

Supporting Information

Visible light-induced living radical polymerization (LRP) mediated by (salen)Co(II)/TPO at ambient temperature

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Experimental

Materials.

Methyl acrylate (MA, Alfa Aesar, 99%), *n*-butyl acrylate (*n*BA, Alfa Aesar, 98+%), and *tert*-butyl acrylate (*t*BA, 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%), 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%) 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. 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.

Typical Procedure for Visible Light Initiated Polymerization.

A typical procedure for polymerization of acrylates, acrylamides and vinyl acetate mediated by (salen)Co(II)/TPO is as follows: (1) a certain amount of (salen)Co(II), TPO and monomers were mixed in C₆D₆ 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 ¹H NMR measurement. When desired conversion (for the polymerization of DMA 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 photo-polymerizations. PMA macroinitiators were synthesized by visible light (3 mW/cm^2) initiated polymerization of MA mediated by (salen)Co(II)/TPO at ambient temperature. After a desired conversion was obtained, remaining MA was removed (TPO was not removed) under vacuum and the resulting PMA ($M_n = 13200 \text{ g/mol}$, $M_w/M_n = 1.16$) was used as macroinitiator for second monomer (*n*BA, *t*BA and DMA). Solvent and excess monomers were removed under vacuum after termination of polymerization. The resulting block copolymers were dissolved in DMF for GPC analysis without purification. Exact polymerization time and monomer conversions were shown in Table 3.

Characterization.

Conversions of monomers were determined by ^1H NMR spectrometry on a Bruker 400 MHz FT spectrometer in C_6D_6 . ^{31}P NMR spectrum was recorded on a Bruker 500 MHz FT 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 2',4',6'-trihydroxyacetophenone monohydrate (THAP) 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 μL), the matrix (9 mg/mL, 10 μL) and the cationizing agent (10 mM, 10 μL) in acetonitrile.

Gel permeation chromatography (GPC) was performed in an Agilent 1200 series system, equipped with two VARIAN PolarGel-M columns ($300 \times 7.5 \text{ mm}$), 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.

UV spectra of (salen)Co(II) and TPO

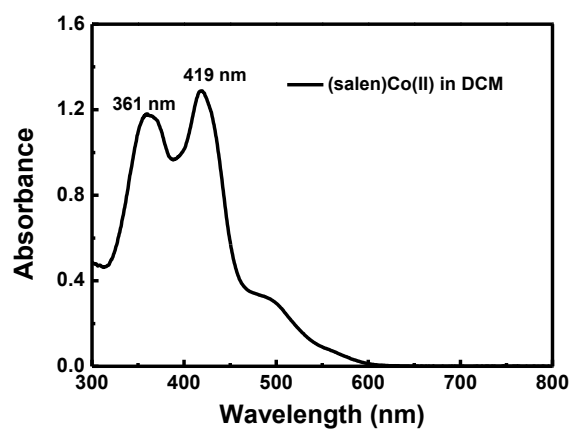


Figure 1S. UV-vis spectrum of (salen)Co(II) in CH₂Cl₂.

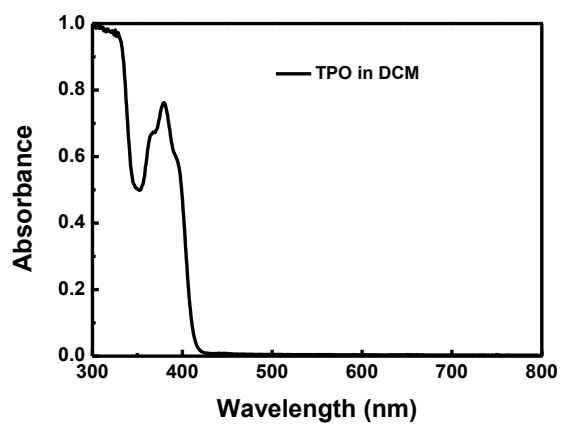


Figure 2S. UV-vis spectrum of TPO in CH₂Cl₂.

GPC traces of homopolymers under different conditions.

