Supporting Information for

Investigation of a Zirconium Compound for Redox Switchable Ring Opening Polymerization

*Ruxi Dai and Paula L. Diaconescu**

Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095

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NMR Spectra

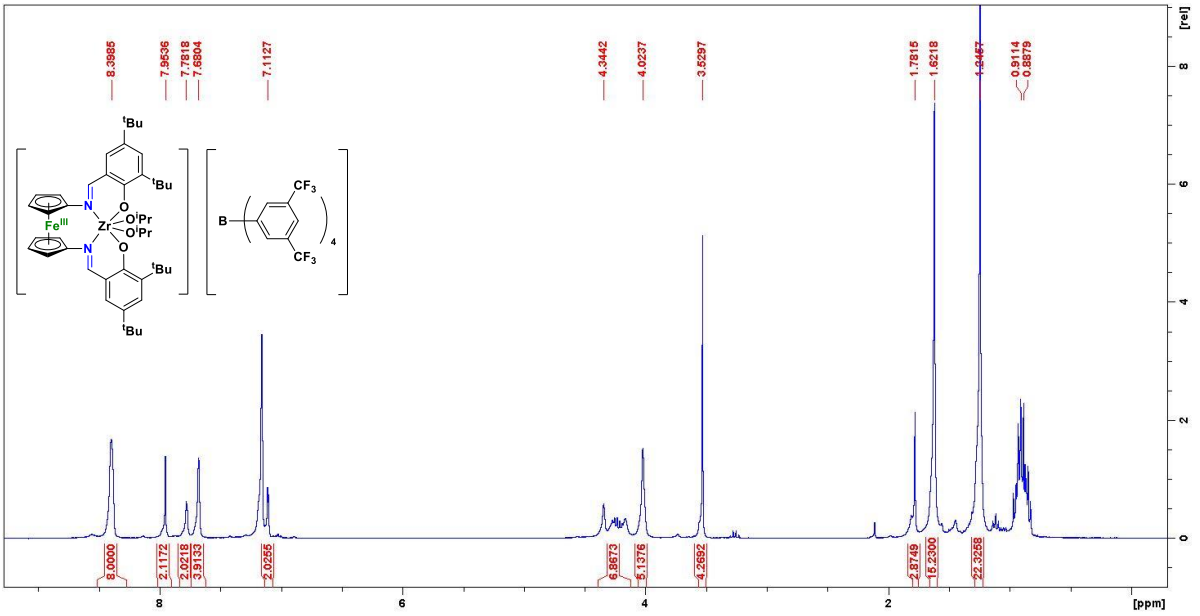

Figure S1. ^{1}H NMR (300 MHz, C_6D_6, 25 °C) spectrum of [(salfen)Zr(O^{i}Pr)$_2$][BAr^{F}]. δ, ppm: 8.40 (s, 8H, *m*-C$_6$*H*$_3$, BAr^{F}), 7.68 (s, 4H, *m*-C$_6$*H*$_3$, BAr^{F}), 7.95 (s, 2H, N=C*H*), 7.82 (s, 2H, *m*-C$_6$H$_2$), 7.11 (s, 2H, *m*-C$_6$H$_2$), 4.34 (br, 8H, C$_5$*H*$_4$), 4.02 (s, 6H, CH(C*H*$_3$)$_2$), 3.53 (s, 6H, CH(C*H*$_3$)$_2$), 1.78 (s, 2H, C*H*(CH$_3$)$_2$), 1.62 (s, 18H, C(C*H*$_3$)$_3$), 1.25 (s, 18H, C(C*H*$_3$)$_3$), 0.90 (hexanes). The other hexanes peaks are blocked by the 1.25 ppm product peak.

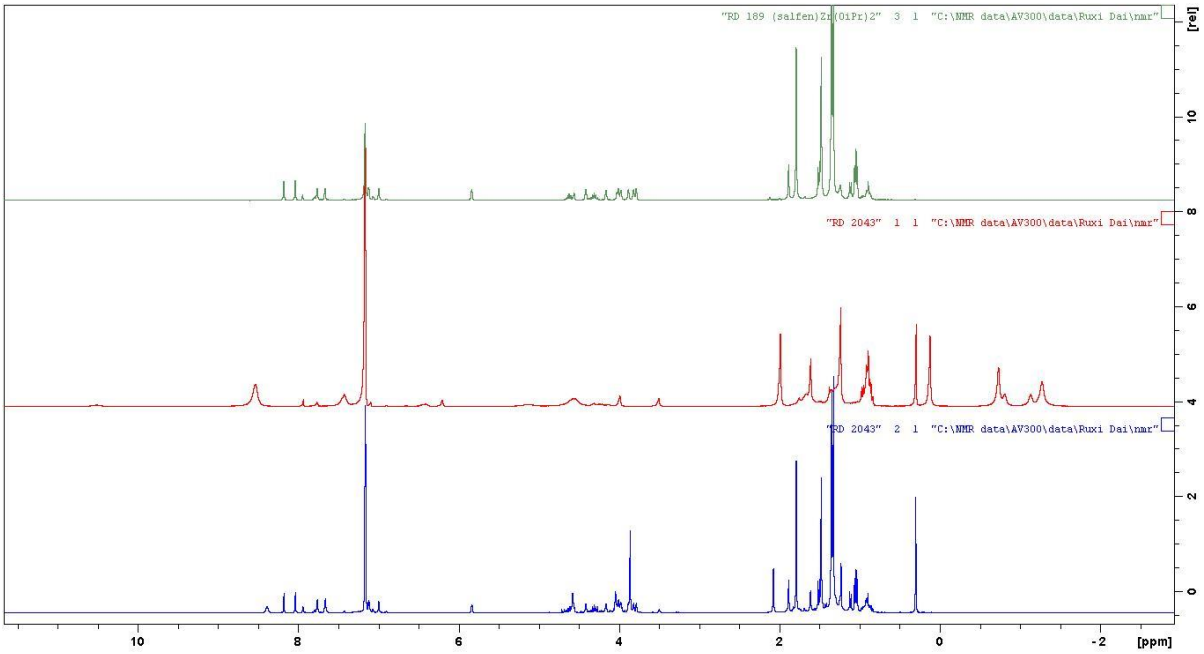

Figure S2. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C) spectrum of (salfen)Zr($O^{i}Pr$)$_2$ (top), [(salfen)Zr($O^{i}Pr$)$_2$][BAr^{F}] generated in situ (middle), and (salfen)Zr($O^{i}Pr$)$_2$ generated from [(salfen)Zr($O^{i}Pr$)$_2$][BAr^{F}] (bottom). All the peaks in the top spectrum match those in the bottom spectrum. The extra peaks in the bottom spectrum belong to ^{Ac}Fc and $CoCp_2$.

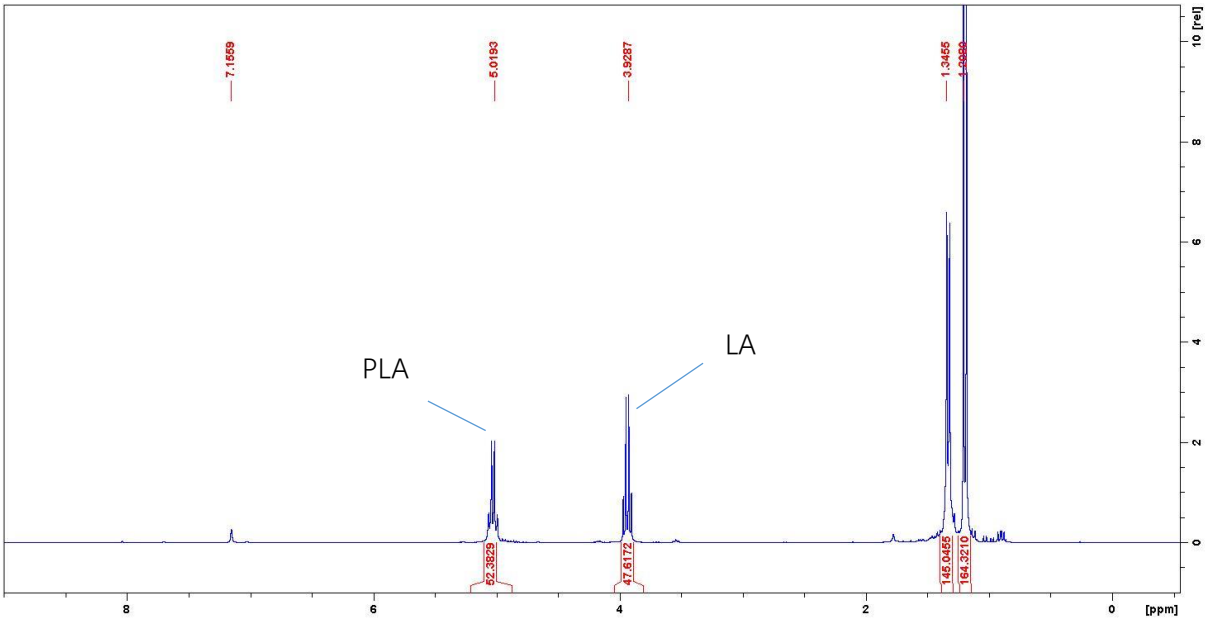

Figure S3. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C) spectrum of 100 equivalents of LA polymerization by (salfen)Zr($O^{i}Pr$)$_2$ (Table 1 entry 1). δ, ppm: 5.02 (t, 1H, C*H*(CH_3)COO, PLA), 3.91 (t, 1H, C*H*(CH_3)COO, LA), 1.34 (d, 3H, CH(C*H*$_3$)COO, PLA), 1.21 (d, 3H, CH(C*H*$_3$)COO, LA).

