Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Immortal Polymerization of LA: the Influence of Steric Effect, Electron Effect and pK_a for Chain Transfer Agents

Na Liu, Jince Zhang, Jingyi Wen, Xiaolei You and Dawei Fang*

Institute of Rare and Scattered Elements, College of Chemistry, Liaoning University, Shenyang 110036, PR China.

*Corresponding author. E-mail: dwfang@lnu.edu.cn. Fax: +86 24 62202380; Tel: +86 24 62202380.

Fig. S1 10 equiv. of PhOH and $Ca[N(SiMe_3)_2]_2(THF)_2$ reacted at room temperature: 1) for 30 min; 2) for 1 h；3) for 1.5 h.

Fig. S2 10 equiv. of *p*-CH_3-PhOH and $Ca[N(SiMe_3)_2]_2(THF)_2$ reacted at room temperature: 1) for 30 min; 2) for 1 h；3) for 1.5 h.

Fig. S3 10 equiv. of $PhCH_2NH_2$ and $Ca[N(SiMe_3)_2]_2(THF)_2$ reacted at room temperature: 1) for 30 min; 2) for 1 h; 3) for 1.5 h.

Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of the afforded PLLA sample ($M_{n,GPC}$ = 3400/1900 g/mol, M_w/M_n = 1.06/1.11) prepared by $Ca[N(SiMe_3)_2]_2(THF)_2$/*p*-CH_3-PhOH.

Fig. S5 MALDI-TOF mass spectrum (Na^+) of a PLLA sample ($M_{n,GPC}$ = 3400/1900 g/mol, M_w/M_n = 1.06/1.11) prepared by the binary catalyst $Ca[N(SiMe_3)_2]_2(THF)_2$/*p*-CH_3-PhOH.

Fig. S6 Semilogarithmic plots of $\ln([LA]_0/[LA]_t)$ for the ROP of L-LA versus time initiated by different $Ca[N(SiMe_3)_2]_2(THF)_2/Ph_2CHOH$ ratios.

Fig. S7. Semilogarithmic plots of $\ln([LA]_0/[LA]_t)$ for the ROP of L-LA versus time initiated by different $Ca[N(SiMe_3)_2]_2(THF)_2/Ph_2CHOH$ ratios.

