Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Preparation of a Highly Reactive Polymer Click Reagent, PEG Nitrile *N*-Oxide, and Its Application to Block and Star Polymer Synthesis

Toyokazu Tsutsuba[†], Hiromitsu Sogawa[†,§], and Toshikazu Takata*[†,§]

[†]Department of Chemical Science and Engineering, and [§] JST-CREST, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Contents

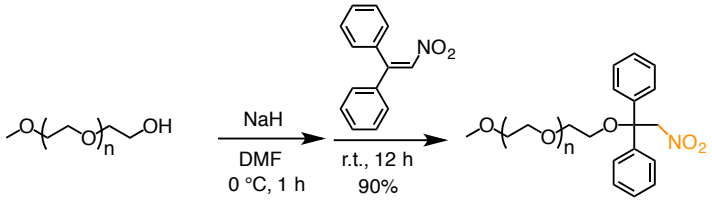
1. Experimental Section

1.1 Materials and instrument

Dichloromethane was dehydrated by activated molecular sieve 4A. δ-Valerolactone (δ-VL) (>98%, TCI) was distilled over CaH_2 under reduced pressure. Sodium hydride (>98%, Kanto Chemical Co., Inc.), poly(ethylene glycol) methyl ether (M_n 2000) (Aldrich), 4-chlorophenyl isocyanate (>98%, TCI), triethylamine (Et_3N) (>98%, Wako), allyltrimethylsilane (>98%, TCI), 3-buten-1-ol (>98%, TCI), diethyl phosphite (>98%, TCI), phenyl isocyanate (>98%, TCI) and other commercially available solvents were used as received. 1,1-diphenylnitroethene was prepared according to literature.[S1] ^1H NMR (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a JEOL AL-400 spectrometer using $CDCl_3$ as a solvent. Tetramethylsilane ($\delta H = 0.00$ ppm) and $CDCl_3$ ($\delta C = 77.0$ ppm) were used as internal standards. 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 were carried out using a HPLC LC-918 instrument by Japan Analysis Industry with a Megapak-Gel 201CP (Guard Column), a Megapak-Gel 201C, and a JAIGEL-H. 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 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

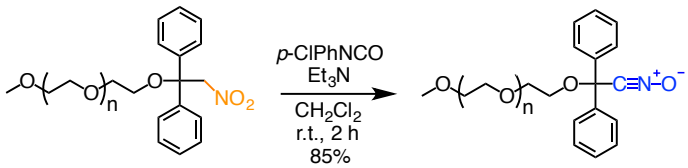
・Synthesis of **PEG-NA**



PEG-OH **PEG-NA**

Sodium hydride (0.65 g, 27 mmol) was washed with hexane. After the remaining hexane was removed by evaporation, dry DMF (40 mL) was added, followed by the dropwise addition of the solution of poly (ethylene glycol) monomethyl ether ($M_{n(SEC)}$ 3100 g/mol, PDI 1.10) (10 g, 5.0 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 (3.4 g, 15 mmol) in dry DMF (10 mL). After stirring at room temperature for 12 h, the reaction was cooled to 0 °C and quenched by a small amount of acetic acid. The mixture was diluted in dichloromethane, washed with 1.0 M HCl aq. and brine, dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by pouring into large amount of Et_2O (0.50 L) at 0 ºC. The precipitate was separated by filtration and dried *in vacuo* to obtain **PEG-NA** (11 g, 90%) as a white solid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.31–7.26 (m, 10H, Ar), 5.34 (s, 2H, –C<u>H</u>$_2$–NO_2), 3.66–3.58 (m, 4H × n, (–OC<u>H</u>$_2$C<u>H</u>$_2$O–)$_n$), 3.38 (s, 3H, C<u>H</u>$_3$O–) ppm; $M_{n(SEC)}$ 3500 g/mol, PDI 1.05.

・Synthesis of **PEG-CNO**

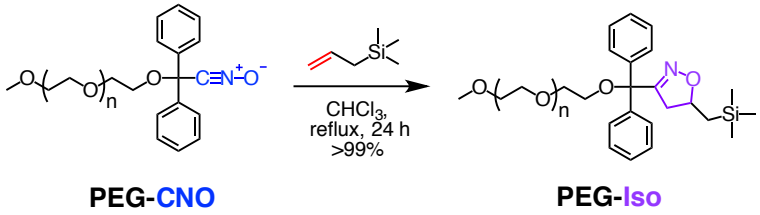


PEG-NA **PEG-CNO**

To a solution of **PEG-NA** (1.1 g, 0.50 mmol) and triethylamine (0.76 g, 7.5 mmol) in dry dichloromethane (20 mL) was added *p*-chlorophenylisocyanate (0.77 g, 5.0 mmol) at room temperature and the mixture was stirred for 2 h under argon atmosphere. After the consumption of **PEG-NA**, generated 1,3-bis(4-chlorophenyl)urea was removed by filtration and the residue was evaporated. It was purified by pouring into large amount of Et_2O (0.10 L) at 0 ºC. The precipitate was separated by filtration and further purified by silica gel column chromatography (eluent: chloroform/ethyl acetate: 1/1 → chloroform/methanol: 9/1) to obtain **PEG-CNO** (0.93 g, 85%) as a white solid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.40–7.37 (m, 4H, Ar), 7.35–7.32 (m, 6H, Ar),

3.66–3.58 (m, 4H × n, (–OC$\underline{H_2}$C$\underline{H_2}$O–)$_n$), 3.38 (s, 3H, C$\underline{H_3}$O–) ppm; IR (NaCl): ν 2883, 2276 (CNO), 1968, 1731, 1467, 1359, 1280, 1118, 1060, 946, 842 cm^{-1}; $M_{n(SEC)}$ 3200 g/mol, PDI 1.08; T_m 48.2 °C; T_{d5} 296 °C.

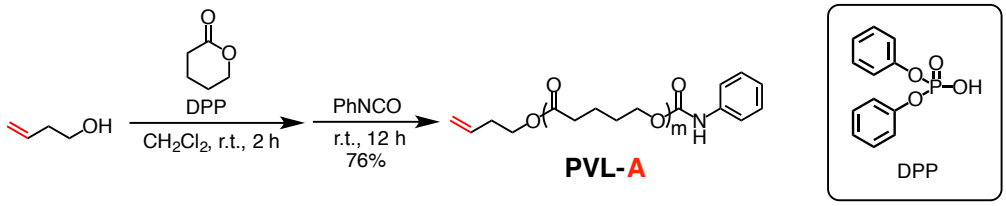
・The reaction of **PEG-CNO** with allyltrimethylsilane



PEG-CNO **PEG-Iso**

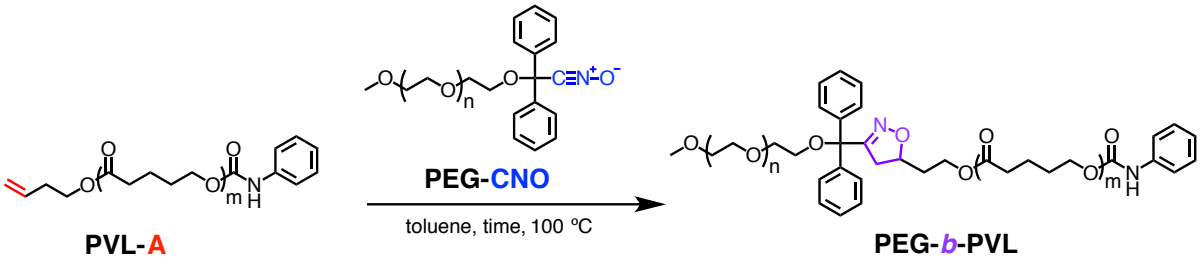
PEG-CNO (0.11 g, 50 μmol) and allyltrimethylsilane (57 mg, 0.5 mmol) were dissolved in $CHCl_3$ (5.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, solvent and excess amount of allyltrimethylsilane were removed under reduced pressure to give the **PEG-Iso** in >99% yield (0.14 g) as a white solid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.59–7.54 (m, 4H, Ar), 7.30–7.22 (m, 6H, Ar), 4.64–4.60 (m, 1H, –CH_2–C$\underline{H}$(CH_2TMS)–O–), 3.67–3.59 (m, 4H × n, (–OC$\underline{H_2}$C$\underline{H_2}$O–)$_n$), 3.38 (s, 3H, C$\underline{H_3}$O–), 2.96–2.94 (m, 1H, –C$\underline{H_A}$$H_B$–CH($CH_2$TMS)–O–), 2.41–2.34 (m, 1H, –C$H_A$$\underline{H_B}$–CH($CH_2$TMS)–O–), 1.11–1.07 (m, 1H, –C$\underline{H_A}$$H_B$TMS), 0.85–0.80 (m, 1H, –C$H_A$$\underline{H_B}$TMS), 0.00 (s, 9H, –Si–(C$\underline{H_3}$)$_3$) ppm; $M_{n(SEC)}$ 3300 g/mol, PDI 1.10.

・Synthesis of **PVL-A**[S2]



Diphenylphosphate (0.13 g, 0.50 mmol) was added to a solution of 3-buten-1-ol (36 mg, 0.50 mmol) and δ-valeroactone (0.40 g, 40 mmol) in CH_2Cl_2 (20 mL), the mixture was stirred for 2 h at room temperature. Then phenylisocyanate (0.60 g, 5.0 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-A** (3.0 g, 76%) as a white solid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.42–7.37 (m, 2H, Ar), 7.32–7.28 (m, 2H, Ar), 7.10–7.03 (m, 1H, Ar), 6.85 (m, NH), 5.82–5.74 (m, 1H, CH_2=C$\underline{H}$–), 5.13–5.06 (m, 2H, C$\underline{H_2}$=CH–), 4.19–4.16 (m, 2H, –CH–CH_2–C$\underline{H_2}$–O–), 4.14–4.12 (m, 2H, CH_2=CH–C$\underline{H_2}$–), 4.11–4.08 (m, 2H × m, (–OC$\underline{H_2}$$CH_2$$CH_2$$CH_2$(C=O)–)$_m$), 2.57–2.44 (m, 2H × m, (–O$CH_2$$CH_2$$CH_2C\underline{H_2}$(C=O)–)$_m$), 1.73–1.68 (m, 4H × m, (–OCH_2C$\underline{H_2}$C$\underline{H_2}$$CH_2$(C=O)–)$_m$) ppm; $DP_{m(NMR)}$ 70, $M_{n(SEC)}$ 6600 g/mol, PDI 1.15; T_m 52.5 °C; T_{d5} 313 °C.

・Synthesis of diblock copolymer **PEG-*b*-PVL** using **PEG-CNO**



・Catalyst-free condition (Table 1, Runs 1–8)

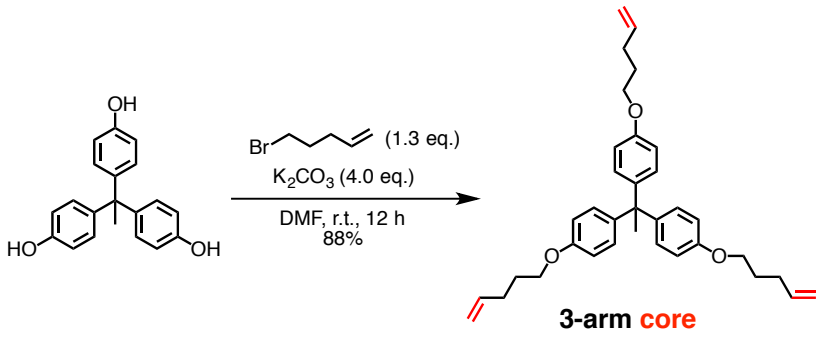
A solution of **PEG-CNO** (0.33 g, 0.15 mmol) and **PVL-A** (0.36 g, 0.05 mmol) in toluene (2.0 mL) was stirred at 100 ºC for several hours. Solvent was removed by evaporation. The residue was poured into Et_2O (80 mL) at room temperature and the precipitate was collected to obtain **PEG-*b*-PVL** (0.42 g, 88%) as a white solid; $M_{n(SEC)}$ 9500 g/mol, PDI 1.10.

・Catalyst- and solvent-free condition (Table 1, Runs 9 and 10)

PEG-CNO (0.33 g, 0.15 mmol) and **PVL-A** (0.36 g, 0.05 mmol) were stirred at 100 ºC for several hours. The resulting mixture was poured into Et_2O at room temperature and collected the precipitate to obtain **PEG-*b*-PVL** (0.42 g, 89%) as a white solid; $M_{n(SEC)}$ 10000 g/mol, PDI 1.13.

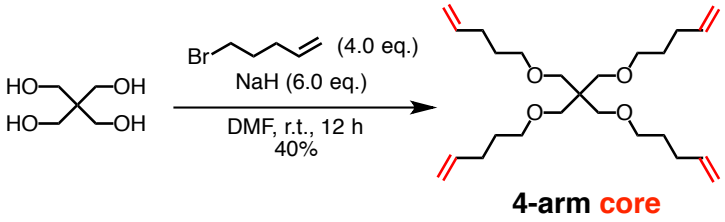
^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.56–7.53 (m, 4H, Ar–H), 7.49–7.47 (m, 3H, Ar–H), 7.44–7.24 (m, 6H, Ar–H), 7.10–7.04 (m, 2H, Ar–H), 6.85 (m, NH), 4.62–4.59 (m, 1H, –CH_2–CH(CH_2–)–O–), 4.10–4.06 (m, 2H × m, (–OC$H_2$$CH_2$$CH_2$$CH_2$(C=O)–)$_m$), 3.66–3.60 (m, 4H × n, (–OCH_2CH_2O–)$_n$), 3.37 (s, 3H, CH_3O–), 3.04–2.98 (m, 1H, –C$H_A$$H_B$–CH($CH_2$)–O–), 2.59–2.52 (m, 1H, –C$H_A$$H_B$–CH($CH_2$)–O–), 2.54–2.39 (m, 2H × m, (–OC$H_2$$CH_2$$CH_2CH_2$(C=O)–)$_m$), 1.68–1.65 (m, 4H × m, (–OCH_2CH_2C$H_2$$CH_2$(C=O)–)$_m$) ppm; IR (NaCl): ν 2956, 2875, 2100, 1729, 1602, 1540, 1473, 1457, 1421, 1403, 1382, 1326, 1259, 1193, 1172, 1106, 1066, 1045, 952, 916, 852, 806, 744, 701 cm^{-1}; T_m 50.3 ºC; T_{d5} 286 °C.