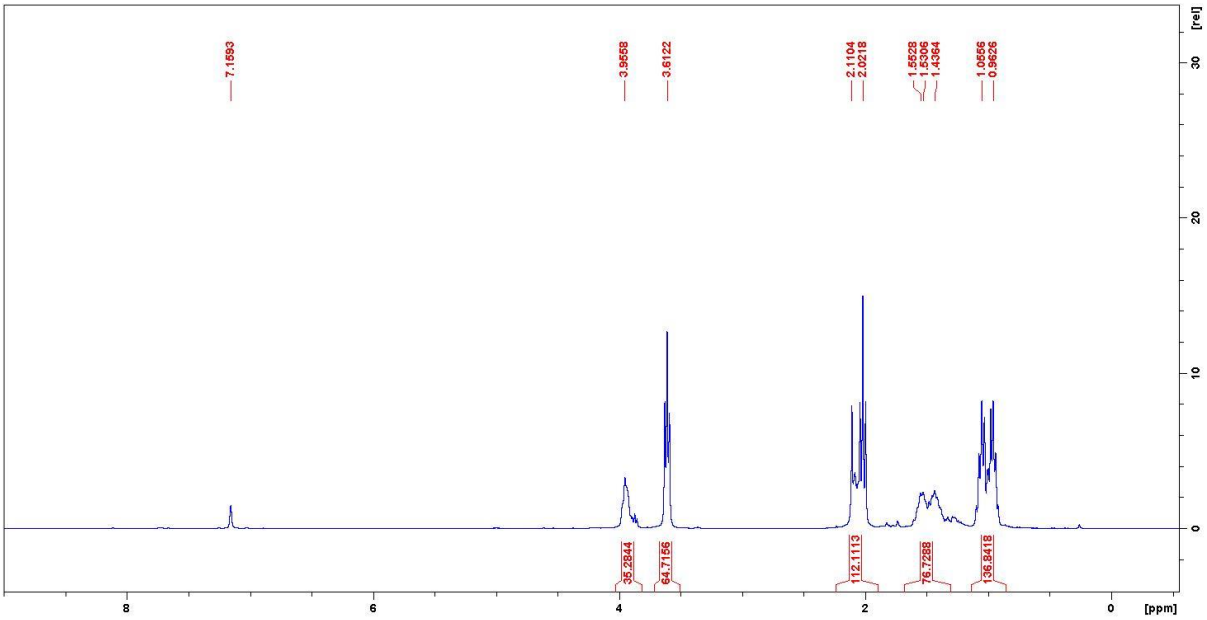

Figure S4. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C) spectrum of 100 equivalents of VL polymerization by (salfen)Zr($O^{i}Pr$)$_2$ (Table 1 entry 3). δ, ppm: 3.96 (br, 2H, CH_2COO, PVL), 3.61 (t, 2H, CH_2COO, VL), 2.11 (m, 2H, CH_2CH$_2$COO, VL), 2.02 (m, 2H, COOCH_2CH$_2$, VL) , 1.55 (br, 2H, CH_2CH$_2$COO, PVL), 1.43 br, 2H, COOCH_2CH$_2$, PVL), 1.06 (m, 2H, COOCH$_2$CH_2, VL), 0.96 (m, 2H, COOCH$_2$CH_2, PVL).

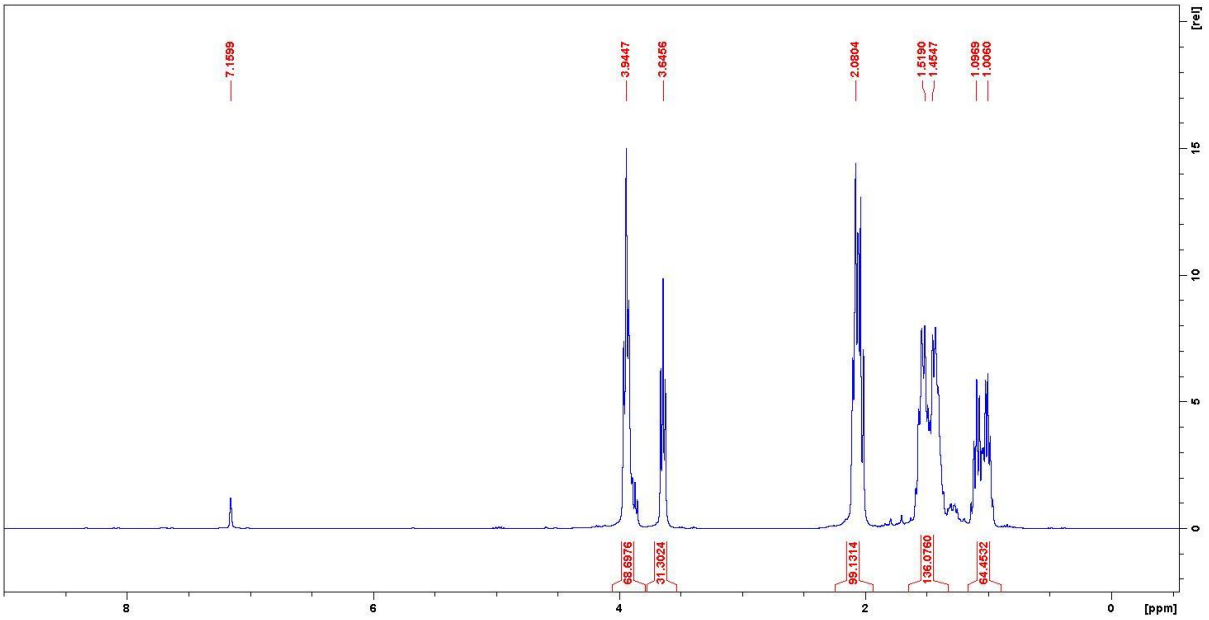

Figure S5. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C) spectrum of 250 equivalents of VL polymerization by (salfen)Zr($O^{i}Pr$)$_2$ (Table 1 entry 4). δ, ppm: 3.94 (br, 2H, C*H*$_2$COO, PVL), 3.65 (t, 2H, C*H*$_2$COO, VL), 2.08 (m, 2H, C*H*$_2$CH$_2$COO, VL), 1.52 (br, 2H, C*H*$_2$CH$_2$COO, PVL), 1.45(br, 2H, COOC*H*$_2$CH$_2$, PVL), 1.10 (m, 2H, COOCH$_2$C*H*$_2$, VL), 1.01 (m, 2H, COOCH$_2$C*H*$_2$, PVL).

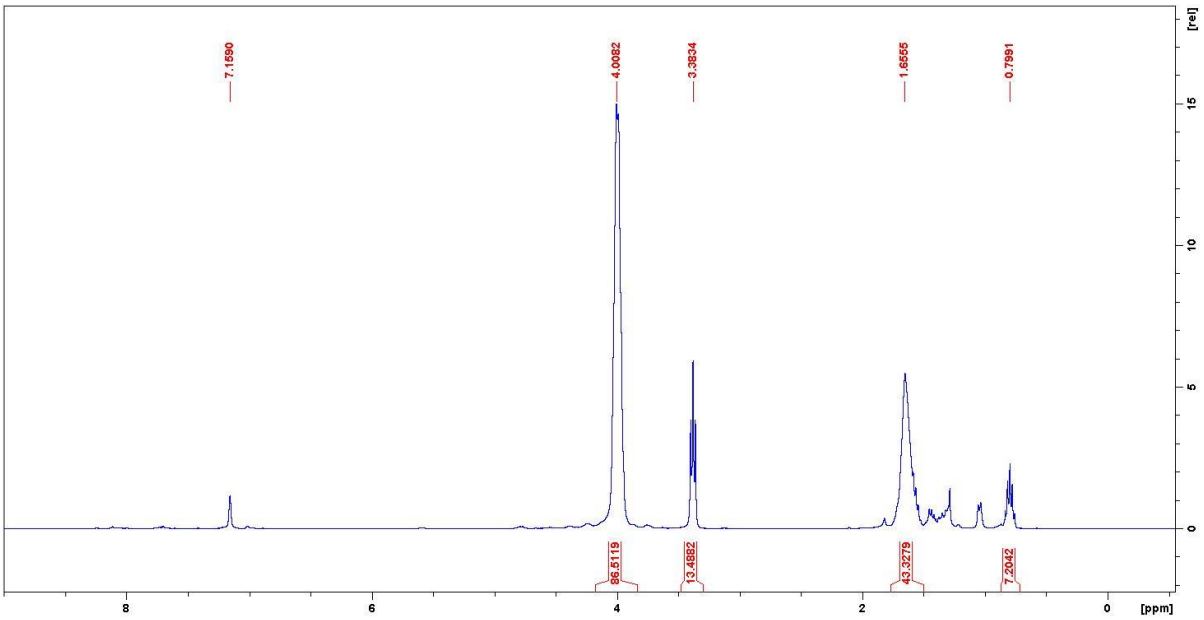

Figure S6. ^{1}H NMR (300 MHz, C_6D_6, 25 °C) spectrum of 100 equivalents of TMC polymerization by (salfen)Zr(O^{i}Pr)$_2$ (Table 1 entry 5). δ, ppm: 4.01 (s, 4H, OC*H*$_2$CH$_2$C*H*$_2$O, PTMC), 3.38 (t, 4H, OC*H*$_2$CH$_2$C*H*$_2$O, TMC), 1.66 (br, 2H, OCH$_2$C*H*$_2$CH$_2$O, PTMC), 0.80 (m, 2H, OCH$_2$C*H*$_2$CH$_2$O, TMC).

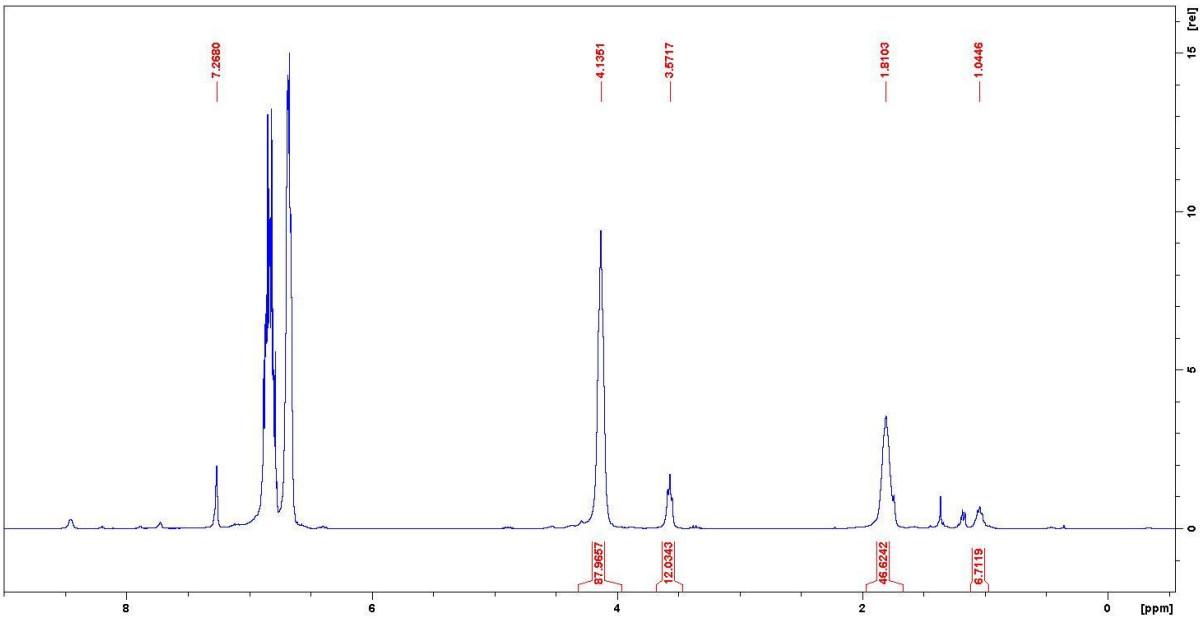

Figure S7. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C) spectrum of 100 equivalents of TMC polymerization by *in situ* generated [(salfen)Zr($O^{i}Pr$)$_2$][BAr^{F}] (Table 1 entry 6). δ, ppm: 4.14 (s, 4H, OC*H*$_2$CH$_2$C*H*$_2$O, PTMC), 3.57 (t, 4H, OC*H*$_2$CH$_2$C*H*$_2$O, TMC), 1.81 (br, 2H, OCH$_2$C*H*$_2$CH$_2$O, PTMC), 1.04 (m, 2H, OCH$_2$C*H*$_2$CH$_2$O, TMC).

