Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

for

Sequences controlled copolymerization of lactide and functional cyclic carbonate using stereoselective aluminum catalysts

Xiufang Hua,[a,b] Xinli Liu *[a] and Dongmei Cui *[a]

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Supplemental Figures:

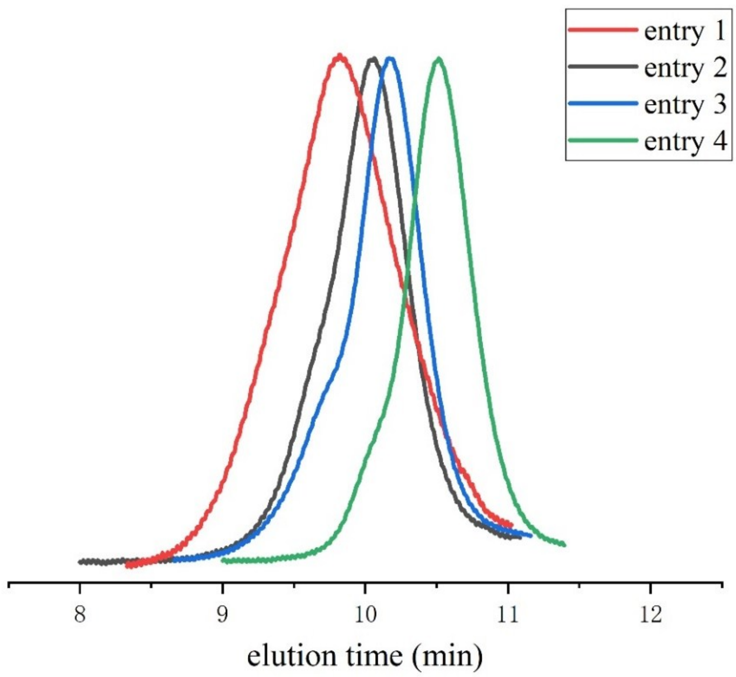


Figure S1. GPC profiles of representative samples, entries 1-4, Table 1.

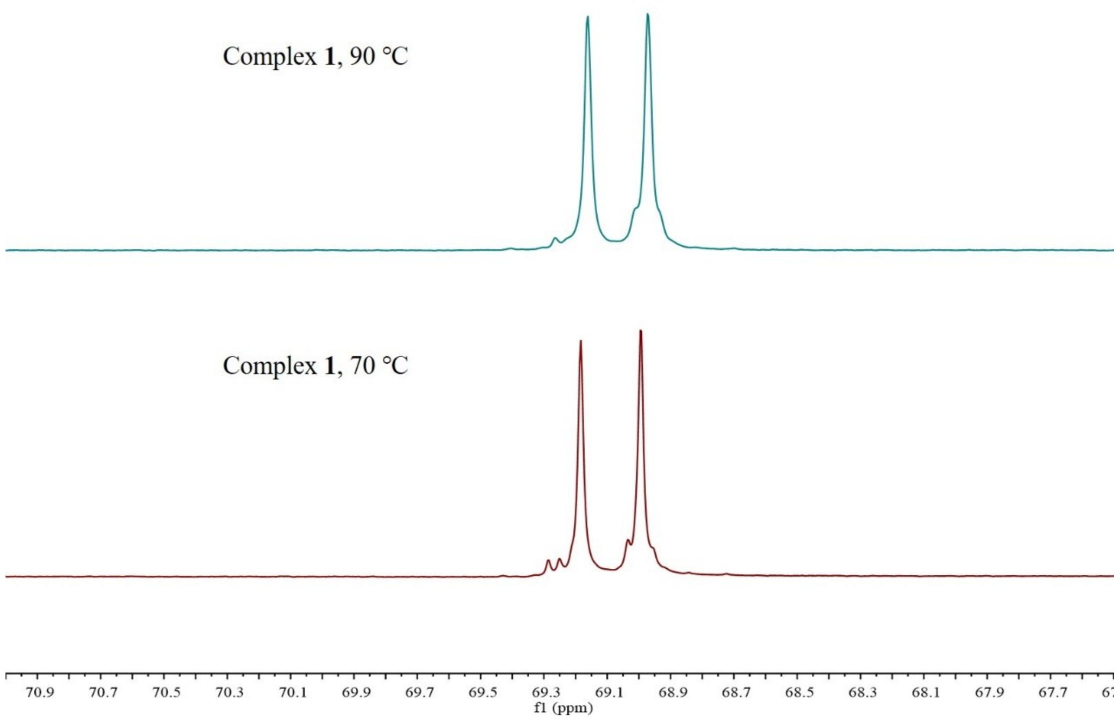


Figure S2. Inverse gated decoupled ^{13}C NMR spectrum for the homopolymerization of *rac*-LA by complex **1** (500 MHz, $CDCl_3$).

