

Electronic Supporting Information

Living Radical Polymerization of Vinyl Acetate and Methyl Acrylate Mediated by Co^{II}(Salen*) Complexes

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I. UV-vis spectrum of cobalt(II) Salen* and cobalt(III) Salen* complexes.

Figure SI 1 is the UV-vis spectrum of cobalt(II) [(R,R)N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine] (Co^{II}(Salen*)) in dichloromethane (DCM) solution (0.1 mM). The absorption bands were near 419 and 361 nm.

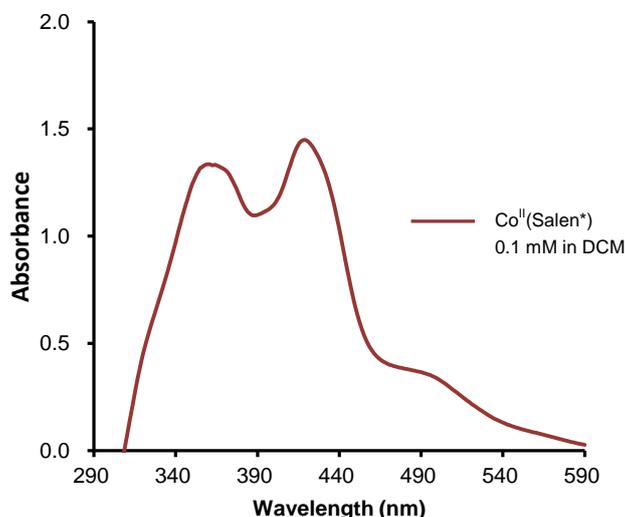


Figure SI 1. The UV-vis spectrum of 0.1mM [(R,R)N,N'-bis(3,5- di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine] cobalt(II) in dichloromethane solution.

Due to the difficulty to obtain the UV-vis spectrum of pure PMA-cobalt(III) Salen* complex, we measured the absorbance of Co^{III}(Salen*)-PVAc (0.6 mM) and Co^{III}(Salen*)-OTs (0.1 mM) in dichloromethane solution to evaluate the influence of cobalt(III) species in UV-vis spectrum. The absorption band was broad and the peak was around 353 nm (Figure SI 2) and 357 nm (Figure SI 3), which are similar to the published results¹ revealing that the Co^{III}(Salen*) complexes usually show a broad absorption band from 290 to 540 nm with the peak value near 390 nm. Therefore, we proposed that the PMA-cobalt(III) species would overlap with cobalt(II) Salen* complex in UV-vis spectrum and the overlapping is much more significant in 361 nm than in 419 nm.

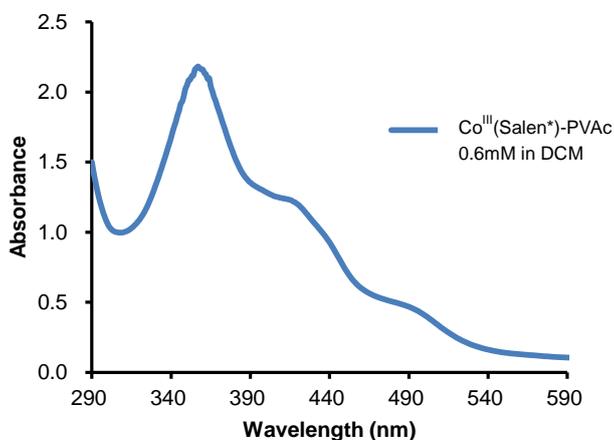


Figure SI 2. The UV-vis spectrum of 0.6 mM Co^{III}(Salen*)-PVAc complex in dichloromethane solution.

