Supporting Information

Chlorophyll derivatives as catalysts and comonomers for atom transfer radical polymerizations

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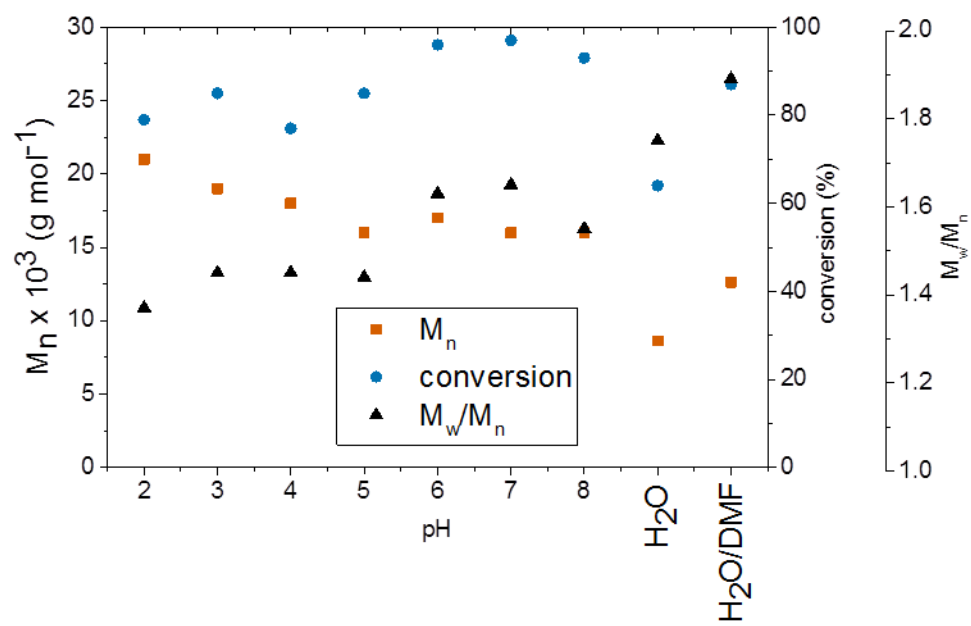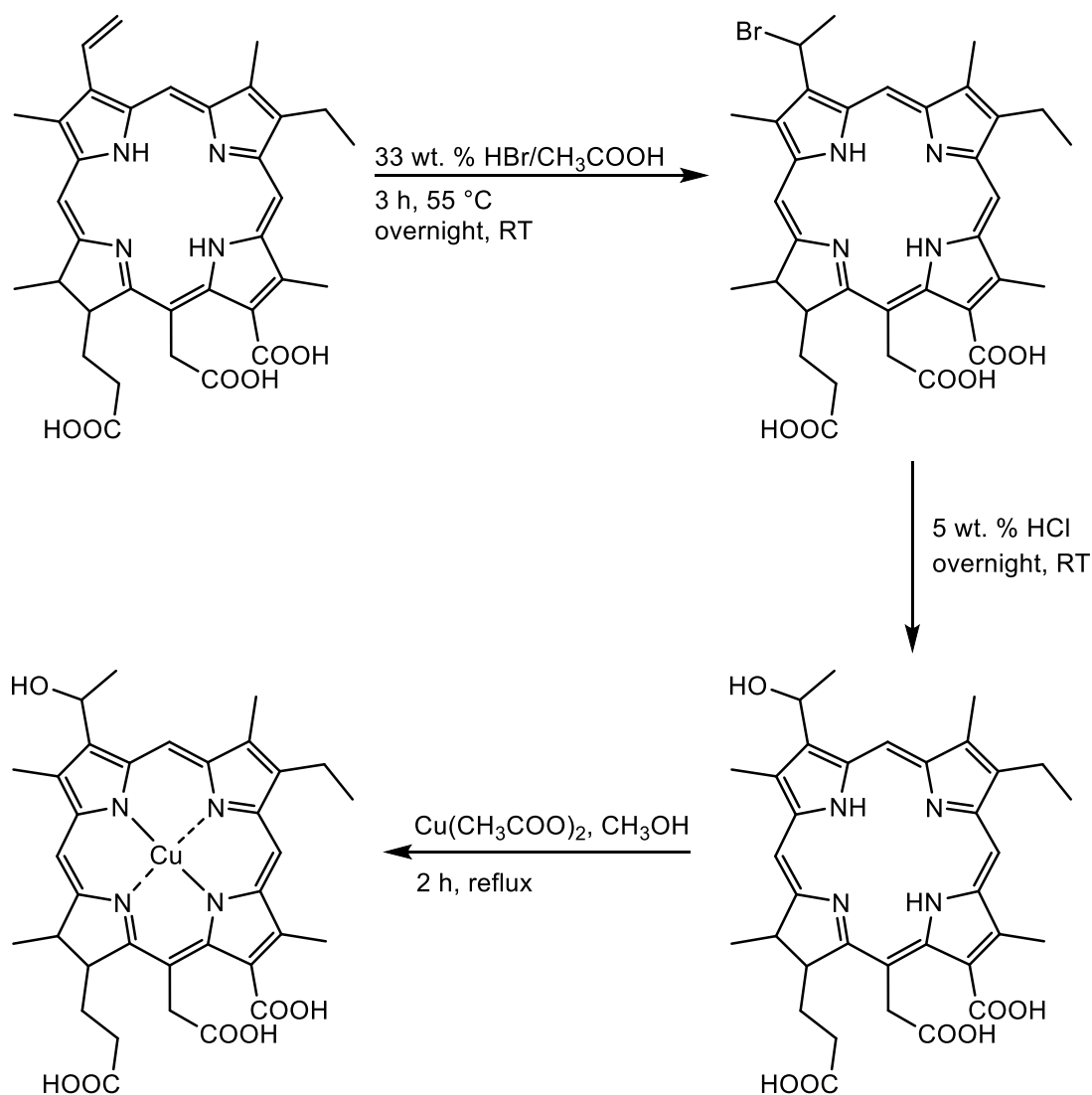
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Figure S1. Influence of pH and cosolvent on the CuChln-catalyzed copolymerization of PEGA and CuChln. Reaction conditions: Ratio PEGA:HEBIB:CuChln:NaAsc: 62.5:1:1:1; no NaBr; reaction time: 24 h; solvent: phosphate-citrate buffer, water, or 20 % v/v DMF in water.

