Supplementary Information for

Synthesis of Dendronized Polymers Through Pd-Initiated C1 Polymerization of Diazoacetates with Different Generation Ester-type Dendron Groups

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Experimental Section

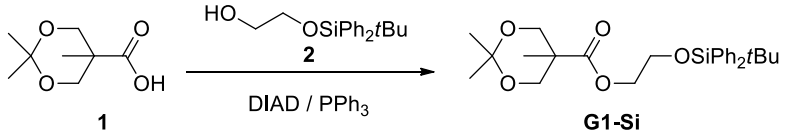
Materials

Tetrahydrofuran (THF, Kanto Chemical, >99.5%, dehydrated Super Plus grade) was used after passage through solvent purification columns (Nikko Hansen & Co., Glass Contour MINI). Diethyl ether (Kanto Chemical, >99.5%, dehydrated), chloroform (Junsei Chemical, 99%), dichloromethane (FUJIFILM Wako Pure Chemical, Guaranteed Reagent), hexane (FUJIFILM Wako Pure Chemical, >95%), ethyl acetate (Nacalai Tesque, >99%), acetonitrile (FUJIFILM Wako Pure Chemical, >99.8%), methanol (Yoneyama Yakuhin Kogyo, 99%; Kanto Chemical, >99.8%, super dehydrated), allylpalladium(II) chloride dimer (π-allylPdCl, Tokyo Chemical Industry, >97.0%), sodium tetraphenylborate ($NaBPh_4$, Tokyo Chemical Industry, >99.5%), diisopropyl azodicarboxylate (DIAD, FUJIFILM Wako Pure Chemical, >90%), triphenylphosphine (PPh_3, Nacalai Tesque, >98.0%), tetrabutylammonium fluoride (TBAF, Kanto Chemical, 1 M THF solution), bromoacetyl bromide (Tokyo Chemical Industry, >98.0%), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU, Tokyo Chemical Industry, >98.0%), copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, FUJIFILM Wako Pure Chemical, >97.0%), hydrochloric acid (Nacalai Tesque, 35–37%), Na_2SO_4 (Nacalai Tesque, > 98.5%), and CaH_2 (Nacalai Tesque, >90.0%) were used as received.

Synthesis of monomers

Ethyl diazoacetate (EDA) were prepared according to the literature,[1] and dried over CaH_2 and stored as a dichloromethane solution. The concentrations of EDA were determined with trichloroethylene (Katayama Chemical) as an internal standard by using ^{1}H NMR spectroscopy. Benzyl diazoacetate (BDA) and *N,N'*-ditosylhydrazine were synthesized according to the procedures reported by Fukuyama and co-workers.[2] ***Caution!*** Extra care must be taken for syntheses and handling of the diazocarbonyl compounds because of their potential explosiveness.

Synthesis of ***G1-Si***

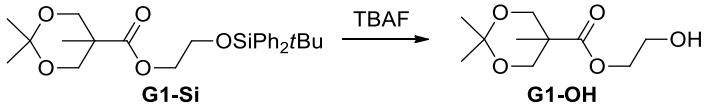


1 **G1-Si**

Under a N_2 atmosphere, a THF (100 mL) solution of acetonide protected bis-MPA **1** (17.0 g, 0.0978 mol) and mono-silyl protected ethylene glycol **2** (14.7 g, 0.0489 mol) was placed in a round bottomed flask equipped with a three-way cock and a dropping funnel. After diisopropyl azodicarboxylate (DIAD, 21.0 ml, 0.108 mol) was added by using a syringe, the mixture was stirred at room temperature for 5 min. Through the dropping funnel, a THF (100 mL) solution of triphenylphosphine (PPh_3, 28.3 g, 0.108 mol) was added dropwise, and the resulting mixture was stirred at room temperature for 12 h. After volatiles were removed under reduced pressure with an evaporator and then, a vacuum pump, hexane (100 mL) was added and the mixture was vigorously stirred for 12 h to precipitate triphenylphosphine oxide as a white solid. After the white solid was removed by filtration, volatiles were removed from the filtrate under reduced pressure. The residue was purified with flash chromatography on silica gel (eluent: AcOEt/$CHCl_3$ = 1/4) to yield **G1-Si** (19.7 g, 88.3%) as pale yellow viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.68–7.66 (m, 4H, Ar-H), 7.45–7.37 (m, 6H, Ar-H), 4.26–4.24 (m, 2H, CH_2), 4.20 (d, J = 12 Hz, 2H, C*H*H), 3.87–3.85 (m, 2H, CH_2), 3.65 (d, J = 12 Hz, 2H, CH*H*), 1.43 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.05 (s, 9H, CH_3).

Synthesis of ***G1-OH***

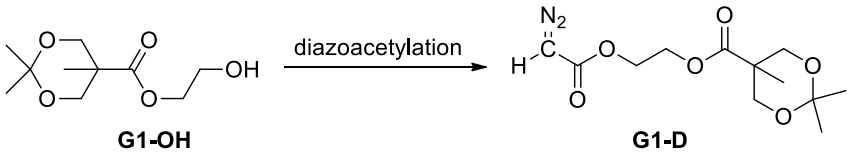


G1-Si **G1-OH**

Under a N_2 atmosphere, a THF (55 mL) solution of **G1-Si** (1.39 g, 3.05 mmol) was placed in a round bottomed flask. After a THF solution of tetrabutylammonium fluoride (in THF, 4.93 ml, 4.93 mmol) was added, the mixture was stirred at room temperature for 3 min. After water (55 mL), 0.1 N HCl aqueous solution (2.75 mL), and $CHCl_3$ (120 mL) were added, the resulting mixture was transferred to a separatory funnel, with which the organic layer was separated. After the organic layer was washed with H_2O (120 mL) and saturated NaCl aqueous solution (120 mL) and dried over Na_2SO_4. After filtration, the volatiles were removed under reduced pressure. The residue was purified by using preparative SEC (eluent: $CHCl_3$) to yield **G1-OH** (0.470 g, 71 %) as colorless viscous oil.