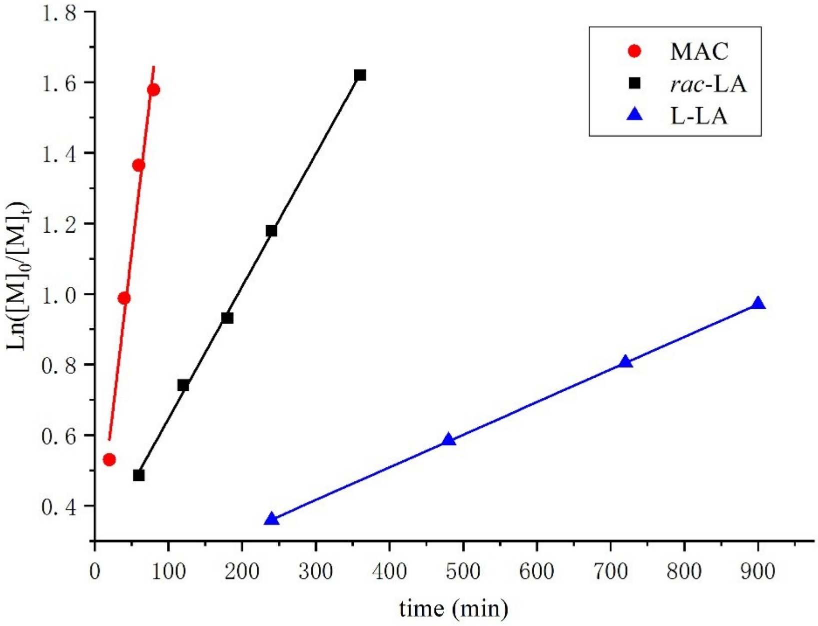


Figure S3. Semilogarithmic kinetic plot in each monomer catalyzed by complex **1** (k_{app} (MAC) = 176.1×10^{-4}, k_{app} (*rac*-LA) = 37.6×10^{-4}, k_{app} (L-LA) = 9.2×10^{-4}), Polymerization conditions: Complex **1** = 10 μmol; T = 90 ℃; Tol. = 2 mL; ratio = [monomer]:[**1**] = 100:1.

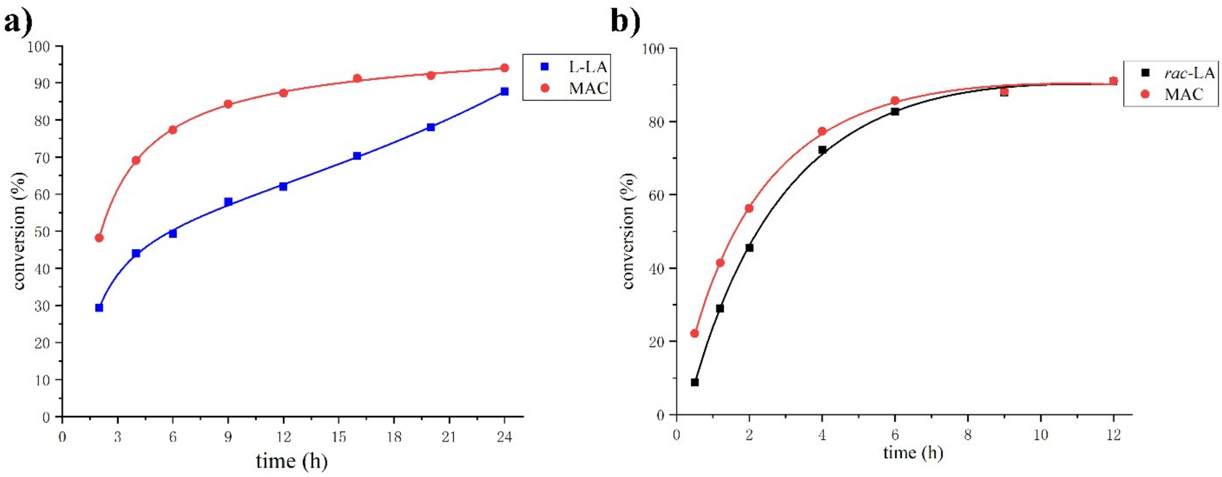


Figure S4. Plots of conversion vs time for the copolymerization with complex **1** of a) L-LA/MAC and b) *rac*-LA/MAC.