Scheme S1. Synthesis of hydrated CuCe6. Hydration of the vinyl bond of Ce6 by a Markovnikov addition of HBr to the vinyl bond, followed by nucleophilic substitution of the bromide with water and insertion of Cu in the porphyrin center.

Table S1. Variation of NaAsc concentration in CuChln-catalyzed ATRP of PEGA. (Reaction time: 24 h, solvent: phosphate-citrate buffer (pH 4)).

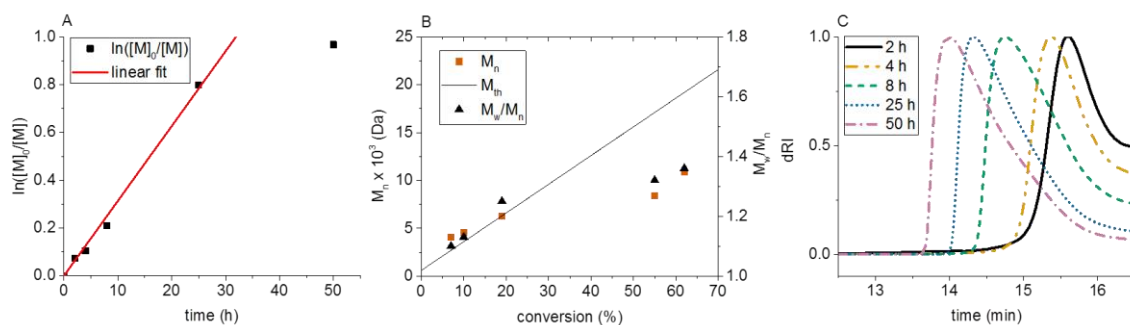| M:I:C:RA	c_{NaAsc} (mg ml^{-1})	Conversion (%)	M_n (g mol^{-1})	M_w/M_n
62.5:1:1:5	22.5	60	18700	1.74
62.5:1:1:2.5	11.3	68	23500	1.92
62.5:1:1:1	4.50	77	18000	1.45
62.5:1:1:0	0.00	-	-	-

