

## Experimental section

Chemicals were received from Aldrich, Fluka, Polymersource and Shearwater and used without further purification unless stated otherwise. Solvents were bought from Biosolve. DMSO was dried over BaO, DMF was dried over molecular sieves and THF was distilled over Na/K. For preparative size exclusion chromatography Bio-Rad SX-1 beads swollen in CH<sub>2</sub>Cl<sub>2</sub> or THF were used. Column chromatography was carried out on Merck silica gel 60. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded on a Varian Mercury spectrometer with frequencies of 400 and 100 MHz respectively and on a Varian Inova spectrometer with frequencies of 500 and 125 MHz respectively. For the metal containing block copolymers at least 200 scans were recorded and the T1 relaxation time was set to 10 seconds. Chemical shifts are given in ppm downfield from TMS. UV/Vis spectra were recorded on a Perkin Elmer Lambda 45P spectrophotometer. Matrix assisted laser desorption/ionization mass spectra were obtained using dithranol as the matrix on a PerSeptive Biosystems Voyager DE PRO spectrometer. All metal containing polymers (*mono*- and *bis*-complexes) were measured on a GPC-system using DMF with 5 mM NH<sub>4</sub>PF<sub>6</sub> as the eluent and calibrated with PMMA-standards:<sup>[13]</sup> the ‘free’ polystyrenes showed unreliable retention times in this eluent<sup>[14]</sup> and were measured on a GPC-system with CHCl<sub>3</sub> having 4% Et<sub>3</sub>N and 2% isopropanol by volume as the eluent and calibrated with PS-standards.<sup>[15]</sup> Tapping Mode AFM measurements were performed using a MultiMode Scanning Probe Microscope from Digital Instruments, Inc. (Santa Barbara, CA, USA). The samples were probed under minimal force tapping conditions using non contact CSC12 silicon cantilevers (MikroMasch), with a force constant of ~1.75 N/m.

**General procedure for the nitroxide mediated polymerization of styrene using the terpyridine functional initiator:** Styrene was subjected to an AlOx-filtration column before use in order to remove the inhibitor. Three degrees of polymerization (DP) were targeted and the corresponding amounts of styrene and the initiator were transferred to the reactors. Three freeze-pump-thaw-cycles were applied for removal of oxygen before the reaction vessels were immersed in an oilbath of 125 °C. The conversion was measured gravimetrically. For DP = 100, 9.998 g styrene and 0.653 g initiator were reacted for 5 h upon which 75% conversion was reached, while for DP = 250, 4.545 g styrene and 0.1026 g initiator were reacted for 8 h and 80% monomer conversion was reached. Finally, for a DP = 450, 4.545 g styrene and 0.0574 g initiator were reacted for 8 h and 60% monomer conversion was reached. The crude polymer was precipitated twice from CH<sub>2</sub>Cl<sub>2</sub> into methanol and dried for 24 h in a vacuumstove at 50 °C. Yields were 7.221 g (72%) for **22**, 3.123 g (74%) for **23** and 2.410 g (56%) for **24**. Molecular weights and polydispersity indices were measured by size exclusion chromatography, whereas <sup>1</sup>H-NMR was used for the determination of end group functionality and molecular weight by careful integration of the polymer backbone to the terpyridine signals. Selected analytical data are for **23**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 8.68 (m, broad, 2H, H<sub>6,6'</sub>), 8.62 (m, broad, 2H, H<sub>3,3'</sub>), 8.21 (m, broad, 2H, H<sub>3',5'</sub>), 7.93 (m, broad, 2H, H<sub>4,4'</sub>), 7.47-6.32 (m, broad, 1023H, H<sub>PS backbone aromatic</sub>; H<sub>aromatic nitroxide</sub>, H<sub>5,5'</sub>), 5.34 (m, broad, 2H, tpyOCH<sub>2</sub>), 4.27-4.07 (broad, 1H, HC-O-N), 3.50-3.15 (broad, 1H, O-N-CH), 2.45-0.53 ppm (m, broad, 621H, H<sub>PS backbone aliphatic</sub>; C(CH<sub>3</sub>)<sub>3</sub>; CH<sub>3</sub>CHCH<sub>3</sub>; CH<sub>3</sub> initiating fragment). GPC (RI): M<sub>n</sub> (PDI): 20500 g mol<sup>-1</sup> (1.14). Analytical data for **22**: GPC (RI): M<sub>n</sub> (PDI): 7700 g mol<sup>-1</sup> (1.08). Analytical data for **24**: GPC (RI): M<sub>n</sub> (PDI): 25500 g mol<sup>-1</sup> (1.17)