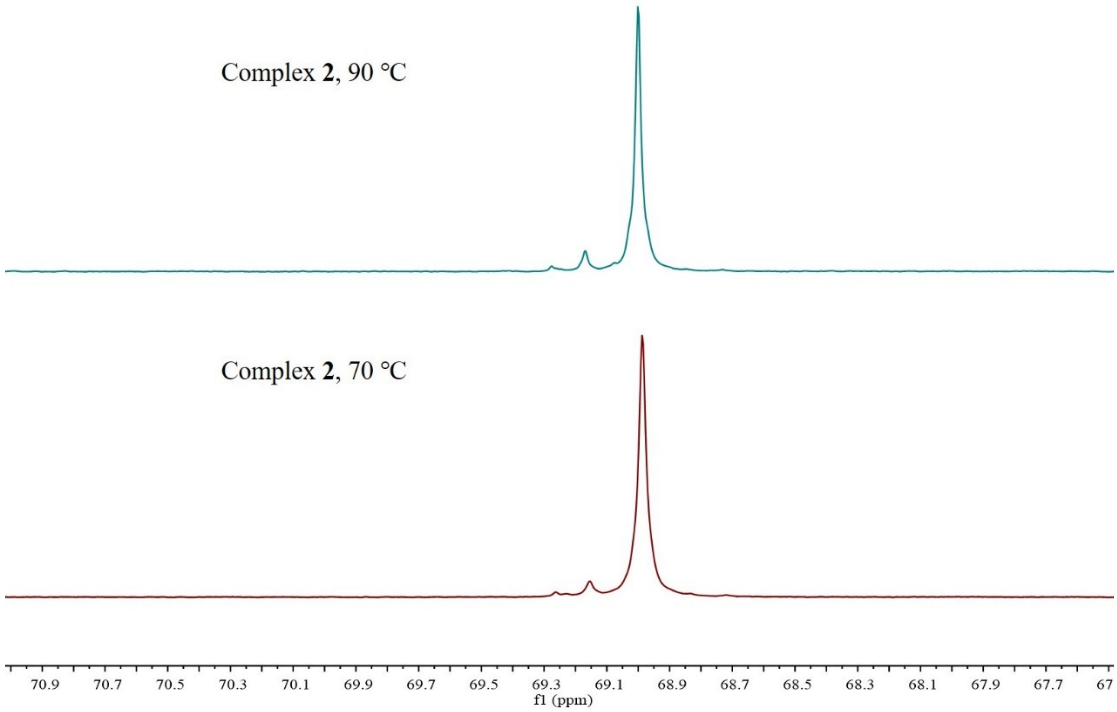


Figure S5. Inverse gated decoupled [13]C NMR spectrum for the homopolymerization of *rac*-LA by complex **2** (500 MHz, $CDCl_3$).