The characterization data was reported in the literature.[3]

Synthesis of ***G1-D***



G1-OH **G1-D**

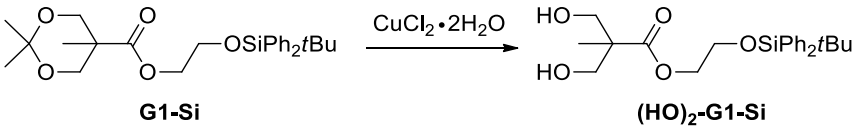
Under a N_2 atmosphere, a THF (19.5 mL) solution of **G1-OH** (0.503 g, 2.30 mmol) and pyridine (3.71 ml, 4.60 mmol) was placed in a round bottomed flask and cooled to 0 °C. After bromoacetyl bromide (3.00 ml, 3.45 mmol) was added, the mixture was stirred at 0 °C for 3 h. After water (19.5 mL) was added, the organic layer was separated from the mixture with CH_2Cl_2 (15 mL × 3). The organic layer was washed with water (45 mL) and saturated NaCl aqueous solution (45 mL), and dried over Na_2SO_4. After filtration, the volatiles were removed under reduced pressure. After the residue was transferred into a round bottomed flask, *N,N'*-ditosylhydrazine (1.56 g, 4.60 mmol) and THF (19.5 mL) were added under a N_2 atmosphere, and the mixture was cooled to 0 °C. After DBU (1.71 mL, 11.5 mmol) was added dropwise, the mixture was stirred at 0 °C for 3 h. After saturated $NaHCO_3$ aqueous solution (19.5 mL) was added, the organic layer was separated from the mixture with Et_2O (15 mL × 3). The organic layer was washed with water (45 mL) and saturated NaCl aqueous solution (45 mL), and dried over Na_2SO_4. After filtration, the volatiles were removed under reduced pressure. The residue was purified by using preparative SEC (eluent: $CHCl_3$) to yield **G1-D** (0.433 g, 65.8 %) as pale yellow viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.77 (br-s, 1H, CH=N_2), 4.40–4.36 (m, 4H, CH_2CH_2), 4.19 (d, J = 12 Hz, 2H, C*H*H), 3.65 (d, J = 12 Hz, 2H, CH*H*), 1.43 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.21 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 174.1 [–CH_3C(*C*=O)O–], 166.6 [br, (N_2=)CH(*C*=O)O–], 98.2 [(–$CH_2O)_2C(CH_3)_2$], 66.0 (CH_2), 62.7 (CH_2), 62.4 (CH_2), 46.4 (–CH=N_2), 42.0 [–CH_3C(C=O)O-], 24.5 (CH_3), 23.0 (CH_3), 18.7 (CH_3).

Anal. Calcd for $C_{12}H_{18}N_2O_6$: C, 50.35; H, 6.34; N, 9.79. Found: C, 50.13; H, 6.72; N, 9.68.

Synthesis of ***(HO)$_2$-G1-Si***



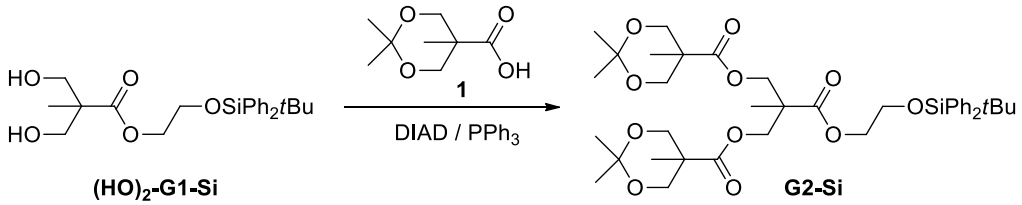
G1-Si **(HO)$_2$-G1-Si**

Under a N_2 atmosphere, an acetonitrile (200 mL) solution of **G1-Si** (16.4 g, 96.0 mmol) was placed in a round-

bottomed flask and cooled to −10 °C. After $CuCl_2 \cdot 2H_2O$ (8.75 g, 19.2 mmol) was added at −10 °C, the mixture was stirred at −5 °C for 20 h. After the mixture was warmed to room temperature, saturated NH_4Cl aqueous solution (60 mL) was added, and an organic layer was separated with AcOEt (50 mL × 3). The organic layer was dried over Na_2SO_4, which was then removed by filtration, and volatiles were removed from the filtrate under reduced pressure. The residue was purified with flash chromatography on silica gel (eluent: AcOEt/hexane = 1/1) to yield **$(HO)_2$-G1-Si** (6.47 g, 80.9% yield) as pale yellow viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ) : 7.68–7.66 (m, 4H, Ar-H), 7.46–7.38 (m, 6H, Ar-H), 4.28–4.26 (m, 2H, CH_2), 3.90 (d, J = 6.8 Hz and 12 Hz, 2H, C*H*H), 3.88–3.86 (m, 2H, CH_2), 3.74 (dd, J = 6.8 and 12 Hz, 2H, CH*H*), 2.79 (t, J = 6.8 Hz, 2H, OH), 1.10 (s, 3H, CH_3), 1.05 (s, 9H, CH_3).

