

## A Well-defined Versatile Photoinitiator (salen)Co-CO<sub>2</sub>CH<sub>3</sub> for Visible Light Initiated Living/Controlled Radical Polymerization

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### Experimental

#### Materials.

Methyl acrylate (MA, Alfa Aesar, 99%), n-butyl acrylate (nBA, Alfa Aesar, 98+%), and tert-butyl acrylate (tBA, Alfa Aesar, 99%) 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%), *N,N*-diethylacrylamide (DEA, TCI, >98.0%), and *N*-acryloylmorpholine (AMO, TCI, >98.0%) were distilled under reduced pressure and stored in the refrigerator before use. Cobalt(II)[*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine] ((salen)Co(II), Aldrich, >99%), (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO, TCI, 98.0%), Potassium peroxymonosulfate (Oxone®, Alfa), Methanol (J&K, 99.9%), toluene (Sinopharm Chemical Reagent Co., Ltd, 99.8%) and <sup>18</sup>O<sub>2</sub> (Beijing Gaisi Chemical Gases Center, 97%) were used as received.

#### 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 the irradiation is modulated by employing neutral density filters with different transmittance. 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.

A household CFL (compact fluorescent lamp, 27 W) was used as the light source; the sample was placed at an approximate distance of 5 cm to the lamp, and the light intensity was measured to be 3–5 mW/cm<sup>2</sup>.

Sunlight was directly used as light source without any optical filters. The intensity of solar irradiation varied between 0.8 and 10 mW/cm<sup>2</sup> within the wavelength range of 400–1000 nm.

#### Synthesis of complex (salen)Co-CO<sub>2</sub>CH<sub>3</sub> I and (salen)Co-<sup>13</sup>CO<sub>2</sub>CD<sub>3</sub>.

Methanol (300 μL) was added into 8.5 mL of a toluene solution containing (salen)Co(II) (0.09 mmol, 55 mg), and Oxone® (0.44 mmol, 135mg). The mixture was reacted for 0.5 h at room temperature. Subsequently, the mixture was filtered, added with Na<sub>3</sub>PO<sub>4</sub>•12H<sub>2</sub>O (1.71 mmol, 650mg), degassed by three freeze-pump-thaw cycles and refilled with carbon monoxide (CO, 1 atm). The sample was shielded

from light and left stirring for 10 minutes at room temperature. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography (basic alumina, CH<sub>2</sub>Cl<sub>2</sub> as eluent). (salen)Co-CO<sub>2</sub>CH<sub>3</sub> **I** (24 mg, 40% yield) was obtained as dark green solid. Recrystallization using CH<sub>2</sub>Cl<sub>2</sub>/hexane gave dark green crystal suitable for single-crystal X-ray diffraction analysis. (salen)Co-CO<sub>2</sub>CH<sub>3</sub> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 303K, δ): 8.06 (s, 1H), 7.86 (s, 1H), 7.40 (t, <sup>4</sup>J = 2.5Hz, 2H), 7.02 (d, <sup>4</sup>J = 2.5 Hz, 1H), 6.98 (d, <sup>4</sup>J = 2.5 Hz, 1H), 3.68 (s, 3H), 3.44 (m, 2H), 2.76 (m, , 2H), 2.04 (m, 2H), 1.65 (m, 2H), 1.58 (s, 9H), 1.54 (s, 9H), 1.46 (m, 2H), 1.31 (s, 9H), 1.30 (s, 9H). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 303K, δ): 7.78 (m, 2H), 7.63 (s, 1H), 7.46 (s, 1H), 7.18 (t, J = 2.5 Hz, 2H), 3.44 (s, 3H), 3.12 (m, 1H), 2.27 (m, 1H), 2.04 (s, 9H), 2.00 (s, 9H), 1.72 (m, 2H), 1.41 (s, 9H), 1.40 (s, 9H), 1.34 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 303K, δ): 24.76, 24.87, 29.42, 29.59, 30.02, 31.52, 34.10, 34.13, 36.22, 56.21, 69.26, 73.07, 118.83, 119.98, 127.28, 127.37, 129.12, 136.42, 136.83, 141.92, 142.45, 161.29, 161.47, 164.02, 164.31. ESI-HRMS calcd for C<sub>38</sub>H<sub>55</sub>CoN<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup>: 662.34883, found: 662.35060.

(salen)Co-<sup>13</sup>C<sub>2</sub>O<sub>2</sub>CD<sub>3</sub> was synthesized under similar conditions simply by replacing CH<sub>3</sub>OH with CD<sub>3</sub>OD and CO with <sup>13</sup>CO. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 303K, δ): 8.06 (s, 1H), 7.86 (s, 1H), 7.40 (t, <sup>4</sup>J = 2.5Hz, 2H), 7.02 (d, <sup>4</sup>J = 2.5 Hz, 1H), 6.98 (d, <sup>4</sup>J = 2.5 Hz, 1H), 3.44 (m, 2H), 2.76 (m, , 2H), 2.04 (m, 2H), 1.65 (m, 2H), 1.58 (s, 9H), 1.54 (s, 9H), 1.46 (m, 2H), 1.31 (s, 9H), 1.30 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, 303K, δ): 24.76, 24.87, 29.42, 29.59, 30.02, 31.52, 34.10, 34.13, 36.22, 69.26, 73.07, 118.83, 119.98, 127.28, 127.37, 129.12, 136.42, 136.83, 141.92, 142.45, 161.29, 161.47, 162.73, 164.02, 164.31. ESI-HRMS calcd for C<sub>37</sub>H<sub>52</sub>CoN<sub>2</sub>O<sub>4</sub><sup>13</sup>CD<sub>3</sub> [M]<sup>+</sup>: 666.37102, found: 666.36959.

**Table 1S.** Crystal Data of (salen)Co-CO<sub>2</sub>CH<sub>3</sub> **I**:

Compound reference	(salen)Co-CO <sub>2</sub> CH <sub>3</sub>
Chemical formula	C <sub>38</sub> H <sub>55</sub> CoN <sub>2</sub> O <sub>4</sub>
Formula Mass	662.77
Crystal system	Monoclinic
<i>a</i> /Å	17.569(4)
<i>b</i> /Å	10.302(2)
<i>c</i> /Å	19.781(4)
<i>α</i> /°	90
<i>β</i> /°	100.629(2)
<i>γ</i> /°	90
Unit cell volume/ Å <sup>3</sup>	3518.8(12)
Temperature/K	173.1500
Space group	P121/n1
No. of formula units per unit cell, <i>Z</i>	4
Radiation type	MoK $\alpha$
Absorption coefficient, $\mu$ /mm <sup>-1</sup>	0.529
No. of reflections measured	23869

No. of independent reflections	8036
$R_{int}$	0.0422
Final $R_I$ values ( $(I > 2\sigma(I))$ )	0.0698
Final $wR(F^2)$ values ( $(I > 2\sigma(I))$ )	0.1519
Final $R_I$ values (all data)	0.0730
Final $wR(F^2)$ values (all data)	0.1534
Goodness of fit on $F^2$	1.260
CCDC number	1031130

### Typical Procedure for Visible Light Initiated Polymerization.

A typical procedure for polymerization of acrylates, acrylamides and vinyl acetate mediated by organocobalt complex is as follows: (1) a certain amount of (salen)Co-CO<sub>2</sub>CH<sub>3</sub> and monomers were mixed in C<sub>6</sub>D<sub>6</sub> or DMSO-d<sub>6</sub> in 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 room temperature water bath and irradiated for a period of time. The progress of polymerization was followed by <sup>1</sup>H NMR measurement. When desired conversion (for the polymerization of DMA, DEA and AMO, 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.