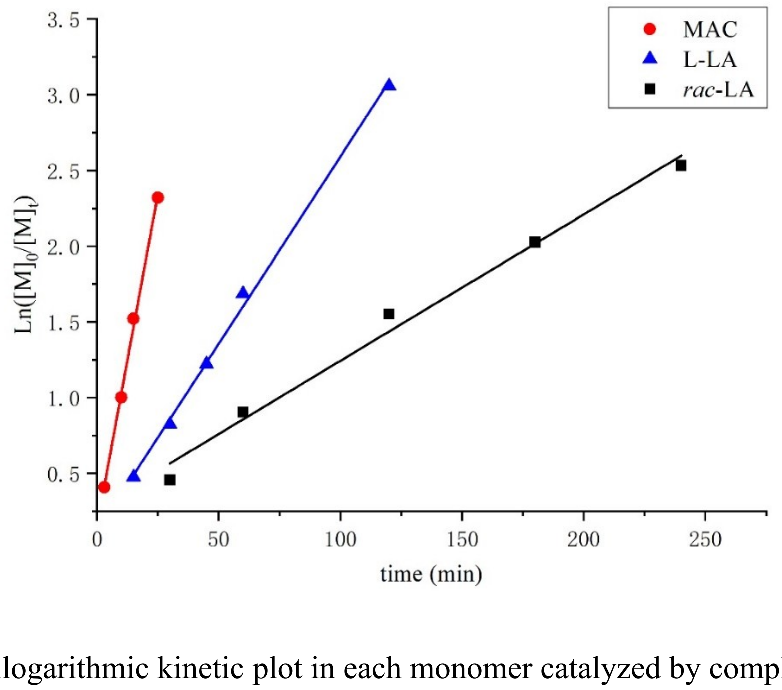


Figure S6. Semilogarithmic kinetic plot in each monomer catalyzed by complex **2** (k_{app} (MAC) = 87.6×10^{-3}, k_{app} (L-LA) = 24.8×10^{-3}), k_{app} (*rac*-LA) = 9.7×10^{-3}, Polymerization conditions: complex **2** = 10 μmol; T = 90 °C; Tol. = 2 mL; ratio = [monomer]:[**2**] = 100:1.

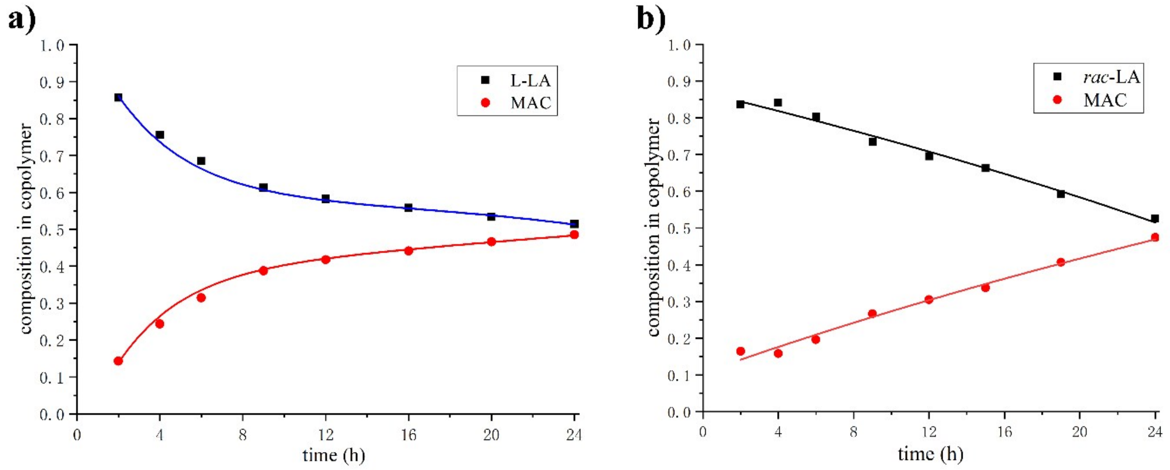


Figure S7. Plots of composition vs time for the copolymerization with complex **2** of a) L-LA/MAC and b) *rac*-LA/MAC.