・Synthesis of **3-arm core**



1,1,1-Tris(4-hydroxyphenyl)ethane) (1.5 g, 5.0 mmol), K_2CO_3 (8.3 g, 60 mmol) and 5-bromo-1-pentene (3.0 g, 20 mmol) were dissolved in DMF (20 mL) and the mixture was stirred at 90 ºC for 12 h. Solvent was removed by evaporation and the residue was diluted in dichloromethane and washed with water, 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 **3-arm core** in 88% yield (2.3 g) as a colorless liquid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 6.98 (d, J = 8.8 Hz, 6H, Ar), 6.78 (d, J = 8.8 Hz, 6H, Ar), 5.88–5.80 (m, 3H, CH_2=C<u>H</u>–), 5.09–4.97 (m, 6H, C<u>H$_2$</u>=CH–), 4.10–3.94 (t, J = 6.5 Hz, 6H, –Ph–O–C<u>H$_2$</u>–CH_2–), 2.25–2.20 (m, 6H, –Ph–O–CH_2–C<u>H$_2$</u>–), 2.10 (s, 3H, –C<u>H$_3$</u>), 19.0–1.83 (m, 6H,–C<u>H$_2$</u>–CH_2=CH_2) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 157.0, 141.7, 137.9, 129.6, 115.1, 113.6, 67.0, 50.5, 30.8, 30.1 28.5 ppm; FAB-HRMS (*m/z*) calc'd for $C_{35}H_{42}O_3$ $[M]^+$, 510.3134; found, 510.3137.

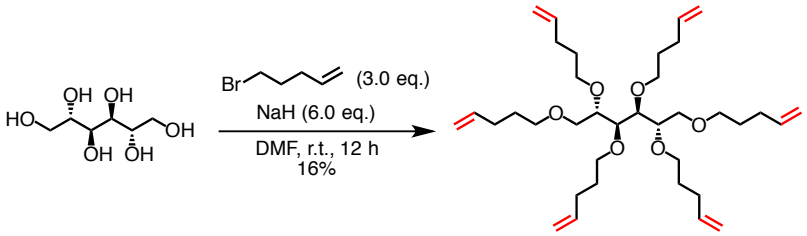
・Synthesis of **4-arm core**



Sodium hydride (3.8 g, 0.16 mol) was washed with hexane. After the remaining hexane was removed by evaporation, dry DMF (45 mL) was added, followed by the dropwise addition of pentaerythritol (1.4 g, 10 mmol) at 0 ºC. The resulting mixture was stirred at the same temperature for 1 h, and added to a 5-bromo-1-pentene (7.8 g, 52 mmol). After stirring at room temperature for 12 h, the reaction was cooled to 0 °C and quenched by a small amount of methanol. The mixture was diluted in dichloromethane, washed with 1.0 M HCl aq. and brine, dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ethyl acetate: 10/1) to obtain **4-arm core** in 40% yield (1.6 g) as a colorless liquid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 5.86–5.78 (m, 4H, CH_2=C<u>H</u>–), 5.04–4.94 (m, 8H, C<u>H$_2$</u>=CH–), 3.40–3.37

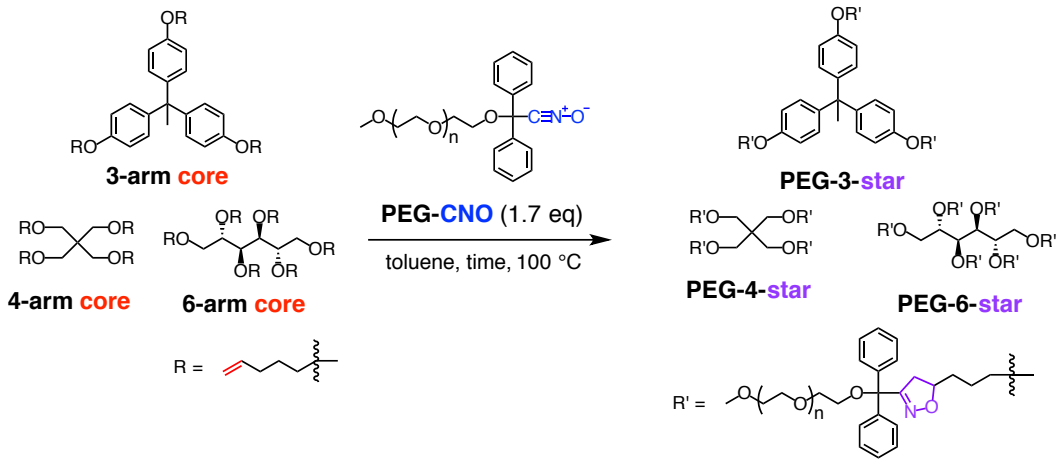
(m, 16H, –C<u>H</u>$_2$–O–C<u>H</u>$_2$–), 2.13–2.07 (m, 8H, –O–CH$_2$–C<u>H</u>$_2$–), 1.67–1.59 (m, 8H,–C<u>H</u>$_2$–CH$_2$=CH$_2$) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 138.6, 114.4, 70.6, 69.7, 45.4, 30.4 28.9 ppm; FAB-HRMS (*m/z*) calc'd for $C_{25}H_{45}O_4$ $[M+H]^+$, 409.3318; found, 409.3311.

・Synthesis of **6-arm core**



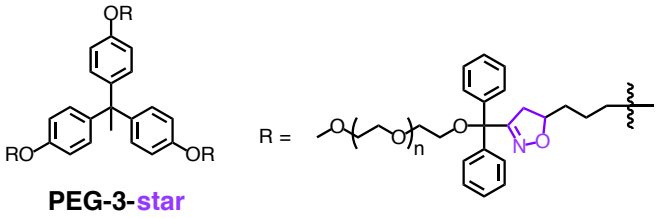
Sodium hydride (9.1 g, 0.38 mol) was washed with hexane. After the remaining hexane was removed by evaporation, dry DMF (45 mL) was added, followed by the dropwise addition of D-mannitol (1.5 g, 8.0 mmol) at 0 ºC. The resulting mixture was stirred at the same temperature for 1 h, and added to a 5-bromo-1-pentene (21 g, 0.14 mol). After stirring at room temperature for 12 h, the reaction was cooled to 0 °C and quenched by a small amount of methanol. The mixture was diluted in dichloromethane, washed with 1.0 M HCl aq. and brine, dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ethyl acetate: 10/1) and preparative GPC ($CHCl_3$) to obtain **6-arm core** in 16% yield (0.76 g) as a colorless liquid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 5.85–5.76 (m, 6H, CH$_2$=C<u>H</u>–), 5.03–4.93 (m, 12H, C<u>H</u>$_2$=CH–), 3.77–3.59 (m, 16H, –C<u>H</u>$_2$–O–C<u>H</u>$_2$– and –CH–O–C<u>H</u>$_2$–), 3.44–3.37 (m, 4H, –O–CH$_2$–(C<u>H</u>)$_4$–CH$_2$–O–), 2.13–2.06 (m, 12H, –O–CH$_2$–C<u>H</u>$_2$–), 1.71–1.63 (m, 12H,–C<u>H</u>$_2$–CH$_2$=CH$_2$) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 138.4, 114.6, 79.0, 78.9, 70.7, 69.6, 68.9, 30.4 29.5, 29.3, 28.9 ppm; FAB-HRMS (*m/z*) calc'd for $C_{36}H_{63}O_6$ $[M+H]^+$, 591.4625; found, 591.4628.

・Typical experimental procedure for the synthesis of star polymer using **PEG-CNO**



A solution of **PEG-CNO** and **3, 4, or 6-arm core** in toluene was stirred at 100 ºC for 24 h. Solvent was removed by evaporation. The residue was poured into Et_2O (80 mL) at room temperature and the precipitate was collected to obtain **PEG-3, 4, or 6-star**.

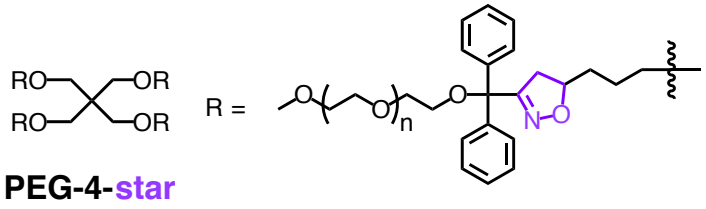
・PEG-3-star



PEG-3-star

PEG-CNO (0.11 g, 50 μmol), **3-arm core** (5.1 mg, 10 μmol) and toluene (6.0 mL) were used for reaction. The precipitate was dried to give **PEG-3-star** in 44% yield (92 mg) as a white solid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.58–7.53 (m, 12H, Ar), 7.31–7.19 (m, 18H, Ar), 6.93 (d, 6H, J = 8.8 Hz, Ar), 6.71 (d, 6H, J = 8.8 Hz, Ar), 4.60–4.56 (m, 3H, –CH_2–C<u>H</u>(CH_2–)–O–), 4.10–3.94 (m, 6H, –Ph–O–C<u>H_2</u>–CH_2–), 3.67–3.60 (m, 4H × n, (–OC<u>H_2</u>C<u>H_2</u>O–)$_n$), 3.38 (s, 9H, C<u>H_3</u>O–), 3.03–2.96 (m, 3H, –C<u>H_A</u>H_B–CH(CH_2)–O–), 2.50–2.35 (m, 3H, –CH_A<u>H_B</u>–CH(CH_2)–O–), 2.07 (s, 3H, –CH_3), 1.80–1.59 (m, 12H, –O–CH_2–C<u>H_2</u>–C<u>H_2</u>–); $M_{n(SEC)}$ 10000 g/mol, PDI 1.06; IR (NaCl): ν 2883, 1965, 1731, 1606, 1508, 1467, 1359, 1344, 1280, 1243, 1145, 1112, 1060, 960, 946, 842, 754, 705 cm^{-1}; T_g -20.4 °C; T_m 45.9 °C; T_{d5} 266 °C.

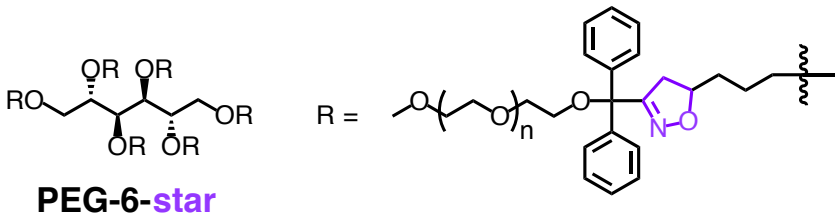
・PEG-4-star



PEG-4-star

PEG-CNO (0.45 g, 0.20 mmol), **4-arm core** (12 mg, 30 μmol) and toluene (10 mL) were used for reaction. The precipitate was dried to give **PEG-4-star** in 86% yield (0.24 g) as a white solid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.57–7.52 (m, 16H, Ar), 7.32–7.18 (m, 24H, Ar), 4.52–4.42 (m, 4H, –CH_2–C<u>H</u>(CH_2–)–O–), 3.67–3.60 (m, 4H × n, (–OC<u>H_2</u>C<u>H_2</u>O–)$_n$), 3.40–3.30 (m, 16H, –C<u>H_2</u>–O–C<u>H_2</u>–), 3.38 (s, 3H, C<u>H_3</u>O–), 2.98–2.85 (m, 8H, –C<u>H_A</u>H_B–CH(CH_2)–O–), 2.50–2.35 (m, 8H, –CH_A<u>H_B</u>–CH(CH_2)–O–), 1.58–1.44 (m, 16H, –O–CH_2–C<u>H_2</u>–C<u>H_2</u>–); $M_{n(SEC)}$ 10500 g/mol, PDI 1.09; IR (NaCl): ν 2883, 1970, 1737, 1600, 1467, 1359, 1344, 1280, 1238, 1149, 1116, 1062, 960, 948, 842, 757, 703 cm^{-1}; T_g -26.2 °C; T_m 45.2 °C; T_{d5} 265 °C.

・PEG-6-star



PEG-6-star

・Catalyst-free condition (Table 2, Runs 3 and 4)

PEG-CNO (0.45 g, 0.20 mmol), **6-arm core** (12 mg, 20 μmol) and toluene (10 mL) were used for reaction. The precipitate was dried to give **PEG-6-star** in 86% yield (0.24 g) as a white solid.

・Catalyst- and solvent-free condition (Table 2, Run 5)

PEG-CNO (0.45 g, 0.20 mmol), **6-arm core** (12 mg, 0.02 μmol) were used for reaction. The precipitate was dried to give **PEG-6-star** in 92% yield (0.27 g) as a white solid.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.57–7.51 (m, 24H, Ar), 7.32–7.18 (m, 36H, Ar), 4.52–4.41 (m, 6H, –CH_2–C<u>H</u>(CH_2–)–O–), 3.67–3.60 (m, 4H × n, (–OC<u>H_2</u>C<u>H_2</u>O–)$_n$), 3.40–3.30 (m, 16 H, –C<u>H_2</u>–O–C<u>H_2</u>–), 3.38 (s, 3H, C<u>H_3</u>O–), 2.98–2.85 (m, 6H, –C<u>H_A</u><u>H_B</u>–CH(CH_2)–O–), 2.50–2.35 (m, 6H, –CH_A<u>H_B</u>–CH(CH_2)–O–), 1.62–1.40 (m, 24H, –O–CH_2–C<u>H_2</u>–C<u>H_2</u>–); IR (NaCl): ν 2883, 1965, 1727, 1594, 1466, 1359, 1344, 1280, 1240, 1145, 1110, 1058, 962, 948, 842, 757, 701 cm^{-1}; $M_{n(SEC)}$ 13000 g/mol, PDI 1.10; T_g -35.2 °C; T_m 43.6 °C; T_{d5} 276 °C.