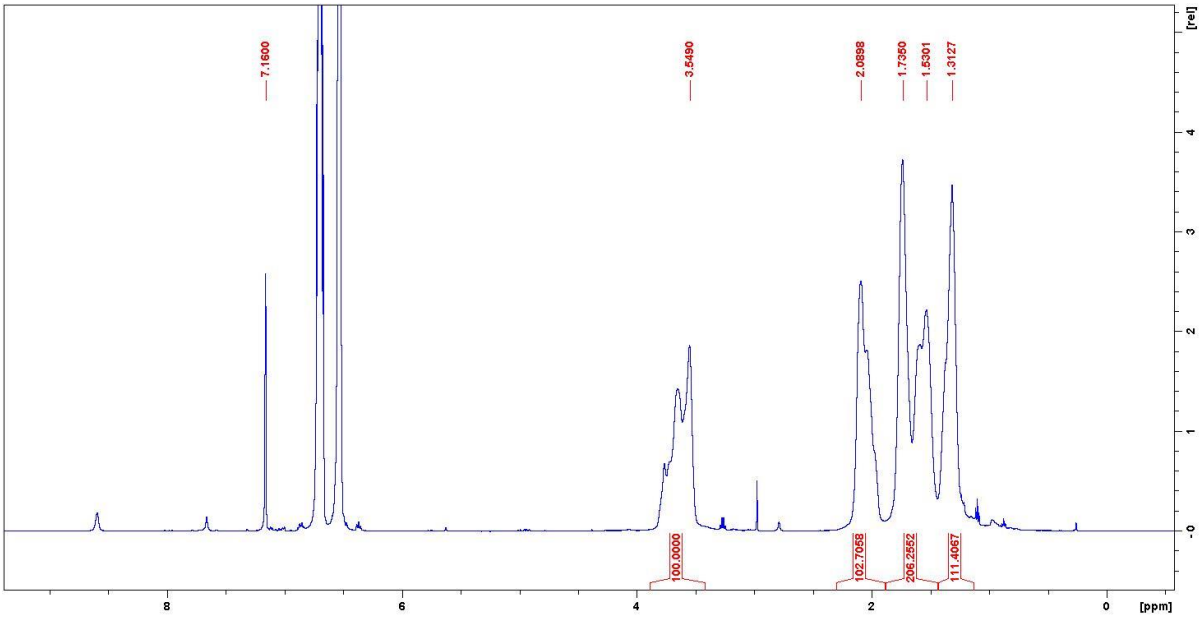

Figure S8. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C) spectrum of 100 equivalents of CHO polymerization by *in situ* generated [(salfen)Zr($O^{i}Pr$)$_2$][BAr^{F}] (Table 1 entry 12). δ, ppm: 3.55 (br, 2H, CH_2CH_2CH(O), PCHO), 2.09 (br, 2H, CH_2CH_2CH(O), PCHO), 1.74 (br, 2H, CH_2CH_2CH(O), PCHO), 1.53 (br, 2H, CH_2CH_2CH(O), PCHO), 1.31 (br, 2H, CH_2CH_2CH(O), PCHO).

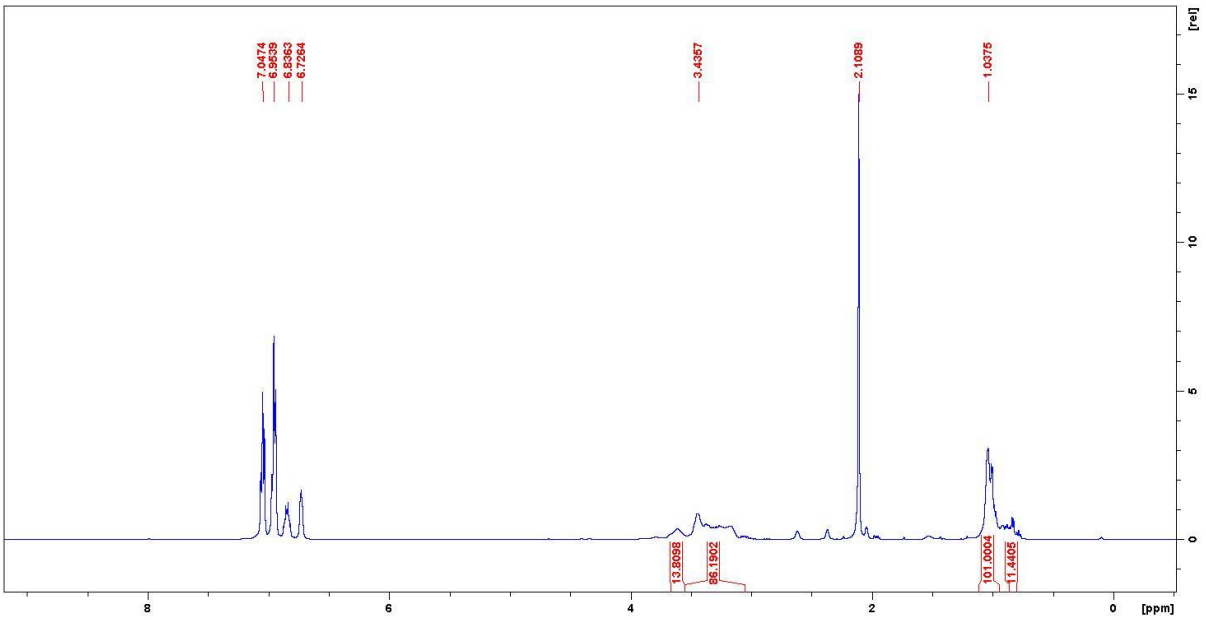

Figure S9. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C) spectrum of 1000 equivalents of PO polymerization by *in situ* generated [(salfen)Zr($O^{i}Pr$)$_2$][BAr^{F}] (Table 1 entry 14). δ, ppm: 7.05 (m, 2H, *m*-C_6H_4, difluorobenzene), 6.95 (m, 2H, *m*-C_6H_4, difluorobenzene), 6.84 (br, 2H, CH_3-C_6H_5, toluene), 6.73 (br, 3H, CH_3-C_6H_5, toluene),3.44 (br, 3H, OC*H*(CH_3)CH_2O, PPO), 2.11 (s, 3H, CH_3-C_6H_5, toluene), 1.04 (br, 3H, OCH(CH_3)CH_2O, PPO).

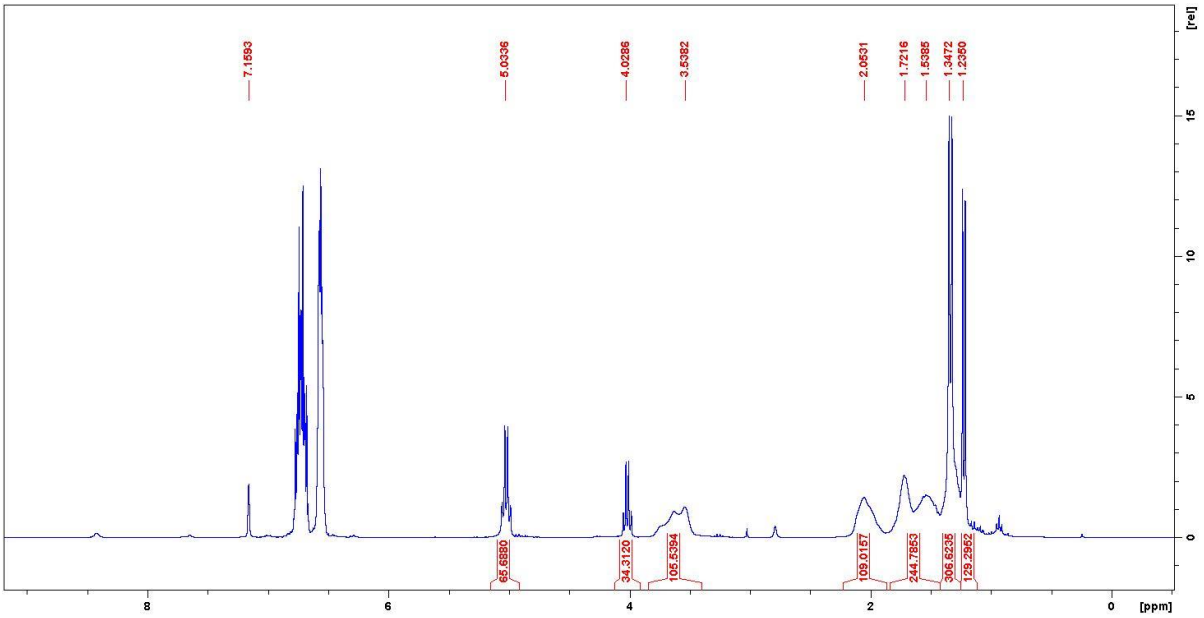

Figure S10. ^{1}H NMR (300 MHz, C_6D_6, 25 ºC) spectrum of PLA-PCHO copolymerization (Table 2 entry 1). δ, ppm: 5.03 (t, 1H, C*H*(CH_3)COO, PLA), 4.03 (t, 1H, C*H*(CH_3)COO, LA), 1.35 (d, 3H, CH(C*H*$_3$)COO, PLA), 1.24 (d, 3H, CH(C*H*$_3$)COO, LA), 3.54 (br, 2H, CH_2CH_2CH(O), PCHO), 2.05 (br, 2H, CH_2CH_2CH(O), PCHO), 1.72 (br, 2H, CH_2CH_2CH(O), PCHO), 1.54 (br, 2H, CH_2CH_2CH(O), PCHO).

