Supporting Information for

Pd-initiated C1 Polymerization of Diazoacetates with Hydroxy-protected Sugar Substituents: Syntheses of a New Type of Protected Sugar-containing C1 Polymers (C1 Glycopolymers)

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Experimental Section

Materials

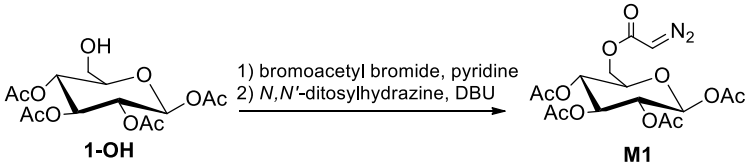
Tetrahydrofuran (THF, Kanto Chemical, >99.5%, dehydrated Super Plus grade) was used after passage through solvent purification columns (Nikko Hansen & Co., Glass Contour MINI). Diethyl ether (Kanto Chemical, >99.5%, dehydrated), chloroform (Junsei Chemical, 99%), dichloromethane (FUJIFILM Wako Pure Chemical, Guaranteed Reagent), hexane (FUJIFILM Wako Pure Chemical, >96.0%), ethyl acetate (FUJIFILM Wako Pure Chemical, >99.5%), methanol (Yoneyama Yakuhin Kogyo, >99%), allylpalladium(II) chloride dimer [(π-allylPdCl)$_2$, Sigma-Aldrich, >98.0%), sodium tetraphenylborate ($NaBPh_4$, Tokyo Chemical Industry, >99.5%), pyridine (Kanto Chemical, >99.5%), bromoacetyl bromide (Sigma-Aldrich, >98.0%), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU, Tokyo Chemical Industry, >98%), hydrochloric acid (Nacalai Tesque, 35–37%), sodium sulfate (Na_2SO_4, Nacalai Tesque, > 98.5%), sodium hydrogen carbonate ($NaHCO_3$, Kanto Chemical, 99.5–100.3%), and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**4-OH**, Tokyo Chemical Industry, >92.0%) were used as received.

N,*N*'-ditosylhydrazine,[1] ethyl diazoacetate (**EDA**),[2] benzyl diazoacetate (**BDA**),[1] 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (**1-OH**),[3] 1,2,3,4-tetra-*O*-benzyl-β-D-glucopyranoside (**2-OH**),[4] **3-OH**[5], (nq)$_2$PdCl[6] were synthesized according to the literatures.

Synthesis of monomers

Caution! Extra care must be taken for syntheses and handling of the diazocarbonyl compounds because of their potential explosiveness.

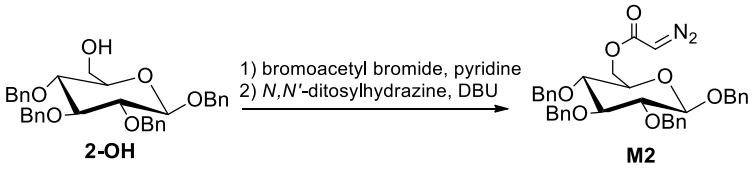
*Synthesis of **M1**.*



Under a N_2 atmosphere, an acetonitrile (38 mL) solution of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (**1-OH**) (2.65 g, 7.61 mmol) and pyridine (0.84 mL, 9.9 mmol) was placed in a round-bottomed flask equipped with a three-way cock, and cooled to 0 °C. After bromoacetyl bromide (0.99 mL, 11 mmol) was added at 0 °C dropwise, the mixture was warmed to room temperature and stirred at room temperature for 30 min. H_2O (38 mL) and $CHCl_3$ (38 mL) were added to the mixture and it was transferred to a separatory funnel to extract the organic phase. After the aqueous phase was extracted with $CHCl_3$ (50 mL × 3), the combined organic phase was washed with saturated NaCl aqueous solution (80 mL) and H_2O (80 mL), and dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel [eluent: AcOEt:hexane (vol/vol) = 3/2] to yield a crude product, which was used for the next step without further purification.

Under a N_2 atmosphere, a THF (30 mL) solution of the crude product and *N,N'*-ditosylhydrazine (4.0 g, 12 mmol) was placed in a round-bottomed flask equipped with a three-way cock, and cooled to 0 °C. After DBU (4.49 mL, 30.1 mmol) was added dropwise at 0 °C, the mixture was stirred at 0 °C for 10 min. After saturated $NaHCO_3$ aqueous solution (30 mL) and Et_2O (30 mL) were added, the mixture was transferred to a separatory funnel to separate the organic phase. After the aqueous phase was extracted with Et_2O (40 mL × 2), the combined organic phase was washed with saturated NaCl aqueous solution (60 mL) and H_2O (60 mL), and dried over Na_2SO_4. After volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel [eluent: AcOEt:hexane (vol/vol) = 2/3] and then, preparative recycling SEC (eluent: $CHCl_3$) to yield **M1** as a yellow solid (1.56 g, 50.0% yield).
^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.71 (d, J = 8.5 Hz, 1H, H-1), 5.25 (t, J = 9.4 Hz, 1H, H-2, H-3, or H-4), 5.05–5.17 (m, 2H, H-2, H-3, or H-4), 4.83 (br-s, 1H, -CH=N_2), 4.23–4.35 (m, 2H, H-6), 3.82–3.90 (m, 1H, H-5), 2.11 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.01 (s, 3H, CH_3).
^{13}C NMR (100 MHz, $CDCl_3$, δ): 170.1, 169.4, 169.2, and 168.9 [-(*C*=O)CH_3 × 4], 166.5 [-(*C*=O)CH=N_2], 91.7 (C-1), 72.8 (overlapping two peaks), 70.2, and 67.8 (C-2, C-3, C-4, and C-5), 61.8 (C-6), 46.5 (-CH=N_2), 20.8 [-(C=O)*C*H_3], 20.7 [overlapping three peaks for -(C=O)*C*H_3].
Anal calcd for $C_{16}H_{20}N_2O_{11}$: C, 46.16; H, 4.84; N, 6.73. Found: C, 46.67; H, 4.98; N, 6.30.

Synthesis of ***M2****.*



Under a N_2 atmosphere, an acetonitrile (15 mL) solution of 1,2,3,4-tetra-*O*-benzyl-β-D-glucopyranoside (**2-OH**) (1.00 g, 1.85 mmol) and pyridine (0.24 mL, 2.8 mmol) was placed in a round-bottomed flask equipped with a three-way cock, and cooled to 0 °C. After bromoacetyl bromide (0.24 mL, 2.8 mmol) was added at 0 °C dropwise, the mixture was warmed to room temperature and stirred at room temperature for 30 min. H_2O (15 mL) and $CHCl_3$ (15 mL) were added to the mixture and it was transferred to a separatory funnel to extract the organic phase. After the aqueous phase was extracted with $CHCl_3$ (25 mL × 3), the combined organic phase was washed with saturated NaCl aqueous solution (50 mL) and H_2O (30 mL), and dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel [eluent: AcOEt:hexane (vol/vol) = 3/2] to yield a crude product, which was used for the next step without further purification.

