Supporting Information for

Direct ATRP of Methacrylic Acid with Iron-porphyrin Based Catalysts

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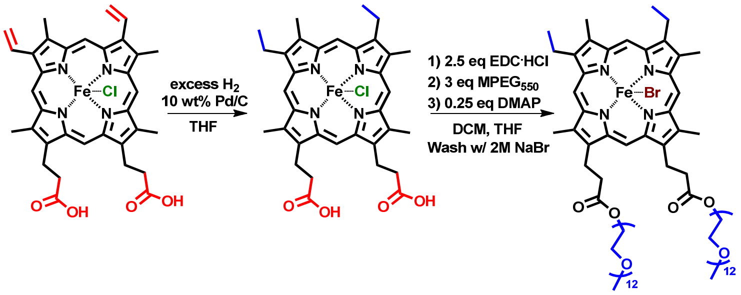
Experimental

Materials: All chemicals were purchased from commercial sources, *e.g.*, Sigma Aldrich, Alfa Aesar, TCI, and Frontier and were used as received if not stated otherwise. Oligo(ethylene oxide) methyl ether methacrylate ($OEOMA_{475}$, 99%, average molecular weight 475, Aldrich) and oligo(ethylene oxide) methyl ether acrylate ($OEOA_{480}$, 99%, average molecular weight 480, Aldrich) were passed over a column of basic alumina (Fisher Scientific) prior to use to remove inhibitor. Poly(ethylene glycol) bromophenyl acetate ($PEG_{2000}BPA$), poly(ethylene oxide) isobutyryl bromide ($PEO_{2000}iBBr$)[1] and mesohemin[2] were prepared as previously reported in prior publications.

Gel Permeation Chromatography (GPC): GPC was used to determine number average molecular weight (M_n) and M_w/M_n values and was conducted with a Waters 515 HPLC Pump and Waters 2414 Refractive Index Detector using PSS columns (SDV 10^2, 10^3, 10^5 Å) in tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min at 35 ^oC. The apparent molecular weights (M_n) and dispersities (M_w/M_n) were determined using linear poly(methyl methacrylate) (M_n = 800 ~ 1,820,000) standards using WinGPC 7.0 software from PSS. The previously reported Mark-Houwink parameters[3] were used for universal calibration using WinGPC 7.0 software from PSS. Conversion was determined using GPC by following the decrease of monomer peak area relative the increase of polymer peak area as previously reported.

Mass spectroscopy: Mass spectra were recorded on a *Varian* Saturn 2100T *MS* with *3900* GC using an EI source. In each case, characteristic fragments with their relative intensities in percentages are shown. Electrospray mass spectra were measured on a Thermo-Fisher LCQ ESI/APCI Ion Trap containing a quadruple field ion trap mass spectrometer with electrospray ionization (ESI).

Electrochemical Analysis: All of the cyclic voltammograms (CV) were recorded at 25 °C with a Gamry Reference 600 potentiostat using a standard three-electrode system consisting of a glassy carbon (GC) working electrode, platinum wire counter electrode, and SCE reference electrode. The GC electrode was polished with a 0.25 µm diamond paste before use. The solution was bubbled with nitrogen for at least 15 minutes. CV measurements were carried out under a nitrogen atmosphere at a scan rate of 100 mV/s.



Scheme S1: Synthetic scheme of Mesohemin-(MPEG$_{550}$)$_2$

Mesohemin synthesis. Mesohemin was synthesized according to the previously reported method for hydrogenation of Hemin (1.1 mmol, 700 mg), Pd/C (10 wt. % to hemin, 105 mg) were mixed in 25 ml Schlenk flask, which was sealed, equipped with balloon and purged with nitrogen. Dry THF (15 ml), obtained from a solvent purification system, was added to the dry components by syringe. The balloon was filled with hydrogen, and refilled every 12 h. Reaction was kept for 30 h, then reaction mixture was diluted with 100 ml of methanol, and filtered through a layer of celite. Solvent was evaporated under reduced pressure yielding 441 mg (yield = 63%) of mesohemin, which was used in further reactions. The obtained compound was analyzed by ESI-MS. m/z [M-Fe+H]$^+$ = 567.5, [M]$^+$ = 620.4, [M+MeOH]$^+$ = 651.3 (**Figure S1**)

