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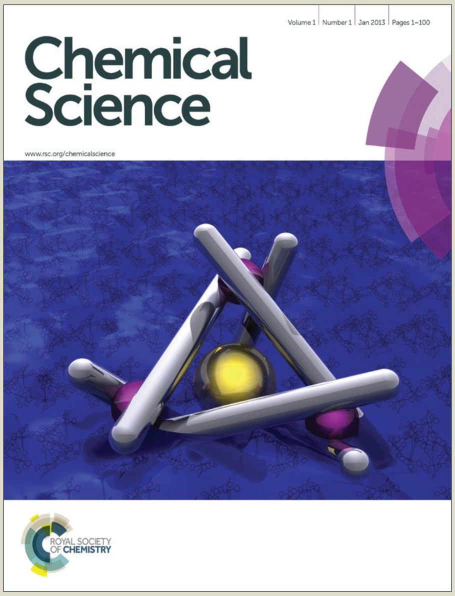

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A Well-defined Versatile Photoinitiator (salen)Co-CO_2CH_3 for Visible Light Initiated Living/Controlled Radical Polymerization

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The control of the polymerization of a wide range of monomers under mild conditions by a single catalyst remains a major challenge in polymer science. We report a versatile well-defined organo-cobalt salen complex to control living radical polymerization of different categories of monomers, including acrylates, acrylamides and vinyl acetate, under visible light irradiation at ambient temperature. Both household light and sunlight were effectively applied in synthesis of polymers with controlled molecular weight and narrow polydispersity. Narrow disperse block copolymers ($Mw/Mn < 1.2$) were obtained under various conditions. The structure of polymers was analyzed by ^{1}H NMR, ^{2}D NMR, ^{13}C NMR, GPC, MALDI-TOF-MS and isotopic labeling experiment which showed that the ω end and α end of polymer chains were capped with (salen)Co and -CO_2CH_3 segments, respectively, from the photoinitiator (salen)Co-CO_2CH_3. The ω end was easily functionalized through oxygen insertion followed by hydrolysis to -^{18}OH from $^{18}O_2$. This robust system could proceeds without any additives, and offers a versatile and green way to produce well-defined homo- and block-copolymers.

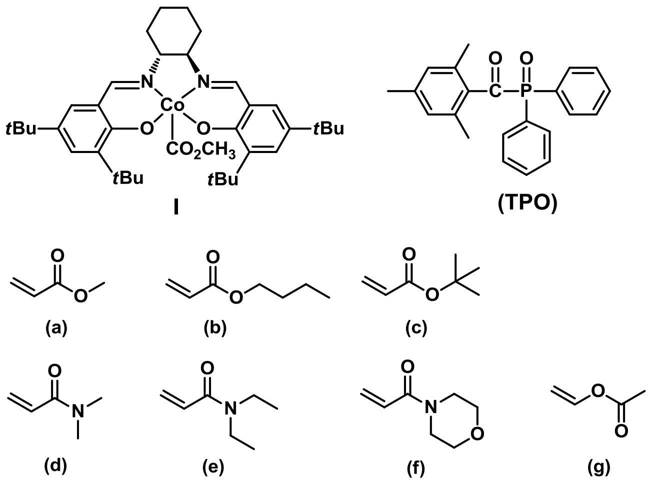
Introduction

Precise control over macromolecular compositions and architectures has long been a challenge in polymer science. The advent of living radical polymerization (LRP) has significantly contributed to this field over the last two decades and gives the possibility to obtain well-defined functional polymeric materials with precisely controlled structures and desired morphologies. So far, based on various strategies to regulate the equilibrium between dormant and active species in LRP, many powerful living radical polymerization technologies have been developed, such as nitroxide mediated radical polymerization (NMP),[1] atom transfer radical polymerization (ATRP),[2] reversible addition-fragmentation chain transfer polymerization (RAFT),[3] organoiodine mediated radical polymerization (IRP),[4] and organometallic mediated radical polymerization (OMRP),[5] etc.

Recently, modulation of external stimuli to control radical polymerization through regulation of the activation and deactivation processes has been employed as an effective method to synthesize polymers with controlled molecular weight, narrow polydispersity and end group functionality.[6] Of the various physical and chemical stimuli used, including heat, metal catalyst, electrochemical,[7] mechanical[6a] and photochemical stimuli,[6] light-induced LRPs[8-10] are receiving growing attention due to its abundance, renewability and simple operation process. Moreover, light-induced LRPs provide opportunities to prepare novel materials through spatial and temporal control of the polymerization.[11] Development of a versatile LRP catalyst suitable for a broader range of monomers, including both conjugated monomers (acrylates, acrylamides) and unconjugated monomers (vinyl esters), under mild conditions, would be desirable and represent a breakthrough in polymeric material synthesis.[3d,12]

Very recently, we reported the visible light induced LRP of acrylates and acrylamides mediated by organo-cobalt porphyrins at room temperature, based on the photo-induced reversible cleavage of Co-C bond.[13] Structurally close related organo-cobalt salen (salen is a common abbreviation for N_2O_2 bis-Schiff-base bis-phenolates) complexes also have relatively weak Co-C bonds. These complexes are supposed to undergo similar photolysis process to generate an organic radical, which could initiate polymerization, and salen cobalt(II) which functions as a persistent metal centered radical to control polymerization. Compared with cobalt porphyrin, cobalt salen is more desirable for industrial application due to its convenient synthesis, allowing facile adjustment of electronic and steric effects.[14] Thus, cobalt salen complexes appear to be an ideal candidate to achieve photo-induced LRP. In fact, cobalt salen complexes have been widely used in hydrolytic kinetic resolution[15] and enantioselective ring opening polymerization of epoxides,[16] however, rarely applied to catalyze living radical polymerization until recently.[17] To the best of our knowledge, there is no report on the success of photo-initiated LRP mediated by cobalt salen complex.

In this article, we report the first example of visible light initiated LRP of a diverse range of monomers (acrylates, acrylamides and vinyl acetate) (Scheme 1) using a novel well-defined methoxylcarbonyl-cobalt salen complex [(salen)Co-CO_2CH_3, **I**, salen = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]. Complex **I** functioned as both initiator and mediator to control the polymerization without any additives under visible light or sunlight irradiation. Furthermore, addition of traditional photoinitiator 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TPO) (Scheme 1) dramatically increased the polymerization efficiency while maintaining good controllability. Visible light was essential in the initiation step, albeit dispensable during chain propagation process, which differed from most photo-LRP processes requiring continuous irradiation after initiation step. Polymer structure was carefully investigated and demonstrated to maintain starting organo-cobalt salen segments at chain ends. Well controlled diblock copolymers were also easily prepared under mild conditions.



Scheme 1. Structures of (salen)Co-CO_2CH_3 **I** and TPO and list of monomers investigated in this study: (a) methyl acrylate (MA), (b) *n*-butyl acrylate (*n*BA), (c) *tert*-butyl acrylate (*t*BA), (d) *N,N*-dimethylacrylamide (DMA), (e) *N,N*-diethylacrylamide (DEA), (f) *N*-acryloylmorpholine (AMO), (g) vinyl acetate (VAc).