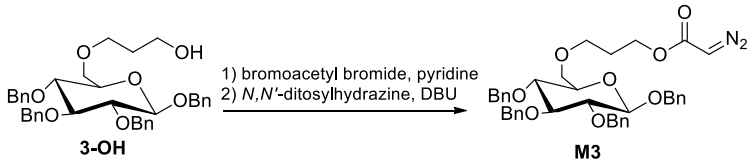
Under a N_2 atmosphere, a THF (12 mL) solution of the crude product and *N,N'*-ditosylhydrazine (0.830 g, 2.44 mmol) was placed in a round-bottomed flask equipped with a three-way cock, and cooled to 0 °C. After DBU (0.91 mL, 6.1 mmol) was added dropwise at 0 °C, the mixture was stirred at 0 °C for 10 min. After saturated $NaHCO_3$ aqueous solution (12 mL) and Et_2O (12 mL) were added, the mixture was transferred to a separatory funnel to separate the organic phase. After the aqueous phase was extracted with Et_2O (20 mL × 2), the combined organic phase was washed with saturated NaCl aqueous solution (15 mL) and H_2O (15 mL), and dried over Na_2SO_4. After volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel [eluent: AcOEt:$CHCl_3$ (vol/vol) = 1/1] and then, preparative recycling SEC (eluent: $CHCl_3$) to yield **M2** as a yellow solid (0.34 g, 30% yield).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.20–7.38 (m, 20H, Ar-H), 4.91–4.98 (m, 3H, H-1 and two of Ph-C*H*H-), 4.86 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.78 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.76 (br-s, overlapping with other peaks, 1H, -CH=N_2), 4.72 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.65 (d, J = 12 Hz, 1H, Ph-C*H*H-), 4.57 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.50 (d, J = 8.0 Hz, 1H, Ph-C*H*H-), 4.48 (d, J = 10 Hz, 1H, H-6), 4.31 (d, J = 10 Hz, 1H, H-6), 3.62 – 3.70 (m, 1H, H-2, H-3, H-4, or H-5), 3.45–3.55 (m, 3H, H-2, H-3, H-4, or H-5).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 166.5 [-(*C*=O)CH=N2], 138.5, 138.4, 137.8, and 137.2 (Ar, *ipso*-C), 128.6, 128.53, 128.50, 128.4, 128.23, 128.20, 128.1, 128.04, 128.00, 127.97, and 127.8 (Ar, CH, one of the peaks contains overlapping two peaks), 102.4 (C-1), 84.7 (C-2, C-3, C-4, or C-5), 82.3 (C-2, C-3, C-4, or C-5), 77.5 (C-2, C-3, C-4, or C-5), 75.8 (Ph-*C*H_2- or C-6), 75.1 (Ph-*C*H_2- or C-6), 75.0 (Ph-*C*H_2- or C-6), 73.1 (C-2, C-3, C-4, or C-5), 71.2 (Ph-*C*H_2- or C-6), 63.5 (Ph-*C*H_2- or C-6), 46.4 (-CH=N_2).

Anal calcd for $C_{36}H_{36}N_2O_7$: C, 71.04; H, 5.96; N, 4.60. Found: C, 71.23; H, 6.17; N, 4.44.

*Synthesis of **M3**.*



Under a N_2 atmosphere, an acetonitrile (5 mL) solution of **3-OH** (0.332 g, 0.554 mmol) and pyridine (0.070 mL, 1.4 mmol) was placed in a round-bottomed flask equipped with a three-way cock, and cooled to 0 °C. After bromoacetyl bromide (0.072 mL, 0.83 mmol) was added at 0 °C dropwise, the mixture was warmed to room temperature and stirred at room temperature for 30 min. H_2O (5 mL) and $CHCl_3$ (5 mL) were added to the mixture and it was transferred to a separatory funnel to extract the organic phase. After the aqueous phase was extracted with $CHCl_3$ (10 mL × 3), the combined organic phase was washed with saturated NaCl aqueous solution (15 mL) and H_2O (15 mL), and dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel [eluent: AcOEt:hexane (vol/vol) = 3/2] to yield a crude product, which was used for the next step without further purification.

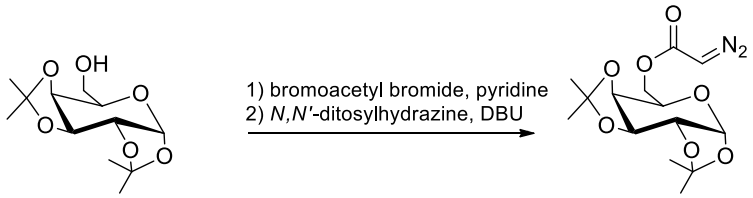
Under a N_2 atmosphere, a THF (12 mL) solution of the crude product and *N,N'*-ditosylhydrazine (0.294 g, 0.431 mmol) was placed in a round-bottomed flask equipped with a three-way cock, and cooled to 0 °C. After DBU (0.32 mL, 2.2 mmol) was added dropwise at 0 °C, the mixture was stirred at 0 °C for 10 min. After saturated $NaHCO_3$ aqueous solution (12 mL) and Et_2O (12 mL) were added, the mixture was transferred to a separatory funnel to separate the organic phase. After the aqueous phase was extracted with Et_2O (20 mL × 2), the combined organic phase was washed with saturated NaCl aqueous solution (20 mL) and H_2O (20 mL), and dried over Na_2SO_4. After volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel [eluent: AcOEt:$CHCl_3$ (vol/vol) = 2/1] and then, preparative recycling SEC (eluent: $CHCl_3$) to yield **M3** as a yellow highly viscous oil (0.17 g, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.22–742 (m, 20H, Ar-H), 4.89–5.00 (m, 3H, H-1 and two of Ph-C*H*H-), 4.86 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.79 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.72 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.66 (d, J = 12 Hz, 1H, Ph-C*H*H-), 4.65 (br-s, overlapping with other peaks, 1H, -CH=N_2), 4.60 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.50 (d, J = 7.6 Hz, 1H, Ph-C*H*H-), 4.27 [t, J = 6.0 Hz, 2H, -CH2O(C=O)], 3.27–3.75 [m, 8H, H-2, H-3, H-4, H-5, H-6, and -OC*H*$_2$CH$_2$CH$_2$O(C=O)], 1.93 (m, 2H, -OCH$_2$C*H*$_2$CH$_2$-).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.9 [-(*C*=O)CH=N_2], 138.6, 138.4, 138.3, and 137.5 (Ar, *ipso*-C), 128.5, 128.44, 128.42, 128.39, 128.2, 128.0, 127.9, 127.83, 127.80, 127.7, and 127.6 (Ar, CH, one of the peaks contains overlapping two peaks), 102.7 (C-1), 84.7 (C-2, C-3, C-4, or C-5), 82.3 (C-2, C-3, C-4, or C-5), 77.9 (C-2, C-3, C-4, or C-5), 75.8 (Ph-*C*H$_2$-, C-6, or -OCH$_2$-), 75.03 (Ph-*C*H$_2$-, C-6 or -OCH$_2$-), 74.94 (Ph-*C*H$_2$-, C-6, or -OCH$_2$-), 74.90 (C-2, C-3, C-4, or C-5), 71.2 (Ph-*C*H$_2$-, C-6, or -OCH$_2$-), 69.8 (Ph-*C*H$_2$-, C-6, or -OCH$_2$-), 68.0 (Ph-*C*H$_2$-, C-6, or -OCH$_2$-), 62.1 (Ph-*C*H$_2$-, C-6, or -OCH$_2$-), 46.2 (-CH=N_2), 29.3 (-OCH$_2$*C*H$_2$CH$_2$O-).

Anal calcd for $C_{39}H_{42}N_2O_8 \cdot (C_6H_6)_{0.2}$: C, 70.25; H, 6.35; N, 4.20. Found: C, 70.35; H, 6.53; N, 3.59.

*Synthesis of **M4**.*



4-OH **M4**

Under a N_2 atmosphere, an acetonitrile (5 mL) solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**4-OH**) (0.360 g, 1.38 mmol) and pyridine (0.30 mL, 3.5 mmol) was placed in a round-bottomed flask equipped with a three-way cock, and cooled to 0 °C. After bromoacetyl bromide (0.18 mL, 2.1 mmol) was added at 0 °C dropwise, the mixture was warmed to room temperature and stirred at room temperature for 30 min. H_2O (5 mL) and $CHCl_3$ (5 mL) were added to the mixture and it was transferred to a separatory funnel to extract the organic phase. After the aqueous phase was extracted with $CHCl_3$ (10 mL × 3), the combined organic phase was washed with saturated NaCl aqueous solution (15 mL) and H_2O (15 mL), and dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel [eluent: AcOEt:hexane (vol/vol) = 3/2] to yield a crude product, which was used for the next step without further purification.

