Supporting Information

Kinetics of Fe-mesohemin-(MPEG₅₀₀)₂-mediated RDRP in Aqueous Solution

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Figure S1: Visible spectra for the reaction of Br-Fe^{III}/L with ascorbic acid in aqueous solution of PEGMA at ambient temperature. The absorbance of Br-Fe^{III}/L does not change significantly within 2 hours after adding 1 equiv of ascorbic acid which indicates of a very slow reduction.



Figure S1: Absorbance spectra in the visible range during PEGMA polymerization with the Fe^{II}-mesohemin-(MPEG₅₀₀)₂ catalyst and with VA-44 in 50 wt% H₂O at 60 °C. (A) The reaction of Fe^{II}/L with PEGMA radicals yields R-Fe^{III}/L on a time scale of 10 min. The arrows indicate the direction of absorbance change. The resulting R-Fe^{III}/L species is marked in red. (B) Dissociation of the R-Fe^{III}/L species upon running the polymerization for more than 30 min.



Figure S2: ⁵⁷Fe Mössbauer spectra recorded on a flash-frozen solution of Cl-Fe^{III}/L after different types of reaction. (A) Cl-Fe^{III}/L in PEGMA with 50 wt% water. (B) Cl-Fe^{III}/L after the reaction with 5 equivalents ascorbic acid (AsAc) in a 50 wt% PEGMA-water mixture. (C) PEGMA polymerization in 50 wt% water according to the procedure described by Simakova *et al.*¹⁵ In all cases the Cl-Fe^{III}/L species is Mössbauer silent and could not be detected due to intermediate spin relaxation.



Figure S3: ⁵⁷Fe Mössbauer spectra recorded at various temperatures for solid Cl-Fe^{III}/L. The asymmetric peak shape is typical for Fe^{III} complexes and results from intermediate spin relaxation. The spectrum at 13 K was fitted with the parameters $\delta = 0.45 \text{ mm s}^{-1}$, $\Delta E_Q = 2.50 \text{ mm s}^{-1}$, $\Gamma = 0.66 \text{ mm s}^{-1}$ and with the intensity ratio of left (I_1) to right (I_r) components being $I_1 : I_r = 1.42$.



Figure S 4: EPR spectrum of PEGMA radicals recorded under stationary conditions as described in the main text. The arrow indicates the magnetic field position used for monitoring the time dependence of radical concentration.



Figure S5: Visible spectra of the individual mesohemin-(MPEG₅₀₀)₂ species in monomer-free model systems, i.e., in mixtures of PEO with 50 wt% H₂O at 22 °C. The black line indicates the initial Br-Fe^{III}/L species which was reduced by $Na_2S_2O_4$ to yield the Fe^{II}/L spectrum (red line). The reaction of Fe^{II}/L with the thermal initiator VA-44 at 65 °C yields the R-Fe^{III}/L species (green line).



Figure S7: Plot of the F([Y]) function vs time, t, for the reaction of Fe^{II}/L with HEMA-Br as described in the main text. A straight line was fitted to the equilibrium data with the slope of 45.9 s⁻¹ taken for the analysis of K_{model} as described in the main text.



Figure S8: (l.h.s.) PREDICI[®] modeling of the [Br-Fe^{III}/L] vs time profiles upon variation of K_{model} , while k_{deact} and k_{add} were kept constant. (r.h.s.) PREDICI[®] modeling of the [Br-Fe^{III}/L] vs time profiles upon variation of k_{deact} , while K_{model} and k_{add} were kept constant. The concentrations of Fe^{II}/L and HEMA-Br used with these simulations are given in the main text.