Photo-Cleavage of Cobalt-Carbon Bond: Visible Light-Induced Living Radical Polymerization Mediated by Organo-Cobalt Porphyrins

Yaguang Zhao, Mengmeng Yu, and Xuefeng Fu*
Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China.

Experimental

Materials.

Methyl acrylate (MA, Alfa, 99%), *N*, *N*-dimethylacrylamide (DMA, Alfa, 99.5%), *N*, *N*-diethylacrylamide (DEA, TCI, >98.0%) and *N*-acryloylmorpholine (AMO, TCI, >98.0%) were distilled and stored in the refrigerator before use. Thermal initiator, 2, 2'-azobissobutyronitrile (AIBN, $((CH_3)_2(CN)C)_2N_2$, Beijing Guoyao Co, 99%) was recrystallized from ethanol. Cobalt porphyrin complex (TMP-OH)Co^{II} or TMPCo^{II} was synthesized and purified according to procedures reported in the literature.[1,2] All other reagents were used as received if otherwise not noted.

Light Source.

A Xe lamp (CHF-XQ-500W, Beijing Trusttech Co. Ltd.) was used as the illumination source with a 400-800 nm filter to provide visible light. The distance of each sample from the light source was 18 cm. The power of the light measured at the sample position was ~80 mW/cm^2.

Analytical Techniques.

The determination of monomer conversions was performed by ^{1}H NMR in C_6D_6 or CD_3OD with benzaldehyde as external reference, using a Bruker 400MHz FT spectrometer. Chemical shifts were calibrated relative to solvent benzene peak at 7.16 ppm and solvent methanol peak at 3.31 ppm.

Analytical gel permeation chromatography (GPC) was performed in an Agilent 1200 series system, equipped with a VARIAN PolarGel-M column (300×7.5mm), an Iso Pump (G1310A), a UV detector at 254nm, and a differential refractive index detector (RI). The number average molecular weight (M_n), weight average molecular weight (M_w), and the polydispersity (PDI) from the RI detector were measured. *N*, *N*-Dimethylformamide (DMF) was used as the eluent at 50^{o}C with a flow rate of 1mL/min. Eight narrowly distributed poly (MMA) samples (molecular weight range of 2710-679000 g/mol, from Polymer Laboratories) were used as the calibration standards for the system.

Synthesis of (TMP-OH)Co-CH$_3$.

The (TMP-OH)Co-CH$_3$ was prepared according to the procedures reported in the literature.[2] (TMP-OH)Co^{II} was reduced with a slight excess of sodium amalgam in THF. The solvent was removed after the reduction. And the (TMP-OH)Co^I was reacted with excess CH_3I in benzene.

The reaction mixture was filtered in the glove box and excess CH_3I was evacuated. The (TMP-OH)Co-CH_3 was identified by ^1H NMR. The ratio of (TMP-OH)Co-CH_3 to (TMP-OH)Co^{II} was determined by integration of the ^{1}HNMR peaks for (TMP-OH)Co^{II} *m*-phenyl proton and (TMP-OH)Co-CH_3 methyl proton. (TMP-OH)Co-CH_3 ^{1}HNMR (CD_3OD, 400 MHz): δ (ppm) -4.64 (s, 3H, -CH_3), 7.22-7.26 (m, 8H, *m*-phenyl), 7.97 (d, 2H, $^3J_{H\text{-}H}$=8.4 Hz, *o*-phenyl), 8.52 (s, 4H, pyrrole), 8.54 (d, 2H, $^3J_{H\text{-}H}$=4.8 Hz, pyrrole), 8.72 (d, 2H, $^3J_{H\text{-}H}$=4.8 Hz, pyrrole).

Synthesis of organo-cobalt initiator I ((TMP-OH)Co-PMA).

The (TMP-OH)Co-PMA macroinitiator was prepared following thermal polymerization procedure using an MA/AIBN/(TMP-OH)Co ratio of 600/6/1 in benzene.[1] The concentration of MA was set at 1.0 M. The sample was sealed in the inert atmosphere glove box and immersed in a thermostated water bath at 60 °C. Organo-cobalt initiator **I** with an M_n of 10300 g/mol and an M_w/M_n of 1.25 (30% conversion after 5 h polymerization) was obtained by removing solvent and excess MA. Remaining AIBN was removed by washing with methanol for at least three times in the glove box and ^1H NMR analysis indicated that there was no observable AIBN presented in the sample.

