Supporting Information

Polyester Nitrile *N*-oxides for Click Reactions Synthesized with Nitroalkane Precursors as the Initiator

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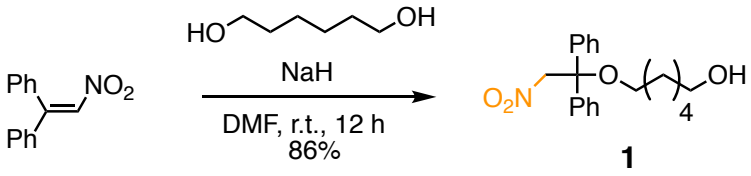
Contents

1. Experimental Section

1.1 Materials and instrument

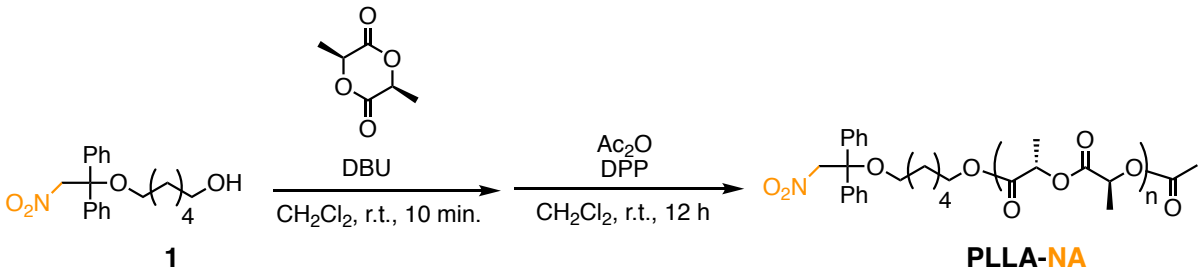
Dichloromethane was dehydrated by activated molecular sieve 4A. δ-Valerolactone (VL) (>98%, TCI) and ε-caprolactone (CL) were distilled over CaH_2 under reduced pressure. L-(-)-Lactide (LLA) (>98%, TCI), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) (>98%, TCI), phenyl isocyanate (>98%, TCI), triethylamine (Et_3N) (>98%, Wako), allyltrimethylsilane (>98%, TCI), acetic anhydride (Ac_2O) (>98%, TCI), diethyl phosphite (DPP) (>98%, TCI) and other commercially available solvents were used as received. 1,1-diphenylnitroethene was prepared according to literature.[S1] ^1H NMR (500 MHz) and ^{13}C NMR spectra (125 MHz) were recorded on a Bruker AVANCE III-HD 500 spectrometer using $CDCl_3$ as the solvent calibrated using residual undeuterated solvents or tetramethylsilane as the internal standard. FT-IR spectra were recorded on a JASCO FT/IR-230 spectrometer. FAB HR-MS were taken by JEOL JMS700 mass spectrometer at the Center for Advanced Materials Analysis, Tokyo Institute of Technology on request. Size exclusion chromatography (SEC) was carried out at 30 °C in $CHCl_3$ (0.85 mL/min) using a JASCO PU-2080 system equipped with a set of Shodex K-804 and Shodex K-805 columns. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of the obtained polymers were calculated on the basis of a polystyrene calibration. Preparative GPC was carried out using a HPLC LC-918 instrument by Japan Analytical Industry with a set of Megapak-Gel 201C and Shodex K-2002.5. TGA analyses were carried out on a Shimadzu TGA-50 instrument under N_2 atmosphere (flow rate of 50 mL/min) to determine 5% weight decomposition temperatures (T_{d5}) at which 5% weight loss was observed (heating rate of 10 °C/min). DSC analyses were carried out with a Shimadzu DSC-60 instrument at N_2 atmosphere (flow rate of 50 mL/min) with liquid N_2 as a refrigerant to determine a glass transition temperature (T_g) and melting points (T_m) (heating rate of 10 °C/min). MALDI-TOF mass spectra were determined on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (l = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. The sample polymer solution (1.0 mg/mL) was prepared in THF, and dithranol (the matrix) and sodium trifluoroacetate (cationizing agent) were dissolved in THF (20 and 1 mg/mL, respectively), and 50 μL of each solution was mixed prior to MALDI analysis.

1.2 Synthetic procedures and characterization data



Scheme S1. Synthesis of **1**

Sodium hydride (1.5 g, 60 mmol) was washed with hexane. After the remaining hexane was removed, dry DMF (40 mL) was added, followed by the dropwise addition of the solution of 1,6-hexanediol (7.1 g, 60 mmol) in dry DMF (10 mL) at 0 ºC. The resulting mixture was stirred at the same temperature for 1 h, and added to a solution of 1,1-diphenylnitroethene (4.1 g, 18 mmol) in dry DMF (10 mL). After stirring at room temperature for 12 h, the reaction was cold to 0 °C and quenched by a small amount of acetic acid. The mixture was diluted with dichloromethane, washed with 1.0 M HCl aq., water and brine, dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ethyl acetate: 3/1) to obtain **1** in 86% yield (5.9 g) as a colorless liquid; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.36–7.25 (m, 10H, Ph–H), 5.34 (s, 2H), 3.65–3.62 (m, 2H,), 3.36 (t, J = 4.2 Hz, 2H), 1.67–1.36 (m, 4H), 2.36 (br, 1H) ppm; ^{13}C NMR (125 MHz, 298 K, $CDCl_3$) δ 141.7, 128.3, 127.9, 126.5, 81.2, 79.8, 62.9, 32.6, 29.6, 25.8, 25.4 (C2) ppm; FAB-HRMS (*m/z*) calc'd for $C_{20}H_{26}NO_4$ $[M+H]^+$, 344.1862; found, 344.1869.



Scheme S2. Synthesis of **PLLA-NA**

DBU was added to a solution of **1** and LLA in dry CH_2Cl_2 under argon atmosphere, and the mixture was stirred for 10 min at room temperature. The resulting mixture was poured into ethanol/ hexane = 1/ 9 (v/ v) and collected the precipitate to obtain OH-terminated PLLA. Ac_2O, DPP and OH-terminated PLLA were dissolved in dry CH_2Cl_2 and the mixture was stirred for 12 h. The resulting mixture was poured into ethanol/ hexane = 1/ 9 (v/ v) and collected the precipitate to obtain **PLLA-NA** as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.38–7.25 (m, 10H), 5.36 (s, 2H), 5.22–5.13 (m, n × 2H), 4.15–4.10 (m, 2H), 3.36 (t, J = 4.0 Hz, 2H), 2.13 (s, 3H), 1.71–1.50 (m, n × 6H), 1.67–1.36 (m, 4H) ppm.

PLLA$_{20}$-NA ([LLA] / [**1**] =20, [M] / [DBU] = 100, [M] = 0.1 M)

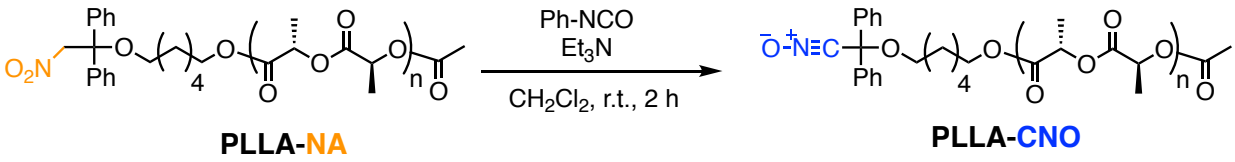
DBU (15 μL, 0.10 mmol), **1** (0.17 g, 0.50 mmol), LLA (1.4 g, 10 mmol), and dry CH_2Cl_2 (10 mL) were used for polymerization. Ac_2O (1.5 g, 15 mmol), DPP (0.33 g 1.5 mmol) and dry CH_2Cl_2 (5.0 mL) were used for acetylation. The precipitate was dried to give **PLLA$_{20}$-NA** in 95% yield (1.5 g); $M_{n(NMR)}$ 3300 g/mol, $DP_{n(NMR)}$ 20, $M_{n(SEC)}$ 4000 g/mol, PDI 1.12; T_g 43.4 °C; T_m 140 °C; T_{d5} 279 °C.

PLLA$_{51}$-NA ([LLA] / [**1**] =50, [M] / [DBU] = 100, [M] = 0.1 M)

DBU (37 μL, 0.25 mmol), **1** (0.17 g, 0.50 mmol), LLA (3.6 g, 25 mmol), and dry CH_2Cl_2 (25 mL) were used for polymerization. Ac_2O (1.5 g, 15 mmol), DPP (0.33 g, 1.5 mmol) and dry CH_2Cl_2 (5.0 mL) were used for acetylation. The precipitate was dried to give **PLLA$_{51}$-NA** in 98% yield (3.7 g); $M_{n(NMR)}$ 7700 g/mol, $DP_{n(NMR)}$ 51, $M_{n(SEC)}$ 9800 g/mol, PDI 1.08; T_g 49.1 °C; T_m 147 °C; T_{d5} 326 °C.

PLLA$_{98}$-NA ([LLA] / [**1**] =100, [M] / [DBU] = 100, [M] = 0.1 M)

DBU (37 μL, 0.25 mmol), **1** (86 mg, 0.25 mmol), LLA (3.6 g, 25 mmol), and dry CH_2Cl_2 (25 mL) were used for polymerization. Ac_2O (0.77 g, 7.5 mmol), DPP (0.18 g, 0.75 mmol) and dry CH_2Cl_2 (2.5 mL) were used for acetylation. The precipitate was dried to give **PLLA$_{98}$-NA** in 99% yield (3.7 g); $M_{n(NMR)}$ 14500 g/mol, $DP_{n(NMR)}$ 98, $M_{n(SEC)}$ 18700 g/mol, PDI 1.05; T_g 51.5 °C; T_m 150 °C; T_{d5} 332 °C.



Scheme S3. Synthesis of **PLLA-CNO**

To a solution of **PLLA-NA** and triethylamine in dry CH_2Cl_2 was added phenylisocyanate at room temperature, and the mixture was stirred for 2 h under argon atmosphere. After the consumption of **PLLA-NA**, generated phenylurea was removed by filtration and solvent was removed by evaporation. The crude was poured into ethanol/ hexane = 2/8 (v/ v) and collected the precipitate to obtain **PLLA-CNO** as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.42–7.36 (m, 10H), 5.22–5.13 (m, n × 2H), 4.15–4.10 (m, 2H), 3.45 (t, J = 4.0 Hz, 2H), 2.13 (s, 3H), 1.71–1.50 (m, n × 6H), 1.67–1.36 (m, 4H) ppm; IR (NaCl): ν 2995, 2943, 2877, 2275, 1758, 1453, 1382, 1363, 1309, 1270, 1213, 1184, 1130, 1097, 1047, 871, 757 cm^{-1}.

PLLA$_{20}$-CNO

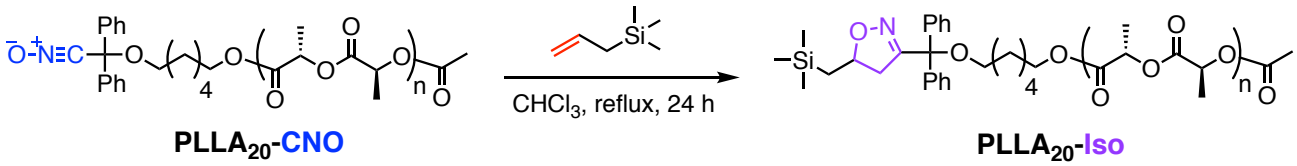
PLLA$_{20}$-NA (1.4 g, 0.44 mmol), phenylisocyanate (0.52 g, 4.4 mmol), triethylamine (0.66 g, 6.6 mmol), and dry CH_2Cl_2 (44 mL) were used for reaction. The precipitate was dried to give **PLLA$_{20}$-CNO** in 92% yield (1.3 g); $M_{n(NMR)}$ 3300 g/mol, $DP_{n(NMR)}$ 20, $M_{n(SEC)}$ 4000 g/mol, PDI 1.12; T_g 43.2 °C; T_m 140 °C; T_{d5} 276 °C.

PLLA$_{51}$-CNO

PLLA$_{51}$-NA (3.5 g, 0.47 mmol), phenylisocyanate (0.56 g, 4.7 mmol), triethylamine (0.72 g, 7.2 mmol), and dry CH_2Cl_2 (47 mL) were used for reaction. The precipitate was dried to give **PLLA$_{51}$-CNO** in 93% yield (3.4 g); $M_{n(NMR)}$ 7700 g/mol, $DP_{n(NMR)}$ 51, $M_{n(SEC)}$ 9800 g/mol, PDI 1.09; T_g 49.6°C; T_m 148 °C; T_{d5} 309 °C.

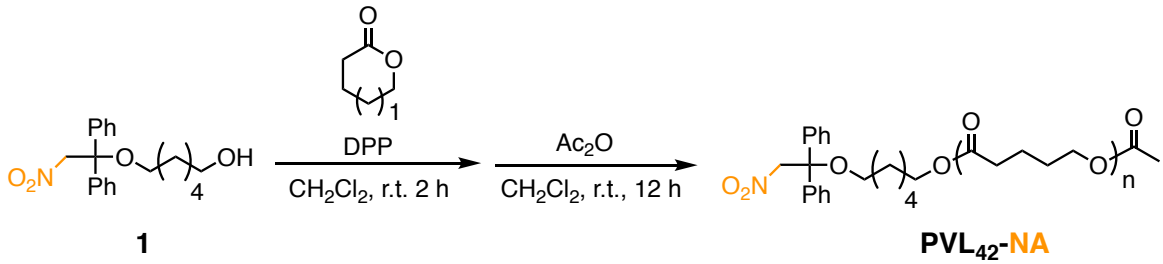
PLLA$_{98}$-CNO

PLLA$_{98}$-NA (3.5 g, 0.23 mmol), phenylisocyanate (0.27 g, 2.3 mmol), triethylamine (0.35 g, 3.5 mmol), and dry CH_2Cl_2 (23 mL) were used for reaction. The precipitate was dried to give **PLLA$_{98}$-CNO** in 93% yield (3.4 g); $M_{n(NMR)}$ 14500 g/mol, $DP_{n(NMR)}$ 98, $M_{n(SEC)}$ 18700 g/mol, PDI 1.08; T_g 52.6 °C; T_m 151 °C; T_{d5} 328 °C.



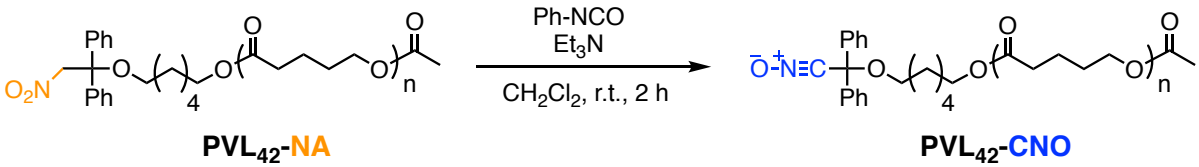
Scheme S4. Synthesis of **PLLA$_{20}$-Iso**

PLLA$_{20}$-CNO (0.17 g, 0.05 mmol) and allyltrimethylsilane (57 mg, 0.50 mmol) were dissolved in $CHCl_3$ (5.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, solvent and excess amount of allyltrimethylsilane were removed under reduced pressure to give the **PLLA$_{20}$-Iso** in >99% yield (0.18 g) as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.57–7.53 (m, 4H), 7.30–7.24 (m, 6H), 5.22–5.13 (m, n × 2H), 4.63–4.59 (m, 1H), 4.15–4.10 (m, 2H), 3.20 (t, J = 4.0 Hz, 2H), 2.91–2.82 (m, 1H), 2.40–2.30 (m, 1H), 2.13 (s, 3H), 1.71–1.50 (m, n × 6H), 1.67–1.36 (m, 4H), 1.13–1.06 (m, 1H), 0.86–0.80 (m, 1H), 0.00 (s, 9H) ppm; $DP_{n(NMR)}$ 20, $M_{n(NMR)}$ 3400 g/mol, $M_{n(SEC)}$ 4100 g/mol, PDI 1.12.



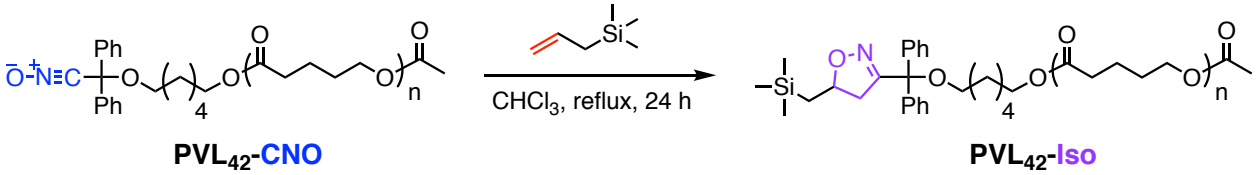
Scheme S5. Synthesis of **PVL$_{42}$-NA**

DPP (0.13 g, 0.50 mmol) was added to a solution of **1** (0.17 g, 0.50 mmol) and VL (2.5 g, 25 mmol) in dry CH_2Cl_2 (25 mL), the mixture was stirred for 2 h at room temperature. Then, Ac_2O (1.5 g, 15 mmol) was added to the mixture and further mixture was stirred for 12 h at same temperature. The resulting mixture was poured into ethanol/hexane = 1/9 (v/v) and collected the precipitate to obtain **PVL$_{42}$-NA** (1.8 g, 67%) as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.38–7.25 (m, 10H), 5.36 (s, 2H), 4.11–4.05 (m, n × 2H), 3.37 (t, J = 4.0 Hz, 2H), 2.49–2.35 (m, n × 2H), 2.05 (s, 3H), 1.73–1.65 (m, n × 4H), 1.67–1.36 (m, 4H) ppm; $M_{n(NMR)}$ 4600 g/mol, $DP_{n(NMR)}$ 42, $M_{n(SEC)}$ 7000 g/mol, PDI 1.18; T_m 50.9 °C; T_{d5} 262 °C.



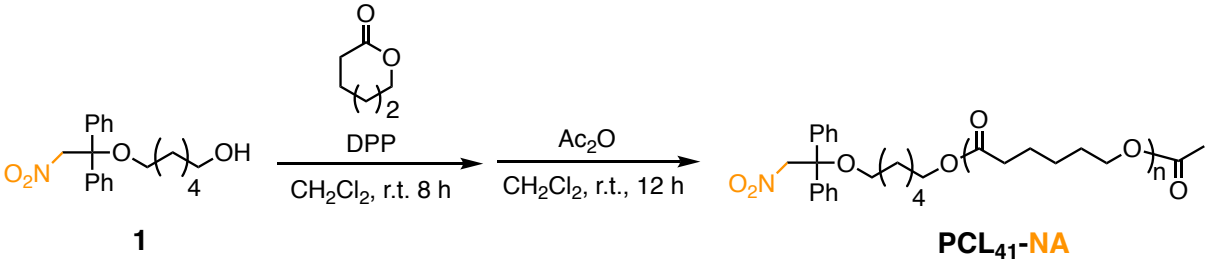
Scheme S6. Synthesis of **PVL$_{42}$-CNO**

To a solution of **PVL$_{42}$-NA** (1.5 g, 0.33 mmol) and triethylamine (0.50 g, 5.0 mmol) in dry CH_2Cl_2 (33 mL) was added phenylisocyanate (0.39 g, 3.3 mmol) at room temperature, and the mixture was stirred for 2 h under argon atmosphere. After the consumption of **PVL$_{42}$-NA**, generated phenylurea was removed by filtration and solvent was removed by evaporation. The crude was poured into ethanol/ hexane = 2/8 (v/ v) and collected the precipitate to obtain **PVL$_{42}$-CNO** (1.4 g, 94%) as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.42–7.35 (m, 10H), 4.11–4.05 (m, n × 2H), 3.45 (t, J = 4.0 Hz, 2H), 2.49–2.35 (m, n × 2H), 2.05 (s, 3H), 1.73–1.65 (m, n × 4H), 1.67–1.36 (m, 4H) ppm; IR (NaCl): ν 2960, 2894, 2874, 2275, 1732, 1474, 1461, 1423, 1402, 1383, 1325, 1259, 1180, 1106, 1067, 1047, 953, 916, 702 cm^{-1}; $M_{n(NMR)}$ 4600 g/mol, $DP_{n(NMR)}$ 42, $M_{n(SEC)}$ 7200 g/mol, PDI 1.21; T_m 51.6 °C; T_{d5} 316 °C.



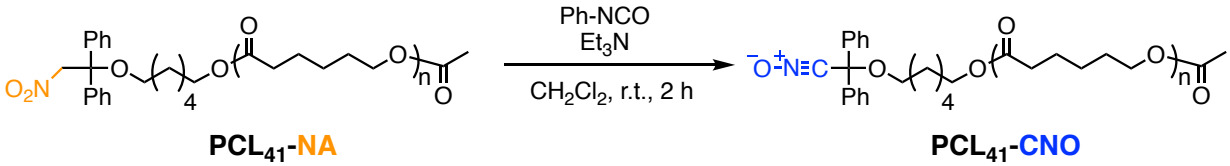
Scheme S7. Synthesis of **PVL$_{42}$-Iso**

PVL$_{42}$-CNO (0.23 g, 0.05 mmol) and allyltrimethylsilane (57 mg, 0.50 mmol) were dissolved in $CHCl_3$ (5.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, solvent and excess amount of allyltrimethylsilane were removed under reduced pressure to give the **PVL$_{42}$-Iso** in >99% yield (0.24 g) as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.57–7.53 (m, 4H), 7.30–7.24 (m, 6H), 4.63–4.59 (m, 1H), 4.11–4.05 (m, n × 2H), 3.20 (t, J = 4.0 Hz, 2H), 2.89–2.83 (m, 1H), 2.49–2.35 (m, n × 2H), 2.40–2.30 (m, 1H), 2.05 (s, 3H), 1.73–1.65 (m, n × 4H), 1.67–1.36 (m, 4H), 1.13–1.06 (m, 1H), 0.86–0.80 (m, 1H), 0.00 (s, 9H) ppm; DP$_{n(NMR)}$ 42, $M_{n(NMR)}$ 4700 g/mol, $M_{n(SEC)}$ 7300 g/mol, PDI 1.22.



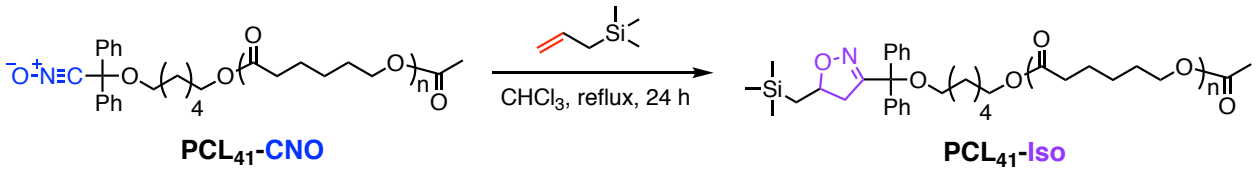
Scheme S8. Synthesis of **PCL$_{41}$-NA**

Diphenylphosphate (0.25 g, 1.0 mmol) was added to a solution of **1** (0.34 g, 1.0 mmol) and CL (5.7 g, 50 mmol) in dry CH_2Cl_2 (50 mL), the mixture was stirred for 8 h at room temperature. Then, Ac_2O (3.1 g, 30 mmol) was added to the mixture and further mixture was stirred for 12 h at same temperature. The resulting mixture was poured into ethanol/hexane = 1/9 (v/v) and collected the precipitate to obtain **PCL$_{41}$-NA** (4.8 g, 80%) as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.38–7.25 (m, 10H), 5.35 (s, 2H), 4.11–4.05 (m, n × 2H), 3.35 (t, J = 4.0 Hz, 2H), 2.49–2.35 (m, n × 2H), 2.04 (s, 3H), 1.73–1.65 (m, n × 4H), 1.40–1.32 (m, n × 2H), 1.67–1.36 (m, 4H) ppm; $M_{n(NMR)}$ 5100 g/mol, DP$_{n(NMR)}$ 41, $M_{n(SEC)}$ 7800 g/mol, PDI 1.09; T_m 51.1 °C; T_{d5} 319 °C.