Results and discussion

Synthesis and Characterization of (salen)Co-CO_2CH_3

The living radical polymerization mediated by cobalt complexes often required induction time to convert cobalt species to trivalent organo-cobalt complexes, which were the actual mediators for the polymerization.[18] Unfortunately, living radical polymerizations using a well-defined molecular organo-cobalt(III) salen complex as the sole radical source were rare due to its sensitivity to air or light and difficulty in purification.[17a,19] Here we synthesized typical trivalent (salen)Co-CO_2CH_3 (**I**) complex from the one-pot reaction of commercial (salen)Co(II), methanol and CO by using Oxone as oxidant. Compound **I** was obtained as dark green solid and characterized using ^1H NMR, ^{13}C NMR, ESI-MS and FT-IR (ESI, Figure 1S-3S). This compound exhibited a strong CO stretching absorption at 1680 cm^{-1}, which was similar to the analogous (TMP)Co-CO_2CH_3 (1695 cm^{-1}, TMP referred to tetramesityl porphyrin).[13b] The single crystal structure of this diamagnetic complex **I** was shown in Figure 1. As with the reported similar cobalt alkyl complexes,[17a,20] the cobalt atom was five-coordinated with a distorted square pyramidal geometry. The Co-O and Co-N bond lengths of ca. 1.868 and 1.872 Å were similar to those results found in analogue (saloph)Co-iC_3H_7 (saloph = dianion of disalicylidene-*o*-phenylenediamine, 1.872(5) and 1.879(5) Å, respectively).[20] The Co-C bond length was 1.895 Å indicating a stronger Co-C bond compared with that reported for (saloph)Co-iC_3H_7 (2.031(8) Å).[20]

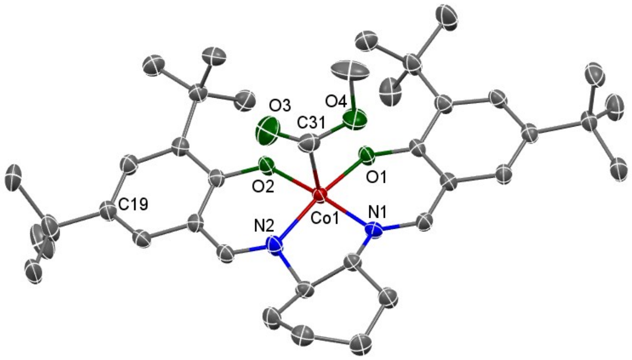


Figure 1. X-ray crystal structure of **I** shown with 50% thermal ellipsoids. One set of disordered *tert*-butyl group (at C19 atom), cyclohexane and H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co-O1 1.858(2), Co-O2 1.878(2), Co-N1 1.872(3), Co-N2 1.872(3), Co-C31 1.895(4); O1-Co-O2 85.32(9), O1-Co-N1 93.84(10), N2-Co-O2 93.96(10), N2-Co-N1 85.37(11), O1-Co-C31 96.95(13), O2-Co-C31 92.32(13), N1-Co-C31 94.67(14), N2-Co-C31 95.40(14).

Photolysis of (salen)Co-CO_2CH_3

(salen)Co-CO_2CH_3 showed a broad absorption band from 300 nm to 700 nm with the peak value around 333 nm and 625 nm (ESI, Figure 4S). To confirm the possibility of using (salen)Co-CO_2CH_3 as the photoinitiator, we carried out a typical radical trapping experiment under visible light irradiation (Figure 2). The light source was a 500W xenon lamp equipped with a 420-780 nm filter with the light intensity of 3 mW/cm^2 at sample position. The benzene-d_6 solution of (salen)Co-CO_2CH_3 (5.0 mM) and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (50 mM) as the radical trap was irradiated for 1 h at ambient temperature. The photolysis occurred companying with the color change of the solution from dark green to red, indicating the formation of (salen)Co(II) (ESI, Figure 5S & 6S). Figure 2

Table 1. Visible Light Initiated LRP of Acrylates and Acrylamides Using **I** as Both Initiator and Mediator at Ambient Temperature[a]

Entry	Monomer(equiv)	Condition[b]	t(h)	Conv.[c] (%)	$M_{n,th}$[d]	$M_{n,GPC}$[e]	M_w/M_n[e]
1	MA(600)	Xe lamp	92	74	38700	38900	1.14
2	MA(600)	CFL	72	67	35300	37300	1.09
3	*n*BA(600)	Xe lamp	72	81	62900	64200	1.23
4	*n*BA(600)	CFL	72	88	68300	71700	1.23
5	*t*BA(600)	Xe lamp	24	73	56800	55000	1.11
6	*t*BA(600)	CFL	24	73	56800	57900	1.15
7[f]	*t*BA(600)	dark	36	0	---	---	---
8[f]	DMA(600)	dark	48	0	---	---	---
9	DMA(600)	Xe lamp	12	76	45800	41200	1.16
10	DMA(600)	CFL	12	79	47600	43100	1.16
11	DEA(600)	Xe lamp	4	71	54100	57200	1.22
12	DEA(600)	CFL	4	70	54800	55900	1.19
13	DEA(600)	Sunlight	4	42	32400	35600	1.23
14	AMO(200)	Xe lamp	12	84	24400	20700	1.12
15	AMO(200)	CFL	12	88	25400	21100	1.13

[a]$[M]_0$ = 1.0 M in benzene-d_6. [b]A 500W Xe lamp was used as light source with a 420-780 nm filter, and light intensity was 3 mW/cm^2; a household CFL (compact fluorescent lamp, 27 W) used as the light source, light intensity was 3 - 5 mW/cm^2 at sample position; sunlight as light source, and sample was placed in a water bath at ambient temperature. [c]The monomer conversion was determined based on ^{1}H NMR spectra. [d]$M_{n,th} = M_{w(\mathbf{I})} + M_{w(Monomer)} \times$ ratio $\times$conv (%), where ratio referred to the equivalent of monomer to **I**. [e]Determined using gel permeation chromatography in DMF calibrated against poly(methyl methacrylate) standards. [f]Sample was protected from light with aluminum foil.

showed the ^{1}H NMR spectrum before and after visible light irradiation. Sharp signals in the region of 1.30-2.10 ppm corresponding to *tert*-butyl group of **I** disappeared after irradiation for 1 h, which suggested the cleavage of the Co-C bond in (salen)Co-CO_2CH_3. Moreover, the resulting CH_3CO_2• radical was trapped by excess TEMPO to form TEMPO-CO_2CH_3 with the yield of 95%.[21] This product was evidenced by the chemical shifts at δ = 1.05-1.30 ppm corresponding to the methyl protons in TEMPO-CO_2CH_3 (ESI, Figure 2). The formation of TEMPO-CO_2CH_3 was also confirmed by ESI-MS (Figure 7S). Simultaneously, broad peaks at -0.49 ppm and downfield in ^{1}H NMR (ESI, Figure 8S) after photolysis clearly indicated the formation of corresponding (salen)Co(II).

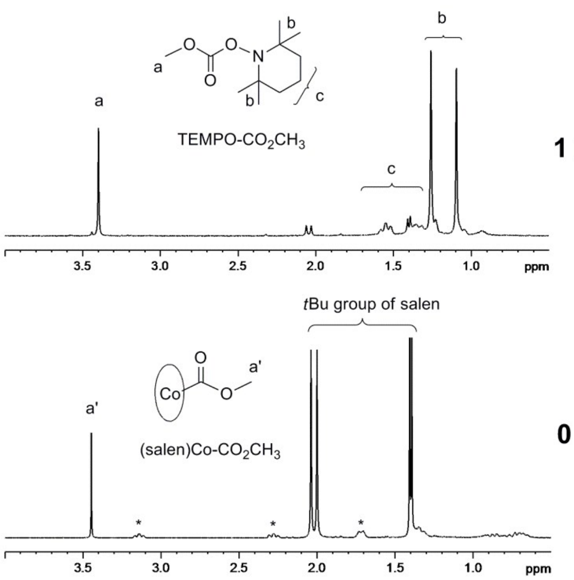


Figure 2. ^{1}H NMR spectrum (in the range of 0.5−4.0 ppm) of (salen)Co-CO_2CH_3 **I** (5.0 mM) and TEMPO (50 mM) in benzene-d_6 under visible light irradiation (I = 3 mW/cm^2 at 420−780 nm wavelength) at room temperature for 1 h (*salen ligand in **I**, see ESI, Figure 2S).