Figure S2. Kinetic data for the CuChln-catalyzed copolymerization of PEGA with 2 equivalents of chlorophyllin. A) $\ln([M]_0/[M])$ vs time, B) molecular weight and dispersity versus conversion, C) GPC elugrams. Reaction conditions: Ratio PEGA:PEG-Br:CuChln:NaAsc: 62:1:2:1; solvent: phosphate-citrate buffer (pH 4) + NaBr.
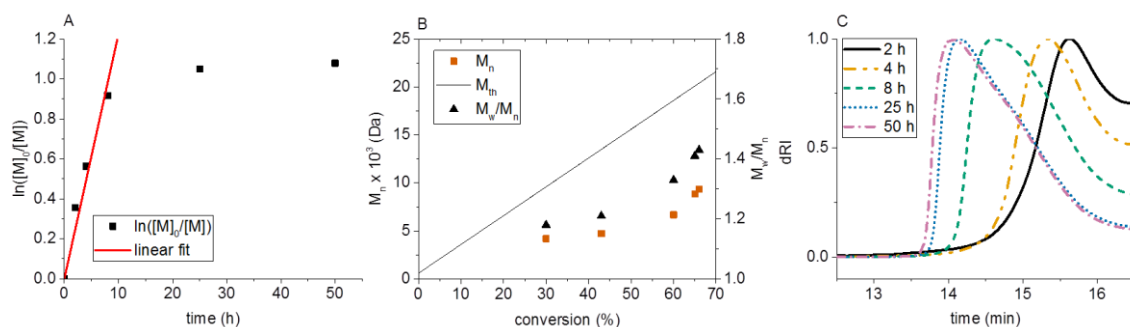

Figure S3. Kinetic data for the CuChln-catalyzed copolymerization of PEGA with 5 equivalents of chlorophyllin. A) $\ln([M]_0/[M])$ vs time, B) molecular weight and dispersity versus conversion, C) GPC elugrams. Reaction conditions: Ratio PEGA:PEG-Br:CuChln:NaAsc: 62:1:5:1; solvent: phosphate-citrate buffer (pH 4) + NaBr.
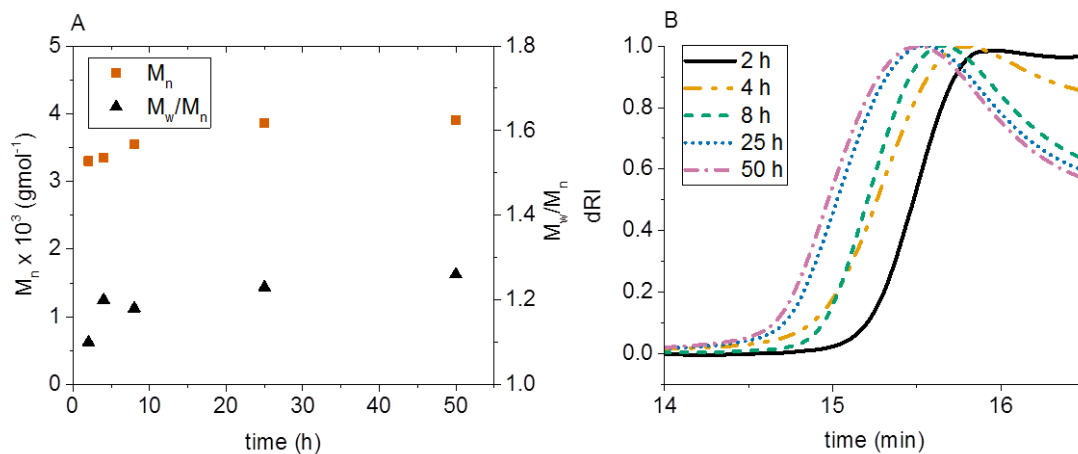

Figure S4. Kinetic data for the CuChln-catalyzed copolymerization of PEGA with 10 equivalents of chlorophyllin. A) molecular weight and dispersity versus time, B) GPC elugrams. Reaction conditions: Ratio PEGA:PEG-Br:CuChln:NaAsc: 62:1:10:1; solvent: phosphate-citrate buffer (pH 4) + NaBr.

Table S2. Content of CuChln in copolymers that were synthesized by CuChln-catalyzed ATRP of PEGA under variation of the CuChln concentration. The polymers were purified from the reaction mixture by precipitation prior to analysis by UV-vis spectroscopy and ICP-OES.