### Synthesis of Block Copolymers.

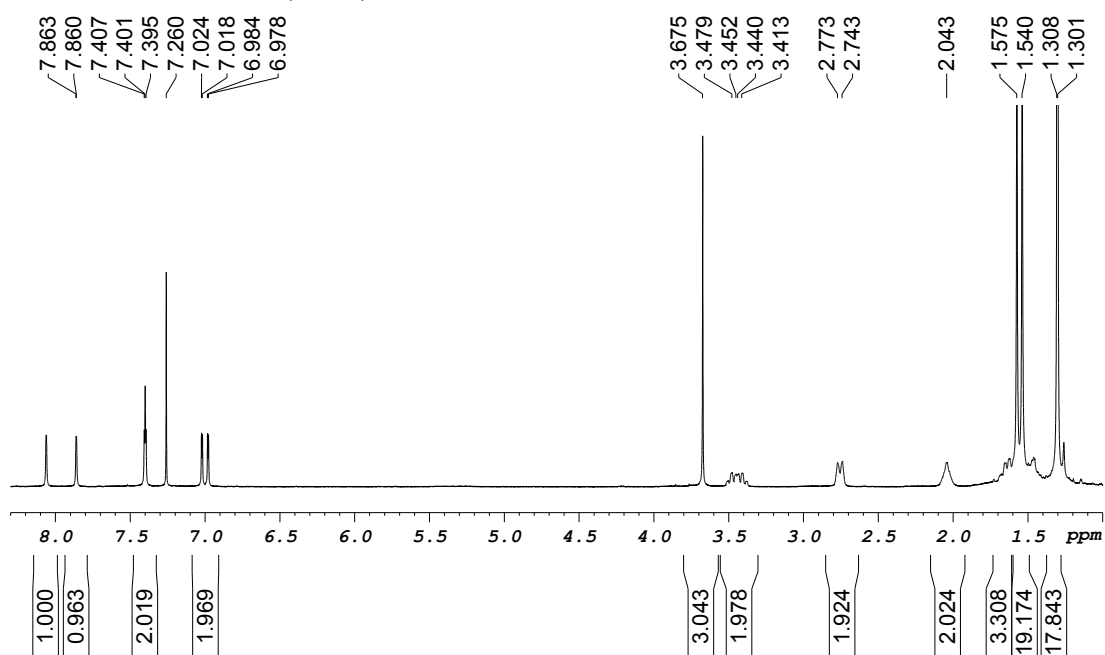
Block copolymers were synthesized by sequential polymerization of MA and DMA. PMA macroinitiators were synthesized by visible light initiated polymerization of MA mediated by (salen)Co-CO<sub>2</sub>CH<sub>3</sub> under different conditions (irradiated by Xe lamp, CFL, or addition of TPO) at ambient temperature. After a desired conversion was obtained, the resulting PMA was used as macroinitiator for DMA under variable conditions. After desired conditions were reached, the polymerizations were stopped. Solvent and excess DMA was removed under vacuum. The resulting PMA-b-PDMA block copolymers were dissolved in DMF for GPC analysis without purification.

### Characterization.

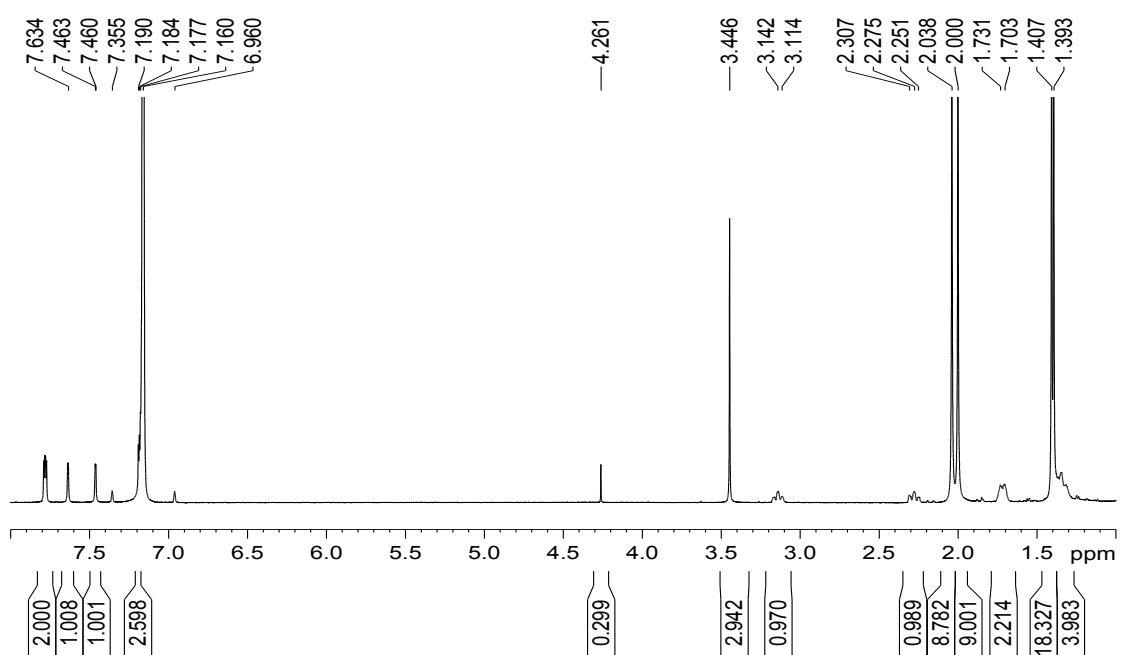
Conversions of monomers were determined by <sup>1</sup>H NMR spectrometry on a Bruker 400 MHz FT spectrometer in C<sub>6</sub>D<sub>6</sub> or DMSO-d<sub>6</sub>. <sup>13</sup>C NMR spectrum was recorded on a Bruker 500 MHz FT spectrometer. IR (film) was recorded with a Nicolet Avatar 330 FT-IR infrared spectrometer. The UV-vis spectra were acquired using a Shimadzu UV3100 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) measurement was performed on a TOF/TOF 5800 system (AB SCIEX) with  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) as a matrix and sodium trifluoroacetate as the cationizing agent in positive reflection mode. Samples for the MALDI-TOF MS measurements were prepared by mixing the polymer (10 mM, 1 $\mu$ L), the matrix (48 mM, 10 $\mu$ L) and the cationizing agent (10 mM, 10 $\mu$ L) in acetonitrile.