Visible Light Initiated LRP Mediated by (salen)Co-CO_2CH_3

The polymerization of different acrylates and acrylamides using **I** as both initiator and mediator at ambient temperature was tested. Three different light sources were used including a 500 W xenon lamp, a commercial household compact fluorescent lamp and direct use of sunlight (Table 1). By using xenon lamp or fluorescent lamp, irradiation of the dark green solution of complex **I** with acrylates in benzene at room temperature yielded corresponding polyacrylates as evidenced by a color change to yellow (ESI, Figure 5S). The polymerizations were all under excellent control over molecular weight with very narrow polydispersity along with the monomer conversions (Table 1, entries 1-6). The experimental molecular weights were all very close to the theoretical values and GPC traces were monomodal and symmetrical. Thus the visible light initiated polymerization of acrylates mediated by **I** demonstrated very good control capability over acrylates using xenon lamp or household light sources. Following the successful polymerization of acrylates, polymerization of acrylamides including DMA, DEA and AMO with **I** also resulted in polyacrylamides with narrow polydispersity (Table 1, entries 9-15). To avoid gel formation due to high viscosity, the ratio of AMO to **I** was reduced to 200 and gave excellent control over molecular weight. Furthermore, direct use of sunlight without filtering was rarely found in photo-LRP examples.[8b,8c,9j,10f,13b,22] However, in our system, the polymerization of DEA with sunlight irradiation gave PDEA with predetermined molecular weight and narrow polydispersity (Table 1, entry 13). To confirm that polymerization was induced only by **I** under light, control experiments in absence of light for the polymerization of *t*BA and DMA were conducted (Table 1, entries 7-8). No polymers were detected in each case and no color change in solution was observed, indicating no polymerization occurring. Thus visible light was essential for successful polymerization. To the best of

Table 2. Visible Light Initiated Polymerization with **I** in the Presence of TPO at Ambient Temperature[a]

Entry	Monomer(equiv)	t(h)	Conv.[b](%)	$M_{n,th}$[c]	$M_{n,GPC}$[d]	M_w/M_n[d]
1	MA(600)	8	76	39900	37200	1.25
2	*n*BA(600)	8	81	62900	55300	1.23
3	*t*BA(600)	5	80	62200	59300	1.24
4	DMA(600)	2	75	45300	40000	1.22
5	DEA(600)	3	71	55000	47200	1.30
6	AMO(200)	3	87	25200	23800	1.24
7[e]	VAc(600)	100	39	20800	20600	1.20
8[f]	VAc(200)	64	78	14100	18600	1.33

[a] A mixture of **I** (1 equiv), TPO (1 equiv) and monomer was irradiated with $[M]_0 = 1.0$ M in benzene-d_6. A 500W Xe lamp was used as light source with a 420-780 nm filter, and light intensity was 3 mW/cm^2. [b] The monomer conversion was determined based on ^1H NMR spectra. [c] $M_{n,th} = M_{w(\mathbf{I})} + M_{w(Monomer)} \times$ ratio $\times$conv (%), where ratio referred to the equivalent of monomer to **I**. [d] Determined using gel permeation chromatography in DMF calibrated against poly(methyl methacrylate) standards. [e] Polymerization in bulk. [f] $[M]_0 = 2.0$ M in dimethyl sulfoxide-d_6.

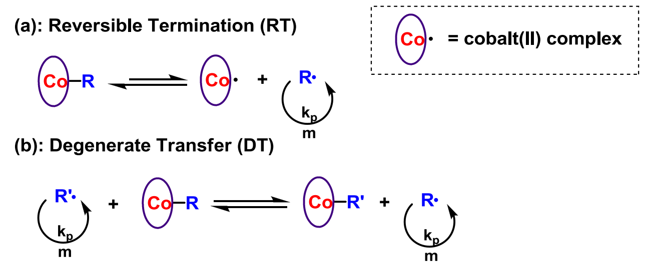
our knowledge, this is the first example that a well-defined five-coordinate cobalt salen complex was used to give well controlled polymerization under visible light irradiation at room temperature.

Visible Light Initiated LRP by Addition of TPO

Although the polymerization by direct irradiation of **I** and different acrylates or acrylamides all gave promising results, the polymerization rate was rather slow. Polymerization of MA required 92 h irradiation to achieve 74% conversion. Switching from reversible termination (RT) to degenerate transfer (DT), by addition of external radicals, could dramatically increase the rate of polymerization.[18b,23] Thus addition of traditional photoinitiator to generate excess radicals would be helpful to improve polymerization efficiency. Indeed, the photo-polymerization of MA (600 equiv) with organo-cobalt complex **I** in the presence of TPO (1 equiv) reached 76% conversion within 8 h at ambient temperature, while 92 h required for similar monomer conversion without TPO (Table 1, entries 1 vs Table 2, entry 1). Significant rate enhancement was also found remarkably effective for the polymerizations of *n*BA, *t*BA, DMA and AMO, and high degree of controllability remained (Table 1, entries 3-15 vs Table 2, entries 2-6). More importantly, (salen)Co-CO_2CH_3 complex could not only mediate the polymerization of conjugated acrylates and acrylamides under visible light irradiation, it was also suitable for typical non-conjugated vinyl acetate (VAc). Bulk polymerization of VAc gave PVAc of narrow polydispersity with excellent control over molecular weight (Table 2, entry 7). But the polymerization was a little bit slow and gel was formed after 39% conversion due to high viscosity. To achieve high conversion and avoid gel formation, the load of VAc to **I** was reduced to 200 equivalents and polymerization was conducted in DMSO-d_6. In this case, PVAc with 78% conversion was obtained with moderate control over molecular weight and polydispersity (Table 2, entry 8). Thus, (salen)Co-CO_2CH_3 was an alternate versatile catalyst to control polymerization of both "more active" monomers (acrylates and acrylamides) and "less activated" monomers (VAc) under visible light irradiation.

Kinetics and Possible Mechanism

Reversible termination (RT) and degenerate transfer (DT) are two competing mechanisms occurred in OMRP and cobalt mediated radical polymerization (Scheme 2).[5,18b,24] Dormant species (organo-cobalt complexes) are the exclusive source of radicals in RT, while the concentration of chain radicals in DT is mainly dependent on the concentration of external radical source. The rate of polymerization via a DT process approaches the rate of a regular free radical polymerization which is much larger than that in a RT process.[18b] In order to investigate the mechanism, the kinetics of polymerization mediated by **I** under different conditions (irradiated by Xe lamp, CFL, or addition of TPO) were investigated (Figure 3a). Mixing **I** with 1 equivalent of TPO in the photo-induced polymerization resulted in a rapid first order kinetics with the conversion of 58% after only 4.5 h (Figure 3a, blue dots). On the other hand, much slower rate was obtained without addition of TPO (Figure 3a, black and red dots). The radical concentration was calculated to be ~8.8×10^{-10} M from the slope of 0.043 h^{-1} and k_p (MA at 298K)[25] of 13500 $M^{-1}S^{-1}$ irradiated by Xe lamp, which was similar to that using CFL (1.0×10^{-9} M) and one order of magnitude smaller than that in the presence of TPO (6.2×10^{-9} M). The lower concentration of propagation chain radical in the absence of TPO arose from the fact that photolysis of organo-cobalt salen was the sole pathway for the formation of chain radicals and the resulting cobalt(II) reversibly grabbed the chain radical.



Scheme 2. (a) Reversible termination and (b) degenerate transfer mechanism in cobalt mediated radical polymerization.

To further understand the polymerization mechanism, the associative equilibrium constant for the formation of organo-cobalt complexes was evaluated ((salen)Co(II) + R• $\rightleftharpoons$ (salen)Co-R, K_{eq} = $[(salen)Co\text{-}R]_{eq}/([(salen)Co(II)]_{eq}\times[R\bullet])$). $[(salen)Co\text{-}R]_{eq}$ and $[(salen)Co(II)]_{eq}$ were the stationary

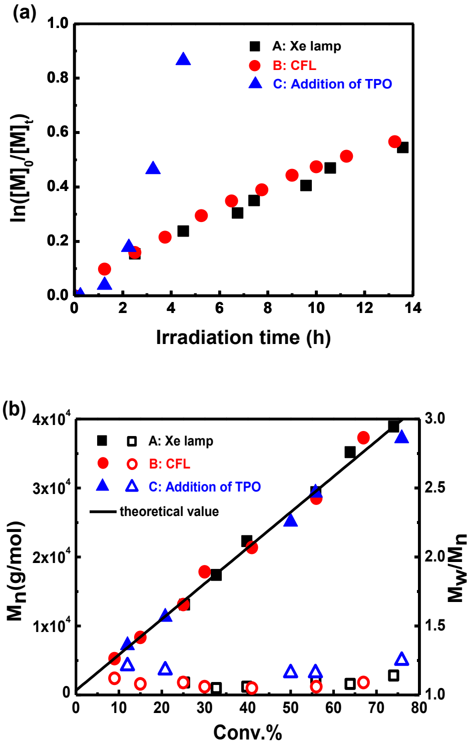


Figure 3. (a) Kinetic plots for polymerization of MA in benzene at ambient temperature with $[MA]_0 = 1.0$ M, $[MA]_0/[\mathbf{I}]_0 = 600/1$. A: t = 13.6 h, conv. = 42%, $M_{n,GPC} = 20300$, $M_w/M_n = 1.07$. B: t = 13.5 h, conv. = 45%, $M_{n,GPC} = 26100$, $M_w/M_n = 1.06$. C: addition of 1 equivalent of TPO, t = 4.5 h, conv. = 58%, $M_{n,GPC} = 28500$, $M_w/M_n = 1.12$. (b) Evolution of molar mass and polydispersity with conversion under different conditions.