Under a N_2 atmosphere, a THF (14 mL) solution of the crude product and *N,N'*-ditosylhydrazine (0.940 g, 2.76 mmol) was placed in a round-bottomed flask equipped with a three-way cock, and cooled to 0 °C. After DBU (1.03 mL, 6.91 mmol) was added dropwise at 0 °C, the mixture was stirred at 0 °C for 10 min. After saturated $NaHCO_3$ aqueous solution (14 mL) and Et_2O (14 mL) were added, the mixture was transferred to a separatory funnel to separate the organic phase. After the aqueous phase was extracted with Et_2O (30 mL × 2), the combined organic phase was washed with saturated NaCl aqueous solution (20 mL) and H_2O (20 mL), and dried over Na_2SO_4. After volatiles were removed under reduced pressure, the residue was subjected to purification with flash chromatography on silica gel [eluent: AcOEt:hexane (vol/vol) = 2/3] and then, preparative recycling SEC (eluent: $CHCl_3$) to yield **M4** as a yellow highly viscous oil (0.28 g, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.54 (d, J = 5.0 Hz, 1H, H-1), 4.82 (br-s, 1H, -CH=N_2), 4.62 (d, J = 8.0 Hz, H-2, H-3, H-4, H-5, or H-6), 4.19–4.38 (m, 4H, H-2, H-3, H-4, H-5, or H-6), 4.05 (t, J = 5.8 Hz, 1H, H-2, H-3, H-4, H-5, or H-6), 1.52, 1.45, 1.34, and 1.33 (s, 3H × 4, -CH_3).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 166.7 [-(*C*=O)CH=N_2], 109.7 [-*C*(CH_3)$_2$], 108.8 [-*C*(CH_3)$_2$], 96.3 (C-1), 71.0, 70.7, 70.5, and 66.1 (C-2, C-3, C-4, and C-5), 63.8 (C-6), 26.0, 25.9, 25.0, and 24.5 (CH_3 × 4).

Anal calcd for $C_{14}H_{20}N_2O_7$: C, 51.22; H, 6.16; N, 8.69. Found: C, 51.47; H, 6.14; N, 8.53.

Polymerization

π-allylPdCl/$NaBPh_4$-initated polymerization of diazoacetates with hydroxy-protected sugar substituents.

As a representative example, the procedure for run 12 in Table 1 is described below.

Under a N_2 atmosphere, a THF (1.7 mL) solution of (π-allylPdCl)$_2$ (0.826 mg, 0.00226 mmol) was placed in a Schlenk tube and cooled to −78 °C. After $NaBPh_4$ (2.1 mg, 0.0061 mmol) was added, the mixture was stirred at −78 °C for 10 min. After a THF (1.8 mL) solution of **M3** (0.153 g, 0.229 mmol) was added to the mixture dropwise with the temperature of the mixture kept at −78 °C and the mixture was stirred at −78 °C for 5 min, it was gradually warmed to −20 °C and stirred at −20 °C for 24 h. After volatiles were removed under reduced pressure, 1N HCl aqueous solution (2 mL), MeOH (2 mL), and $CHCl_3$ (10 mL) were added, and the mixture was stirred for 30 min. The mixture was transferred to a separately funnel to extract the organic phase, and the aqueous phase was extracted with $CHCl_3$ (10 mL × 3). The combined organic phase was washed with 1N HCl aqueous solution (10 mL), H_2O (10 mL), and saturated NaCl aqueous solution (10 mL), and dried over Na_2SO_4. After volatiles were removed under reduced pressure, the residue was subjected to purification using preparative recycling SEC (eluent: $CHCl_3$) to yield poly**M3'** as a pale yellow solid (68 mg, 47% yield).

(nq)$_2$Pd/$NaBPh_4$-initated polymerization of diazoacetates with hydroxy-protected sugar substituents.

As a representative example, the procedure for run 14 in Table 1 is described below.

Under a N_2 atmosphere, a THF (1.2 mL) solution of (nq)$_2$PdCl (1.29 mg, 0.00305 mmol) was placed in a Schlenk tube and cooled to −78 °C. After $NaBPh_4$ (1.46 mg, 0.00426 mmol) was added, the mixture was stirred at −78 °C for 10 min. The mixture was warmed to 0 °C, and a THF (1.3 mL) solution of **M3** (0.100 g, 0.150 mmol) was added to the mixture dropwise with the temperature of the mixture kept at 0 °C. After the mixture was stirred at 0 °C for 10 min, it was gradually warmed to room temperature and stirred at room temperature for 13 h. After volatiles were removed under reduced pressure, 1N HCl aqueous solution (2 mL), MeOH (2 mL), and $CHCl_3$ (10 mL) were added, and the mixture was stirred for 30 min. The mixture was transferred to a separately funnel to extract the organic phase, and the aqueous phase was extracted with $CHCl_3$ (10 mL × 3). The combined organic phase was washed with 1N HCl aqueous solution (10 mL), H_2O (10 mL), and saturated NaCl aqueous solution (10 mL), and dried over Na_2SO_4. After volatiles were removed under reduced pressure, the residue was subjected to purification using preparative recycling SEC (eluent: $CHCl_3$) to yield poly**M3'** as a pale yellow solid (27 mg, 28% yield).

*Copolymerization of galactose-based monomer **M4** with **EDA**.*

As a representative example, the procedure for run 2 in Table 2 is described below.

Under a N_2 atmosphere, a THF (4.0 mL) solution of (π-allylPdCl)$_2$ (1.08 mg, 0.00295 mmol) was placed in a Schlenk tube and cooled to −78 °C. After $NaBPh_4$ (3.90 mg, 0.0114 mmol) was added, the mixture was stirred at −78 °C for 10 min. A mixture of a THF (6.0 mL) solution of **M4** (0.101 g, 0.308 mmol) and a CH_2Cl_2 solution of **EDA** (0.15 mL of 2.04 M solution, 0.31 mmol) was added to the initiator solution at −78 °C, and the mixture was stirred at −78 °C for 5 min. After the mixture was gradually warmed to room temperature, it was stirred at room temperature for 13 h. After volatiles were removed under reduced pressure, 1N HCl aqueous solution (3 mL), MeOH (3 mL), and $CHCl_3$ (15 mL) were added, and the mixture was stirred for 30 min. The mixture was transferred to a separately funnel to extract the organic phase, and the aqueous phase was extracted with $CHCl_3$ (15 mL × 3). The combined organic phase was washed with 1N HCl aqueous solution (15 mL), H_2O (15 mL), and saturated NaCl aqueous solution (15 mL), and dried over Na_2SO_4. After volatiles were removed under reduced pressure, the residue was subjected to purification using preparative

recycling SEC (eluent: CHCl3) to yield poly(**M4'**-*co*-**EDA'**) as a pale yellow solid (62 mg, 52% yield).

*Copolymerization of galactose-based monomer **M4** with **BDA**.*

Under a N_2 atmosphere, a THF (5.0 mL) solution of $(nq)_2PdCl$ (4.10 mg, 0.00969 mmol) was placed in a Schlenk tube and cooled to −78 °C. After $NaBPh_4$ (4.20 mg, 0.0123 mmol) was added, the mixture was stirred at −78 °C for 10 min. The mixture was warmed to 0 °C, and a THF (11.2 mL) solution of **M4** (0.0810 g, 0.247 mmol) and **BDA** (0.131 g, 0.744 mmol) was added to the initiator solution at 0 °C, and it was stirred at 0 °C for 10 min. The mixture was gradually warmed to room temperature and it was stirred at room temperature for 13 h. After volatiles were removed under reduced pressure, 1N HCl aqueous solution (3 mL), MeOH (3 mL), and $CHCl_3$ (15 mL) were added, and the mixture was stirred for 30 min. The mixture was transferred to a separately funnel to extract the organic phase, and the aqueous phase was extracted with $CHCl_3$ (15 mL × 3). The combined organic phase was washed with 1N HCl aqueous solution (15 mL), H_2O (15 mL), and saturated NaCl aqueous solution (15 mL), and dried over Na_2SO_4. After volatiles were removed under reduced pressure, the residue was subjected to purification using preparative recycling SEC (eluent: $CHCl_3$) to yield poly(**M4'**-*co*-**BDA'**) as a pale yellow solid (36 mg, 31% yield).