Gel permeation chromatography (GPC) was performed in an 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.

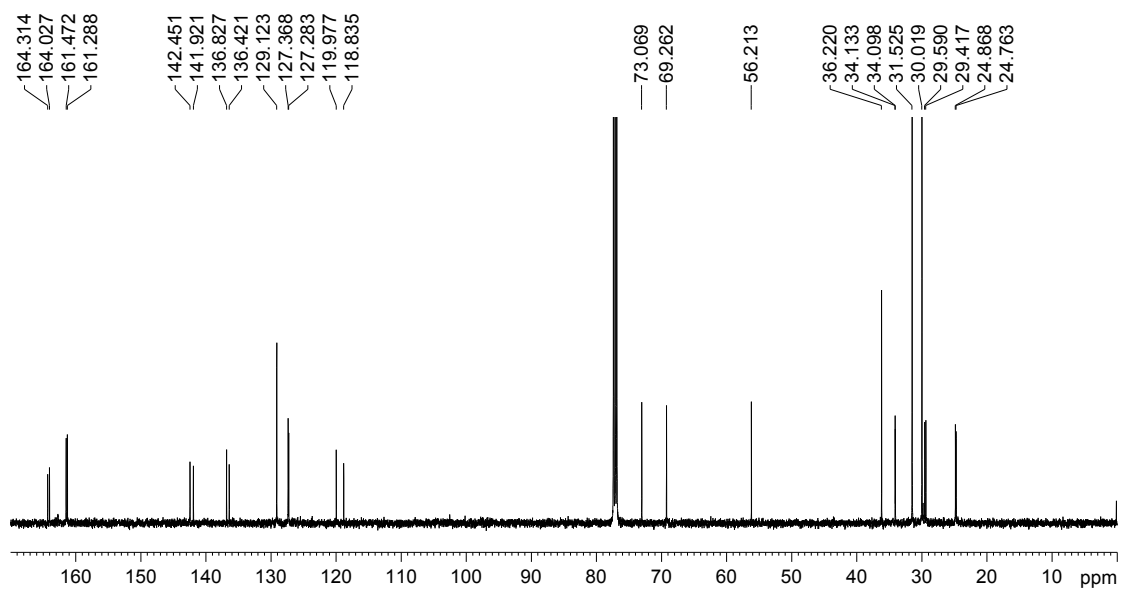
### Characterization of (salen)Co-CO<sub>2</sub>CH<sub>3</sub> I:



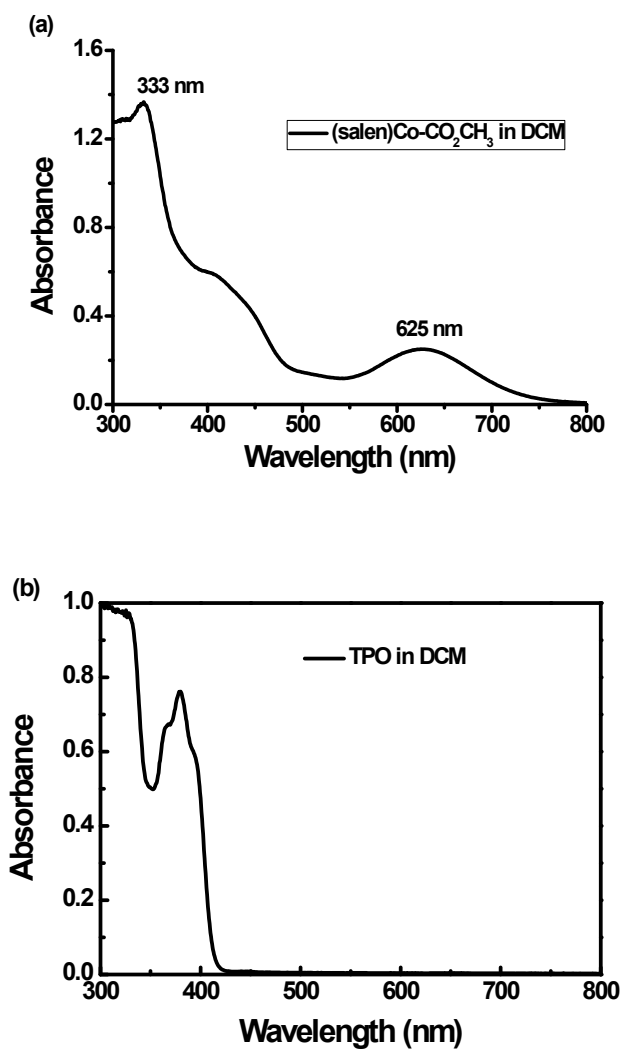
**Figure 1S.** <sup>1</sup>H NMR spectrum of (salen)Co-CO<sub>2</sub>CH<sub>3</sub> in CDCl<sub>3</sub>.



**Figure 2S.**  $^1\text{H}$  NMR spectrum of (salen)Co-CO<sub>2</sub>CH<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>.



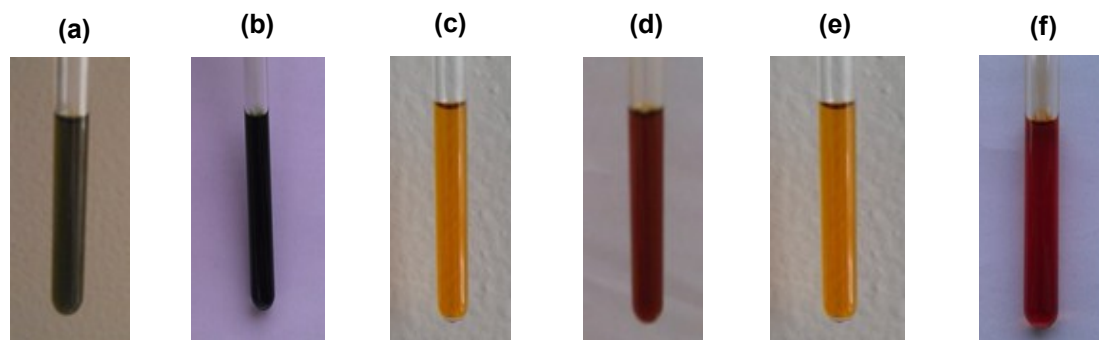
**Figure 3S.**  $^{13}\text{C}$  NMR spectrum of (salen)Co-CO<sub>2</sub>CH<sub>3</sub> in CDCl<sub>3</sub>.



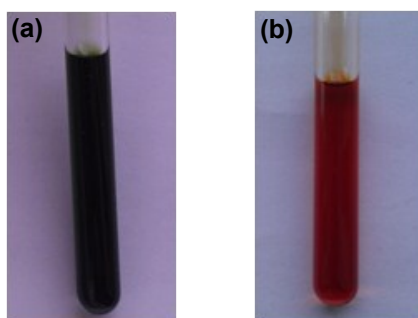
**Figure 4S.** UV-vis spectra of (a) (salen)Co-CO<sub>2</sub>CH<sub>3</sub> **I** and (b) TPO in CH<sub>2</sub>Cl<sub>2</sub>.

