Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Ring-opening copolymerization of cyclic epoxide and anhydride using a five-coordinate chromium complex with a sterically demanding amino triphenolate ligand

Ho Kyun Ryu,[a] Dae Young Bae,[b] Hyeongi Lim,[a] Eunsung Lee,*[b] and Kyung-sun Son*[a]

[a] Department of Chemistry, Chungnam National University, Daejeon, Republic of Korea
[b] Department of Chemistry, Pohang University of Science and Technology, Pohang, Republic of Korea

Contents

Synthesis of 1-Cr

The complex **1-Cr** was prepared according to the previously reported procedures (*Dalton Trans.,* 2019, 48, 9617-9624). The chemical yield was improved by modification. NaH (17.2 mg, 3.3 equiv.) and **1** (205.0 mg, 0.217 mmol, 1.0 equiv.) were added to a 30 mL vial. Dry THF (10 mL) was added to the vial. The resulting mixture was stirred at 23 °C for 30 min. $CrCl_3(THF)_3$ (82.0 mg, 0.217 mmol, 1.0 equiv.) was then added to the vial. The mixture was stirred at 60 °C for 24 h. The solvents were removed *in vacuo*. The solid residue was extracted with pentane (4 × 5 mL). The extracted solution was removed *in vacuo* to afford **1-Cr** as a green solid (198.4 mg, 86 %). Solution magnetic moment (C_6D_6): 3.76 μ_B. IR (KBr, cm^{-1}): 2958 (s (br), C–H), 2927 (s, C–H), 2868 (s, C–H), 1589 (s), 1430 (m), 1360 (s), 1274(m), 1043(m), 859 (s), 752 (s).

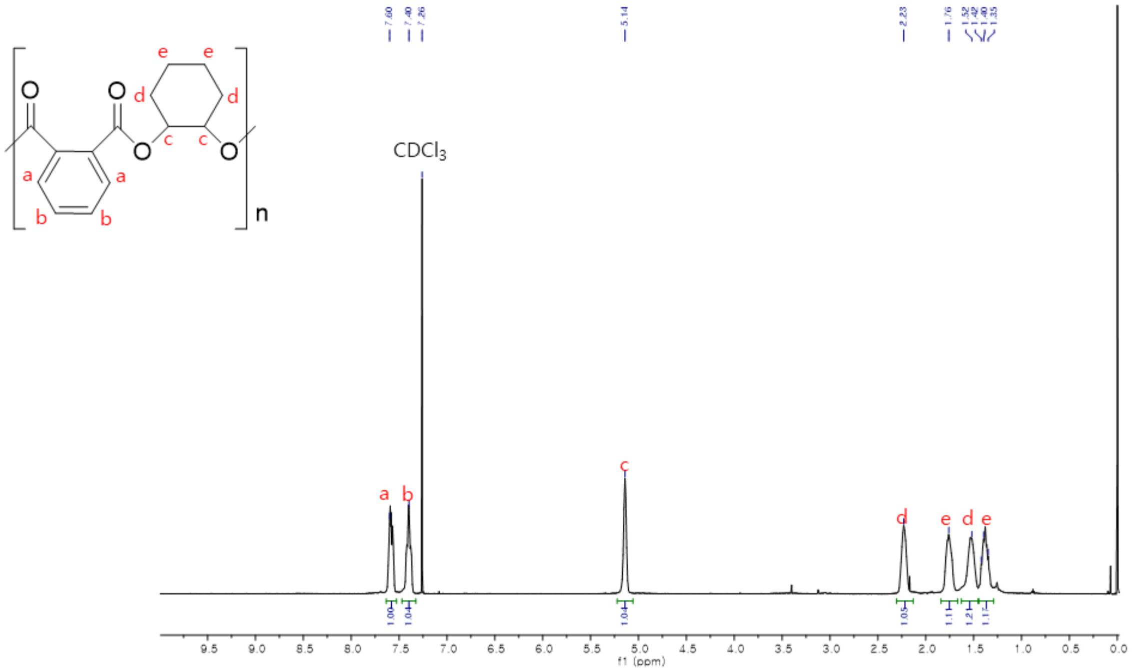


Figure S1. ^{1}H NMR spectrum of poly(PA-*alt*-CHO) (entry 1 in Table 1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.60 (m, 2H, CH_{ar}), 7.40 (m, 2H, CH_{ar}), 5.14 (m, 2H, OCH), 2.23 (m 2H, CH_2), 1.76 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.42-1.35 (m, 2H, CH_2).

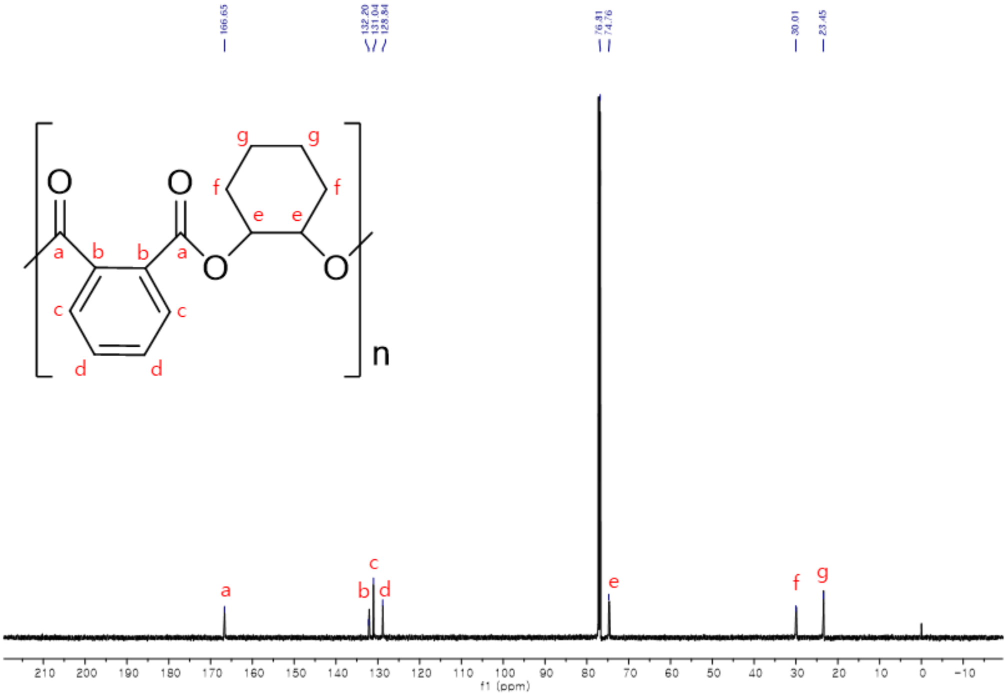


Figure S2. ^{13}C NMR spectrum of poly(PA-*alt*-CHO) (entry 1 in Table 1). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 166.7 (C=O), 132.2 (C_{ar}), 131.0 (C_{ar}), 128.8 (C_{ar}), 74.8 (OCH), 30.0 (CH_2), 23.5 (CH_2).