Measurements

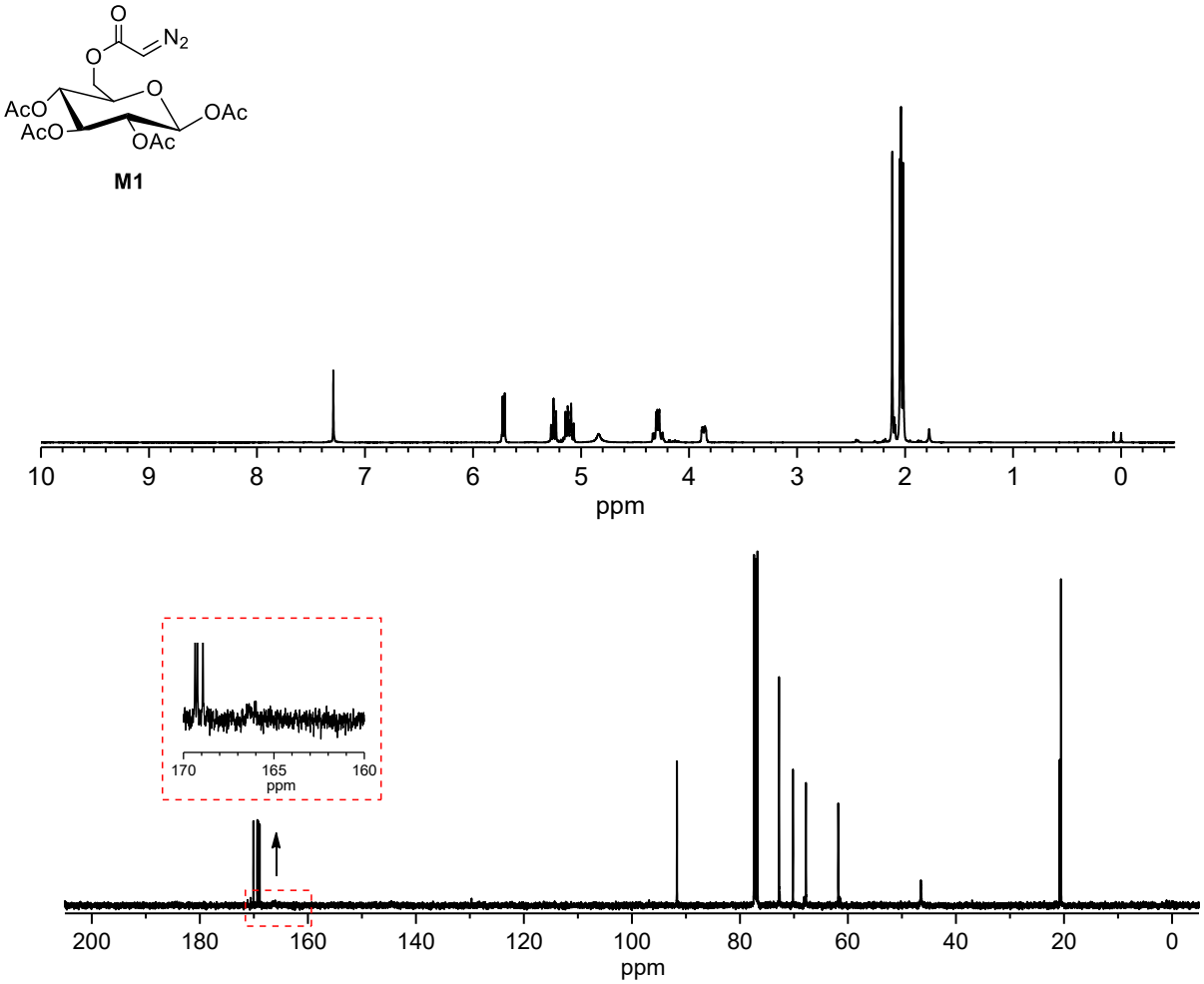
The molar mass distributions of polymers were measured via SEC in THF (flow rate = 1.0 mL/min) at 40 °C on polystyrene gel columns [Styragel HR4 and Styragel HR2 (Waters, molar-mass exclusion limit = 600 kDa and 20 kDa for polystyrene, respectively)] connected to a pump (JASCO, PU-4180), a column oven (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). Purification by preparative recycling SEC was performed on a LaboACE LC-5060 (Japan Analytical Industry) 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.) using chloroform as eluent at a flow rate of 7.5 mL/min at room temperature. 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.

NMR spectra were recorded on a Bruker Avance 400 (400 MHz for ^1H and 100 MHz for ^{13}C) or Avance 500 (500 MHz for ^1H and 126 MHz for ^{13}C) spectrometer at room temperature (monomers and their precursors) or at 50 °C (polymers).

MALDI-TOF-MS (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) data were recorded on a JMS-S3000 (JEOL, spiral mode) using super-DHB (Merck, a mixture of 2,5-dihydroxybenzoic acid and 2-hydroxy-5-methoxybenzoic acid) as a matrix and sodium trifluoroacetate as an ion source. The calibration was carried out using poly(ethylene glycol) (M_n = 2700−3500).

Glass transition temperature (T_g) of polymers were determined by differential scanning calorimetry (DSC; Seiko Instruments Inc., EXSTAR DSC6000). The heating and cooling rates were 10 °C/min. The T_g was defined as the temperature of the midpoint of a heat capacity change on the second heating scan.