state concentrations of dormant and deactivate species during the polymerization. A certain amount of (salen)Co(II) (>5 mol% of the initial concentration of **I**) was added at the beginning of polymerization in order to shift the activation-deactivation equilibrium towards the dormant species so that only a tiny proportion of (salen)Co-CO_2CH_3 was dissociated during the polymerization. Thus, the equilibrium concentration of $[(salen)Co\text{-}R]_{eq}$ and $[(salen)Co(II)]_{eq}$ was assumed to be equal to the initial concentration of $[(salen)Co\text{-}CO_2CH_3]_0$ and $[(salen)Co(II)]_0$. To determine the K_{eq}, 8% and 16% excess of (salen)Co(II) to (salen)Co-CO_2CH_3 were added before the irradiation and the polymerization kinetics were shown in Figure 4. Both the polymerizations gave linear consumption of MA with decreased polymerization rate due to the addition of excess (salen)Co(II). The radical concentration was calculated to be 3.56×10^{-10} M and 1.83×10^{-10} M, respectively. The ratio of $[(salen)Co\text{-}CO_2CH_3]_0/[(salen)Co(II)]_0$ combined with the radical concentration gave the equilibrium constant $K_{eq} = 3.5\times10^{10}$ M^{-1} and 3.4×10^{10} M^{-1}, respectively. The K_{eq} was three orders of magnitude larger than that measured under thermal polymerization of MA at 60 °C mediated by (salen)Co(II) ($K_{eq} \sim 2.4\times10^7$ M^{-1})[17b] and close to the value for thermal polymerization by cobalt porphyrin system ($K_{eq} \sim 8.7\times10^9$ M^{-1}).[26] With such a large K_{eq}, when TPO was added, the major radical source would mainly from external TPO other than from organo-cobalt (salen)Co-CO_2CH_3. Thus, the visible light initiated polymerization mediated by complex **I** without TPO was suggested to mainly undergo a RT process, while DT process was predominant in photo-polymerization in the presence of TPO. Furthermore, addition of TPO had insignificant influence to α end fidelity because only a tiny amount of polymer chain derived from TPO segment was found in MALDI-TOF-MS detection. (ESI, Figure 9S & 10S)

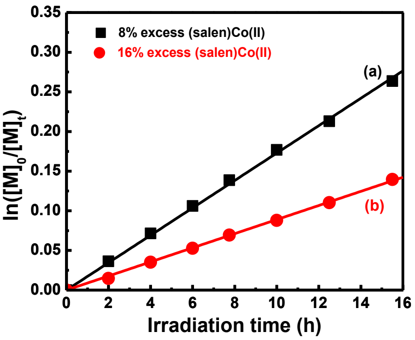


Figure 4. Kinetic plots for the polymerization of MA with excess amount of (salen)Co(II). $[MA]_0 = 1.0$ M, $[MA]_0/[\mathbf{I}]_0 = 600/1$. ■ 8% (salen)Co(II) added, conv. = 23%, $M_{n,th} = 12500$, $M_{n,GPC} = 11600$, $M_w/M_n = 1.08$. ● 16% (salen)Co(II) added, conv. = 13%, $M_{n,th} = 7380$, $M_{n,GPC} = 7370$, $M_w/M_n = 1.09$.

Living character of the visible light initiated radical polymerization of MA was further demonstrated by the evolution of molecular weight versus conversion under different conditions (Figure 3b). Gel permeation chromatography analysis revealed a linear increase in molecular weight with respect to conversion of MA under all conditions. The polydispersity index was small ($M_w/M_n < 1.25$) from the early stage of polymerization up to high MA conversions in all cases. The GPC traces for photo-polymerization under these conditions were all monomodal and symmetrical throughout the whole processes (ESI, Figure 11S-13S). Furthermore, it was worth mentioning that in the thermal polymerization of MA mediated by (salen)Co(II), there was a significant deviation between measured and calculated molecular weights because the relative small K_{eq} (2.4×10^7 M^{-1}) under thermal condition resulted in incomplete conversion of cobalt(II) complexes to organo-cobalt species.[17b] However, the large K_{eq} of this photo system at room temperature maintained nearly all cobalt species as organo-cobalt complexes and fulfilled the ideal assumption of one polymer chain per cobalt. So that the experimental molecular weights are all close to theoretical values, indicating high initiation efficiency for this visible light initiated polymerization.

Effect of Visible Light

Surprisingly, we found that after initiation stage, the rate of polymerization was approximately the same with/without continuing irradiation. For example, after passing the initiation stage, one sample was protected from light by covering aluminum foil and the other was continuing irradiated under light intensity of 3 mW/cm^2, however, both of these two samples of DMA gave similar conversions (45% and 46%).

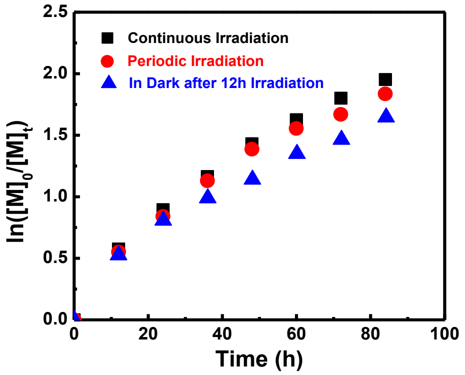


Figure 5. Kinetic plots for polymerization of MA in benzene at ambient temperature under variable conditions. $[MA]_0$ = 1.0 M, $[MA]_0/[I]_0$ = 200/1. ■ conv. = 87%, $M_{n,th}$ = 15600, $M_{n,GPC}$ = 18200, M_w/M_n = 1.11. ● conv. = 85%, $M_{n,th}$ = 15300, $M_{n,GPC}$ = 17900, M_w/M_n = 1.09. ▲ conv. = 81%, $M_{n,th}$ = 14600, $M_{n,GPC}$ = 17700, M_w/M_n = 1.10.

This observation definitely indicated that polymerization also occurred with similar rate in dark after initiation. This was interesting since visible light was essential for the successful polymerization (Table 1, entry 8).

To assess the influence of visible light on the polymerization process at ambient temperature, MA was chosen as model monomer and kinetic studies were conducted under three different conditions. The molar ratio of MA to **I** was all set at 200/1, one sample was conducted by continuous irradiation under Xe lamp irradiation and the second sample was subjected to a periodic light on-off process for every 12 hours. The third sample was irradiated for the first 12 hours and then stored in dark. Polymerization rate under continuous irradiation was slightly faster than that in dark, and no significant rate difference was observed under continuous and periodic irradiation within 40 h (Figure 5). So the visible light of 3 mW/cm^2 has negligible influence over the polymerization rate after initiation. However, after a fairly long reaction time (more than 40 h), the polymerization under visible light irradiation showed a little bit higher monomer conversion than that in dark (Figure 5 & ESI Figure 14S). These results indicated that Co-C bonds in (salen)Co-PMA and (salen)Co-PDMA could undergo homolysis to give propagating radicals even in dark at ambient temperature although **I** did not initiate polymerization in dark (Table 1, entries 7-8). The bond dissociation energy of Co-C bonds in Co-C(O)OR was much stronger than in Co-CHR$_1$R$_2$ due to the sp^2 hybridized carbon in **I**.

