

### Physical properties of initiators

**Free-base initiator**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300.13 MHz)  $\delta$  8.88-8.81 (m, 8H,  $\beta$ -pyrroleH)  $\delta$  8.24 (d, 2H, ArHO,  $^3J = 8.5$  Hz)  $\delta$  8.09 (d, 6H, ArHCH<sub>3</sub>,  $^3J = 7.7$ )  $\delta$  7.56 (d, 6H, ArHCH<sub>3</sub>,  $^3J = 7.7$ )  $\delta$  7.54 (d, 2H, ArHO,  $^3J = 8.22$  Hz),  $\delta$  2.71 (s, 9H, ArCH<sub>3</sub>),  $\delta$  2.23 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>Br),  $\delta$  -2.78 (s, 2H, NH) ppm. Maldi-TOF mass spectrometry (reflective mode)  $m/z$  820, 821, 822, 823, 824, 825 (isotopic pattern  $M^+$ ). UV-vis ( $\text{CHCl}_3$ )  $\lambda$  420, 517, 553, 594, 648 nm. IR (KBr pellet)  $\nu_{\text{C=O}}$  1756  $\text{cm}^{-1}$ .

**Cu(II) initiator** UV-vis ( $\text{CHCl}_3$ )  $\lambda$  417, 541, 574 nm.

**Mn(III) initiator** UV-vis ( $\text{CHCl}_3$ )  $\lambda$  382, 486, 586, 626 nm.

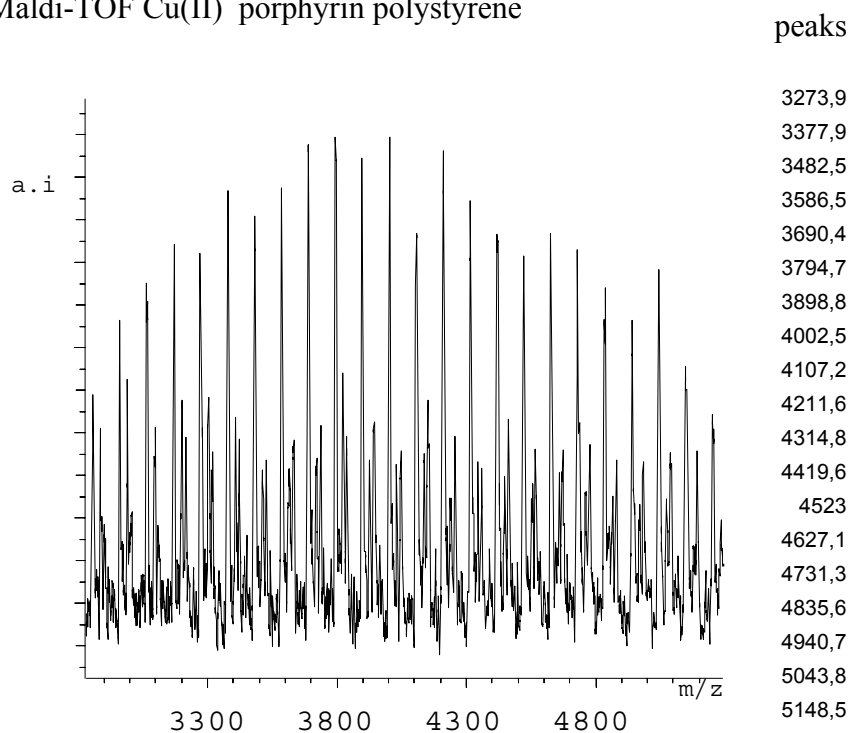
**Zn(II) initiator** UV-vis ( $\text{CHCl}_3$ )  $\lambda$  421, 549, 586 nm.

### ATRP procedure

A schlenk tube was charged with the porphyrin initiator and CuBr and vacuum-nitrogen refilled three times. Subsequently, the schlenk tube was capped with a septum and styrene and anisole were added with a syringe. The resulting mixture was purged with nitrogen for 5 min. and placed in an ice-bath, after which PMDETA was added as the ligand. Next, the tube was placed in an oil bath with a temperature of 90 °C and the reaction mixture was sampled periodically to determine the ratio styrene/anisole with gas chromatography.

### Characterization of Cu(II) porphyrin polystyrene

Maldi-TOF Cu(II) porphyrin polystyrene



UV-VIS Cu(II) porphyrin polystyrene (toluene)  $\lambda$  417, 540, 575 nm.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300.13 MHz)  $\delta$  1.22-1.71 ((CH<sub>2</sub>-CHPh)<sub>n</sub>)  $\delta$  1.71-2.35 ((CH<sub>2</sub>-CHPh)<sub>n</sub>)  $\delta$  6.28-7.25 ((CH<sub>2</sub>-CHPh)<sub>n</sub>) ppm, The paramagnetic Cu(II) porphyrin is not visible with NMR.

### Sample treatment

After polymerization the mixture was dissolved in toluene and purified over a short size exclusion column (Bio-beads S-X1) with toluene as the eluents to remove traces of copper and unreacted monomer from the polymer batch. Preparation of the (Cu)porphyrin

polystyrene samples for TEM and SEM studies was performed by injecting 100  $\mu\text{l}$  of a THF solution (0.3 mg/ml) of the compound into 1 ml of milliQ water while sonicating at 60  $^{\circ}\text{C}$ . A drop of the resulting cloudy solution was placed on a carbon coated copper grid and the water was drained off after 2 min.

For the (Mn) porphyrin polystyrene studies, to 100  $\mu\text{l}$  of a THF solution (3 mg/ml) of the compound was slowly added 200  $\mu\text{l}$  of water. A drop of the resulting solution was placed on a carbon coated copper grid and the drop was drained off after 2 min.

TEM images were obtained with a JEOL JEM-1010 microscope (60 kV) equipped with a CCD camera. SEM images were recorded with a JEOL JSM-6330F microscope.