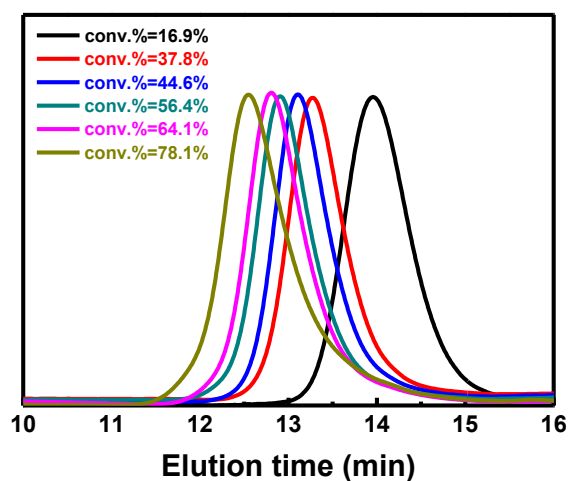


Figure 3S. GPC traces for photo-polymerization of MA in benzene with (salen)Co(II)/TPO under visible light irradiation (50 mw/cm²) at ambient temperature. Experimental conditions: [MA]₀ = 1.0 M; [MA]₀/[(salen)Co(II)]₀/[TPO]₀ = 600/1/1.

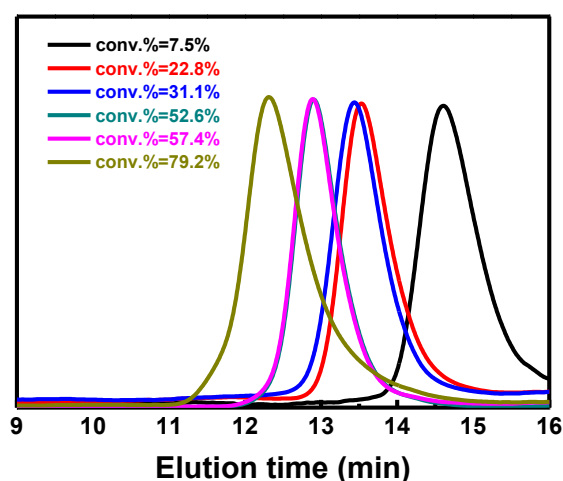


Figure 4S. GPC traces for photo-polymerization of MA in benzene with (salen)Co(II)/TPO under visible light irradiation (20 mw/cm²) at ambient temperature. Experimental conditions: [MA]₀ = 1.0 M; [MA]₀/[(salen)Co(II)]₀/[TPO]₀ = 600/1/1.

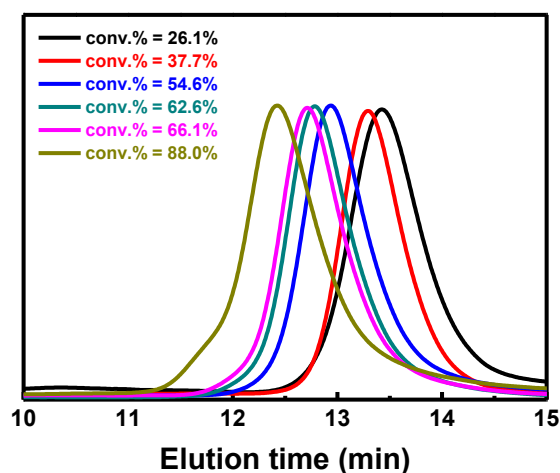


Figure 5S. GPC traces for photo-polymerization of MA in benzene with (salen)Co(II)/TPO under visible light irradiation (**10** mw/cm²) at ambient temperature. Experimental conditions: [MA]₀ = **1.0** M; [MA]₀/[(salen)Co(II)]₀/[TPO]₀ = **600/1/1**.

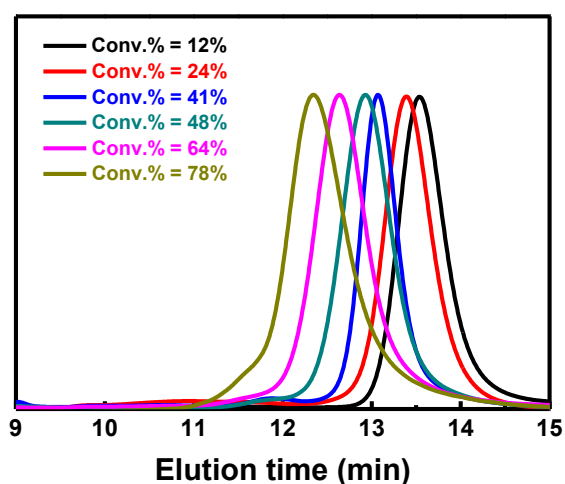


Figure 6S. GPC traces for photo-polymerization of MA in benzene with (salen)Co(II)/TPO under visible light irradiation (**3** mw/cm²) at ambient temperature. Experimental conditions: [MA]₀ = **1.0** M; [MA]₀/[(salen)Co(II)]₀/[TPO]₀ = **600/1/1**.