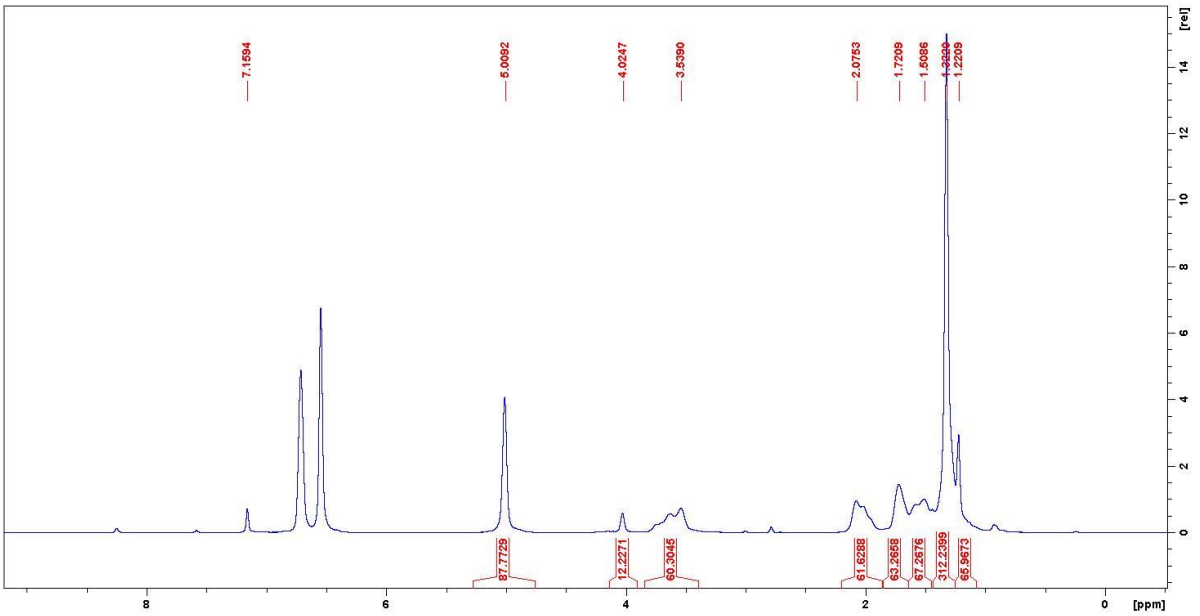

Figure S11. ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C) spectrum of PLA-PCHO-PLA copolymerization (Table 2 entry 2). δ, ppm: 5.04 (t, 1H, C*H*(CH_3)COO, PLA), 4.10 (t, 1H, C*H*(CH_3)COO, LA), 1.33 (d, 3H, CH(C*H*$_3$)COO, PLA), 1.25 (d, 3H, CH(C*H*$_3$)COO, LA), 3.54 (br, 2H, CH_2CH_2C*H*(O), PCHO), 2.05 (br, 2H, CH_2C*H*$_2$CH(O), PCHO), 1.71 (br, 2H, CH_2C*H*$_2$CH(O), PCHO).

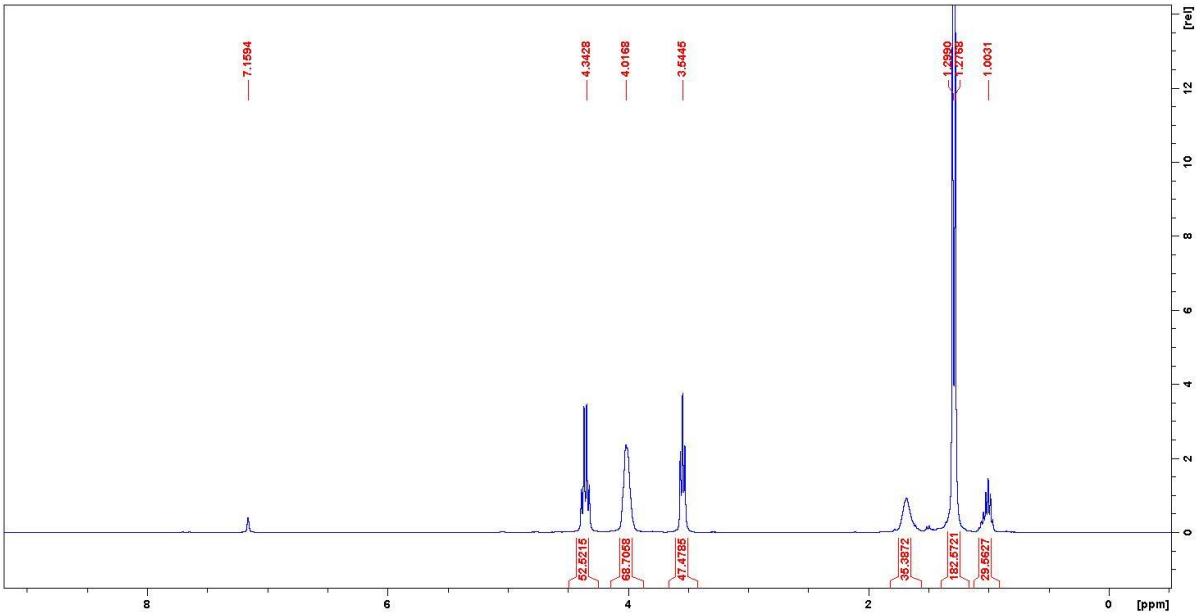

Figure S12. ^{1}H NMR (300 MHz, C_6D_6, 25 ºC) spectrum of PTMC-PLA copolymerization (Table 1 entry 3). δ, ppm: 4.34 (t, 1H, C*H*(CH_3)COO, PLA), 3.54 (t, 1H, C*H*(CH_3)COO, LA), 1.30 (d, 3H, CH(C*H*$_3$)COO, PLA), 1.28 (d, 3H, CH(C*H*$_3$)COO, LA), 4.02 (s, 4H, OC*H*$_2$CH$_2$C*H*$_2$O, PTMC), 3.54 (t, 4H, OC*H*$_2$CH$_2$C*H*$_2$O, TMC), 1.68 (br, 2H, OCH$_2$C*H*$_2$CH$_2$O, PTMC), 1.00 (m, 2H, OCH$_2$C*H*$_2$CH$_2$O, TMC).

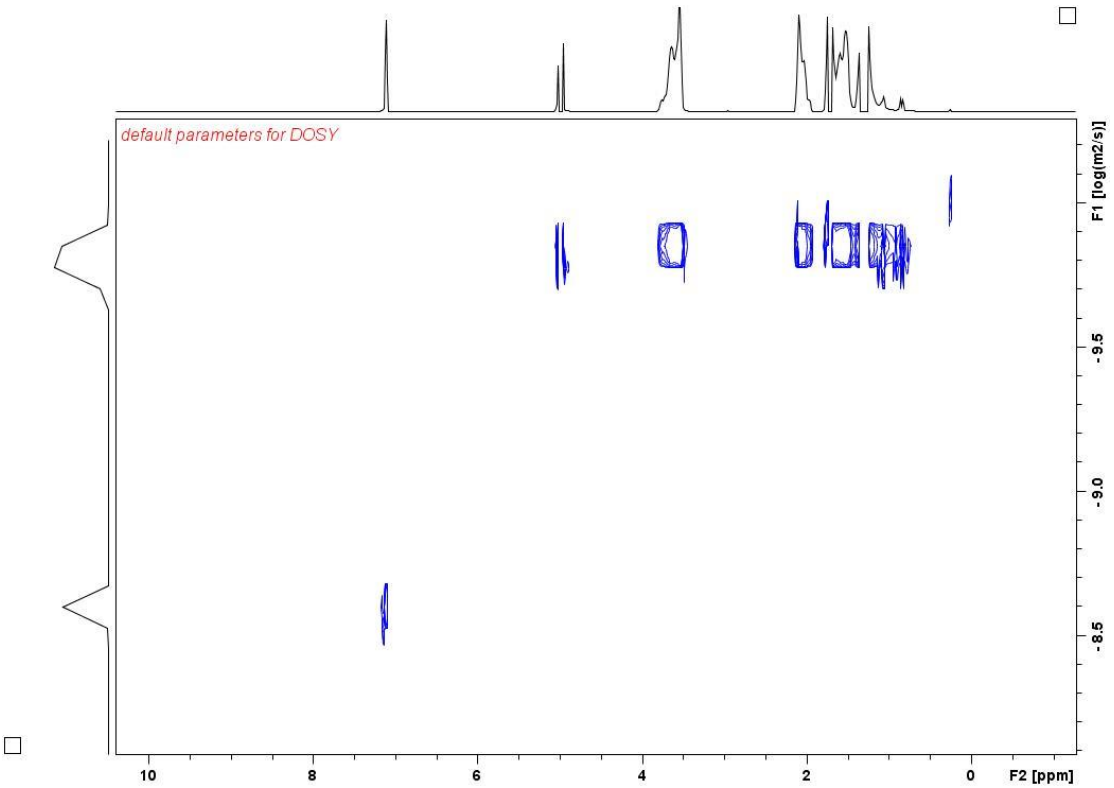

Figure S13. DOSY NMR for PLA-PCHO copolymer (Table 2 entry 1).

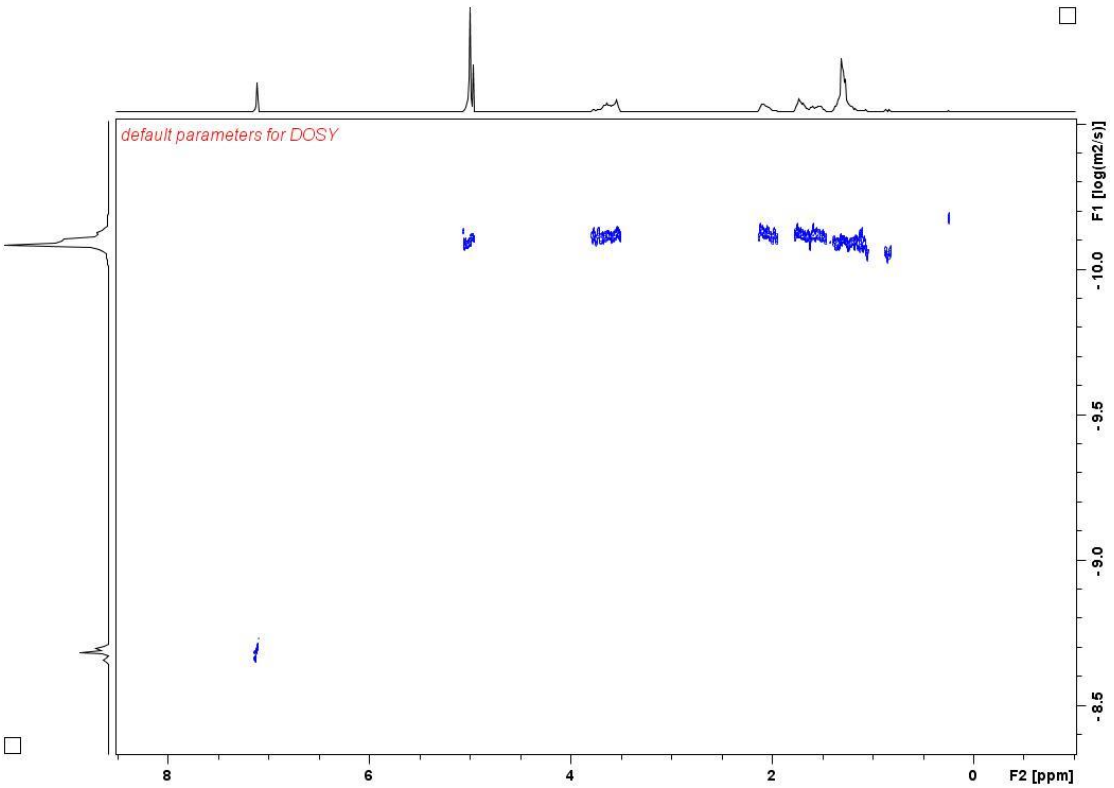

Figure S14. DOSY NMR for PLA-PCHO-PLA copolymer (Table 2 entry 2).