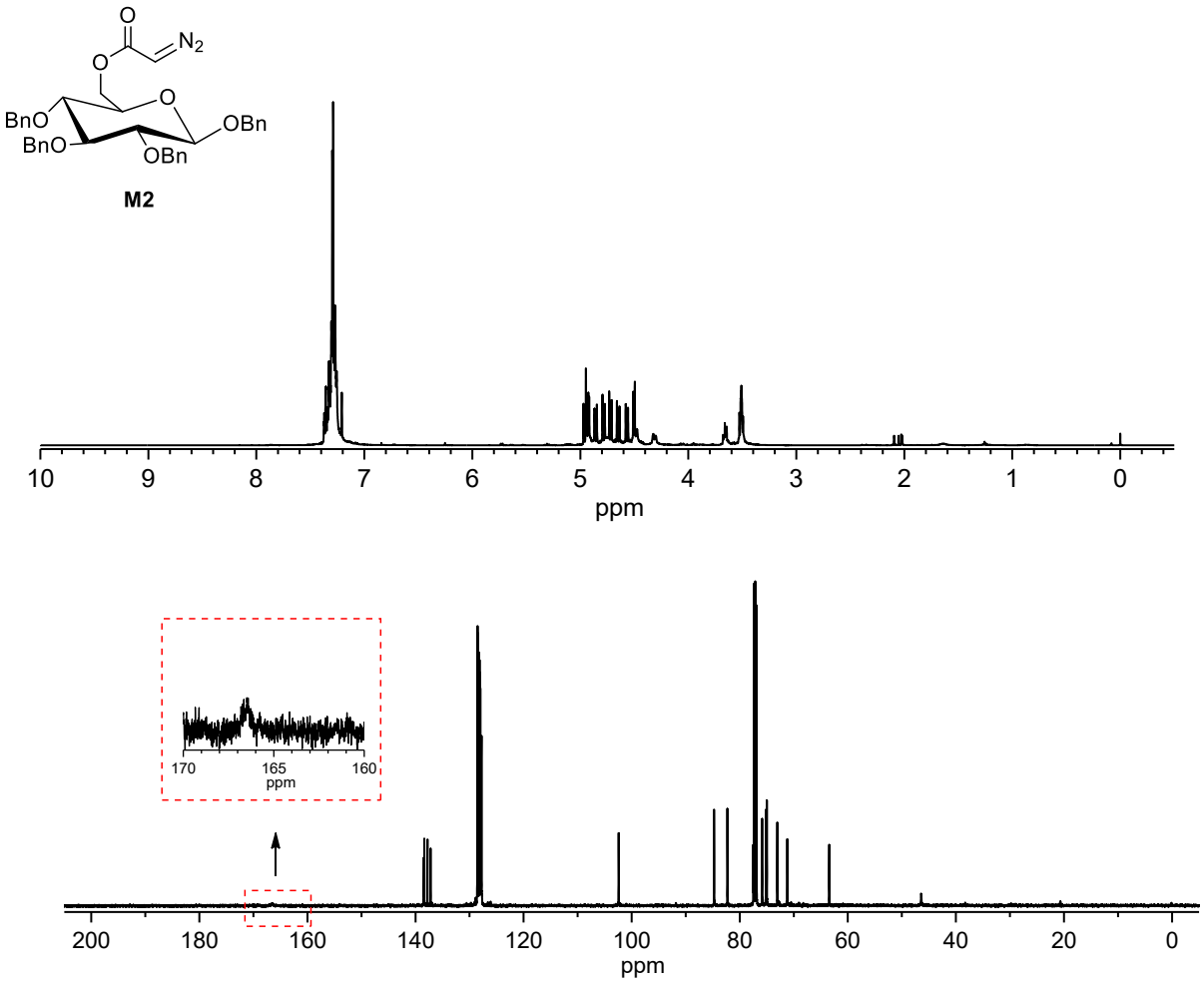
Elemental analyses were performed on a MICRO CORDER JM10T (J-SCIENCE LAB).



^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.71 (d, J = 8.5 Hz, 1H, H-1), 5.25 (t, J = 9.4 Hz, 1H, H-2, H-3, or H-4), 5.05–5.17 (m, 2H, H-2, H-3, or H-4), 4.83 (br-s, 1H, -CH=N_2), 4.23–4.35 (m, 2H, H-6), 3.82–3.90 (m, 1H, H-5), 2.11 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.01 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 170.1, 169.4, 169.2, and 168.9 [-(*C*=O)CH_3 × 4], 166.5 [-(*C*=O)CH=N_2], 91.7 (C-1), 72.8 (overlapping two peaks), 70.2, and 67.8 (C-2, C-3, C-4, and C-5), 61.8 (C-6), 46.5 (-CH=N_2), 20.8 [-(C=O)*C*H_3], 20.7 [overlapping three peaks for -(C=O)*C*H_3].

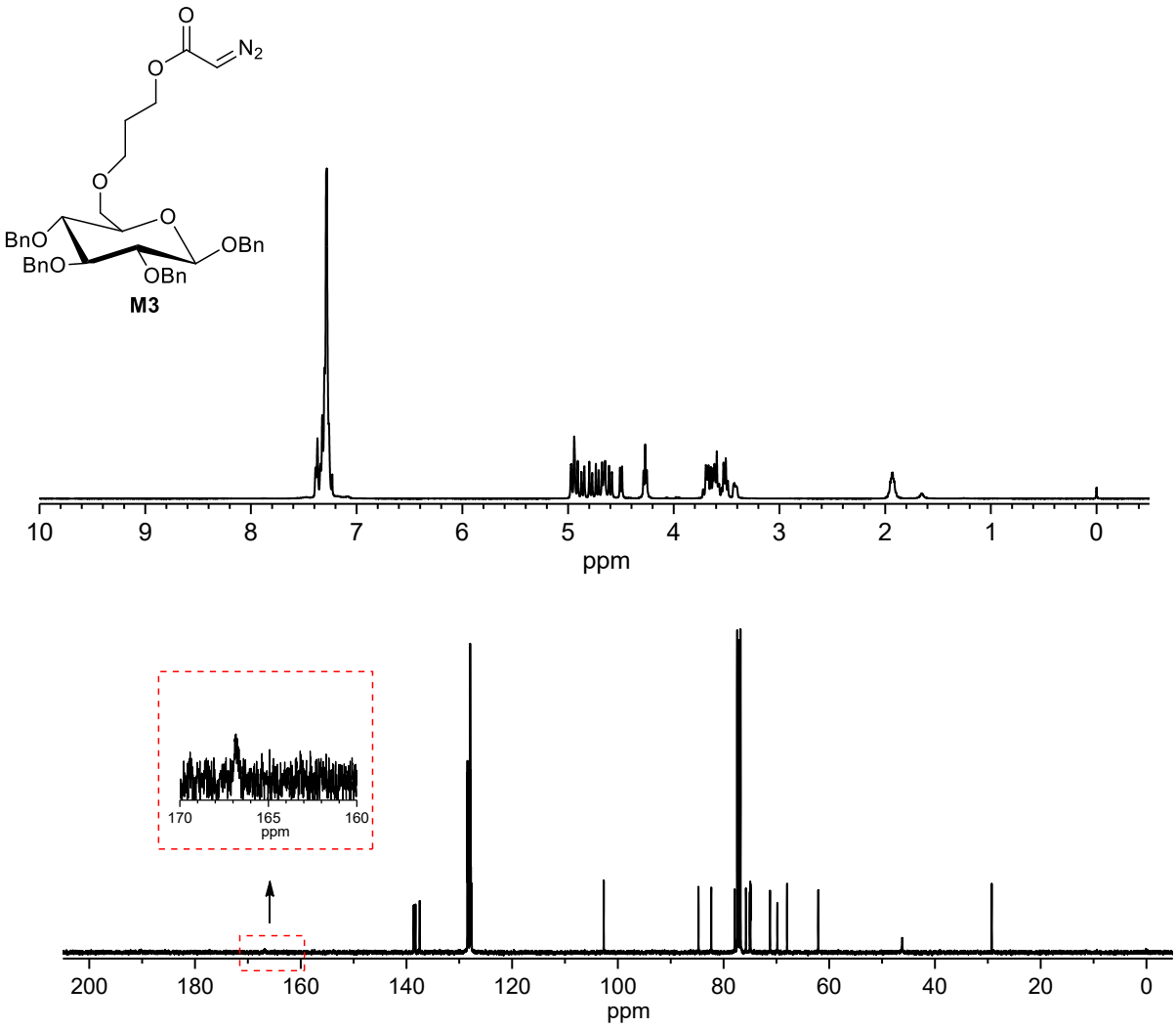
Figure S1. ^{1}H (upper) and ^{13}C (lower) NMR spectra of **M1**.



^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.20–7.38 (m, 20H, Ar-H), 4.91–4.98 (m, 3H, H-1 and two of Ph-C*H*H-), 4.86 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.78 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.76 (br-s, overlapping with other peaks, 1H, -CH=N_2), 4.72 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.65 (d, J = 12 Hz, 1H, Ph-C*H*H-), 4.57 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.50 (d, J = 8.0 Hz, 1H, Ph-C*H*H-), 4.48 (d, J = 10 Hz, 1H, H-6), 4.31 (d, J = 10 Hz, 1H, H-6), 3.62 – 3.70 (m, 1H, H-2, H-3, H-4, or H-5), 3.45–3.55 (m, 3H, H-2, H-3, H-4, or H-5).