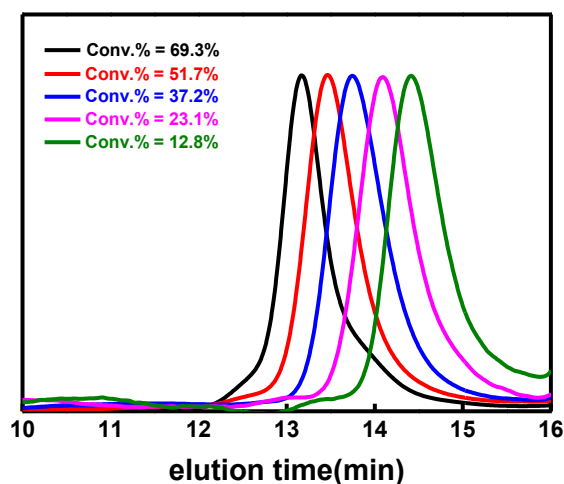


Figure 7S. GPC traces for photo-polymerization of MA in benzene with (salen)Co(II)/TPO under visible light irradiation (3 mw/cm^2) at ambient temperature. Experimental conditions: $[\text{MA}]_0 = 0.5 \text{ M}$; $[\text{MA}]_0/[(\text{salen})\text{Co}(\text{II})]_0/[\text{TPO}]_0 = 300/1/1$.

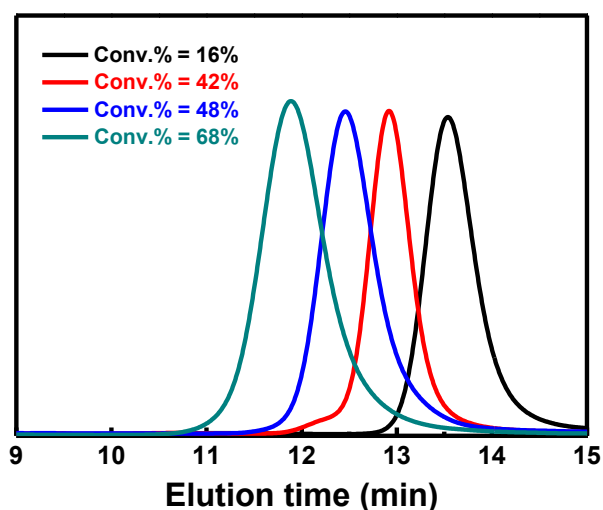


Figure 8S. GPC traces for photo-polymerization of MA in benzene with (salen)Co(II)/TPO under visible light irradiation (3 mw/cm^2) at ambient temperature. Experimental conditions: $[\text{MA}]_0 = 1.5 \text{ M}$; $[\text{MA}]_0/[(\text{salen})\text{Co}(\text{II})]_0/[\text{TPO}]_0 = 900/1/1$.

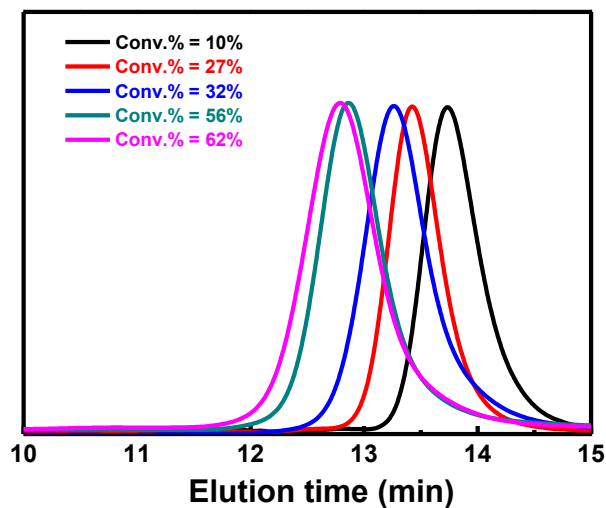


Figure 9S. GPC traces for photo-polymerization of MA in benzene with (salen)Co(II)/TPO under visible light irradiation (3 mw/cm^2) at ambient temperature. Experimental conditions: $[\text{MA}]_0 = 1.0 \text{ M}$; $[\text{MA}]_0/[(\text{salen})\text{Co}(\text{II})]_0/[\text{TPO}]_0 = 600/1/2$.