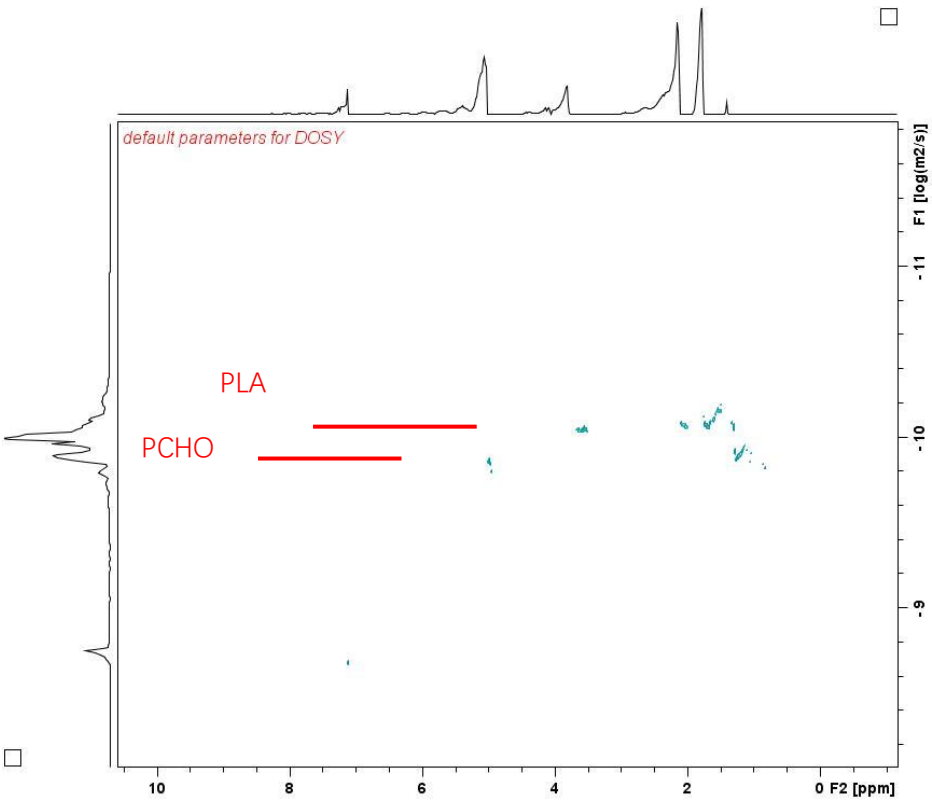

Figure S15. DOSY NMR for a mixture of PLA and PCHO homopolymers.

Table S1. Homopolymerizations by [(salfen)Zr(O^iPr)$_2$] or [(salfen)Zr(O^iPr)$_2$][BAr^F].[a]

Entry	Monomer[b]	catalyst oxidation state	Equiv. monomer	Time (h)	Temp. (°C)	Conv. (%)	Exp. Mw (10^3 g/mol)	Calcd. Mw (10^3 g/mol)	Đ
1	LA	red	100	24	100	71	6.4	5.5	1.02
2		ox	100	24	25	<3	--	--	--
3	VL	red	100	24	100	39	--	--	--
4		red	250	24	100	64	10.8	8.7	1.13
5		ox	100	14	25	<3	--	--	--
6	TMC	red	100	24	100	92	10.0	9.4	1.29
7		ox	100	24	25	88	8.7	9.0	1.13
8	PC	red	100	24	100	<3	--	--	--
9		ox	100	24	25	<3	--	--	--
10	BL	red	100	24	100	<3	--	--	--
11		ox	100	24	25	<3	--	--	--
12	CHO	red	100	24	100	<3	--	--	--
13		ox	100	0.1	25	100	22	5.0	1.23
14	PO	red	100	24	100	<3	--	--	--
15		ox	100	24	25	51	--	--	--
16		ox	1000	24	25	88	1.8	30	1.62

[a] All polymerization reactions were done with 4 μmol precatalysts, 0.6 mL of C_6D_6 as a solvent and hexamethylbenzene as an internal standard. [b]VL stands for δ-valerolactone, TMC stands for 1,3-trimethylene carbonate, BL stands for β-butyrolactone, PC stands for propylene carbonate and PO stands for propylene oxide.

Table S2. Redox-controlled copolymerizations.[a]

Entry	Monomer 1 (conv. %)	Monomer 2 (conv. %)	Monomer 3 (conv. %)	catalyst oxidation state	Exp. Mw (10^3 g/mol)	Calcd. Mw (10^3 g/mol)	Đ
1	LA (70 %)	CHO (100 %)	--	red-ox	14.0	9.8	1.37
2	LA (66 %)	CHO (100 %)	LA (88%, overall)	red-ox-red	1.72	1.69	1.55
3	TMC (60 %)	LA (87 %)	--	red-red	14.7	12.4	1.09
4	LA (70 %)	TMC (0 %)	--	red-red	--	--	--
5	LA (70 %)	TMC (0 %)	--	red-ox	--	--	--

[a] All polymerization reactions were done with 4 μmol precatalysts, 0.6 mL of C_6D_6 as the solvent and hexamethylbenzene as an internal standard. 100 equivalents of monomer was used unless otherwise mentioned. All reactions with $[Zr]^{red}$ were done at 100 °C and all reactions with $[Zr]^{ox}$ were done at 25 °C.

GPC

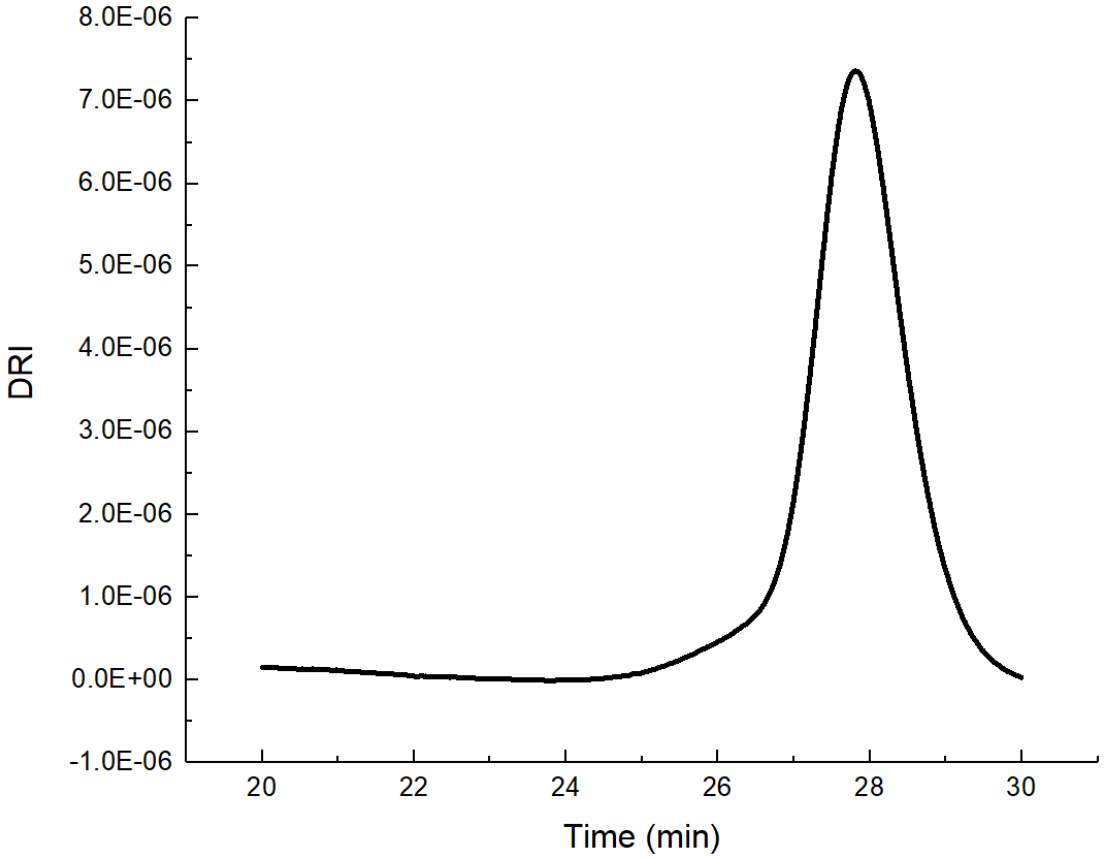

Figure S16. SEC trace for the reaction between 100 equivalents of LA and (salfen)Zr(O^iPr)$_2$ (Table 1, entry 1).