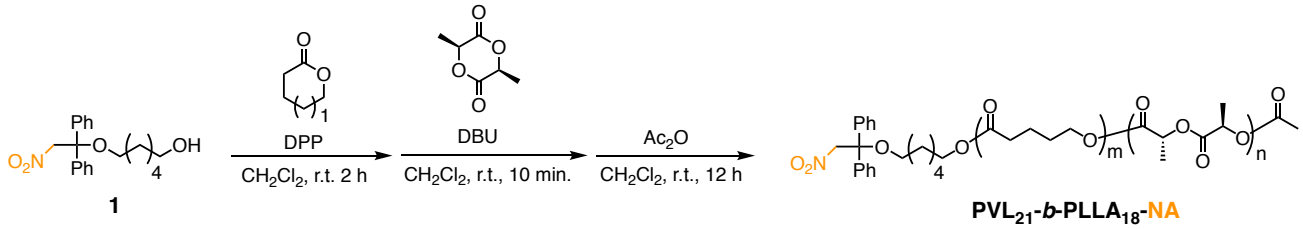
Scheme S9. Synthesis of **PCL$_{41}$-CNO**

To a solution of **PCL$_{41}$-NA** (2.0 g, 0.39 mmol) and triethylamine (0.59 g, 5.9 mmol) in dry CH_2Cl_2 (39 mL) was added phenylisocyanate (0.46 g, 3.9 mmol) at room temperature, and the mixture was stirred for 2 h under argon atmosphere. After the consumption of **PCL$_{41}$-NA**, generated phenylurea was removed by filtration and solvent was removed by evaporation. The crude was poured into ethanol/ hexane = 2/8 (v/ v) and collected the precipitate to obtain **PCL$_{41}$-CNO** (1.7 g, 86%) as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.42–7.35 (m, 10H), 4.11–4.05 (m, n × 2H), 3.45 (t, J = 4.0 Hz, 2H), 2.49–2.35 (m, n × 2H), 2.04 (s, 3H), 1.73–1.65 (m, n × 4H), 1.40–1.32 (m, n × 2H), 1.67–1.36 (m, 4H) ppm; IR (NaCl): ν 2943, 2910, 2864, 2275, 1724, 1470, 1419, 1398, 1365, 1294, 1242, 1189, 1108, 1065, 1048, 961, 935, 702 cm^{-1}; $M_{n(NMR)}$ 5100 g/mol, $DP_{n(NMR)}$ 41, $M_{n(SEC)}$ 7800 g/mol, PDI 1.10; T_m 52.0 °C; T_{d5} 332 °C.



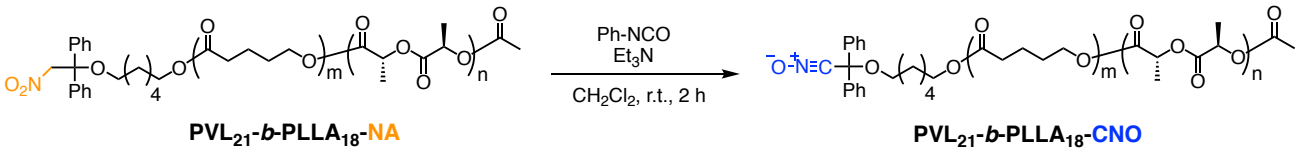
Scheme S10. Synthesis of **PCL$_{41}$-Iso**

PCL$_{41}$-CNO (0.24 g, 0.05 mmol) and allyltrimethylsilane (57 mg, 0.50 mmol) were dissolved in $CHCl_3$ (5.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, solvent and excess amount of allyltrimethylsilane were removed under reduced pressure to give the **PCL$_{41}$-Iso** in >99% yield (0.25 g) as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.57–7.53 (m, 4H), 7.30–7.24 (m, 6H), 4.64–4.60 (m, 1H), 4.11–4.05 (m, n × 2H), 3.21 (t, J = 4.0 Hz, 2H), 2.88–2.84 (m, 1H), 2.49–2.35 (m, n × 2H), 2.40–2.30 (m, 1H), 2.04 (s, 3H), 1.73–1.65 (m, n × 4H), 1.41–1.32 (m, n × 2H), 1.67–1.36 (m, 4H), 1.14–1.05 (m, 1H), 0.87–0.82 (m, 1H), 0.00 (s, 9H) ppm; $DP_{n(NMR)}$ 41, $M_{n(NMR)}$ 5200 g/mol, $M_{n(SEC)}$ 7900 g/mol, PDI 1.12.



Scheme S11. Synthesis of **PVL_{21}-*b*-$PLLA_{18}$-NA**

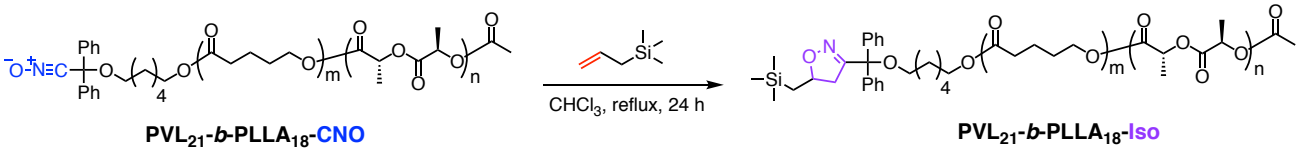
Diphenylphosphate (0.25 g, 1.0 mmol) was added to a solution of **1** (0.34 g, 1.0 mmol) and VL (2.0 g, 20 mmol) in dry CH_2Cl_2 (20 mL), the mixture was stirred for 2 h at room temperature. The resulting mixture was poured into ethanol/hexane = 1/9 (v/v) and collected the precipitate to obtain **PVL_{21}-NAOH**. Subsequently, DBU (14 mg, 0.09 mmol) was added to a solution of **PVL_{21}-NAOH** (1.1 g, 0.45 mmol) and LLA (1.2 g, 9.0 mmol) in CH_2Cl_2 (9.0 mL), the mixture was stirred for 10 min at room temperature. The resulting mixture was poured into ethanol/ hexane = 1/ 9 (v/ v) and collected the precipitate. Ac_2O (1.4 g, 14 mmol), DPP (0.34 g, 1.4 mmol) and obtained polymer were dissolved in CH_2Cl_2 (9.0 mL) and the mixture was stirred for 12 h. The resulting mixture was poured into ethanol/ hexane = 1/ 9 (v/ v) and collected the precipitate to obtain **PVL_{21}-*b*-$PLLA_{18}$-NA** in 44% yield (2.3 g) as a white powder; δ 7.38–7.25 (m, 10H), 5.36 (s, 2H), 5.22–5.13 (m, n × 2H), 4.11–4.05 (m, n × 2H), 3.35 (t, J = 4.0 Hz, 2H), 2.49–2.35 (m, n × 2H), 2.13 (s, 3H), 1.73–1.65 (m, n × 4H), 1.71–1.50 (m, n × 6H), 1.67–1.36 (m, 4H) ppm; $M_{n(NMR)}$ 5100 g/mol, $DP_{n(NMR,\ PVL)}$ 21, $DP_{n(NMR,\ PLLA)}$ 18, $M_{n(SEC,\ \textbf{PVL-NAOH})}$ 4800 g/mol, $M_{n(SEC)}$ 14600 g/mol, $PDI_{(\textbf{PVL-NAOH})}$ 1.22, PDI 1.12; T_m 141 °C; T_{d5} 202 °C.



PVL$_{21}$-*b*-PLLA$_{18}$-NA **PVL$_{21}$-*b*-PLLA$_{18}$-CNO**

Scheme S12. Synthesis of **PVL$_{21}$-*b*-PLLA$_{18}$-CNO**

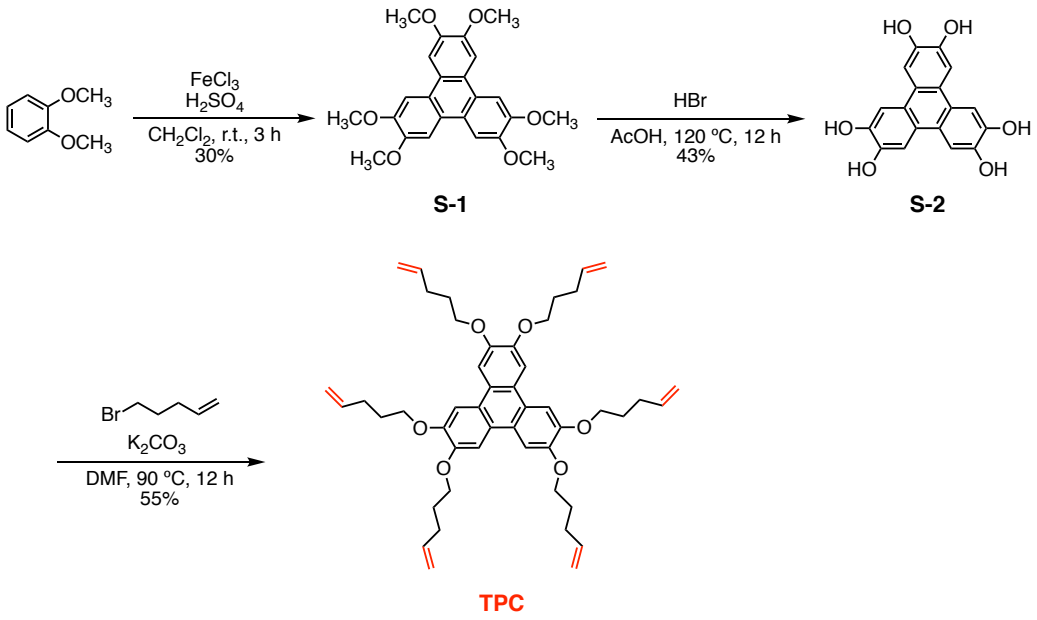
To a solution of **PCL$_{21}$-*b*-PLLA$_{18}$-NA** (1.9 g, 0.37 mmol) and triethylamine (0.57 g, 5.6 mmol) in dry CH_2Cl_2 (37 mL) was added phenylisocyanate (0.45 g, 3.7 mmol) at room temperature and the mixture was stirred for 2 h under argon atmosphere. After the consumption of **PCL$_{21}$-*b*-PLLA$_{18}$-NA**, generated phenylurea was removed by filtration and solvent was removed by evaporation. The crude was poured into ethanol/ hexane = 2/8 (v/ v) and collected the precipitate to obtain **PCL$_{21}$-*b*-PLLA$_{18}$-CNO** (1.7 g, 86%) as a white powder; δ 7.42–7.35 (m, 10H), 5.22–5.13 (m, n × 2H), 4.11–4.05 (m, n × 2H), 3.46 (t, J = 4.0 Hz, 2H), 2.49–2.35 (m, n × 2H), 2.13 (s, 3H), 1.73–1.65 (m, n × 4H), 1.71–1.50 (m, n × 6H), 1.67–1.36 (m, 4H) ppm; IR (NaCl): ν 2997, 2947, 2897, 2275, 1758, 1735, 1455, 1420, 1385, 1358, 1316, 1294, 1268, 1246, 1213, 1185, 1132, 1094, 1046, 960, 872, 756, 703 cm^{-1}; $M_{n(NMR)}$ 5100 g/mol, DP$_{n(NMR, PVL)}$ 21, DP$_{n(NMR, PLLA)}$ 18, $M_{n(SEC)}$ 14700 g/mol, PDI 1.14; T_m 142 °C; T_{d5} 315 °C.



PVL$_{21}$-*b*-PLLA$_{18}$-CNO **PVL$_{21}$-*b*-PLLA$_{18}$-Iso**

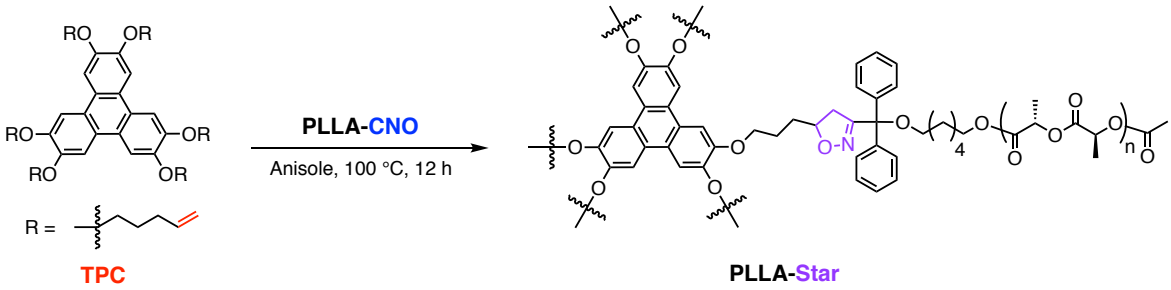
Scheme S13. Synthesis of **PVL$_{21}$-*b*-PLLA$_{18}$-Iso**

PVL$_{21}$-*b*-PLLA$_{18}$-CNO (0.15 g, 0.03 mmol) and allyltrimethylsilane (34 mg, 0.30 mmol) were dissolved in $CHCl_3$ (3.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, solvent and excess amount of allyltrimethylsilane were removed under reduced pressure to give **PVL$_{21}$-*b*-PLLA$_{18}$-Iso** in >99% yield (0.16 g) as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.57–7.53 (m, 4H), 7.30–7.24 (m, 6H), 5.21–5.11 (m, n × 2H), 4.64–4.60 (m, 1H), 4.10–4.05 (m, n × 2H), 3.21 (t, J = 4.0 Hz, 2H), 2.88–2.84 (m, 1H), 2.48–2.30 (m, n × 2H), 2.40–2.30 (m, 1H), 2.13 (s, 3H), 1.71–1.50 (m, n × 6H), 1.73–1.65 (m, n × 4H), 1.67–1.36 (m, 4H), 1.14–1.05 (m, 1H), 0.87–0.82 (m, 1H), 0.00 (s, 9H) ppm; $M_{n(NMR)}$ 5200 g/mol, DP$_{n(NMR, PVL)}$ 21, DP$_{n(NMR, PLLA)}$ 18, $M_{n(SEC)}$ 15000 g/mol, PDI 1.14.



Scheme S14. Synthesis of **TPC**

TPC was synthesized according to literature.[S2] **TPC** (1.1 g, 1.4 mmol) was obtained in 7.1 % overall yield (3 steps) as a brown solid; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.83 (s, 6H), 5.85–5.76 (m, 6H), 5.03–4.93 (m, 12H), 4.25 (d, J = 6.5 Hz, 12H), 2.40–2.33 (m, 12H), 2.10–2.00 (m, 12H) ppm.



Scheme S15. Synthesis of **PLLA-star**

A solution of **PLLA-CNO** and **TPC** in anisole was stirred at 100 ºC for 12 h. The reaction mixture was poured into excess amount of hexane. The crude was purified by preparative GPC, and obtained polymer was precipitated into excess amount of hexane to obtain **PLLA-star** as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.77 (s, 6H), 7.55–7.53 (m, 24H), 7.30–7.23 (m, 36H), 5.22–5.11 (m, n × 12H), 4.63–4.59 (m, 6H), 4.15–4.10 (m, 12H), 4.27–4.07 (m, 12H), 3.21–3.17 (m, 12H), 2.91–2.82 (m, 6H), 2.40–2.30 (m, 6H), 2.13 (s, 18H), 2.40–2.33 (m, 12H), 2.10–2.00 (m, 12H), 1.71–1.50 (m, n × 36H), 1.67–1.36 (m, 24H), 1.13–1.06 (m, 6H), 0.86–0.80 (m, 6H) ppm; IR (NaCl): ν 2995, 2943, 2877, 1759, 1517, 1452, 1436, 1382, 1363, 1344, 1309, 1270, 1250, 1213, 1184, 1145, 1097, 1169, 1047, 960, 871, 755, 705 cm^{-1}.

PLLA$_{20}$-star (run 1 in Table 3)

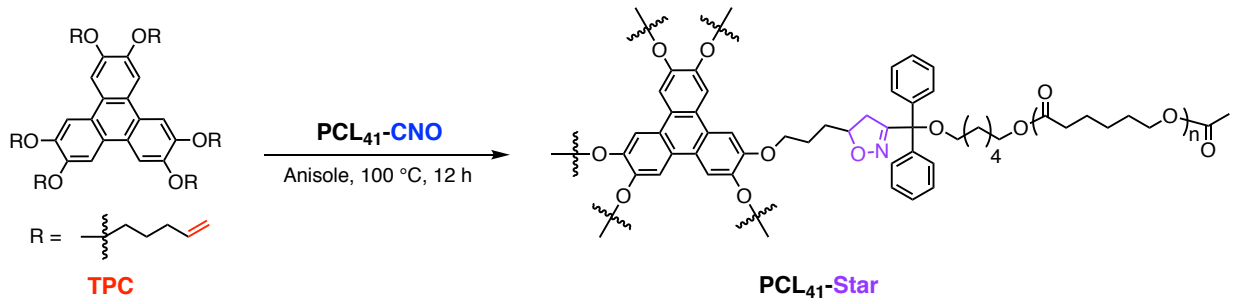
PLLA$_{20}$-CNO (0.33 g, 0.10 mmol), **TPC** (7.3 mg, 10 μmol) and anisole (10 mL) were used for reaction. The conversion was >99% determined by ^{1}H NMR. After the purification, the precipitate was dried to give **PLLA$_{20}$-star** in 61% yield (0.13 g); $M_{n(SEC)}$ 23600 g/mol, PDI 1.07; T_g 44.1 °C; T_m 138 °C; T_{d5} 283 °C.

PLLA$_{51}$-star (run 2 in Table 3)

PLLA$_{51}$-CNO (0.77 g, 0.10 mmol), **TPC** (7.3 mg, 10 μmol) and anisole (10 mL) were used for reaction. The conversion was >99% determined by ^{1}H NMR. After the purification, the precipitate was dried to give **PLLA$_{51}$-star** in 65% yield (0.31 g); $M_{n(SEC)}$ 58800 g/mol, PDI 1.07; T_g 51.2 °C; T_m 142 °C; T_{d5} 311 °C.

PLLA$_{98}$-star (run 3 in Table 3)

PLLA$_{98}$-CNO (0.72 g, 0.05 mmol), **TPC** (3.7 mg, 5.0 μmol) and anisole (5.0 mL) were used for reaction. The conversion was >99% determined by ^{1}H NMR. After the purification, the precipitate was dried to give **PLLA$_{98}$-star** in 60% yield (0.26 g); $M_{n(SEC)}$ 99600 g/mol, PDI 1.05; T_g 54.2 °C; T_{d5} 331 °C.



Scheme S16. Synthesis of **PCL$_{41}$-star**

A solution of **PCL$_{41}$-CNO** and **TPC** in anisole was stirred at 100 ºC for 12 h. The reaction mixture was poured into excess amount of hexane. The crude was purified by preparative GPC, and obtained polymer was precipitated into excess amount of hexane to obtain **PCL$_{41}$-star** as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.77 (s, 6H), 7.54–7.53 (m, 24H), 7.30–7.23 (m, 36H), 4.63–4.59 (m, 6H), 4.15–4.10 (m, 12H), 4.11–4.05 (m, n × 12H), 4.27–4.07 (m, 12H), 3.21–3.17 (m, 12H), 2.91–2.82 (m, 6H), 2.49–2.35 (m, n × 12H), 2.40–2.30 (m, 6H), 2.04 (s, 18H), 2.40–2.33 (m, 12H), 2.10–2.00 (m, 12H), 1.73–1.65 (m, n × 4H), 1.67–1.36 (m, 24H), 1.40–1.32 (m, n × 12H), 1.67–1.3 (m, 6H), 0.86–0.80 (m, 6H) ppm; IR (NaCl): ν 2943, 2910, 2864, 1725, 1517, 1470, 1437, 1420, 1398, 1367, 1294, 1254, 1187, 1114, 1065, 1048, 959, 935, 754, 704 cm^{-1}.

PCL$_{41}$-star (run 4 in Table 3)

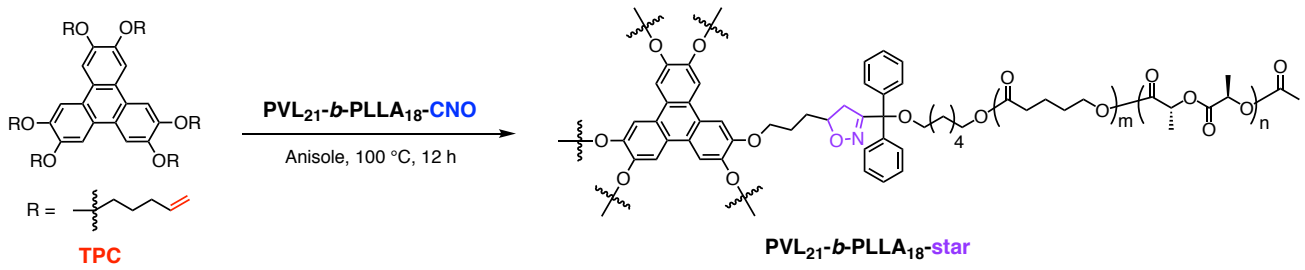
PCL$_{41}$-CNO (0.51 g, 0.10 mmol), **TPC** (7.3 mg, 10 μmol) and anisole (10 mL) were used for reaction. The conversion was >99% determined by ^{1}H NMR. After the purification, the precipitate was dried to give **PCL$_{41}$-star** in 70% yield (0.22 g); $M_{n\,(SEC)}$ 43700 g/mol, PDI 1.06; T_m 48.1 °C; T_{d5} 322 °C.

PCL$_{41}$-star (run 5 in Table 3)

The reaction was carried out for 1 h. The conversion was 45% determined by ^{1}H NMR.

PCL$_{41}$-star (Solvent-free reaction, run 6 in Table 3)

PCL$_{41}$-CNO (0.51 g, 0.10 mmol) and **TPC** (7.3 mg, 10 μmol) were heated at 100 ºC for 1 h. The conversion was >99% determined by ^{1}H NMR.