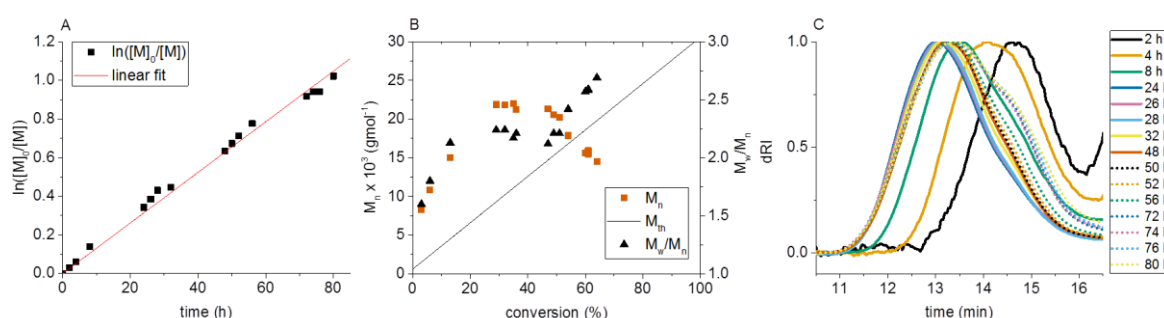| Eq. chlorophyllin	Conversion at which the polymerization was stopped (%)	M_n (g mol^{-1})	M_w/M_n	c_{CuChln}(UV-vis) (wt. %) 405 nm	c_{CuChln}(ICP-OES) (wt. %)
1	47	3890	1.15	1.47 ± 0.05	2.37 ± 0.04
2	62	4300	1.19	5.0 ± 0.4	7.78 ± 0.08
5	66	4270	1.17	9.7 ± 1.1	16.5 ± 0.6
10	n.d.	3620	1.17	16.1 ± 1.0	43.1 ± 1.4

Figure S5. Kinetic data for CuChln-catalyzed copolymerization of PEGA and ChChln with NaAsc feeding every 24 h: A) $\ln([M]_0/[M])$ vs time, B) molecular weight and dispersity versus conversion, C) GPC elugrams. Reaction conditions: Ratio PEGA:PEG-Br:CuChln: 62:1:1; 1 equiv. NaAsc was present at the beginning of the reaction, 1 additional equiv. NaAsc were added every 24 h; solvent: phosphate-citrate buffer (pH 4) + NaBr.
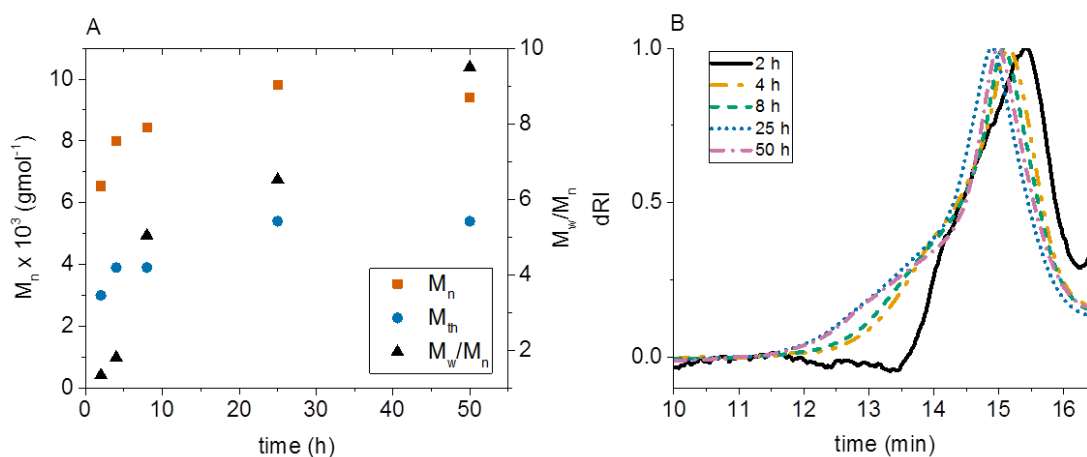