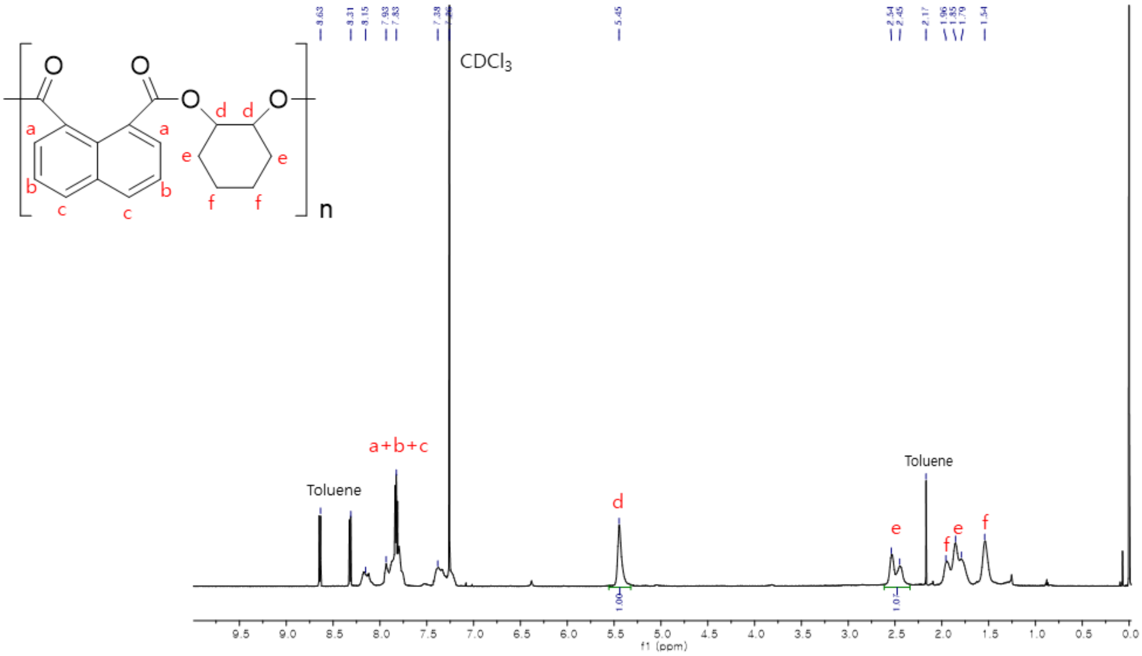


Figure S3. ^{1}H NMR spectrum of poly(NA-*alt*-CHO) (entry 1 in Table 2). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.15 (m, 1H, CH_{ar}), 7.93 – 7.83 (m, 3H, CH_{ar}), 7.39 (m, 2H, CH_{ar}), 5.45 (m, 2H, OCH), 2.54–2.45 (m, 2H, CH_2), 1.96–1.79 (m, 4H, CH_2), 1.54 (m, 2H, CH_2).

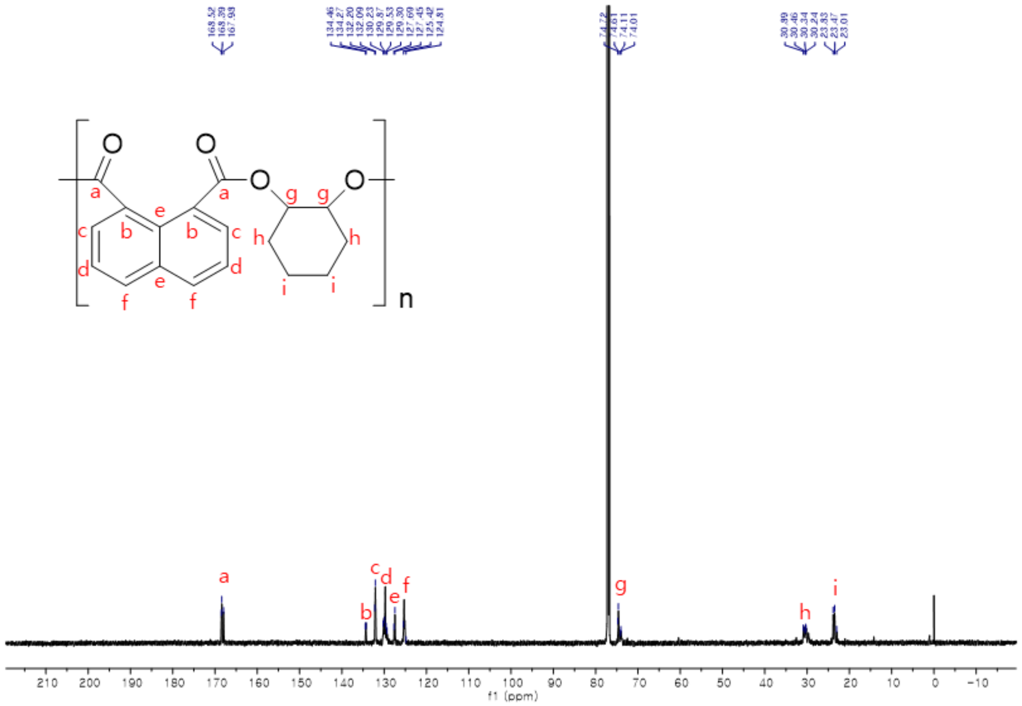


Figure S4. ^{13}C NMR spectrum of poly(NA-*alt*-CHO) (entry 1 in Table 2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 168.5 - 167.9 (C=O), 134.5 – 134.3 ($C_{ar}C$=O), 132.2 – 132.1 (C_{ar}), 130.2 – 129.5(C_{ar}), 127.7 – 127.4 (C_{ar}), 125.4 – 124.8 (C_{ar}), 74.7 – 74.0 (OCH), 30.9 – 30.2 (CH_2), 23.8 – 23.0 (CH_2).