Scheme S17. Synthesis of **PVL$_{21}$-*b*-PLLA$_{18}$-star** (run 7 in Table 3)

A solution of **PVL$_{21}$-*b*-PLLA$_{18}$-CNO** (0.51 g, 0.10 mmol) and **TPC** (7.3 mg, 0.01 mmol) in anisole (10 mL) was stirred at 100 ºC for 12 h. The reaction mixture was poured into excess amount of hexane. The crude was purified by preparative GPC, and obtained polymer was precipitated into excess amount of hexane to obtain **PVL$_{21}$-*b*-PLLA$_{18}$-star** (0.17 g) in 54% yield as a white powder; ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) δ 7.77 (s, 6H), 7.54–7.53 (m, 24H), 7.30–7.23 (m, 36H), 5.22–5.11 (m, n × 12H), 4.63–4.59 (m, 6H), 4.15–4.10 (m, 12H), 4.10–4.05 (m, n × 12H), 4.27–4.07 (m, 12H), 3.21–3.17 (m, 12H), 2.91–2.82 (m, 6H), 2.48–2.30 (m, n × 12H), 2.40–2.30 (m, 6H), 2.13 (s, 18H), 2.40–2.33 (m, 12H), 2.10–2.00 (m, 12H), 1.73–1.65 (m, n × 4H), 1.71–1.50 (m, n × 36H), 1.67–1.36 (m, 24H), 1.41–1.32 (m, n × 12H), 1.13–1.06 (m, 6H), 0.86–0.80 (m, 6H) ppm; IR (NaCl): ν 2996, 2943, 2897, 1759, 1734, 1517, 1455, 1436, 1420, 1385, 1350, 1316, 1288, 1251, 1213, 1185, 1169, 1132, 1094, 1052, 961, 872, 755, 705 cm^{-1}; $M_{n\,(SEC)}$ 55900 g/mol, PDI 1.04; T_m 137 °C; T_{d5} 298 °C.

2. *Spectrum data of new compounds*

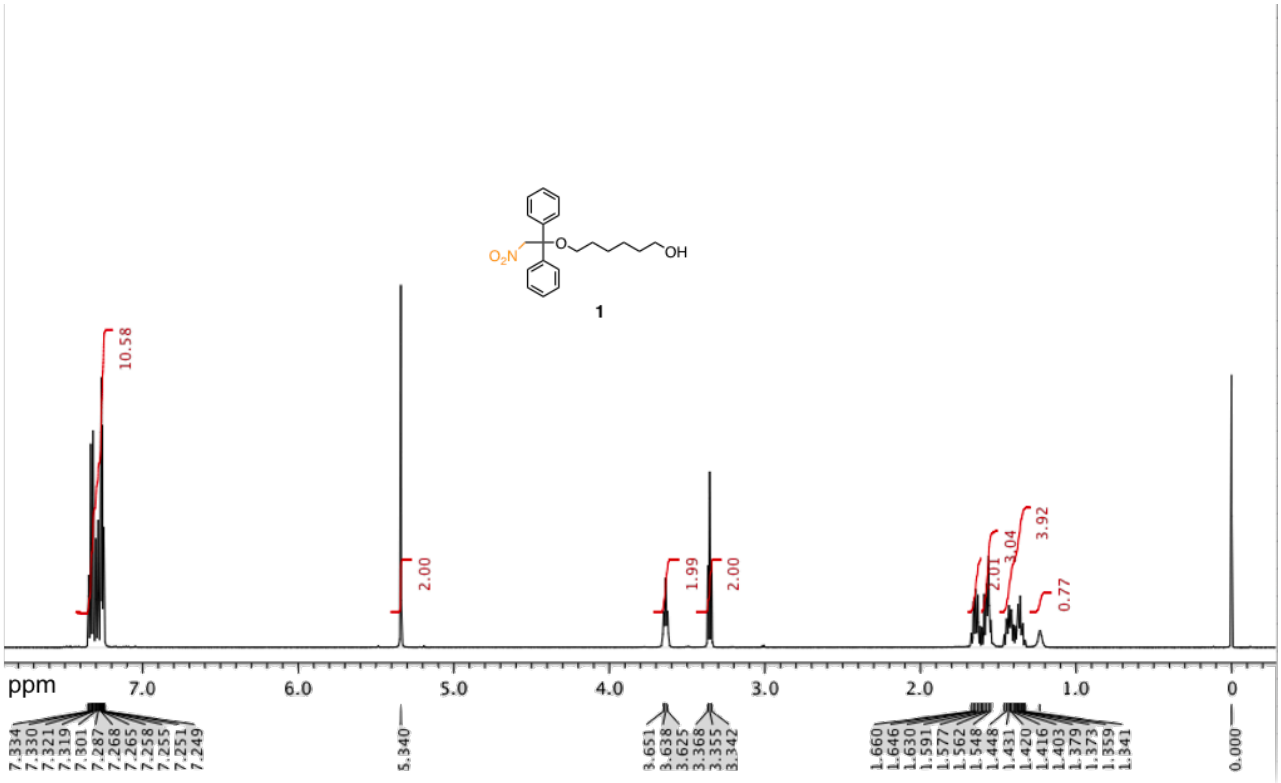


Figure S1. ^{1}H NMR spectrum of **1** (500 MHz, 298 K, $CDCl_3$)

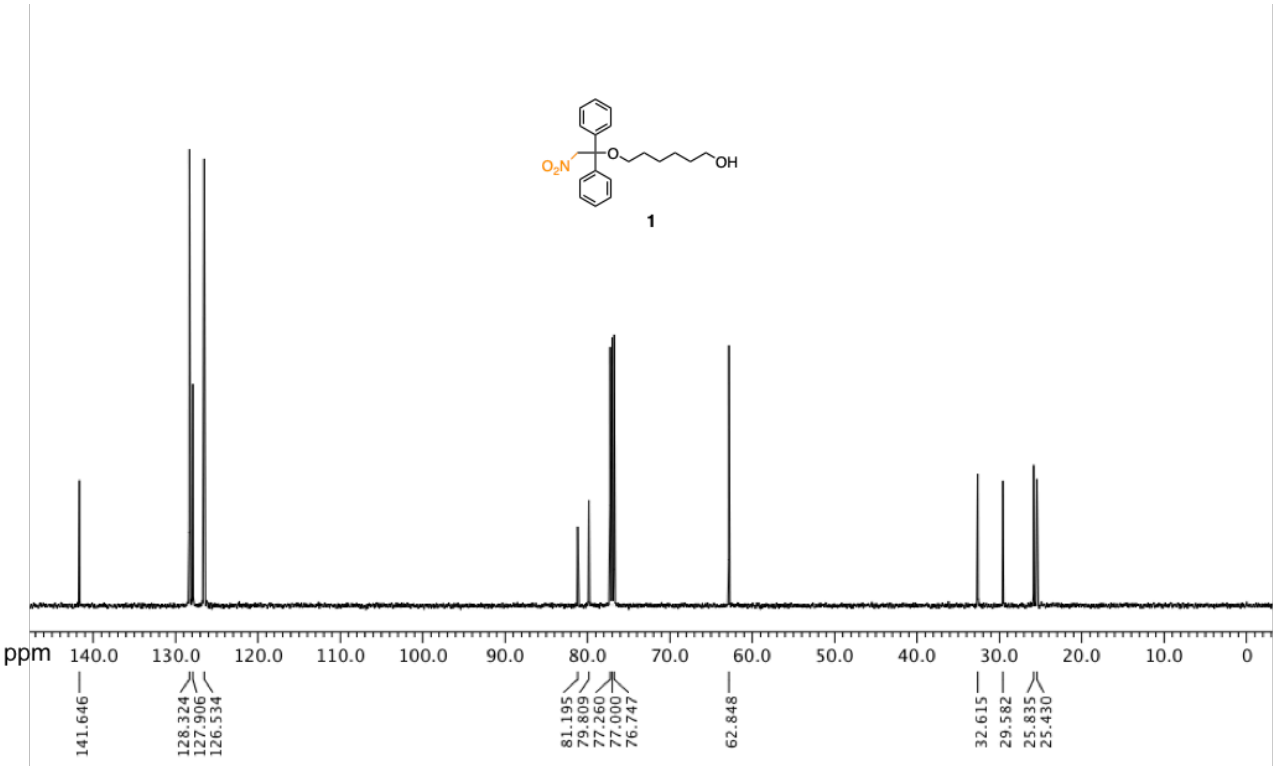


Figure S2. ^{13}C NMR spectrum of **1** (125 MHz, 298 K, $CDCl_3$)

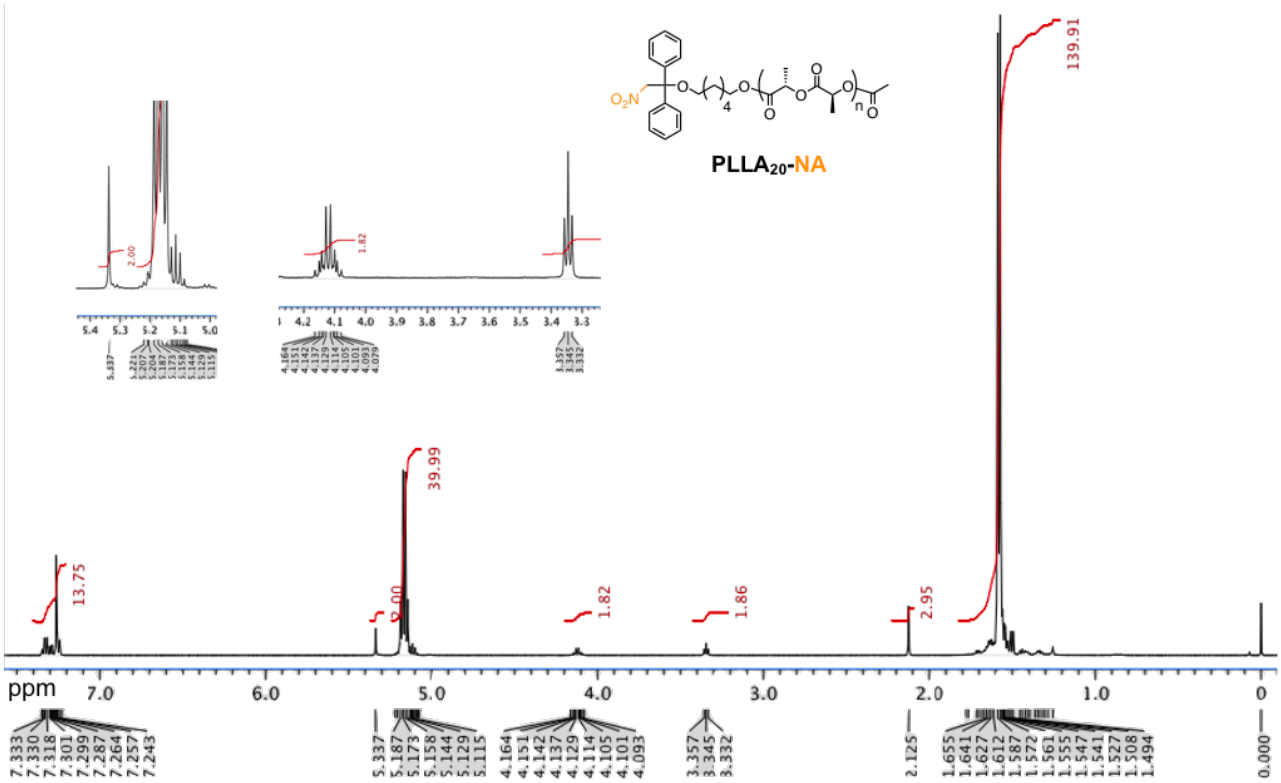


Figure S3. ^{1}H NMR spectrum of **PLLA$_{20}$-NA** (500 MHz, 298 K, $CDCl_3$)

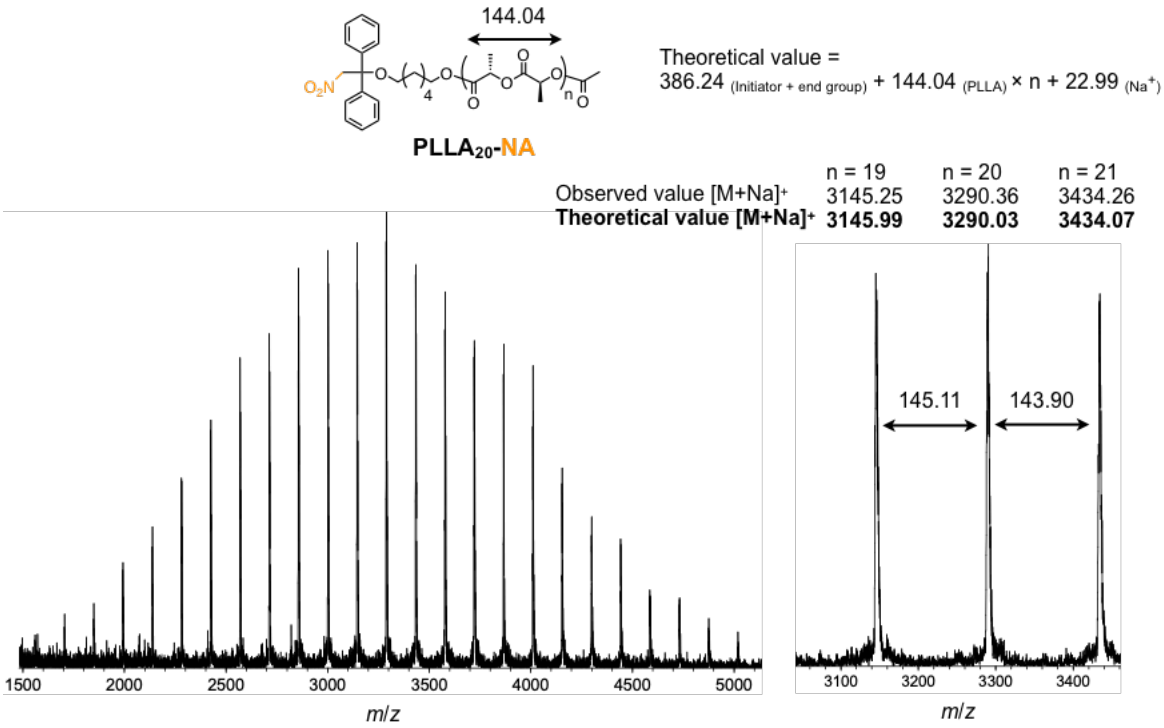


Figure S4. MALDI-TOF MS spectrum of **PLLA$_{20}$-NA** (marix: dithranol)

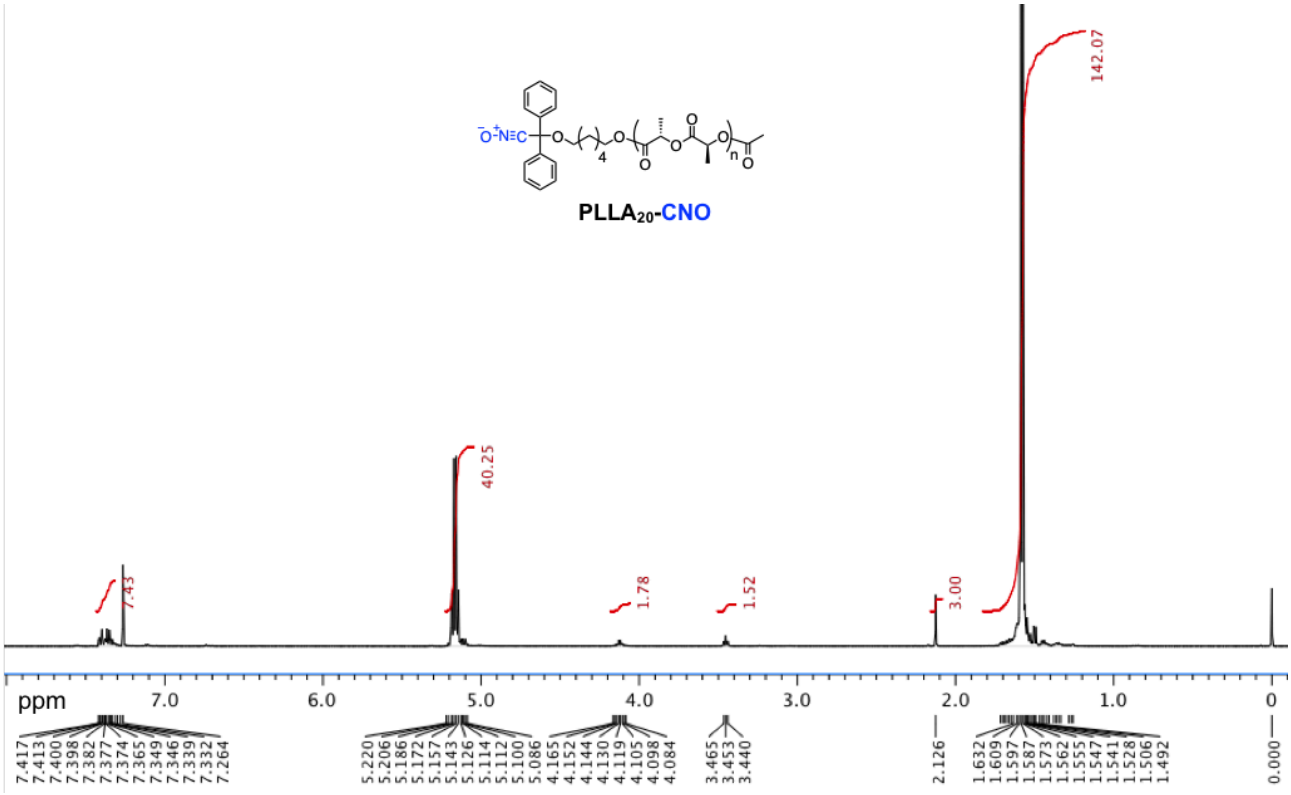


Figure S5. ^{1}H NMR spectrum of **PLLA$_{20}$-CNO** (500 MHz, 298 K, $CDCl_3$)

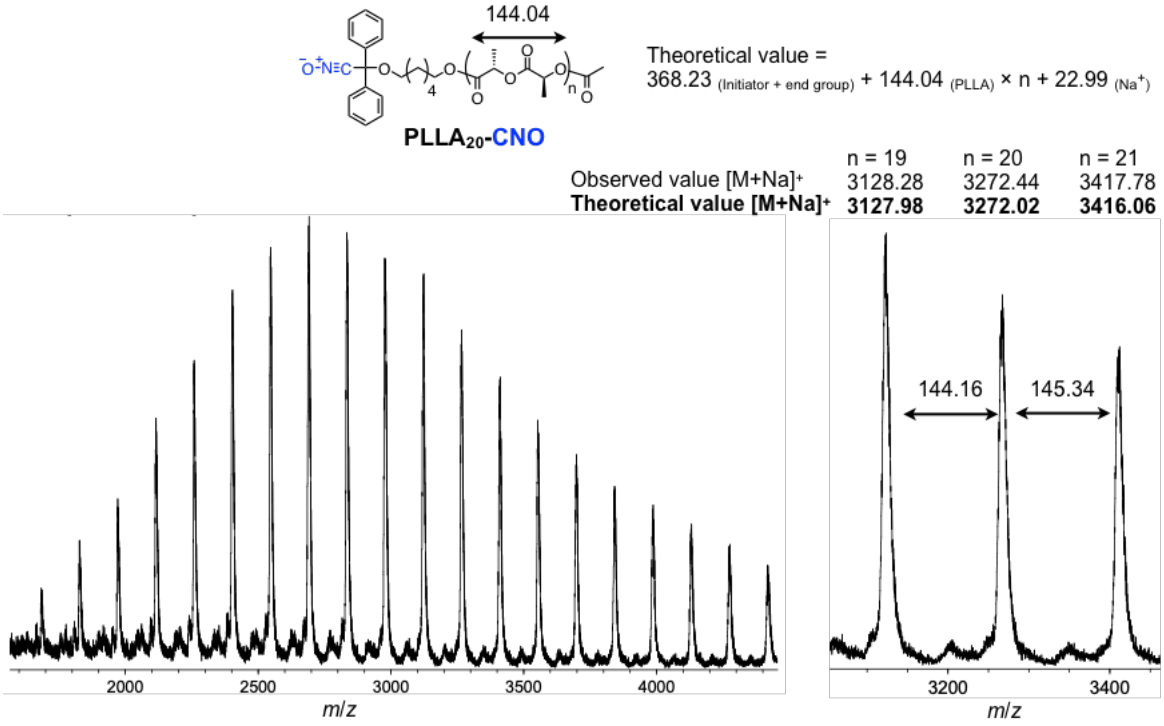


Figure S6. MALDI-TOF MS spectrum of **PLLA$_{20}$-CNO** (marix: dithranol)

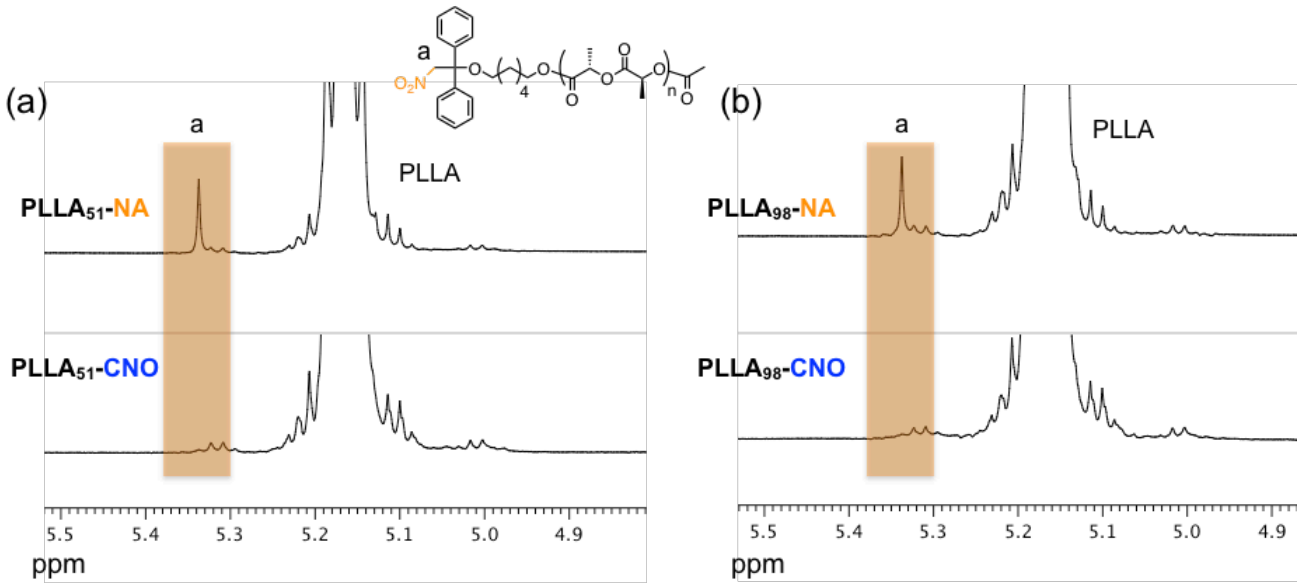
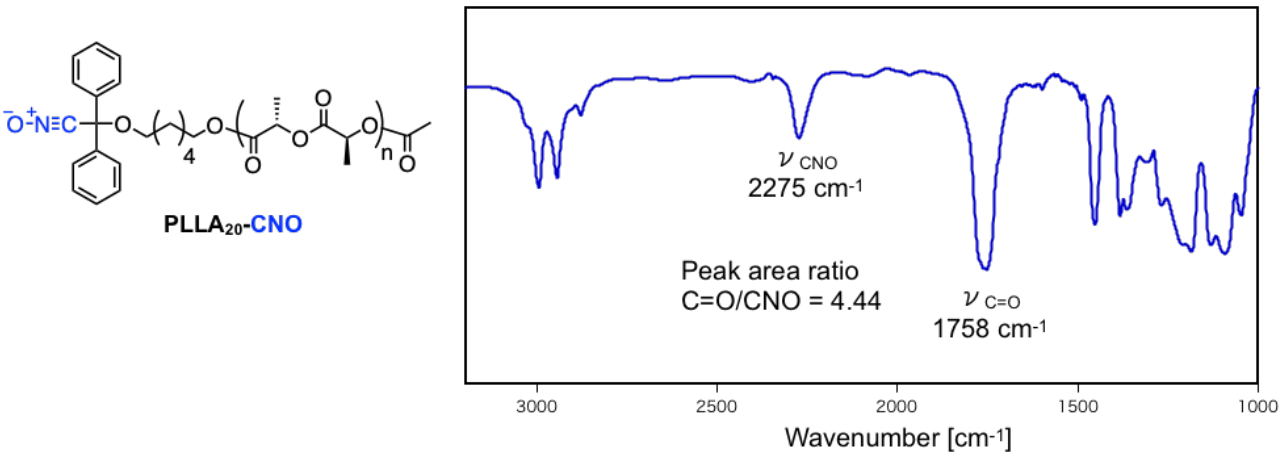


