Electronic Supplementary Information

Hydrophilic Bio-Based Polymers by Radical Copolymerization of Cyclic Vinyl Ethers Derived from Glycerol

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Contents

Experimental Section

Materials

Glycerol (Sigma-Aldrich, >99.5%), acetone (Wako, >99.5%), *p*-toluenesulfonic acid monohydrate (TCI, >98.0%), *p*-toluenesulfonyl chloride (TCI, >99.0%), triethylamine (Nacalai, >99.0%), valeraldehyde (TCI, >95.0%), cyclohexanecarboxaldehyde (TCI, >98.0%), benzaldehyde (Wako, >98.0%), chloroform (Wako, >99.0%), potassium *tert*-butoxide (Sigma-Aldrich, >98.0%), 2-cyano-2-propyl benzodithioate (CPBD) (Sigma-Aldrich, >97.0%), cyanomethyl dodecyl trithiocarbonate (CMDTTC) (Sigma-Aldrich, >98.0%), and aq. HCl (Nacalai, 35–37.0%) were used as received. 1,2,3,4-tetrahydronaphthalene (TCI, >97.0%), methyl acrylate (MA) (TCI, >99.0%), butyl acrylate (BA) (TCI, >99.0%), methyl methacrylate (MMA) (Wako, >98.0%), styrene (St) (TCI, >99.0%) were distilled over calcium hydride under reduced pressure before use. *N*-isopropylacrylamide (NIPAM) (TCI, >98.0%) was recrystallized before use. tert-Butyldimethylsilyl vinyl ether (TBDMSVE) was synthesized according to the literature.[1] *N*,*N*-dimethylformamide (DMF) (KANTO, >99.5%; H_2O <0.001%), toluene (KANTO, >99.5%; H_2O <0.001%), and THF (KANTO, >99.5%; H_2O <0.001%) were dried and deoxygenized by passage through columns of Glass Contour Solvent Systems before use. 2,2'-Azobisisobutyronitrile (AIBN) (Wako, >98.0%) was purified by recrystallization from methanol. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako, >95.0%) was purified by washing with acetone at –15 °C and evaporated until dryness under reduced pressure.

Synthesis of 1,2-Isopropylidene Glycerol

1,2-Isopropylidene glycerol was synthesized by the reaction between glycerol and acetone. In a 2000 ml three-necked flask with 4 Å molecular sieves, glycerol (210.8 g, 2.29 mol) and acetone (960 ml) were added. *p*-Toluenesulfonic acid (10.0 g, 52.6 mmol) was dissolved in acetone (40 mL) and added to the flask with glycerol and acetone. The reaction mixture was stirred at 40 °C for 15 h. $NaHCO_3$ was added to the mixture in an ice bath to stop the reaction. After removing residue acetone via rotary evaporation, extraction was conducted with chloroform, and the organic layer was washed with water. The organic layer was concentrated by rotary evaporation to yield 1,2-isopropylidene glycerol as a viscous liquid (120.2 g, 40%). This product was used in the next step without purification. ^{1}H NMR ($CDCl_3$, r.t.): δ 4.27–3.57 (m, 5H, C*H*$_2$C*H*C*H*$_2$), 2.08–2.04 (br, 1H, O*H*), 1.44 (s, 3H, O–C(C*H*$_3$)$_2$–O), and 1.38 (s, 3H, O–C(C*H*$_3$)$_2$–O).

Synthesis of 2,2-dimethyl-4-tosyloxymethyl-1,3-dioxolane

2,2-Dimethyl-4-tosyloxymethyl-1,3-dioxolane was synthesized by the toslyation of the hydroxyl group remaining in 1,2-isopropylidene glycerol. *p*-Toluenesulfonyl chloride (78.7 g, 0.42 mol) and triethylamine (120 ml) were added to a 500 ml round-bottomed flask. 1,2-Isopropylidene glycerol (44.7 g, 0.34 mol) was added dropwise to the reaction mixture at 0 °C, and the mixture was stirred at

0 °C for 2 h. Chloroform was added, and extraction was conducted with chloroform. The organic layer was washed with aq. $NaHCO_3$ and water, then was concentrated by rotary evaporation to yield 2,2-dimethyl-4-tosyloxymethyl-1,3-dioxolane as a white solid (95.3 g, 98%). This product was used in the next step without purification. ^{1}H NMR ($CDCl_3$, r.t.): δ 7.79 (d, J = 8.2 Hz, 2H, Ar*H*), 7.36 (d, J = 8.2 Hz, 2H, Ar*H*), 4.30–3.07 (m, 5H, CH_2C*H*CH_2), 2.45 (s, 3H, ArCH_3), 1.34 (s, 3H, O–C(CH_3)$_2$–O), and 1.31 (s, 3H, O–C(CH_3)$_2$–O).