Polymer Structure Analysis

The chain growth process is through monomer insertion into cobalt carbon bond in organo-cobalt dormant species. Thus in the final polymer structure, α ends was anticipated to be CO_2CH_3 in (salen)Co-CO_2CH_3, while ω ends should be cobalt salen. In order to investigate the α ends of polymer chains, both deuterated and ^{13}C labeled organo-cobalt complex (salen)Co-$^{13}CO_2CD_3$ was synthesized under similar conditions (Electronic supplementary information, ESI). It was characterized by ^{1}H NMR, ^{13}C NMR, ^{2}D NMR and ESI-MS. The ^{2}D NMR spectrum gave a clear peak at -1.315 ppm, corresponding to the deuterium atoms of methyl group in (salen)Co-$^{13}CO_2CD_3$ (Figure 6a). After polymerization of MA, the isotopic labeled methyl group in PMA shifted to -1.455 ppm corresponding to the deuterium atoms at α ends. The structure of PMA synthesized from (salen)Co-$^{13}CO_2CD_3$ was further investigated by ^{13}C NMR and compared with PMA prepared from regular (salen)Co-CO_2CH_3 (Figure 7). The PMAs formed were highly linear as no signal was detected in the range of δ(^{13}C) = 37-40 and 47-49 ppm that are characteristic of acrylate branching.[27] The two spectra were nearly identical except for the signal at 172 ppm which was assigned to the ^{13}C labeled carbon atom in the ester group from the starting (salen)Co-$^{13}CO_2CD_3$. Both the ^{2}D NMR and ^{13}C NMR detections demonstrated that α ends of

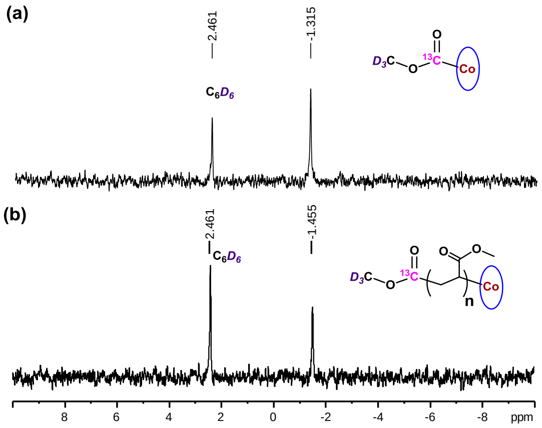


Figure 6. ^{2}D NMR spectra of benzene solutions of (salen)Co-$^{13}CO_2CD_3$ and PMA synthesized by photo-LRP mediated by (salen)Co-$^{13}CO_2CD_3$ ($M_{n,GPC}$ = 9060, M_w/M_n = 1.08, $M_{n,th}$ = 9125).

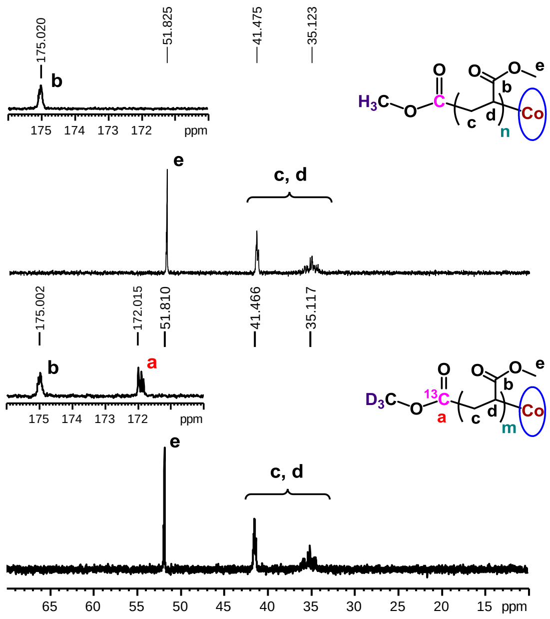


Figure 7. ^{13}C NMR spectrum of PMA synthesized by photo-LRP mediated by (salen)Co-CO_2CH_3 ($M_{n,GPC}$ = 7370, M_w/M_n = 1.09) and (salen)Co-$^{13}CO_2CD_3$ ($M_{n,GPC}$ = 9060, M_w/M_n = 1.08). $CDCl_3$ was used as the solvent.

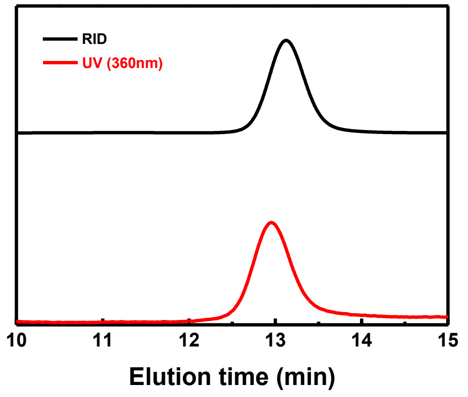


Figure 8. Gel permeation chromatography (GPC) traces of the PMA produced by photo-LRP mediated by **I** ($M_{n,th}$ =21800, $M_{n,GPC}$ = 21400, M_w/M_n = 1.05). Black line indicated the refractive index detection trace, and red line indicated the UV-visible (360 nm) detection trace.

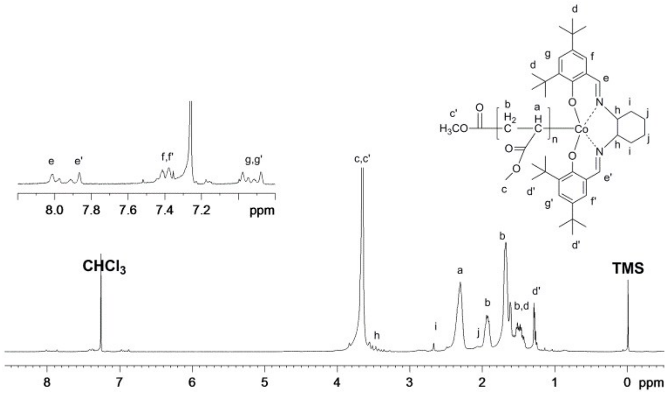


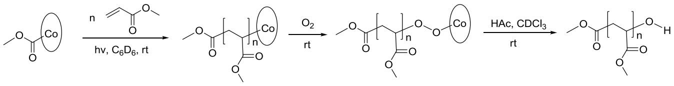
Figure 9. ^{1}H NMR spectrum of PMA synthesized by visible light initiated polymerization with Xe lamp irradiation at ambient temperature. $[MA]_0 = 1.0$ M, $[MA]_0/[(salen)Co\text{-}CO_2CH_3]_0 = 200/1$, conversion = 50%. $M_{n,GPC}$ = 10300, $M_{n,th}$ = 9270, $M_{n,NMR}$ = 9530, M_w/M_n = 1.10. $M_{n,th} = M_{w(I)} + M_{w(MA)} \times$ ratio $\times$ conv (%); $M_{n,NMR} = I^{2.3ppm}/(I^{7.9ppm}/2) \times M_{W(MA)} + M_{W(I)}$, where $I^{2.3ppm}$ and $I^{7.9ppm}$ were integrals of signals at δ 2.3 ppm and 7.9 ppm corresponding to methane group of MA and imine group of salen, respectively.

the formed polymers mediated by organo-cobalt salen complexes were CO_2CH_3 from (salen)Co-CO_2CH_3.[13b]

To analyze the structure of ω chain ends, GPC traces of PMA were detected by both refractive index and UV-visible detectors (Figure 8 & ESI, Figure 15S). Polymers with (salen)Co chromophore showed a strong UV-visible absorption band around 360 nm. GPC traces of typical PMA samples by RID and UV-vis detectors were nearly the same except for delay in RID signal due to series connection of equipment. The elution curves were narrow and symmetrical, indicating that each polymer chain contained one cobalt complex at ω end.

PMA obtained in our system was further characterized by ^{1}H NMR (Figure 9). The chemical shift at 6.9 ppm, 7.4 ppm, and 7.8-8.0 ppm clearly demonstrated the presence of (salen)Co group in the polymer chain. Furthermore, the molecular weight calculated from ^{1}H NMR analysis was 9530 g/mol, which fitted very well with theoretical value (9270 g/mol) and experimental molar mass (10300 g/mol), indicating high initiator efficiency.

Polymer End Group Functionalization



Scheme 3. The strategy of modification of ω end of (salen)Co-PMA synthesized.