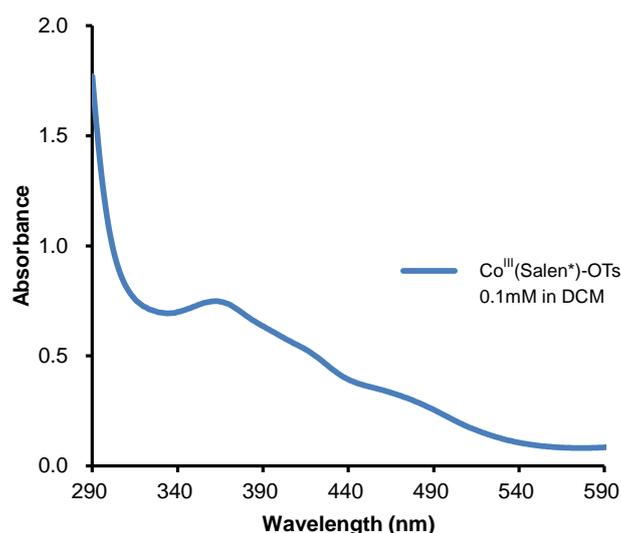


Figure SI 3. The UV-vis spectrum of 0.1 mM Co^{III}(Salen*)-OTs complex in dichloromethane solution.

Since the MA polymerization was performed in benzene but our background studies were performed in dichloromethane (DCM), the effect of different solvents to the absorbance should be concerned. A stock solution of $[\text{Co}^{\text{II}}]_0/[\text{AIBN}]_0/[\text{MA}]_0 = 1/10/1000$ and $[\text{MA}] = 3.7 \text{ M}$ in benzene was prepared to mimic the sample solution taken from the MA polymerization. Two UV-vis samples were prepared by diluting 0.3 ml of the stock solution to 5 ml using benzene and DCM, respectively. Their electronic spectra showed very limited difference and were displayed in Figure SI 4. This high similarity of UV-vis spectra in benzene and DCM should be due to the use of double beam detector so that the results of our background measurements should be able to be adopted by our polymerization results.

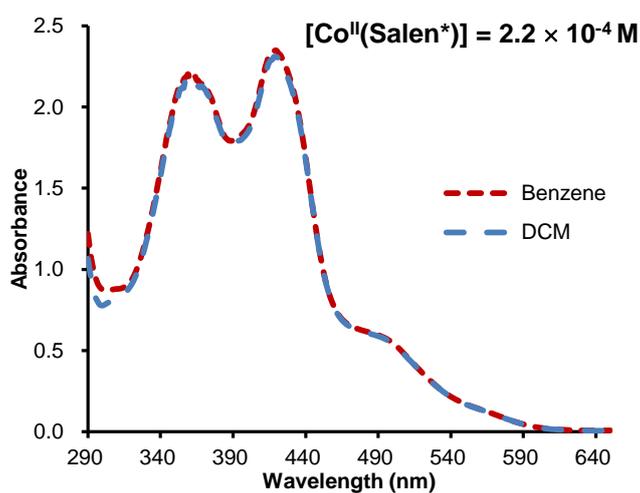


Figure SI 4. The UV-vis spectra of $2.2 \times 10^{-4} \text{ M}$ Co^{II}(Salen*) complex in benzene and dichloromethane solution.

II. The estimation of $[\text{Co}^{\text{II}}]$ and $[\text{Co}^{\text{III}}\text{-R}]$ by time-dependent UV-vis spectrum and numerical method.

We used the time-dependent UV-vis spectrum with numerical method to estimate the equilibrium of $[\text{Co}^{\text{II}}(\text{Salen}^*)]$ and $[\text{Co}^{\text{III}}(\text{Salen}^*)\text{-R}]$. According to Figure SI 1, the characteristic absorption of $\text{Co}^{\text{II}}(\text{Salen}^*)$ was at 419 nm and 361 nm and the extinction coefficients could be obtained as $\epsilon_{\text{Co}^{\text{II}}419\text{nm}} = 1.04 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{\text{Co}^{\text{II}}361\text{nm}} = 9.59 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ by the linear regression analysis with four different concentration of $\text{Co}^{\text{II}}(\text{Salen}^*)$ complex (Figure SI 5).

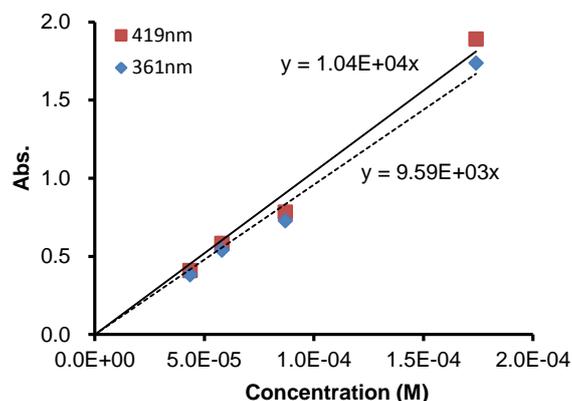


Figure SI 5. The linear regression analysis of $\text{Co}^{\text{II}}(\text{Salen}^*)$ in dichloromethane, the slope is equal to the extinction coefficient.