Synthesis of 2-butyl-4-tosyloxymethyl-1,3-dioxolane

The acetal exchange reaction was carried out to introduce a *n*-butyl group. *p*-Toluenesulfonic acid (8.3 g, 44.0 mmol) and 2,2-dimethyl-4-tosyloxymethyl-1,3-dioxolane (51.0 g, 0.18 mol) were dissolved in 130 ml and 30 ml of $CHCl_3$, respectively, and mixed. Valeraldehyde (22.7 ml, 0.22 mol) was added to the round-bottomed flask and the reaction mixture was stirred at 55 °C for 40 h. Aq. $NaHCO_3$ was added to the mixture to stop the reaction. The mixture was washed with aq. $NaHCO_3$ and water. The organic layer was concentrated by rotary evaporation to yield 2-butyl-4-tosyloxymethyl-1,3-dioxolane (53.1 g, 94%). This product was used in the next step without purification. ^{1}H NMR ($CDCl_3$, r.t.): δ 7.80 (d, J = 8.2 Hz, 2H, Ar*H*), 7.35 (d, J = 8.2 Hz, 2H, Ar*H*), 4.87–4.82 (m, 1H, O–C*H*(*n*-Bu)–O), 4.28–3.60 (m, 5H, CH_2C*H*CH_2), 2.46 (s, 3H, ArCH_3), 1.57–1.55 (m, 2H, CH_2(CH$_2$)$_2$CH$_3$), 1.36–1.29 (m, 4H, CH$_2$(CH_2)$_2$CH$_3$), and 0.92–0.86 (m, 3H, CH$_2$(CH$_2$)$_2$CH_3).

Synthesis of 2-butyl-4-methylene-1,3-dioxolane (BuMDO)

An elimination reaction was performed to synthesize 2-butyl-4-methylene-1,3-dioxolane. Potassium *tert*-butoxide (54.0 g, 0.48 mol) was dissolved in DMF (450 ml). At 0 °C, 2-butyl-4-tosyloxymethyl-1,3-dioxolane was added dropwise slowly to the reaction mixture and was stirred for 30 min. Diethyl ether was added to stop the reaction. The organic layer was washed with brine and was concentrated by rotary evaporation. The crude compound was distilled under reduced pressure to yield 2-butyl-4-methylene-1,3-dioxolane as a clear liquid (7.9 g, 32%). ^{1}H NMR ($CDCl_3$, r.t.): δ 5.22 (t, J = 4.8 Hz, 1H, O–C*H*(*n*-Bu)–O), 4.52 (dt, J = 12.3, 1.4 Hz, 1H, CCH_2O), 4.36 (dt, J = 12.2, 1.9 Hz, 1H, CCH_2O), 4.31 (q, J = 2.1 Hz, 1H, CH_2=C), 3.88 (q, J = 1.8 Hz, 1H, CH_2=C), 1.76–1.71 (m, 2H, CH_2(CH$_2$)$_2$CH$_3$), 1.47–1.32 (m, 4H, CH$_2$(CH_2)$_2$CH$_3$), and 0.92 (t, J = 7.1 Hz, 3H, CH$_2$(CH$_2$)$_2$CH_3). ^{13}C NMR ($CDCl_3$, r.t.): δ 156.6 (CH$_2$=*C*), 107.5 (O–*C*H(*n*-Bu)–O), 77.8 (*C*H$_2$=C), 67.5 (C*C*H$_2$O), 33.7 (*C*H$_2$(CH$_2$)$_2$CH$_3$), 25.9 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 22.8 (CH$_2$CH$_2$*C*H$_2$CH$_3$), and 14.1 (CH$_2$CH$_2$CH$_2$*C*H$_3$).

Synthesis of 2-cyclohexyl-4-tosyloxymethyl-1,3-dioxolane

The acetal exchange reaction was carried out to introduce a cyclohexyl group. *p*-Toluenesulfonic acid (23.4 g, 0.12 mol) and 2,2-dimethyl-4-tosyloxymethyl-1,3-dioxolane (150.1 g, 0.52 mol) were dissolved in 420 ml and 100 ml of $CHCl_3$, respectively, and mixed in a 1000 ml round-bottomed flask.

