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Synthesis and Self-Assembly of Styrene–[1]Dimethylsilaferrocenophane–Methyl Methacrylate Pentablock Copolymers

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Experimental Section

Methods

NMR spectra were recorded on a Bruker ARX-500 spectrometer at 500 MHz (^1H) and 125 MHz (^{13}C). Molecular weights were determined by SEC using a Waters Associates Liquid Chromatograph equipped with a 515 HPLC pump, U6K injector, PSS ultrastyrigel columns with pore sizes of 10^3 , 10^5 , 10^6 Å and a Waters 410 differential refractometer. A flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$ was used. Samples were dissolved in THF containing toluene as a flow rate marker. Calculation of the molecular weights was carried out with respect to PS standards (purchased from PSS Polymer Standards Service GmbH, Mainz, Germany). Transmission Electron Microscopy (TEM) was carried out on films of around 1 mm thickness. These were cast from 5 % (w/v) solutions in dichloromethane, tetrahydrofuran and toluene, and allowed to evaporate slowly over 3–4 weeks at room temperature. Most thin films were annealed under vacuum at $180\text{ }^\circ\text{C}$ for 24 h. Ultrathin slices of cast films were cut to ca. 50 nm by means of LEICA Ultra Cut microtome at room temperature. Bright field TEM was performed using a Zeiss CEM902 transmission electron microscope operated at 80 kV and 50 μA beam current.

Materials

n-Butyl lithium (*n*-BuLi) (Aldrich, 2.5 M solution in hexane) was used as received. Tetrahydrofuran (THF) and diethyl ether were purified by distillation from deep purple sodium benzophenone. Hexane was distilled from sodium metal. While THF and hexane were stored over

red 1,1-diphenylhexyl lithium (DPHLi), diethylether was used directly. Dichlorodimethylsilane (Aldrich, 99 %) was distilled and carefully degassed in order to remove dissolved HCl. Ferrocene (Aldrich, 98 %) was purified by recrystallization from hexane. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) (Aldrich, 99.5 %) was distilled over CaH₂ (Fluka, ≥ 95 %). Methylmethacrylate (MMA) (Aldrich, 99 %) was first dried by stirring over CaH₂. After distillation it was titrated further with a small amount of triethylaluminium (Aldrich, 1.0 M solution in hexane) until a slight yellowish green color appeared and then stored in the glove-box refrigerator at -20 °C. Just prior to use it was condensed in vacuo and kept in liquid nitrogen in order to avoid autopolymerization. For purification of the 1,1-diphenylethylene (DPE) (Acros, 99 %), a small amount of *n*-BuLi was added until a deep red color appeared and distilled using a short-path distillation apparatus under high vacuum. The DPE purified and degassed in this manner was divided into small portions and stored in the glove-box refrigerator until used. 1,1-Dimethylsilacyclobutane (DMSB) (Fluka) was stirred over CaH₂, degassed, distilled and stored in the glove box. Methanol was dried by refluxing over magnesium metal in an atmosphere of N₂, distilled and carefully degassed by repeated freeze-pump-thaw cycles.

Unless otherwise noted, all manipulations were carried out using either a MBraun glove box equipped with a refrigerator or an all-glass high-vacuum line, equipped with Teflon valves and a removable four-inlet glass reactor. Both were operated with purified nitrogen. The preparation of polymeric precursors and other reagents and solutions involved the use of ampoules, also equipped with Teflon valves, which can be directly attached to the reactor. All the reactions including living anionic polymerizations were performed under an inert atmosphere (ultra-pure nitrogen), using either high vacuum techniques or a vacuum atmosphere glove box (MBraun).

[1]Dimethylsilaferrocenophane was synthesized according to a previously described procedure^[1] and further purified so as to obtain a product of “high purity” suitable for living anionic polymerizations by slight modifications which involved alternating cycles of recrystallization from *n*-hexane (- 60 °C), stirring over CaH₂ (600-700 mg) in THF for 24 h (20 mL) and high vacuum sublimations (10⁻⁵ mm Hg, 40 °C) until no impurities could be observed by ¹H NMR.^[1] High purity implies that no signals other than those for the silaferrocenophane and benzene were observed in a 20 times expansion of the vertical scale of the ¹H NMR spectrum of a solution containing 10 mg of silaferrocenophane in 0.5 mL of C₆D₆.