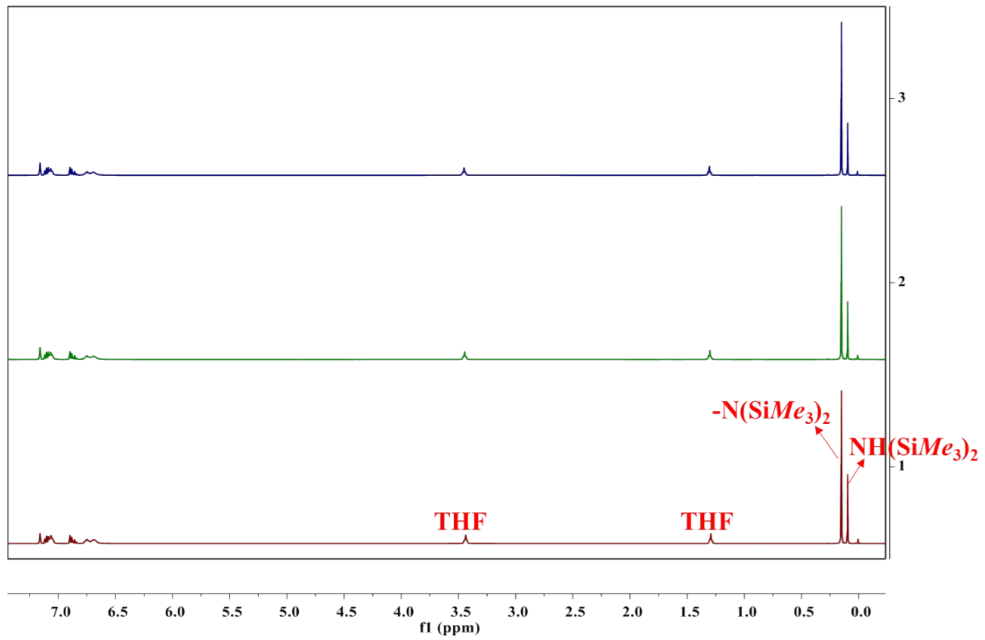

Fig. S1 10 equiv. of PhOH and $Ca[N(SiMe_3)_2]_2(THF)_2$ reacted at room temperature: 1) for 30 min; 2) for 1 h； 3) for 1.5 h.

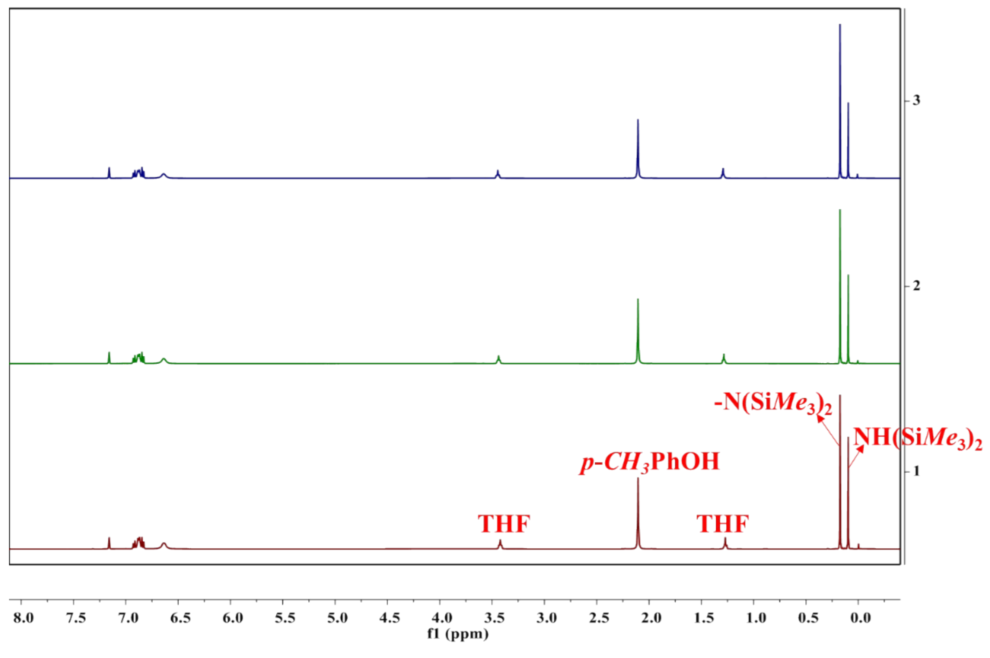

Fig. S2 10 equiv. of *p*-CH_3-PhOH and $Ca[N(SiMe_3)_2]_2(THF)_2$ reacted at room temperature: 1) for 30 min; 2) for 1 h； 3) for 1.5 h.