2. *Spectrum data of new compounds*

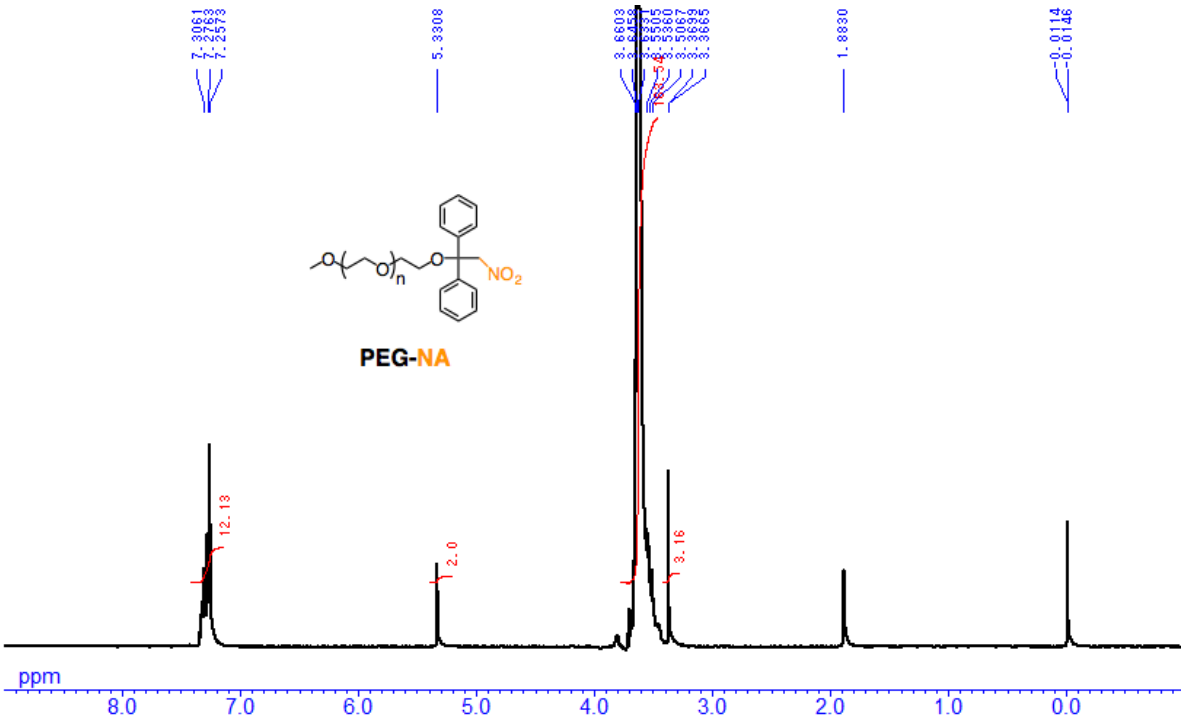


Figure S1. ^{1}H NMR spectrum of **PEG-NA** (400 MHz, 298 K, $CDCl_3$)

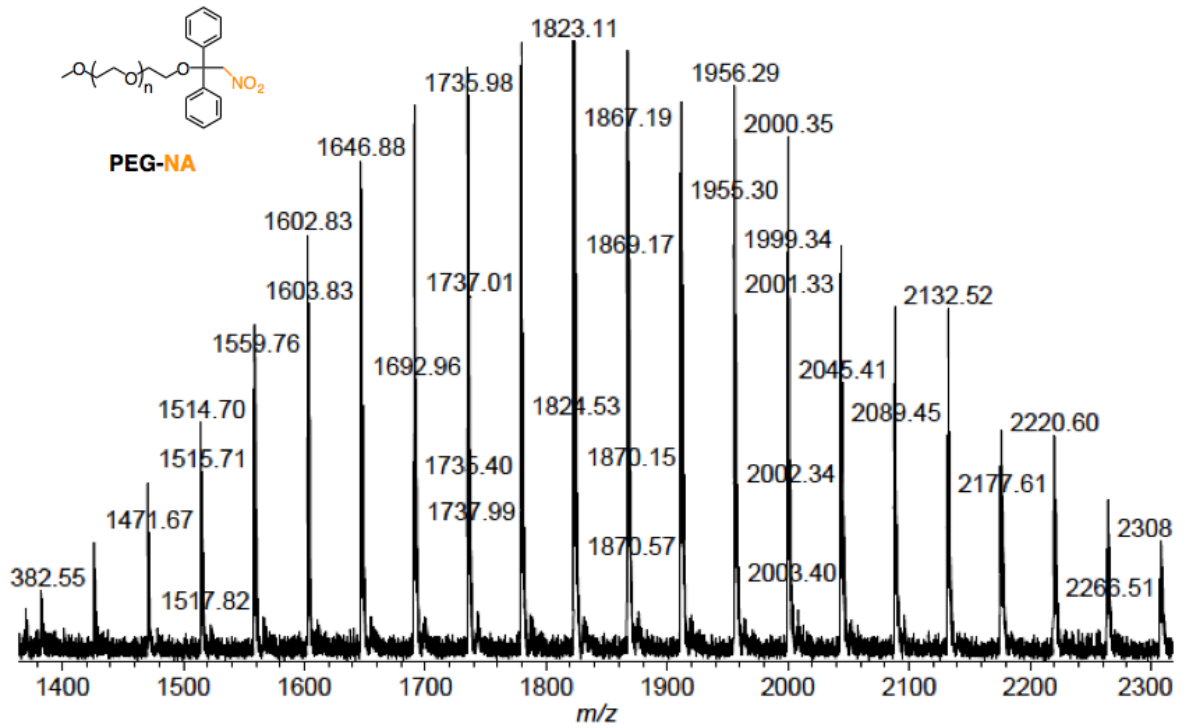


Figure S2. MALDI-TOF MS spectrum of **PEG-NA** (marix: dithranol)

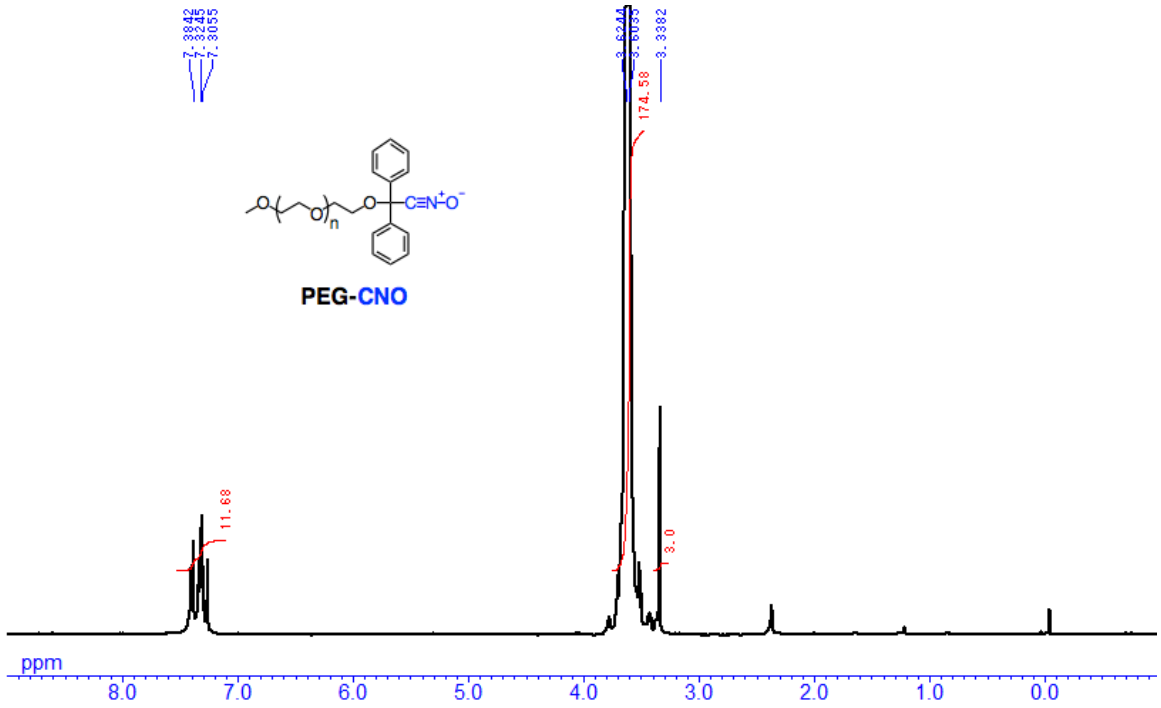


Figure S3. ^{1}H NMR spectrum of **PEG-CNO** (400 MHz, 298 K, $CDCl_3$)

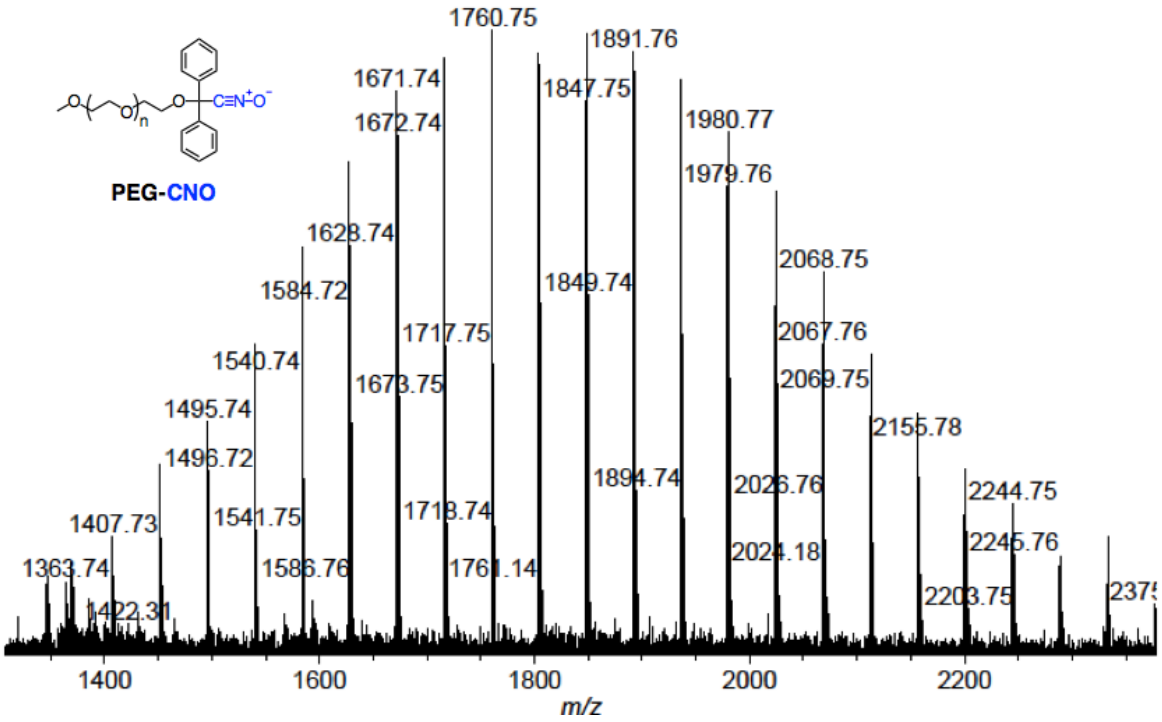


Figure S4. MALDI-TOF MS spectrum of **PEG-NA** (marix: dithranol)

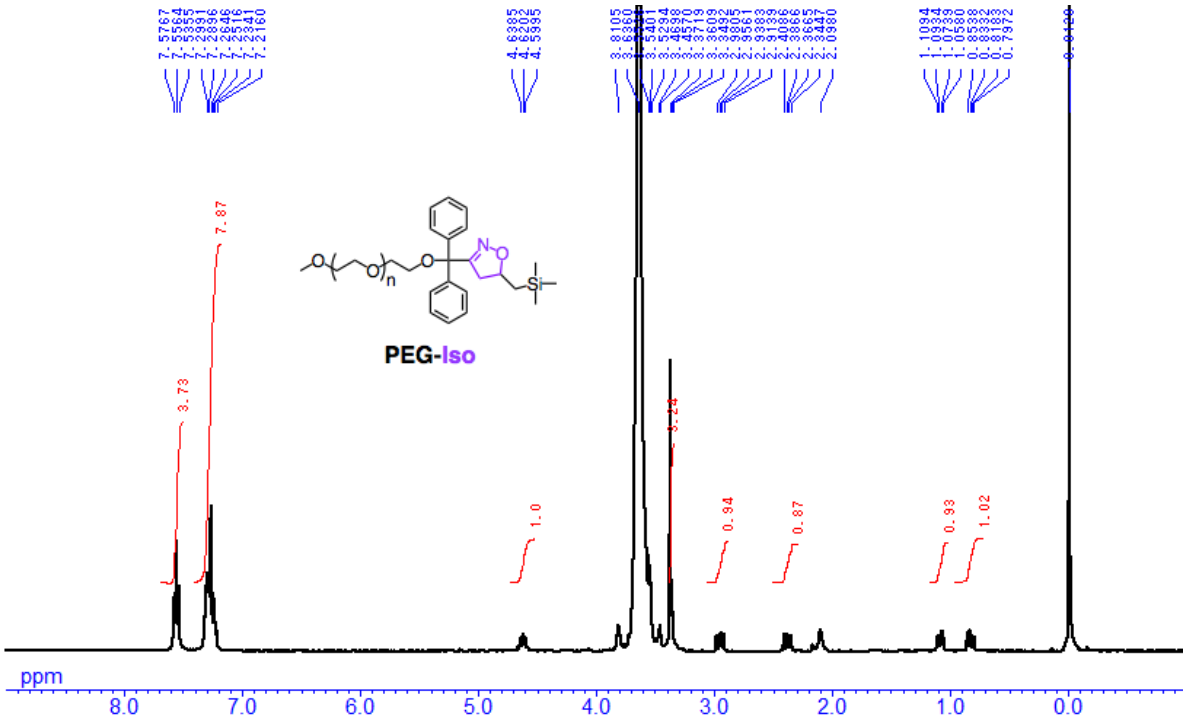


Figure S5. ^{1}H NMR spectrum of **PEG-Iso** (400 MHz, 298 K, $CDCl_3$)