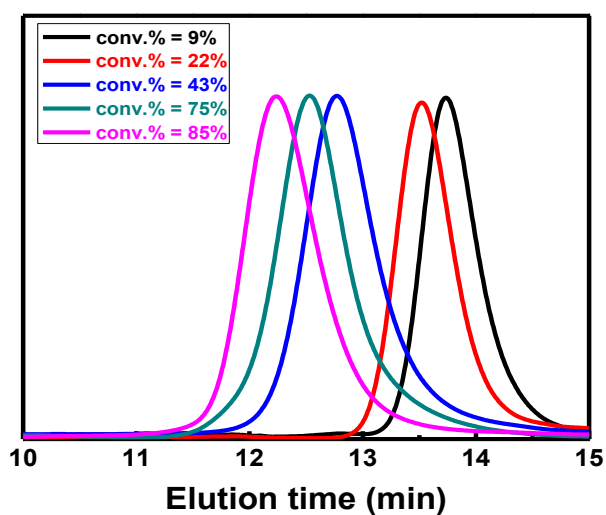


Figure 10S. GPC traces for photo-polymerization of MA in benzene with (salen)Co(II)/TPO under visible light irradiation (3 mw/cm^2) at ambient temperature. Experimental conditions: $[\text{MA}]_0 = 1.0 \text{ M}$; $[\text{MA}]_0/[(\text{salen})\text{Co}(\text{II})]_0/[\text{TPO}]_0 = 600/1/3$.

³¹P NMR spectrum of PMA

After the polymerization of MA mediated by (salen)Co(II)/TPO under visible light was stopped, solvent and excess MA were removed under vacuum. To avoid the influence of TPO, the remaining TPO in PMA was removed by washing with methanol. The ¹H NMR spectra of PMA before and after washing with methanol were shown in Figure 11S, indicating total disappearance of TPO in PMA. Then the ³¹P NMR of PMA sample was detected with saturated phosphoric acid as external reference (Figure 5 in main text). The ³¹P NMR of pure TPO was also detected and showed a single peak at 13.78 ppm (Figure 12S). The spectrum of PMA had no peak in this region (Figure 5 in main text), which further confirmed the removal of TPO from final polymer.