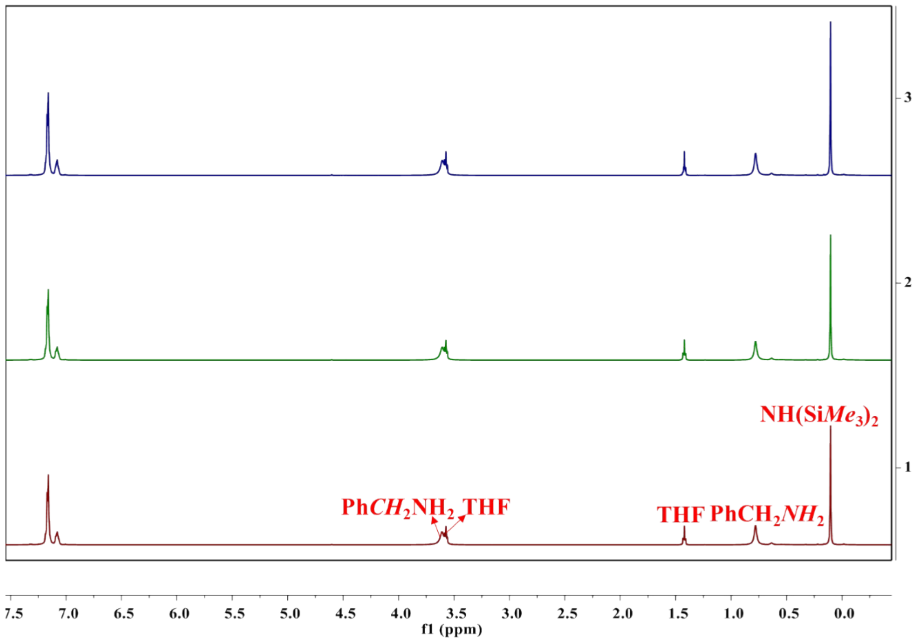

Fig. S3 10 equiv. of $PhCH_2NH_2$ and $Ca[N(SiMe_3)_2]_2(THF)_2$ reacted at room temperature: 1) for 30 min; 2) for 1 h; 3) for 1.5 h.