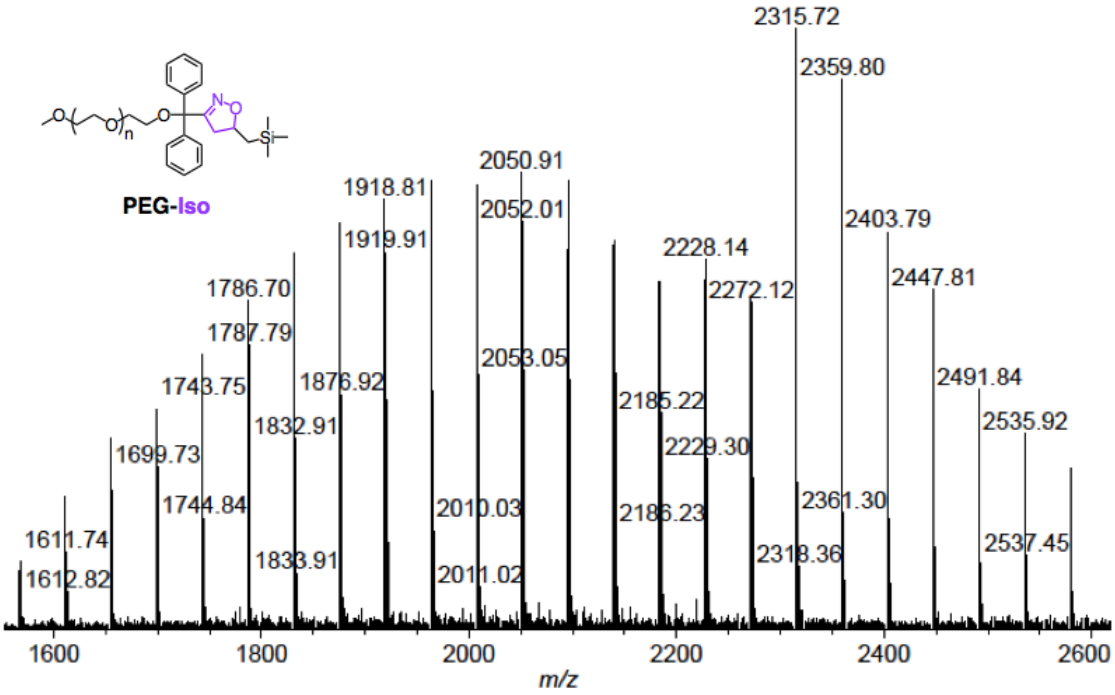


Figure S6. MALDI-TOF MS spectrum of **PEG-Iso** (marix: dithranol)

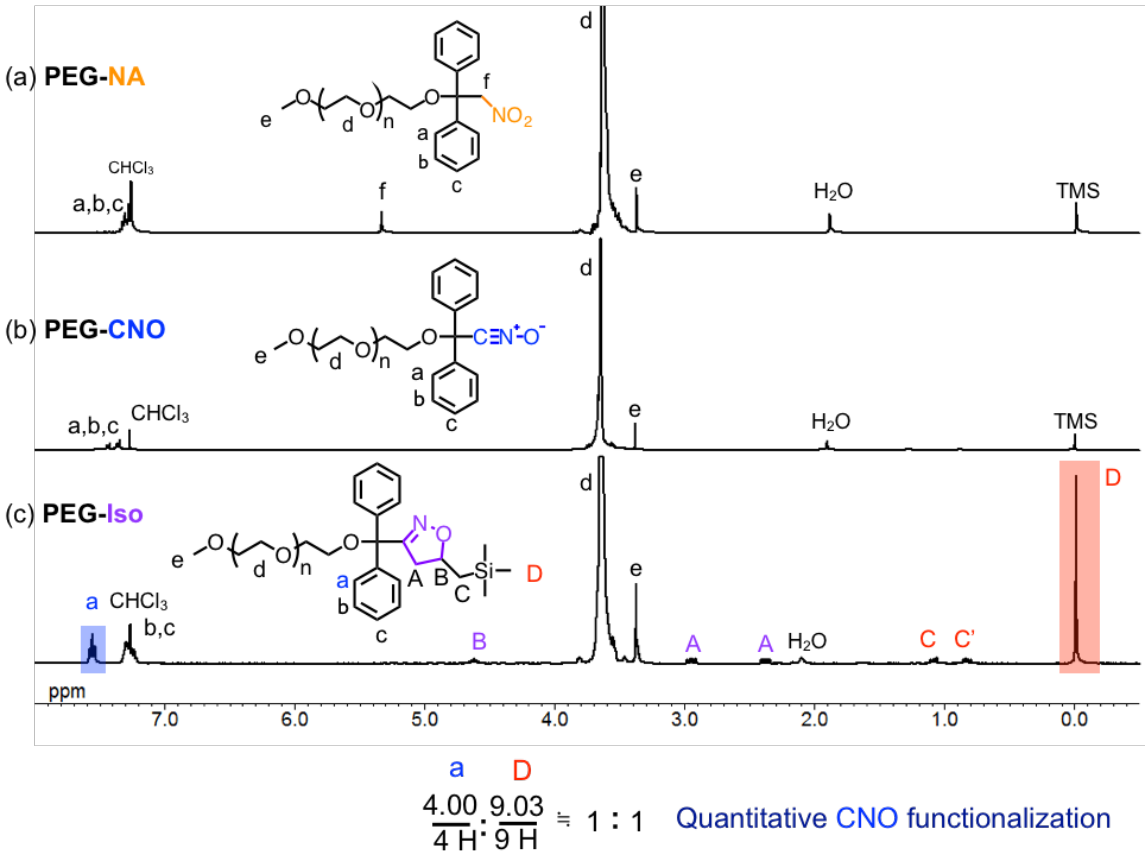


Figure S7. ^{1}H NMR spectra change of (a) **PEG-NA**, (b) **PEG-CNO** and (b) **PEG-Iso** (400 MHz, 298 K, $CDCl_3$)

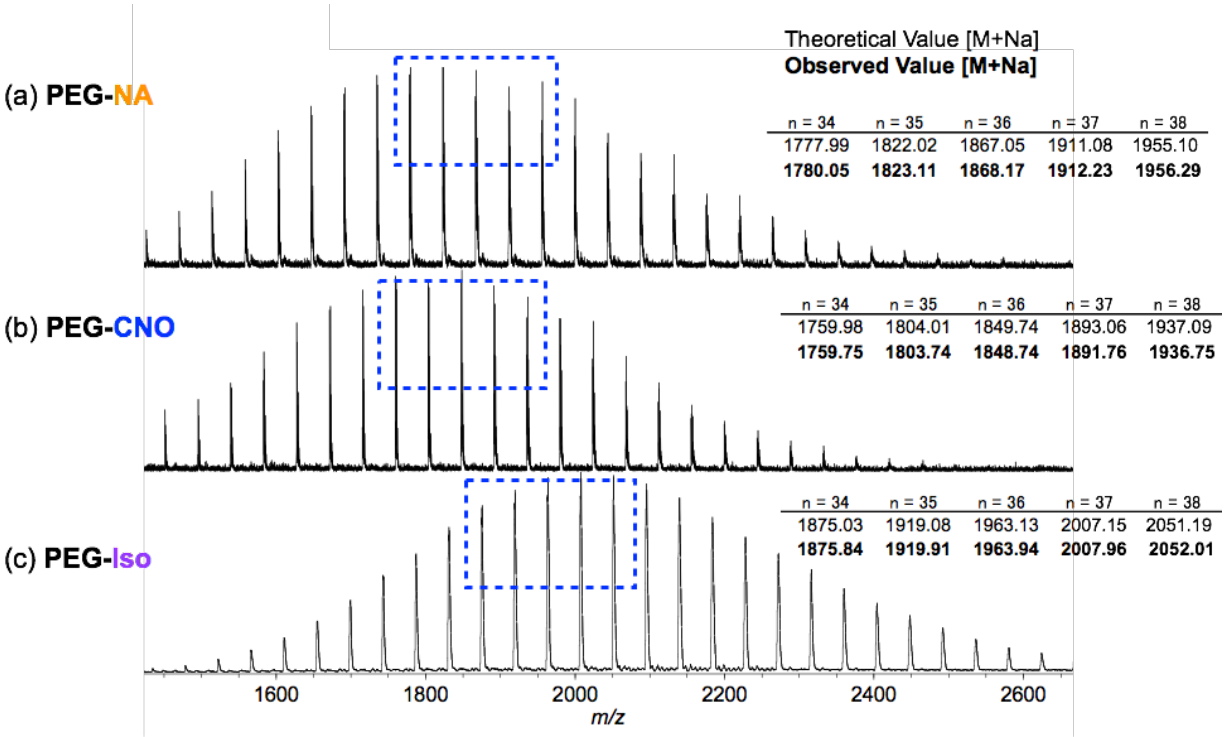


Figure S8. MALDI-TOF MS spectra change of (a) **PEG-NA**, (b) **PEG-CNO**, and (c) **PEG-Iso** (marix: dithranol)

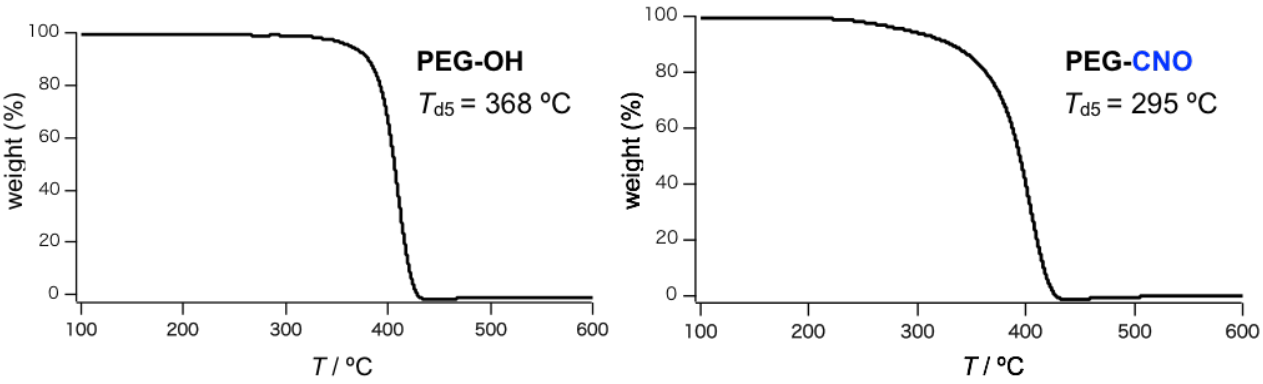


Figure S9. TGA (10 °C/min, under N_2) charts of (a) **PEG-OH** and (b) **PEG-CNO**

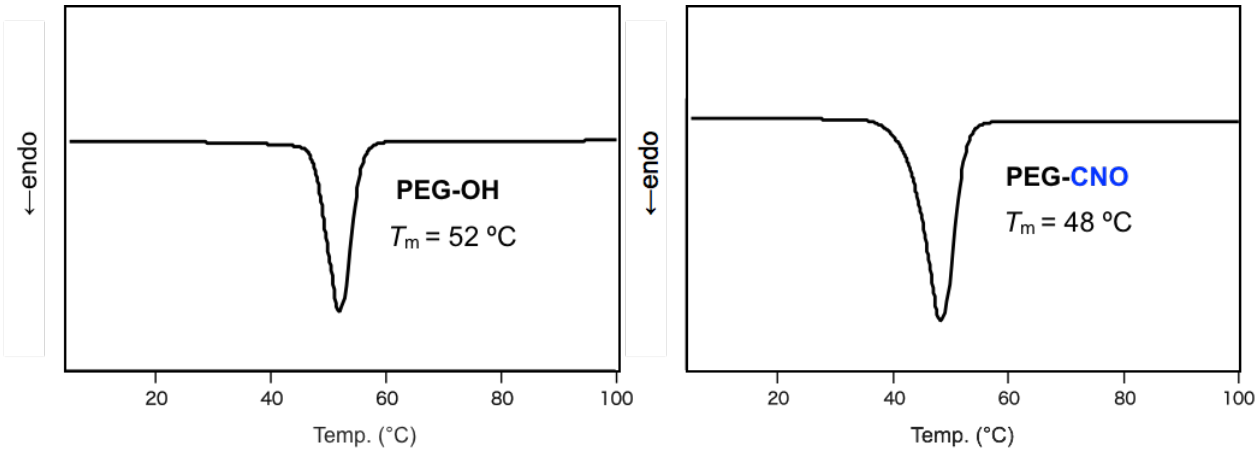


Figure S10. DSC (10 °C/min, 2nd heating under N_2) charts of (a) **PEG-OH** and (b) **PEG-CNO**

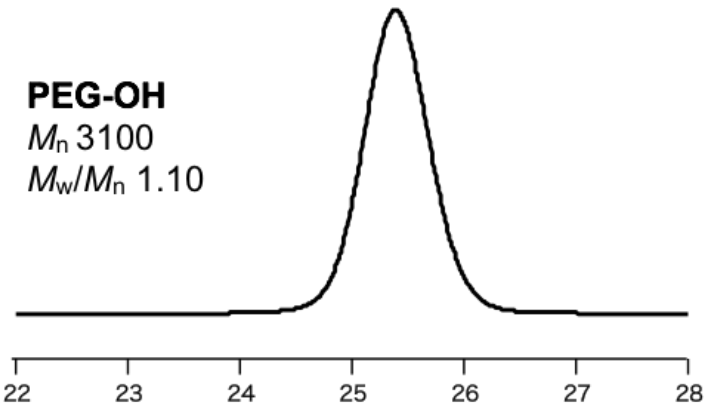


Figure S11. SEC chart of **PEG-OH** (PS standard, eluent, $CHCl_3$; flow rate,1.0 mL/min, detected by RI)