The concentration of cobalt(II) Salen^* ($[\text{Co}^{\text{II}}]_0$) was recorded by the measured extinction coefficient and Beer-Lambert law:

$$\epsilon_{\text{Co}^{\text{II}}419\text{nm}} \times [\text{Co}^{\text{II}}]_0 = \text{Abs}_{0,419\text{nm}}$$

Because there was only small amount of organo-cobalt(III) at 10 minutes and the absorbance of $[\text{Co}^{\text{III}}\text{-R}]$ at 419nm was much smaller than that at 361nm (Figure SI 2), we assumed the absorbance of $[\text{Co}^{\text{III}}\text{-R}]$ at 419nm was 0 to obtain the $[\text{Co}^{\text{II}}]_{10}$ and to calculate $[\text{Co}^{\text{III}}]_{10}$ by $[\text{Co}^{\text{III}}]_{10} = [\text{Co}^{\text{II}}]_0 - [\text{Co}^{\text{II}}]_{10}$. With the known $[\text{Co}^{\text{II}}]_{10}$, $[\text{Co}^{\text{III}}]_{10}$, and $\epsilon_{\text{Co}^{\text{II}}361\text{nm}}$, the extinction coefficient of organo-cobalt(III) at 361 nm ($\epsilon_{\text{Co}^{\text{III}}361\text{nm}}$) can be obtained by:

$$\epsilon_{\text{Co}^{\text{II}}361\text{nm}} \times [\text{Co}^{\text{II}}]_{10} + \epsilon_{\text{Co}^{\text{III}}361\text{nm}} \times [\text{Co}^{\text{III}}]_{10} = \text{Abs}_{10,361\text{nm}}$$

Given by the extinction coefficients of cobalt(II) and organo-cobalt(III) species ($\epsilon_{\text{Co}^{\text{II}}361\text{nm}}$ and $\epsilon_{\text{Co}^{\text{III}}361\text{nm}}$), the concentration of $\text{Co}^{\text{II}}(\text{Salen}^*)$ and $\text{Co}^{\text{III}}(\text{Salen}^*)\text{-R}$ ($[\text{Co}^{\text{II}}]_{20}$ and $[\text{Co}^{\text{III}}]_{20}$) at 20 minutes could be measured by following equation:

$$\epsilon_{\text{Co}^{\text{II}}361\text{nm}} \times [\text{Co}^{\text{II}}]_{20} + \epsilon_{\text{Co}^{\text{III}}361\text{nm}} \times ([\text{Co}^{\text{II}}]_0 - [\text{Co}^{\text{II}}]_{20}) = \text{Abs}_{20,361\text{nm}}$$

Then $[\text{Co}^{\text{II}}]_{20}$, $[\text{Co}^{\text{III}}]_{20}$ and $\epsilon_{\text{Co}^{\text{II}}419\text{nm}}$ were used to estimate the value of $\epsilon_{\text{Co}^{\text{III}}419\text{nm}}$ by following equation:

$$\epsilon_{\text{Co}^{\text{II}}419\text{nm}} \times [\text{Co}^{\text{II}}]_{20} + \epsilon_{\text{Co}^{\text{III}}419\text{nm}} \times [\text{Co}^{\text{III}}]_{20} = \text{Abs}_{20,419\text{nm}}$$

However, the values of $[\text{Co}^{\text{II}}]_t$, $[\text{Co}^{\text{III}}]_t$, $\epsilon_{\text{Co}^{\text{III}}361\text{nm}}$, and $\epsilon_{\text{Co}^{\text{III}}419\text{nm}}$ were obtained by a preliminary estimation

and thus were needed to be refined by repeating above steps with the time dependent UV-vis spectrum (Figure SI 6 and Figure 7).