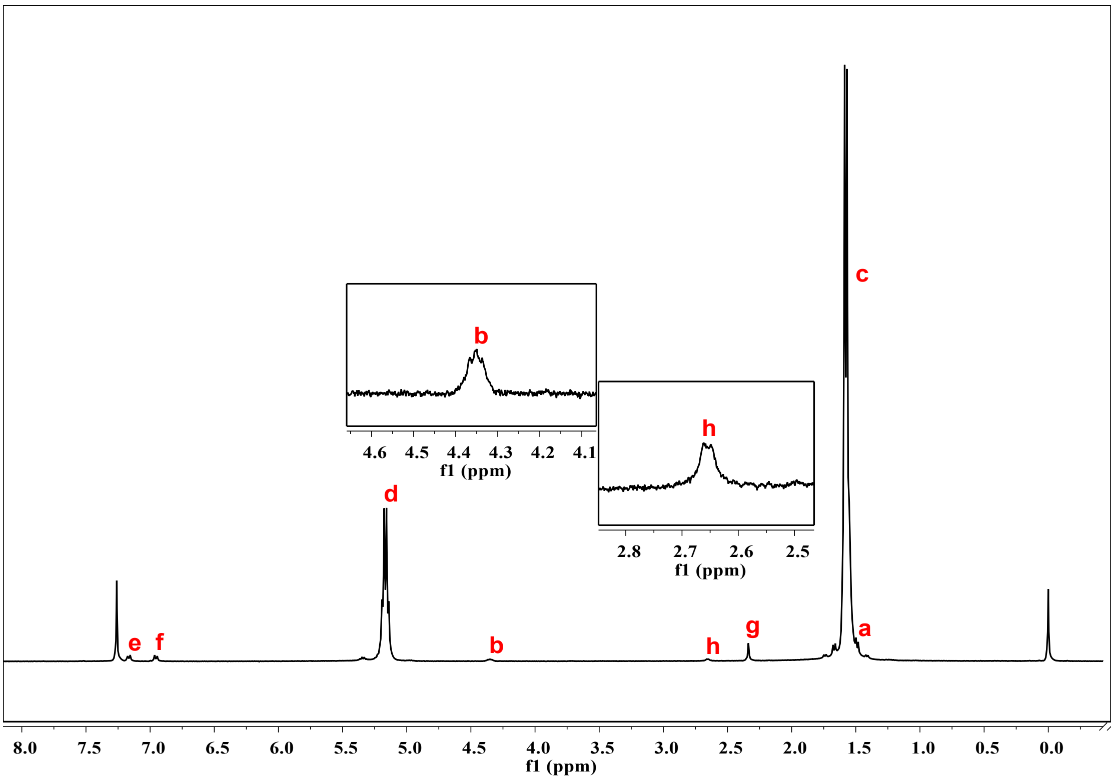

Fig. S4 ^1H NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of the afforded PLLA sample ($M_{n,GPC}$ = 3400/1900 g/mol, M_w/M_n = 1.06/1.11) prepared by $Ca[N(SiMe_3)_2]_2(THF)_2$/p-CH_3-PhOH.

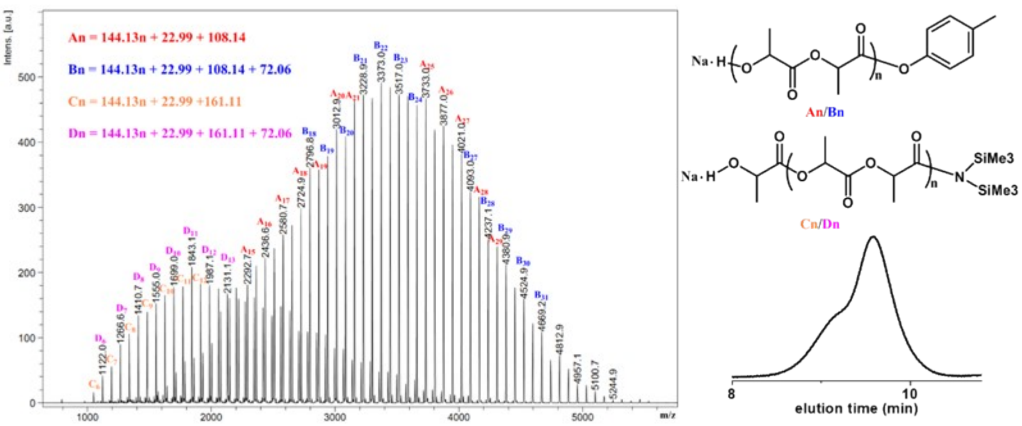

Fig. S5 MALDI-TOF mass spectrum (Na^+) of a PLLA sample ($M_{n,GPC}$ = 3400/1900 g/mol, M_w/M_n = 1.06/1.11) prepared by the binary catalyst $Ca[N(SiMe_3)_2]_2(THF)_2$/*p*-CH_3-PhOH (A_n = 144.13n + 22.99 + 108.14, B_n = 144.13n + 22.99 + 108.14 + 72.06, C_n = 144.13n + 22.99 + 161.11, D_n = 144.13n + 22.99 + 161.11 + 72.06, where n is the degree of polymerization, M_{Na} = 22.99 g/mol, M_{LA} = 144.13 g/mol, $M_{NH(SiMe3)2}$ = 161.11 g/mol and $M_{p\text{-}CH3\text{-}PhOH}$ = 108.14 g/mol).