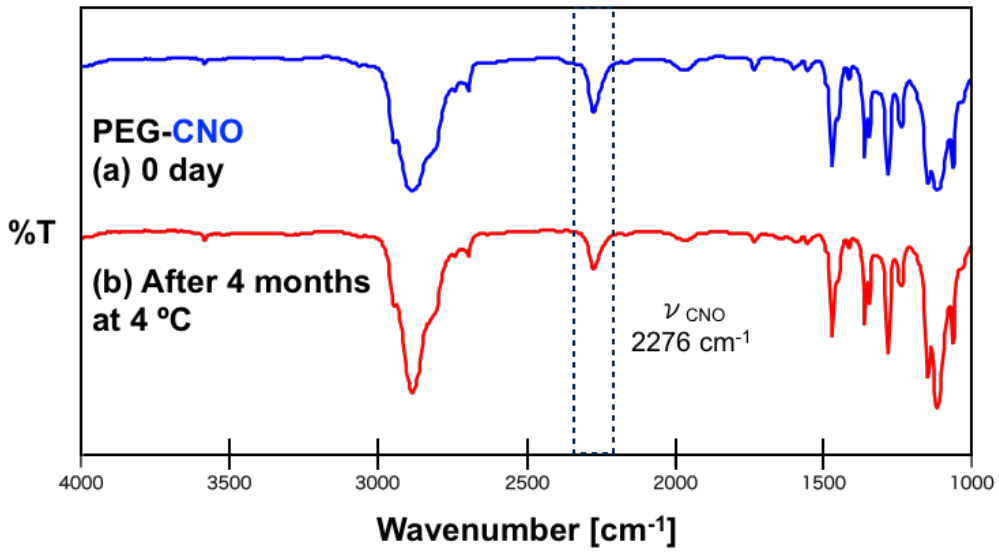


Figure S12. FT-IR spectra of (a) **PEG-CNO** and (b) **PEG-CNO** after standing at 4 ºC for 4 months (NaCl)

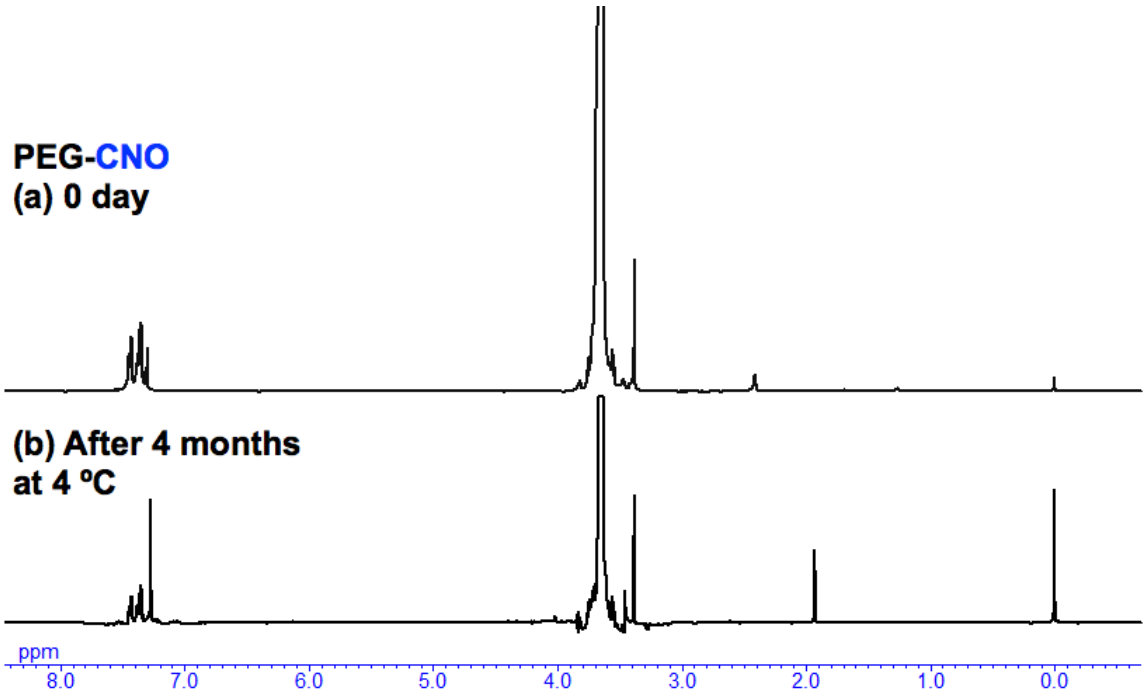


Figure S13. ^{1}H NMR spectra of (a) **PEG-CNO** and (b) **PEG-CNO** after standing at 4 ºC for 4 months (400 MHz, 298 K, $CDCl_3$)

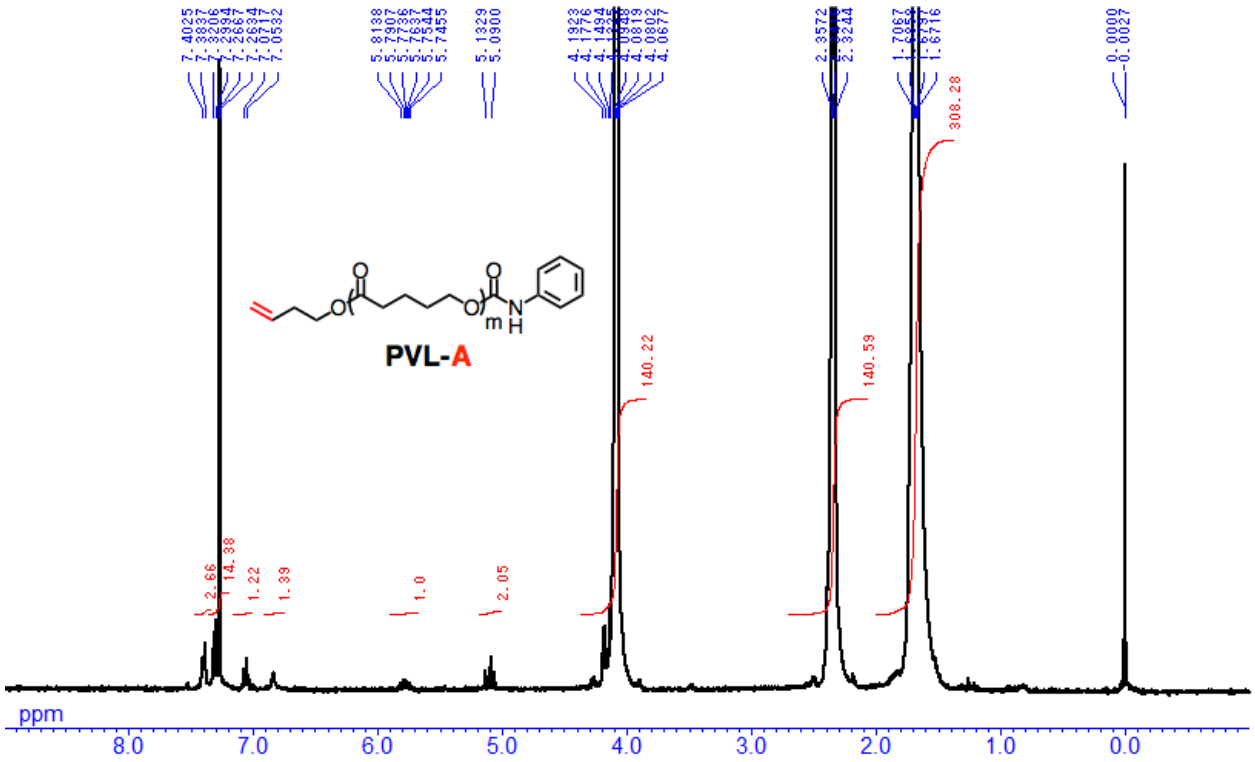


Figure S14. ^{1}H NMR spectrum of **PVL-A** (400 MHz, 298 K, $CDCl_3$)

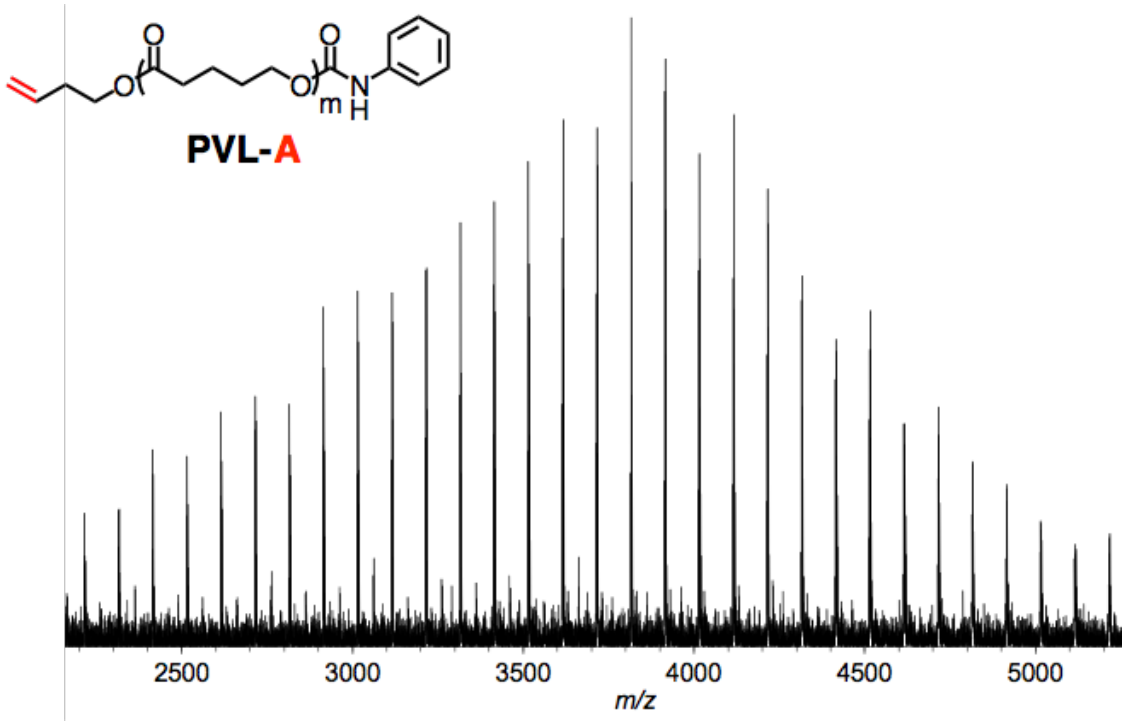


Figure S15. MALDI-TOF MS spectrum of **PVL-A** (marix: dithranol)

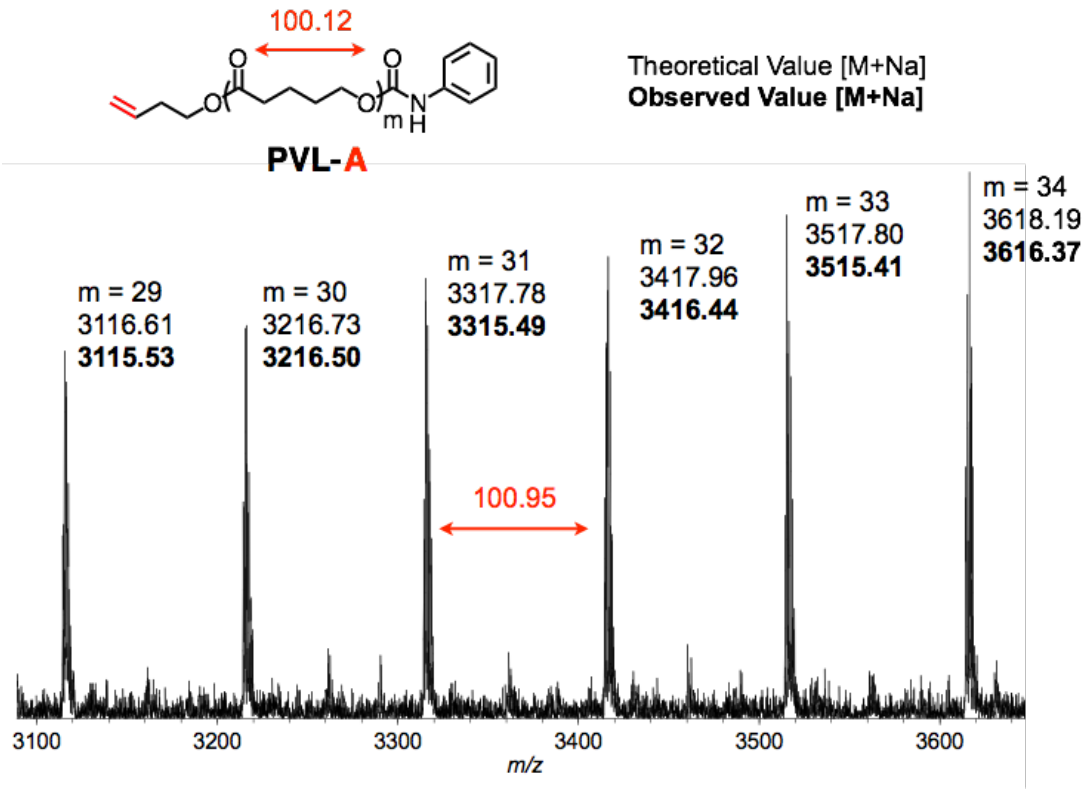


Figure S16. MALDI-TOF MS spectrum of **PVL-A** (marix: dithranol)