**Typical Colors of Different Compounds.**

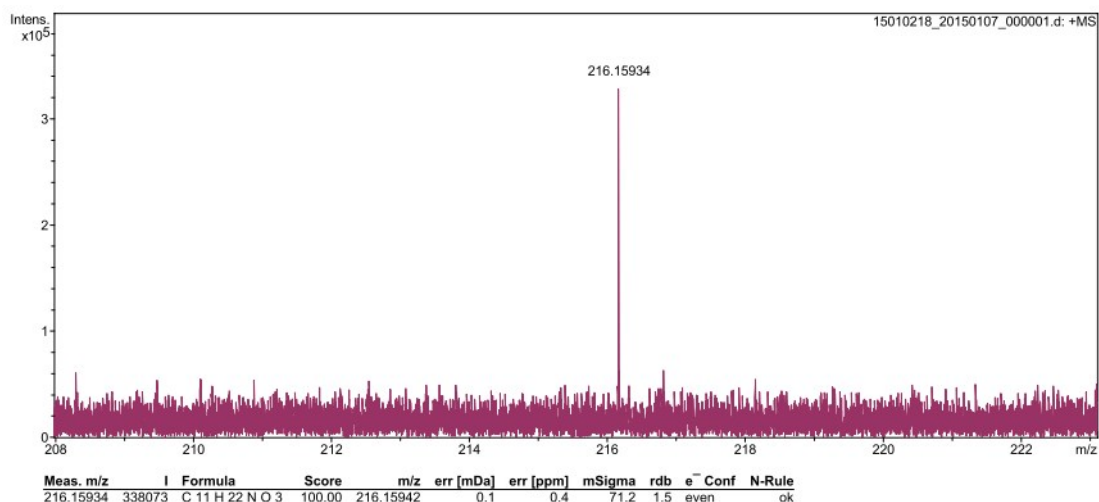
Both the polymerization of acrylates and transformation of **I** was followed by the color change. Here we show typical colors of different compounds in C<sub>6</sub>D<sub>6</sub> during this research.



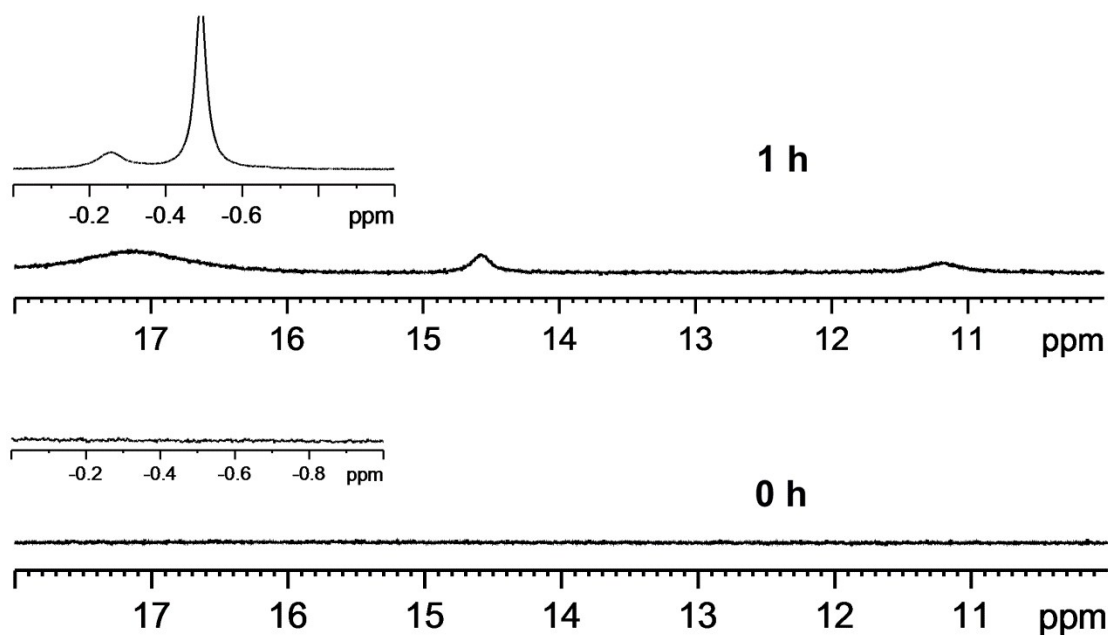
**Figure 5S.** Typical colors of several compounds during the research. (a) (salen)Co-CO<sub>2</sub>CH<sub>3</sub>,  $1.6 \times 10^{-3}$  M, light green; (b) (salen)Co-CO<sub>2</sub>CH<sub>3</sub>,  $5 \times 10^{-3}$  M, dark green; (c) (salen)Co-PMA,  $1.6 \times 10^{-3}$  M, yellow; (d) (salen)Co-PMA,  $5 \times 10^{-3}$  M, orange; (e) (salen)Co(II),  $1.6 \times 10^{-3}$  M, yellow; (f) (salen)Co(II),  $5 \times 10^{-3}$  M, red.



**Figure 6S.** Color change during radical trapping experiment: the benzene-d<sub>6</sub> solution of (salen)Co-CO<sub>2</sub>CH<sub>3</sub> **I** (5 mM) and TEMPO (50 mM) was irradiated by visible light ( $I = 3 \text{ mW/cm}^2$  at 420–780 nm wavelength) at ambient temperature. (a) 0h; (b) 1h.



**Figure 7S.** ESI spectra of TEMPO-CO<sub>2</sub>CH<sub>3</sub> formed according to procedure mentioned in photolysis of (salen)Co-CO<sub>2</sub>CH<sub>3</sub> and TEMPO.