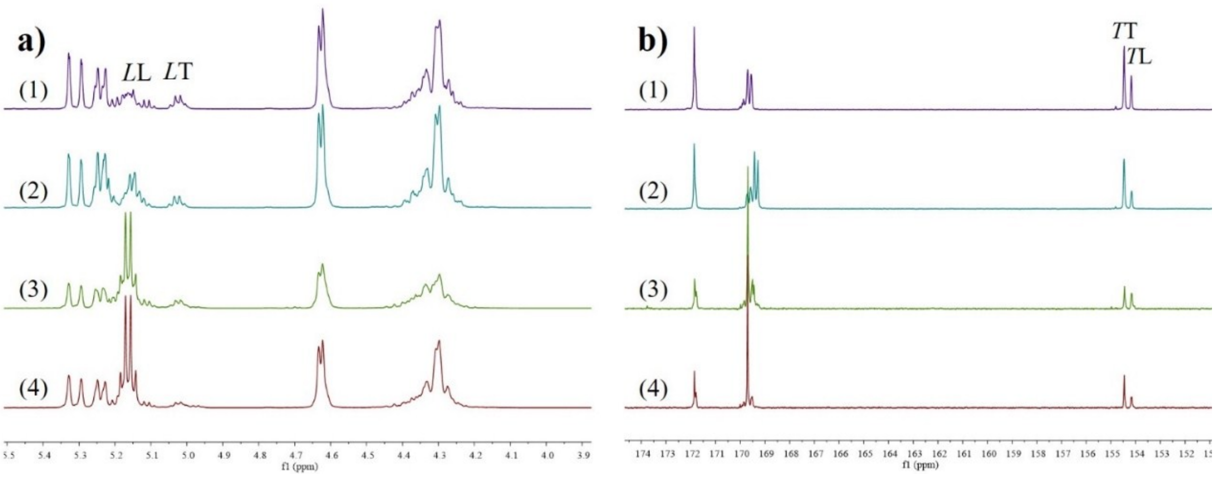


Figure S8. (a) ^{1}H NMR and (b) ^{13}C NMR spectroscopy in $CDCl_3$:

(1) poly(MAC-*r*-L-LA), $L_{\text{L-LA}} = 3.40/L_{\text{MAC}} = 3.08$, (table 1, entry 9);

(2) poly(MAC-*grad*-*rac*-LA), $L_{rac\text{-LA}} = 4.45/L_{\text{MAC}} = 3.76$, (table 1, entry 13);

(3) poly(*rac*-LA-*tapered*-MAC), $L_{rac\text{-LA}} = 6.83/L_{\text{MAC}} = 2.29$, (table 2, entry 9);

(4) *quasi*-diblock poly(L-LA-*b*-MAC), $L_{\text{L-LA}} = 7.43/L_{\text{MAC}} = 3.68$, (table 2, entry 4).

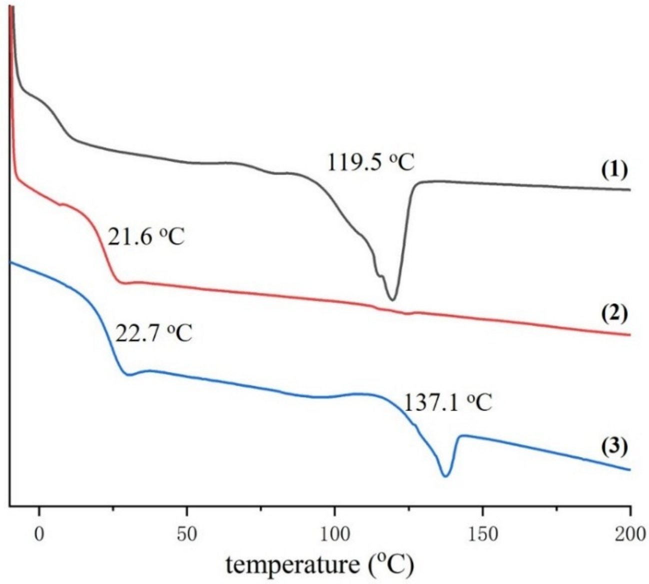


Figure S9. DSC thermograms of *quasi*-diblock Poly(L-LA-*b*-MAC) (table 2, entry 4) (T_g value was calculated by STAR^e method with heating/cooling rate of 10 °C/min and using second cycle from -10 ℃ to 200 ℃): (1) first heating cycle; (2) after eliminating thermal history; (3) after isothermal crystallization.

Table S1. Homopolymerization of *rac*-LA or MAC with complex **1** and **2**.

entry[a]	Cat.	M	$[Cat.]_0$:$[CTA]_0$:$[M]_0$	conv.[b](%)	$M_{n,calcd}$[c](KDa)	$M_{n,SEC}$[d](KDa)	M_w/M_n[d]	T_g/T_m[e](°C)
1	**1**	*rac*-LA	1:3:100	94	4.70	6.06	1.04	40.0/-
2	**2**	*rac*-LA	1:3:100	91	4.55	7.75	1.28	49.8/188.5
3	**1**	MAC	1:3:100	95	6.52	7.24	1.20	-10.5/-