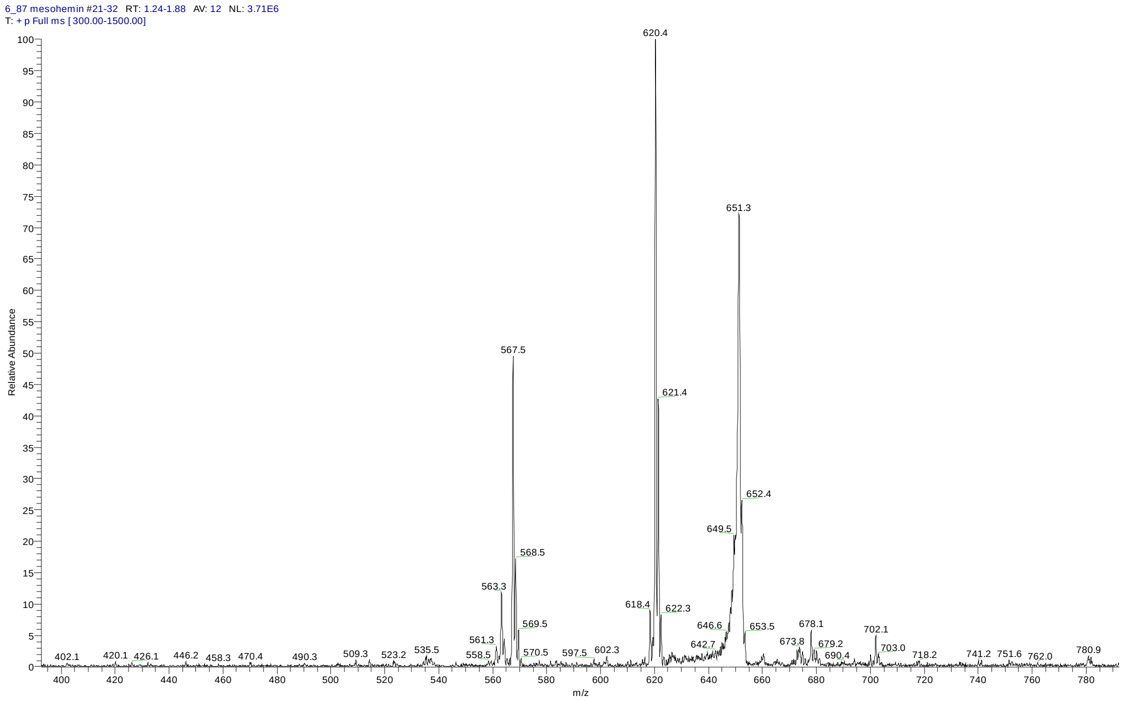


Figure S1: ESI-MS of mesohemin: 250μM in water:methanol = 1:3

Mesohemin-(MPEG$_{550}$)$_2$ synthesis. Mesohemin (550 mg, 0.838 mmol) was dissolved in 50 ml of THF. N-(3-dimethylaminopropyl)-N (ethylcarbodiimide hydrochloride (EDC·HCl) (401.6 mg, 2.095 mmol) and DMAP (25.5 mg, 0.209 mmol) were mixed in 200 mL of 50/50 THF/DCM in a round bottom flask and reacted for 1 hour prior to the addition of poly(ethylene glycol) methyl ether (MPEG$_{550}$, MW$_{avg.}$=550) (1.38 g, 2.514 mmol). The mesohemin solution was immersed in ice bath, and the second mixture was added slowly. The reaction mixture was brought to room temperature and stirred for 24h. After completion of the reaction the solution was washed with 0.1 M HCl (2x50 ml), and with saturated $NaHCO_3$ (2x50 ml). After that mixture was dried over $MgSO_4$ and solvent was removed under reduced pressure. The residue was purified by column chromatography on alumina with chloroform/methanol (9/1) mixture. Fractions were collected, solvent was removed, and then the residue was dissolved in 1M HCl in DCM, and washed with saturated $NaHCO_3$. The solution of the product was dried over $MgSO_4$ and solvent was removed under reduced pressure yielding 750 mg of mesohemin-(MPEG$_{550}$)$_2$ (75 % yield). The final compound was analyzed by ESI-MS. m/z $[M]^+$: 1266.1 – 1971.8 with interval of 44, $[M]^{2+}$: 755.1 – 1064.0 with interval of 22 (**Figure S2**)