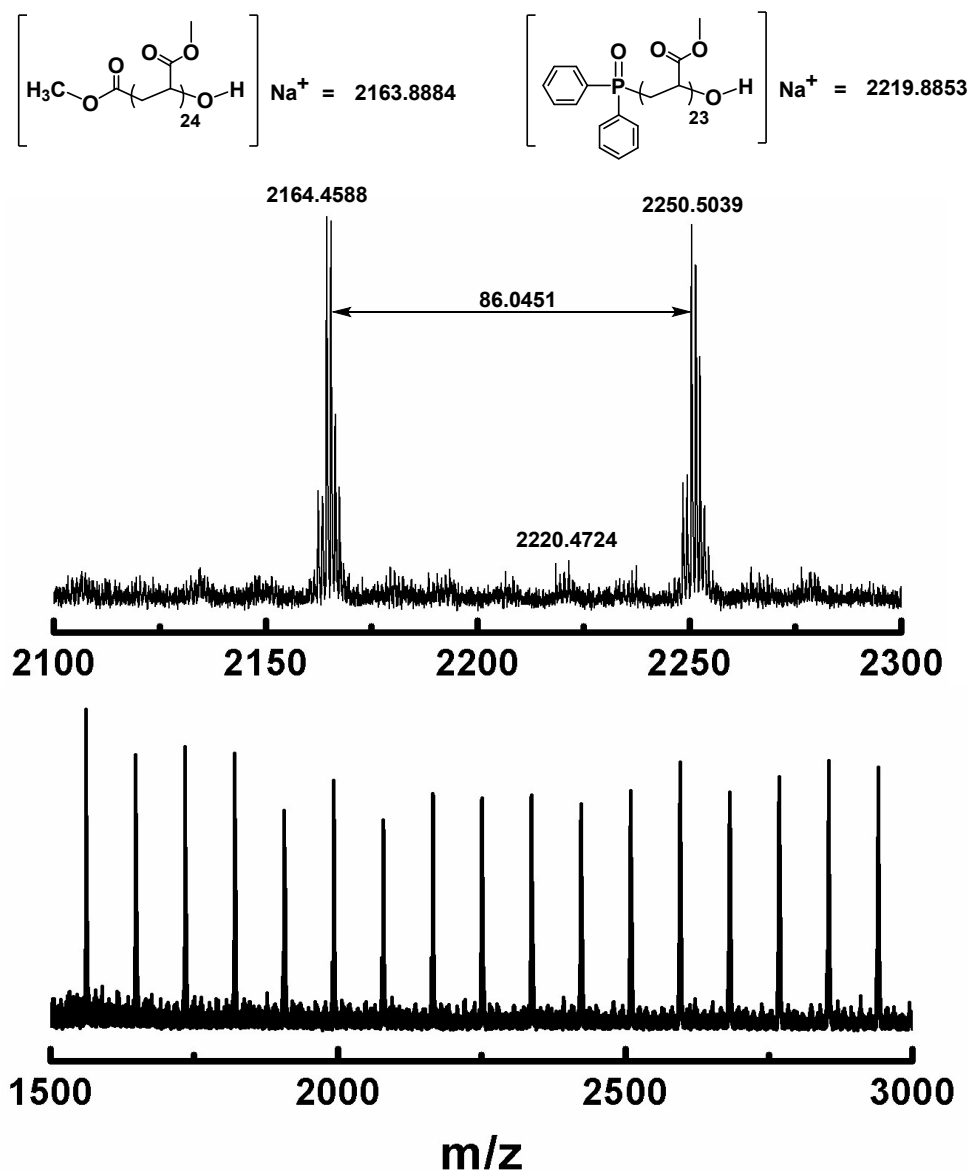


**Figure 8S.** <sup>1</sup>H NMR (400 MHz) spectra (low field) in C<sub>6</sub>D<sub>6</sub> during the visible light irradiation of (TMP)Co-CO<sub>2</sub>CH<sub>3</sub> in the presence of TEMPO indicating the formation of corresponding (salen)Co(II).

### Influence of TPO to the $\alpha$ -end fidelity of final polymer

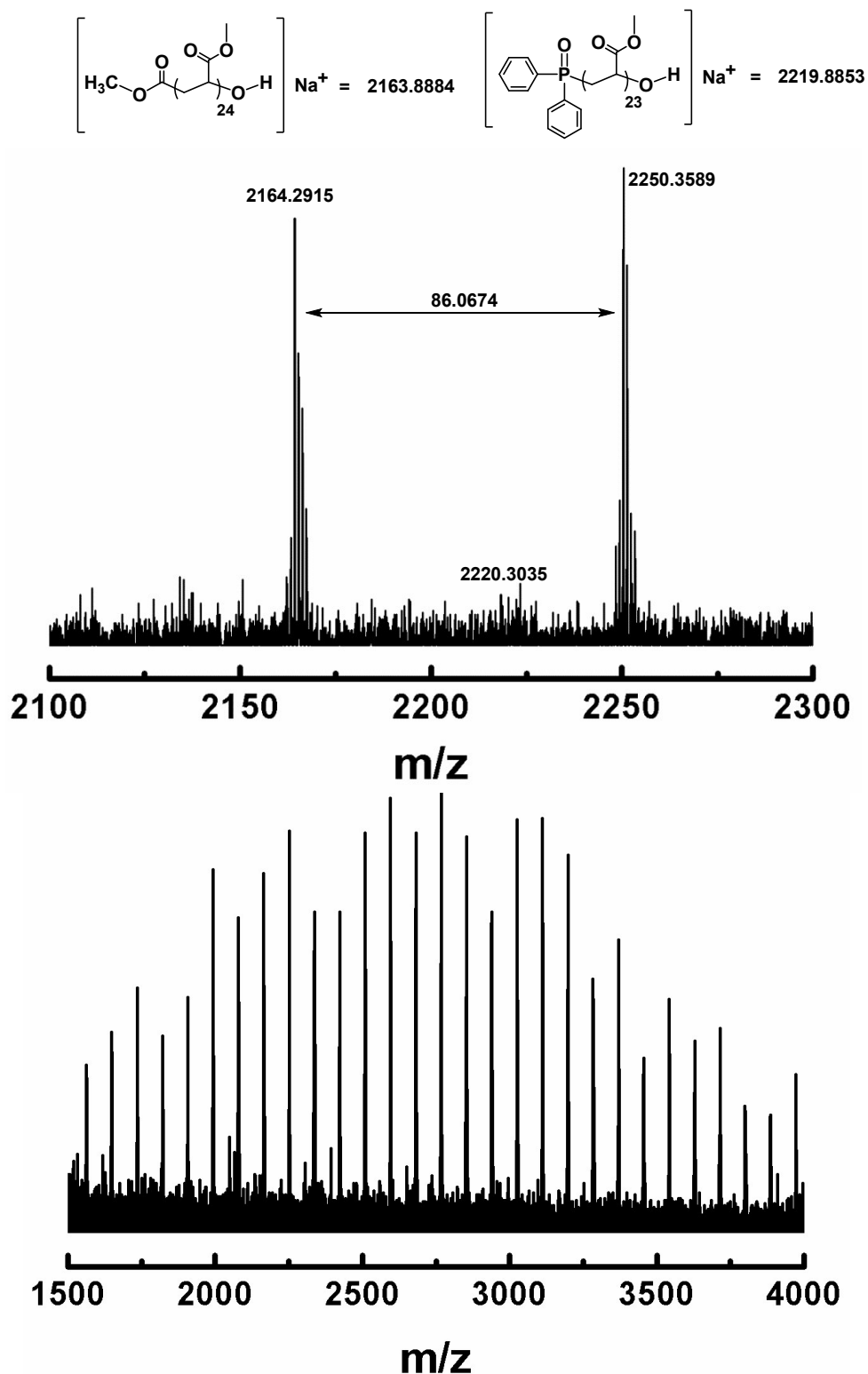
During the polymerization of acrylates under Xe lamp irradiation with addition of TPO, TPO was used to accelerate the polymerization while maintain good control over molecular weight and polydispersity. But since TPO could also initiate new polymer chain, it might influence the  $\alpha$ -end fidelity by polymer chains with TPO segments. To evaluate the  $\alpha$ -end fidelity, two PMA samples were prepared by irradiation with addition of TPO and analyzed by MALDI-TOF-MS (Figure 9S & 10S). The results indicated that there were only one main series of peaks with MA

repeating unit. The experimental isotopic mass values of the main peak series agreed well with the theoretical values, as shown in the upper part of Figure 9S and 10S. The peak series referring to polymer chains initiated by TPO could be ignored as only tiny proportion of signal (< 5% of main peak series) was found. Thus when one equivalent of TPO was addition before polymerization, it could significantly increase the polymerization rate but gave insignificant influence to the  $\alpha$ -end fidelity of final polymer.