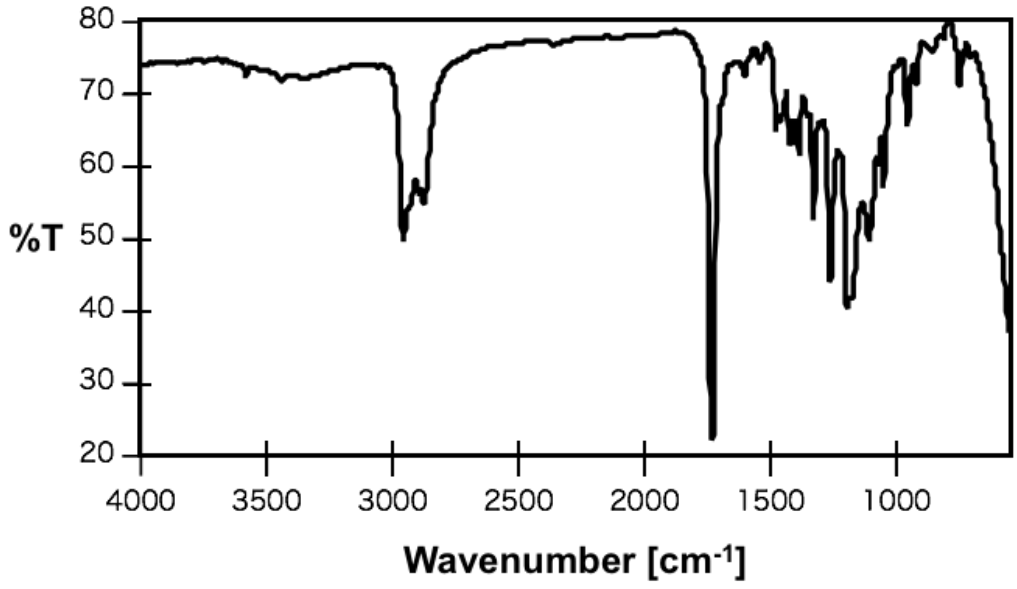
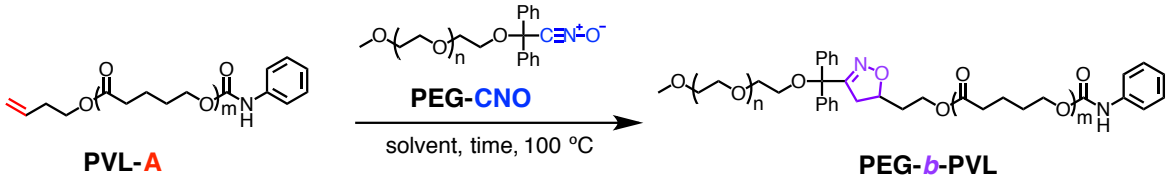


Figure S17. FT-IR spectrum of **PEG-*b*-PVL** (NaCl)

Table S1. Catalyst-free synthesis of **PEG-*b*-PVL** by click reaction of **PEG-CNO** and **PVL-A**.



Run[a)]	Solvent	Time (min.)	Conv.[b)] (%)
1	toluene	10	81
2	DMF	10	78
3	chlorobenzene	10	83

a) Reaction conditions: at 100 °C, [**PEG-CNO**] / [**PVL-A**] = 3.0, [**PVL-A**] = 0.025 M. b) Determined by ^{1}H NMR.

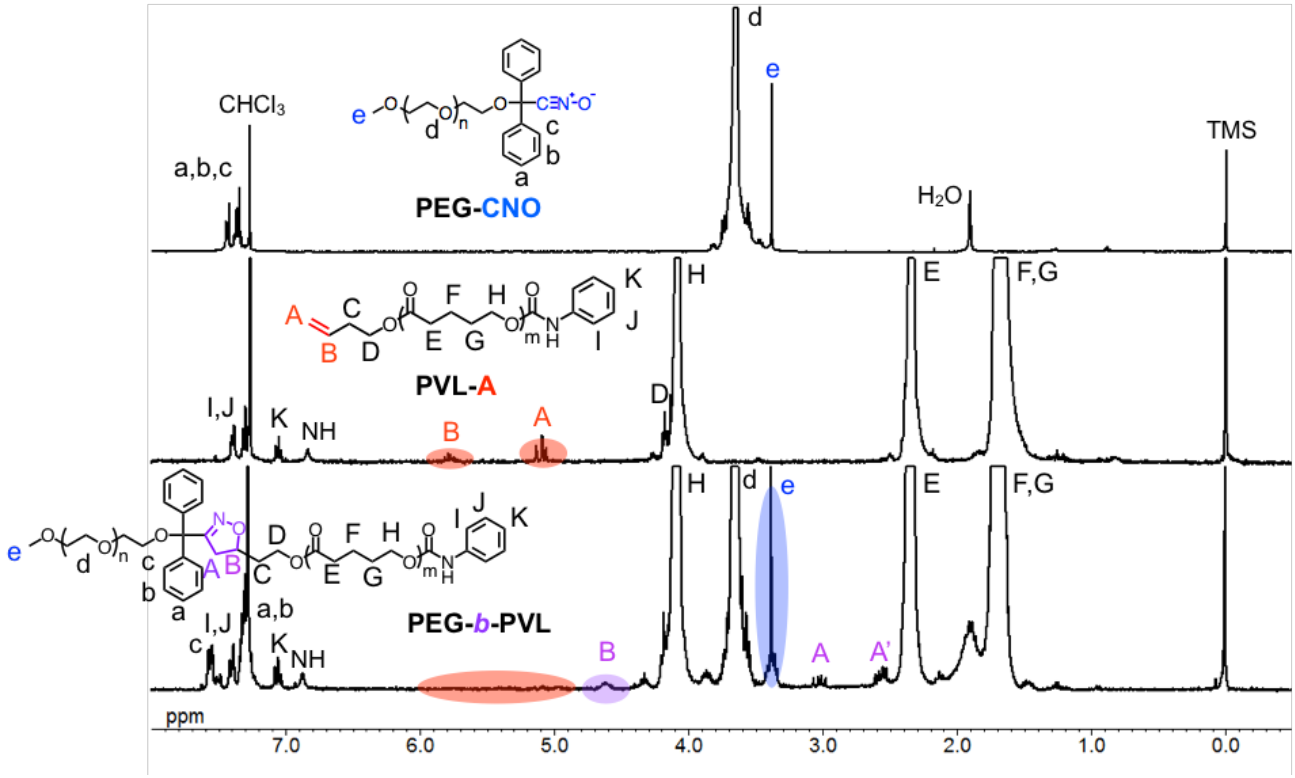


Figure S18. ^{1}H NMR spectra of **PEG-CNO**, **PVL-A** and **PEG-*b*-PVL** (400 MHz, 298 K, $CDCl_3$)

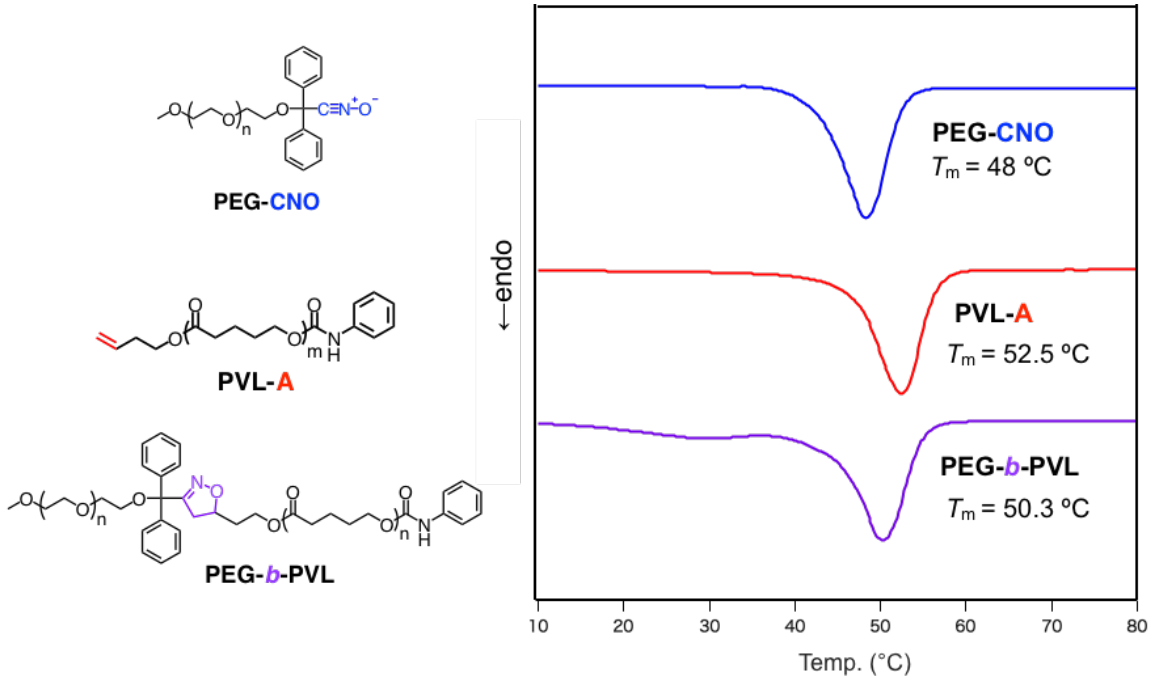


Figure S19. DSC (10 °C/min, 2nd heating under N_2) charts of **PEG-CNO**, **PVL-A** and **PEG-*b*-PVL**

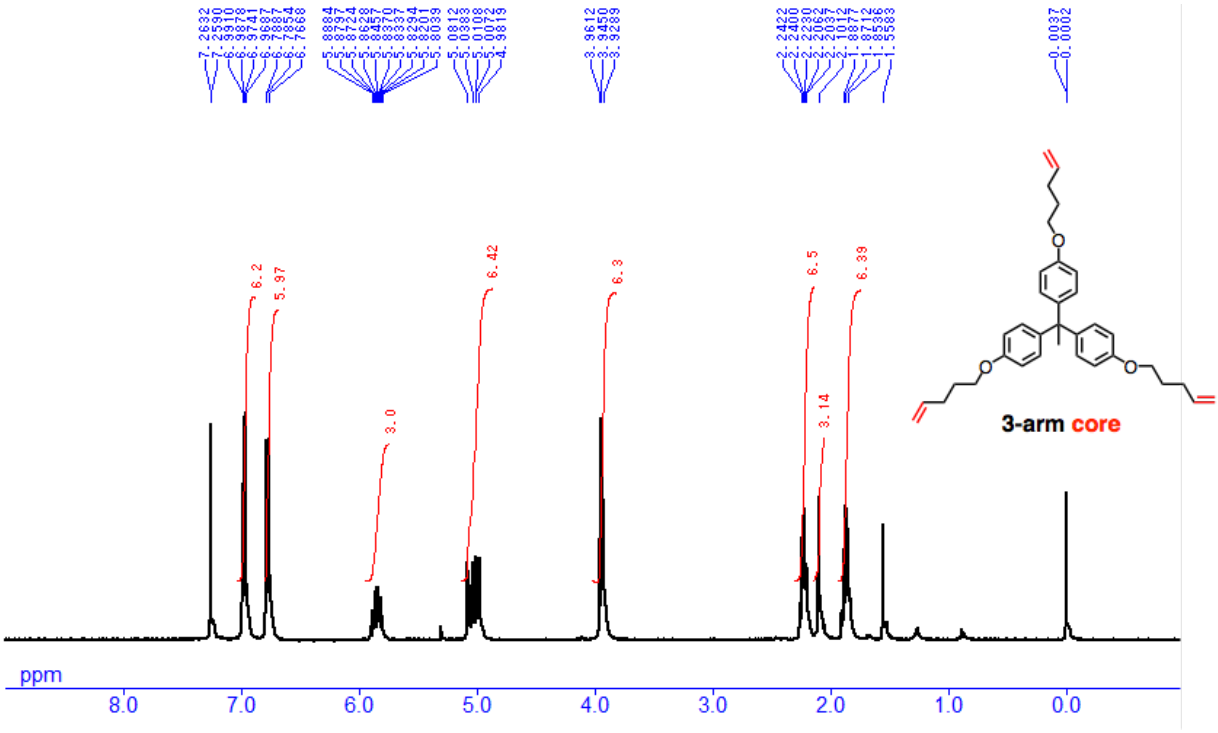


Figure S20. ^{1}H NMR spectrum of **3-arm core** (400 MHz, 298 K, $CDCl_3$)

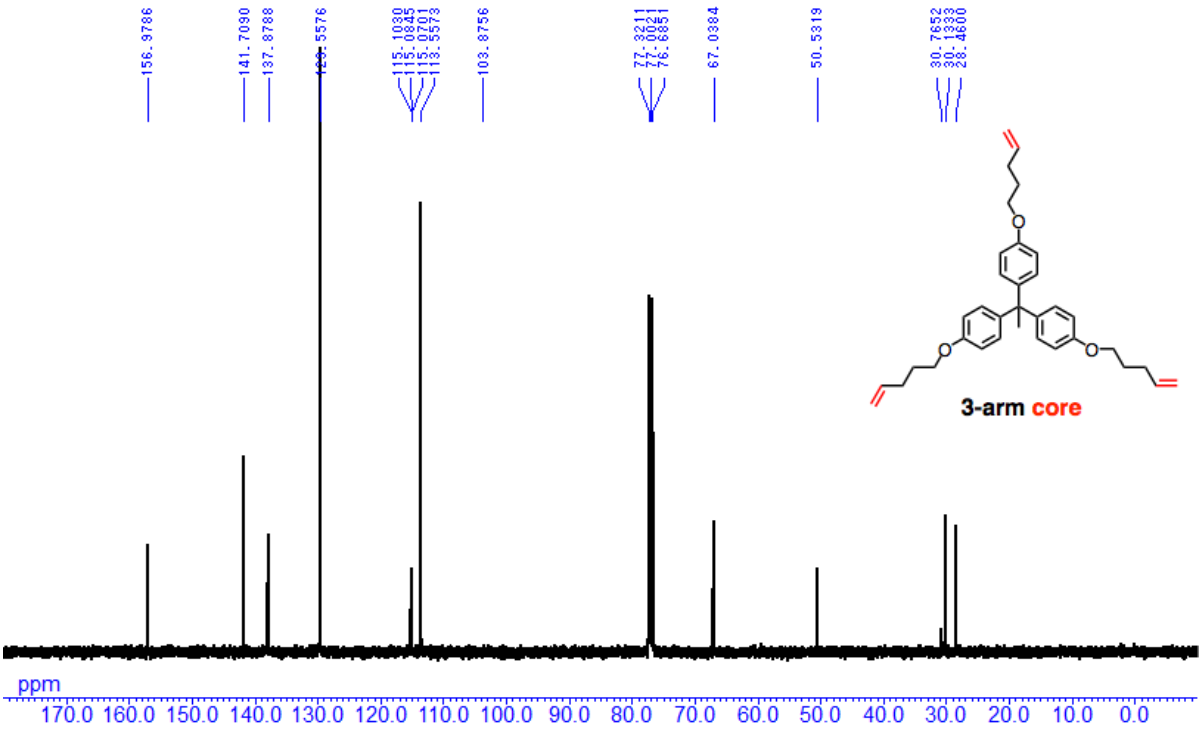


Figure S21. ^{13}C NMR spectrum of **3-arm core** (100 MHz, 298 K, $CDCl_3$)