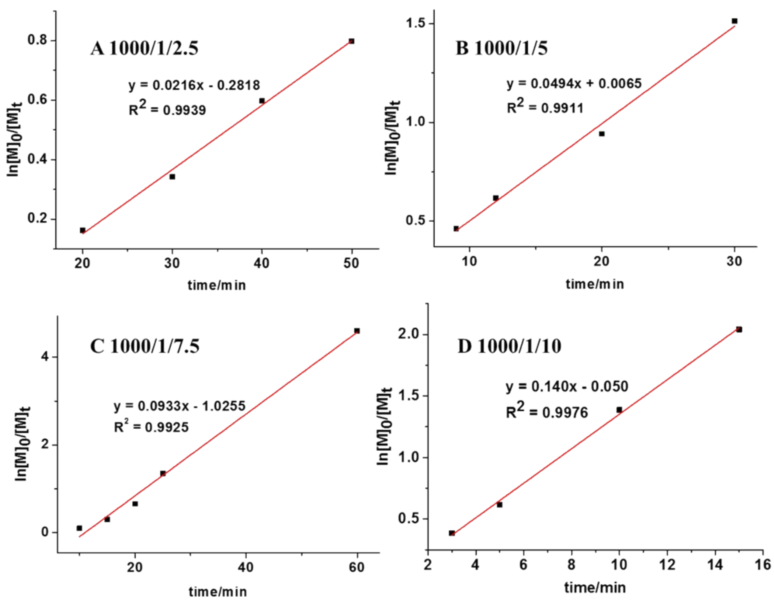

Fig. S6 Semilogarithmic plots of ln($[LA]_0/[LA]_t$) for the ROP of L-LA versus time initiated by different $Ca[N(SiMe_3)_2]_2(THF)_2/Ph_2CHOH$ ratios: A) **1000/1/2.5**, k_{app} = 2.16×10^{-2} min^{-1}, R^2 = 0.9772; B) **1000/1/5**, k_{app} = 4.94×10^{-2} min^{-1}, R^2 = 0.9984; C) **1000/1/7.5**, k_{app} = 9.33×10^{-2} min^{-1}, R^2 = 0.9844; D) **1000/1/10**, k_{app} = 1.40×10^{-1} min^{-1}, R^2 = 0.9947 (Conditions: T = 50 °C, in toluene, $[LA]_o$ = 2.0 M).

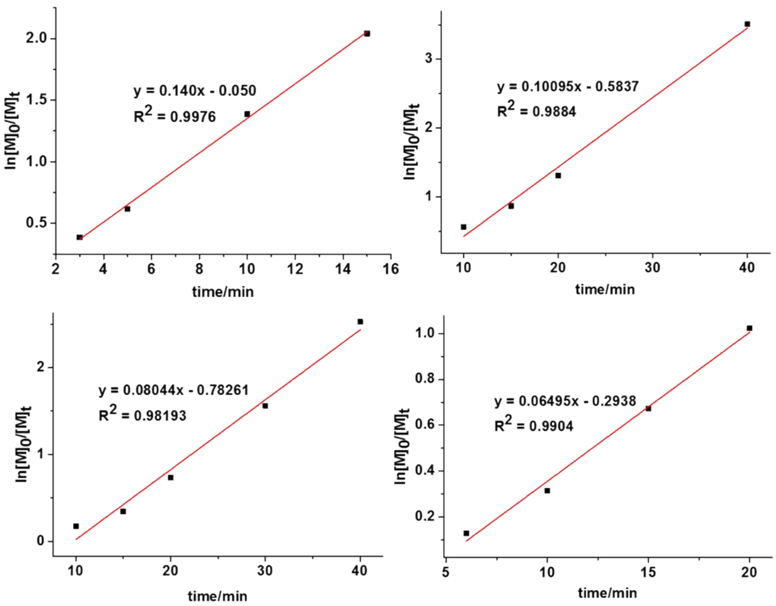

Fig. S7 Semilogarithmic plots of $\ln([LA]_0/[LA]_t)$ for the ROP of L-LA versus time initiated by different $Ca[N(SiMe_3)_2]_2(THF)_2/Ph_2CHOH$ ratios: A) **1000/1/10**, $k_{app} = 1.40 \times 10^{-1}$ min^{-1}, $R^2 = 0.9772$; B) **1000/1/15**, $k_{app} = 1.01 \times 10^{-1}$ min^{-1}, $R^2 = 0.9984$; C) **1000/1/30**, $k_{app} = 8.04 \times 10^{-2}$ min^{-1}, $R^2 = 0.9844$; D) **1000/1/40**, $k_{app} = 6.50 \times 10^{-1}$ min^{-1}, $R^2 = 0.9947$ (Conditions: $T = 50$ °C, in toluene, $[LA]_o = 2.0$ M).