*Synthesis of **G2-Si***

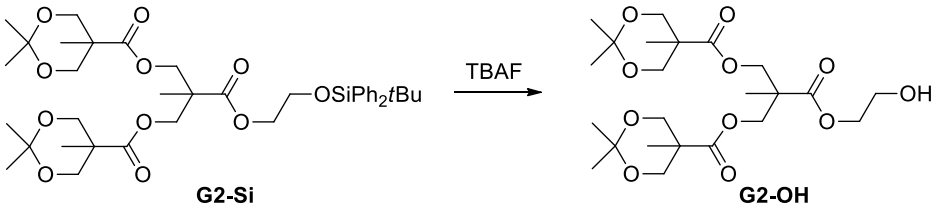


$(HO)_2$-G1-Si **G2-Si**

Under a N_2 atmosphere, a THF (120 mL) solution of **1** (11.25 g, 64.2 mmol) and **$(HO)_2$-G1-Si** (8.91 g, 21.4 mmol) was placed in a round bottomed flask equipped with a three-way cock and a dropping funnel. After DIAD (14.28 ml, 70.6 mmol) was added by using a syringe, the mixture was stirred at room temperature for 5 min. Through the dropping funnel, a THF (120 mL) solution of triphenylphosphine (PPh_3, 18.5 g, 70.6 mmol) was added dropwise, and the resulting mixture was stirred at room temperature for 46 h. After volatiles were removed under reduced pressure with an evaporator and then, a vacuum pump, hexane (100 mL) was added and the mixture was vigorously stirred for 24 h to precipitate triphenylphosphine oxide as a white solid. After the white solid was removed by filtration, volatiles were removed from the filtrate under reduced pressure. The residue was purified with flash chromatography on silica gel (eluent: AcOEt/$CHCl_3$ = 1/4) to yield **G2-Si** (11.3 g, 72.3 % yield) as pale yellow viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.67–7.65 (m, 4H, Ar-H), 7.45–7.37 (m, 6H, Ar-H), 4.33 (s, 2H, CO_2CH_2), 4.22 (t, J = 5.3 Hz, 4H, CH_2), 4.27 (d, J = 12 Hz, 4H, C*H*H), 3.85 (t, J = 5.3 Hz, 4H, CH_2), 3.60 (d, J = 12 Hz, 4H, CH*H*), 1.41 (s, 6H, CH_3), 1.34 (s, 6H, CH_3), 1.29 (s, 3H, CH_3), 1.13 (s, 6H, CH_3), 1.05 (s, 9H, CH_3).

*Synthesis of **G2-OH***

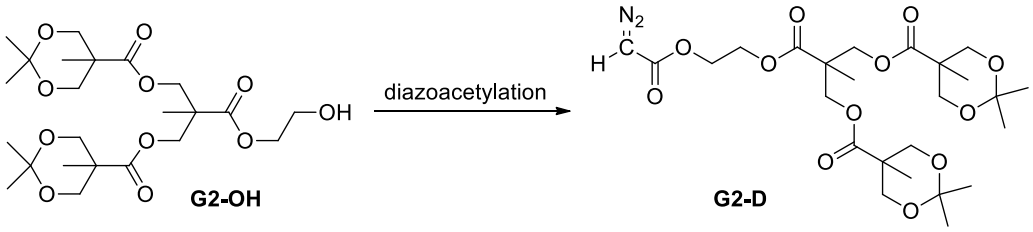


G2-Si **G2-OH**

Under a N_2 atmosphere, a CH_2Cl_2 (10 mL) solution of **G2-Si** (0.446 g, 0.612 mmol) was placed in a round bottomed flask. After a THF solution of TBAF (in THF, 0.918 ml, 0.918 mmol） was added, the mixture was stirred at room temperature for 15 h. After water (3 mL) was added, the resulting mixture was transferred to a separatory funnel, with which the organic layer was separated with Et_2O (10 mL × 3). The organic layer was washed with water (30 mL) and saturated NaCl solution (30 mL), and dried over Na_2SO_4. After filtration, volatiles were removed under reduced pressure. The residue was purified by using preparative SEC (eluent: $CHCl_3$) to yield **G2-OH** (0.199 g, 66.2 %) as colorless viscous oil.

The characterization data was reported in the literature.[3]

Synthesis of ***G2-D***



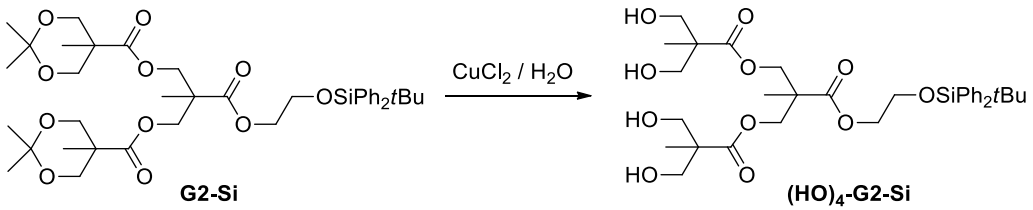
Under a nitrogen atmosphere, a THF (20 mL) solution of **G2-OH** (0.813 g, 1.66 mmol) and pyridine (0.263 ml, 3.32 mmol) was placed in a round bottomed flask and cooled to 0 °C. After bromoacetyl bromide (0.216 ml, 2.49 mmol) was added, the mixture was stirred at 0 °C for 5 h. After water (6 mL) was added, the organic layer was separated from the mixture with CH_2Cl_2 (15 mL × 3). The organic layer was washed with water (45 mL) and saturated NaCl aqueous solution (45 mL), and dried over Na_2SO_4. After filtration, the volatiles were removed under reduced pressure. After the residue was transferred into a round bottomed flask, *N,N'*-ditosylhydrazine (1.13 g, 3.32 mmol) and THF (20 mL) was added under a N_2 atmosphere, and the mixture was cooled to 0 °C. After DBU (1.24 ml, 8.30 mmol) was added dropwise, the mixture was stirred at 0 °C for 5 h. After saturated $NaHCO_3$ aqueous solution (6 mL) was added, an organic layer was separated from the mixture with Et_2O (15 mL × 3). The organic layer was washed with water (45 mL) and saturated NaCl aqueous solution (45 mL), and dried over Na_2SO_4. After filtration, the volatiles were removed under reduced pressure. The residue was purified by using flash chromatography on silica gel (eluent: AcOEt/$CHCl_3$ = 7/3) followed by preparative SEC (eluent: $CHCl_3$) to yield **G2-D** (0.589 g, 63.5 % yield) as pale yellow viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.77 (br-s, 1H, CH=N_2), 4.40–4.26 (m, 8H, CO_2CH_2), 4.15 (d, *J* = 12 Hz, 4H, C*H*H), 3.62 (d, *J* = 12 Hz, 4H, CH*H*), 1.42 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.28 (s, 3H, CH_3), 1.14 (s, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.6 [–CH_3C(*C*=O)O–], 172.5 [–CH_3C(*C*=O)O–], 166.6 [br, (N_2=)CH(*C*=O)O–], 98.2 [(–$CH_2O)_2C(CH_3)_2$], 66.1 (CH_2), 66.0 (CH_2), 65.4 (CH_2), 63.2 (CH_2), 62.2 (CH_2), 46.9 [–CH_3C(C=O)O-], 46.4 (–CH=N_2), 42.2 [–CH_3C(C=O)O-], 25.3 (CH_3), 22.2 (CH_3), 18.6 (CH_3), 17.8 (CH_3).