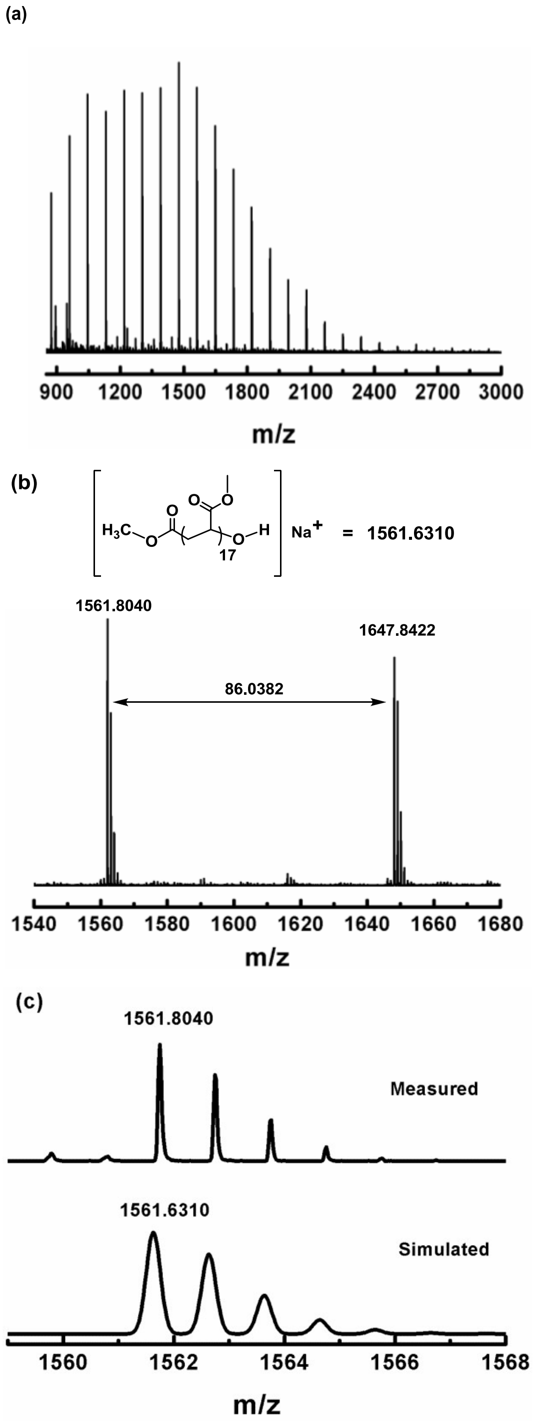


Figure 10. (a) Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) of PMA after modification of ω polymer end ($M_{n,GPC}$ = 3450, M_w/M_n = 1.16). (b) the expanded main peak series and theoretical molecular weight. (c) the simulation of the isotopic pattern.

Photo induced dioxygen insertion into Co-C bond was reported previously[28] and Co(III)-alkylperoxo complexes were important intermediates in cobalt-catalyzed hydrocarbon oxidation

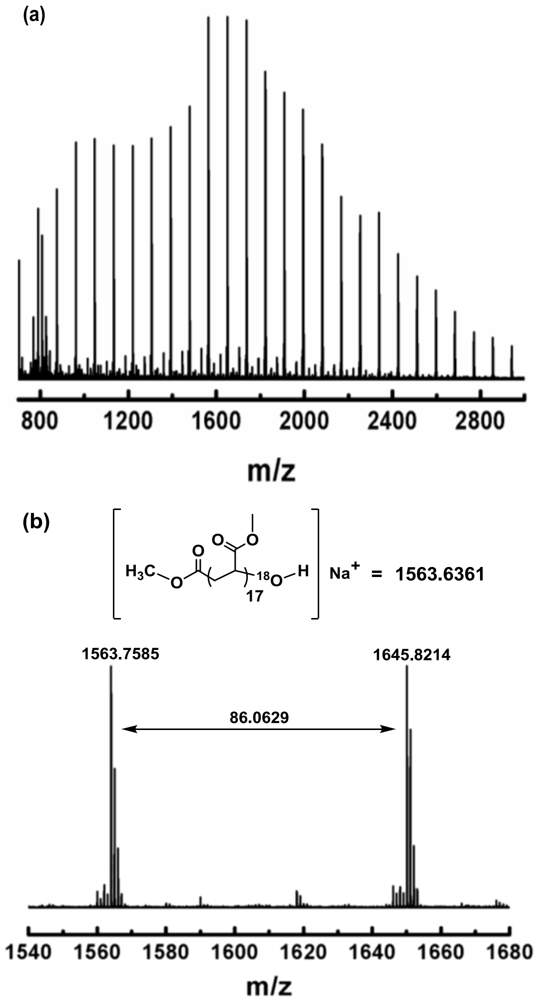


Figure 11. (a) Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) of PMA ($M_{n,GPC}$ = 3870, M_w/M_n = 1.19) after modification of ω polymer end using $^{18}O_2$. (b) the expanded main peak series and theoretical molecular weight.

reactions.[29] Our strategy for modification of ω end of polymers obtained was illustrated in Scheme 3. As investigated in periodic irradiation experiment, the Co-C bond in (salen)Co-PMA could undergo homolysis to give PMA• and (salen)Co(II). Schiff-base cobalt(II) complexes were well-known to bind dioxygen reversibly.[30] Thus photolysis of (salen)Co-PMA in the presence of dioxygen resulted in the formation of Co(III)-alkylperoxo complex [(salen)Co-O-O-PMA] accompanying with the color change from yellow to dark brown (ESI, Figure 16S). Coordination of alkylperoxide to cobalt was presumed to weaken the O-O bond and assist O-O bond cleavage.[29b] Subsequently, hydrolysis of (salen)Co-O-O-PMA complex under acidic condition led to the formation of PMA with terminal hydroxyl group (Scheme 3). Figure 10a showed the MALDI-TOF-MS spectrum of OH group functionalized PMA sample ($M_{n,GPC}$ = 3450, M_w/M_n = 1.16) with a series of molecular ion peaks, regularly separated by the molar mass of MA monomer. Experimental isotopic mass values of the main peak series were equal to that expected for the PMA with CH_3CO_2- at the α end and hydroxyl group at the ω end, plus a sodium ion from externally added salt for ionization, as shown in the upper part of Figure 10b. More specifically, the observed isotopic pattern (m/z) of the main series at m/z = 1561.8040 g/mol indicated the assigned species with DP (degree of polymerization) of 17 and matched well with the simulated pattern, m/z = 1561.6310 g/mol (Figure 7c). The observed isotopic pattern also agreed well with the simulation result.

To gain more evidence for the modification process (scheme 3), isotopic labeling experiment was conducted by reaction of (salen)Co-PMA with $^{18}O_2$. The resulting PMA-^{18}OH was also characterized by MALDI-TOF-MS (Figure 11). The end-capped sample also gave a series of molecular ion peaks separated by MA unit. The absolute mass of each peak clearly indicated the ^{18}O labeled structure. Thus the isotopic labeling and MALDI-TOF-MS analysis all suggested end group successfully functionalized by OH group which would be highly useful for further application.

Synthesis of Block Copolymers

To further probe the living nature of this visible light initiated system, as well as provide additional evidence for the presence of cobalt salen complexes at ω chain ends, block copolymers were prepared by sequential polymerization of acrylates and acrylamides. MA and DMA were chosen as model monomers. Three (salen)Co-PMAs with narrow molecular weight distributions were prepared by photo-polymerization under different conditions (irradiated by Xe lamp, CFL, or addition of TPO) and used as macroinitiators (ESI, Figure 17S-19S). After addition of fresh DMA, all the polymerizations under these conditions proved to be well-behaved processes leading to the desired PMA-b-PDMA with predetermined molar mass and low polydispersity (Figure 20S). GPC traces all showed substantial shift with negligible residual of macroinitiators after block-copolymerization. The successful block copolymer synthesis further indicated efficient reversible activation of the cobalt-carbon chain end and minimal termination under all polymerization conditions.