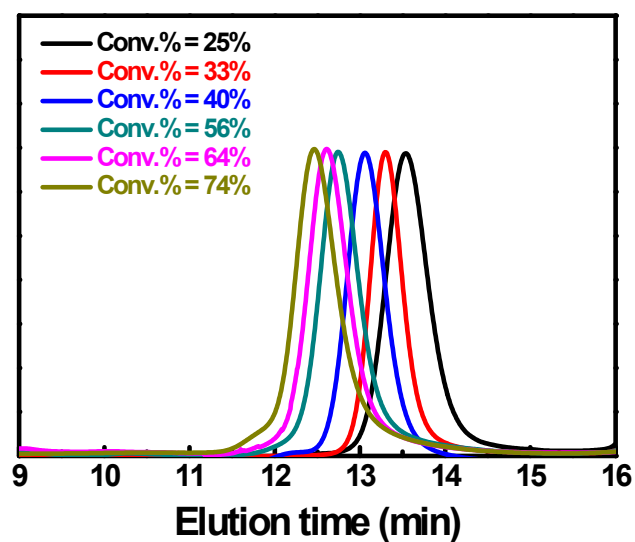


**Figure 9S.** Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) of PMA obtained from photo-LRP mediated by (salen)Co-CO<sub>2</sub>CH<sub>3</sub> with addition of one equivalent TPO at room temperature. [MA]<sub>0</sub> = 1.0M, [MA]<sub>0</sub>/[Co-R]<sub>0</sub>/[TPO]<sub>0</sub> = 600/1/1, t = 1h, Conv% = 8.7%, M<sub>n,th</sub> = 5140, M<sub>n,GPC</sub> = 5630, M<sub>w</sub>/M<sub>n</sub> = 1.15.

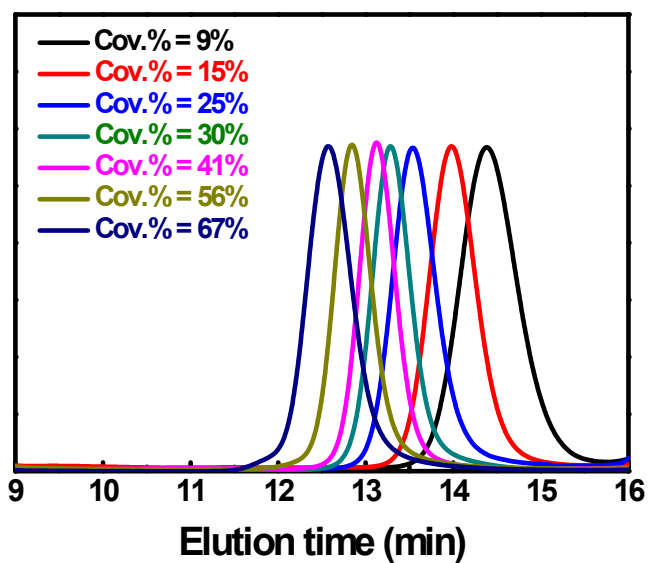




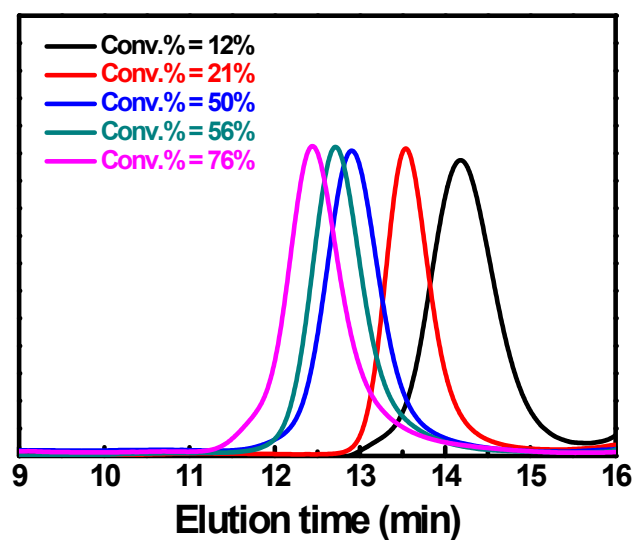
**Figure 10S.** Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) of PMA obtained from photo-LRP mediated by (salen)Co-CO<sub>2</sub>CH<sub>3</sub> with addition of one equivalent TPO at room temperature. [MA]<sub>0</sub> = 1.0M, [MA]<sub>0</sub>/[Co-R]<sub>0</sub>/[TPO]<sub>0</sub> = 200/1/1, t = 4.5h, Conv% = 14.1%, M<sub>n,th</sub> = 3090, M<sub>n,GPC</sub> = 3430, M<sub>w</sub>/M<sub>n</sub> = 1.13.



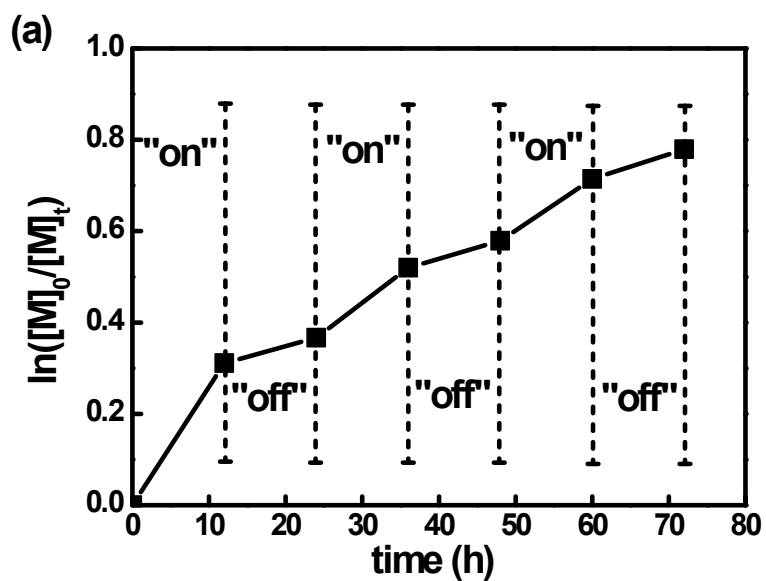
**Figure 11S.** GPC traces for photo-polymerization of MA in benzene with **I** under Xe lamp irradiation (3 mw/cm<sup>2</sup>) at ambient temperature. Experimental conditions: [MA]<sub>0</sub> = 1.0 M; [MA]<sub>0</sub>/[**I**]<sub>0</sub> = 600/1.