^{13}C NMR (126 MHz, $CDCl_3$, δ): 166.5 [-(*C*=O)CH=N2], 138.5, 138.4, 137.8, and 137.2 (Ar, *ipso*-C), 128.6, 128.53, 128.50, 128.4, 128.23, 128.20, 128.1, 128.04, 128.00, 127.97, and 127.8 (Ar, CH, one of the peaks contains overlapping two peaks), 102.4 (C-1), 84.7 (C-2, C-3, C-4, or C-5), 82.3 (C-2, C-3, C-4, or C-5), 77.5 (C-2, C-3, C-4, or C-5), 75.8 (Ph-*C*H_2- or C-6), 75.1 (Ph-*C*H_2- or C-6), 75.0 (Ph-*C*H_2- or C-6), 73.1 (C-2, C-3, C-4, or C-5), 71.2 (Ph-*C*H_2- or C-6), 63.5 (Ph-*C*H_2- or C-6), 46.4 (-CH=N_2).

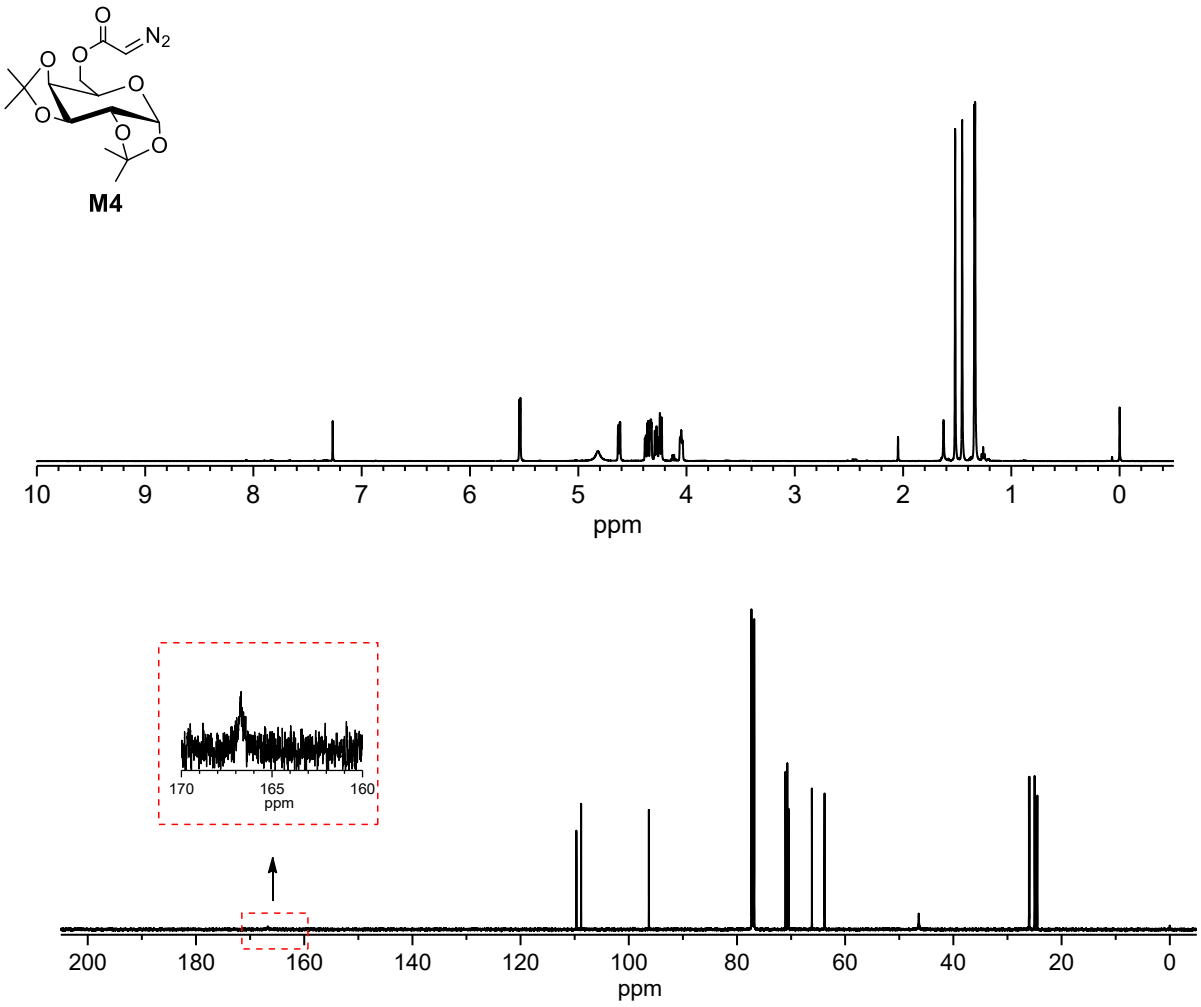
Figure S2. ^{1}H (upper) and ^{13}C (lower) NMR spectra of **M2**.



^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.22–742 (m, 20H, Ar-H), 4.89–5.00 (m, 3H, H-1 and two of Ph-C*H*H-), 4.86 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.79 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.72 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.66 (d, J = 12 Hz, 1H, Ph-C*H*H-), 4.65 (br-s, overlapping with other peaks, 1H, -CH=N_2), 4.60 (d, J = 11 Hz, 1H, Ph-C*H*H-), 4.50 (d, J = 7.6 Hz, 1H, Ph-C*H*H-), 4.27 [t, J = 6.0 Hz, 2H, -CH2O(C=O)], 3.27–3.75 [m, 8H, H-2, H-3, H-4, H-5, H-6, and -OCH_2CH_2CH_2O(C=O)], 1.93 (m, 2H, -OCH_2CH_2CH_2-).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.9 [-(*C*=O)CH=N_2], 138.6, 138.4, 138.3, and 137.5 (Ar, *ipso*-C), 128.5, 128.44, 128.42, 128.39, 128.2, 128.0, 127.9, 127.83, 127.80, 127.7, and 127.6 (Ar, CH, one of the peaks contains overlapping two peaks), 102.7 (C-1), 84.7 (C-2, C-3, C-4, or C-5), 82.3 (C-2, C-3, C-4, or C-5), 77.9 (C-2, C-3, C-4, or C-5), 75.8 (Ph-*C*H_2-, C-6, or -OCH_2-), 75.03 (Ph-*C*H_2-, C-6 or -OCH_2-), 74.94 (Ph-*C*H_2-, C-6, or -OCH_2-), 74.90 (C-2, C-3, C-4, or C-5), 71.2 (Ph-*C*H_2-, C-6, or -OCH_2-), 69.8 (Ph-*C*H_2-, C-6, or -OCH_2-), 68.0 (Ph-*C*H_2-, C-6, or -OCH_2-), 62.1 (Ph-*C*H_2-, C-6, or -OCH_2-), 46.2 (-CH=N_2), 29.3 (-OCH_2*C*H_2CH_2O-).