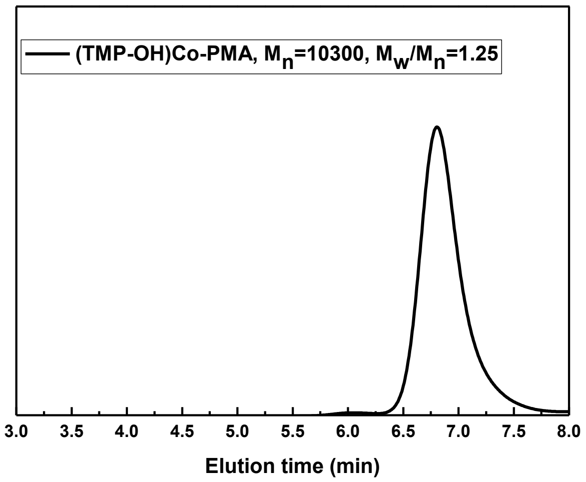

Figure S1. GPC trace of organo-cobalt initiator **I** (TMP-OH)Co-PMA.

Synthesis of organo-cobalt initiator II ((TMP-OH)Co-PDMA).

The (TMP-OH)Co-PDMA macroinitiator was synthesized following thermal polymerization procedure with an DMA/AIBN/(TMP-OH)Co ratio of 600:6:1 in benzene.[1] The concentration of DMA was set at 1.0 M. The sample was sealed in the inert atmosphere glove box and immersed in a thermostated water bath at 60 °C. Organo-cobalt initiator **II** with an M_n of 14100 g/mol and M_w/M_n of 1.26 (30% conversion after 4.5h polymerization) was obtained by removing solvent and excess DMA. Remaining AIBN was removed by washing with diethyl ether for at least three times in the glove box.

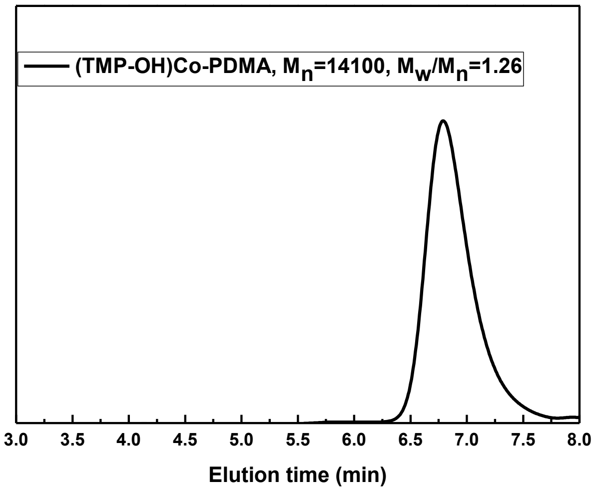

Figure S2. GPC trace of organo-cobalt initiator **II** (TMP-OH)Co-PDMA.

Synthesis of organo-cobalt initiator III [TMPCo-PMA].

The TMPCo-PMA macroinitiator was synthesized following thermal polymerization procedure with an MA/AIBN/TMPCo ratio of 600/6/1 in benzene.[1] The concentration of MA was set at 1.0 M. The sample was sealed in the inert atmosphere glove box and immersed in a thermostated water bath at 60 °C. Organo-cobalt initiator **III** with an M_n of 17800 g/mol and an M_w/M_n of 1.24 (40% conversion after 4.5h polymerization) was obtained by removing solvent and excess MA. Remaining AIBN was removed by washing with methanol for at least three times in the glove box.

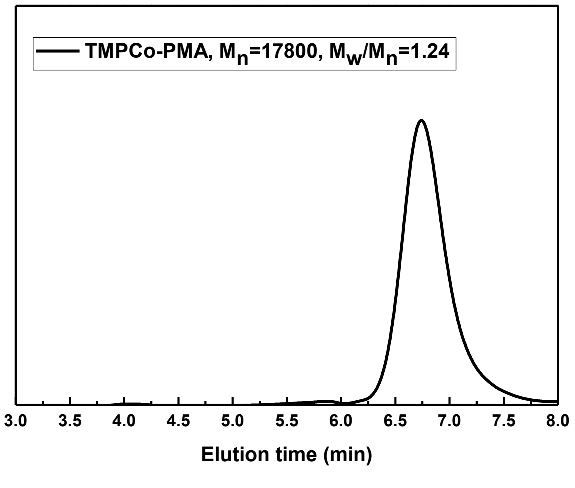

Figure S3. GPC trace of organo-cobalt initiator **III** TMPCo-PMA.

