Supporting Information

When CMRP Met Alkyl Vinyl Ketone: Visible Light Induced Living Radical Polymerization (LRP) of Ethyl Vinyl Ketone (EVK)

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Experimental Materials.

Methyl acrylate (MA, Alfa Aesar, 99%), Ethyl Vinyl Ketone (EVK, Alfa Aesar, 97%) were purified by passing through a neutral alumina column and distilled under reduced pressure to remove the inhibitor. *N*,*N*-dimethylacrylamide (DMA, Alfa, 99.5%) were distilled under reduced pressure and stored in the refrigerator before use.

Potassium peroxymonosulfate (Oxone®, Alfa), Methanol (J&K, 99.9%), toluene (Sinopharm Chemical Reagent Co., Ltd, 99.8%) were used as received.

Synthesis of the catalyst.

Organo-cobalt porphyrin complex (TMPCo-CO₂CH₃) was synthesized according to previous reported method^[1].

Light Source.

A 500 W xenon lamp (CEL-S500, Aulight, Beijing, China) was used as the light source with a 420–780 nm filter to give visible light. The intensity of visible light irradiation was measured by a FZ-A radiometer (Photoelectric Instrument Factory of Beijing Normal University) equipped with a 400-1000 nm sensor.

Typical Procedure for Visible Light Initiated Polymerization.

A typical procedure for polymerization of vinyl ketones mediated by organo-cobalt complex is as follows: (1) a certain amount of TMPCo-CO₂CH₃ and monomers were mixed in C₆D₆or DMSO-d₆in a J. Young valve NMR tube; (2) after being thoroughly mixed and three freeze–pump–thaw cycles, the sample was refilled with nitrogen; (3) the sample was placed in a water bath at room temperature and irradiated for a period of time. The progress of polymerization was followed by ¹H NMR measurement. When desired conversion (benzaldehyde sealed in capillary tube was used as external

reference) was reached, the reaction was stopped by exposure to air. The solvent and excess monomers were removed under vacuum. The resulting product without further purification was dissolved in DMF for GPC analysis.

Coordination experiments

(TMP)CoCOOMe (6.67mM in C_6D_6) and the mixture solution of (TMP)CoCOOMe(6.67mM in C_6D_6) and EVK (6.67mM in C_6D_6) were detected by ¹H NMR respectively (Fig. S1, A, B).¹H NMRresults showed no change in both chemical shift and integral of each resonances of (TMP)CoCOOMe, indicating that the existence of EVK led to insignificant coordination to (TMP)CoCOOMe. Moreover, the resonances of (TMP)CoCOOMestill stayed the same even after 8 hours (Fig. S1, C). In addition, the signals of the remained (TMP)CoCOOMe(Fig. S1, D) after removing the EVK by reduced pressure distillation was the same as that of the initial (TMP)CoCOOMe (Fig. S1, A), which further confirmed that there is no interaction between (TMP)CoCOOMe and EVK.



Fig S1. From bottom to top: ¹H NMR of (TMP)CoCOOMe(6.67mM in C₆D₆);¹H NMR of the mixture solution of (TMP)CoCOOMe(6.67mM in C₆D₆)and EVK (6.67mM in C₆D₆);¹H NMR of the mixture solution of (TMP)CoCOOMe (6.67mM in C₆D₆) and EVK (6.67mM in C₆D₆) after 8 hours; ¹H NMR of the remained (TMP)CoCOOMe after removing the EVK.

Synthesis of Block Copolymers.

Block copolymers were synthesized by sequential polymerization of EVK, MA and DMA. PEVKmacroinitiators were synthesized by visible light initiated polymerization of EVK mediated by TMPCo-CO₂CH₃at 25°C. After a desired conversion was obtained, the resulting PEVK was used as macroinitiator for next DMA under variable conditions. After desired condition was reached, the polymerization was stopped. Solvent and excess DMA was removed under vacuum. The resulting PEVK-b-PDMA block copolymers were dissolved in DMF for GPC analysis without purification. Other block copolymers were obtained similarly.

Characterization.

Conversions of monomers were determined by ¹H NMR spectrometry on a Bruker 400 MHz FT spectrometer in C₆D₆. ¹H NMR spectrums of the block copolymers were recorded on a Bruker 400 MHz FT spectrometer in DMSO-d₆.

Gel permeation chromatography (GPC) was performed in Agilent 1200 series system, equipped with two VARIAN PolarGel-M columns (300×7.5 mm), an Iso Pump (G1310A), a UV detector at 420 nm, and a differential refractive index detector (RID). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersity (PDI) were measured in DMF at 50 °C with a flow rate of 1.0 mL/min. A series of poly(methyl methacrylate)s (molecular weight range of 2710–679 000 g/mol, from Polymer Laboratories) were used as standards for calibration.



Fig S2.GPC traces for photo-polymerization of EVK in benzenemediated by (TMP)Co-CO₂CH₃under visible light irradiationat ambient temperature. Experimental conditions: $[EVK]_0 = 1.0 \text{ M}$; $[EVK]_0/[(TMP)Co-CO_2CH_3]_0=215/1$, $I = 30 \text{ mw/cm}^2$.



Fig S3. Gel permeation chromatography (GPC) traces of the PEVK produced by photo-LRP mediated by (TMP)Co-CO₂CH₃ ($M_{n,GPC}$ = 31400, M_w/M_n = 1.25). Black line indicated the refractive index detection trace, and red line indicated the UV-visible (420 nm) detection trace.

¹H NMR Characterization of Block Copolymers

PEVK-b-PDMA



Fig S4.¹H NMR of PEVK-*b*-PDMA (Table 2, entry 1) in DMSO-d₆

PDMA-b-PEVK



Fig S5.¹H NMR of PDMA-*b*-PEVK (Table 2, entry 3) in DMSO-d₆.





Fig S6.¹H NMR of PEVK-*b*-PMA (Table 2, entry 2) in DMSO-d₆.

PMA-b-PEVK



Fig S7.¹H NMR of PMA-*b*-PEVK (Table 2, entry 4) in DMSO-d₆.





Fig S8.¹H NMR of PMA-*b*-PEVK-*b*-PDMA(Table 2, entry 5) in DMSO-d₆

Reference

[1] Y. G. Zhao, M. M. Yu, S. L. Zhang, Y. C. Liu and X. F. Fu, *Macromolecules*, 2014, **47**, 6238-6245.