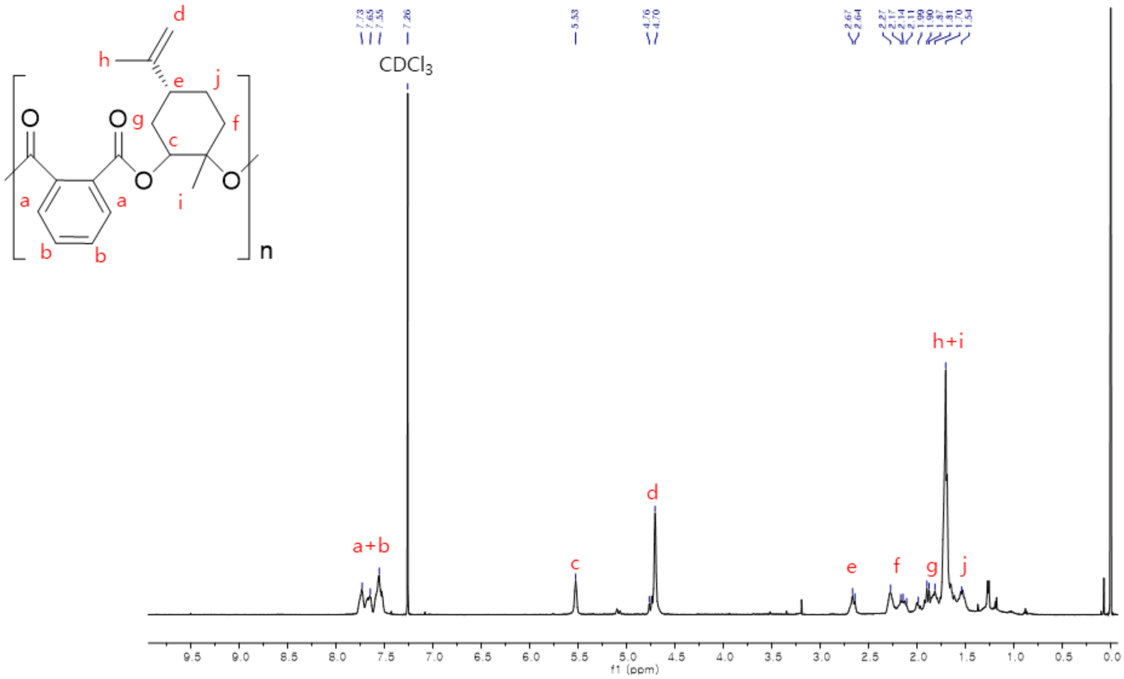


Figure S5. ^1H NMR spectrum of poly(PA-*alt*-LO) (entry 3 in Table 2). ^1H NMR ($CDCl_3$, 600 MHz): δ = 7.73 – 7.65 (m, 2H, CH_{ar}), 7,55 (m, 2H, CH_{ar}), 5.53 (s br, 1H, OCH), 4.76 - 4.70 (m, 2H, $C{=}CH_2$), 2.67 – 2.64 (m, 1H, CH), 2.27 – 2.11 (m, 2H, CH_2), 1.99 – 1.81 (m, 2H, CH_2), 1.70 (m, 3H, CH_3), 1.69 (m, 3H, CH_3), 1.54 (m, 2H, CH_2).

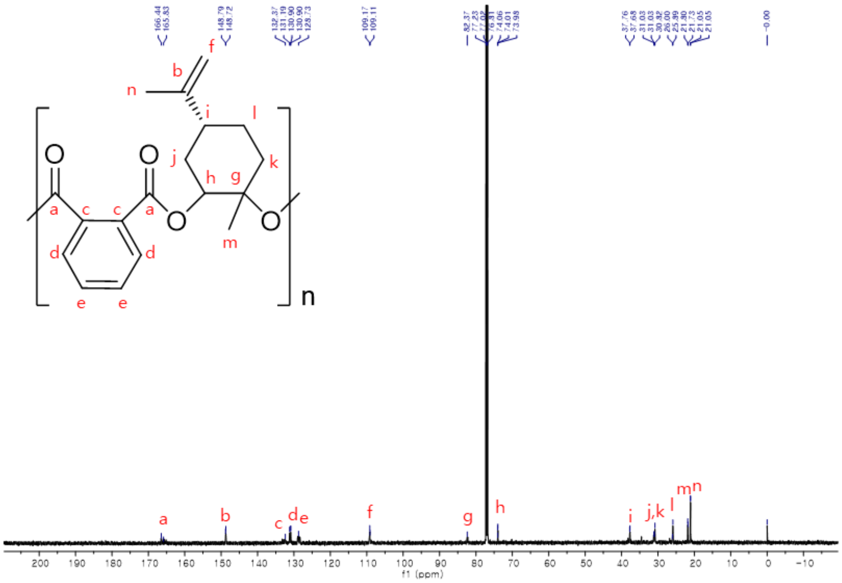


Figure S6. ^{13}C NMR spectrum of poly(PA-*alt*-LO) (entry 3 in Table 2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 166.4 – 165.8 (C=O), 148.8 – 148.7 (C=C), 132.4 (C_{ar}), 131.2 – 130.9 (C_{ar}), 128.7 (C_{ar}), 109.2 – 109.1 (C=C), 82.4 (OCMe), 74.1 – 74.0 (OCH), 37.8 – 37.7 (CH-C=C), 31.0 – 30.9 (CH_2), 26.0 (CH_2), 21.9 – 21.7 ($OCCH_3$), 21.1 ($C{=}CCH_3$).