Typical Photo-polymerization Procedure.

A certain amount of organo-cobalt initiator and freshly prepared monomer C_6D_6/CD_3OD solution was mixed in a J. Young Valve NMR tube and subjected to three freeze-pump-thaw cycles. Benzaldehyde sealed in a capillary glass tube was added to the NMR tube as an external reference. The reaction mixture was irradiated by visible light through a 400-800 nm filter at room temperature in the oil bath. The temperature of the oil bath slightly increased and remained around 27-29 °C. The distance of each sample from the light source was 18 cm. The power of the light measured at the sample position was ~80 mW/cm^2. The progress of polymerization was followed by ^{1}HNMR detection. When desired conversion was reached, the reaction was stopped by exposed to air. Solvent and excess monomers were removed under vacuum. The resulting polymer products were dissolved in DMF for GPC analysis without further purification.

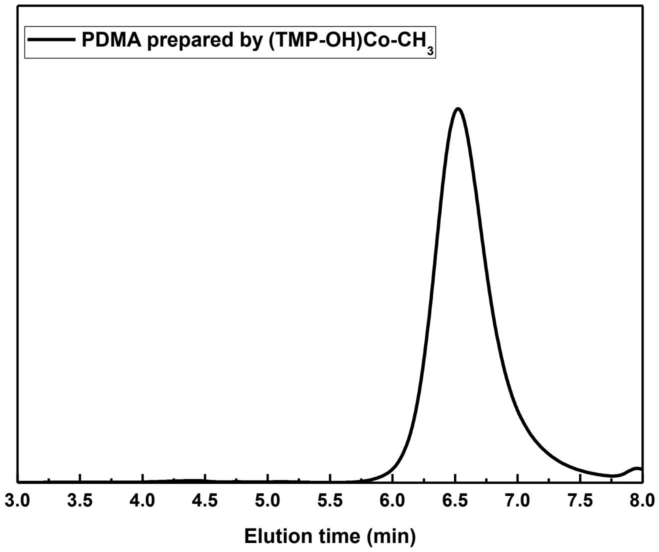

Figure S4. GPC trace of PDMA prepared by photo-initiated polymerization of DMA with (TMP-OH)Co-CH_3 in CD_3OD at rt. $[DMA]_0$=1.0M, $[(TMP\text{-}OH)Co\text{-}CH_3]_0=1.50\times10^{-3}$ M, $[(TMP\text{-}OH)Co^{II}]_0=0.17\times10^{-3}$ M, t=18h, conv%=68%, M_n=27300, M_w/M_n=1.27.

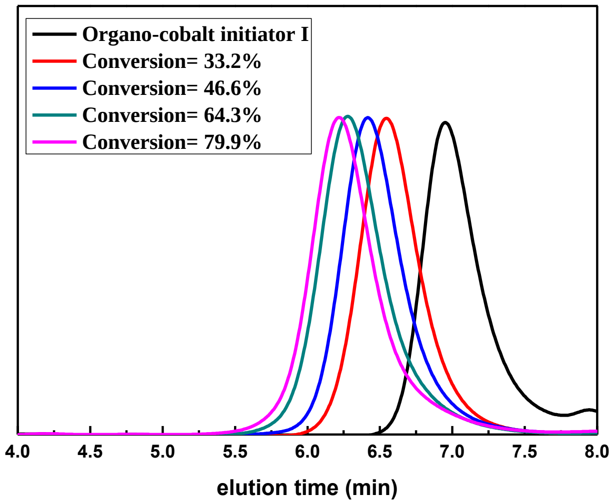

Figure S5. The shift of GPC traces with evolution of DMA conversion. $[DMA]_0$=1.0M, $[\mathbf{I}]_0=1.67\times10^{-3}$ M.

Table S1. Photo-polymerization of methyl acrylate (MA) with organo-cobalt initiator **III**

Entry	M(equiv)	t/h	Conv%	M_n	M_w/M_n
1	MA(600)	8	48	37200	1.63
2[a]	MA(600)	14	50	35500	1.27

$[MA]_0$=1.0 M. Solvent was benzene. [a] 50% density filter combined with 400-800nm filter was employed.

Photo-polymerization of MA with the same condition as DMA was not controlled (Table S1, entry 1). This may results from over-photolysis due to relative weak Co-C bond in (TMP)Co-PMA. Thus a 50% density filter combined with 400-800nm filter was employed. PMA with a relatively small polydispersity was obtained (Table S1, entry 2) which indicates the versatility of this photo-polymerization.