Cyclohexanecarboxaldehyde (65.0 ml, 0.54 mol) was added to the round-bottomed flask and the reaction mixture was stirred at 60 °C for 18 h. Aq. $NaHCO_3$ was added to the mixture to stop the reaction. The mixture was washed with aq. $NaHCO_3$ and water. The organic layer was concentrated by rotary evaporation to yield 2-cyclohexyl-4-tosyloxymethyl-1,3-dioxolane (172.0 g, 97%). This product was used in the next step without purification. ^{1}H NMR ($CDCl_3$, r.t.): δ 7.80 (d, J = 8.2 Hz, 2H, Ar*H*), 7.35 (d, J = 7.9 Hz, 2H, Ar*H*), 4.59 (dd, 1H, O–C*H*(Cy)–O), 4.24–3.59 (m, 5H, CH_2C*H*CH_2), 2.46 (s, 3H, ArCH_3), 1.69 (m, 5H, Cy), 1.47–1.42 (m, 1H, Cy), 1.25–1.10 (m, 3H, Cy), and 1.04–0.94 (m, 2H, Cy).

Synthesis of 2-cyclohexyl-4-methylene-1,3-dioxolane (CyMDO)

An elimination reaction was performed to synthesize 2-butyl-4-methylene-1,3-dioxolane. Potassium *tert*-butoxide (80.1 g, 0.71 mol) was dissolved in DMF (485 ml). At 0 °C, 2-cyclohexyl-4-tosyloxymethyl-1,3-dioxolane was added dropwise slowly to the reaction mixture and was stirred for 30 min. Diethyl ether was added to stop the reaction. The organic layer was washed with brine and was concentrated by rotary evaporation. The residue was distilled under reduced pressure to yield 2-cyclohexyl-4-methylene-1,3-dioxolane as a clear liquid (43.4 g, 53%). ^{1}H NMR ($CDCl_3$, r.t.): δ 4.96 (d, J = 5.0 Hz, 1H, O–C*H*(Cy)–O), 4.50 (dt, J = 12.2, 1.5 Hz, 1H, CCH_2O), 4.35 (dt, J = 12.2, 2.1 Hz, 1H, CCH_2O), 4.30 (q, J = 2.1 Hz, 1H, CH_2=C), 3.91–3.83 (m, 1H, CH_2=C), 1.83–1.75 (m, 4H, Cy), 1.71–1.58 (m, 2H, Cy), and 1.31–1.05 (m, 5H, Cy). ^{13}C NMR ($CDCl_3$, r.t.): δ 156.9 (CH_2=*C*), 110.5 (O–*C*H(Cy)–O), 77.8 (*C*H_2=C), 67.7 (C*C*H_2O), 42.1, 27.3, 27.2, 26.8, and 26.1 (Cy).

Synthesis of 2-phenyl-4-tosyloxymethyl-1,3-dioxolane

The acetal exchange reaction was carried out to introduce a phenyl group. *p*-Toluenesulfonic acid (20.9 g, 0.11 mol) and 2,2-dimethyl-4-tosyloxymethyl-1,3-dioxolane (127.9 g, 0.45 mol) were dissolved in 360 ml and 100 ml of $CHCl_3$, respectively, and mixed in a 1000 ml round-bottomed flask. Benzaldehyde (228.0 ml, 2.23 mol) was added to the round-bottomed flask and the reaction mixture was stirred at 55 °C for 19 h. Aq. $NaHCO_3$ was added to the mixture to stop the reaction. The mixture was washed with aq. $NaHCO_3$ and water. The organic layer was concentrated by rotary evaporation at 50 °C to yield 2-phenyl-4-tosyloxymethyl-1,3-dioxolane (125.5 g, 83%). This product was used in the next step without purification. ^{1}H NMR ($CDCl_3$, r.t.): δ 7.90–7.32 (m, 9H, Ph + Ar*H*), 5.79 (d, 1H, O–C*H*(Ph)–O), 4.47–3.95 (m, 5H, CH_2C*H*CH_2), and 2.45 (s, 3H, ArCH_3).

