Universal Methodology for Block Copolymer Synthesis

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Instrumentation

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker ARX-500 spectrometer operating at 500 and 125 MHz, respectively, in CDCl$_3$ at 25 °C. Size exclusion chromatography (SEC) analysis was performed with THF as the mobile phase at a flow rate of 1 mL/min on a modular setup consisting of a Waters 515 pump, a Waters 410 differential refractometer, a Waters 486 UV-detector, and a three column set (PSS-SDV-gel; 5 μm, 10$^6$, 10$^5$, 10$^4$ Å). MALDI-TOF MS spectra were recorded on a Kratos Compact MALDI 3 instrument operating with a 20 kV acceleration voltage in linear mode. The irradiation source was a pulsed nitrogen laser delivering 3 ns pulses at a wavelength of 337 nm.
Figure S-1. $^1$H-NMR spectrum of the reaction product between 1 and 2.

Figure S-2. MALDI-TOF mass spectrum of the product obtained from the first coupling step according to Scheme 2. The inset corresponds to a magnified view of the peaks around m/z ≈ 3500. All peaks are in full agreement with structure 3.
Figure S-3. $^{13}$C-NMR spectrum of the crude PS-$b$-PFS-$b$-PS product. No polystyrene head-to-head dimerization was observed at the 50 ppm region, evidencing the absence of side reactions.

Figure S-4. $^1$H-NMR spectrum of the crude PS-$b$-PFS-$b$-PS product. The absence of the CH$_2$-Cl signal evidences quantitative coupling.
Figure S-5. SEC pattern of an asymmetric PS-\textit{b}-PFS-\textit{b}-PS triblock copolymer. The shoulder corresponds to the excess of living PS-Li that used during the final coupling step.

Figure S-6. SEC pattern of \textit{ω}-chloropropyl polyisoprene.
Figure S-7. MALDI-TOF mass spectrum of the product obtained from the reaction between living polystyrene, endcapped with a few isoprene units, and silane 2. The inset corresponds to a magnified view of the peaks around m/z ≈ 4200. All peaks fit exactly to the expected structure.
Figure S-8. SEC pattern of a PS-\textit{b}-PI diblock copolymer. The shoulders correspond to the excess of living PI-(CH$_2$CH$_2$S)$_6$CH$_2$CH$_2$S-Li which upon exposure to ambient conditions affords the H-terminated analogue as well as the dimer due to oxidative coupling. (E. Nicol, C. Bonnans-Plaisance, P. Dony, G. Levesque, \textit{Macromol. Chem. Phys.} \textbf{2001}, 202, 2843.) However, the dimer formation could be eliminated by deactivation of the thianions prior to the exposure at ambient conditions e.g. by addition of EtBr. (M. Morton, R. F. Kammereck, L. J. Fetters, \textit{Macromolecules} \textbf{1971}, \textit{4}, 11.)
Figure S-9. SEC traces of the addition products of living polymers (PFS-Li, PMMA-Li, PS-CH$_2$CH(CH$_3$)O-Li) with 4-(chloromethyl)benzoyl chloride 4.
Figure S-10. MALDI-TOF mass spectrum of the product after the room temperature treatment of polystyryllithium with propylene oxide (2 equiv) at cyclohexene, followed by the addition of diethyl ether (20 equiv). The inset corresponds to a magnified view. All the peaks fit to the expected structure as Cu$^+$ cationized species. The same results were obtained also at pure cyclohexene, i.e. without added diethyl ether.
Figure S-11. MALDI-TOF mass spectrum of ω-chlorobenzyl-functionalized PS. The inset corresponds to a magnified view. The main peak distribution fits to the expected structure as Cu$^+$ cationized species. The higher intensity minor distribution corresponds to the non-chlorinated counterpart, caused by fragmentation during the ionization process, whereas the low intensity one to the expected cationized structure without integrated copper.