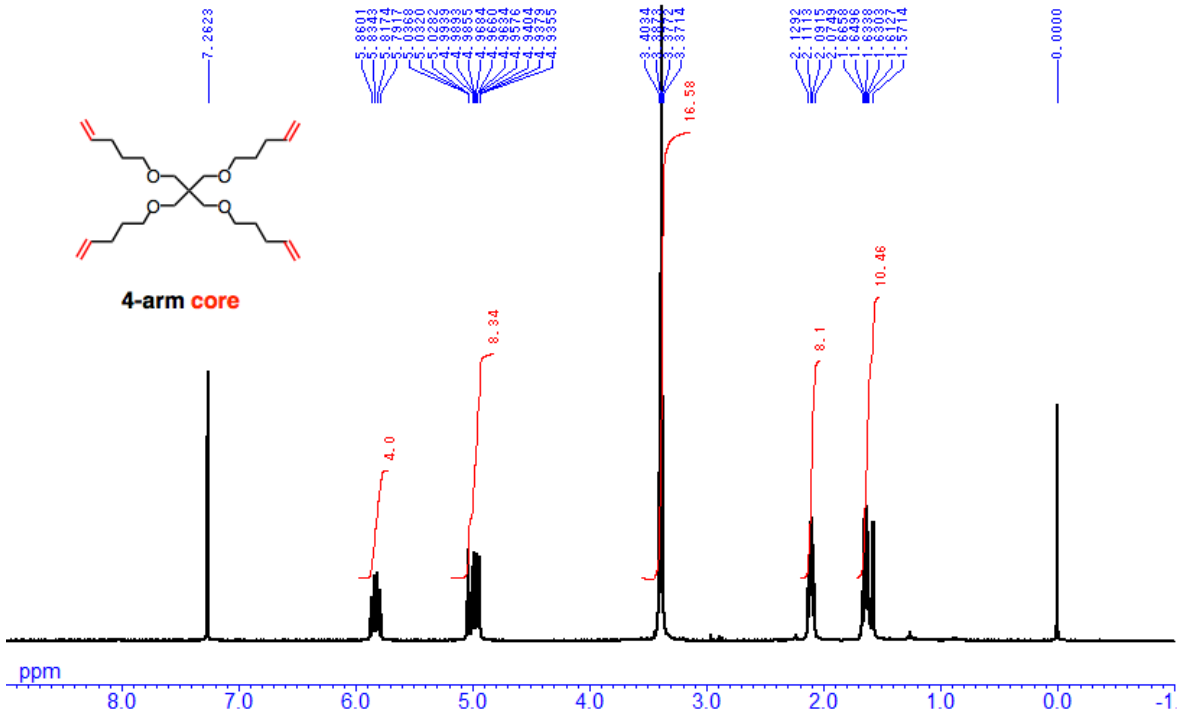


Figure S22. ^{1}H NMR spectrum of **4-arm core** (400 MHz, 298 K, $CDCl_3$)

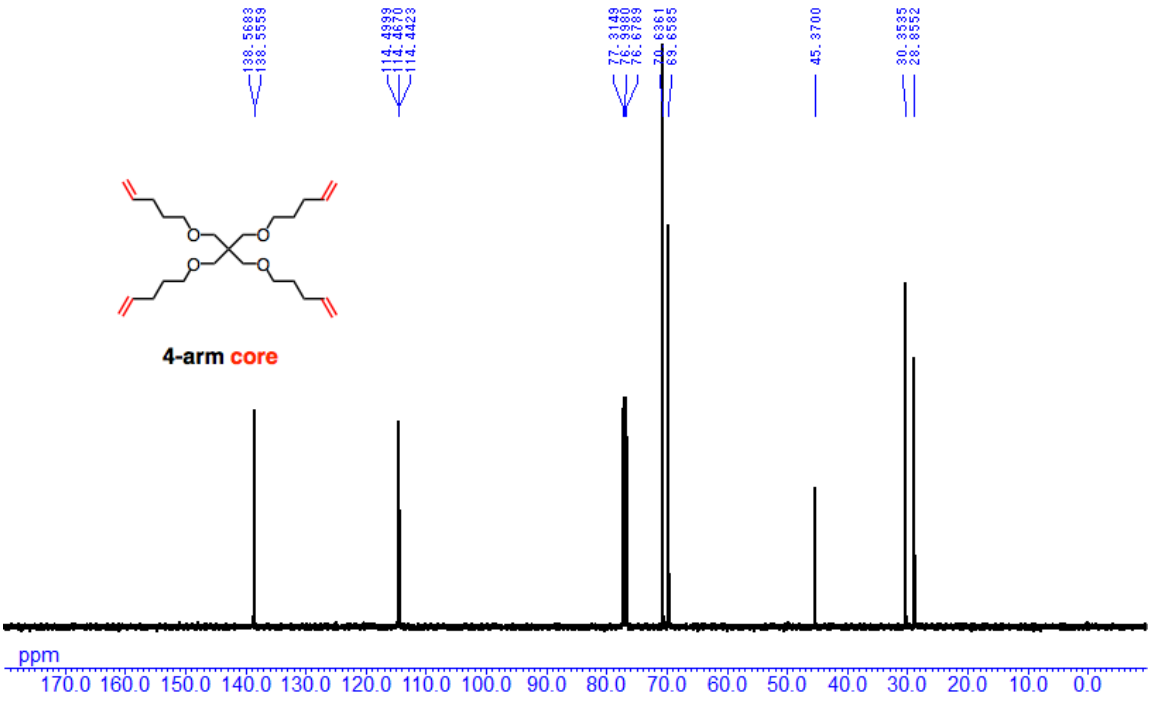


Figure S23. ^{13}C NMR spectrum of **4-arm core** (100 MHz, 298 K, $CDCl_3$)

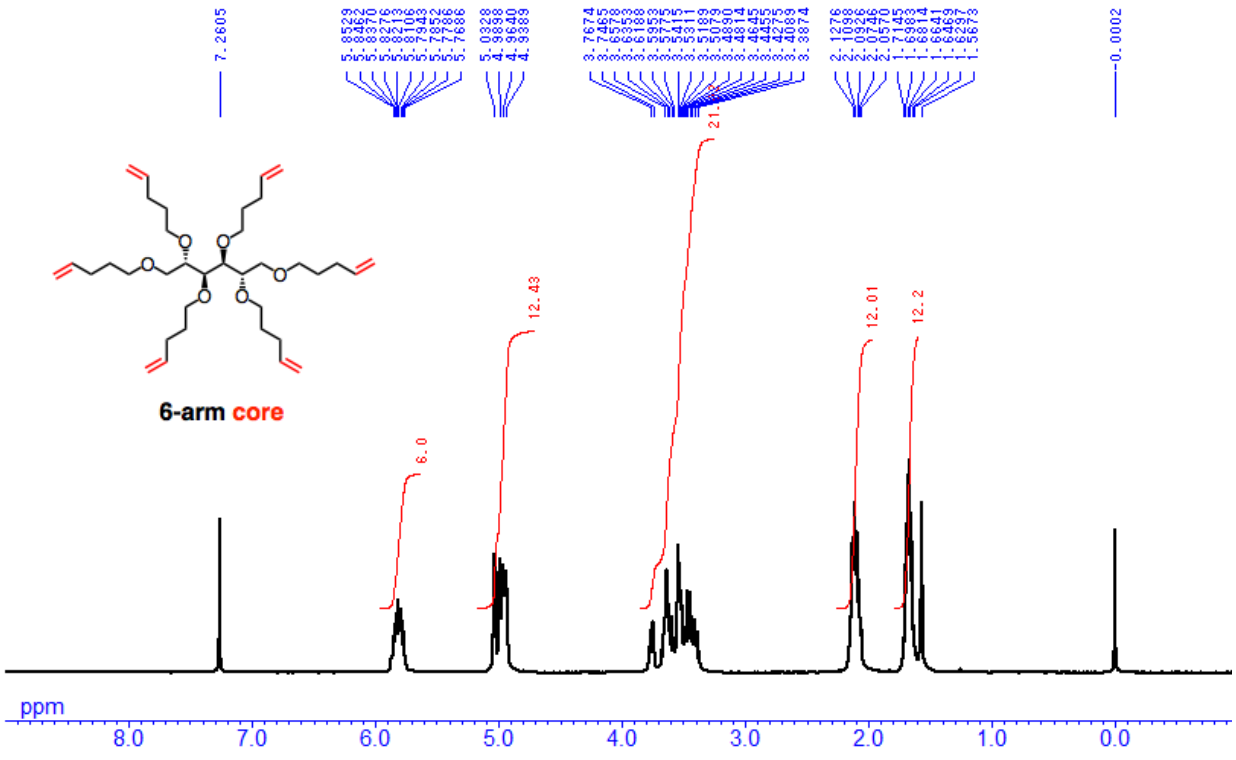


Figure S24. ^{1}H NMR spectrum of **6-arm core** (400 MHz, 298 K, $CDCl_3$)

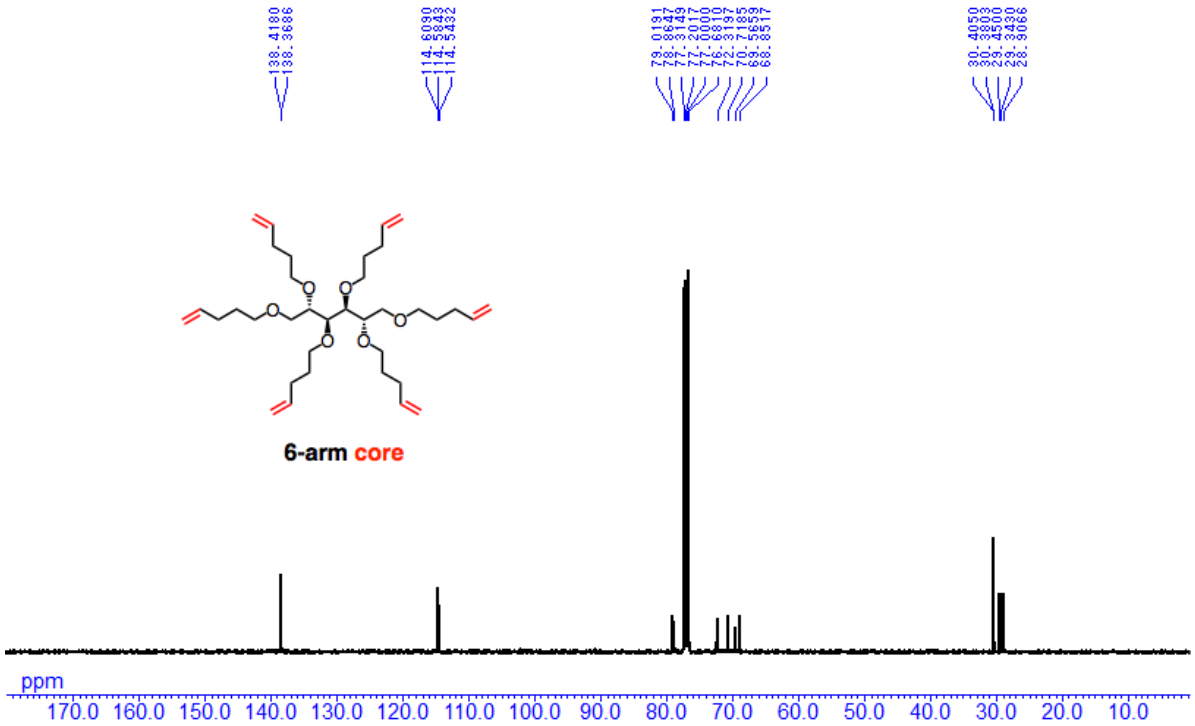


Figure S25. ^{13}C NMR spectrum of **6-arm core** (100 MHz, 298 K, $CDCl_3$)