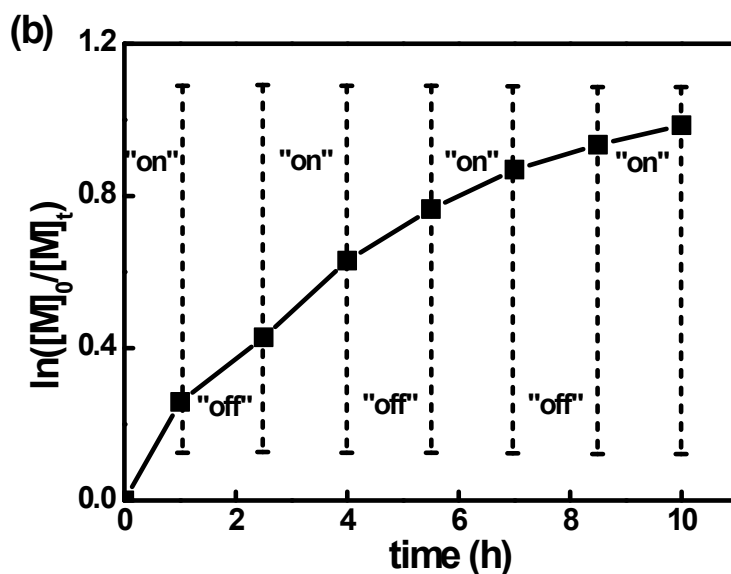


**Figure 12S.** GPC traces for photo-polymerization of MA in benzene with **I** under CFL irradiation (3-5 mw/cm<sup>2</sup>) at ambient temperature. Experimental conditions: [MA]<sub>0</sub> = 1.0 M; [MA]<sub>0</sub>/[**I**]<sub>0</sub> = 600/1.

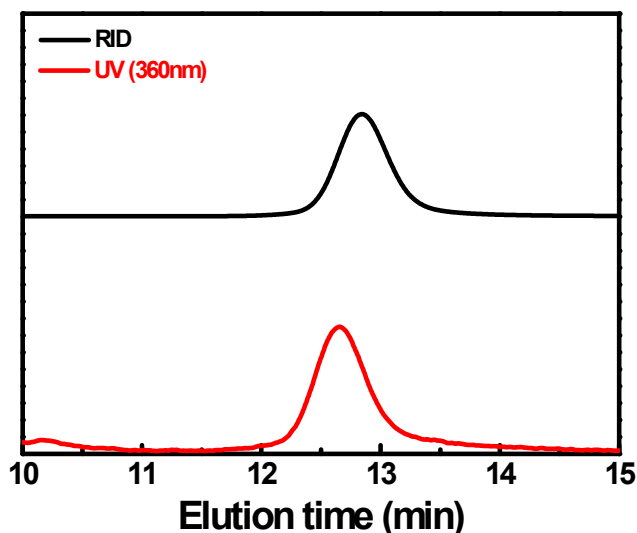


**Figure 13S.** GPC traces for photo-polymerization of MA in benzene with I under Xe lamp irradiation ( $3 \text{ mw/cm}^2$ ) with addition of 1 equivalent of TPO at ambient temperature. Experimental conditions:  $[\text{MA}]_0 = 1.0 \text{ M}$ ;  $[\text{MA}]_0/[\text{I}]_0/[\text{TPO}]_0 = 600/1/1$ .





**Figure 14S.** Effect of visible light during the intermittent visible light initiated polymerization of MA and DMA in benzene mediated by **I** under Xe lamp irradiation (3 mw/cm<sup>2</sup>) at ambient temperature: (a) [MA]<sub>0</sub> = 1.0 M; [MA]<sub>0</sub>/[**I**]<sub>0</sub> = 600/1; (b) [DMA]<sub>0</sub> = 1.0 M; [DMA]<sub>0</sub>/[**I**]<sub>0</sub> = 600/1.

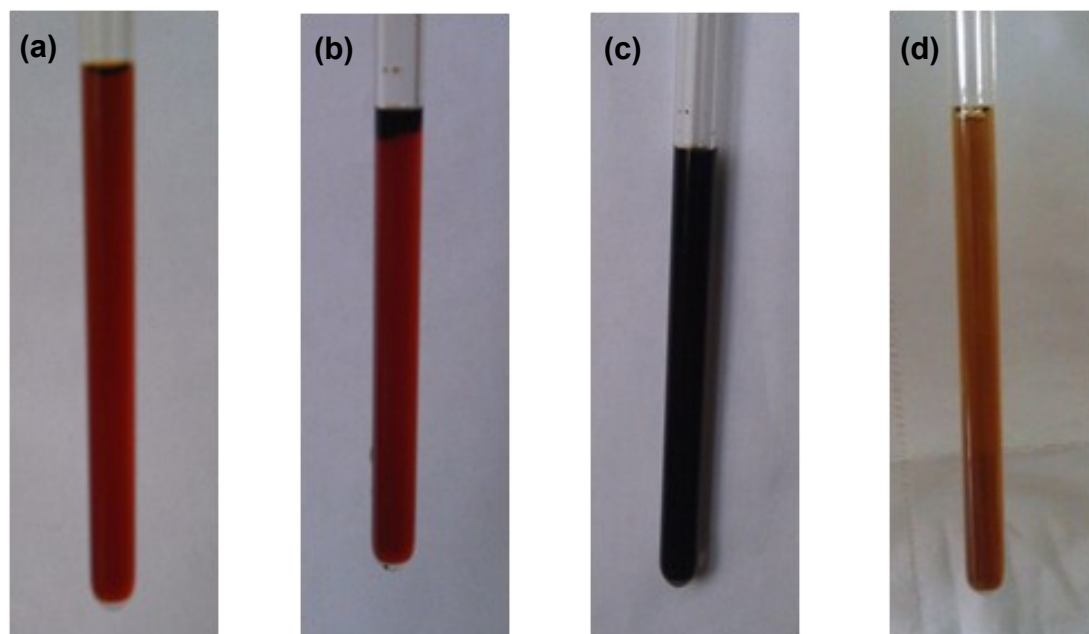


**Figure 15S.** Gel permeation chromatography (GPC) traces of the PMA produced by photo-CRP mediated by **I** ( $M_{n,th} = 29600$ ,  $M_{n,GPC} = 28500$ ,  $M_w/M_n = 1.06$ ). Black line indicated the refractive index detection trace, and red line indicated the UV-visible (360 nm) detection trace.