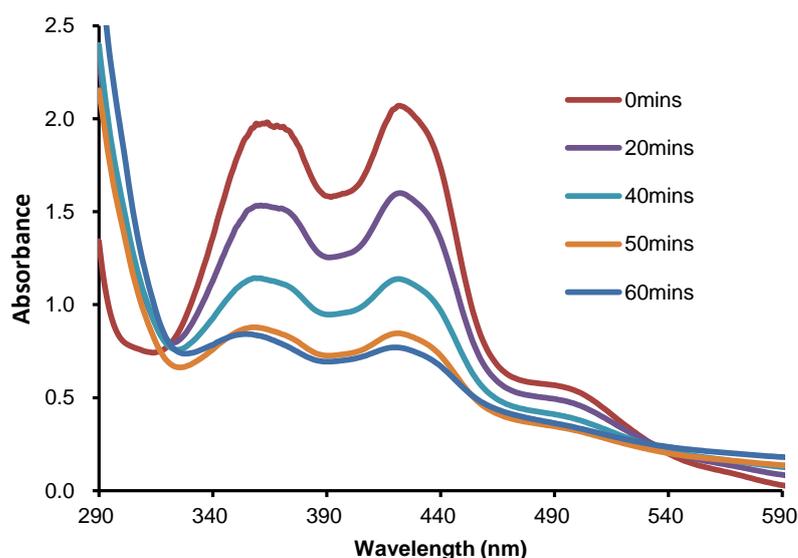


Figure SI 6. The time dependent UV-vis spectrum illustrating the transformation of $\text{Co}^{\text{II}}(\text{Salen}^*)$ to $\text{Co}^{\text{III}}(\text{Salen}^*)\text{-R}$ during the induction period of methyl acrylate polymerization with the condition of $[\text{Co}^{\text{II}}]_0/[\text{AIBN}]_0/[\text{MA}]_0 = 1/10/500$, $[\text{AIBN}]_0 = 0.074\text{M}$ in benzene at 60°C (Table 1, entry 3).

Table SI 1 summarized the refined values of $[\text{Co}^{\text{II}}]_t$, $[\text{Co}^{\text{III}}]_t$, $\epsilon_{\text{Co}^{\text{III}}361\text{nm}}$, and $\epsilon_{\text{Co}^{\text{III}}419\text{nm}}$ for the $\text{Co}^{\text{II}}(\text{Salen}^*)$ mediated MA polymerization with the condition of $[\text{Co}^{\text{II}}(\text{Salen}^*)]_0/[\text{AIBN}]_0/[\text{MA}]_0 = 1/10/500$, $[\text{AIBN}]_0 = 0.074\text{M}$ in benzene at 60°C (Table 1, entry 3). The change of $\text{Co}^{\text{II}}(\text{Salen}^*)$ and $\text{Co}^{\text{III}}(\text{Salen}^*)\text{-R}$ concentration shown in Table SI 1 was plotted in Figure SI 7 to better illustrate the approach of the $\text{Co}^{\text{II}}(\text{Salen}^*)$ and $\text{Co}^{\text{III}}(\text{Salen}^*)\text{-R}$ equilibrium.

Table SI 1. The change of $\text{Co}^{\text{II}}(\text{Salen}^*)$ and $\text{Co}^{\text{III}}(\text{Salen}^*)\text{-R}$ concentration during the induction period of MA polymerization with the condition of $[\text{Co}^{\text{II}}(\text{Salen}^*)]_0/[\text{AIBN}]_0/[\text{MA}]_0 = 1/10/500$, $[\text{AIBN}]_0 = 0.074\text{M}$ in benzene at 60°C .

Entry	t (sec)	$[\text{Co}^{\text{II}}(\text{Salen}^*)]_t$	$[\text{Co}^{\text{III}}(\text{Salen}^*)\text{-R}]_t$
1	0	7.40E-03	0
2	600	7.14E-03	2.57E-04
3	1200	6.53E-03	8.65E-04
4	1800	5.69E-03	1.71E-03
5	2400	5.12E-03	2.28E-03
6	3000	4.16E-03	3.24E-03
7	3600	4.00E-03	3.40E-03

$$\epsilon_{\text{Co}^{\text{III}}419\text{nm}} = 68 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

$$\epsilon_{\text{Co}^{\text{III}}361\text{nm}} = 3215 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