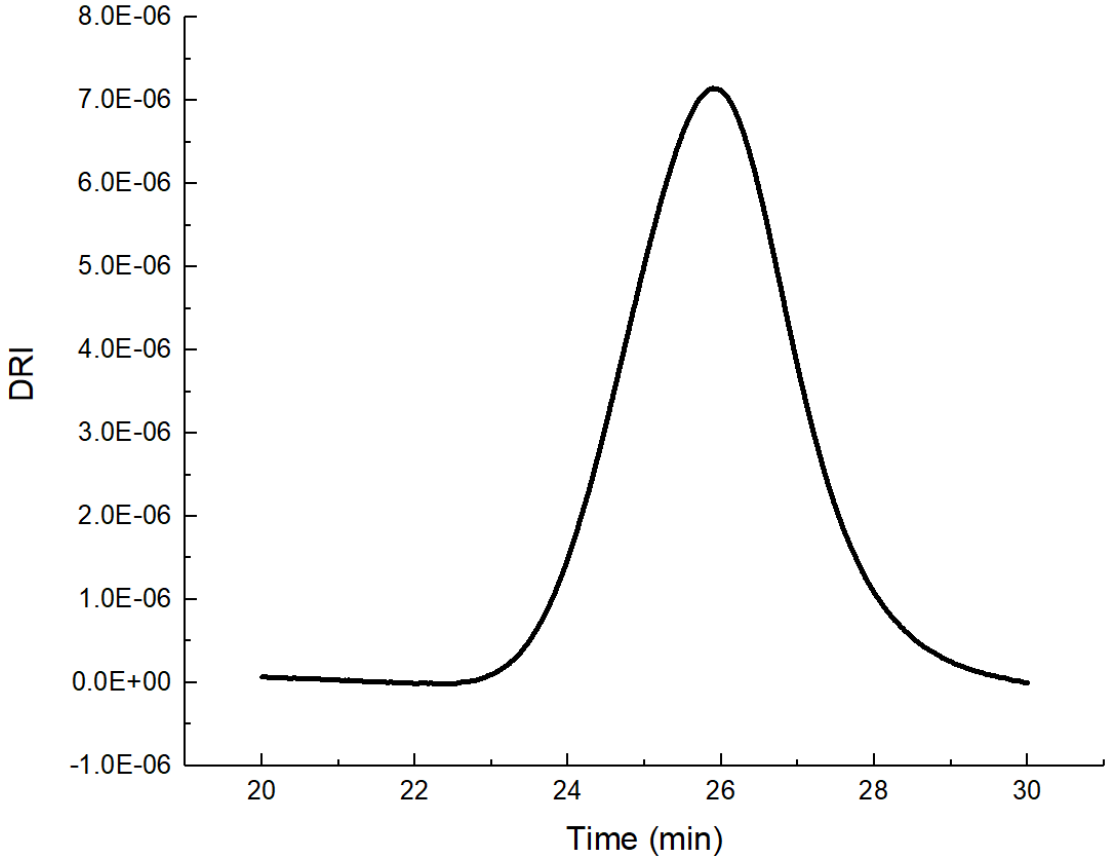

Figure S17. SEC trace for the reaction between 250 equivalents of VL and (salfen)Zr(O^iPr)$_2$ (Table 1, entry 4).

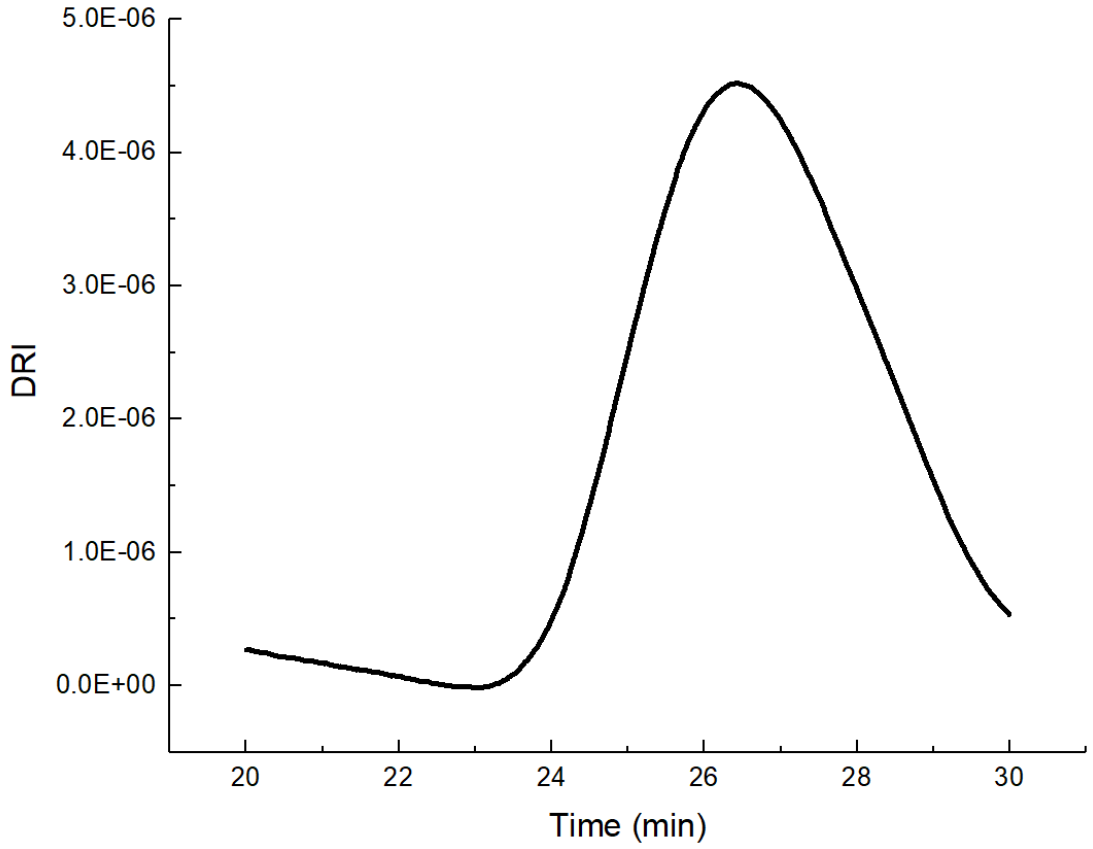

Figure S18. SEC trace for the reaction between 100 equivalents of TMC and (salfen)Zr(O^iPr)$_2$ (Table 1, entry 5).

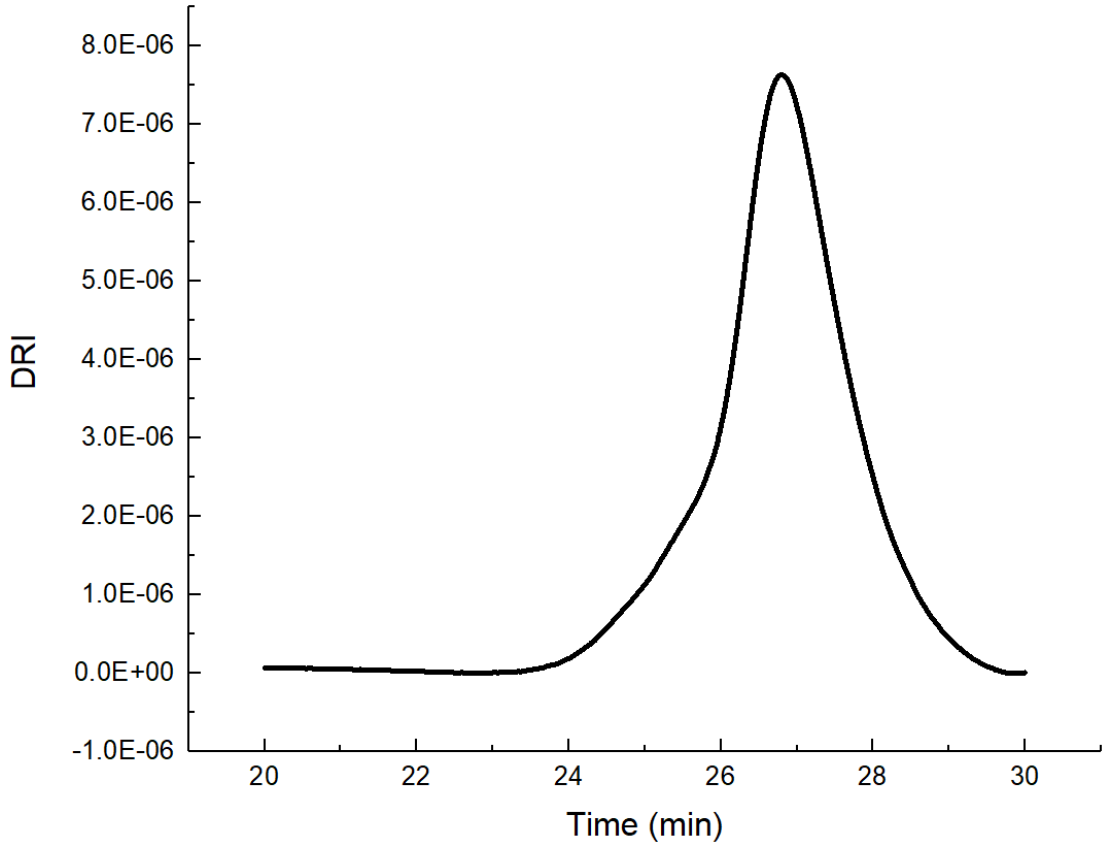

Figure S19. SEC trace for the reaction between of 100 equivalents of TMC and in situ generated [(salfen)Zr(O^{i}Pr)$_2$][BAr^{F}] (Table 1, entry 6).

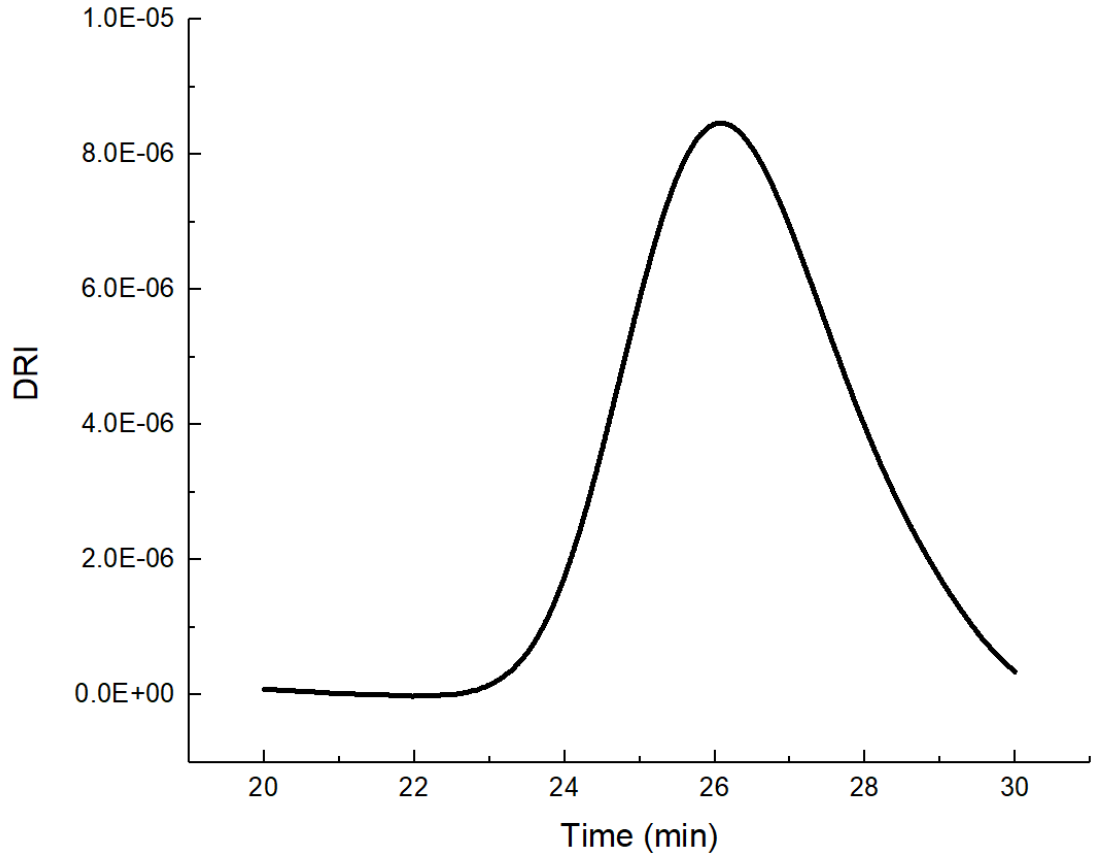

Figure S20. SEC trace for the reaction between 100 equivalents of CHO and in situ generated [(salfen)Zr(O^iPr)$_2$][BAr^F] (Table 1, entry 12).