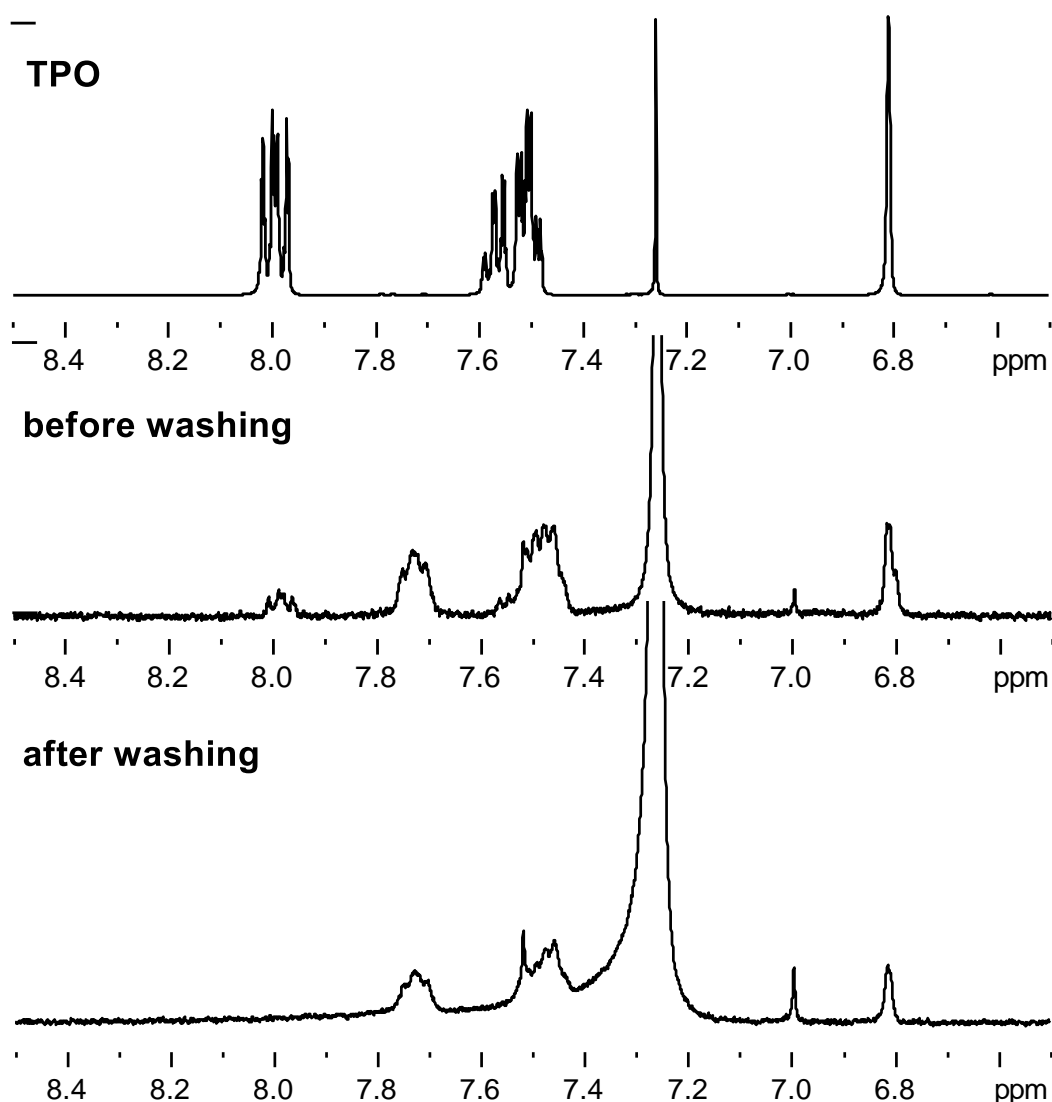


Figure 11S. ¹H NMR of TPO and PMA before and after washing with methanol in CDCl₃.