Figure S6. Free radical polymerization of PEGA in the presence of CuChln. A) molecular weight and dispersity versus time, B) GPC elugrams. The reaction yielded 18 % monomer conversion after 50 h and gave a copolymer with M_n = 9410 g mol^{-1} and M_w/M_n = 9.49. The dispersity is very high, as expected for polymers produced via free radical polymerization. Reaction conditions: Ratio PEGA:CuChln:NaAsc 62:1:1; APS/TEMED = 1/1 ; solvent: phosphate-citrate buffer (pH 4).
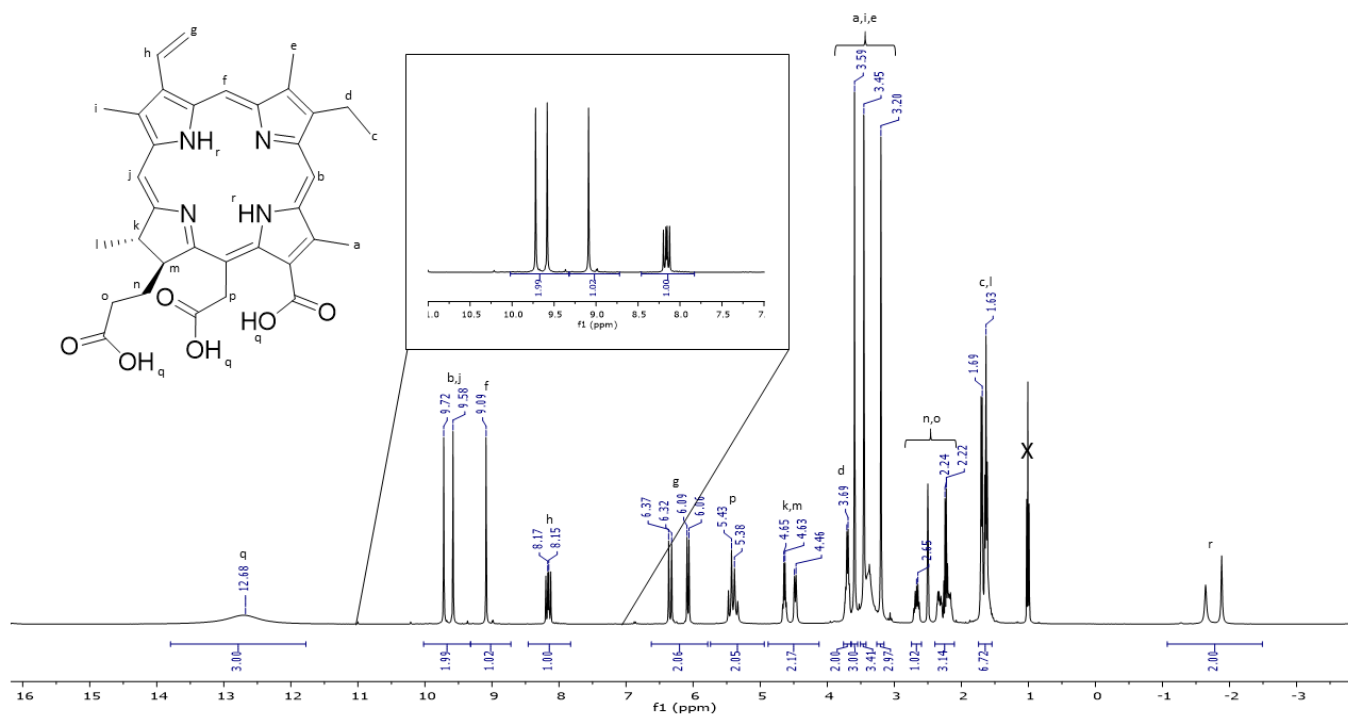
Figure S7. ¹H NMR (300 MHz, DMSO-d_6) spectrum of chlorin-e6. Expansion highlights the region containing peaks corresponding to the vinyl proton (h) and the meso protons (b,f,j) of the macrocycle.
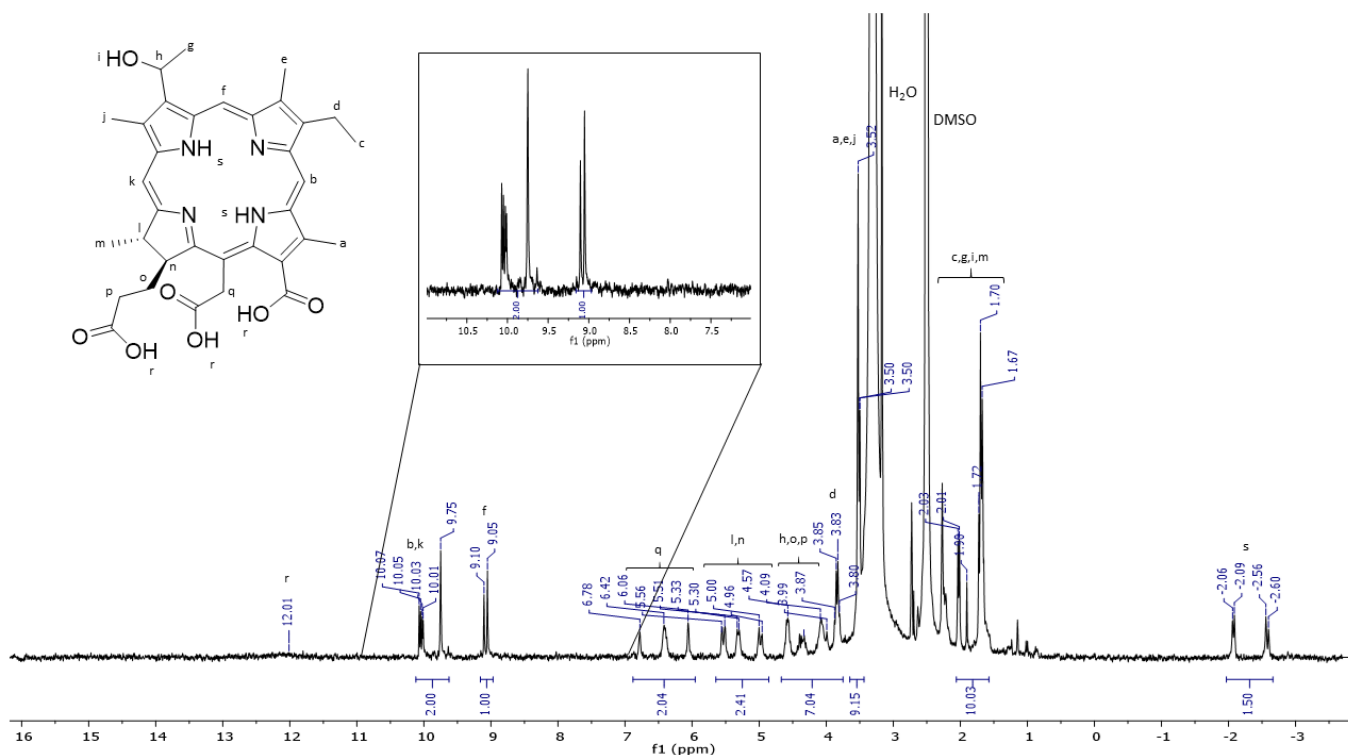