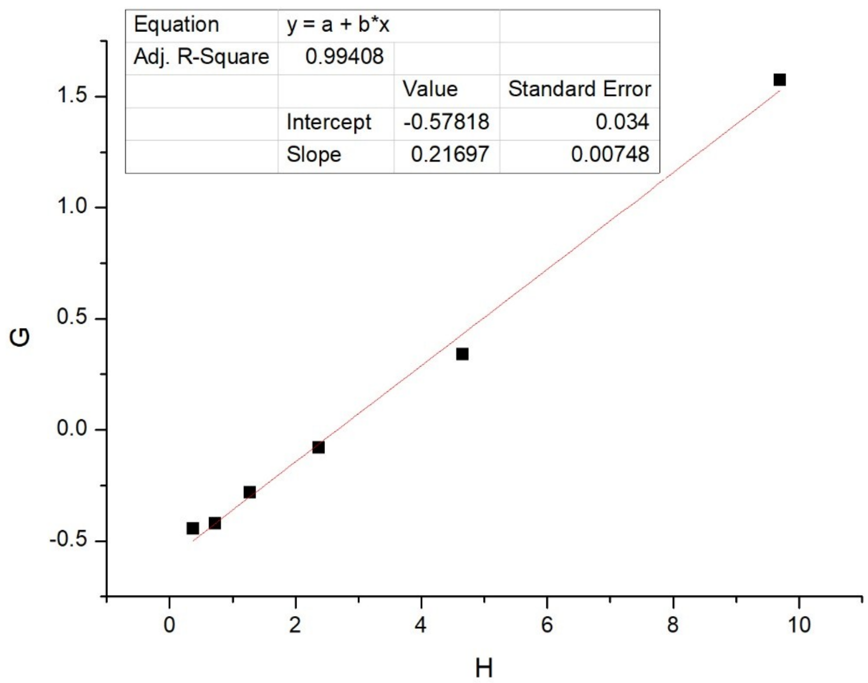
[a]Polymerization conditions: $[M]_0$ = 0.5 M; CTA = Ph_2CHOH; T = 90 °C; time = 24 h; toluene = 2 mL [b]Measured by ^{1}H NMR. [c]$M_{n,calcd}$ = molar mass of M × $[M]_0/[CTA]_0$ × conversion % + the molar mass of CTA. [d]Molecular weight (M_n) and dispersity values (M_w/M_n) determined by SEC in THF at 40 °C using polystyrene standards. [e]Calculated by DSC measurement (Figure 4)

Reactivity Ratio Calculation:

Table S2. Reactivity ratio calculation for copolymerization of L-LA and MAC catalyzed by complex **1.**

entry	L-LA (f_1)[a]	MAC (f_2)[a]	f_1 / f_2	conversion			
				LA (%)	MAC(%)	LA (F_1)[b]	MAC (F_2)[b]
1	0.8	0.2	4	5.67	13.76	0.622	0.378
2	0.7	0.3	2.333	4.67	9.32	0.539	0.461
3	0.6	0.4	1.5	8.67	13.70	0.487	0.513
4	0.5	0.5	1	6.00	7.69	0.438	0.562
5	0.4	0.6	0.667	10.67	11.63	0.380	0.620
6	0.3	0.7	0.429	10.67	9.34	0.329	0.671

[a] f_1 and f_2 are defined as mole fractions of monomers LA and MAC in the feed and $f_1 = 1 - f_2$.
[b] F_1 and F_2 represents the mole fraction of each monomer in the copolymer and $F_1 = 1 - F_2$



$$H = \frac{f_1^2(1-F_1)}{(1-f_1)^2 F_1}, \qquad G = \frac{f_1(2F_1-1)}{(1-f_1)F_1}$$

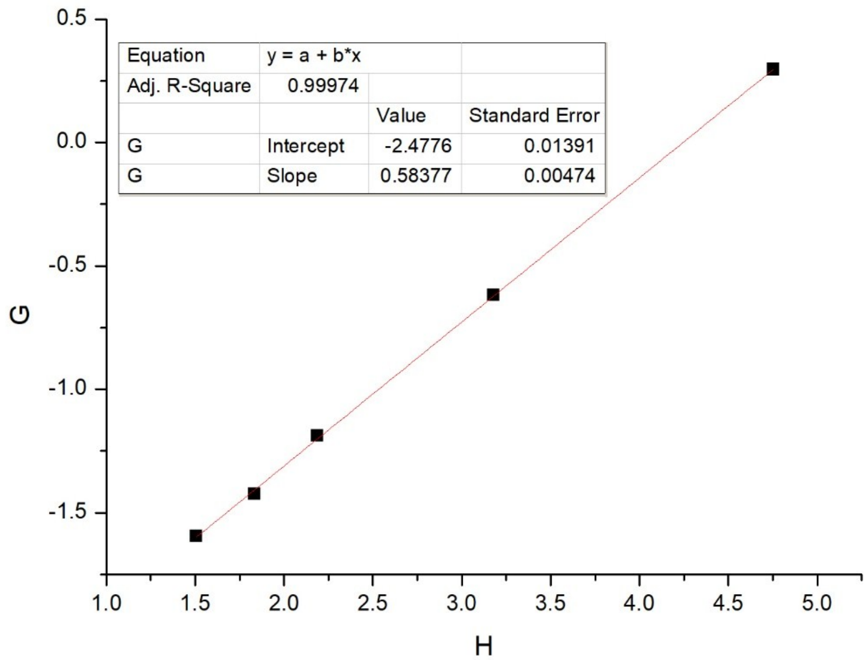
Where $G = Hr_1 - r_2$, a plot of H versus G yields a straight line with slope r_1 and intercept $-r_2$.