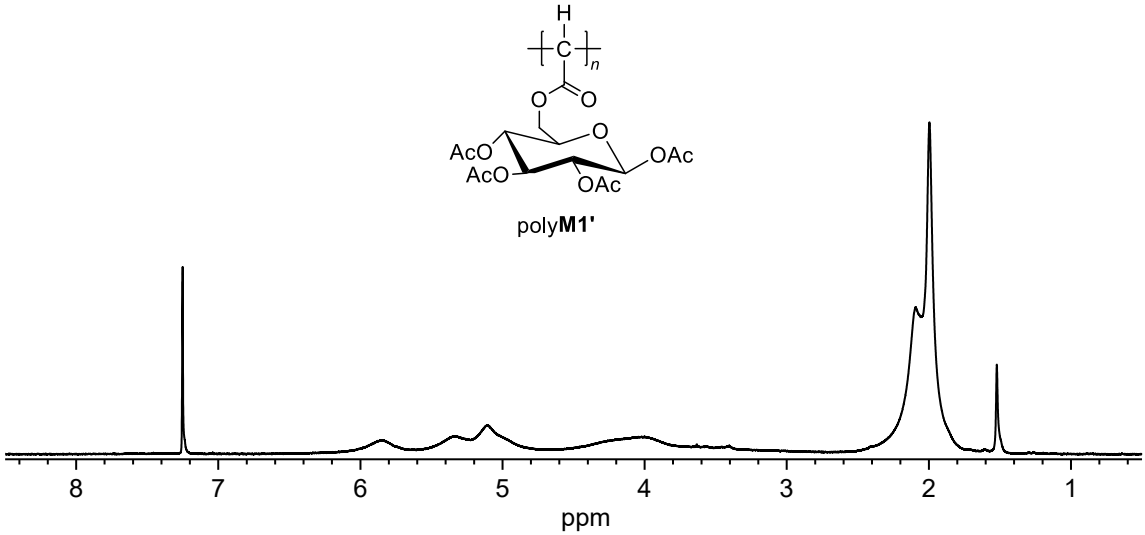
Figure S3. ^{1}H (upper) and ^{13}C (lower) NMR spectra of **M3**.



^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.54 (d, J = 5.0 Hz, 1H, H-1), 4.82 (br-s, 1H, -CH=N_2), 4.62 (d, J = 8.0 Hz, H-2, H-3, H-4, H-5, or H-6), 4.19–4.38 (m, 4H, H-2, H-3, H-4, H-5, or H-6), 4.05 (t, J = 5.8 Hz, 1H, H-2, H-3, H-4, H-5, or H-6), 1.52, 1.45, 1.34, and 1.33 (s, 3H × 4, -CH_3).

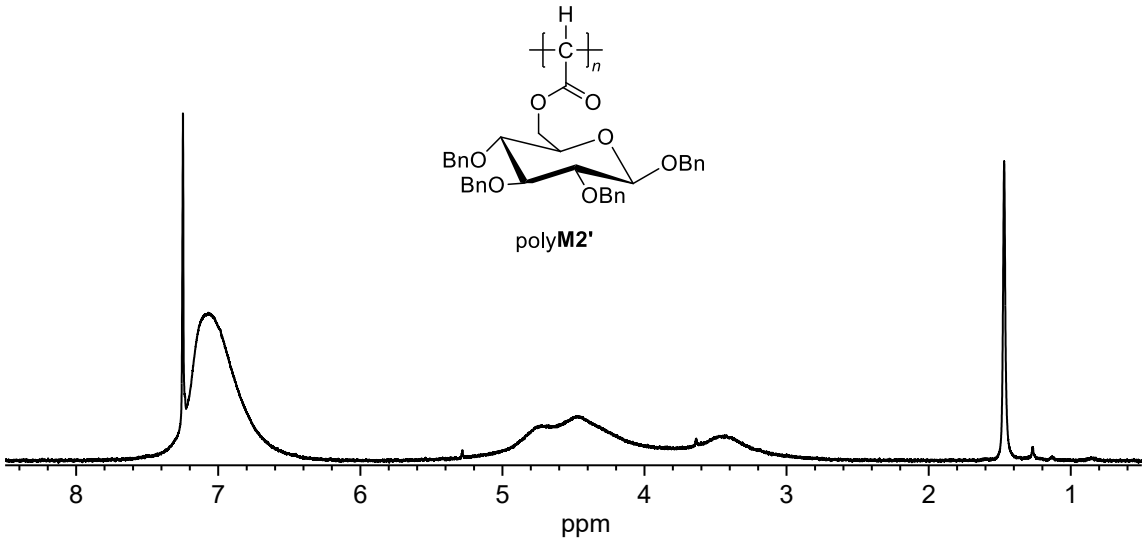
^{13}C NMR (126 MHz, $CDCl_3$, δ): 166.7 [-(*C*=O)CH=N_2], 109.7 [-*C*(CH_3)$_2$], 108.8 [-*C*(CH_3)$_2$], 96.3 (C-1), 71.0, 70.7, 70.5, and 66.1 (C-2, C-3, C-4, and C-5), 63.8 (C-6), 26.0, 25.9, 25.0, and 24.5 (CH_3 × 4).

Figure S4. ^{1}H (upper) and ^{13}C (lower) NMR spectra of **M4**.



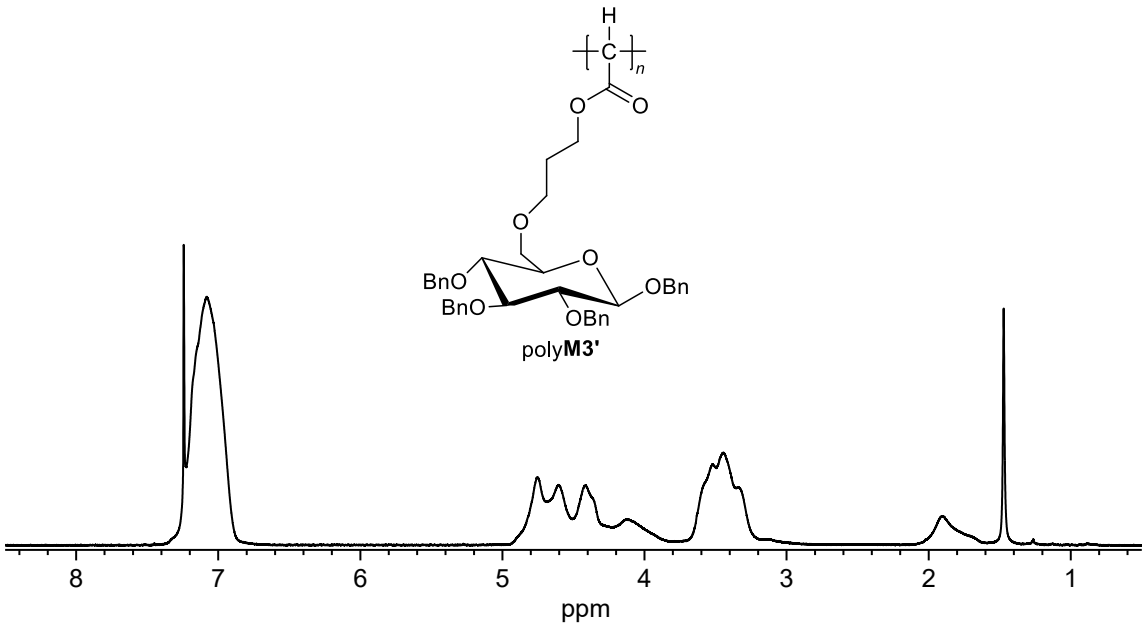
^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.6–6.4 (br, 1H × *n*, H-1), 4.6–5.6 (br, 3H × *n*, H-2, H-3, and H-4), 2.8–4.6 (br, 4H × *n*, H-5, H-6, and main chain CH), 1.7–2.6 (br, 12H × *n*, CH_3).

Figure S5. ^{1}H NMR spectrum of poly**M1'**.