Figure S8. ¹H NMR (300 MHz, DMSO-d_6) spectrum of hydrated chlorin-e6. Expansion highlights the absence of the peaks corresponding to the vinyl proton seen in Figure S7. Additional evidence of hydration is seen between 1.00-2.50 ppm where the peaks corresponding to the newly formed methyl group and hydroxyl proton are present.
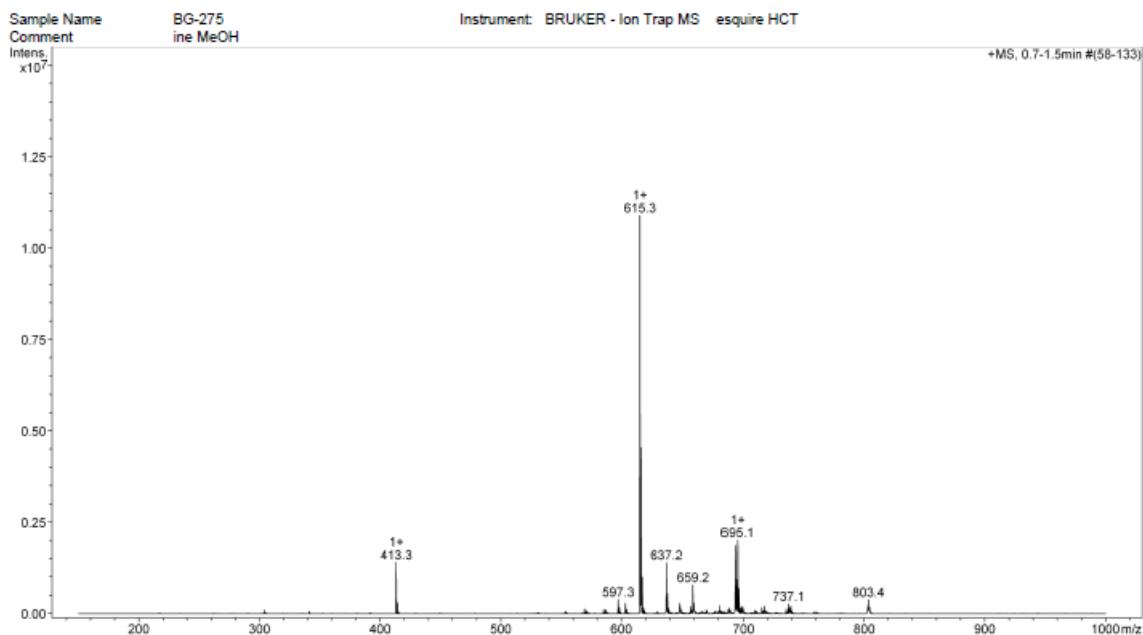
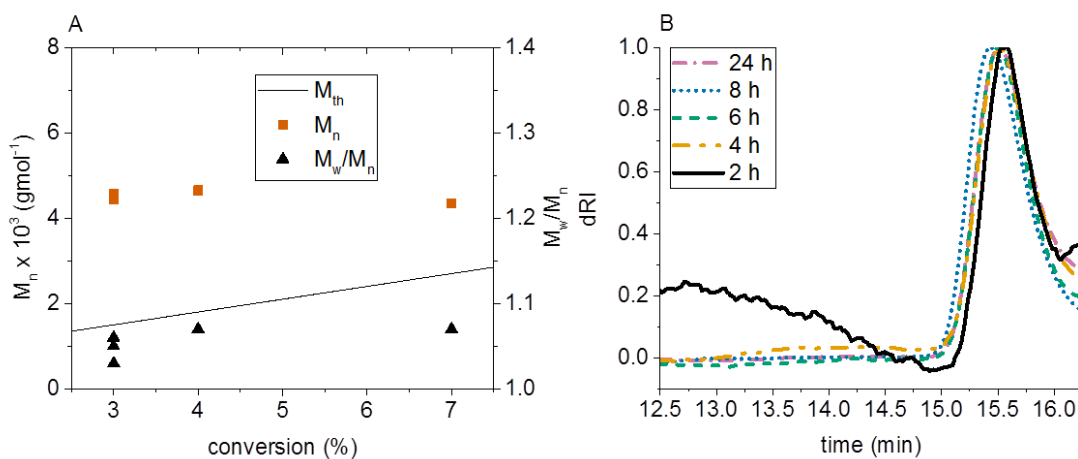Figure S9. ESI-MS spectrum of hydrated chlorin-e6 with a m/z= 615.3+.