Synthesis of Pentablock Copolymer 3

Block copolymerization was carried out in a 250 mL five-necked reactor equipped with an appropriate magnetic stirring bar under a dry nitrogen atmosphere attached to a high-vacuum line. The concentration of the lithium naphthalide initiator solution used for the synthesis of pentablock copolymers was calculated back from the polymerization of styrene at $-50\text{ }^{\circ}\text{C}$. A solution containing 100 μL of green colored lithium naphthalide in 20 mL of THF was cooled to $-50\text{ }^{\circ}\text{C}$ in the polymerization reactor. Styrene (1 g, 9.6 mmol) was added to this quickly with stirring, upon which the solution immediately turned yellow. After stirring for 35 min the living polystyrene was terminated by addition of a few drops of CH_3OH and isolated by precipitation in methanol (100 mL). SEC analysis gave $M_n = 19,850\text{ g}\cdot\text{mol}^{-1}$, $\text{PDI} = 1.02$, from which the concentration of the lithium naphthalide initiator solution was calculated to be 0.504 M.

Styrene (see Table for quantities) was rapidly injected into a green solution of lithium naphthalide in 20 mL THF (0.0252 mmol, 50 μL , 0.504 M) at $-50\text{ }^{\circ}\text{C}$. The solution became yellow immediately. The styrene was polymerized for 35 min at this temperature, and then the reaction mixture was allowed to warm up to room temperature. Silaferrocenophane, dissolved in 10 mL THF, was added with stirring. The resulting red solution gradually changed to amber over 20 min. After 45 min the living polymer was trapped by means of dimethylsilacyclobutane (DMSB) mediated end-capping with 1,1-diphenylethylene so as to yield the living macroinitiator. A molar ratio of 1:4:2 for initiator:DPE:DMSB, respectively, was employed for the trapping reaction in all the block polymerizations. DPE (0.101 mmol, 18 μL) and DMSB (0.05 mmol, 6 μL) were immediately added in succession. The solution changed color from amber to red in 10-15 min and was stirred for 30 min during which the color deepened further. Next the red solution was cooled to $-80\text{ }^{\circ}\text{C}$ and MMA was added to it upon which the solution immediately turned yellow. MMA block polymerization was carried out for 75 min after which the living copolymer was terminated by addition of a few drops of methanol. The block copolymer was then isolated by precipitation into methanol (150 mL) and dried under high vacuum (4 h). Thus an orange-yellow powdery pentablock copolymer was isolated in about 90-95 % yield.

Table: Quantities of monomers and initiator used for the synthesis of the pentablock copolymers described in this paper.

Sample	S (g, mmol)	FS (g, mmol)	MMA (g, mmol)	I (μ mol)
A	0.28, 2.688	0.2, 0.8261	0.9, 8.989	25.2
B	0.25, 2.4	0.2, 0.8261	0.8, 7.9904	25.2
C	0.85, 8.16	0.4, 1.6522	1.2, 11.985	50.4
D	0.45, 4.32	0.2, 0.8261	0.65, 6.4919	25.2
E	0.6, 5.76	0.2, 0.8261	0.6, 5.9925	25.2
F	0.7, 6.72	0.2, 0.8261	0.5, 4.9938	25.2
G	0.75, 7.2	0.2, 0.8261	0.35, 3.4958	25.2

S: styrene, FS: [1]dimethylsilaferrocenophane, MMA: methylmethacrylate, I: lithium naphthalide (50/100 μ L of 0.504 M), solvent 30 mL in total.