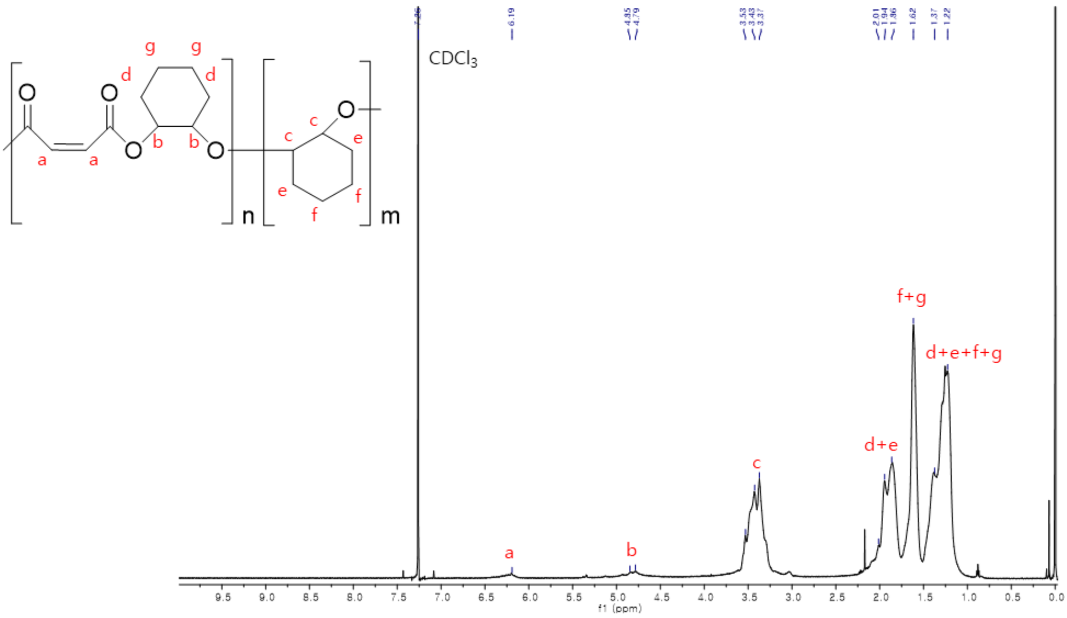


Figure S7. ^{1}H NMR spectrum of poly(MA-*co*-CHO) (entry 6 in Table 2). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 6.19 (m, 2H, HC=CH), 4.95 – 4.79 (m, 2H, OCH_{ester}), 3.53 – 3.37(m, 2H, OCH_{ether}), 2.01 – 1.96 (m, 4H, CH_2), 1.62 (m, 4H, CH_2), 1.37 – 1.22 (m, 8H, CH_2).

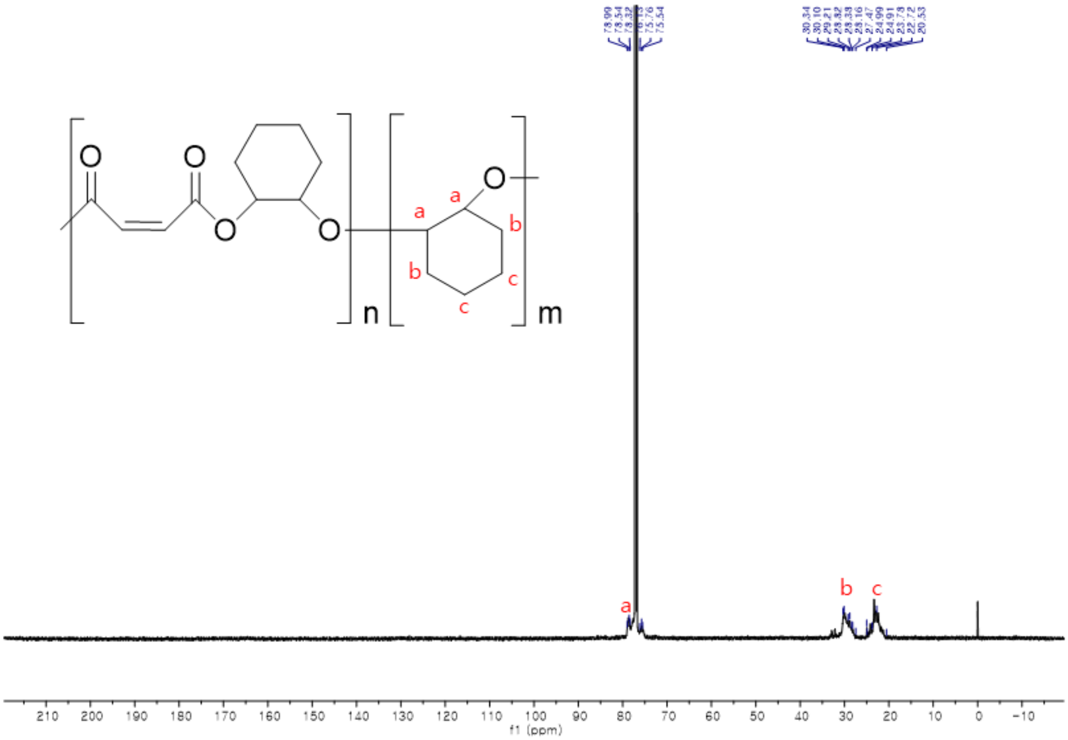


Figure S8. ^{13}C NMR spectrum of poly(MA-*co*-CHO) (entry 6 in Table 2). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 79.0 – 75.6 (OCH), 30.3 – 27.5 (CH_2), 25.0 – 20.6 (CH_2). No signal for carbonyl carbon in ester (C=O) was detected due to the low polyester ratio.

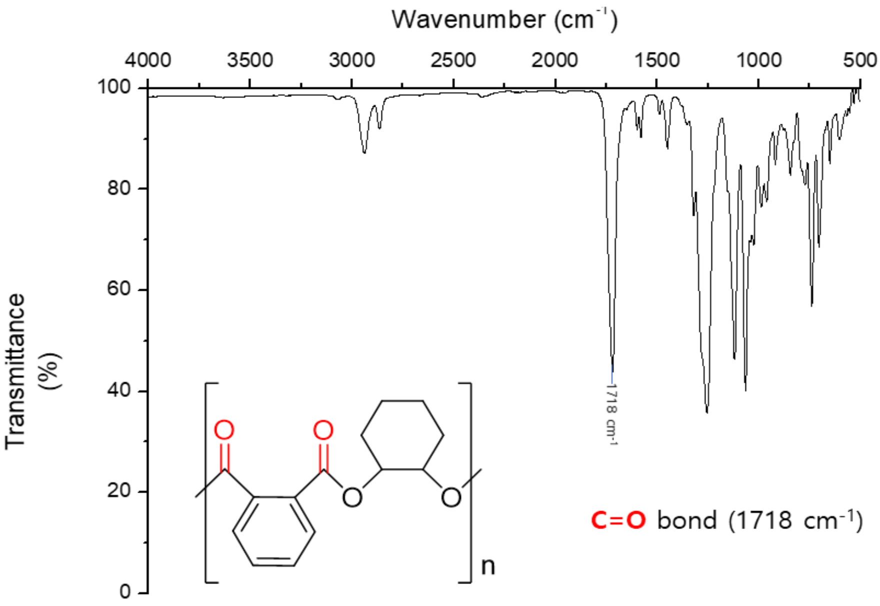


Figure S9. IR spectrum of poly(PA-*alt*-CHO) (entry 1 in Table 1).