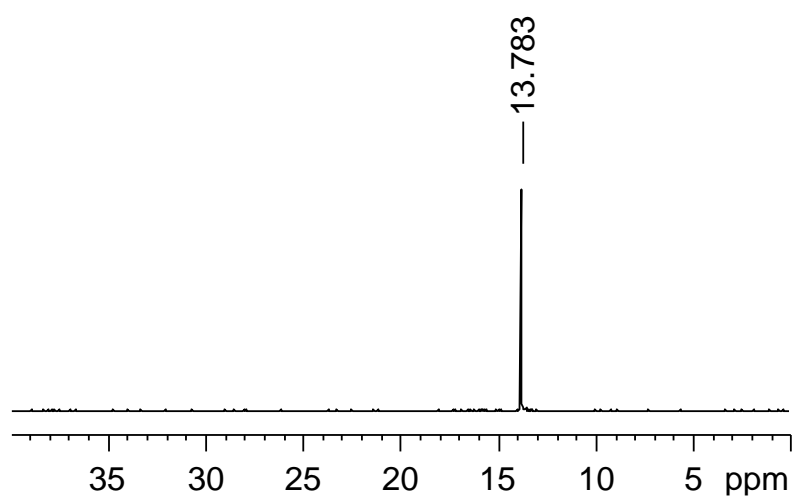
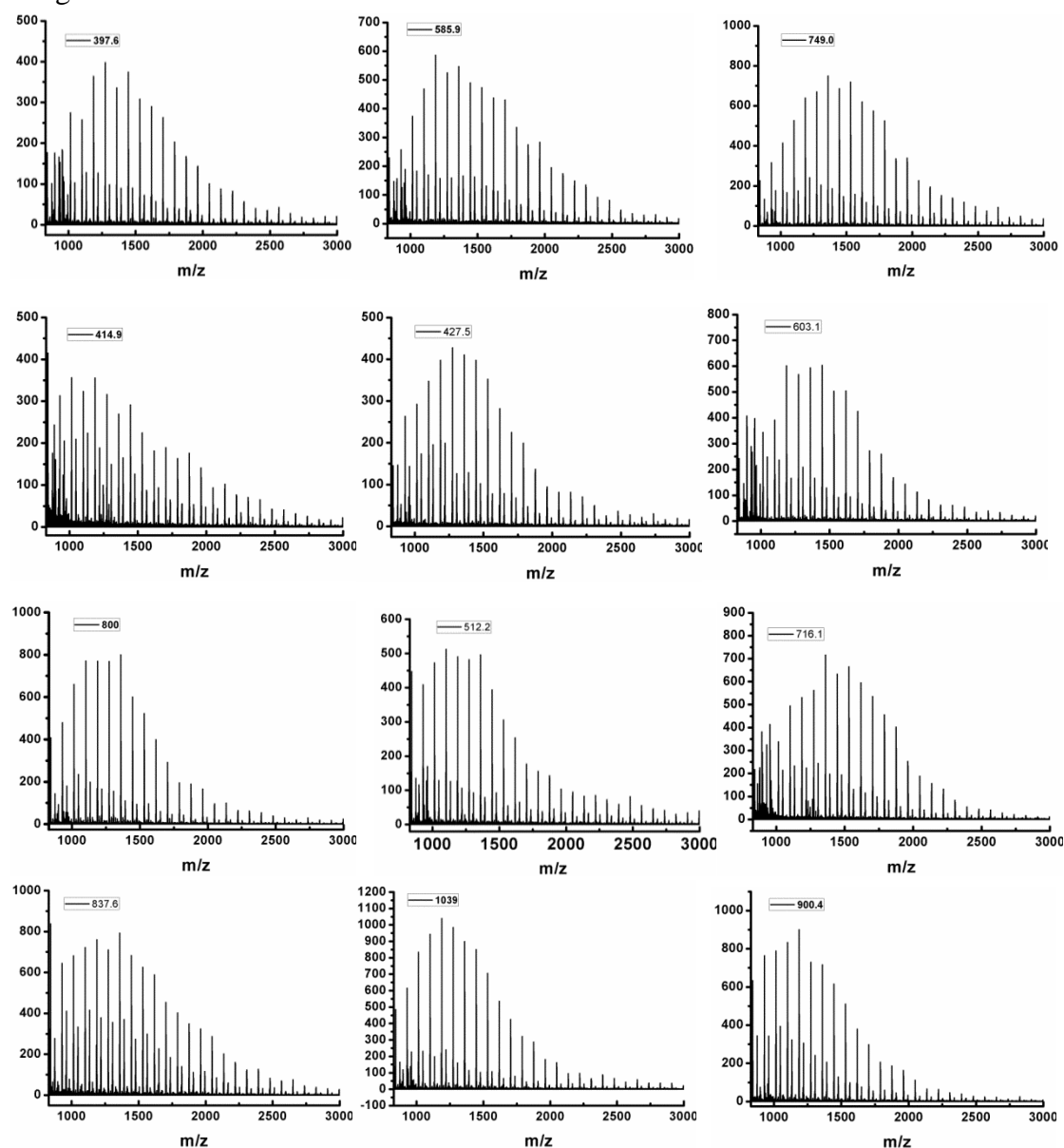


Figure 12S. ^{31}P NMR spectrum of TPO.

MALDI-TOF analysis of proportion of polymer chains initiated by phosphorus centered radical

To quantitatively determine the proportion of polymer chains with two different initiating radical driven from TPO, three parallel photo-polymerizations of MA were conducted. The feeding ratio of $[MA]_0/[(salen)Co(II)]_0/[TPO]_0$ was set at 600/1/1. Irradiation with 3 mW/cm² visible light for 20 h gave MA conversions between 6% and 8%. The ω end was functionalized through oxygen insertion reaction to form P-OH and then the three samples were analyzed by MALDI-TOF-MS. For each sample, 16 to 28 sites were analyzed and gave corresponding MS spectra.

For example, 28 MS spectra for sample 1 were shown in Figure 13S. These spectra were distinguished from each other by the highest intensity of peak as marked in the images.