Figure S7. Partial ^{1}H NMR spectra of (a) **PLLA$_{51}$-NA**, **PLLA$_{51}$-CNO** and (b) **PLLA$_{98}$-NA**, **PLLA$_{98}$-CNO** (500 MHz, 298 K, $CDCl_3$)

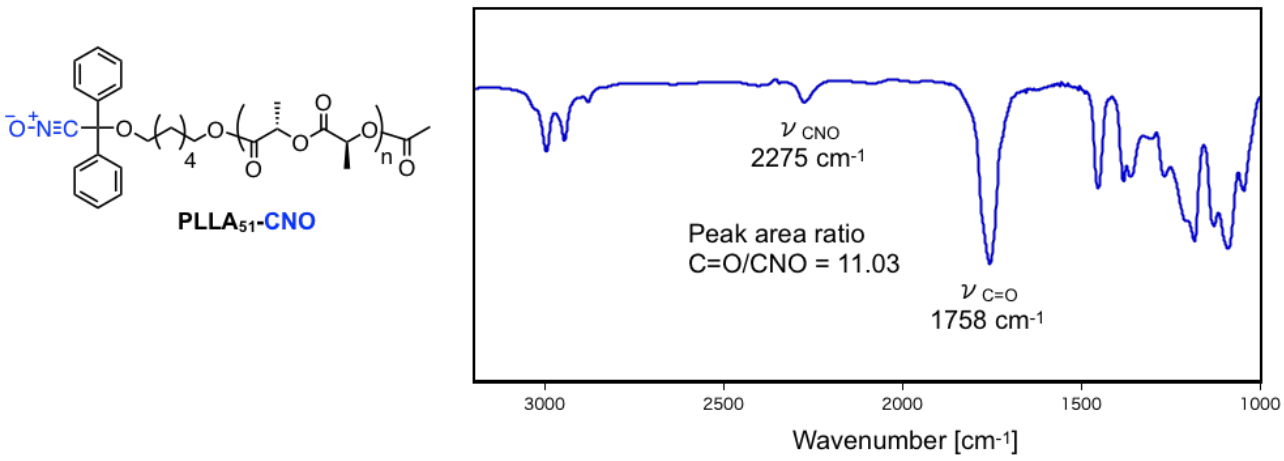


PLLA$_{20}$-CNO (20 mer) : C=O/CNO = 4.44, conversion (^{1}H NMR) : >99%

When the conversion of nitroalkane is >99%, the peak area ratio of **PLLA$_{51}$-CNO** and **PLLA$_{98}$-CNO** (theoretical) are assessed as below;

PLLA$_{51}$-CNO (51 mer) : C=C/CNO = 11.32
PLLA$_{98}$-CNO (98 mer) : C=C/CNO = 21.75

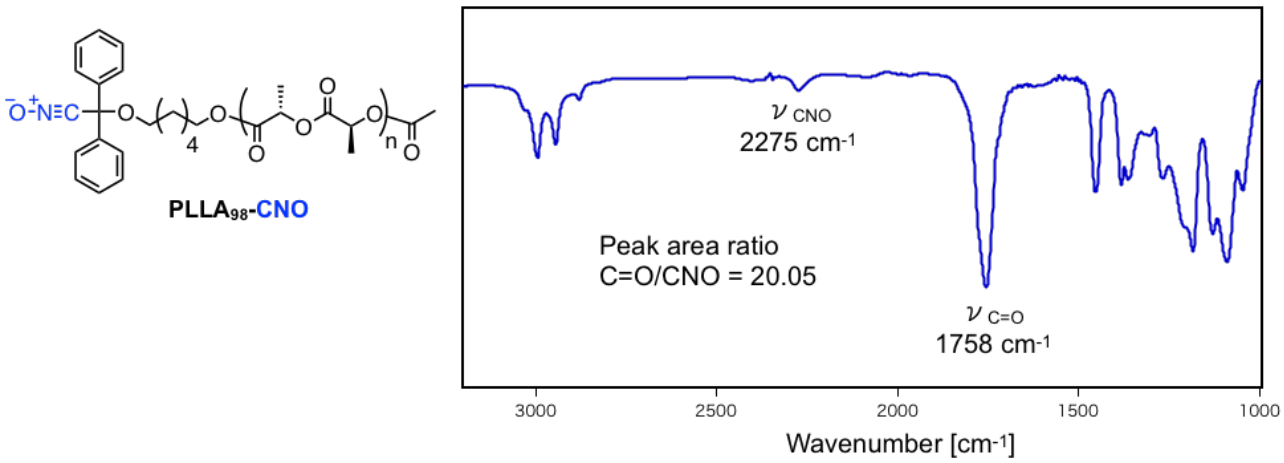
Figure S8. FT-IR spectrum of **PLLA$_{20}$-CNO** (NaCl)



Peak area ratio
Theoretical value : C=C/CNO = 11.32
Observed value : C=O/CNO = 11.03

Conversion (IR) = 11.03/11.32 × 100 = 97%

Figure S9. FT-IR spectrum of **PLLA$_{51}$-CNO** (NaCl)



Peak area ratio
Theoretical value : C=C/CNO = 21.75
Observed value : C=O/CNO = 20.67

Conversion (IR) = 20.05/21.75 × 100 = 95%

Figure S10. FT-IR spectrum of **PLLA$_{98}$-CNO** (NaCl)

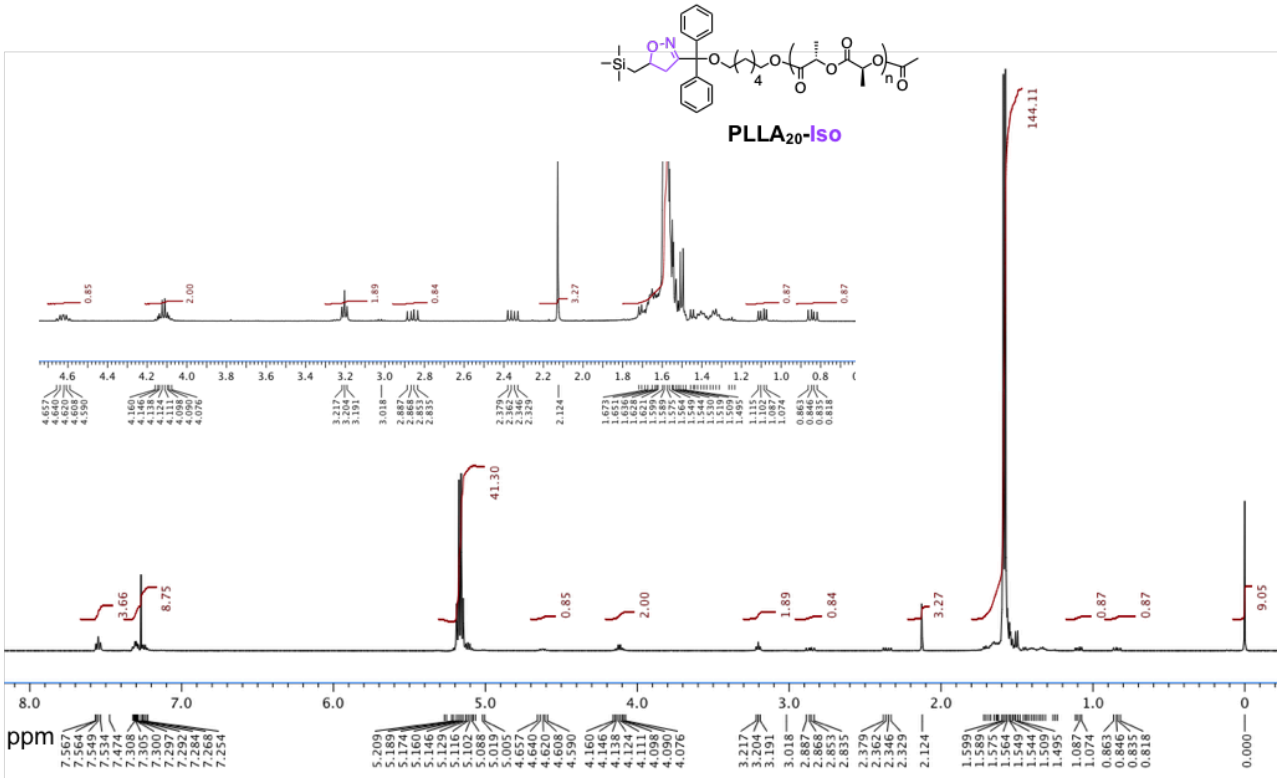


Figure S11. ^{1}H NMR spectrum of **PLLA$_{20}$-Iso** (500 MHz, 298 K, $CDCl_3$)

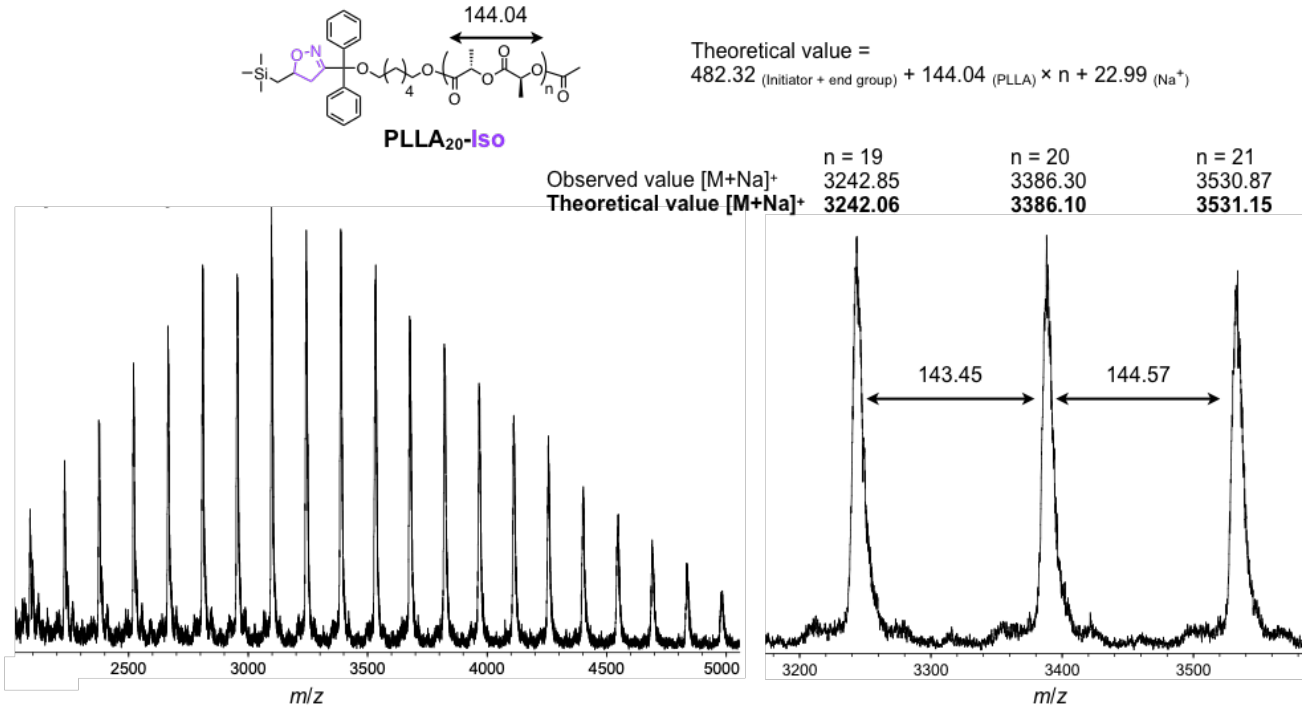


Figure S12. MALDI-TOF MS spectrum of **PLLA$_{20}$-Iso** (marix: dithranol)

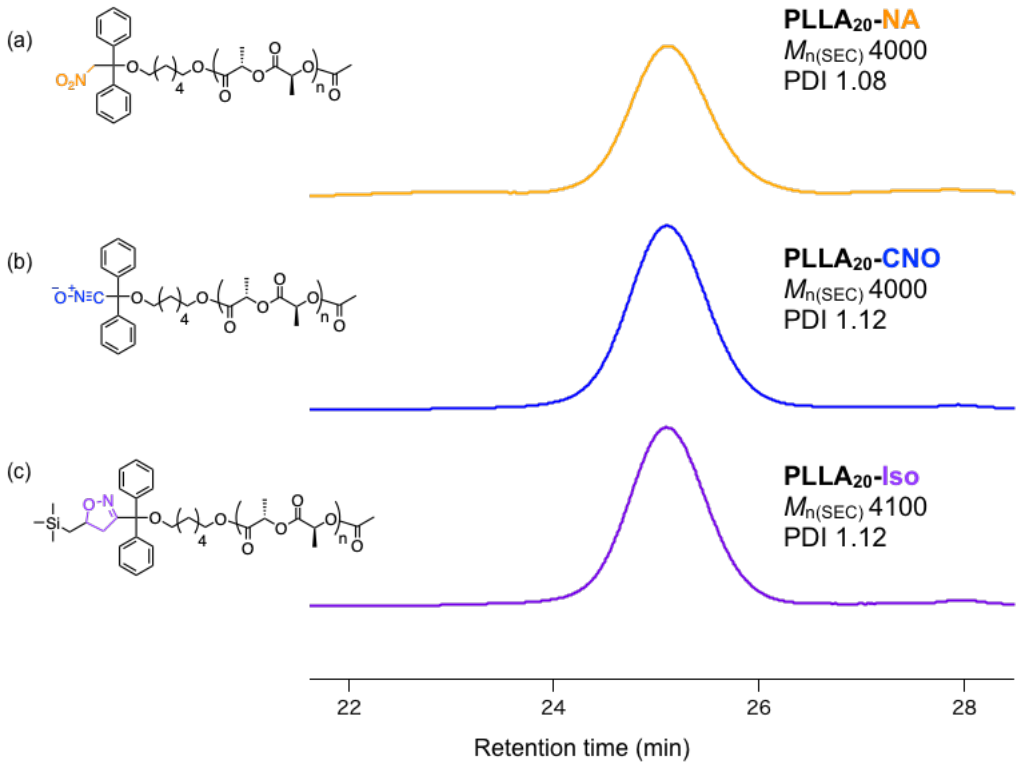


Figure S13. SEC charts of (a) **PLLA$_{20}$-NA**, (b) **PLLA$_{20}$-CNO** and (c) **PLLA$_{20}$-Iso** (PS standard, eluent, $CHCl_3$; flow rate, 0.85 mL/min, detected by RI)

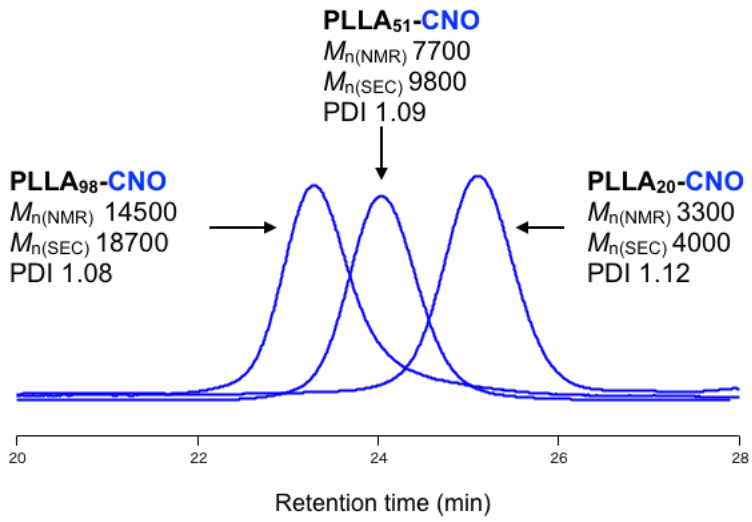


Figure S14. SEC charts of **PLLA$_{20}$-CNO**, **PLLA$_{51}$-CNO** and **PLLA$_{98}$-CNO** (PS standard, eluent, $CHCl_3$; flow rate, 0.85 mL/min, detected by RI)

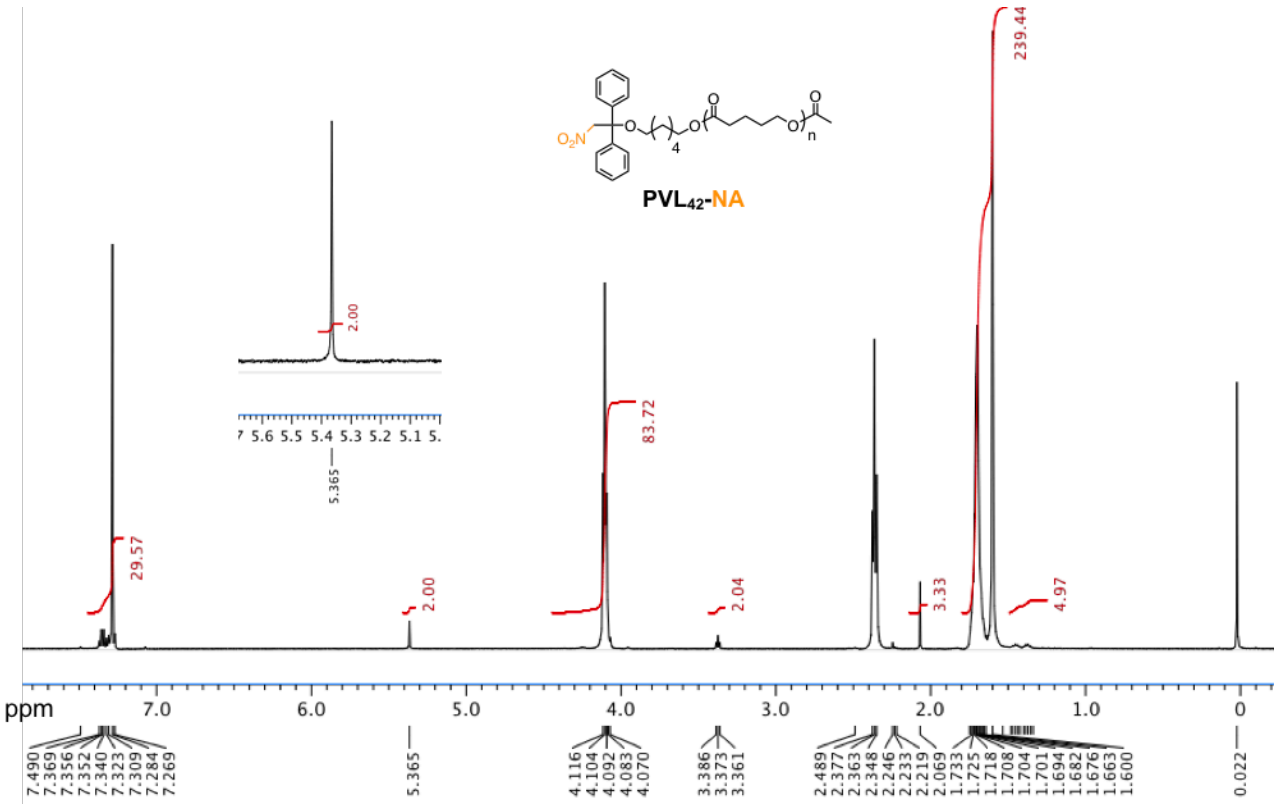


Figure S15. ^{1}H NMR spectrum of **PVL$_{42}$-NA** (500 MHz, 298 K, $CDCl_3$)

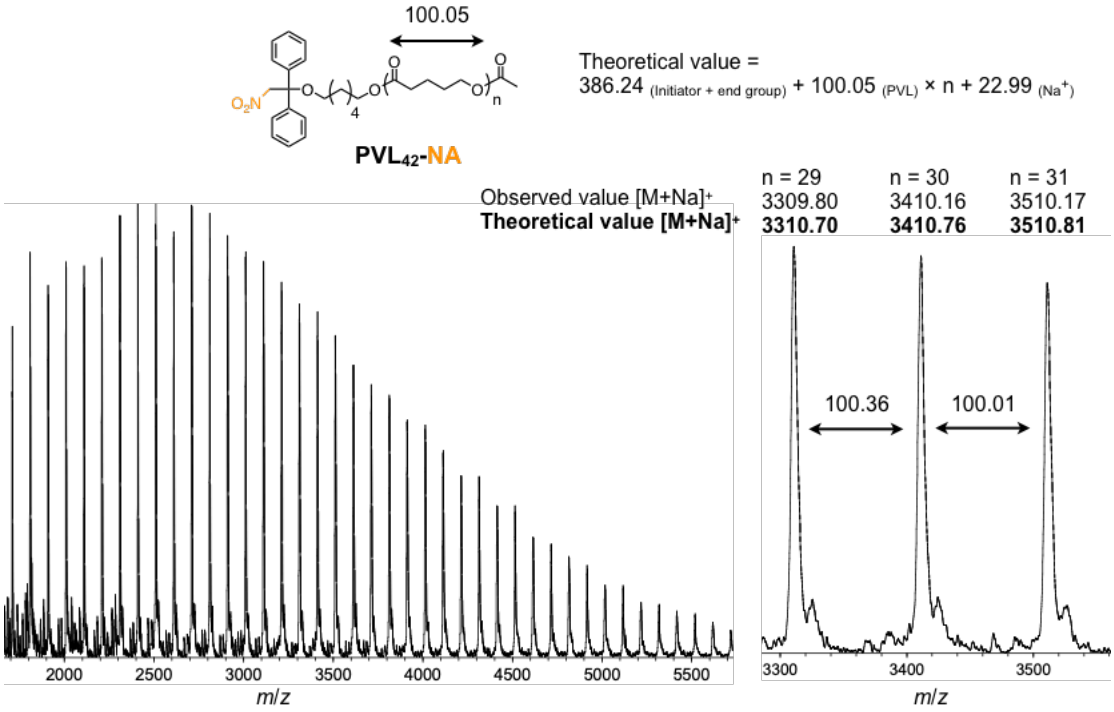


Figure S16. MALDI-TOF MS spectrum of **PVL$_{42}$-NA** (marix: dithranol)