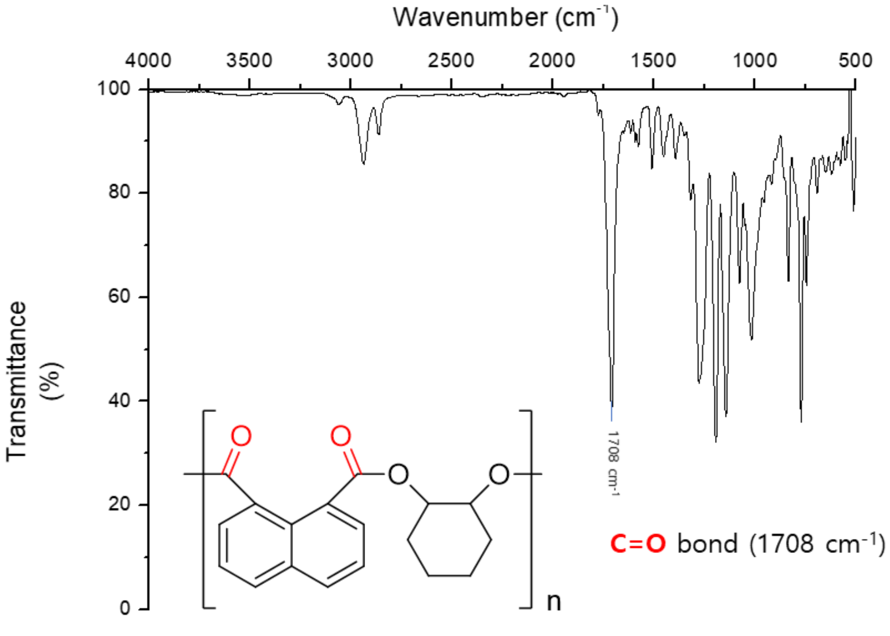


Figure S10. IR spectrum of poly(NA-*alt*-CHO) (entry 1 in Table 2).

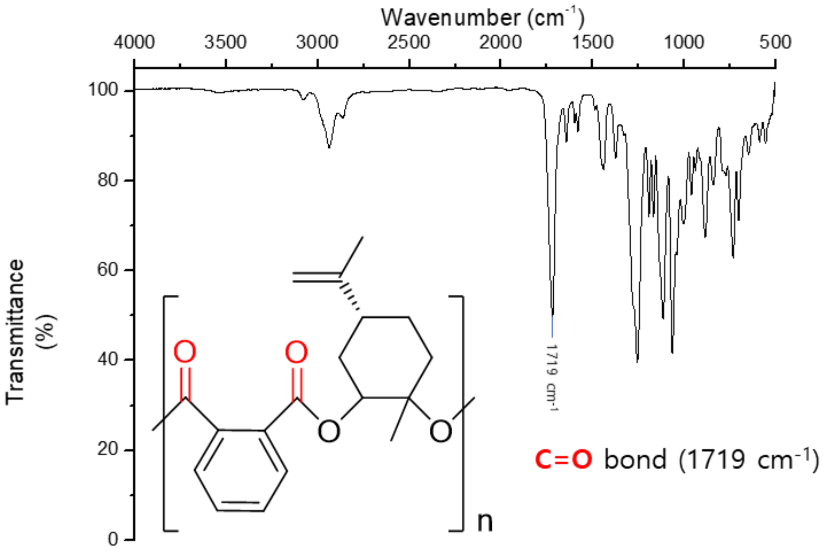


Figure S11. IR spectrum of poly(PA-*alt*-LO) (entry 3 in Table 2).

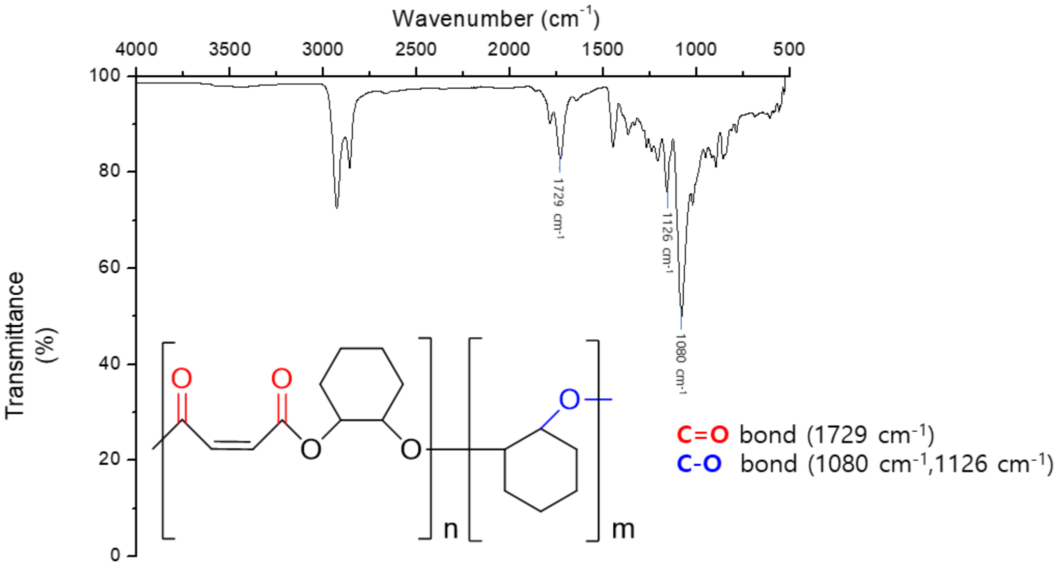


Figure S12. IR spectrum of poly(MA-*co*-CHO) (entry 6 in Table 2).

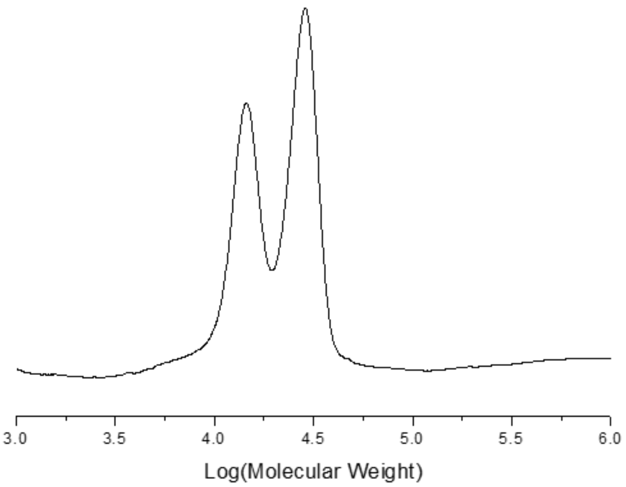


Figure S13. GPC trace of poly(PA-*alt*-CHO) (entry 1 in Table 1; M_n = 19.3 kDa, Đ = 1.13).