Anal Calcd for $C_{25}H_{38}N_2$: C, 53.76; H, 6.86; N, 5.02. Found : C, 54.04; H, 7.27; N, 5.24

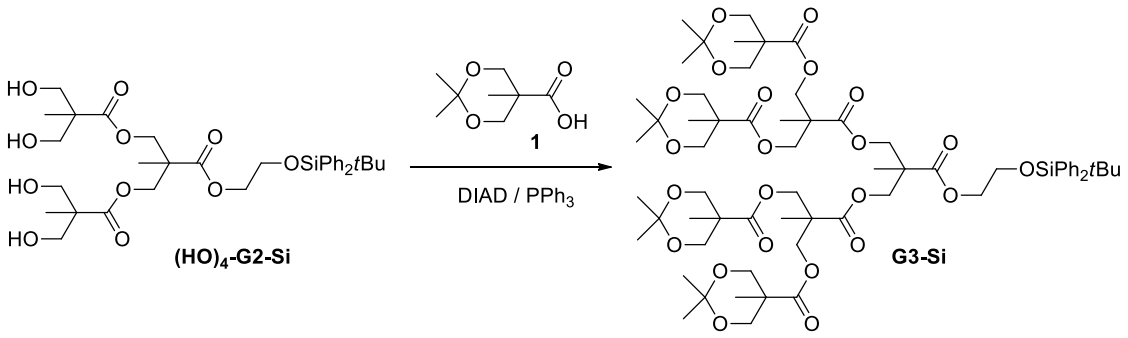
Synthesis of **$(HO)_4$-G2-Si**



Under a N_2 atmosphere, an acetonitrile (100 mL) solution of **G2-Si** (2.30 g, 3.16 mmol) was placed in a round-bottomed flask and cooled to −10 °C. After $CuCl_2 \cdot 2H_2O$ (5.39 g, 31.6 mmol) was added at −10 °C, the mixture was stirred at −5 °C for 20 h. After the mixture was warmed to room temperature, saturated NH_4Cl aqueous solution (54 mL) was added, and an organic layer was separated with AcOEt (40 mL × 3). The organic layer was washed with water (100 mL) and saturated NaCl aqueous solution (100 mL) and dried over Na_2SO_4. After filtration, volatiles were removed from the filtrate under reduced pressure. The residue was purified with flash chromatography on silica gel (eluent: AcOEt/hexane = 1/1) to yield **$(HO)_4$-G2-Si** (1.44 g, 70.3% yield) as colorless viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ) : 7.68–7.66 (m, 4H, Ar-H), 7.47–7.38 (m, 6H, Ar-H), 4.46 (d, *J* = 12 Hz, 2H, C*H*H), 4.29 (d, *J* = 12 Hz, 2H, C*H*H), 4.25–4.23 (m, 2H, C*H*H), 3.88–3.83 (m, 6H, CH_2), 3.74–3.67 (m, 4H, CH_2), 3.06 (m, 4H, OH), 1.32 (s, 3H, CH_3), 1.05 (s, 9H, CH_3), 1.02 (s, 6H, CH_3).