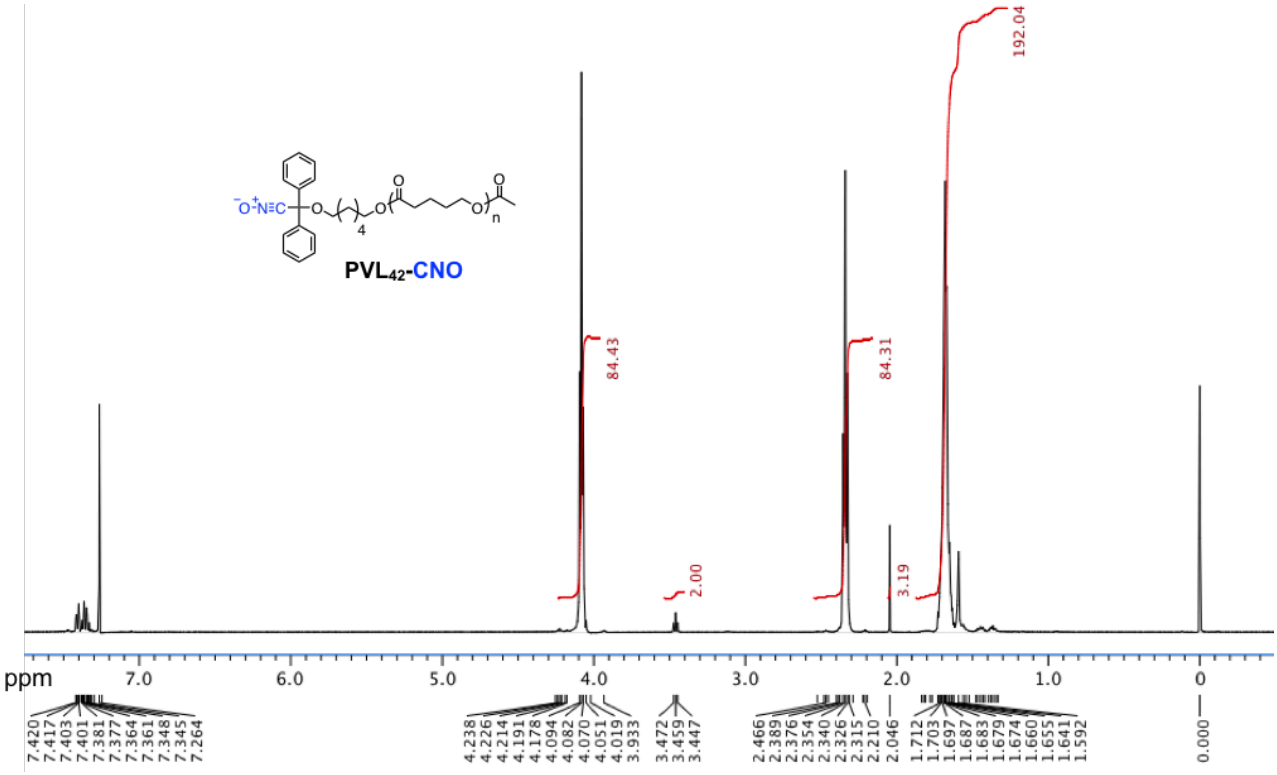


Figure S17. ^{1}H NMR spectrum of **PVL$_{42}$-CNO** (500 MHz, 298 K, $CDCl_3$)

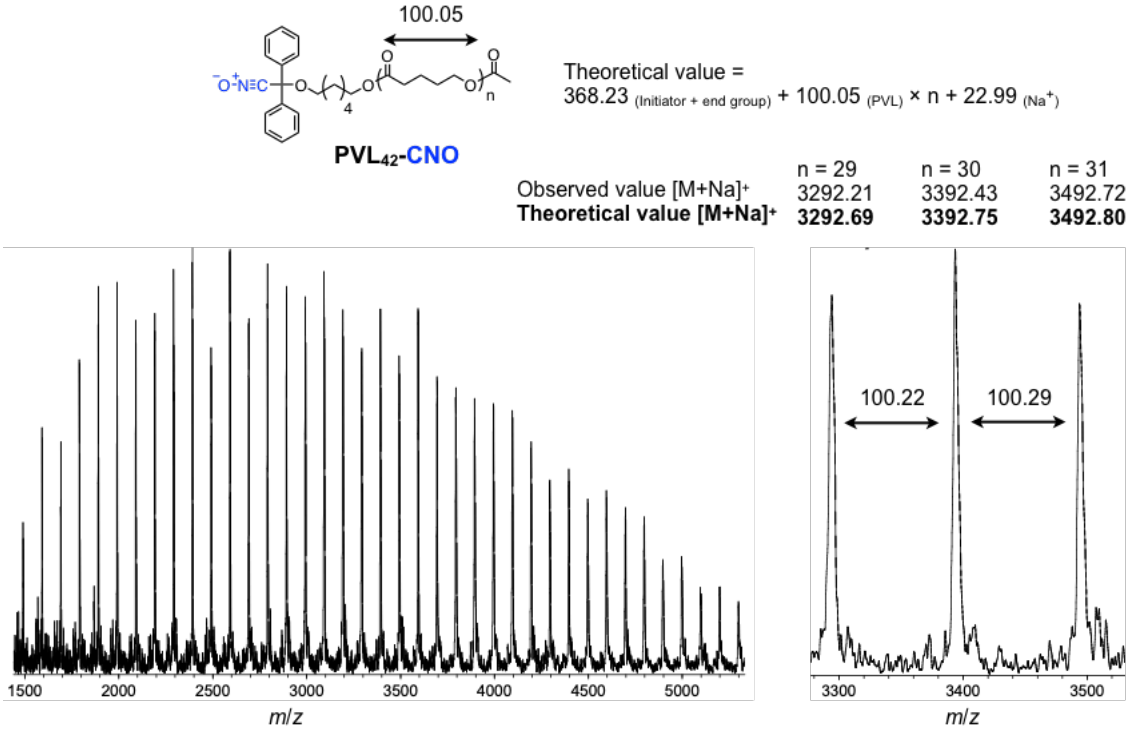


Figure S18. MALDI-TOF MS spectrum of **PVL$_{42}$-CNO** (marix: dithranol)

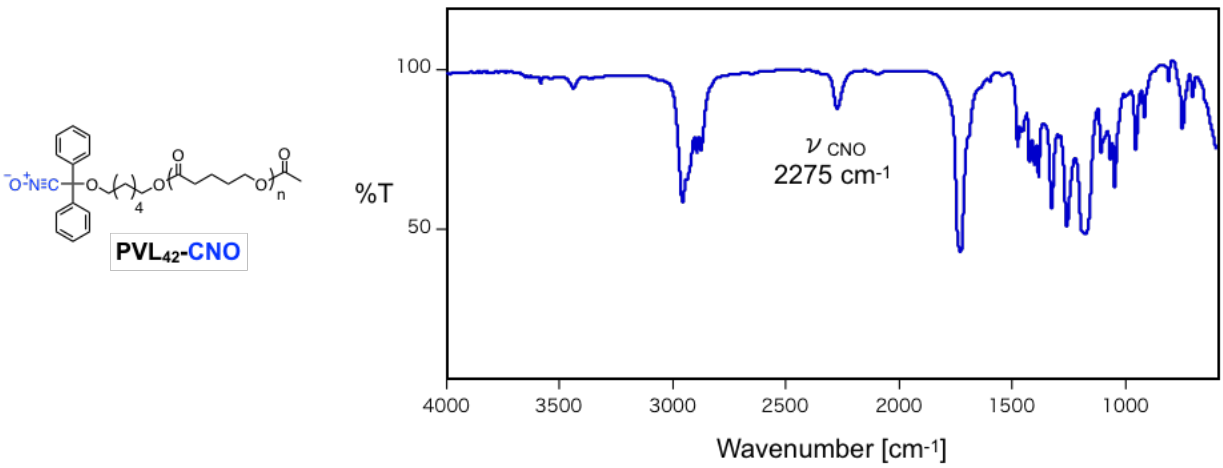


Figure S19. FT-IR spectrum of **PVL$_{42}$-CNO** (NaCl)

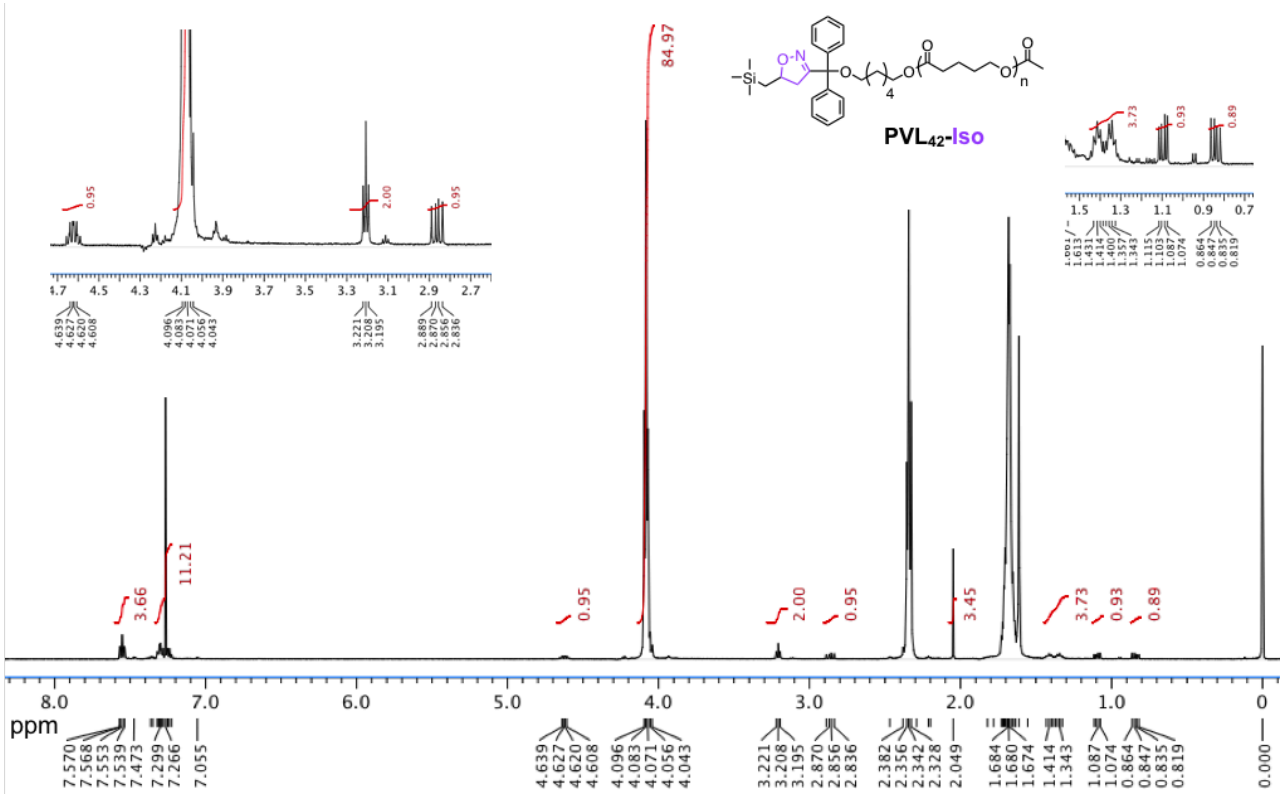


Figure S20. ^{1}H NMR spectrum of **PVL$_{42}$-Iso** (500 MHz, 298 K, $CDCl_3$)

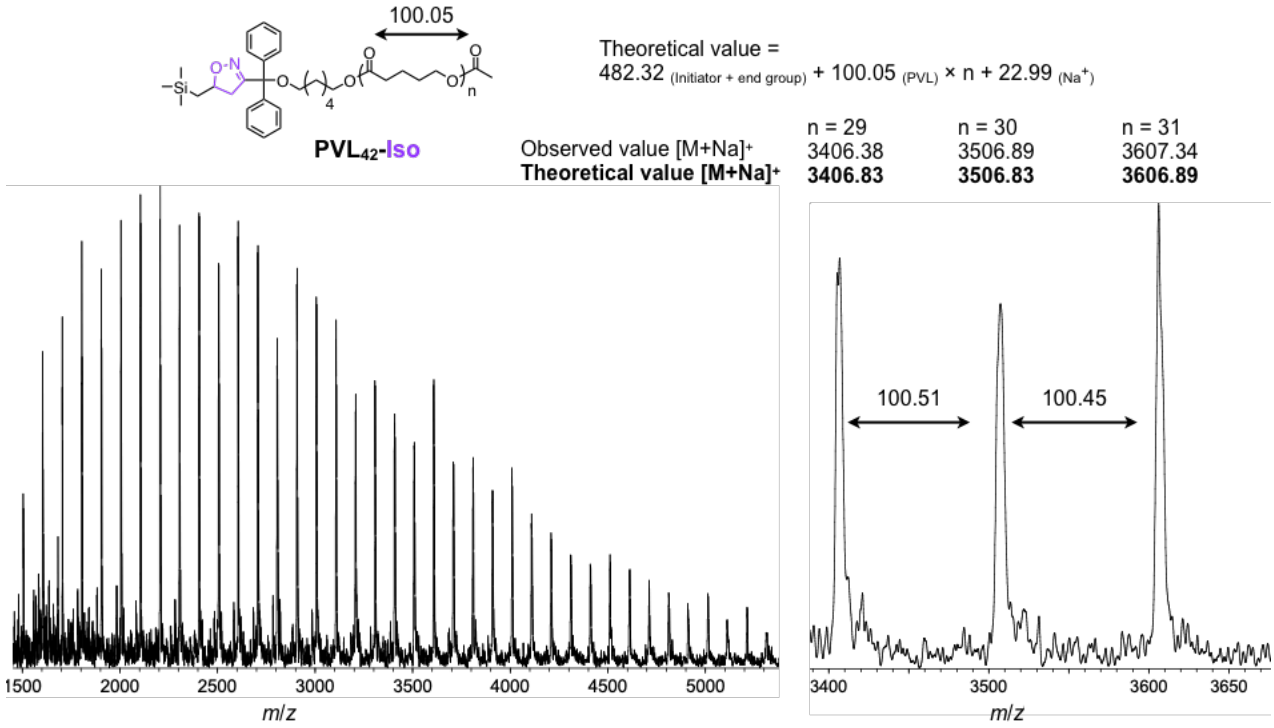


Figure S21. MALDI-TOF MS spectrum of **PVL$_{42}$-Iso** (marix: dithranol)

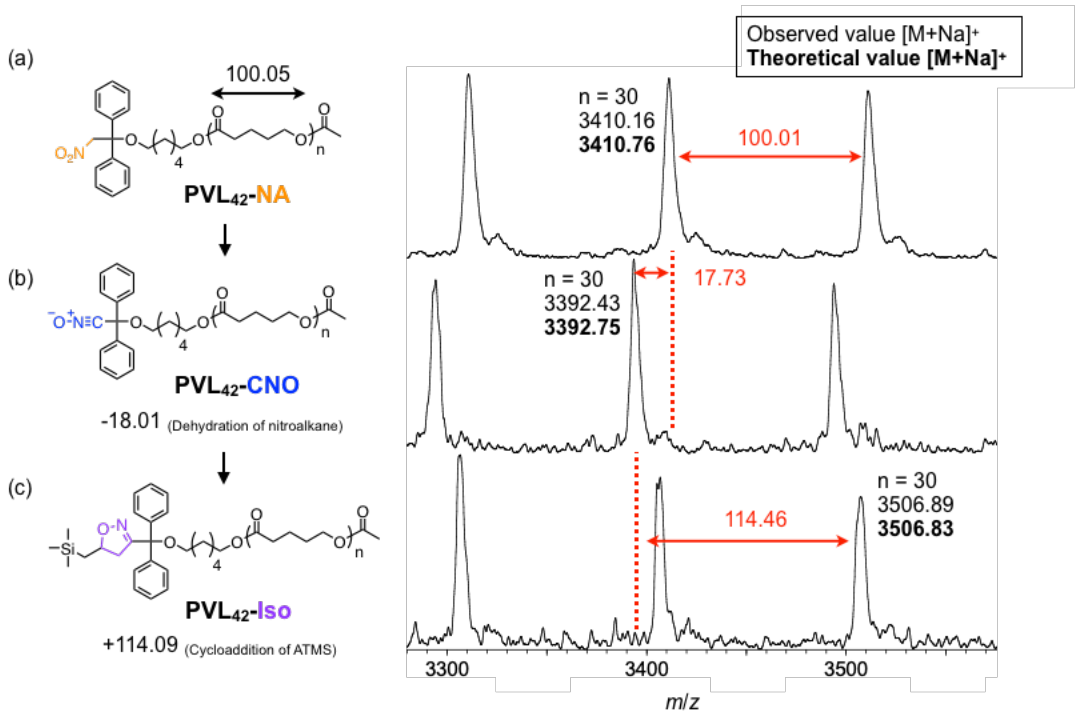


Figure S22. MALDI-TOF MS spectra change of (a) **PVL$_{42}$-NA**, (b) **PVL$_{42}$-CNO** and (c) **PVL$_{42}$-Iso** (matrix: dithranol)

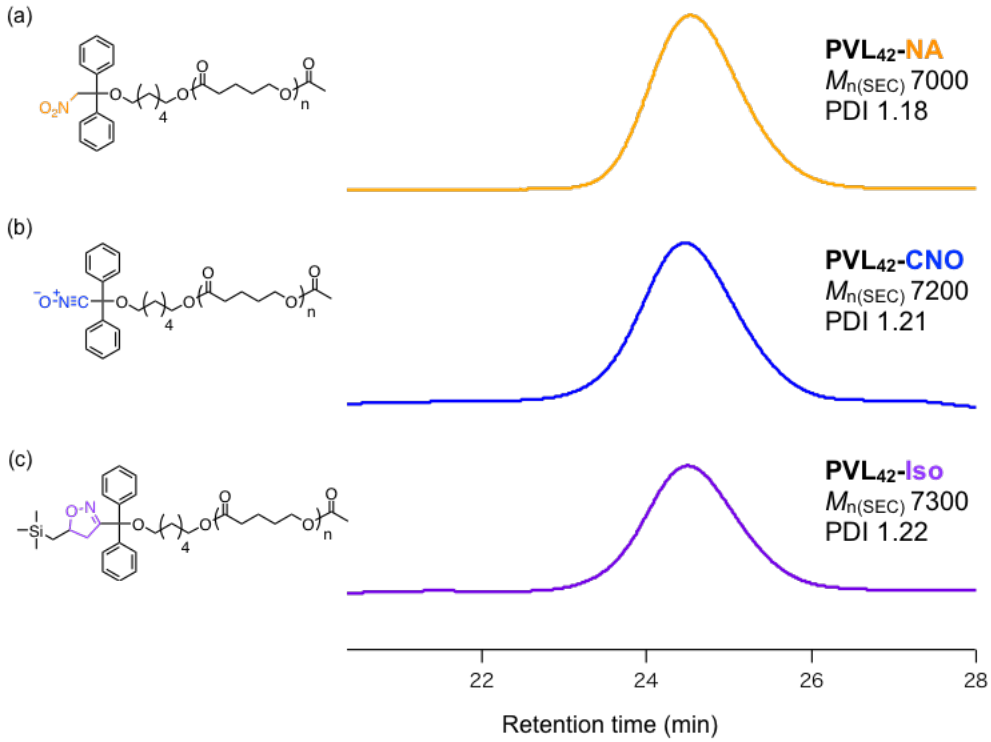


Figure S23. SEC charts of (a) **PVL$_{42}$-NA**, (b) **PVL$_{42}$-CNO** and (c) **PVL$_{42}$-Iso** (PS standard, eluent, $CHCl_3$; flow rate, 0.85 mL/min, detected by RI)

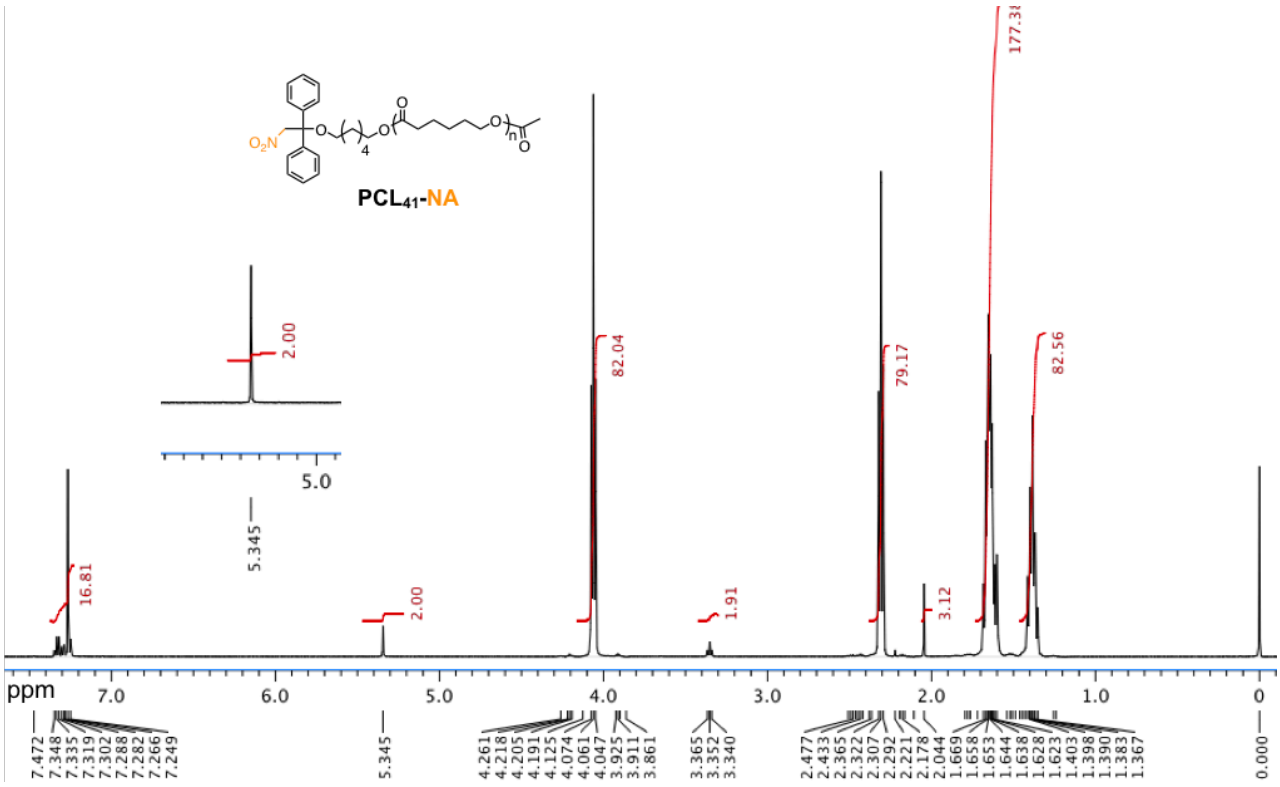


Figure S24. ^{1}H NMR spectrum of **PCL$_{41}$-NA** (500 MHz, 298 K, $CDCl_3$)