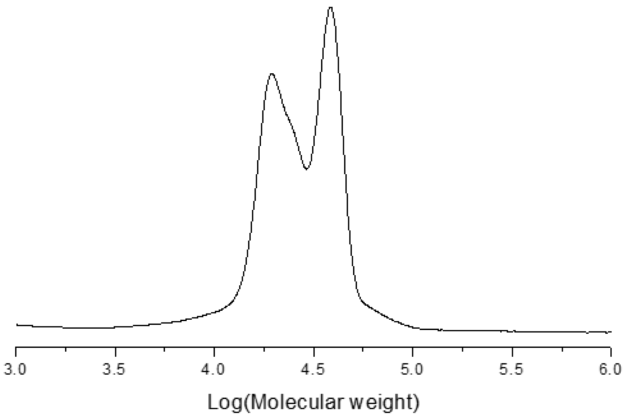


Figure S14. GPC trace of poly(PA-*alt*-CHO) (entry 4 in Table 1; M_n = 43.8 kDa, Đ = 1.21).

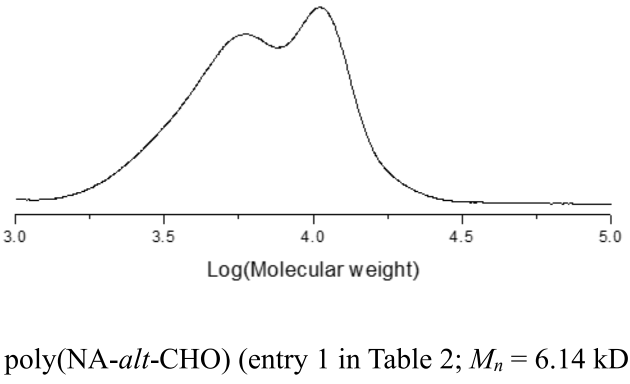


Figure S15. GPC trace of poly(NA-*alt*-CHO) (entry 1 in Table 2; M_n = 6.14 kDa, Đ = 1.23).

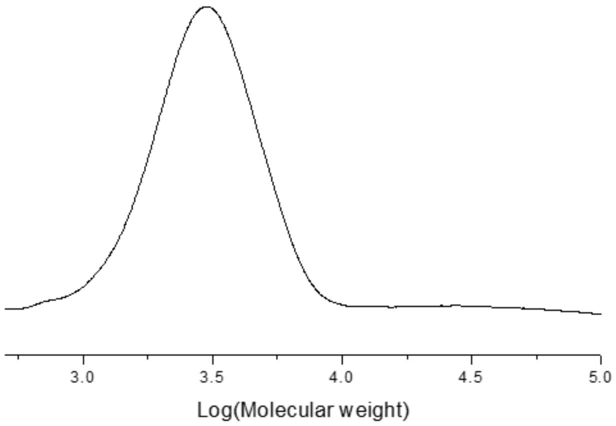


Figure S16. GPC trace of poly(PA-*alt*-LO) (entry 3 in Table 2; M_n = 2.78 kDa, Đ = 1.17).

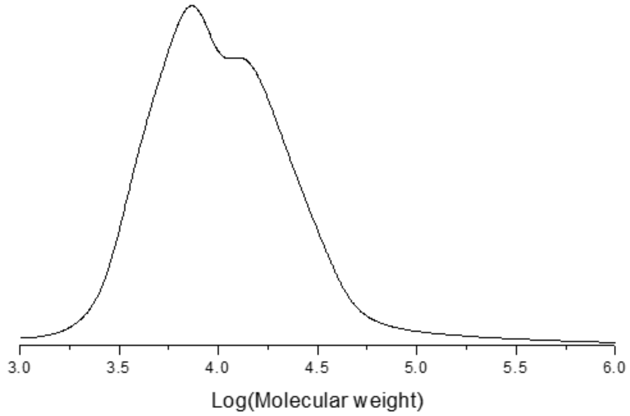


Figure S17. GPC trace of poly(MA-*co*-CHO) (entry 6 in Table 2; M_n = 7.75 kDa, Đ = 1.45).

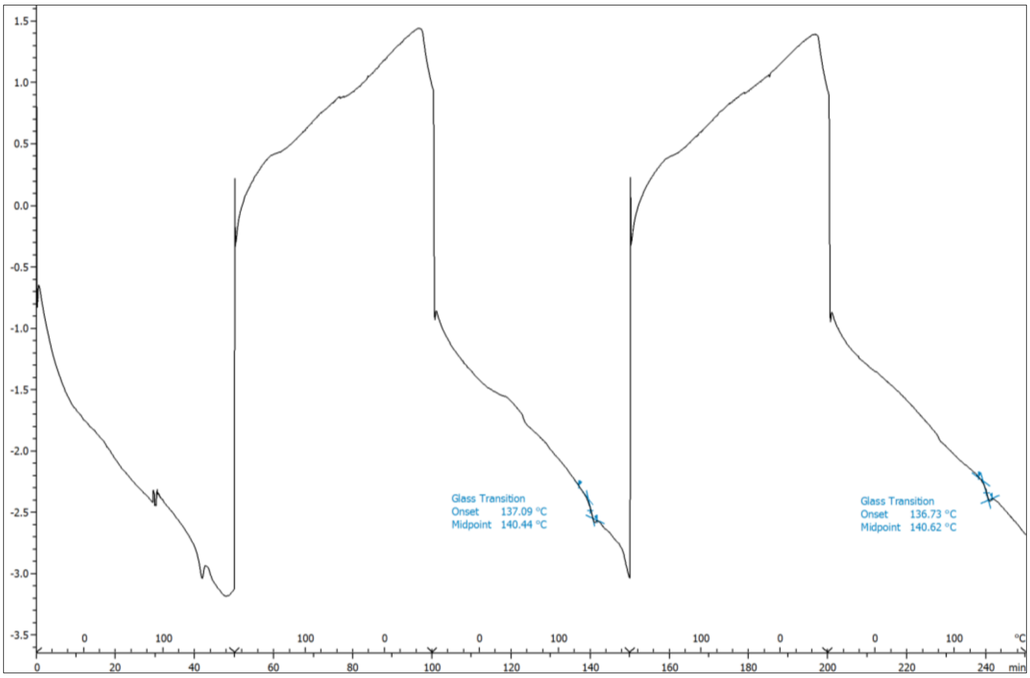


Figure S18. DSC thermogram of poly(PA-*alt*-CHO) (entry 1 in Table 1).