$r_{L\text{-}LA} = 0.217$, $r_{MAC} = 0.578$.

entry	*rac*-LA (f_1)[a]	MAC (f_2)[a]	f_1 / f_2	conversion			
				LA (%)	MAC(%)	LA (F_1)[b]	MAC (F_2)[b]
1	0.7	0.3	2.333	4.81	9.80	0.534	0.466
2	0.6	0.4	1.5	4.75	10.07	0.414	0.586
3	0.5	0.5	1	3.52	7.70	0.314	0.686
4	0.45	0.55	0.818	5.67	12.71	0.267	0.733
5	0.4	0.6	0.667	3.53	7.98	0.228	0.772

Table S3. Reactivity ratio calculation for copolymerization of *rac*-LA and MAC catalyzed by complex **1.**

[a] f_1 and f_2 are defined as mole fractions of monomers LA and MAC in the feed and $f_1 = 1 - f_2$.
[b] F_1 and F_2 represents the mole fraction of each monomer in the copolymer and $F_1 = 1 - F_2$.



entry	L-LA	MAC	f_1 / f_2	conversion			
	$(f_1)^a$	$(f_2)^a$		LA (%)	MAC(%)	LA $(F_1)^b$	MAC $(F_2)^b$
1	0.55	0.45	1.222	11.37	4.30	0.764	0.236
2	0.5	0.5	1	11.67	4.33	0.729	0.271
3	0.45	0.55	0.818	11.55	4.11	0.697	0.303
4	0.4	0.6	0.667	14.09	4.54	0.674	0.326
5	0.3	0.7	0.429	16.00	4.62	0.597	0.403

$$H = \frac{f_1^2(1-F_1)}{(1-f_1)^2F_1}, \qquad G = \frac{f_1(2F_1-1)}{(1-f_1)F_1}$$

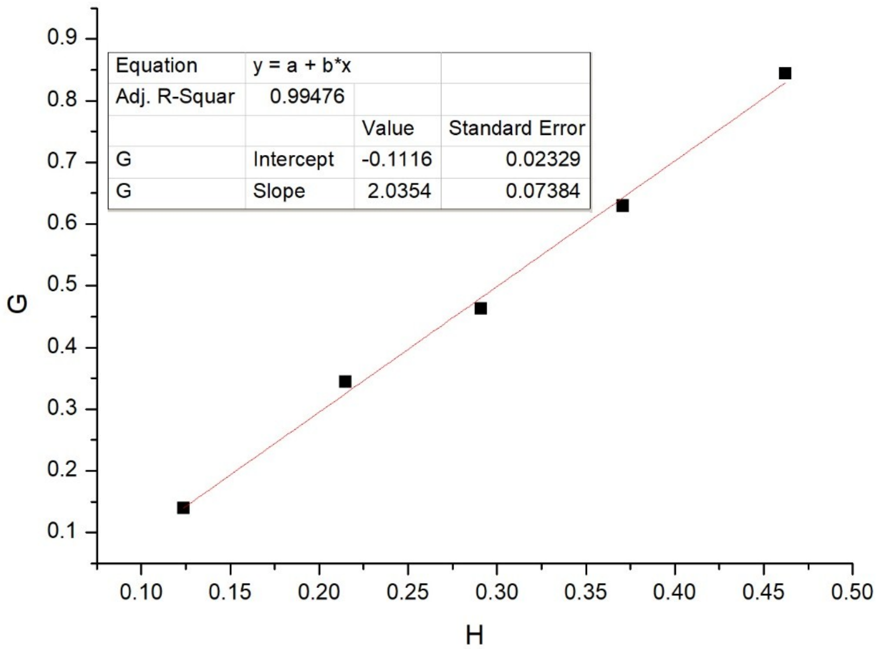
Where $G = Hr_1 - r_2$, a plot of H versus G yields a straight line with slope r_1 and intercept $-r_2$.