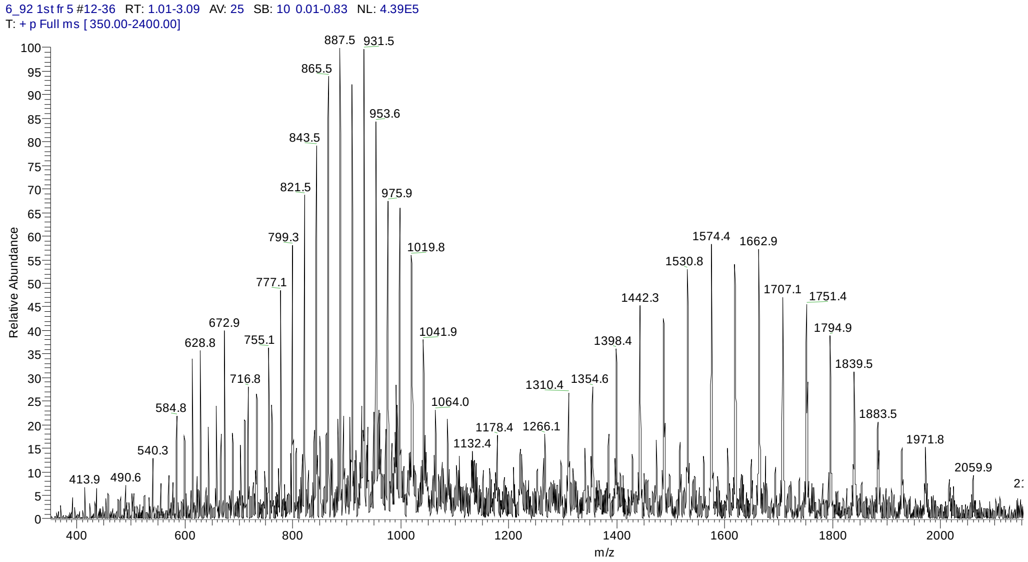


Figure S2: ESI of mesohemin-$(MPEG_{550})_2$: 250μM in water:methanol = 1:3

General procedure for synthesis of poly(methacrylic acid) (PMAA) by A(R)GET ATRP: A series of aqueous A(R)GET ATRP reactions were carried out. The following procedure describes a typical polymerization of MAA catalyzed by mesohemin-$(MPEG_{550})_2$. NaBr (51.5 mg, 0.5 mmol), MAA (1.01 g, 11.74 mmol), and mesohemin-$(MPEG_{550})_2$ (17.9 mg, 0.01 mmol) were dissolved in H_2O (3.6 ml). The mixture was added to a 10 ml Schlenk flask wrapped in aluminum foil and purged with nitrogen for 20 minutes, then placed in an oil bath at 30 °C. An ascorbic acid solution (100 mM) was purged with nitrogen, and then added into reaction mixture (0.1 ml) by either single injection or by continuous feeding at a rate of 16nmol/min. Then 33 mM stock solution of BPAA/PEG_{2000}BPA in DMF, purged with nitrogen, was added to the reaction mixture (0.3 ml). Samples were taken throughout the reaction and methylated by TMS-diazomethane for THF GPC analysis.

Polymerization with different amount of NaBr

Table S1: Effect of pH on ATRP of MAA initiated by BiBA.[a]

Entry	[M]/[I]/RA/ Cat.	NaBr	pH	Conversion	$M_{n,th}\times10^{-3}$	$M_{n,app}\times10^{-3}$	M_w/M_n

1	200:1:1:0.1	100 mM	2.79	11.1%	5.4	12.6	1.71
2	200:1:1:0.1	200 mM	2.63	9.4%	4.8	23.1	1.55
3	200:1:1:0.1	300 mM	2.65	8.0%	6.9	17.7	1.61

[a][M] = 20 vol% in water/DMF = 80/20, [RX] = 12 mM, reaction time = 4h, T = 30°C; $M_{\mathrm{n,app}}$ measured by THF GPC using universal PMMA standards after methylation of reaction samples.