**General procedure for the preparation of RuCl<sub>3</sub> mono-terpyridine complexes:** A three-fold excess of anhydrous RuCl<sub>3</sub> with respect to the terpyridine end functionalized polymer was heated in dry degassed DMF to 130 °C. After the color of the suspension changed from blue to green to brown, a solution of the corresponding poly(ethylene oxide) in dry degassed DMF was added dropwise. For DP = 70, 125, 225 and 375 of the poly(ethylene oxide) this required 0.800 g, 0.200 g, 0.250 g and 0.500 g of polymer and 0.096 g, 0.050 g, 0.011 g and 0.011 g of RuCl<sub>3</sub> respectively. Stirring was continued overnight at 130 °C and then the solution was allowed to cool to room temperature. The resulting mixture was partitioned between water and CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated *in vacuo*. The brown residue was taken up in a minimum amount of THF and precipitated twice in ice-cold diethyl ether. Yields were between 79-88%. Selected analytical data: UV/vis:  $\lambda$  / nm ( $\epsilon$  / L mol<sup>-1</sup> cm<sup>-1</sup>): **25**: 401 (8700), 311 (16500), 276 (31000); **26**: 400 (8700), 311 (16300), 277 (30600); **27**: 397 (8800), 311 (16900), 277 (30900); **28**: 395 (8200), 311 (15900), 277 (29800); GPC (RI): M<sub>n</sub> (PDI): **25**: 7000 g mol<sup>-1</sup> (1.08); **26**: 11000 g mol<sup>-1</sup> (1.12); **27**: 17000 g mol<sup>-1</sup> (1.08); **28**: 28000 g mol<sup>-1</sup> (1.08).

#### AFM-studies

All of the prepared thin films had a thickness between 35 and 60 nm with a deviation of ~1 nm in thickness over the whole sample except for the thin films of **15** and **16** that showed holes of up to 20 nm deep.

**General procedure for the synthesis of the PS<sub>m</sub>-[Ru]-PEO<sub>n</sub> block copolymers 1-16:** Terpyridine functionalized polystyrene and the RuCl<sub>3</sub> mono-complex of terpyridine functional poly(ethylene oxide) were reacted in a 1.05:1 molar ratio in a 4:1 solvent mixture of chloroform and methanol at reflux under argon. After 30 minutes a catalytic amount of *N*-ethylmorpholine was added and a color change from brown to purple to red was observed. Stirring was continued overnight, after which a ten-fold excess of NH<sub>4</sub>PF<sub>6</sub> was added. The solution was then allowed to cool to room temperature and poured into water. The water-layer was extracted twice with chloroform and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated *in vacuo*. The crude product was purified by a combination of preparative size exclusion chromatography on BioBeads SX-1 swollen in THF and/or CH<sub>2</sub>Cl<sub>2</sub> and column chromatography (SiO<sub>2</sub>, THF to wash down uncomplexed material, followed by 10% MeOH in THF to separate the *mono*-, if any, from the *bis*-complex, which was isolated by addition of NH<sub>4</sub>PF<sub>6</sub> to the eluent). Selected analytical details for **10**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.41 (bm, 2H, H<sub>3:3'</sub> PEO), 8.34-8.22 (bm, 6H, H<sub>3:3'</sub> PS, H<sub>3':5'</sub> PS & PEO), 7.83 (bm, 4H, H<sub>4:4'</sub> PS & PEO), 7.47 (bm, 2H, *H*-PhCH<sub>2</sub>Otpy), 7.36 (m, 6H, H<sub>5:5'</sub> PS & PEO, *H*-PhCH<sub>2</sub>Otpy), 7.21-6.28 (m, 349 H, PS backbone, H<sub>6:6'</sub> PS & PEO, *H*-Ph-nitroxide), 5.58 (m, 2H, tpyOCH<sub>2</sub>, PS), 4.77 (m, 2H, tpyOCH<sub>2</sub>, PEO), 4.11 (m, 2H, tpyOCH<sub>2</sub>CH<sub>2</sub>), 3.88-3.46 (m, 901 H, PEO-backbone, Ph-CH-O-N), 3.38 (s, 3H, OCH<sub>3</sub>, PEO), 2.20-1.20 (m, 205 H, PS backbone, O-N-CH), 0.88 (m, 9H, C(CH<sub>3</sub>)<sub>3</sub> nitroxide), 0.66-0.28 (m, 7H, isopropyl nitroxide); UV/vis (THF):  $\lambda$  / nm ( $\epsilon$  / L mol<sup>-1</sup> cm<sup>-1</sup>): 487 (14800), 306 (52100), 270 (69100), 263 (69000); GPC (RI): M<sub>n</sub> (PDI): 27000 g mol<sup>-1</sup> (1.10).