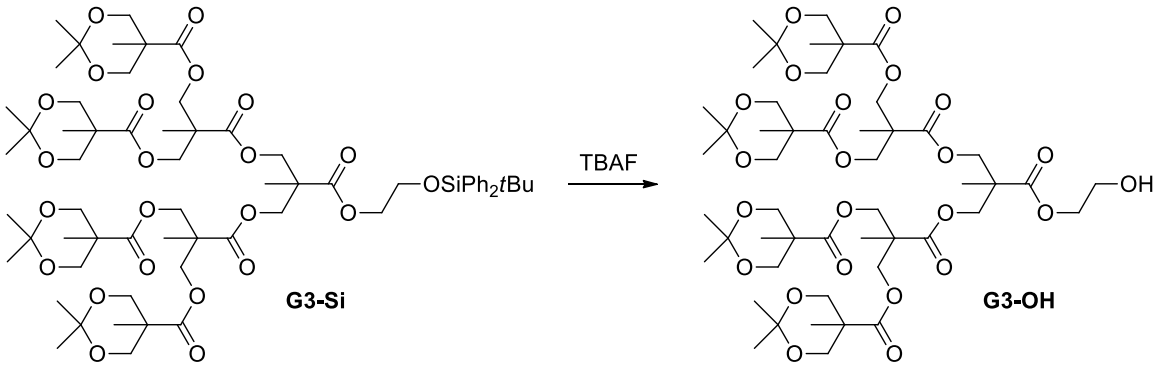
Synthesis of ***G3-Si***



Under a N_2 atmosphere, a THF (26 mL) solution of **1** (1.67 g, 9.60 mmol) and **$(HO)_4$-G2-Si** (0.778 g, 1.20 mmol) was placed in a round bottomed flask equipped with a three-way cock and a dropping funnel. After DIAD (1.87 ml, 9.60 mmol) was added by using a syringe, the mixture was stirred at room temperature for 5 min. Through the dropping funnel, a THF (26 mL) solution of triphenylphosphine (PPh_3, 2.52 g, 9.60 mmol) was added dropwise, and the resulting mixture was stirred at 50 °C for 72 h. After volatiles were removed under reduced pressure with an evaporator and then, a vacuum pump, hexane (50 mL) was added and the mixture was vigorously stirred for 24 min to precipitate triphenylphosphine oxide as a white solid. After the white solid was removed by filtration, volatiles were removed from the filtrate under reduced pressure. The residue was purified with flash chromatography on silica gel (eluent: AcOEt/$CHCl_3$ = 2/3) to yield **G3-Si** (0.968 g, 63.3% yield) as pale yellow viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.67–7.64 (m, 4H, Ar-H), 7.50–7.36 (m, 6H, Ar-H), 4.30–4.26 (m, 12H, CH_2), 4.21 (t, J = 5.3 Hz, 2H, CH_2), 4.12 (d, J = 12 Hz, 8H, C*H*H), 3.84 (t, J = 5.3 Hz, 2H, CH_2), 3.59 (d, J = 12 Hz, 8H, CH*H*), 1.39 (s, 12H, CH_3), 1.33 (s, 12H, CH_3), 1.25 (s, 3H, CH_3), 1.23 (s, 6H, CH_3), 1.12 (s, 12H, CH_3), 1.03 (s, 9H, CH_3).

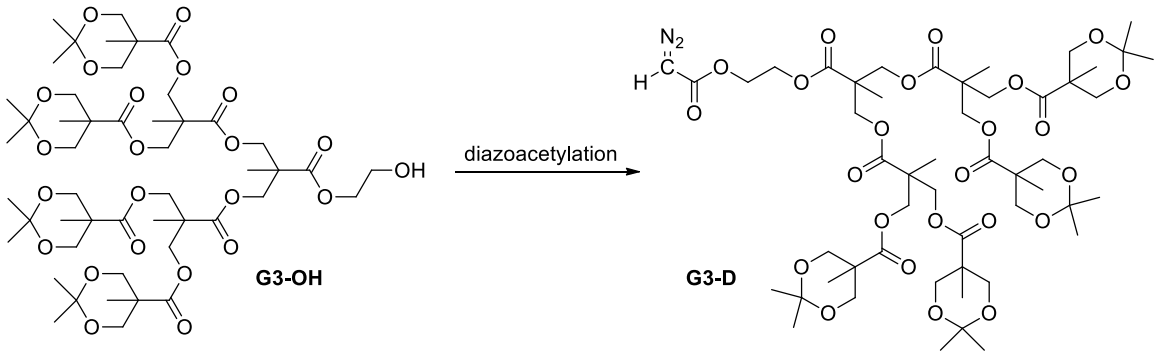
Synthesis of ***G3-OH***



Under a N_2 atmosphere, a THF (50 mL) solution of **G3-Si** (0.968 g, 0.760 mmol) was placed in a round bottomed flask. After a THF solution of TBAF (1 M in THF, 1.14 ml, 1.14 mmol） was added, the mixture was stirred at room temperature for 30 min. After water (100 mL), 0.1 N HCl aqueous solution (0.7 mL) were added, the resulting mixture was transferred to a separatory funnel, with which an organic layer was separated with $CHCl_3$ (50mL). The organic layer was washed with water (150 mL) and saturated NaCl aqueous solution (150 mL) and dried over Na_2SO_4. After the organic layer was dried over Na_2SO_4, Na_2SO_4 was removed by filtration and volatiles were removed under reduced pressure. The residue was purified by using preparative SEC (eluent: $CHCl_3$) to yield **G3-OH** (1.51g, 77.4 % yield) as colorless viscous oil.

The characterization data was reported in the literature.[3]

*Synthesis of **G3-D***



Under a N_2 atmosphere, a THF (20 mL) solution of **G3-OH** (0.609 g, 0.588 mmol) and pyridine (0.095 ml, 1.18 mmol) was placed in a round bottomed flask and cooled to 0 °C. After bromoacetyl bromide (0.077 ml, 0.887 mmol) was added, the mixture was stirred at 0 °C for 7 h. After water (20 mL) was added, an organic layer was separated from the mixture with CH_2Cl_2 (15 mL × 3). The organic layer was washed with water (45 mL) and saturated NaCl aqueous solution (45 mL), and dried over Na_2SO_4. After filtration, the volatiles were removed under reduced pressure. After the residue was transferred into a round bottomed flask, *N,N'*-ditosylhydrazine (0.400 g, 1.18 mmol) and THF (20 mL) was added under a N_2 atmosphere, and the mixture was cooled to 0 °C. After DBU (0.448 ml, 2.94 mmol) was added dropwise, the mixture was stirred at 0 °C for 7 h. After saturated $NaHCO_3$ aqueous solution (20 mL) was added, an organic layer was separated from the mixture with Et_2O (15 mL × 3). The organic layer was washed with water (45 mL) and saturated NaCl aqueous solution (45 mL), and dried over Na_2SO_4. After filtration, the volatiles were removed under reduced pressure. The residue was purified by preparative SEC (eluent: $CHCl_3$) to yield **G3-D** (0.466 g, 54.9 % yield) as pale yellow viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.84 (br-s, 1H, CH=N_2), 4.40–4.24 (m, 16H, CO_2CH_2), 4.15 (d, J = 12 Hz, 4H, C*H*H), 3.62 (d, J = 12 Hz, 4H, CH*H*), 1.41 (s, 12H, CH_3), 1.35 (s, 12H, CH_3), 1.28 (s, 9H, CH_3), 1.14 (s, 12H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.7 [–CH_3C(*C*=O)O–], 172.1 [–CH_3C(*C*=O)O–], 172.0 [–CH_3C(*C*=O)O–], 98.3 [(–$CH_2O)_2C(CH_3)_2$], 66.2 (CH_2), 66.1 (CH_2), 65.1 (CH_2), 63.6 (CH_2), 62.2 (CH_2), 47.0 [–CH_3C(C=O)O-], 46.8 [–CH_3C(C=O)O–], 46.5 (–CH=N_2), 42.2 [–CH_3C(C=O)O-], 25.4 (CH_3), 22.2 (CH_3), 18.7 (CH_3), 17.8 (CH_3), 17.7 (CH_3). The signal for the carbonyl-C [(N_2=)CH(*C*=O)O–] could not be observed.