Figure S10. Kinetic data for polymerization of PEGA catalyzed by hydrated CuCe6 at pH 4 with PEG-Br as the initiator. A) molecular weight and dispersity versus conversion, B) GPC elugrams. Reaction conditions: Ratio PEGA:PEG-Br:hydrated CuCe6:NaAsc: 62:1:1:1; solvent: phosphate-citrate buffer (pH 4) + NaBr.
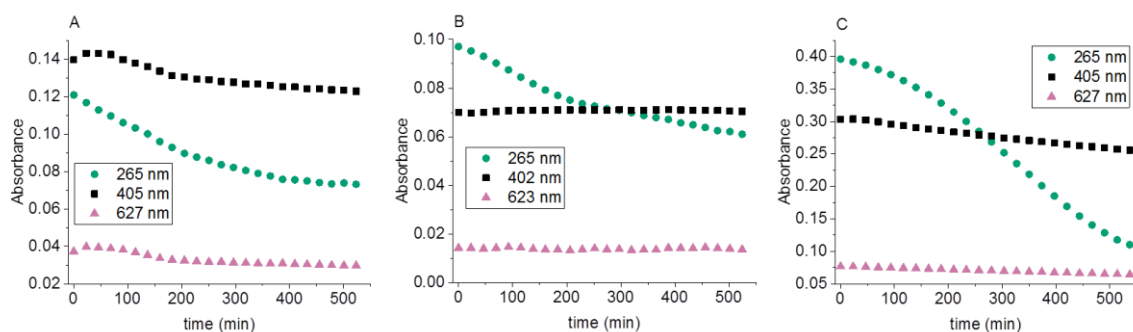
Figure S11. Development of absorbance at 265 nm, 405 nm, and 627 nm A) during the copolymerization of PEGA with chlorophyllin at pH 4, B) during the polymerization of PEGA catalyzed by hydrated CuCe6 at pH 8, and C) during the reaction of NaAsc with chlorophyllin in water (every 4th data value from the original 96 were depicted for the comparison).
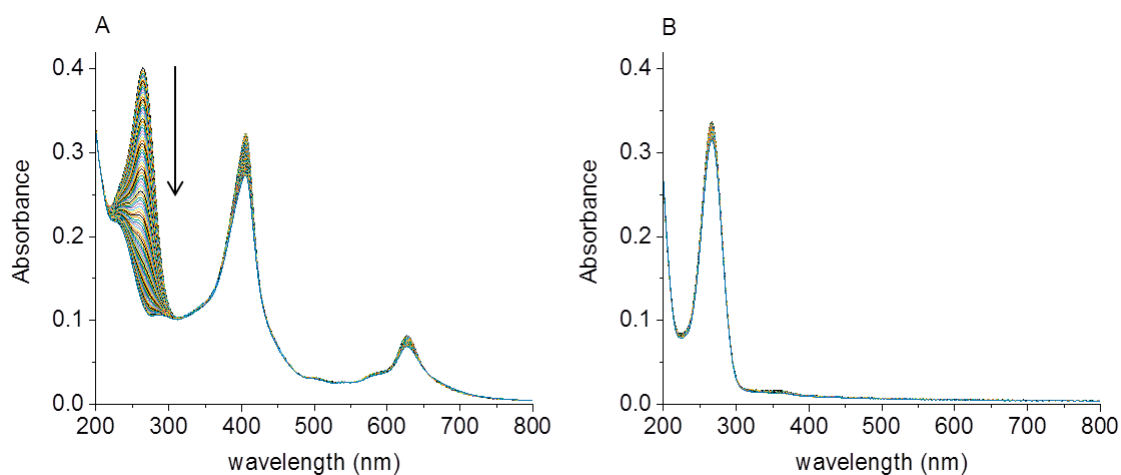