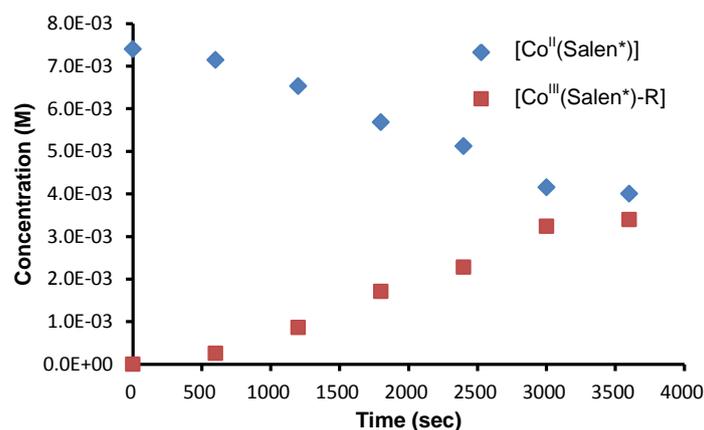


Figure SI 7. The change of [Co^{II}(Salen*)] and [Co^{III}(Salen*)-R] during the induction period in the polymerization of methyl acrylate with condition of [Co^{II}]₀/[AIBN]₀/[MA]₀ = 1/10/500, [AIBN]₀ = 0.074M in benzene at 60°C (Table 1, entry 3).

The refined values of [Co^{II}]_t, [Co^{III}]_t, ε_{Co^{III}361nm}, and ε_{Co^{III}419nm} for MA polymerization shown in Table 1, entry 4 were listed in Table SI 2 and Figure 8. The extinction coefficients shown in Table SI 2 were close to that in Table SI 1, which supported the accuracy of our estimation.

Table SI 2. The change of Co^{II}(Salen*) and Co^{III}(Salen*)-R concentration during the induction period of MA polymerization with the condition of [Co^{II}(Salen*)]₀/[AIBN]₀/[MA]₀ = 1/10/1000, [AIBN]₀ = 0.037M in benzene at 60°C.

Entry	t (sec)	[Co ^{II} (Salen*)] _t	[Co ^{III} (Salen*)-R] _t
1	0	3.70E-03	0.00E+00
2	600	3.54E-03	1.57E-04
3	1200	3.15E-03	5.53E-04
4	1800	2.85E-03	8.48E-04
5	2400	2.28E-03	1.09E-03
6	3000	2.22E-03	1.48E-03
7	3600	2.21E-03	1.49E-03

$$\epsilon_{\text{Co}^{\text{III}}419\text{nm}} = 40 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

$$\epsilon_{\text{Co}^{\text{III}}361\text{nm}} = 2849 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

III. Molecular weight of PVAc-*b*-PMA evaluated by Mark–Houwink equation

The measured molecular weight of PVAc-*b*-PMA was re-evaluated using Mark–Houwink equation and parameters for PVAc and PMA since the Mark–Houwink parameters for PVAc-*b*-PMA are not available and the results were shown in Table SI 3. The M_n became smaller when calibrated by parameters of PVAc ($M_{n,cal,PVAc}$) but became larger when calibrated by parameters of PMA ($M_{n,cal,PMA}$). Nevertheless, all three values showed a limited difference so that we just reported the measured M_n directly for the molecular weight of block copolymers.

Table SI 3. Molecular weight of PVAc-*b*-PMA evaluated by Mark–Houwink equation

Polymer	Figure	$M_{n,GPC}$	$M_{n,cal,PVAc}$	$M_{n,cal,PMA}$
PVAc- <i>b</i> -PMA	Fig. 9b	44,000	41,000	49,000
	Fig. 10b	49,000	46,000	55,000
	Fig. 11a	20,000	19,000	22,000
	Fig. 11b	42,000	39,000	47,000
	Fig. 11b	3,500	3,200	3,500

Mark–Houwink parameters for PVAc: $K = 15.6 \times 10^{-5} \text{ dL g}^{-1}$, $a = 0.708$; for PMA: $K = 19.5 \times 10^{-5} \text{ dL g}^{-1}$, $a = 0.66$; for PSt: $K = 11.7 \times 10^{-5} \text{ dL g}^{-1}$, $a = 0.725$.