Typical Procedure for the Synethesis of Functional Triblock Copolymers.

Diblock copolymer macroinitiator (PMA-b-PDMA, M_n=44600, M_w/M_n=1.16) was prepared according to the photo-polymerization procedure described above. A benzene solution of an macroinitiator and fresh monomer (DEA, AMO) were mixed in the glove box. Benzaldehyde sealed in a capillary glass tube was added to the NMR tube as an external reference. The NMR tube was immerged in a preheated water bath (60 °C) or irradiated by Xe lamp equipped with a 400-800 nm filter at room temperature. The conversion of third monomer was followed by ^{1}HNMR detection. The polymerization was quenched by exposing to air. Solvent and excess monomers were pumped out. The functional triblock copolymers PMA-b-PDMA-b-PDEA, PMA-b-PDMA-b-PAMO were dissolved in DMF for GPC analysis without further purification.

^{1}H NMR of typical block copolymers.

Organo-cobalt initiator **I** **(**(TMP-OH)Co-PMA, M_n=10300, M_w/M_n=1.25**)** together with diblock copolymer macroinitiator (PMA-b-PDMA, M_n=44600, M_w/M_n=1.16) and functional triblock copolymers PMA-b-PDMA-b-PDEA and PMA-b-PDMA-b-PAMO (see above and Fig. 3 for synthetic procedure) were characterized with ^{1}H NMR in C_6D_6.