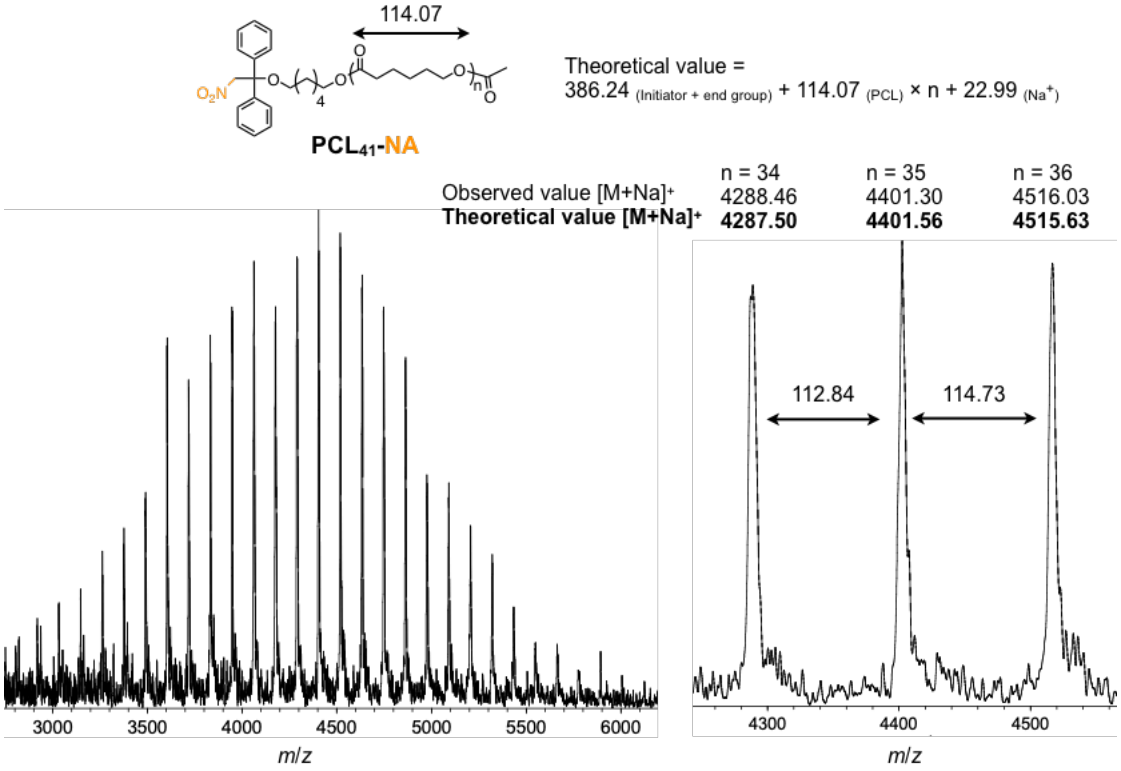


Figure S25. MALDI-TOF MS spectrum of **PCL$_{41}$-NA** (marix: dithranol)

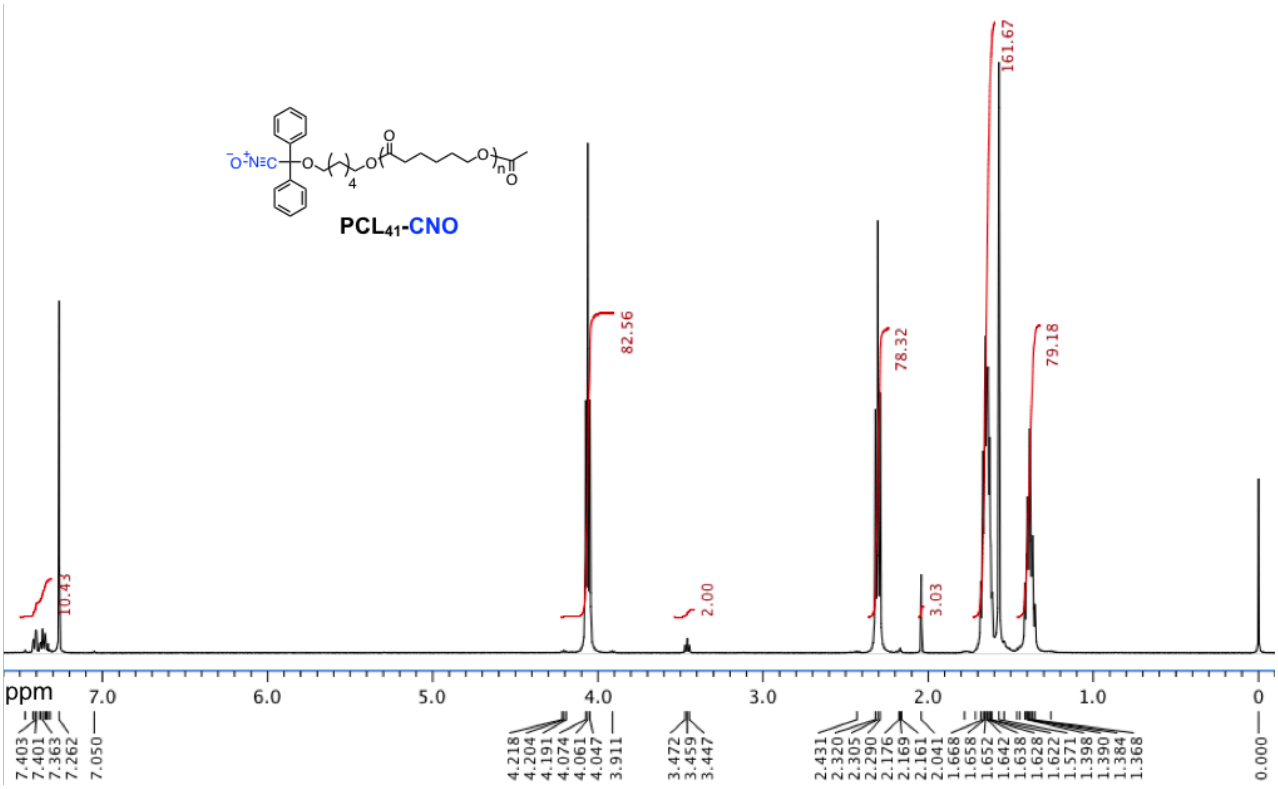


Figure S26. ^{1}H NMR spectrum of **PCL$_{41}$-CNO** (500 MHz, 298 K, $CDCl_3$)

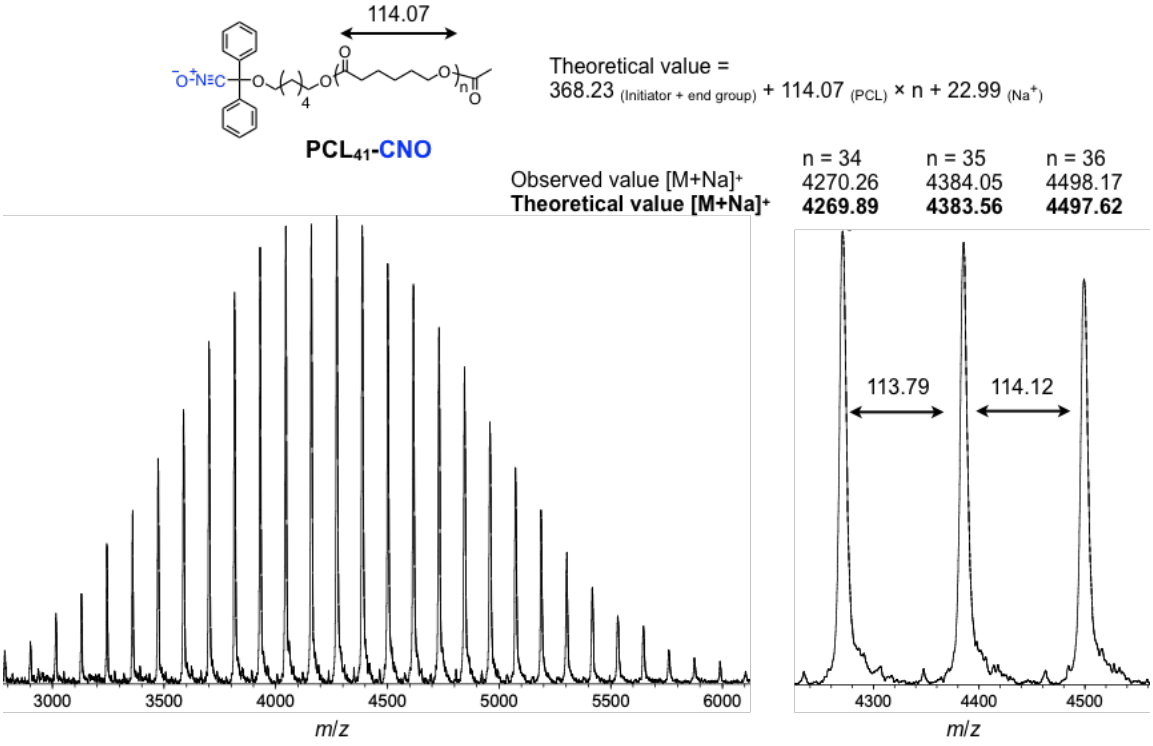


Figure S27. MALDI-TOF MS spectrum of **PCL_{41}-CNO** (marix: dithranol)

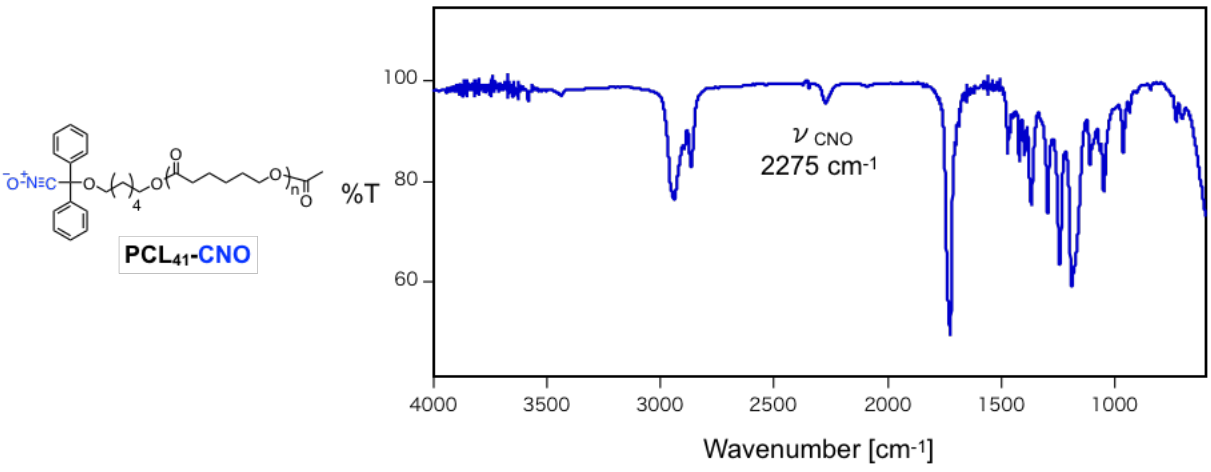


Figure S28. FT-IR spectrum of **PCL_{41}-CNO** (NaCl)

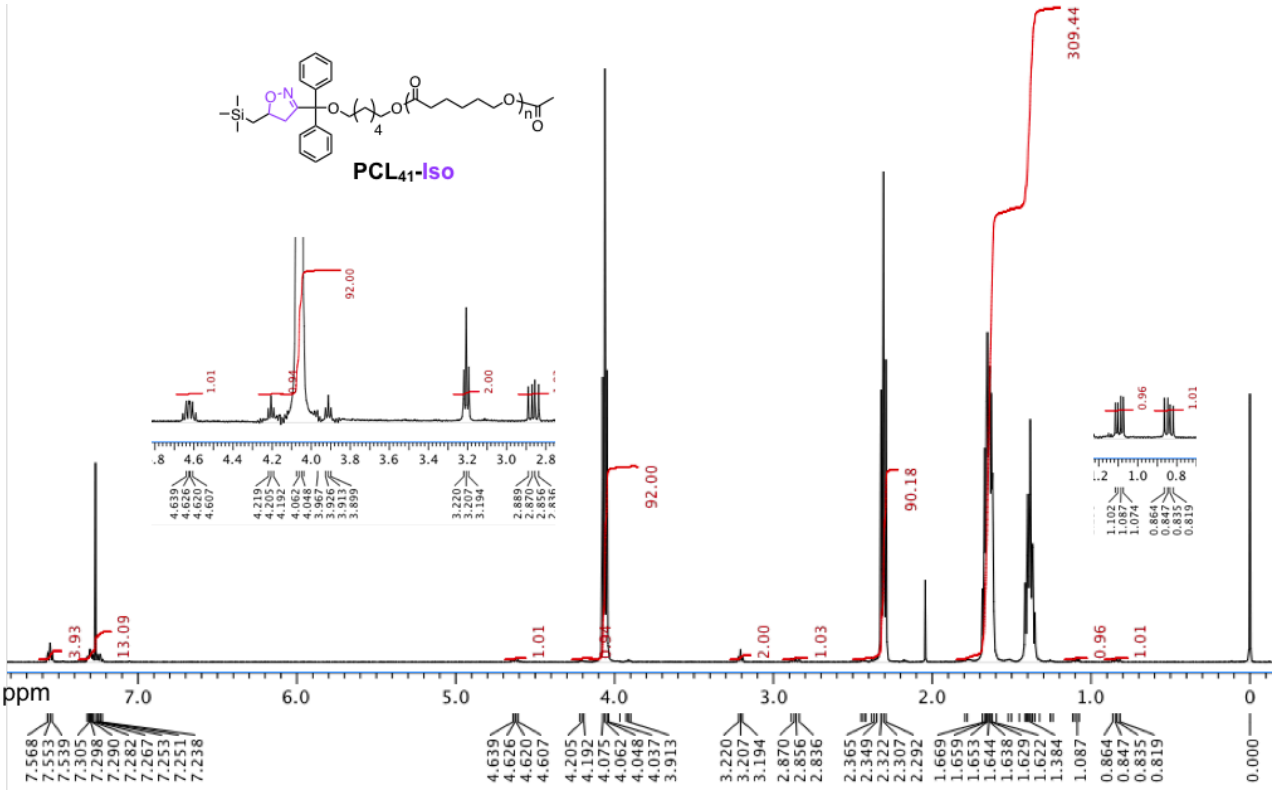


Figure S29. ^{1}H NMR spectrum of **PCL$_{41}$-Iso** (500 MHz, 298 K, $CDCl_3$)

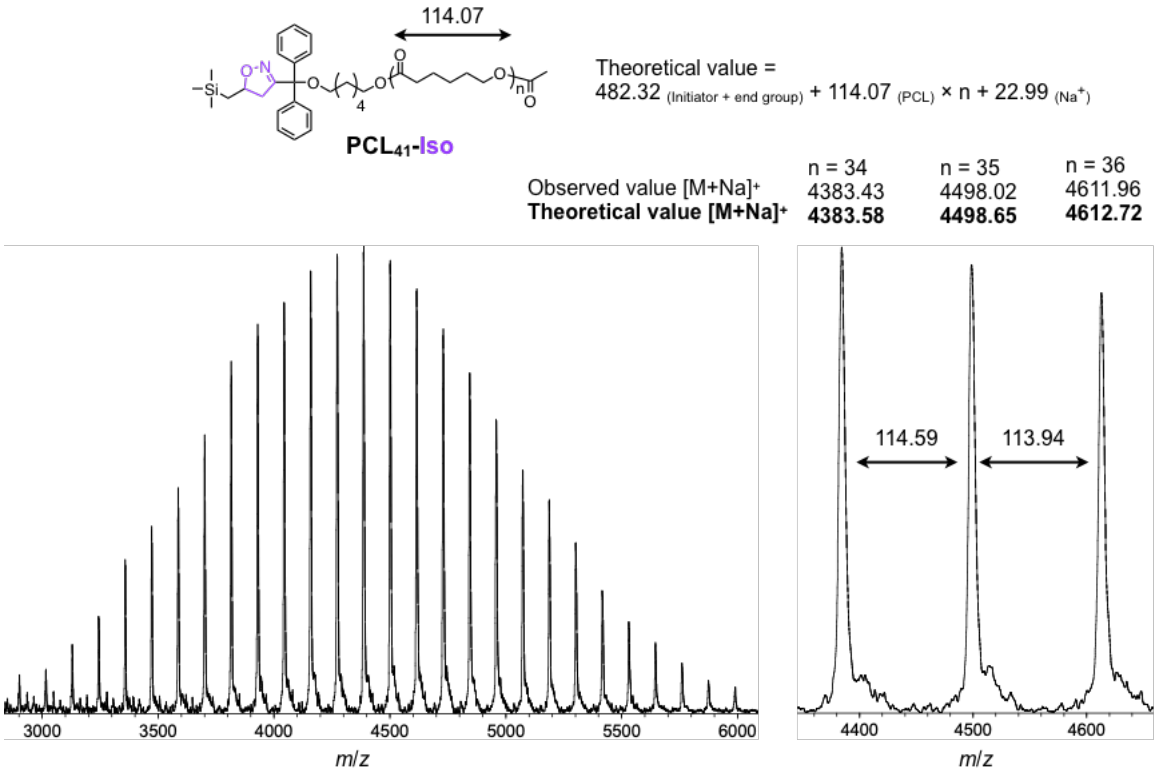


Figure S30. MALDI-TOF MS spectrum of **PCL$_{41}$-Iso** (marix: dithranol)

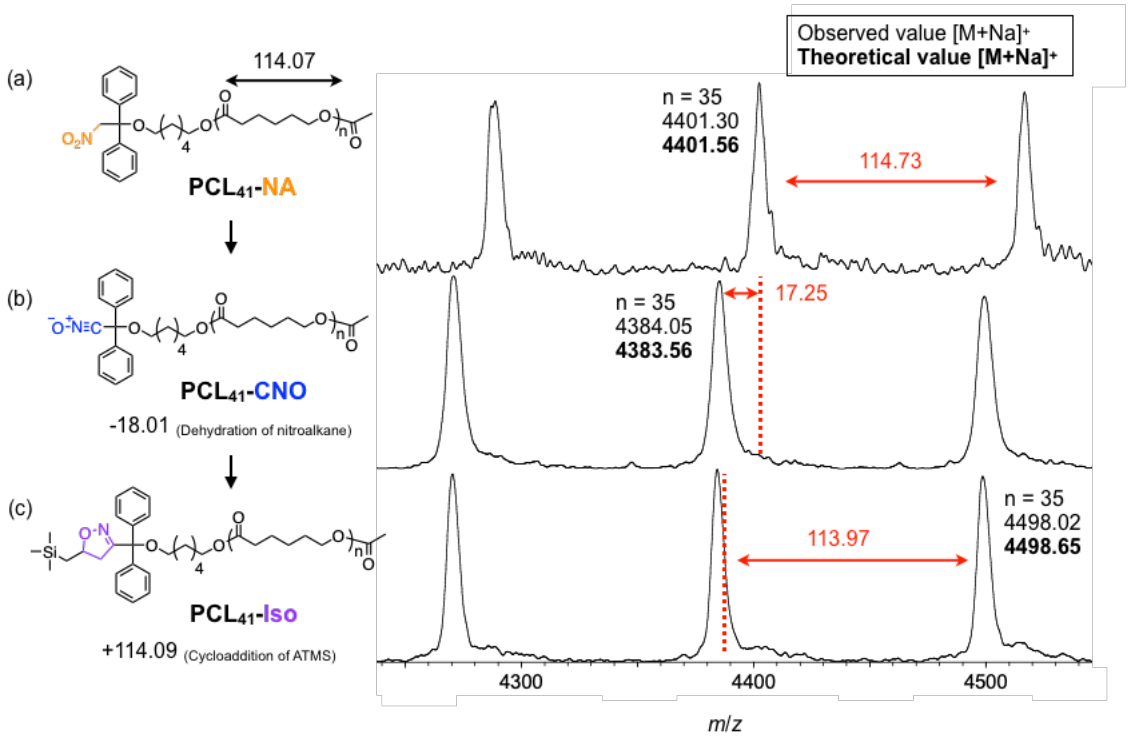


Figure S31. MALDI-TOF MS spectra change of (a) **PCL$_{41}$-NA**, (b) **PCL$_{41}$-CNO** and (c) **PCL$_{41}$-Iso** (matrix: dithranol)

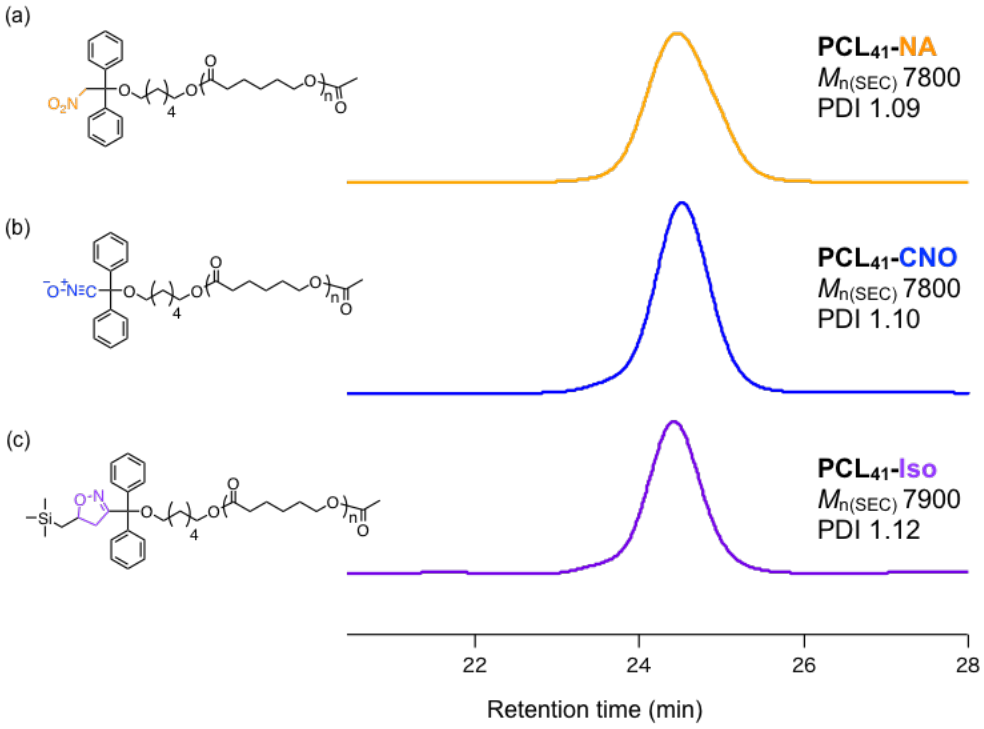


Figure S32. SEC charts of (a) **PCL$_{41}$-NA**, (b) **PCL$_{41}$-CNO** and (c) **PCL$_{41}$-Iso** (PS standard, eluent, $CHCl_3$; flow rate, 0.85 mL/min, detected by RI)