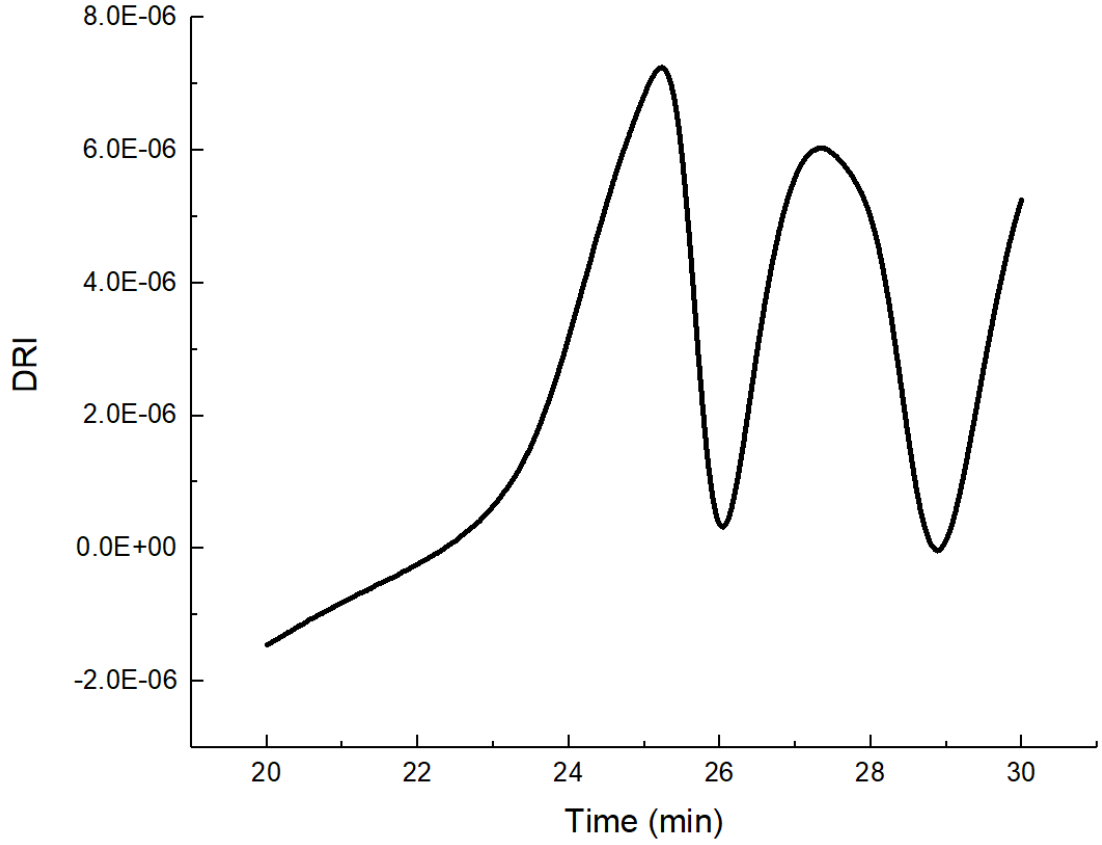

Figure S21. SEC trace for the reaction between 1000 equivalents of PO and in situ generated [(salfen)Zr(O^iPr)$_2$][BAr^F] (Table 1, entry 14).

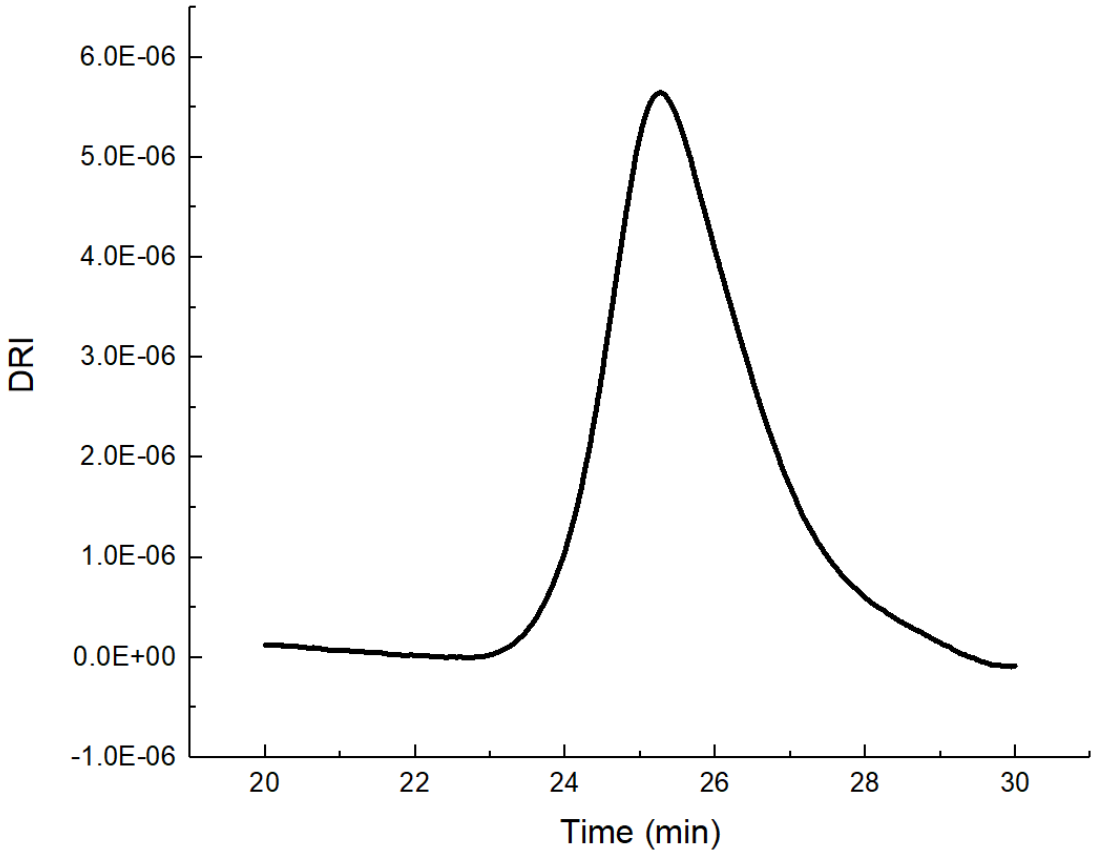

Figure S22. SEC trace for the PTMC-PLA copolymer by (salfen)Zr(O^iPr)$_2$ (Table 2, entry 3).

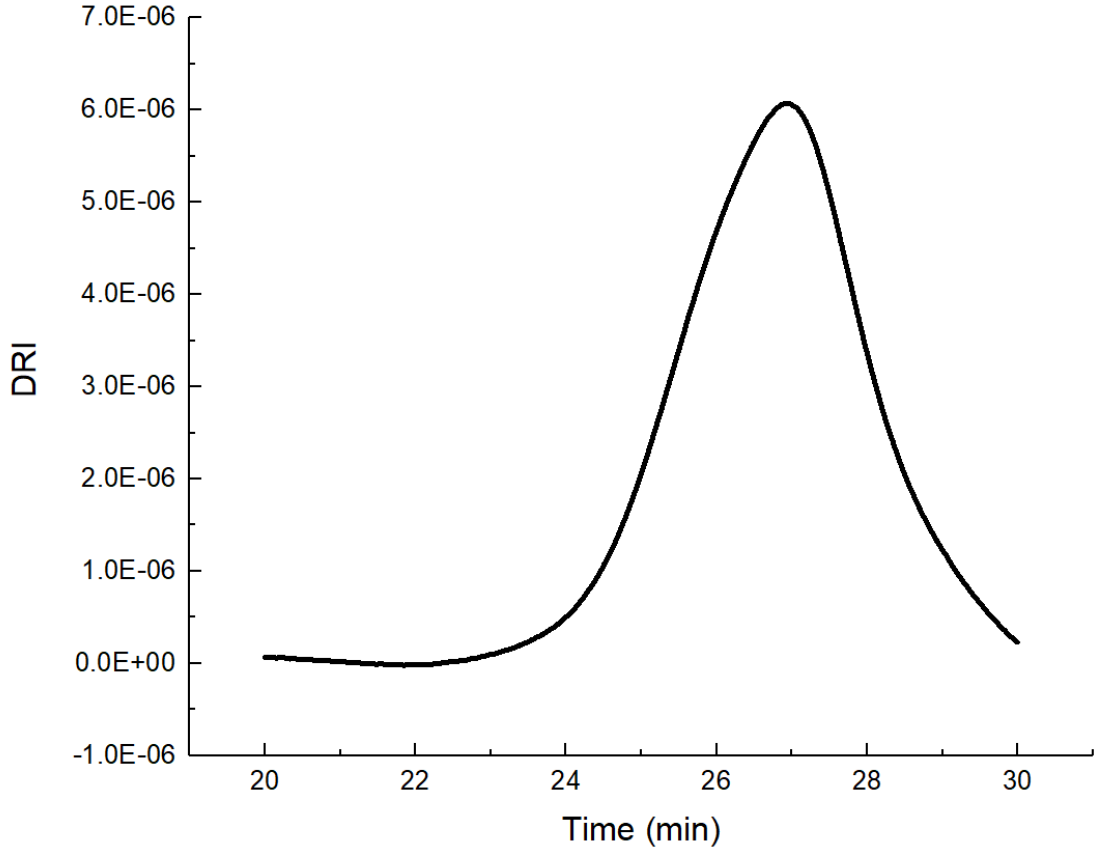

Figure S23. SEC trace for the PLA-PCHO copolymers (Table 2, entry 1).