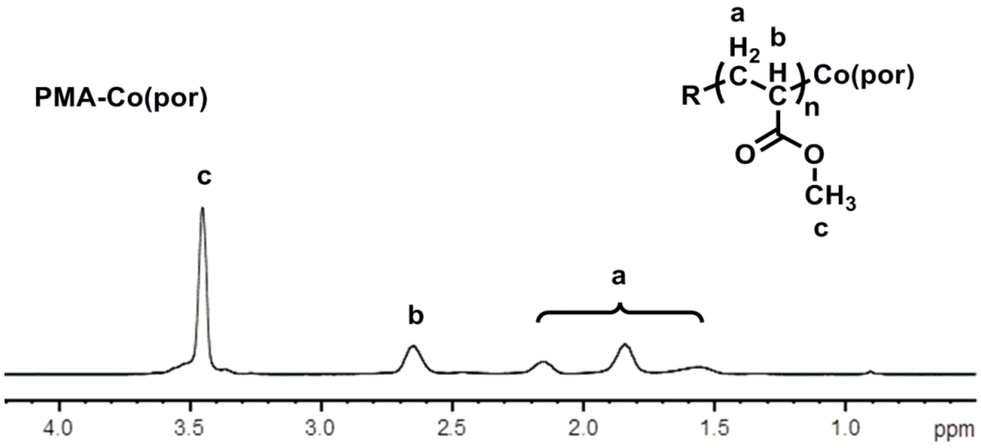

Figure S6. ^{1}H NMR spectrogram of organo-cobalt initiator **I** in C_6D_6

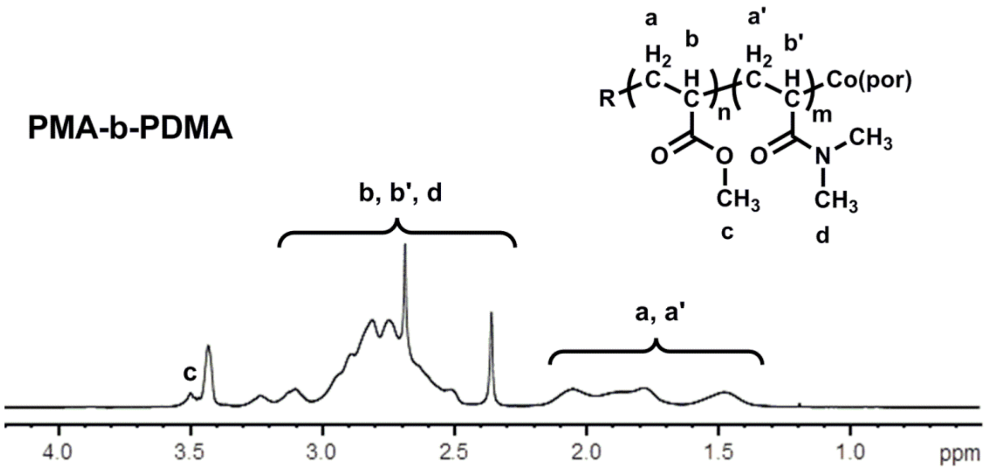

Figure S7. ^{1}HNMR spectrogram of PMA-b-PDMA in C_6D_6

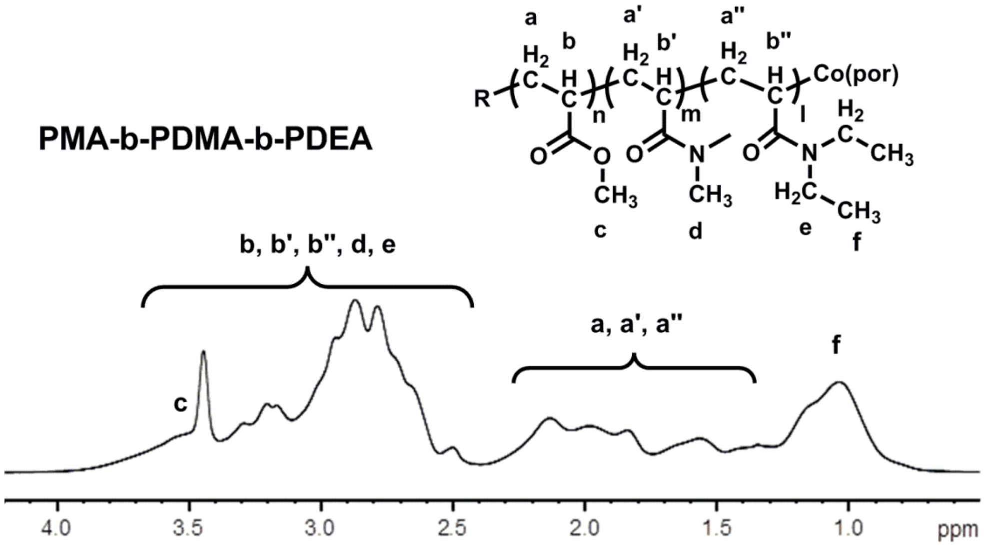

Figure S8. ^{1}HNMR spectrogram of PMA-b-PDMA-b-PDEA in C_6D_6

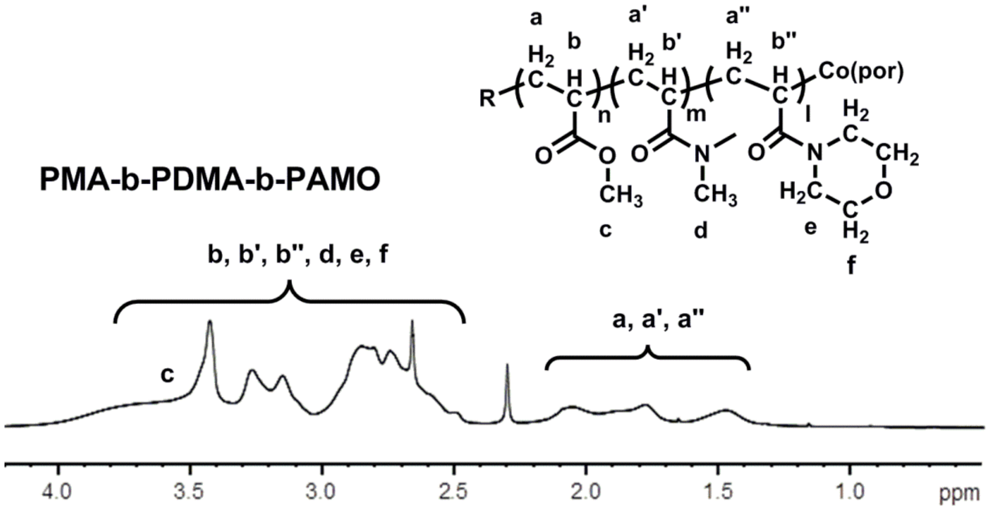

Figure S9. ^{1}HNMR spectrogram of PMA-b-PDMA-b-PAMO in C_6D_6

Reference:

(1) Zhao, Y.; Dong, H.; Li, Y.; Fu, X. *Chem. Commun.*, 2012, **48**, 3506.

(2) Wayland, B. B.; Basickes, L.; Mukerjee, S.; Wei, M.; Fryd, M. *Macromolecular* 1997, **30**, 8109.