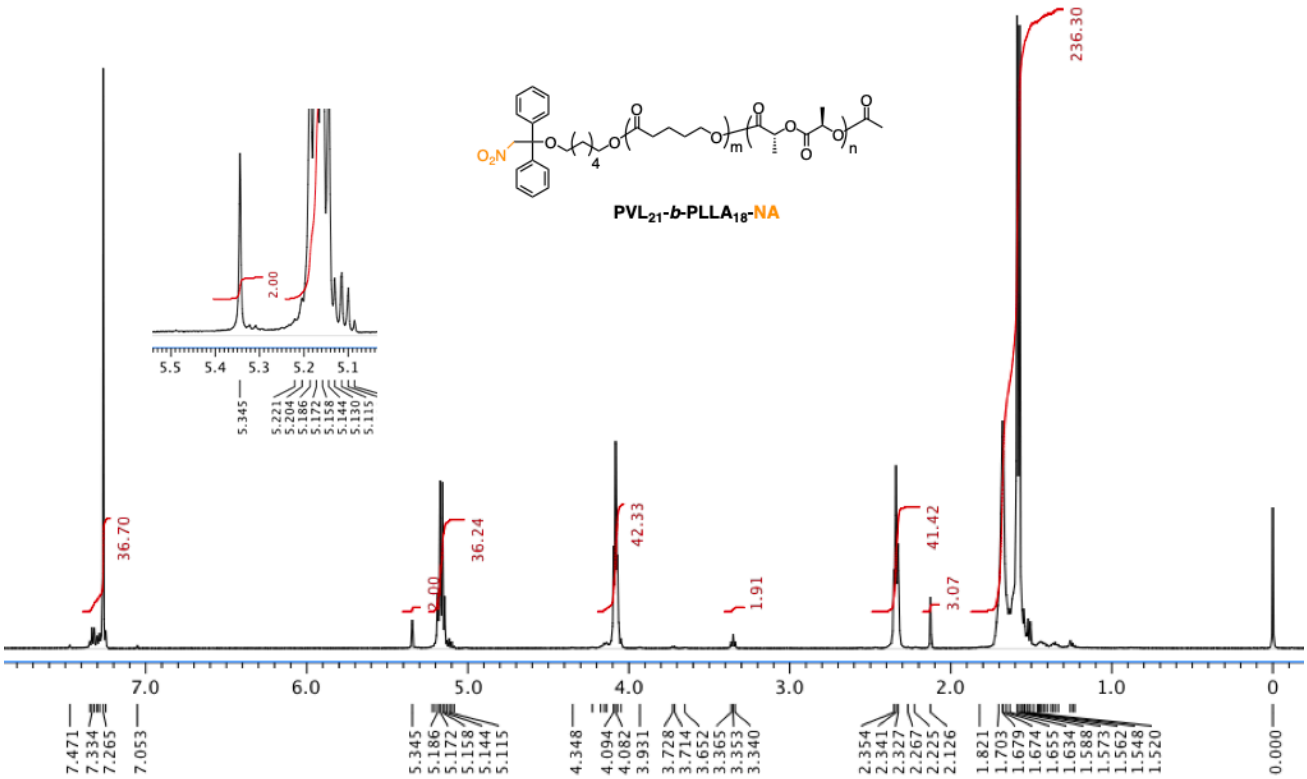


Figure S33. ^{1}H NMR spectrum of **PVL$_{21}$-*b*-PLLA$_{18}$-NA** (500 MHz, 298 K, $CDCl_3$)

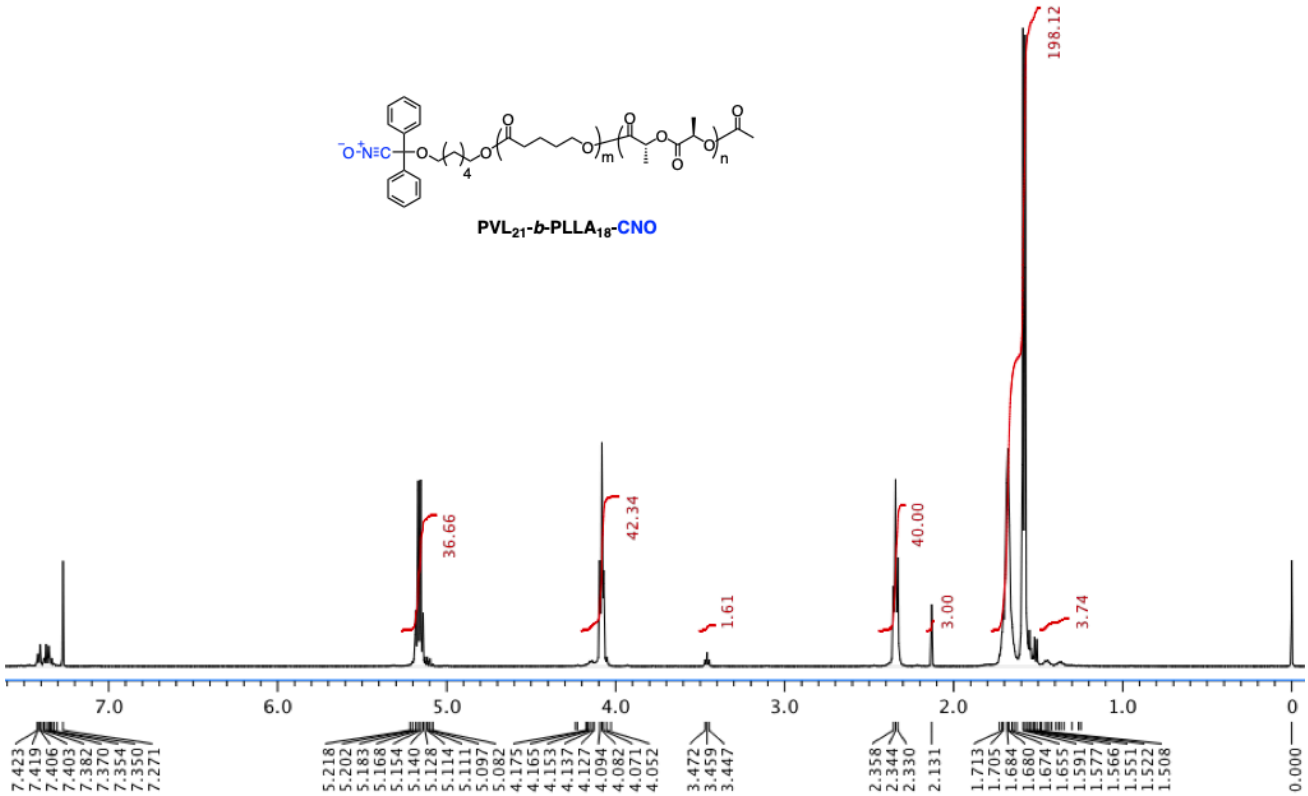


Figure S34. ^{1}H NMR spectrum of **PVL$_{21}$-*b*-PLLA$_{18}$-CNO** (500 MHz, 298 K, $CDCl_3$)

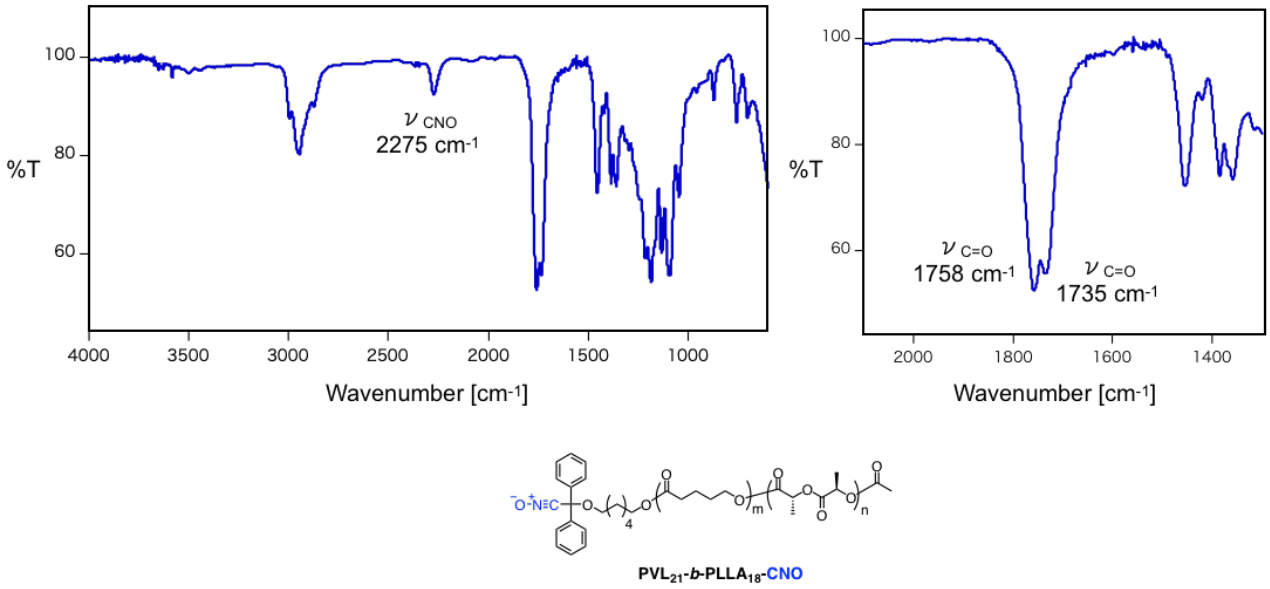


Figure S35. FT-IR spectrum of **PVL$_{21}$-*b*-PLLA$_{18}$-CNO** (NaCl)

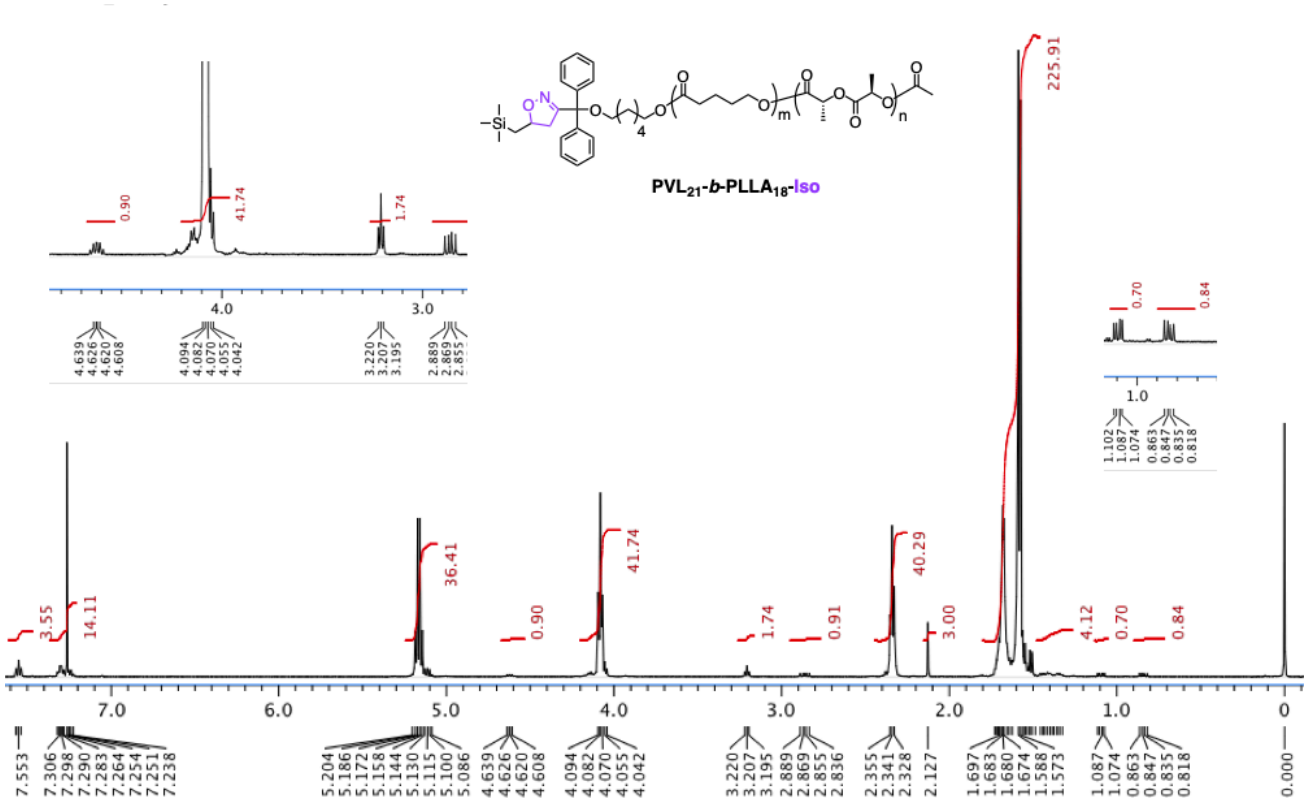


Figure S36. ^{1}H NMR spectrum of **PVL$_{21}$-*b*-PLLA$_{18}$-Iso** (500 MHz, 298 K, $CDCl_3$)

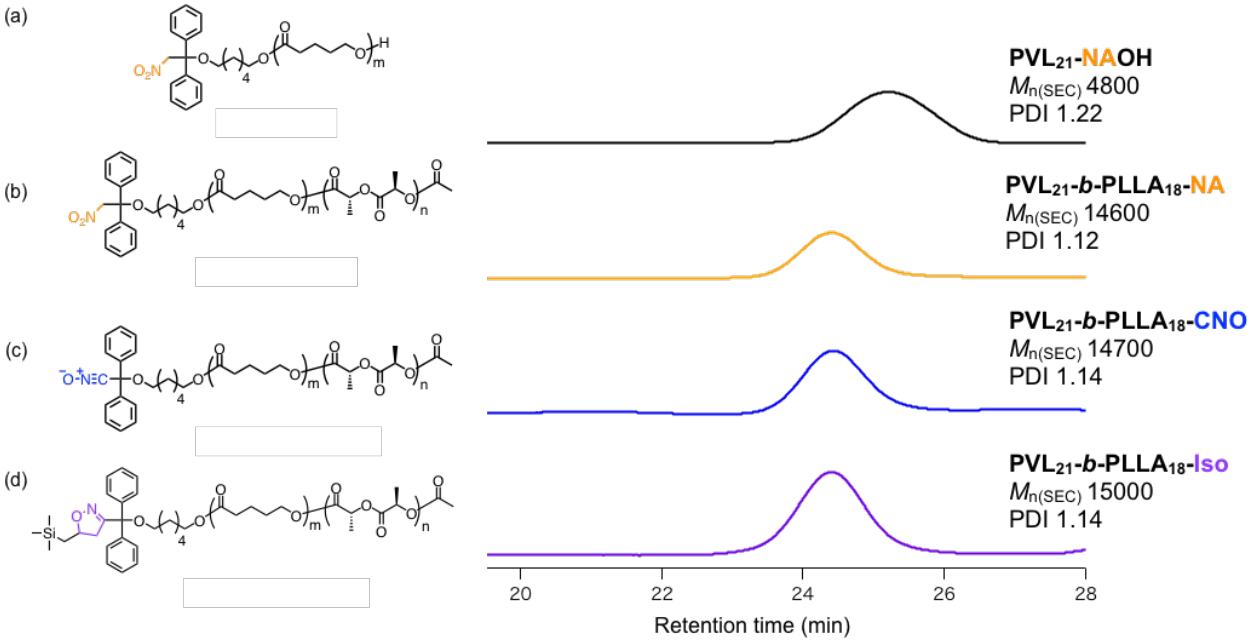


Figure S37. SEC charts of (a) **PVL$_{21}$-*b*-PLLA$_{18}$-NA**, (b) **PVL$_{21}$-*b*-PLLA$_{18}$-CNO** and (c) **PVL$_{21}$-*b*-PLLA$_{18}$-Iso** (PS standard, eluent, $CHCl_3$; flow rate, 0.85 mL/min, detected by RI)

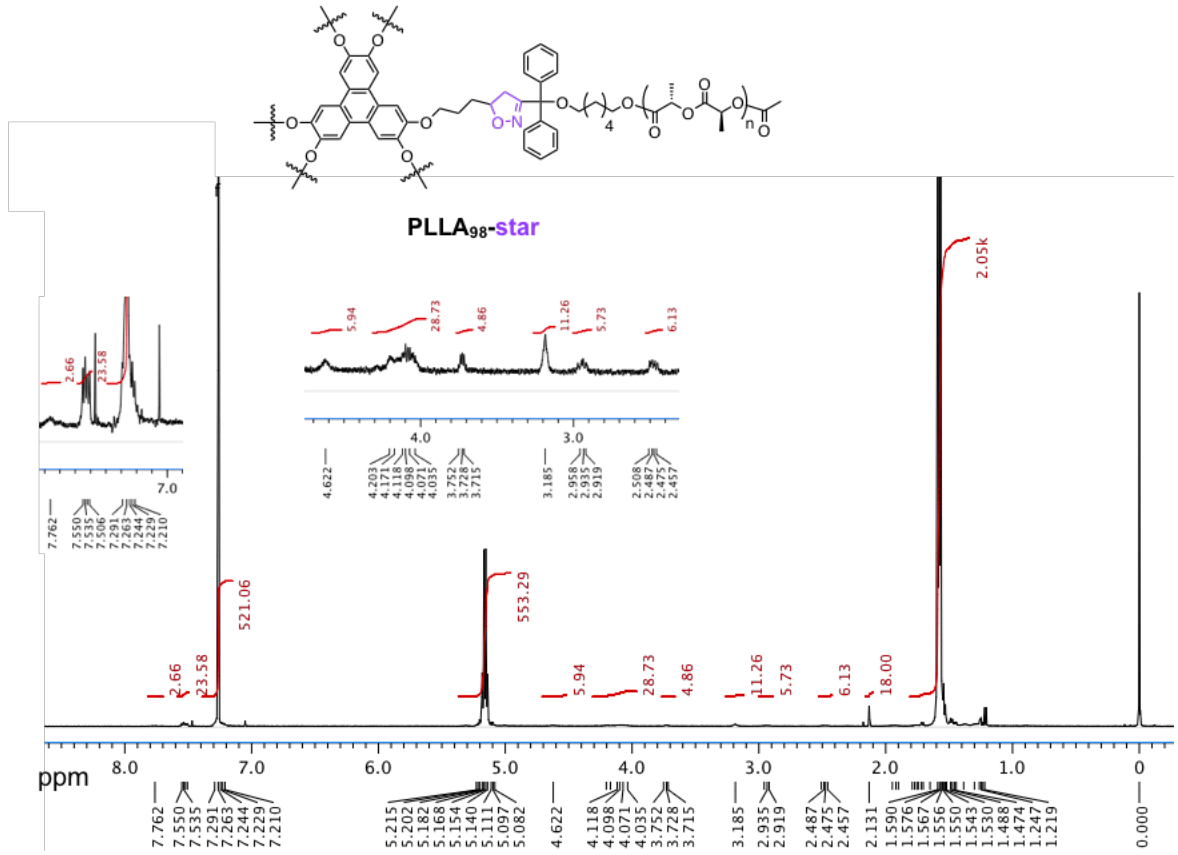


Figure S38. ^{1}H NMR spectrum of **PLLA$_{98}$-star** (500 MHz, 298 K, $CDCl_3$)

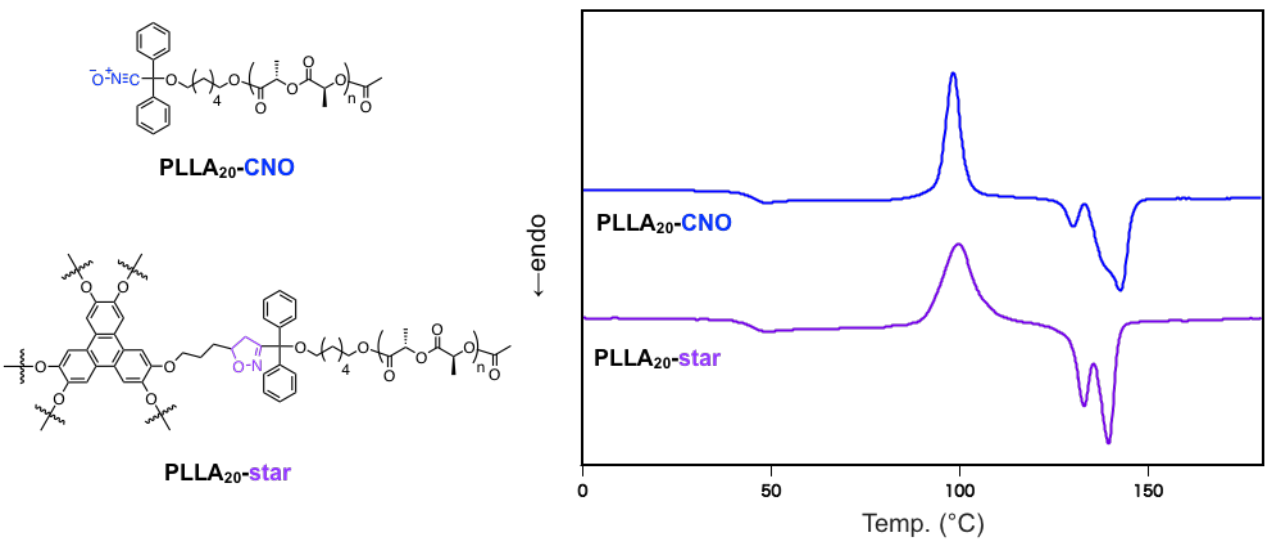


Figure S39. DSC charts of **PLLA$_{20}$-CNO** and **PLLA$_{20}$-star** (10 °C/min, 2nd heating under N_2)

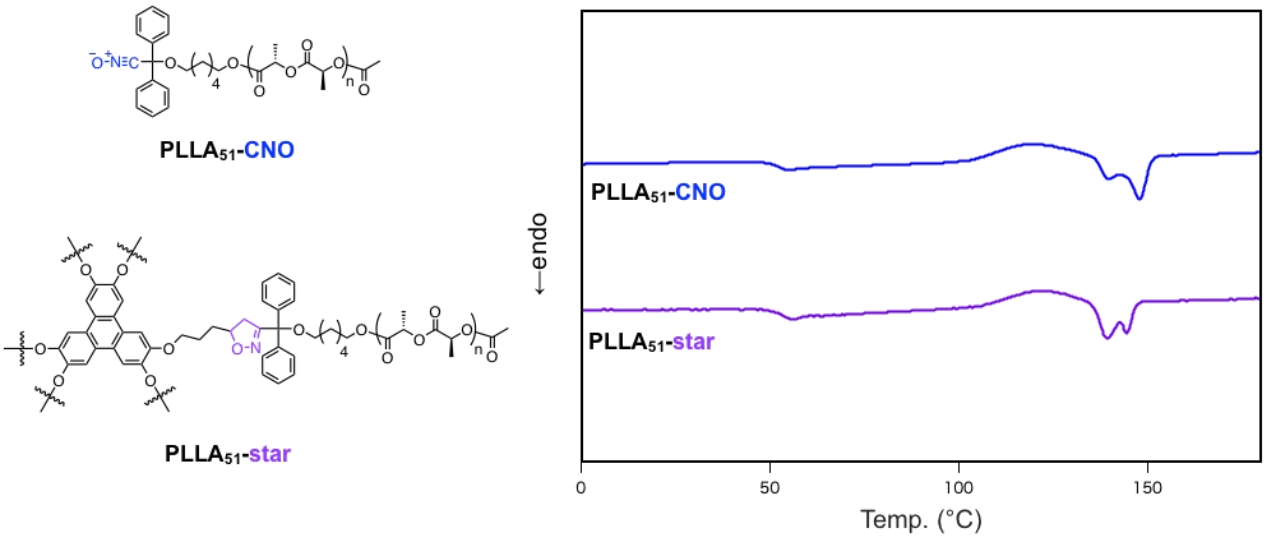


Figure S40. DSC charts of **PLLA$_{51}$-CNO** and **PLLA$_{51}$-star** (10 °C/min, 2nd heating under N_2)