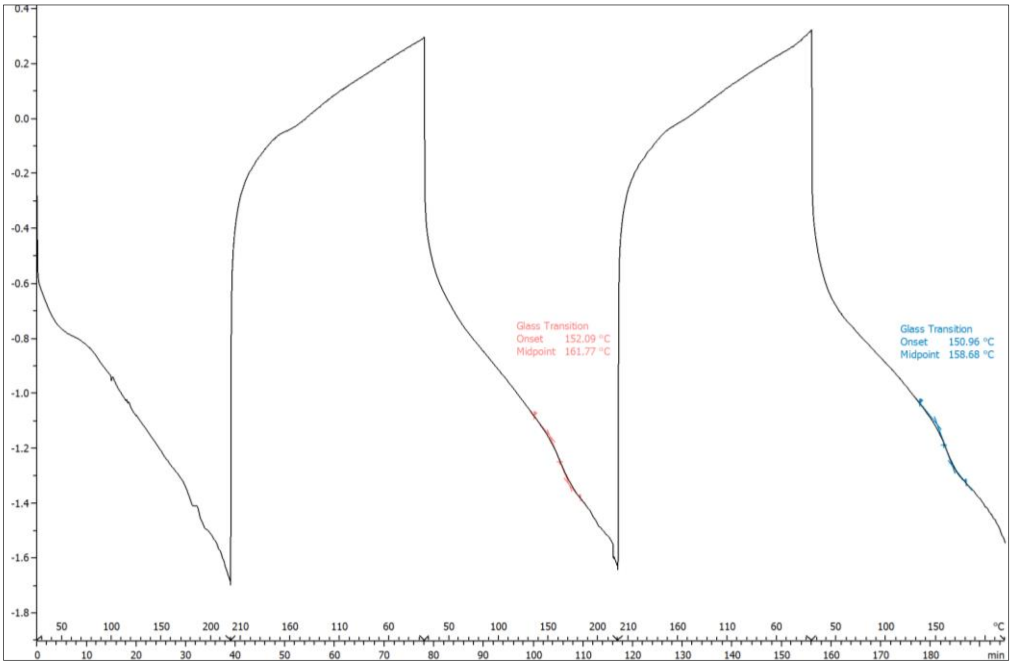


Figure S19. DSC thermogram of poly(NA-*alt*-CHO) (entry 1 in Table 2).

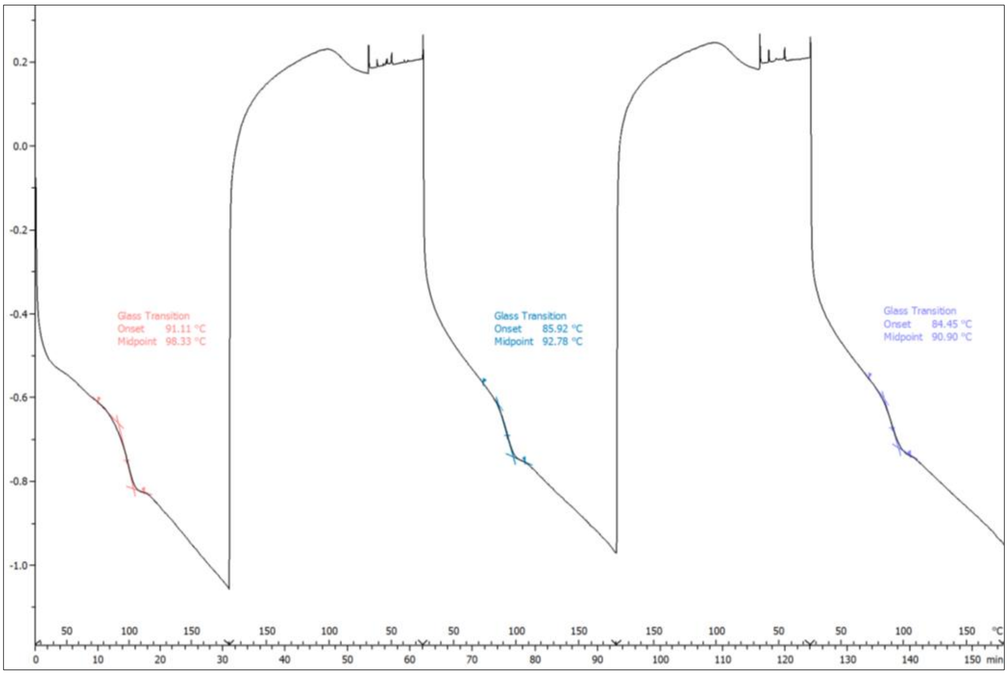


Figure S20. DSC thermogram of poly(PA-*alt*-LO) (entry 3 in Table 2).

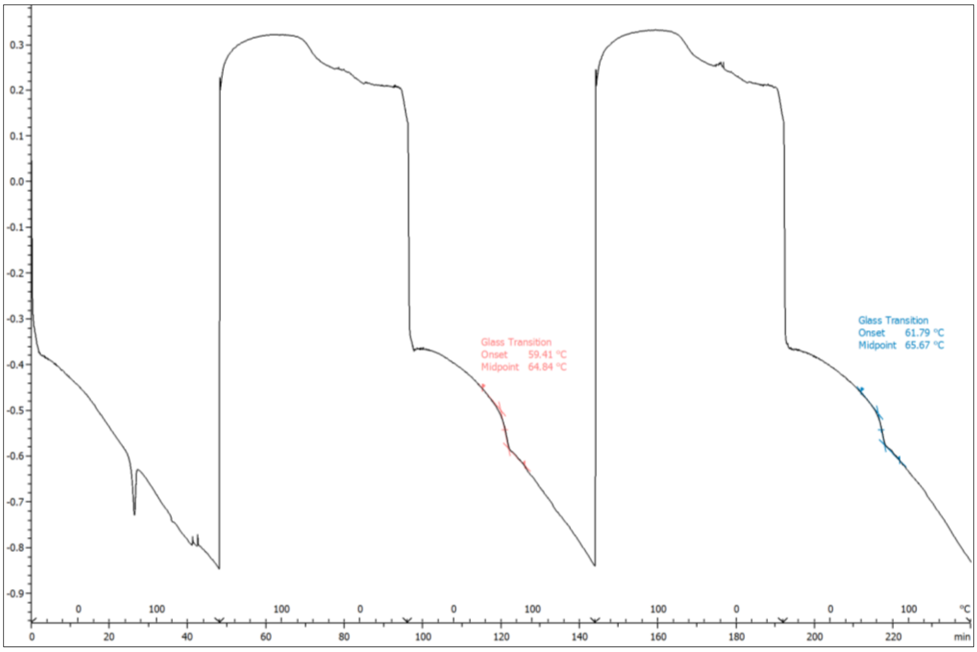
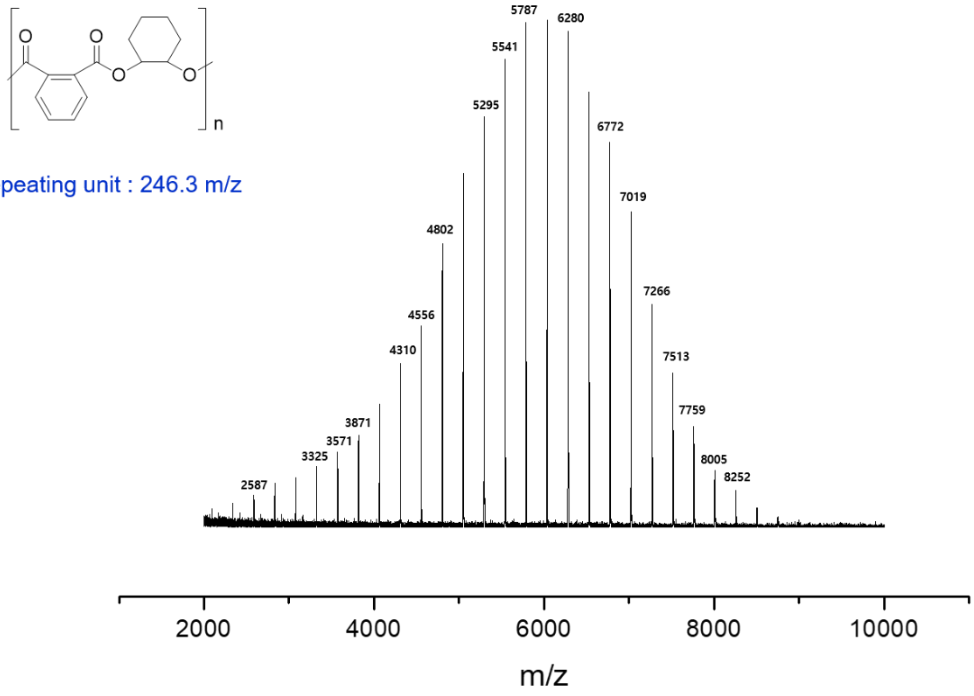