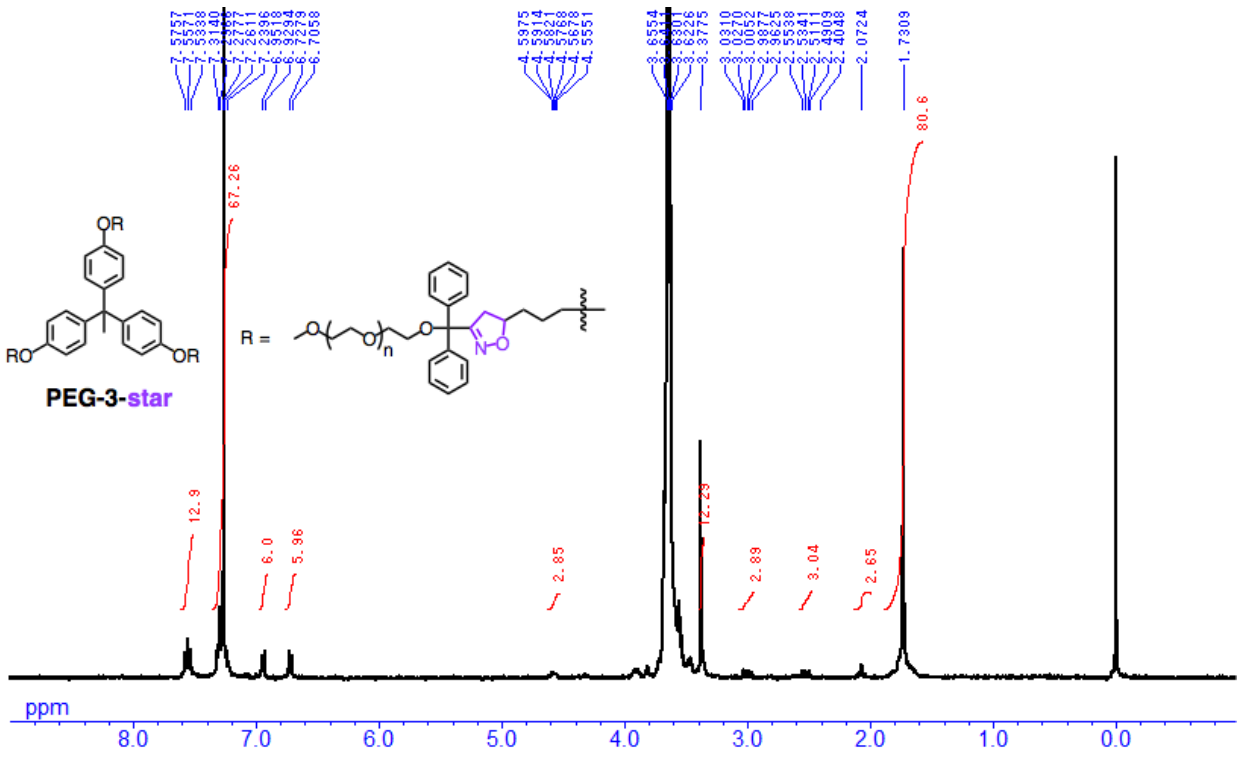


Figure S26. ^{1}H NMR spectrum of **PEG-3 star** (400 MHz, 298 K, $CDCl_3$)

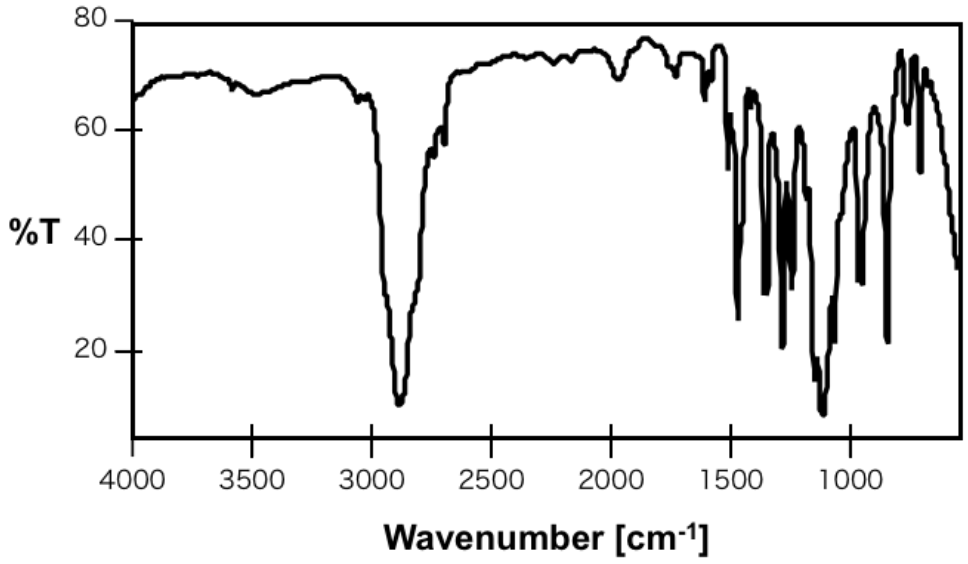


Figure S27. FT-IR spectrum of **PEG-3 star** (NaCl)

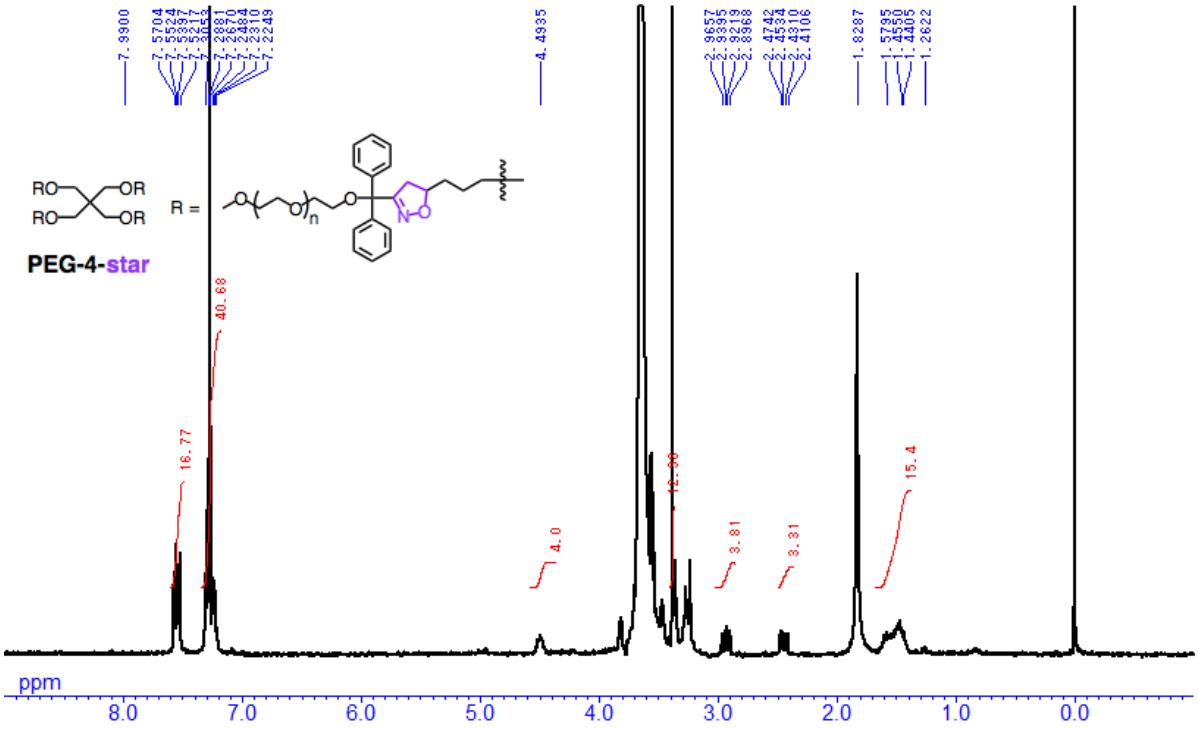


Figure S28. ^{1}H NMR spectrum of **PEG-4 star** (400 MHz, 298 K, $CDCl_3$)

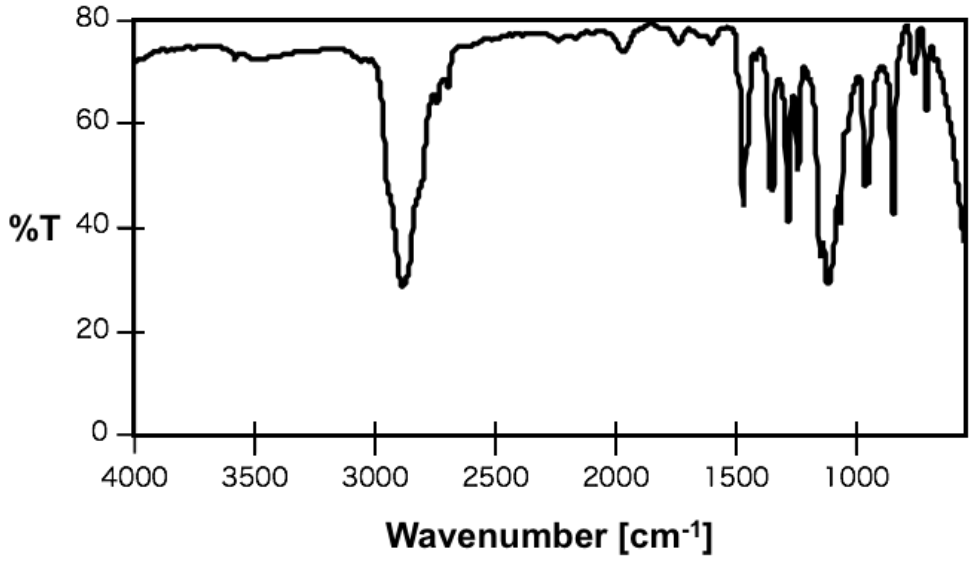


Figure S29. FT-IR spectrum of **PEG-4 star** (NaCl)

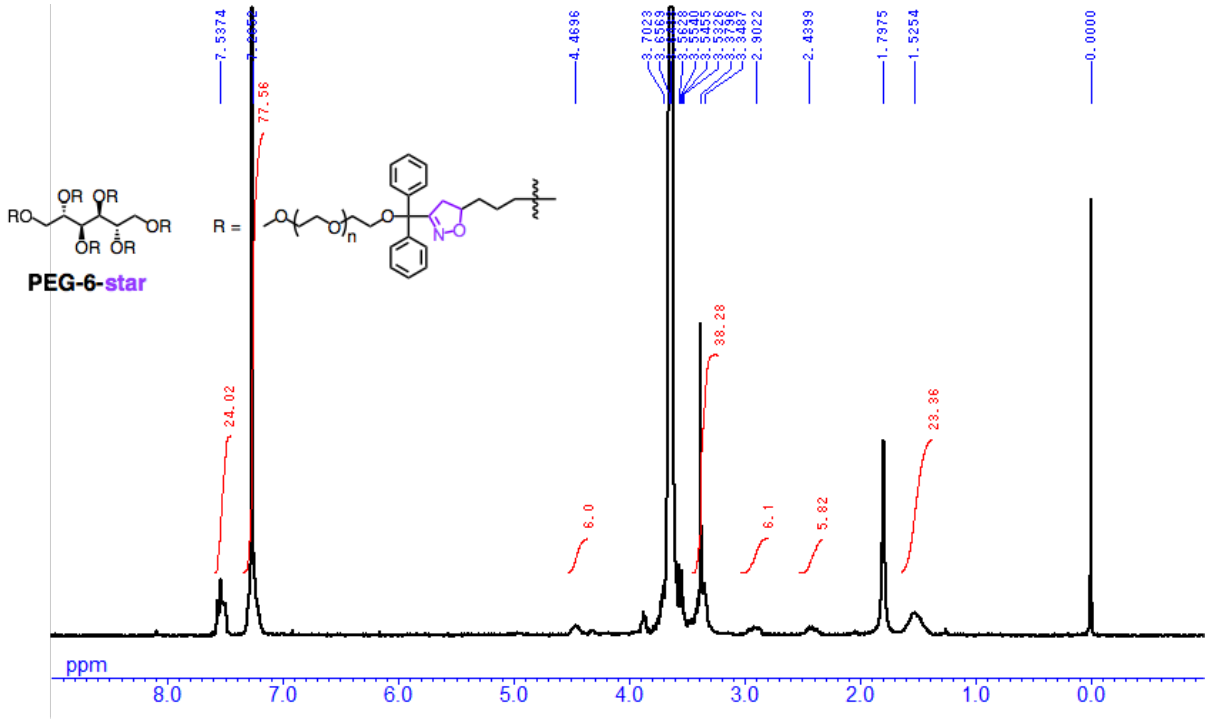


Figure S30. ^{1}H NMR spectrum of **PEG-6 star** (400 MHz, 298 K, $CDCl_3$)

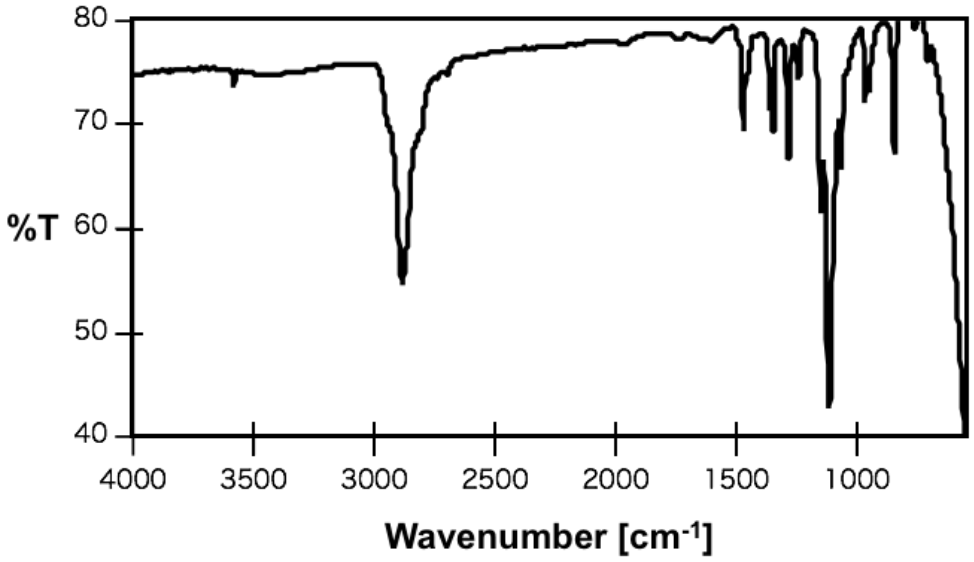


Figure S31. FT-IR spectrum of **PEG-6 star** (NaCl)

3. Reference

S1. C-G. Wang, Y. Koyama, M. Yonekawa, S. Uchida and T. Takata, *Chem. Commun.,* 2013, **49**, 7723.
S2. K. Makiguchi, T. Satoh and T. Kakuchi, *Macromolecules*, 2011, **44**, 1999.