Anal Calcd for C51H78N2O24: C, 55.53; H, 7.13; N, 2.54. Found : C, 54.52; H, 6.80; N, 2.05.

Polymerization procedure

As a representative example, the polymerization procedures for run 7 in Table 1 is described.

Under a N_2 atmosphere, a THF (1.0 mL) solution of π-allylPdCl (0.76 mg, 2.1×10^{-3} mmol) was placed in a Schlenk flask and was cooled to −78 °C. At −78 °C, $NaBPh_4$ (1.71 mg, 4.99×10^{-3} mmol) was added to the Schlenk tube and the mixture was stirred for 10 min. Then, at −78 °C, a THF (0.9 mL) solution of **G2-D** (0.116 g, 0.208 mmol) dried over CaH_2 was added dropwise to the Schlenk tube, and the temperature of the mixture was raised to −20 °C, and the mixture was stirred at −20 °C for 15 h. After the volatiles were removed under reduced pressure, the residue was transferred to a separatory funnel with $CHCl_3$ (2 mL) and H_2O (2 mL) to extract the organic layer. The aqueous layer was extracted with $CHCl_3$ (10 mL × 3) and the combined organic layer was washed with H_2O (30 mL) and saturated NaCl aqueous solution (30 mL). After the organic layer was dried over Na_2SO_4. Na_2SO_4 was removed by filtration and volatiles were removed under reduced pressure. The residue was subjected to purification with preparative SEC using $CHCl_3$ as an eluent to afford **p(G2-D)'** as pale yellow solid (53.5 mg, 48.6 % yield).

As a representative example for copolymerization, the polymerization procedures for run 1 in Table 2 is described.

Under a N_2 atmosphere, a THF (1.5 mL) solution of π-allylPdCl (0.932 mg, 2.54×10^{-3} mmol) was placed in a Schlenk flask and was cooled to −78 °C. At −78 °C, $NaBPh_4$ (2.08 mg, 6.09×10^{-3} mmol) was added to the Schlenk tube and the mixture was stirred for 10 min. Then, at −78 °C, a THF (1.5 mL) solution of **G3-D** (9.37×10^{-2} g, 0.0849 mmol) and BDA (7.20×10^{-2} g, 0.425 mmol) dried over CaH_2 was added dropwise to the Schlenk tube, and the temperature of the mixture was raised to −20 °C, and the mixture was stirred at −20 °C for 15 h. After volatiles were removed under reduced pressure, the residue was transferred to a separatory funnel with $CHCl_3$ (3 mL) and H_2O (3 mL) and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ (10 mL × 3) and the combined organic layer was washed with H_2O (30 mL) and saturated NaCl aqueous solution (30 mL). After the organic layer was dried over Na_2SO_4, Na_2SO_4 was removed by filtration and volatiles were removed under reduced pressure. The residue was subjected to purification with preparative SEC using $CHCl_3$ as an eluent to afford **p[(G3-D)'-*co*-BDA']** as pale yellow solid (0.080 g, 52 % yield).

Hydrolysis procedure

The copolymer sample of **p[(G3-D)'-*co*-BDA']** obtained in run 1 in Table 2 was dissolved in a mixture of THF (4.2 mL) and MeOH (1.8 mL) and the solution was placed in a round-bottomed flask. To the solution, 0.1 M aqueous solution of HCl (0.5 mL) was added, and the mixture was stirred at room temperature for 24 h. After H_2O (5 mL) was added, the mixture was transferred to a separatory funnel, with which organic layer was separated with $CHCl_3$ (10 mL × 3). After the organic layer was dried over Na_2SO_4, Na_2SO_4 was removed by filtration and volatiles were removed under reduced pressure to afford a hydrolyzed polymer as a colorless solid (59.0 mg, 84.1 % yield).

Measurements

The molar mass distributions of polymers were measured via SEC in THF (flow rate = 1.0 mL/min) at 40 °C on polystyrene gel columns [Styragel HR4 and Styragel HR2 (Waters, molar-mass exclusion limit = 600 kDa and 20 kDa for polystyrene, respectively)] connected to a pump (JASCO, PU-4180), a column oven (JASCO, CO-2065 Plus), an ultraviolet detector (JASCO, UV-4075), and a refractive index detector (JASCO, RI-2031 Plus). The number-average molar mass (M_n) and dispersity [$Đ$; weight-average molar mass/number-average molar mass (M_w/M_n)] were calculated from the chromatographs on the basis of six poly(methyl methacrylate) (PMMA) standards (Shodex M-75; M_p = 2400–212000, $Đ$ < 1.1) and dibutyl sebacate (molar mass = 314.5).

The absolute molecular weight of the polymers was determined by SEC coupled with multiangle light scattering (SEC-MALS) on a Dawn HELEOS II 8+ (Wyatt Technology; λ = 661.5 nm). The refractive index increment (dn/dc) values were measured assuming 100% mass recovery.

Purification by preparative recycling SEC was performed on a JAI LaboACE LC-5060 equipped with a combination of JAIGEL-3HH and JAIGEL-2HH (Japan Analytical Industry, molar mass exclusion limit = 70 kDa and 5 kDa for polystyrene, respectively; column size = 600 mm × 20 mm i.d.) or on a JAI LaboACE LC-5060 equipped with a combination of JAIGEL-2HH and JAIGEL-1HH (Japan Analytical Industry, molar mass exclusion limit = 5 kDa and 1 kDa for polystyrene, respectively; column size = 600 mm × 20 mm i.d.), using chloroform as eluent at a flow rate of 7.5 mL/min at room temperature.

^1H (400 MHz or 500 MHz) and ^{13}C (100 MHz or 126 MHz) NMR spectra of polymers were recorded on a Bruker Avance 400 or on a Bruker Avance III HD 500 spectrometer in $CDCl_3$ at 50 °C.

Elemental analyses were performed on a YANAKO CHN Corder MT-5.