Figure S12. Development of UV-vis spectra A) during the reaction of chlorophyllin with NaAsc in water, B) during the reaction of HEBIB with NaAsc in water. The arrow indicates the direction of the evolution of the spectra.
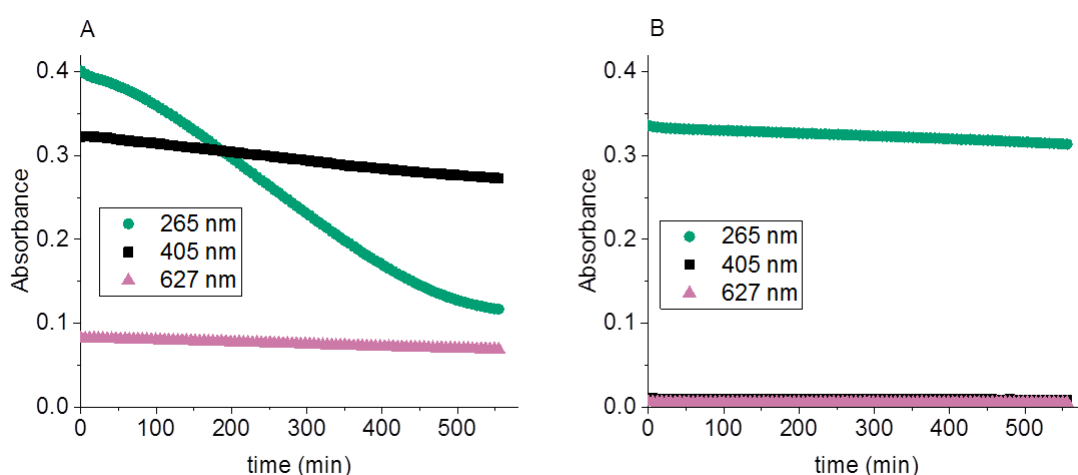

Figure S13. Development of absorbance at 265 nm, 405 nm, and 627 nm A) during the reaction of chlorophyllin with NaAsc in water, B) during the reaction of HEBIB with NaAsc in water.

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