SEC analysis of pentablock copolymer 3:

Without any purification, the SEC traces of the obtained polymers look as follows:

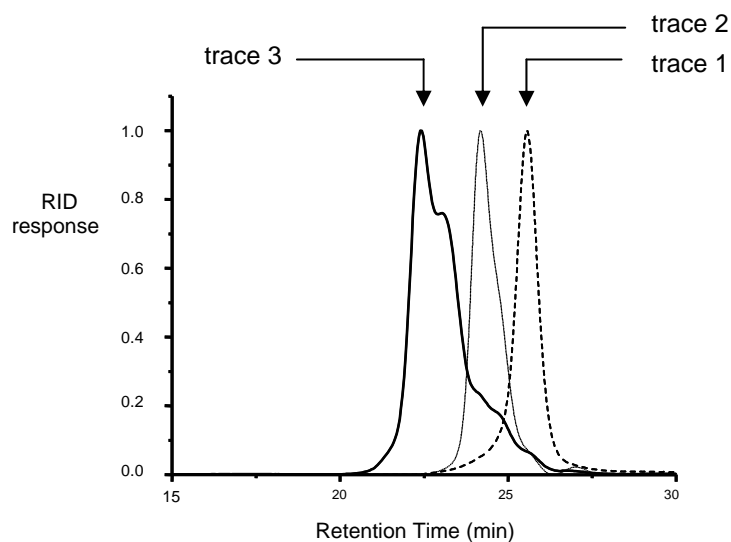


Figure 1. Characteristic SEC traces of PS **1** (trace 1), the PFS-*b*-PS-*b*-PFS intermediate **2** (trace 2), and the final PMMA-*b*-PFS-*b*-PS-*b*-PFS-*b*-PMMA pentablock copolymer **3** (trace 3). Samples are taken during a typical polymerization experiment according to Scheme 1 and analyzed without any further purification.

The pentablock can be purified by three cycles of repetitive precipitation in cyclohexane. Three solvents namely hexane, cyclohexane and toluene, were employed for the experiments. The best results were found for cyclohexane: about 0.7 g of the crude pentablock were dissolved in 10 mL of THF. To this solution, cyclohexane was added drop wise, initially fast but later slowly. After addition of 150 mL (total amount 190 mL) the solution turned turbid and the first grains of precipitate appeared. After addition of all the cyclohexane, the precipitate was separated off using a centrifuge (4000 rpm for 10 min). By this method, around 0.66g of the pentablock (+ some tetrablock) copolymer was obtained, and the triblock copolymer was efficiently separated off. The procedure can be repeated several times, depending on the required purity of the material.

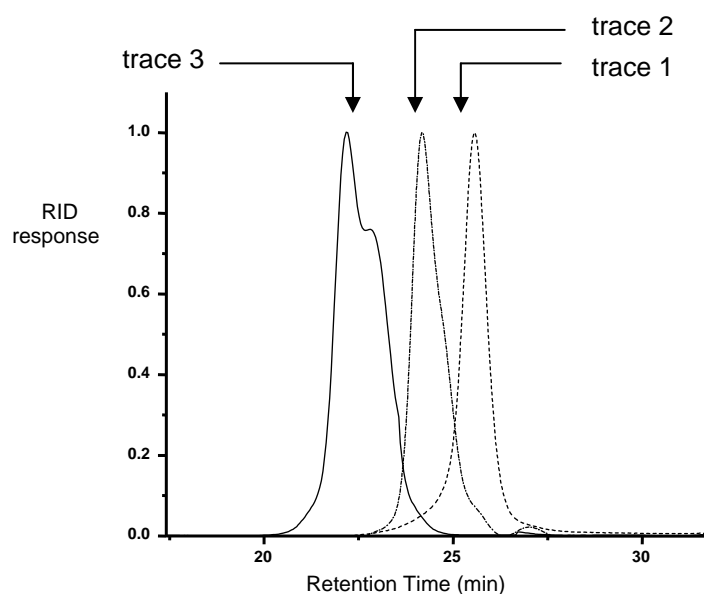


Figure 2. Characteristic SEC traces of PS **1** (trace 1), the PFS-*b*-PS-*b*-PFS intermediate **2** (trace 2), and the PMMA-*b*-PFS-*b*-PS-*b*-PFS-*b*-PMMA pentablock copolymer **3** (trace 3) after threefold precipitation according to the above purification procedure.

References:

- [1] C. Kloninger, M. Rehahn *Macromolecules* **2004**, 37, 1720.