Conclusions

In summary, we have demonstrated that the (salen)Co-CO_2CH_3 acted as versatile photoinitiator to mediate polymerization of acrylates, acrylamides and non-conjugated VAc. All the polymerizations showed controlled behavior evidenced by formation of polymers with predetermined molecular weight and low polydispersity. The equilibrium constant ((salen)Co(II) + R• $\rightleftharpoons$ (salen)Co-R, $K_{eq} = [(salen)Co\text{-}R]_{eq}/([(salen)Co(II)]_{eq} \times [R\bullet])$) between organo radical, cobalt(II) and organo-cobalt(III) species was determined to be 3.5×10^{10} M^{-1}. Addition of 1 equivalent of TPO dramatically increased the polymerization rate while maintaining high controllability, indicating a switch from RT polymerization to DT mechanism. Visible light was found to be essential for the initiation but show negligible effect during propagation, which might result from difference in cobalt carbon bond energy in (salen)Co-

$C(sp^2)$ and (salen)Co-$C(sp^3)$. Polymer structure analysis demonstrated the presence of (salen)Co segments in polymer chain ω end and -CO_2CH_3 segments in polymer chain α end. Efficient block copolymer synthesis under Xe lamp, CFL, and with addition of TPO, respectively, further confirmed the versatile capability of this novel complex in controlled/living radical polymerization. The convenient synthesis of salen complexes offered a unique and appreciable approach for preparation of functional polymeric materials.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental details, characterization of (salen)Co-CO_2CH_3, Figure S1-S20]. See DOI: 10.1039/b000000x/

1. (a) C. J. Hawker, A. W. Bosman and E. Harth, *Chem. Rev.*, 2001, **101**, 3661-3688; (b) V. Sciannamea, R. Jerome and C. Detrembleur, *Chem. Rev.*, 2008, **108**, 1104-1126; (c) J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes and B. Charleux, *Prog. Polym. Sci*, 2013, **38**, 63-235.
2. (a) J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1995, **117**, 5614-5615; (b) M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 1995, **28**, 1721-1723; (c) K. Matyjaszewski and J. H. Xia, *Chem. Rev.*, 2001, **101**, 2921-2990; (d) M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev*., 2001, **101**, 3689-3745; (e) M. Ouchi, T. Terashima and M. Sawamoto, *Chem. Rev.*, 2009, **109**, 4963-5050; (f) K. Matyjaszewski and N. V. Tsarevsky, *J. Am. Chem. Soc*., 2014, **136**, 6513-6533.
3. (a) G. Moad, E. Rizzardo and S. H. Thang, *Polymer*, 2008, **49**, 1079-1131; (b) G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem*, 2009, **62**, 1402-1472; (c) C. Boyer, V. Bulmus, T. P. Davis, V. Ladmiral, J. Q. Liu and S. Perrier, *Chem. Rev*., 2009, **109**, 5402-5436; (d) D. J. Keddie, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 2012, **45**, 5321-5342.
4. G. David, C. Boyer, J. Tonnar, B. Ameduri, P. Lacroix-Desmazes and B. Boutevin, *Chem. Rev*., 2006, **106**, 3936-3962.
5. (a) A. Debuigne, R. Poli, C. Jerome, R. Jerome and C. Detrembleur, *Prog. Polym. Sci*, 2009, **34**, 211-239; (b) M. Hurtgen, C. Detrembleur, C. Jerome and A. Debuigne, *Polym. Rev*, 2011, **51**, 188-213; (c) L. E. N. Allan, M. R. Perry and M. P. Shaver, *Prog. Polym. Sci*, 2012, **37**, 127-156.
6. (a) F. A. Leibfarth, K. M. Mattson, B. P. Fors, H. A. Collins and C. J. Hawker, *Angew. Chem., Int. Ed*, 2013, **52**, 199-210; (b) S. Yamago and Y. Nakamura, *Polymer*, 2013, **54**, 981-994.
7. (a) A. J. D. Magenau, N. C. Strandwitz, A. Gennaro and K. Matyjaszewski, *Science*, 2011, **332**, 81-84; (b) N. Bortolamei, A. A. Isse, A. J. D. Magenau, A. Gennaro and K. Matyjaszewski, *Angew. Chem., Int. Ed*, 2011, **50**, 11391-11394; (c) A. J. D. Magenau, N. Bortolamei, E. Frick, S. Park, A. Gennaro and K. Matyjaszewski, *Macromolecules*, 2013, **46**, 4346-4353.
8. For selected examples for photo-induced ATRP, see: (a) M. A. Tasdelen, M. Uygun and Y. Yagci, *Macromol. Rapid. Commun*, 2011, **32**, 58-62; (b) D. Konkolewicz, K. Schröder, J. Buback, S. Bernhard and K. Matyjaszewski, *ACS Macro Lett*, 2012, **1**, 1219-1223; (c) M. Ciftci, M. A. Tasdelen and Y. Yagci, *Polym. Chem*, 2014, **5**, 600; (d) B. P. Fors and C. J. Hawker, *Angew. Chem., Int. Ed*, 2012, **51**, 8850-8853; (e) N. V. Alfredo, N. E. Jalapa, S. L. Morales, A. D. Ryabov, R. Le Lagadec and L. Alexandrova, *Macromolecules*, 2012, **45**, 8135-8146; (f) J. Mosnáček and M. Ilčíková, *Macromolecules*, 2012, **45**, 5859-5865; (g) S. Dadashi-Silab, M. Atilla Tasdelen, A. Mohamed Asiri, S. Bahadar Khan and Y. Yagci, *Macromol. Rapid. Commun*, 2014, **35**, 454-459; (h) A. Anastasaki, V. Nikolaou, A. Simula, J. Godfrey, M. Li, G. Nurumbetov, P. Wilson and D. M. Haddleton, *Macromolecules*, 2014, **47**, 3852-3859; (i) A. Anastasaki, V. Nikolaou, G. S. Pappas, Q. Zhang, C. Wan, P. Wilson, T. P. Davis, M. R. Whittaker and D. M. Haddleton, *Chem. Sci*, 2014, **5**, 3536; (j) N. J. Treat, B. P. Fors, J. W. Kramer, M. Christianson, C.-Y. Chiu, J. R. d. Alaniz and C. J. Hawker, *ACS Macro Lett*, 2014, **3**, 580-584; (k) N. J. Treat, H. Sprafke, J. W. Kramer, P. G. Clark, B. E. Barton, J. Read de Alaniz, B. P. Fors and C. J. Hawker, *J. Am. Chem. Soc*, 2014, **136**, 16096-16101; (l) S. Dadashi-Silab, M. A. Tasdelen and Y. Yagci, *J. Polym. Sci., Polym. Chem*, 2014, **52**, 2878-2888; (m) T. G. Ribelli, D. Konkolewicz, S. Bernhard and K. Matyjaszewski, *J. Am. Chem. Soc*, 2014, **136**, 13303-13312; (n) G. M. Miyake and J. C. Theriot, *Macromolecules*, 2014, **47**, 8255-8261; (o) X. Jiang, J. Wu, L. Zhang, Z. Cheng and X. Zhu, *Macromol. Rapid. Commun*, 2014, **35**, 1879-1885; (p) A. Anastasaki, V. Nikolaou, Q. Zhang, J. Burns, S. R. Samanta, C. Waldron, A. J. Haddleton, R. McHale, D. Fox, V. Percec, P. Wilson and D. M. Haddleton, *J. Am. Chem. Soc*., 2014, **136**, 1141-1149; (q) X. Pan, M. Lamson, J. Yan and K. Matyjaszewski, *ACS Macro Lett*, 2015, DOI: 10.1021/mz500834g; (r) A. Anastasaki, V. Nikolaou, F. Brandford-Adams, G. Nurumbetov, Q. Zhang, G. J. Clarkson, D. J. Fox, P. Wilson, K. Kempe and D. M. Haddleton, *Chem. Commun*, 2015, DOI: 10.1039/c4cc09916h.
9. For selected examples for photo-induced RAFT, see: (a) J. F. Quinn, L. Barner, C. Barner-Kowollik, E. Rizzardo and T. P. Davis, *Macromolecules*, 2002, **35**, 7620-7627; (b) L. Lu, N. Yang and Y. Cai, *Chem. Commun*, 2005, 5287-5288; (c) L. Lu, H. J. Zhang, N. F. Yang and Y. L. Cai, *Macromolecules*, 2006, **39**, 3770-3776; (d) Y. Shi, H. Gao, L. Lu and Y. Cai, *Chem. Commun*, 2009, 1368-1370; (e) H. Wang, Q. B. Li, J. W. Dai, F. F. Du, H. T. Zheng and R. K. Bai, *Macromolecules*, 2013, **46**, 2576-2582; (f) G. H. Liu, H. Shi, Y. R. Cui, J. Y. Tong, Y. Zhao, D. J. Wang and Y. L. Cai, *Polym. Chem*, 2013, **4**, 1176-1182; (g) C. Fu, J. Xu, L. Tao and C. Boyer, *ACS Macro Lett*, 2014, **3**, 633-638; (h) J. Xu, K. Jung, N. A. Corrigan and C. Boyer, *Chem. Sci*, 2014, **5**, 3568; (i) J. Xu, K. Jung, A. Atme, S. Shanmugam and C. Boyer, *J. Am. Chem. Soc*, 2014, **136**, 5508-5519; (j) X. T. Miao, J. J. Li, Z. B. Zhang, Z. P. Cheng, W. Zhang, J. Zhu and X. T. Zhu, *Polym. Chem*, 2014, **5**, 4641-4648; (k) M. Y. Khan, M.-S. Cho and Y.-J. Kwark, *Macromolecules*, 2014, **47**, 1929-1934; (l) S. Shanmugam, J. T. Xu and C. Boyer, *Macromolecules*, 2014, **47**, 4930-4942.