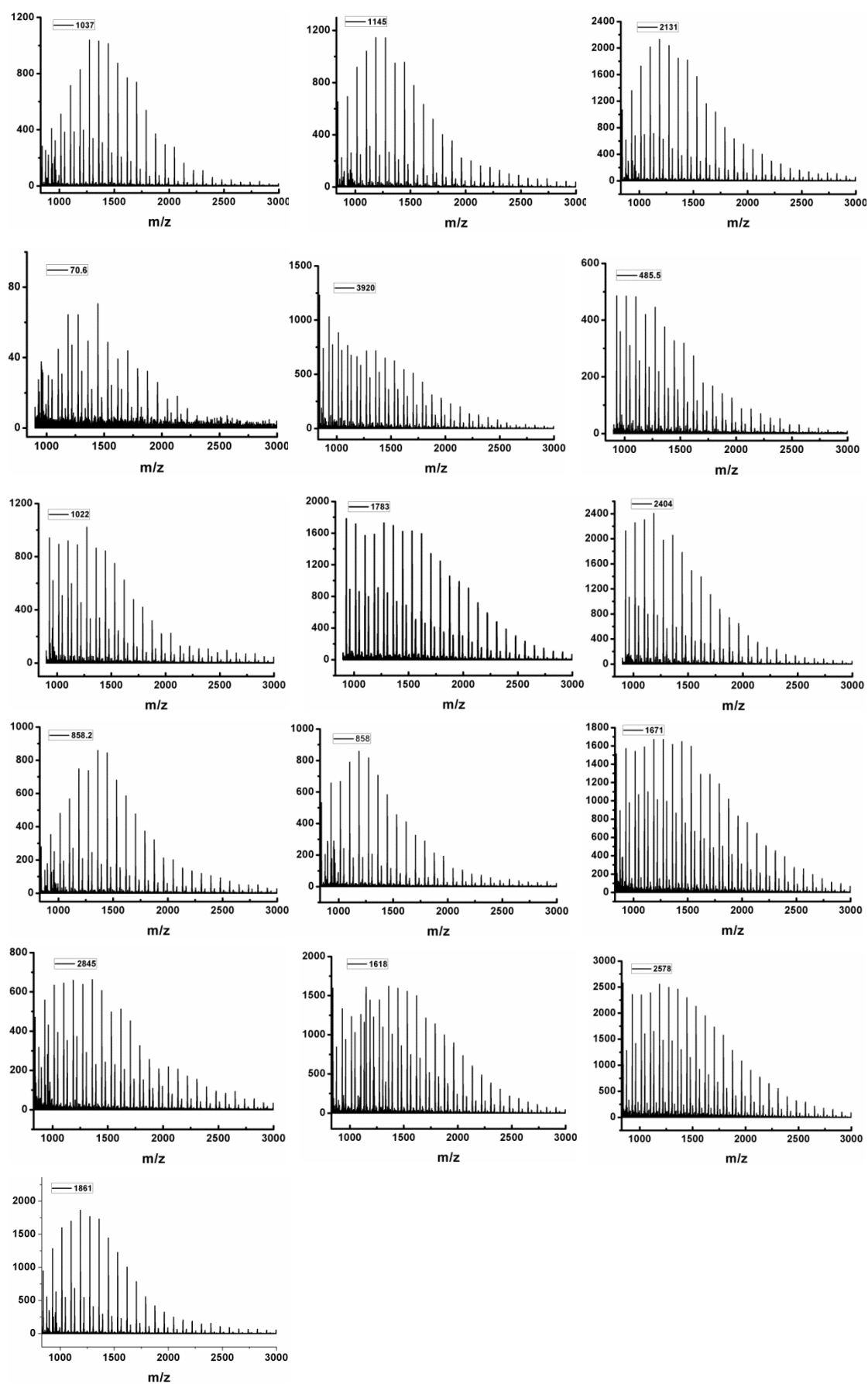


Figure 13S. MALDI-TOF-MS spectra of sample 1 obtained by laser desorption at 28

different sites.

In each spectrum, the polymer chains initiated by phosphorus and carbon centered radicals could be observed (Figure 6 in main text). For each spectrum, the integrals for the series of peaks initiated by P and C radicals were calculated separately. Then the percentage of polymer chains initiated by P radical was obtained. For sample 1, the results for these 28 spectra were summarized in Figure 14S and gave average value of 70.15%.