NMR analysis

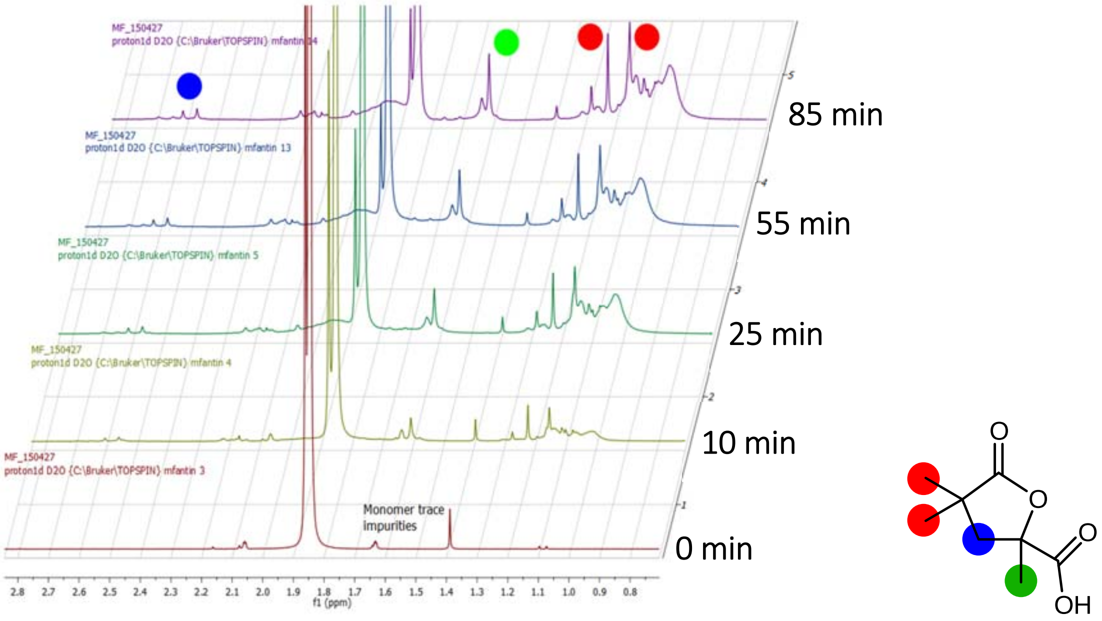


Figure S3: NMR of polymerization of MAA using Cu$^{\mathrm{II}}$-TPMA, visualizing intramolecular lactone formation. Proton peaks on lactone chain end are located at 1.62 ppm and 2.56 ~ 2.64 ppm, as labeled in the figure. Reproduced with permission from reference[4], Copyright 2016 American Chemical Society.

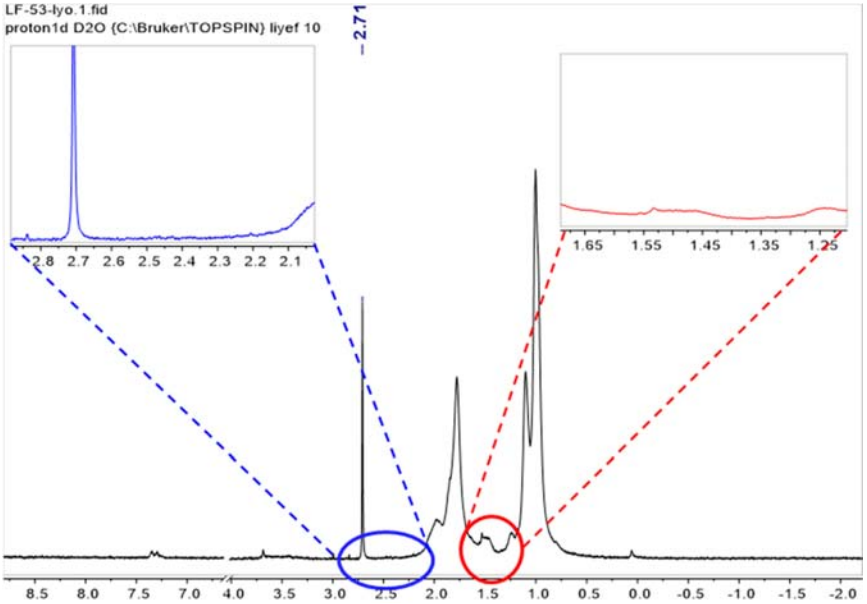
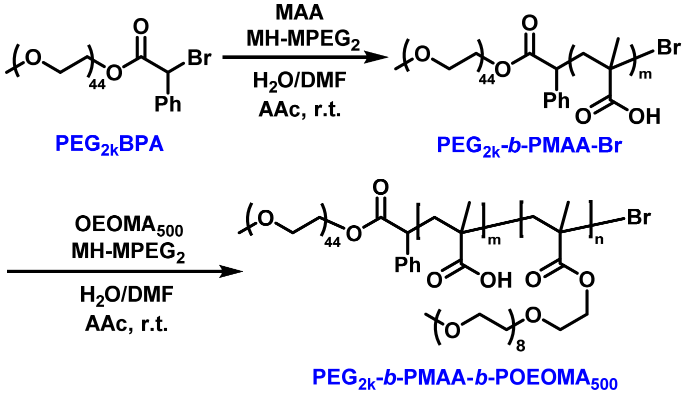


Figure S4: NMR of polymerization of MAA using Mesohemin-$(MEPG_{550})_2$, without formation of intramolecular lactonization. Singlet at 2.64 ppm = DMSO solvent peak.



Scheme S2: Preparation of PEG_{2k}-PMAA-$POEOMA_{500}$ triblock copolymer.

References

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