannot be provided, rationalization of the unexpected micro-morphologies is possible by assuming partial miscibility of the (rather short) PFMMA block and the polystyrene at least in the solvent-swollen state: if under these conditions some PS blocks penetrate the PFMMA domains, the resulting increase in the PFMMA volume fraction might result in thermodynamically governed development of a layer morphology. Later on, during removal of the swelling medium, *i.e.* during evaporation of the methylene chloride, local de-mixing of PFMMA and PS segments might still occur, but certainly not fundamental re-organization of the overall micro-morphology, even though requested by changed volume fractions of the respective block. As a consequence, a non-equilibrium morphology remains frozen in the film samples finally obtained.

Finally, several attempts were made to polymerize ferrocene-containing monomers in grafting-from processes. Indeed, we could cover various colloidal particles by metal-containing corona chains of narrow polydispersity. Chain lengths and grafting densities of corona chains could be varied over a broad range. As an example, Figure 3 shows a TEM picture of a core-shell system of polystyrene cores and poly(dimethylsilaferrocenophane) (PFS) corona chains.

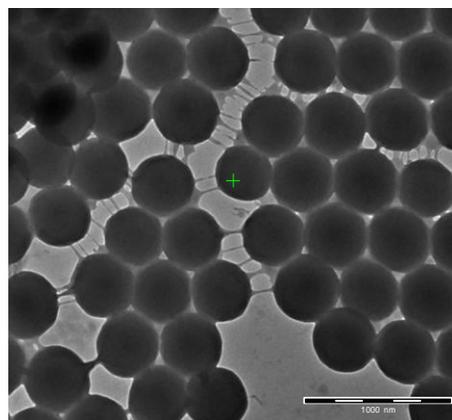


Figure 3. TEM picture of a core-shell system of polystyrene core particles and poly(dimethylsilaferrocenophane) (PFS) corona chains; prepared by drop-casting onto graphite-covered copper grid.

Conclusions

Efficient procedures have been described for living anionic polymerization of various ferrocene-containing polymers, thereby providing very powerful and versatile access to highly defined and homogeneous homo and block copolymers. The overall molar masses and block ratios can be varied over a broad range. Depending on the preparation conditions, “frustrated” micro-morphologies can be observed. Currently, we are broadening the scope of the presented synthetic route further, and are analyzing the microphase behavior of the materials in detail.

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