10. For selected examples for other photo-induced LRP, see: (a) Y. Guillaneuf, D. Bertin, D. Gigmes, D.-L. Versace, J. Lalevée and J.-P. Fouassier, *Macromolecules*, 2010, **43**, 2204-2212; (b) S. Yamago, Y. Ukai, A. Matsumoto and Y. Nakamura, *J. Am. Chem. Soc*., 2009, **131**, 2100-2101; (c) A. Debuigne, M. Schoumacher, N. Willet, R. Riva, X. Zhu, S. Rutten, C. Jerome and C. Detrembleur, *Chem. Commun*, 2011, **47**, 12703-12705; (d) C. Detrembleur, D. L. Versace, Y. Piette, M. Hurtgen, C. Jerome, J. Lalevee and A. Debuigne, *Polym. Chem*, 2012, **3**, 1856-1866; (e) K. Koumura, K. Satoh and M. Kamigaito, *Macromolecules*, 2008, **41**, 7359-7367; (f) A. Ohtsuki, A. Goto and H. Kaji, *Macromolecules*, 2013, **46**, 96-102; (g) X. Miao, W. Zhu, Z. Zhang, W. Zhang, X. Zhu and J. Zhu, *Polym. Chem*, 2014, **5**, 551.

11. (a) J. F. Yan, B. Li, F. Zhou and W. M. Liu, *ACS Macro Lett*, 2013, **2**, 592-596; (b) J. E. Poelma, B. P. Fors, G. F. Meyers, J. W. Kramer and C. J. Hawker, *Angew. Chem., Int. Ed*, 2013, **52**, 6844-6848; (c) B. P. Fors, J. E. Poelma, M. S. Menyo, M. J. Robb, D. M. Spokoyny, J. W. Kramer, J. H. Waite and C. J. Hawker, *J. Am. Chem. Soc*., 2013, **135**, 14106-14109.

12. M. Benaglia, J. Chiefari, Y. K. Chong, G. Moad, E. Rizzardo and S. H. Thang, *J. Am. Chem. Soc*., 2009, **131**, 6914-6915.

13. (a) Y. G. Zhao, M. M. Yu and X. F. Fu, *Chem. Commun*., 2013, **49**, 5186-5188; (b) Y. G. Zhao, M. M. Yu, S. L. Zhang, Y. C. Liu and X. F. Fu, *Macromolecules*, 2014, **47**, 6238-6245; (c) C. H. Peng, T. Y. Yang, Y. G. Zhao and X. F. Fu, *Org. Biomol. Chem*., 2014, **12**, 8580-8587.

14. L. Chiang, L. E. N. Allan, J. Alcantara, M. C. P. Wang, T. Storr and M. P. Shaver, *Dalton Trans.*, 2014, **43**, 4295-4304.

15. (a) M. Tokunaga, *Science*, 1997, **277**, 936-938; (b) S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow and E. N. Jacobsen, *J. Am. Chem. Soc*., 2002, **124**, 1307-1315.

16. (a) Z. Q. Qin, C. M. Thomas, S. Lee and G. W. Coates, *Angew. Chem., Int. Ed*, 2003, **42**, 5484-5487; (b) K. L. Peretti, H. Ajiro, C. T. Cohen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc*., 2005, **127**, 11566-11567; (c) W. Hirahata, R. M. Thomas, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc*., 2008, **130**, 17658-17659; (d) R. M. Thomas, P. C. B. Widger, S. M. Ahmed, R. C. Jeske, W. Hirahata, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc*., 2010, **132**, 16520-16525; (e) S. M. Ahmed, A. Poater, M. I. Childers, P. C. B. Widger, A. M. LaPointe, E. B. Lobkovsky, G. W. Coates and L. Cavallo, *J. Am. Chem. Soc*., 2013, **135**, 18901-18911; (f) M. I. Childers, J. M. Longo, N. J. Van Zee, A. M. LaPointe and G. W. Coates, *Chem. Rev*., 2014, **114**, 8129-8152; (g) G. P. Wu, W. M. Ren, Y. Luo, B. Li, W. Z. Zhang and X. B. Lu, *J. Am. Chem. Soc*., 2012, **134**, 5682-5688; (h) Y. Liu, W. M. Ren, J. Liu and X. B. Lu, *Angew. Chem., Int. Ed*, 2013, **52**, 11594-11598.

17. (a) R. K. Sherwood, C. L. Kent, B. O. Patrick and W. S. McNeil, *Chem. Commun*, 2010, **46**, 2456-2458; (b) C.-M. Liao, C.-C. Hsu, F.-S. Wang, B. B. Wayland and C.-H. Peng, *Polym. Chem*, 2013, **4**, 3098; (c) A. Kermagoret, C. Jérôme, C. Detrembleur and A. Debuigne, *Eur. Polym. J.*, 2015, **62**, 312-321.

18. (a) Z. Lu, M. Fryd and B. B. Wayland, *Macromolecules*, 2004, **37**, 2686-2687; (b) B. B. Wayland, C. H. Peng, X. F. Fu, Z. Lu and M. Fryd, *Macromolecules*, 2006, **39**, 8219-8222; (c) C. H. Peng, J. Scricco, S. Li, M. Fryd and B. B. Wayland, *Macromolecules*, 2008, **41**, 2368-2373; (d) Y. G. Zhao, H. L. Dong, Y. Y. Li and X. F. Fu, *Chem. Commun*., 2012, **48**, 3506-3508; (e) Y. C. Lin, Y. L. Hsieh, Y. D. Lin and C. H. Peng, *Macromolecules*, 2014, **47**, 7362-7369.

19. W. H. Leung, E. Y. Y. Chan, E. K. F. Chow, I. D. Williams and S. M. Peng, *J. Chem. Soc., Dalton Trans*., 1996, 1229-1236.

20. L. G. Marzilli, M. F. Summers, N. Brescianipahor, E. Zangrando, J. P. Charland and L. Randaccio, *J. Am. Chem. Soc*., 1985, **107**, 6880-6888.

21. (a) D. J. Coveney, V. F. Patel, G. Pattenden and D. M. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2721-2728; (b) V. F. Patel, G. Pattenden and D. M. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2729-2734.

22. W. D. Jiang, L. C. Lu and Y. L. Cai, *Macromol. Rapid Commun*., 2007, **28**, 725-728.

23. A. Goto, Y. Kwak, T. Fukuda, S. Yamago, K. Iida, M. Nakajima and J. Yoshida, *J. Am. Chem. Soc*., 2003, **125**, 8720-8721.

24. A. Debuigne, Y. Champouret, R. Jerome, R. Poli and C. Detrembleur, *Chem-Eur J*, 2008, **14**, 4046-4059.

25. C. Barner-Kowollik, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, M. L. Coote, R. A. Hutchinson, T. Junkers, I. Lacik, G. T. Russell, M. Stach and A. M. van Herk, *Polym. Chem*, 2014, **5**, 204-212.

26. C. H. Peng, S. Li and B. B. Wayland, *Inorg. Chem*., 2009, **48**, 5039-5046.

27. (a) N. M. Ahmad, F. Heatley and P. A. Lovell, *Macromolecules*, 1998, **31**, 2822-2827; (b) C. Farcet, J. Belleney, B. Charleux and R. Pirri, *Macromolecules*, 2002, **35**, 4912-4918.

28. (a) M. J. Kendrick and W. Alakhdar, *Inorg. Chem*., 1987, **26**, 3971-3972; (b) J. Watanabe and J. Setsune, *Organometallics*, 1997, **16**, 3679-3683.

29. (a) F. A. Chavez, J. M. Rowland, M. M. Olmstead and P. K. Mascharak, *J. Am. Chem. Soc*., 1998, **120**, 9015-9027; (b) F. A. Chavez and P. K. Mascharak, *Acc. Chem. Res*., 2000, **33**, 539-545; (c) B. B. Corden, R. S. Drago and R. P. Perito, *J. Am. Chem. Soc*., 1985, **107**, 2903-2907.

30. A. Huber, L. Muller, H. Elias, R. Klement and M. Valko, *Eur. J. Inorg. Chem*., 2005, 1459-1467.