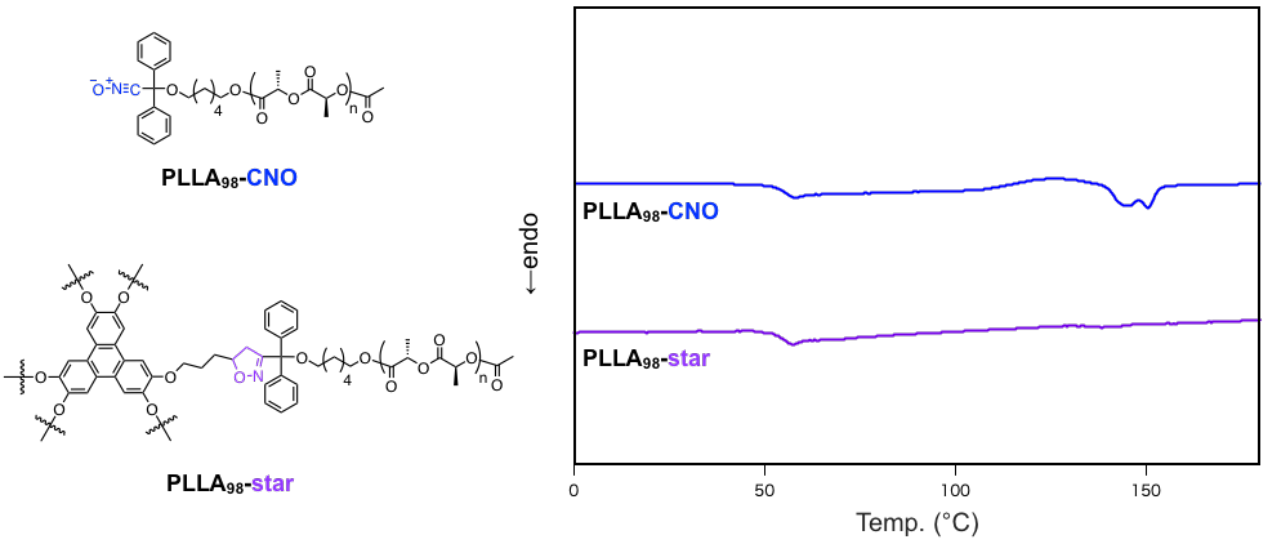


Figure S41. DSC charts of **PLLA$_{98}$-CNO** and **PLLA$_{98}$-star** (10 °C/min, 2nd heating under N_2)

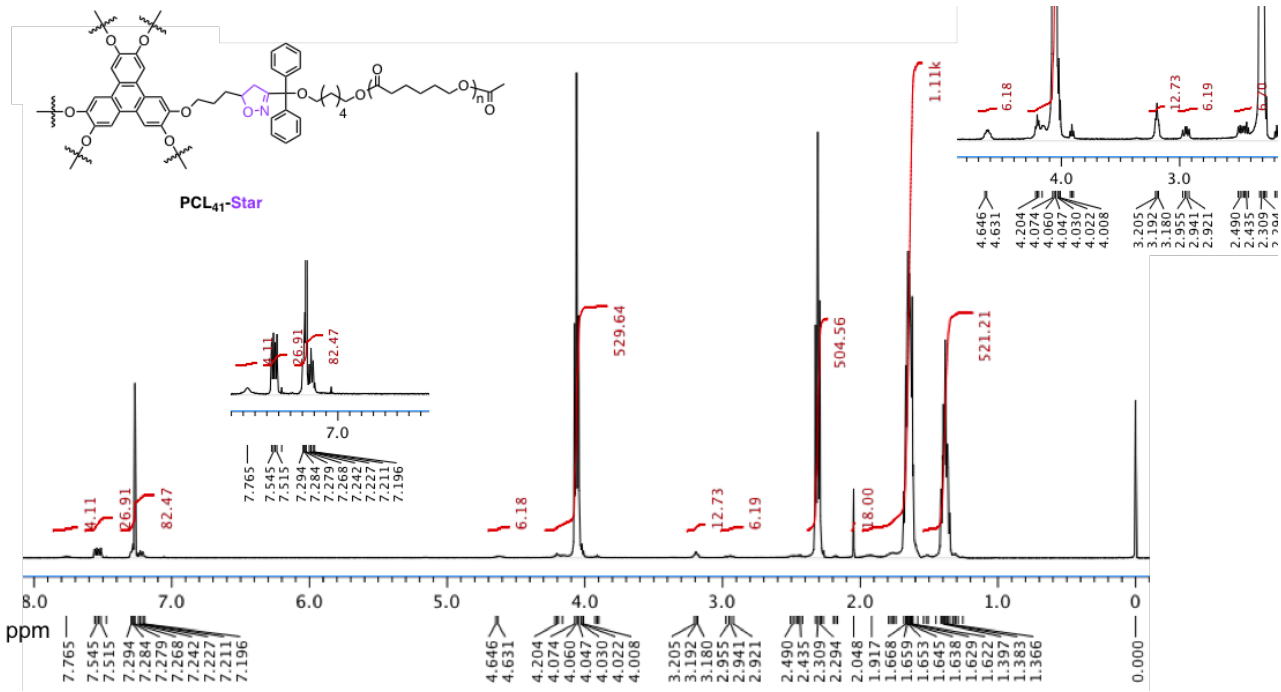


Figure S42. ^{1}H NMR spectrum of **PCL$_{41}$-star** (500 MHz, 298 K, $CDCl_3$)

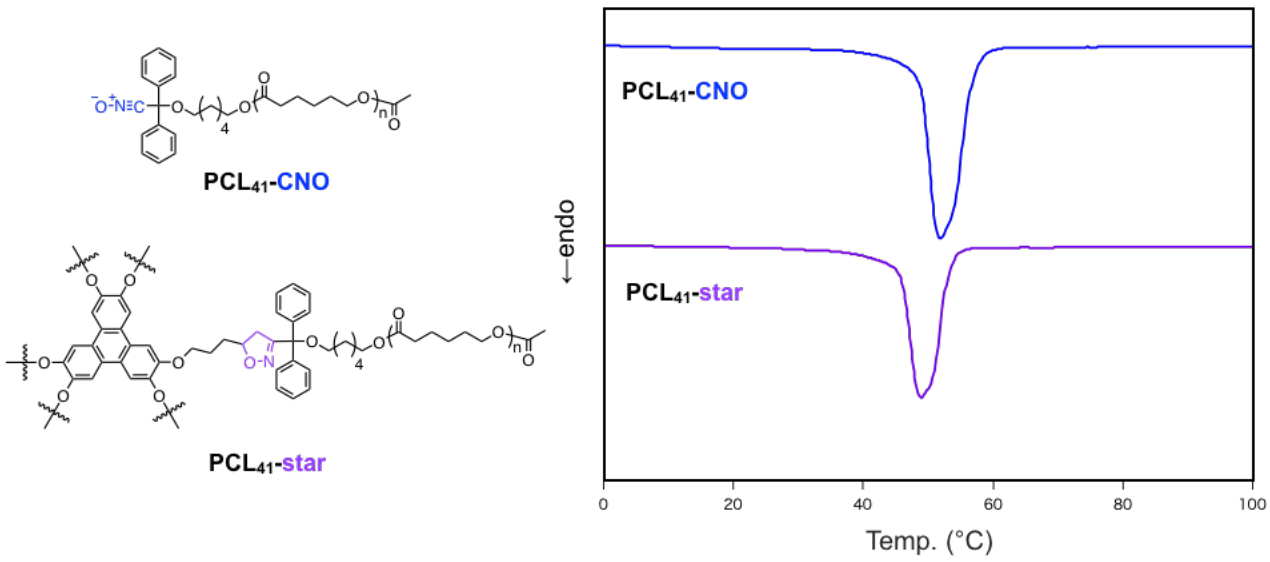


Figure S43. DSC charts of **PCL_{41}-CNO** and **PCL_{41}-star** (10 °C/min, 2nd heating under N_2)

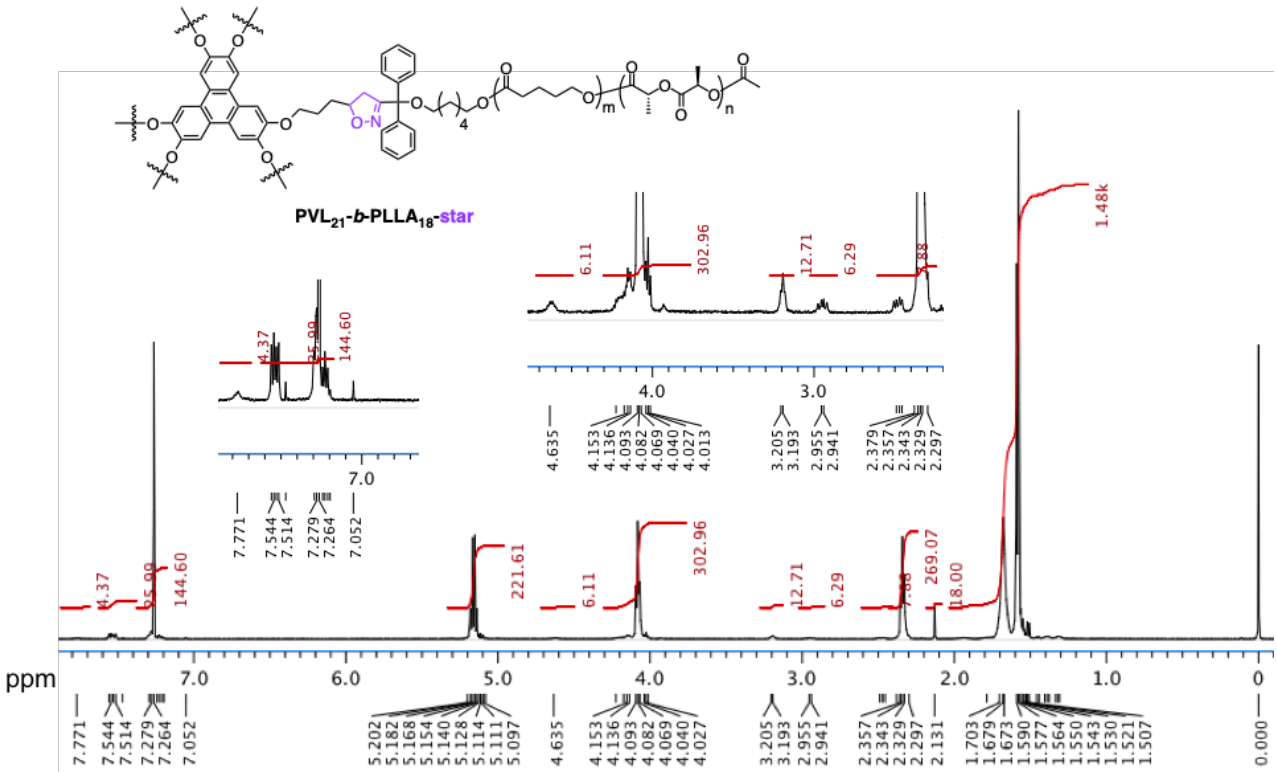


Figure S44. ^{1}H NMR spectrum of **PVL_{21}-*b*-$PLLA_{18}$-star** (500 MHz, 298 K, $CDCl_3$)

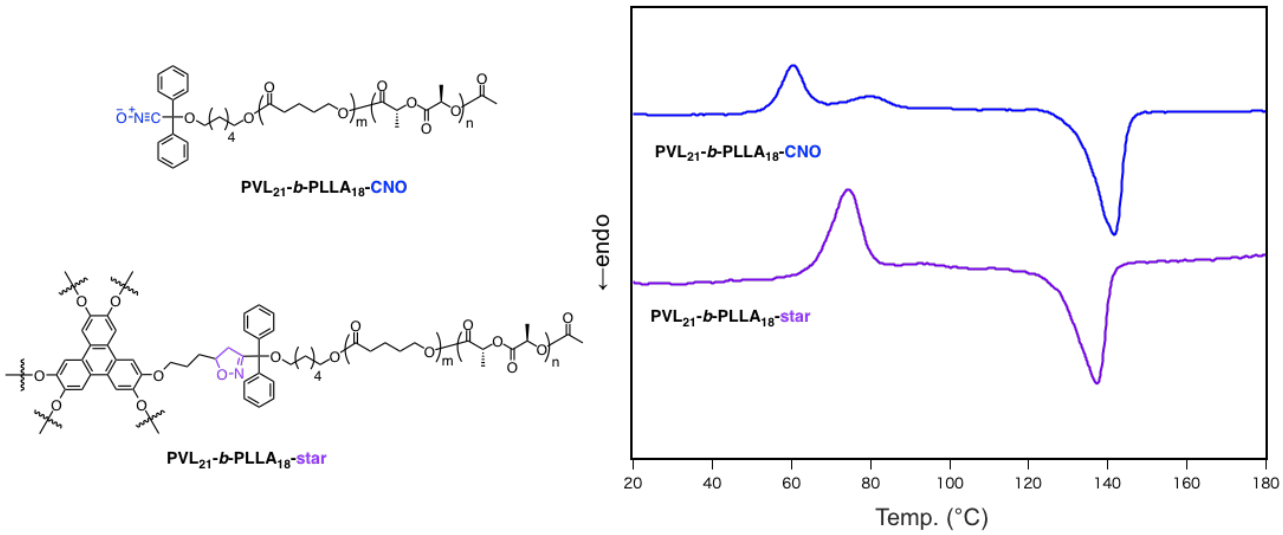


Figure S45. DSC charts of **PVL_{21}-*b*-$PLLA_{18}$-CNO** and **PVL_{21}-*b*-$PLLA_{18}$-star** (10 °C/min, 2nd heating under N_2)

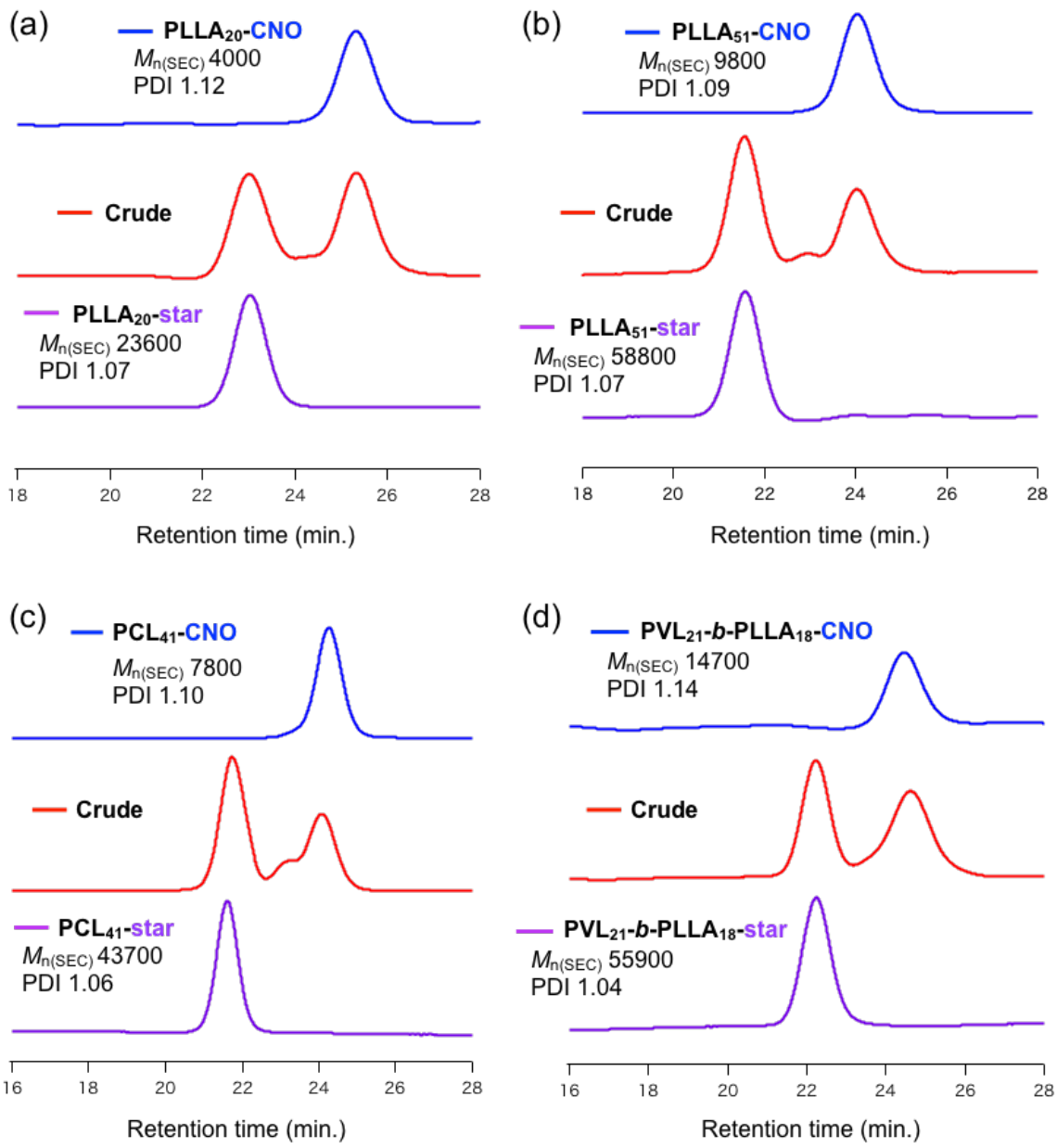


Figure S46 SEC charts of (a) **PLLA$_{20}$-CNO**, crude and **PLLA$_{20}$-star**, (b) **PLLA$_{51}$-CNO**, crude and **PLLA$_{51}$-star**, (c) **PCL$_{41}$-CNO**, crude and **PCL$_{41}$-star** and (d) **PVL$_{21}$-*b*-PLLA$_{18}$-CNO**, crude and **PVL$_{21}$-*b*-PLLA$_{18}$-star** (PS standard, eluent, $CHCl_3$; flow rate, 0.85 mL/min, detected by RI)

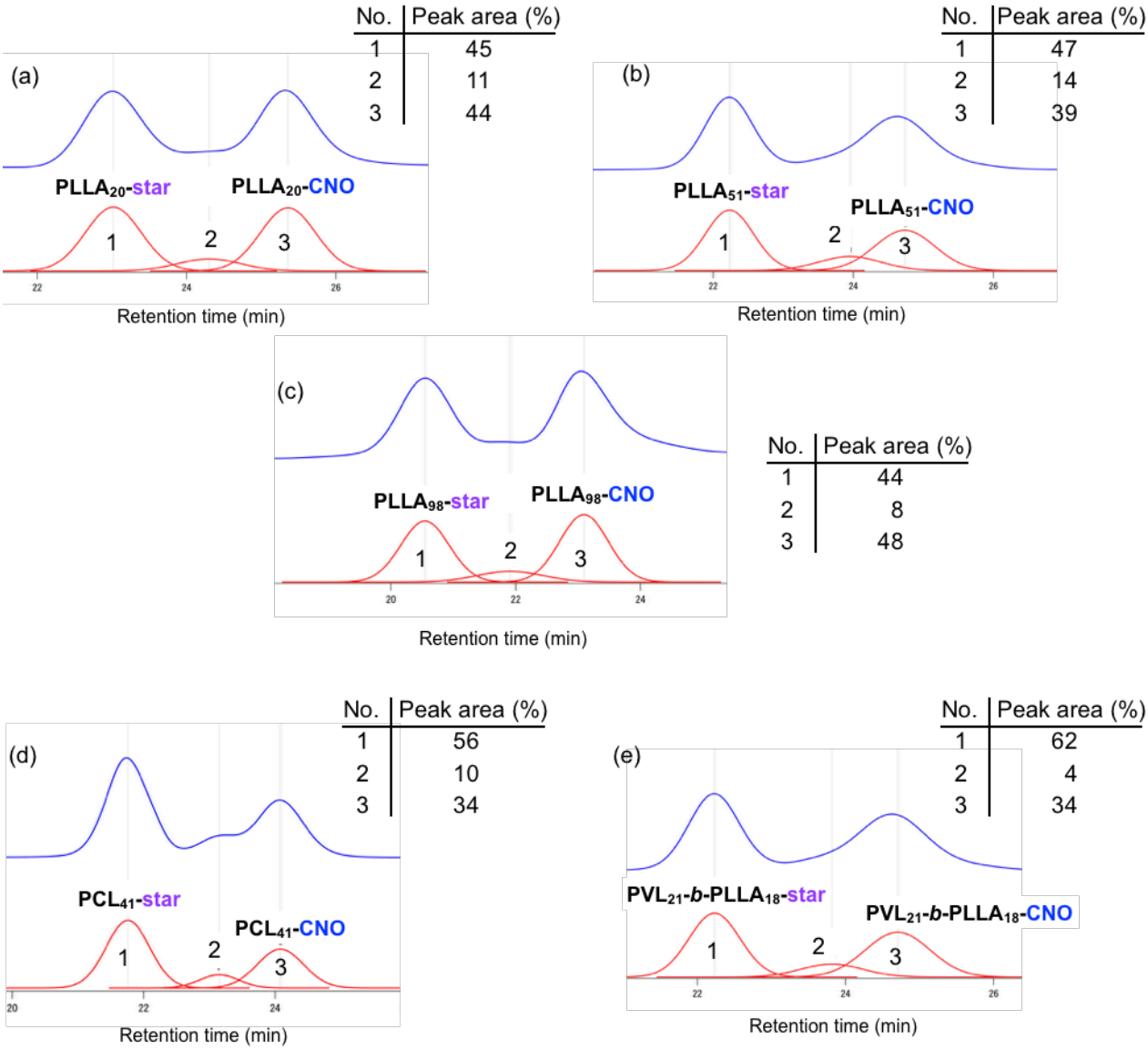


Figure S47 Peak separation of crude SEC charts of (a) **PLLA$_{20}$-star**, (b) **PLLA$_{51}$-star**, (e) **PLLA$_{51}$-star**, (d) **PCL$_{41}$-star** and (e) **PVL$_{21}$-*b*-PLLA$_{18}$-star**.

Table S1. Thermal properties of **PX-CNO** and **PX-star**

Polyester	T_{d5} (°C)[a)]	T_g (°C)[b)]	T_m (°C)[b)]
PLLA$_{20}$-CNO	276	43.2	140
PLLA$_{20}$-star	283	44.1	138
PLLA$_{51}$-CNO	309	49.6	148
PLLA$_{51}$-star	311	51.2	142
PLLA$_{98}$-CNO	328	52.6	151
PLLA$_{98}$-star	331	54.2	-[c)]
PCL$_{41}$-CNO	332	-[c)]	52.0
PCL$_{41}$-star	322	-[c)]	48.1
PVL$_{21}$-*b*-PLLA$_{18}$-CNO	315	-[c)]	142
PVL$_{21}$-*b*-PLLA$_{18}$-star	298	-[c)]	137

a) Determined by TGA. b) Determined by DSC. c) Not observed.

3. Reference

S1. C-G. Wang, Y. Koyama, M. Yonekawa, S. Uchida and T. Takata, *Chem. Commun.,* 2013, **49**, 7723.
S2. A. Zelcer, B. Donnio, C. Bourgogne, F. D. Cukiernik, and D. Guillon, *Chem*. *Mater*., 2007, **19**, 1992.