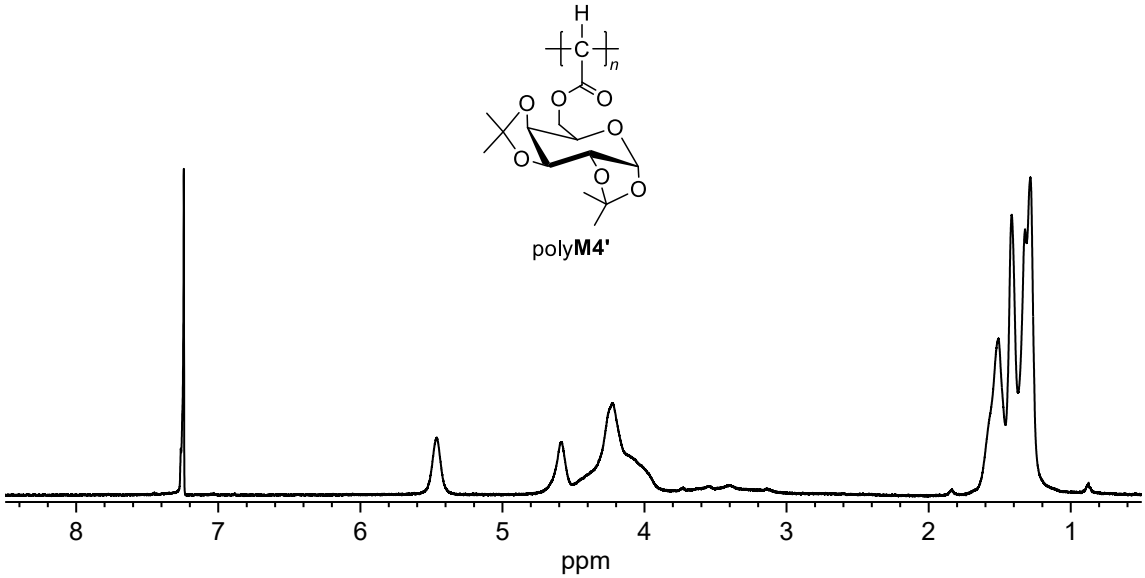
^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.2–7.5 (br, 20H × *n*, Ph-H), 3.8–5.6 (br, 10H × *n*, $PhCH_2$- , H-1 and H-6), 2.7–3.8 (br, 5H × *n*, H-2, H-3, H-4, H-5, and main chain CH).

Figure S6. ^{1}H NMR spectrum of poly**M2'**.



^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.6–7.5 (br, 20H × *n*, Ph-H), 3.8–5.0 [br, 11H × *n*, $PhCH_2$- , H-1 and $CH_2O(C=O)$-], 2.7–3.8 (br, 9H × *n*, H-2, H-3, H-4, H-5, H-6, -$CH_2OCH_2CH_2$-, main chain CH), 1.6–2.2 (br, 2H × *n*, -$OCH_2CH_2CH_2O$-).

Figure S7. ^{1}H NMR spectrum of poly**M3'**.



^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.3–5.7 (br, 1H × *n*, H-1), 3.8–4.9 (br, 6H × *n*, H-2, H-3, H-4,H-5 and H-6), 2.8–3.8 (br, 1H × *n*, main chain CH), 1.0 – 1.8 (br, 12H × *n*, CH_3).

Figure S8. ^{1}H NMR spectrum of poly**M4'**.

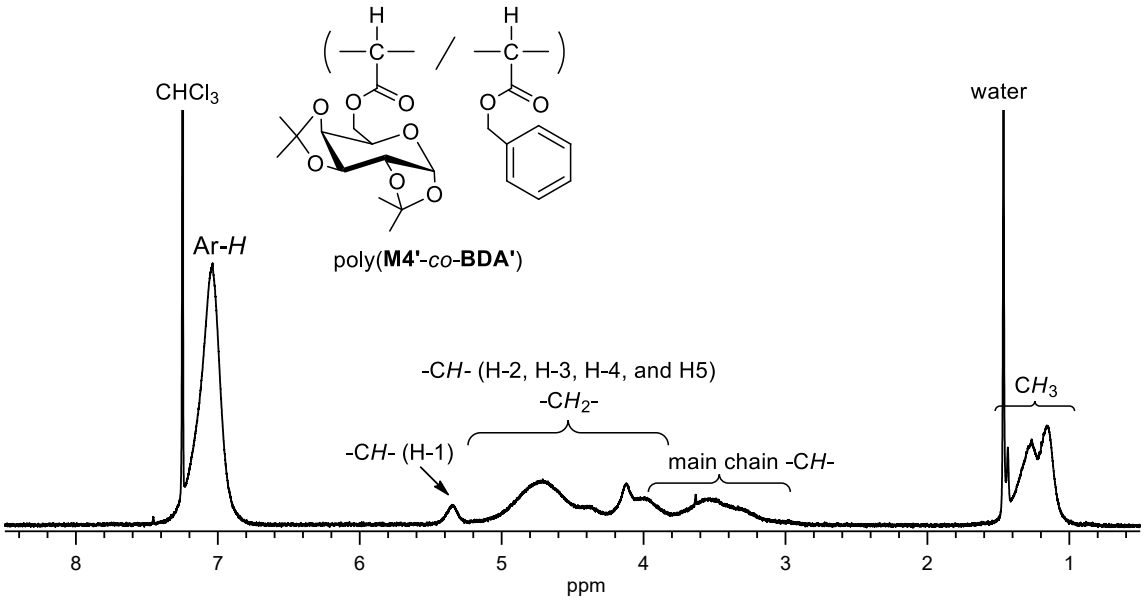


Figure S9. ^{1}H NMR spectrum of poly(**M4'**-*co*-**BDA'**) (run 5 in Table 2).

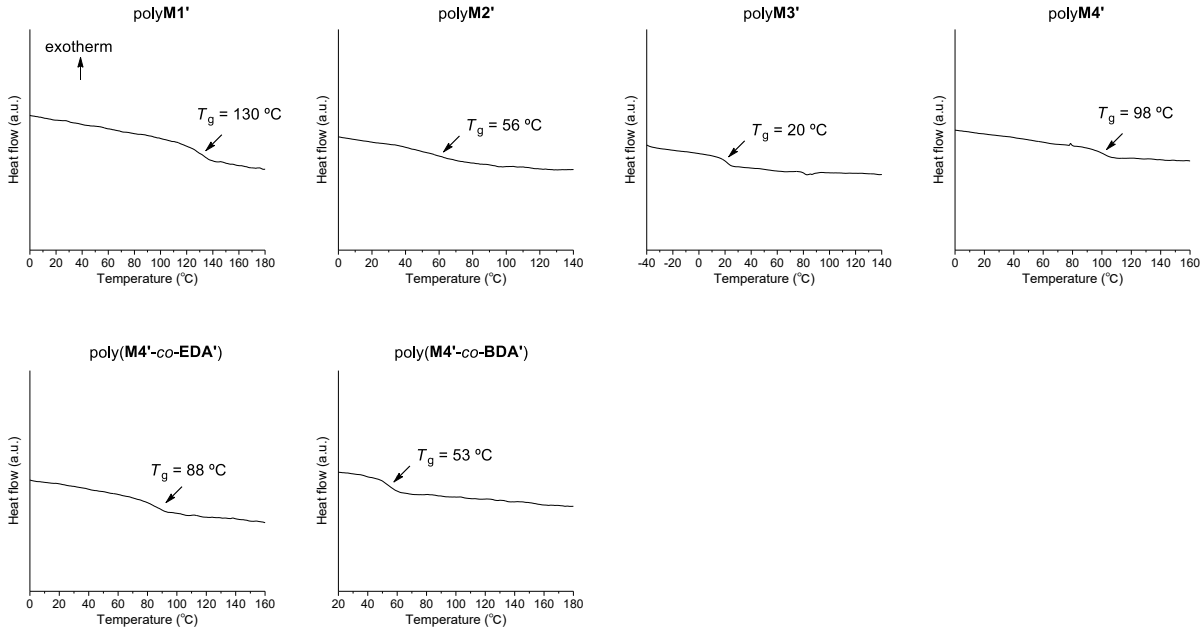


Figure S10. DSC thermograms of poly**M1'** (run 1 in Table 1), poly**M2'** (run 8 in Table 1), poly**M3'** (run 12 in Table 1), poly**M4'** (run 19 in Table 1), poly(**M4'**-*co*-**EDA'**) (run 4 in Table 2), and poly(**M4'**-*co*-**BDA'**) (run 5 in Table 2).

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