$r_{rac\text{-LA}} = 0.584$, $r_{MAC} = 2.478$.

Table S4. Reactivity ratio calculation for copolymerization of L-LA and MAC catalyzed by complex **2.**

[a] f_1 and f_2 are defined as mole fractions of monomers LA and MAC in the feed and $f_1 = 1 - f_2$.

[b] F_1 and F_2 represents the mole fraction of each monomer in the copolymer and $F_1 = 1 - F_2$.



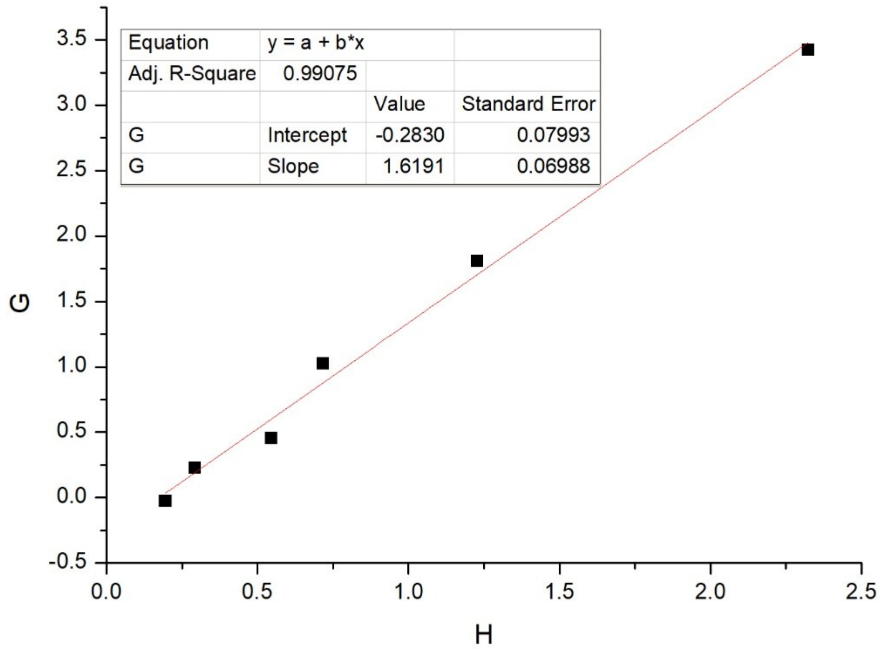
$$H = \frac{f_1^2(1-F_1)}{(1-f_1)^2F_1}, \qquad G = \frac{f_1(2F_1-1)}{(1-f_1)F_1}$$

Where $G = Hr_1 - r_2$, a plot of H versus G yields a straight line with slope r_1 and intercept $-r_2$.
$r_{\text{L-LA}} = 2.035$, $r_{\text{MAC}} = 0.112$.

Table S5. Reactivity ratio calculation for copolymerization of *rac*-LA and MAC catalyzed by complex **2.**

[a]f_1 and f_2 are defined as mole fractions of monomers LA and MAC in the feed and $f_1 = 1 - f_2$.
[b]F_1 and F_2 represents the mole fraction of each monomer in the copolymer and $F_1 = 1 - F_2$.

entry	*rac*-LA	MAC	f_1 / f_2	conversion			
	$(f_1)^a$	$(f_2)^a$		LA (%)	MAC(%)	LA $(F_1)^b$	MAC $(F_2)^b$
1	0.8	0.2	4	13.58	7.89	0.873	0.127
2	0.7	0.3	2.333	11.82	6.22	0.816	0.184
3	0.6	0.4	1.5	11.67	5.59	0.758	0.242
4	0.5	0.5	1	10.11	5.53	0.646	0.354
5	0.4	0.6	0.667	11.52	5.08	0.602	0.398
6	0.3	0.7	0.429	11.95	5.48	0.483	0.517



$$H = \frac{f_1^2(1 - F_1)}{(1 - f_1)^2 F_1}, \qquad G = \frac{f_1(2F_1 - 1)}{(1 - f_1)F_1}$$

Where $G = Hr_1 - r_2$, a plot of H versus G yields a straight line with slope r_1 and intercept $-r_2$.
$r_{rac\text{-LA}} = 1.619$, $r_{MAC} = 0.283$.