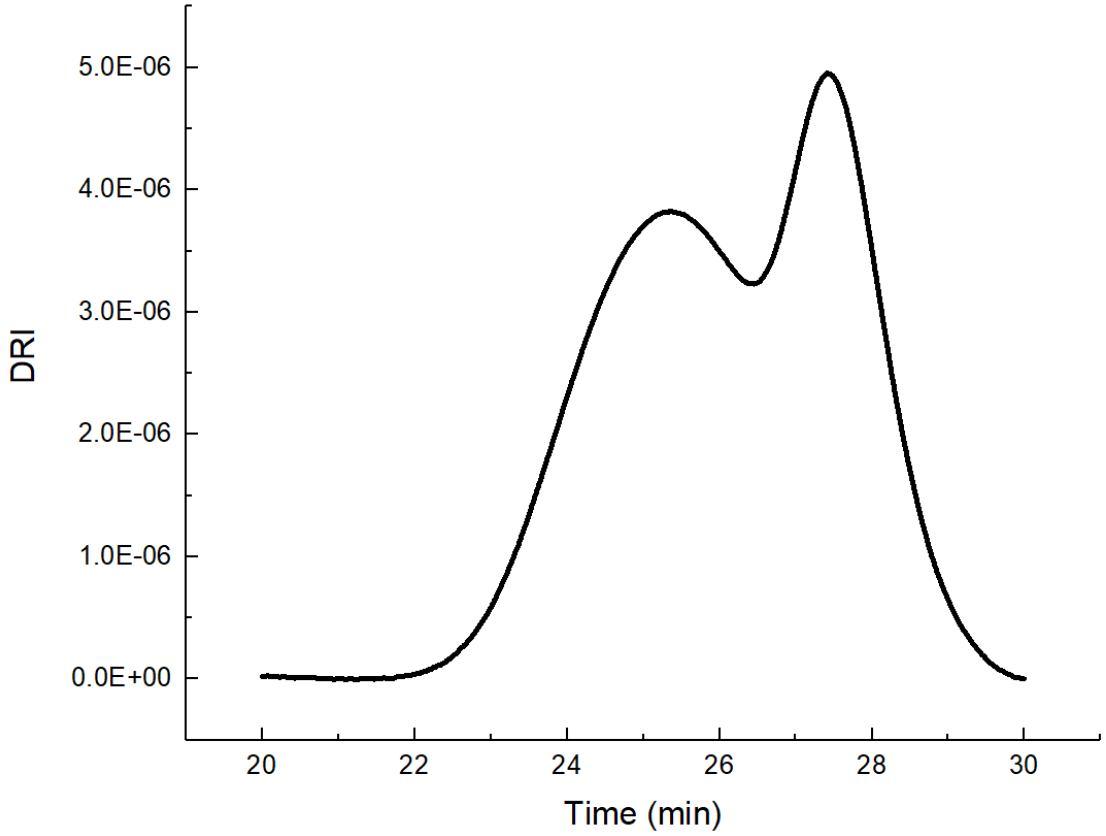

Figure S24. SEC trace for a mixture of PLA homopolymers and PCHO homopolymers.

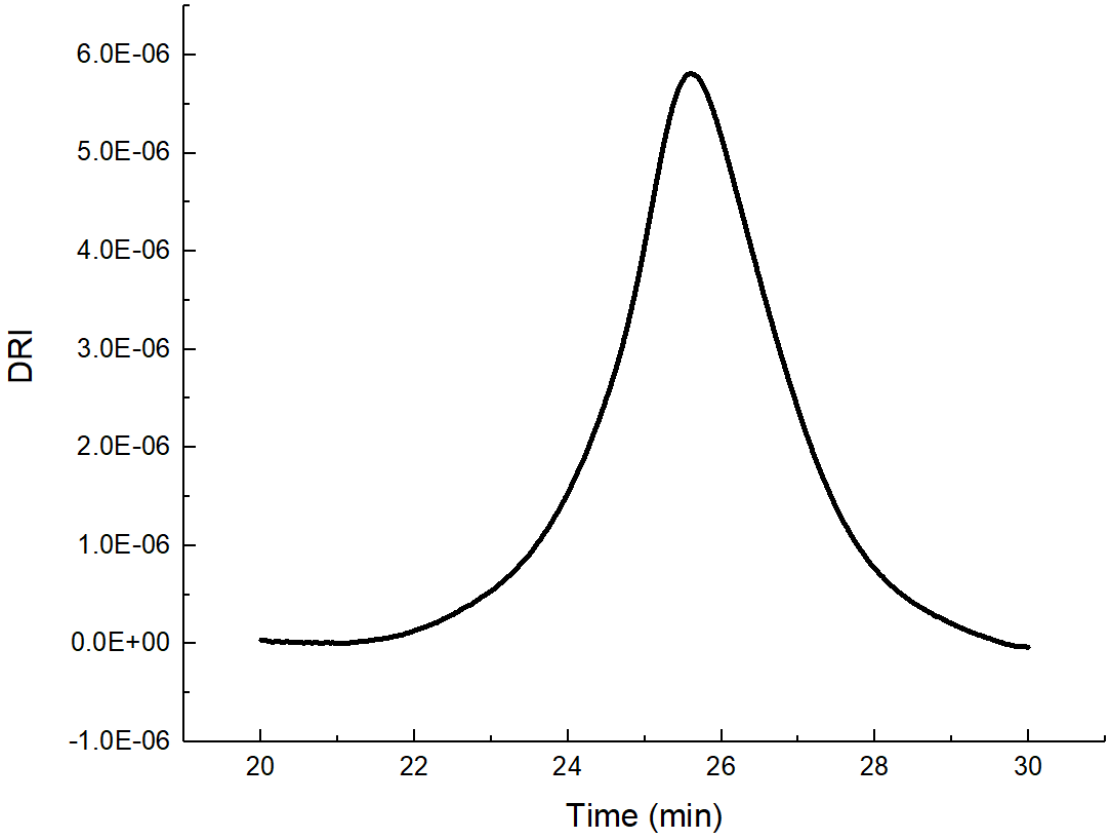

Figure S25. SEC trace for the PLA-PCHO-PLA triblock copolymer (Table 2, entry 2).

Polymerization Kinetics Study: Mn vs Conversion

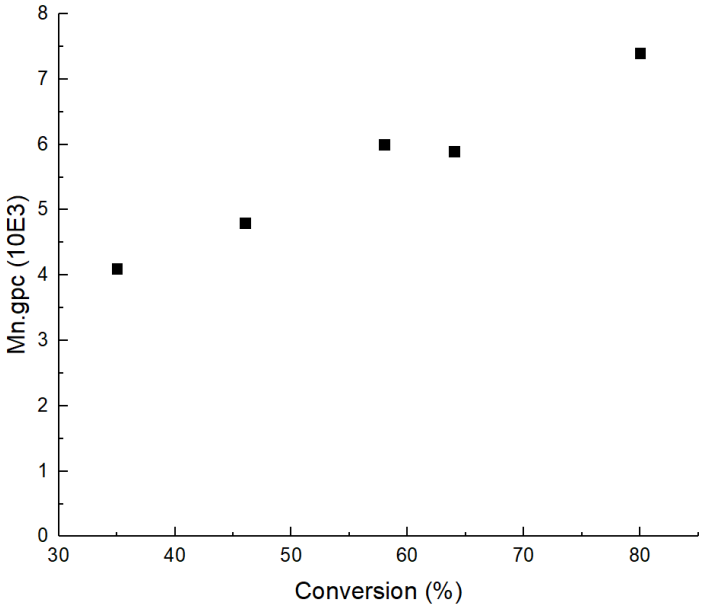

Figure S26. Mn vs conversion plot for LA polymerization by (salfen)Zr(O^iPr)$_2$.

Table S3. Kinetics study: Mn vs conversion for LA polymerization by (salfen)Zr(O^iPr)$_2$.

Entry	Conversion	Exp. Mn (10^3 Da)	Calcd. Mn (10^3 Da)	Đ
1	35%	4.1	3.1	1.06
2	46%	4.8	4.0	1.03
3	58%	6.0	5.0	1.01
4	64%	5.9	5.5	1.03
5	80%	7.4	6.9	1.05

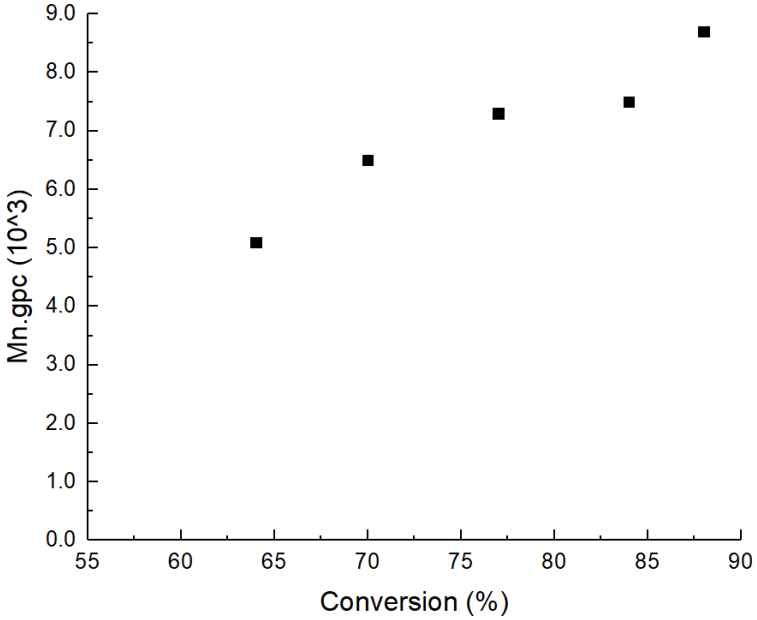

Figure S27. Mn vs conversion plot for TMC polymerization by [(salfen)Zr(O^iPr)$_2$][BAr^F].

Table S4. Kinetics study: Mn vs conversion for TMC polymerization by [(salfen)Zr(O^iPr)$_2$][BAr^F].

Entry	Conversion	Exp. Mn (10^3 Da)	Calcd. Mn (10^3 Da)	Đ
1	64%	5.1	6.5	1.03
2	70%	6.5	7.1	1.09
3	77%	7.3	7.8	1.11
4	84%	7.5	8.4	1.06
5	88%	8.7	9.0	1.13