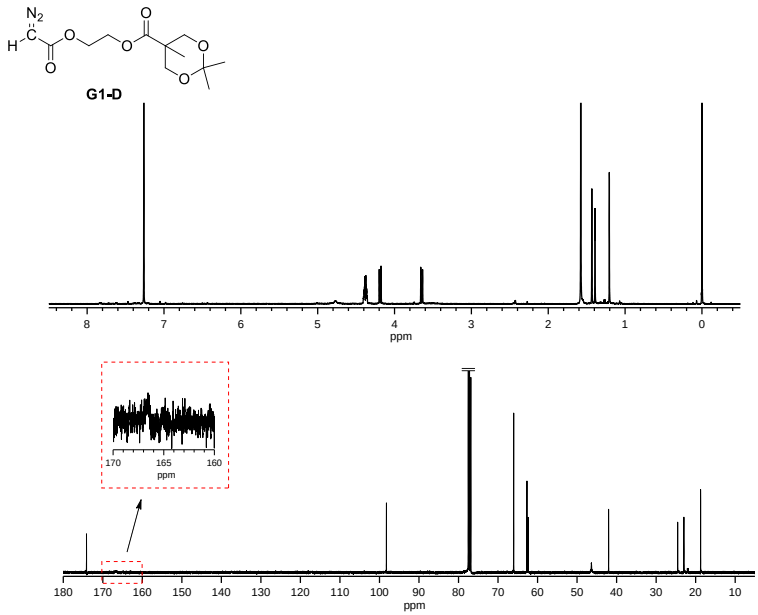


Figure S1. ^{1}H and ^{13}C NMR spectra of **G1-D** recorded in $CDCl_3$.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.77 (br-s, 1H, $CH{=}N_2$), 4.40–4.36 (m, 4H, CH_2CH_2), 4.19 (d, J = 12 Hz, 2H, C*H*H), 3.65 (d, J = 12 Hz, 2H, CH*H*), 1.43 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.21 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 174.1 [–CH_3C(*C*=O)O–], 166.6 [br, (N_2=)CH(*C*=O)O–], 98.2 [(–$CH_2O)_2C(CH_3)_2$], 66.0 (CH_2), 62.7 (CH_2), 62.4 (CH_2), 46.4 (–$CH{=}N_2$), 42.0 [–CH_3C(C=O)O-], 24.5 (CH_3), 23.0 (CH_3), 18.7 (CH_3).

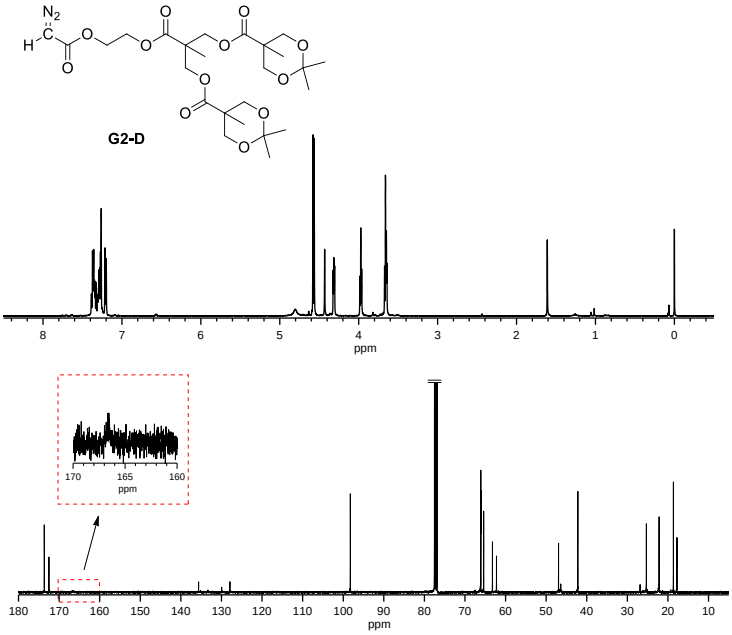


Figure S2. ^{1}H and ^{13}C NMR spectra of **G2-D** recorded in $CDCl_3$.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.77 (br-s, 1H, $CH{=}N_2$), 4.40–4.26 (m, 8H, CO_2CH_2), 4.15 (d, J = 12 Hz, 4H, C*H*H), 3.62 (d, J = 12 Hz, 4H, CH*H*), 1.42 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.28 (s, 3H, CH_3), 1.14 (s, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.6 [–CH_3C(*C*=O)O–], 172.5 [–CH_3C(*C*=O)O–], 166.6 [br, (N_2=)CH(*C*=O)O–], 98.2 [(–$CH_2O)_2C(CH_3)_2$], 66.1 (CH_2), 66.0 (CH_2), 65.4 (CH_2), 63.2 (CH_2), 62.2 (CH_2), 46.9 [–CH_3C(C=O)O-], 46.4 (–$CH{=}N_2$), 42.2 [–CH_3C(C=O)O-], 25.3 (CH_3), 22.2 (CH_3), 18.6 (CH_3), 17.8 (CH_3).