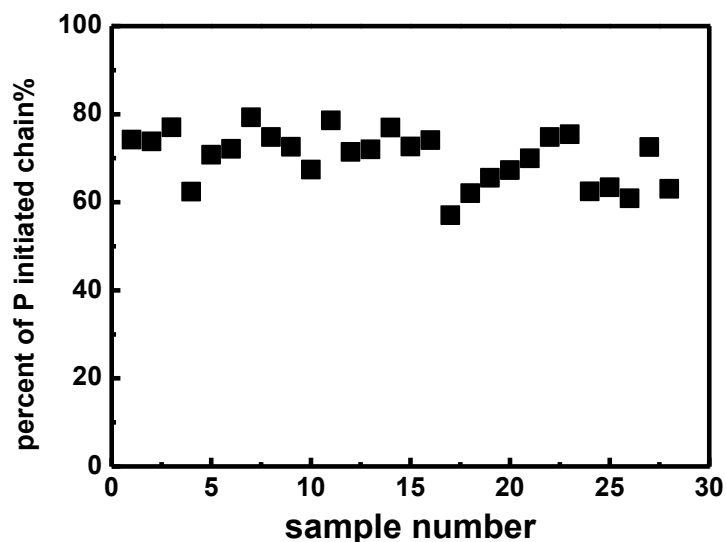


Figure 14S. The percentage of chains initiated by P radicals determined in 28 MS spectra of sample 1.

The independently prepared samples were analyzed with the same method (Figure 15S & 16S) and gave the average percentage of 67.49% and 71.09%, respectively. Thus the average percent of chains initiated by phosphorus radical from the three PMA samples was 69%.

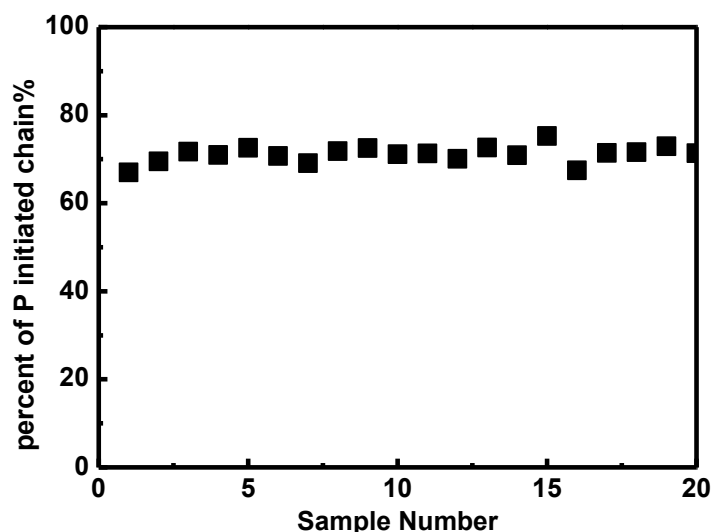


Figure 15S. The Percentage of chains initiated by P radicals determined in 20 MS spectra of sample 2.

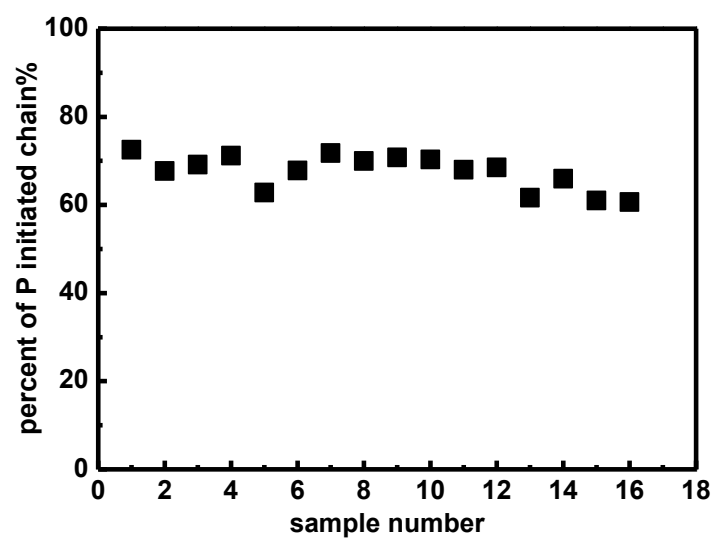


Figure 16S. The percentage of chains initiated by P radicals determined in 16 MS spectra of sample 3.