IV. The deconvolution of GPC trace of PVAc-*b*-PMA

The Figure SI 8 is the GPC trace of poly(vinyl acetate)-*b*-poly(methyl acrylate) (PVAc-*b*-PMA) with $M_n = 44,000$ and PDI = 1.61. The elution time was converted to molecular weight (Figure SI 9) by the calibration curve using the polystyrene as a standard (Figure SI 10).

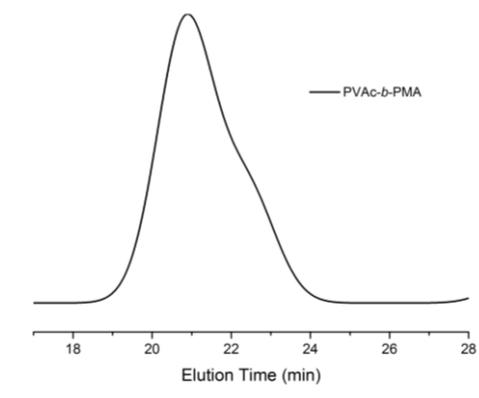


Figure SI 8. The GPC trace of block copolymer of PVAc-*b*-PMA with $M_n = 44,000$ and PDI = 1.61.

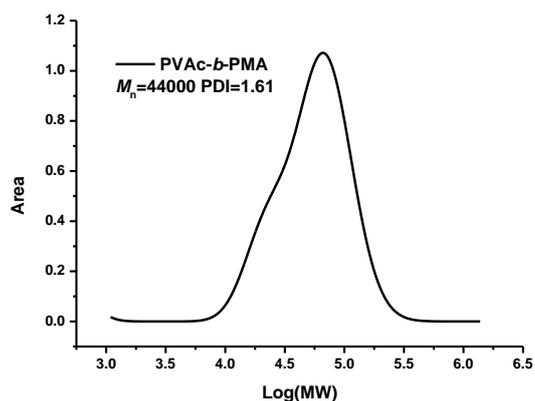


Figure SI 9. The molecular weight distribution of PVAc-*b*-PMA.

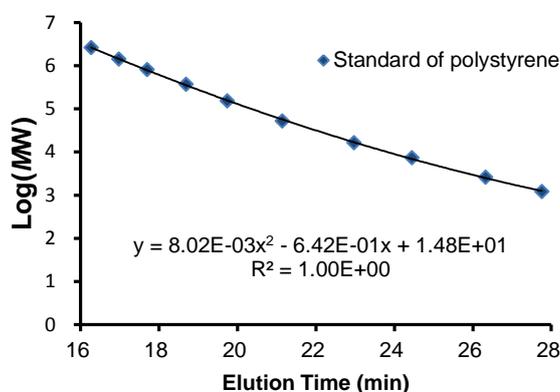


Figure SI 10. The calibration curve in GPC to convert the elution time to molecular weight using polystyrene as a standard.

The distribution of molecular weight was then deconvoluted to two peaks by Gaussian function as shown in Figure SI 11. The M_n and PDI values thus can be calculated as 59,000 and 1.32 for the higher peak and 19,700 and 1.26 for the lower peak by the data generated from the deconvolution program. In addition, the molar ratio of terminated chains and living chains can also be estimated by the same set of data and the value is 1.16 which was very close the ratio of $[Co^{II}]_{eq}/[Co^{III}]_{eq}$ in Table 1, entry 3 (1.18).

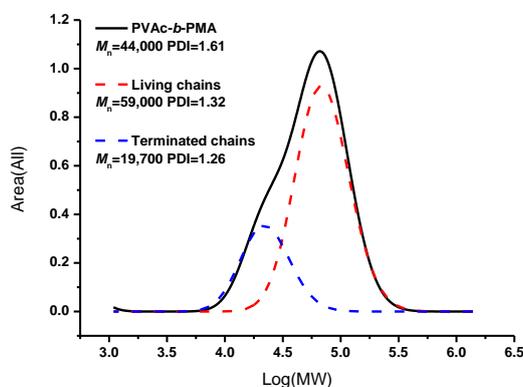


Figure SI 11. The deconvolution of the molecular weight distribution of PVAc-*b*-PMA by Gaussian function. The red line was supposed to be the living chains and the blue line was supposed to be the terminated chains.

V. Reference

- (1) Kim, S.; Lee, C. Y.; Kim, G. J. *Bull. Korean Chem. Soc.* **2010**, 31, 2793