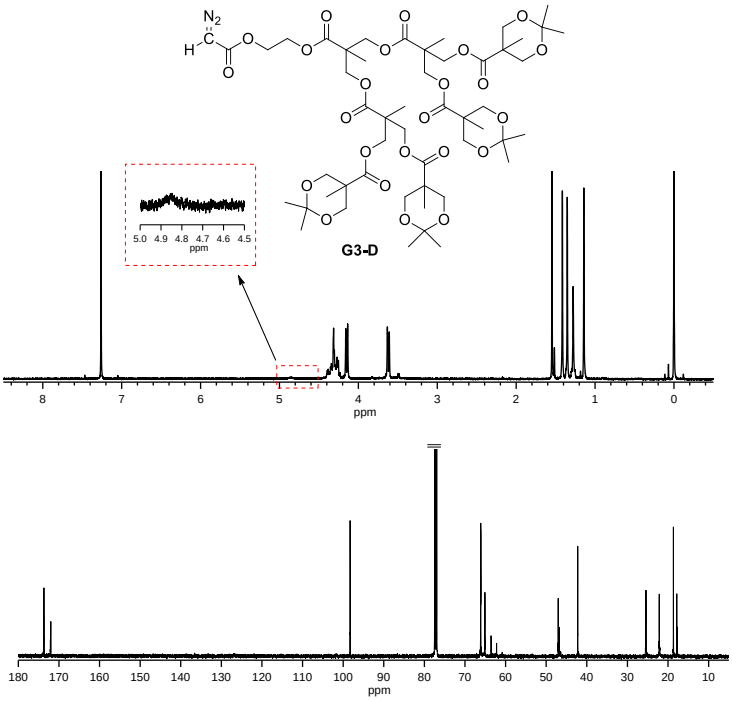


Figure S3. ^{1}H and ^{13}C NMR spectra of **G3-D** recorded in $CDCl_3$.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.84 (br-s, 1H, $CH{=}N_2$), 4.40–4.24 (m, 16H, CO_2CH_2), 4.15 (d, J = 12 Hz, 4H, C*H*H), 3.62 (d, J = 12 Hz, 4H, CH*H*), 1.41 (s, 12H, CH_3), 1.35 (s, 12H, CH_3), 1.28 (s, 9H, CH_3), 1.14 (s, 12H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.7 [–CH_3C(*C*=O)O–], 172.1 [–CH_3C(*C*=O)O–], 172.0 [–CH_3C(*C*=O)O–], 98.3 [(–$CH_2O)_2C(CH_3)_2$], 66.2 (CH_2), 66.1 (CH_2), 65.1 (CH_2), 63.6 (CH_2), 62.2 (CH_2), 47.0 [–CH_3C(C=O)O-], 46.8 [–CH_3C(C=O)O–], 46.5 (–$CH{=}N_2$), 42.2 [–CH_3C(C=O)O-], 25.4 (CH_3), 22.2 (CH_3), 18.7 (CH_3), 17.8 (CH_3), 17.7 (CH_3). The signal for the carbonyl-C [$(N_2{=})CH(C{=}O)O$–] could not be observed.

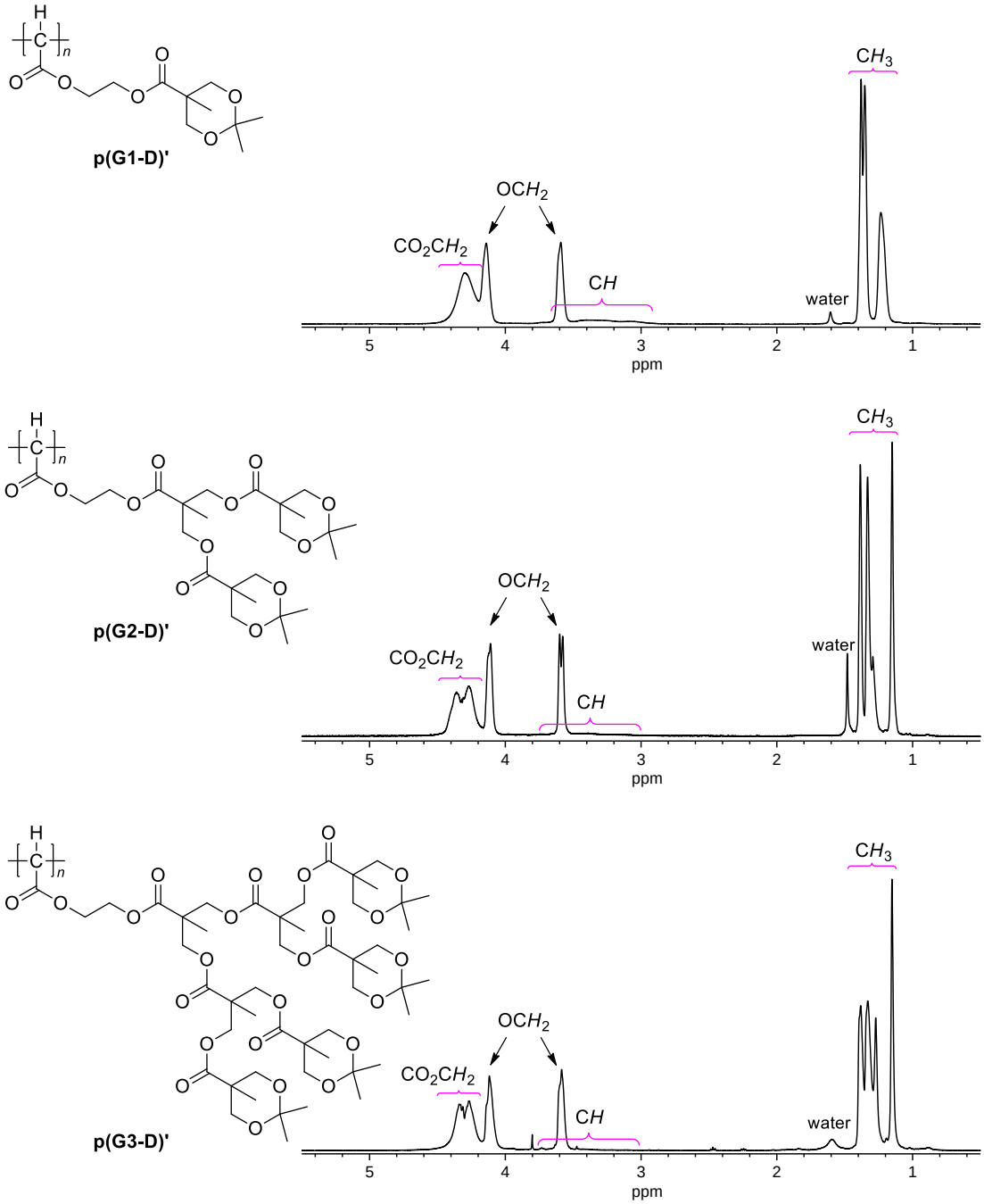


Figure S4. ^{1}H NMR spectra of **p(G1-D)'** (top), **p(G2-D)'** (middle), and **p(G3-D)'** (bottom) recorded in $CDCl_3$.

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