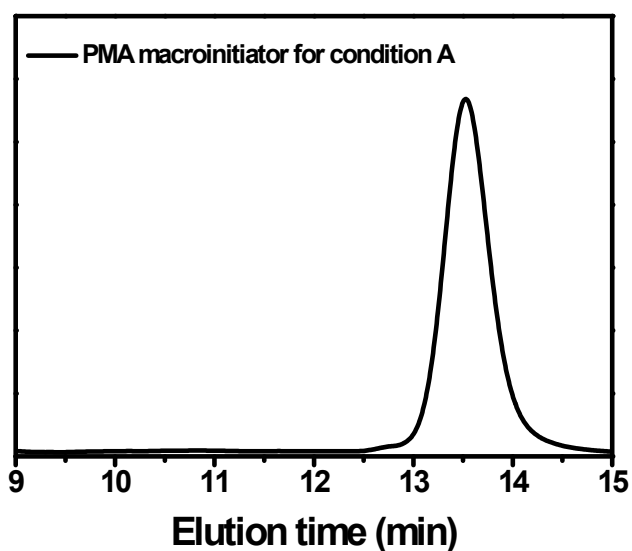
#### Modification of $\omega$ end of (salen)Co-PMA.

After the visible light initiated polymerization of MA, excess MA and C<sub>6</sub>D<sub>6</sub> was removed under vacuum. The resulting (salen)Co-PMA was dissolved in CDCl<sub>3</sub> in the

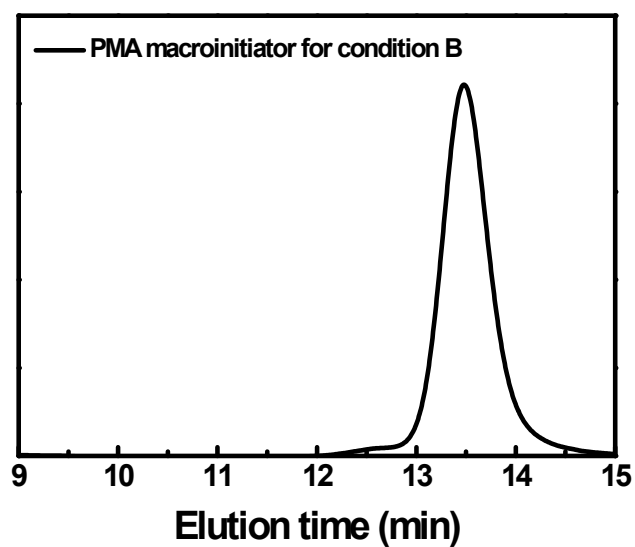
glove box and detected by  $^1\text{H}$  NMR to ensure the complete removal of monomer. Then the solution was degassed by three freeze–pump–thaw cycles and back filled with  $^{16}\text{O}_2$  or  $^{18}\text{O}_2$  using vacuum line. After thoroughly mixed for 1 h, excess acetic acid was added. The solvent and acetic acid was removed under vacuum after 1h and the resulting product was analyzed by both MALDI-TOF-MS and GPC.



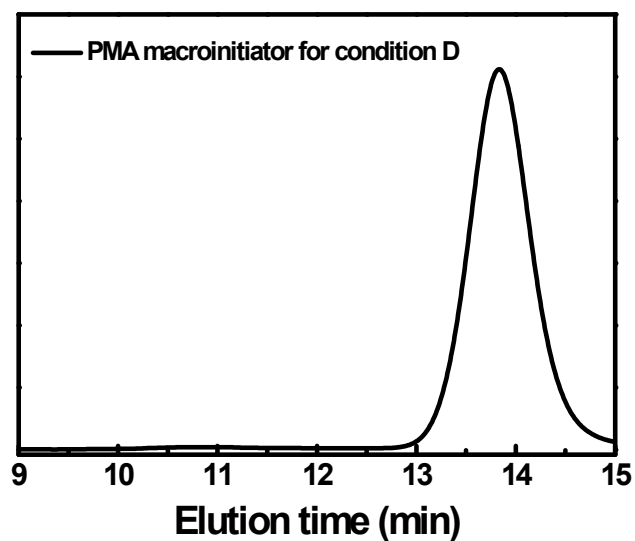
**Figure 16S.** Color change during the modification of  $\omega$  end of (salen)Co-PMA : (a) before  $\text{O}_2$  addition; (b) 0.5 min after  $\text{O}_2$  addition; (c) 1 h after  $\text{O}_2$  addition; (d) after acetic acid addition.



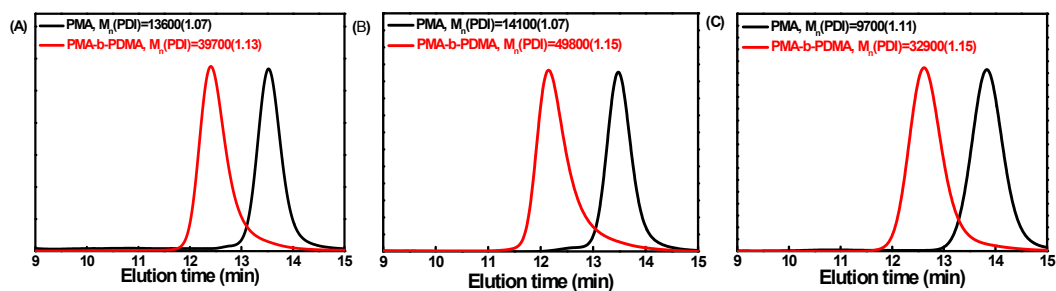
**Figure 17S.** PMA macroinitiator for irradiation with Xe lamp,  $[\text{MA}]_0/[\text{I}]_0 = 600/1$ ,  $I = 3 \text{ mw/cm}^2$ , room temperature,  $t = 10\text{h}$ , conversion = 26%,  $M_{n,\text{GPC}} = 13600$ ,  $M_w/M_n = 1.07$ .



**Figure 18S.** PMA macroinitiator for irradiation with CFL lamp,  $[MA]_0/[I]_0 = 600/1$ ,  $I = 3-5 \text{ mW/cm}^2$ , room temperature,  $t = 12.5\text{h}$ , conversion = 26%,  $M_{n, \text{GPC}} = 14100$ ,  $M_w/M_n = 1.07$ .



**Figure 19S.** PMA macroinitiator for irradiation with Xe lamp with addition of 1 equivalent of TPO,  $[M]_0/[I]_0/[TPO]_0 = 600/1/1$ ,  $I = 3 \text{ mw/cm}^2$ , room temperature,  $t = 1.5\text{h}$ , conversion = 23%,  $M_{n, \text{GPC}} = 9700$ ,  $M_w/M_n = 1.11$ .



**Figure 20S.** GPC traces of block copolymer PMA-b-PDMA (black line = macroinitiator, red line = block copolymer) with  $[\text{DMA}]_0 = 1.0 \text{ M}$ ,  $[\text{DMA}]_0/[(\text{salen})\text{Co-PMA}]_0 = 600/1$ : (A) irradiated by Xe lamp,  $t = 12 \text{ h}$ , conv. = 54%,  $M_{n,\text{GPC}} = 39700$ ,  $M_w/M_n = 1.13$ ; (B) irradiated by CFL,  $t = 18 \text{ h}$ , conv. = 51%,  $M_{n,\text{GPC}} = 49800$ ,  $M_w/M_n = 1.15$ ; (C) irradiated by Xe lamp with addition of 1 equivalent of TPO,  $t = 2 \text{ h}$ , conversion = 36%,  $M_{n,\text{GPC}} = 32900$ ,  $M_w/M_n = 1.15$ .