Figure S21. DSC thermogram of poly(MA-*co*-CHO) (entry 6 in Table 2).



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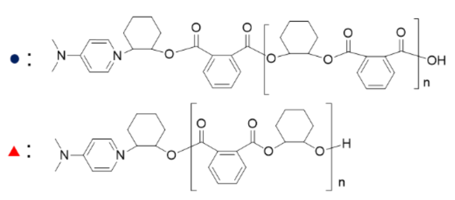

n = 11, M : 246.3 x 11 (repeat unit) + 98.15 (CHO) + 148.15 (PA) + 122.17 (DMAP) = 3077.77 (3078)

n = 12, M : 246.3 x 12 (repeat unit) + 122.17 (DMAP) + 98.15 (CHO) = 3175.92 (3176)

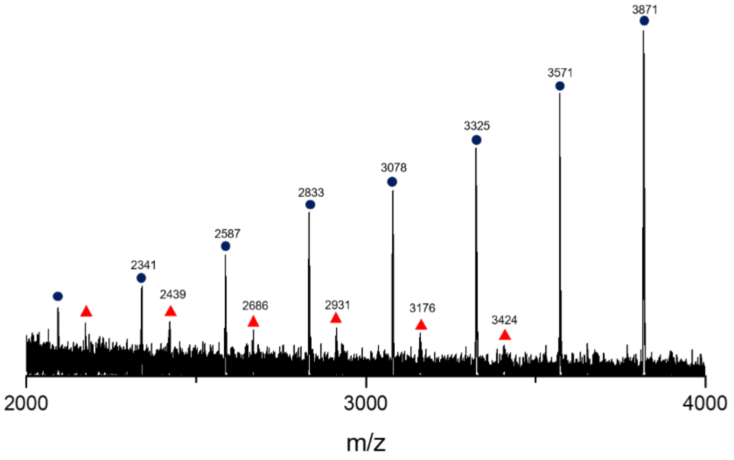

Figure S22. Representative MALDI-TOF MS analysis of poly(PA-*alt*-CHO) (entry 2 in Table 1).

Table S1. Control experiments of ROCOP using PA and CHO[a]

Entry	Cocatalyst (mmol)	Catalyst	[PA]:[CHO]	Time (h)	Conversion (%)[b]	Ester (%)[b]	M_n (kDa)[c]	Đ[c,d]	T_g (°C)[e]
2 (Table 1)	DMAP (0.025)	**1-Cr**	1:1	2	69	>99	9.67	1.12	134
S1	DMAP (0.025)	–	1:1	2	3	>99	–[f]	–[f]	–[f]
9 (Table 1)	PPNCl (0.005)	**1-Cr**	1:2	3	92	97	17.4	1.13	133
S2	PPNCl (0.005)	–	1:2	3	7	99	7.85	1.12	128

[a] General conditions: 4 mmol of PA, 0.005 mmol **1-Cr**, 100 °C, in a nitrogen atmosphere. [b] Determined by proton nuclear magnetic resonance (^1H NMR) analysis ($CDCl_3$); “Conversion” corresponds to the conversion of epoxides to polyester; “Ester” refers to the ratio of ester linkages in the product. [c] Determined by GPC in THF using polystyrene standards for calibration. [d] Polydispersity index ($Đ) = M_w/M_n$. [e] Determined by differential scanning calorimetry (DSC); the third cycle values are recorded. [f] No polymer was isolated.

Table S2. Control experiments of ROCOP using NA/CHO and PA/LO[a]

Entry	Anhydride	Epoxide	Cocatalyst	Catalyst	Temp. (°C)	Time (h)	Conversion (%)[b]	Ester (%)[b]	M_n (kDa)[c]	Đ[c,d]	T_g (°C)[e]
1(Table 2)[f]	NA	CHO	DMAP	**1-Cr**	100	72	44	>99	6.14	1.23	159
S3[f]	NA	CHO	DMAP	–	100	72	<1	–	–[g]	–[g]	–[g]
3(Table 2)	PA	LO	DMAP	**1-Cr**	130	24	98	>99	2.78	1.17	91
S4	PA	LO	DMAP	–	130	24	10	>99	–[g]	–[g]	–[g]

[a] General conditions: 4 mmol of anhydride, 8 mmol of epoxide, 0.005 mmol **1-Cr**, 0.025 mmol DMAP, in a nitrogen atmosphere. [b] Determined by proton nuclear magnetic resonance (^1H NMR) analysis ($CDCl_3$); “Conversion” corresponds to the conversion of epoxides to polyester; “Ester” refers to the ratio of ester linkages in the product. [c] Determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) using polystyrene standards for calibration. [d] Polydispersity index ($Đ) = M_w/M_n$. [e] Determined by differential scanning calorimetry (DSC); the third cycle values are recorded. [f] Toluene 2 mL was added. [g] No polymer was isolated.