Synthesis of 4-methylene-2-phenyl-1,3-dioxolane (PhMDO)

An elimination reaction was performed to synthesize 4-methylene-2-phenyl-1,3-dioxolane. Potassium *tert*-butoxide (100.2 g, 0.90 mol) was dissolved in DMF (660 ml). At 0 °C, 2-phenyl-4-tosyloxymethyl-1,3-dioxolane was added dropwise slowly to the reaction mixture and was stirred for

30 min. Diethyl ether was added to stop the reaction. The organic layer was washed with aqueous NaCl and was concentrated by rotary evaporation. The residue was distilled under reduced pressure to yield 4-methylene-2-phenyl-1,3-dioxolane as a clear viscous liquid (23.6 g, 38%). ^{1}H NMR ($CDCl_3$, r.t.): δ 7.50 (m, 2H, Ph), 7.40 (m, 3H, Ph), 6.13 (s, 1H, O–C*H*(Ph)–O), 4.66 (dt, J = 12.3, 1.5 Hz, 1H, CCH_2O), 4.54 (dt, J = 12.3, 1.9 Hz, 1H, CCH_2O), 4.43 (q, J = 2.1 Hz, 1H, CH_2=C), and 3.99 (q, J = 2.0 Hz, 1H, CH_2=C). ^{13}C NMR ($CDCl_3$, r.t.): δ 156.1 (CH_2=*C*), 136.8, 129.8, 128.5 and 126.6 (Ph), 106.0 (O–*C*H(Ph)–O), 78.5 (*C*H_2=C), and 67.6 (C*C*H_2O).

RAFT Radical Copolymerization

RAFT copolymerization was carried out by syringe technique under dry nitrogen in sealed glass tubes. A typical example for polymerization of BuMDO and methyl acrylate (MA) with CPBD as RAFT agent in the presence of AIBN is given below: BuMDO (1.01 ml, 7.5 mmol), MA (0.68 ml, 7.5 mmol), CPBD (0.50 ml of 200 mM solution in toluene, 0.10 mmol), AIBN (0.50 ml of 50 mM solution in toluene, 0.025 mmol), 1,2,3,4-tetrahydronaphthalene (0.20 ml) as an internal standard, and toluene were placed in a 25 ml round-bottomed flask equipped with a three-way stopcock at room temperature. The total volume of the reaction mixture was 5.0 ml. Immediately after mixing, the solution was evenly charged in eight glass tubes, and the tubes were sealed by flame under a nitrogen atmosphere. The tubes were immersed in a thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to –78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2,3,4-tetrahydronaphthalene as an internal standard (e.g., 98 h, BuMDO/MA = 60/87%). The quenched reaction solutions were evaporated to dryness to give poly(MA-*co*-BuMDO) (M_n = 9 100, M_w/M_n = 1.29). The obtained polymer was purified by preparative size-exclusion chromatography (SEC) for the ^{1}H NMR analysis.

Free Radical Copolymerization of Cyclic Vinyl Ethers with Common Vinyl Monomers

The free radical copolymerization with common vinyl monomers was carried out in a Schlenk flask equipped with a three-way stopcock. A typical example for polymerization of PhMDO and MA in the presence of AIBN is given below: PhMDO (0.27 ml, 2.0 mmol), MA (0.18 ml, 2.0 mmol), AIBN (0.40 ml of 100 mM solution in toluene, 0.040 mmol), 1,2,3,4-tetrahydronaphthalene (0.10 ml) as an internal standard, and toluene were placed in a Schlenk flask, and immersed in a thermostatic oil bath at 60 °C. The total volume of the reaction mixture was 2.0 ml. The polymerization was terminated by cooling the reaction mixture to –78 °C after 24 hours. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2,3,4-tetrahydronaphthalene as an internal standard (e.g., 24 h, PhMDO/MA = 61/97%). The quenched reaction solution was evaporated to dryness and purified by preparative size-exclusion chromatography (SEC) to give poly(MA-*co*-PhMDO) (M_n = 14 100, M_w/M_n = 2.00). The obtained polymer was purified by preparative size-

exclusion chromatography (SEC) for the ^{1}H NMR analysis.

Free Radical Copolymerization of TBDMSVE with MA

The free radical copolymerization of TBDMSVE with MA was carried out by syringe technique under dry nitrogen in sealed glass tubes. A typical example for polymerization of TBDMSVE and MA in the presence of AIBN is given below: TBDMSVE (0.99 ml, 5.0 mmol), MA (0.45 ml, 5.0 mmol), AIBN (0.016 g, 0.10 mmol), and toluene were placed in a 25 ml round-bottomed flask equipped with a three-way stopcock at room temperature. The total volume of the reaction mixture was 5.0 ml. Immediately after mixing, the solution was evenly charged in four glass tubes, and the tubes were sealed by flame under a nitrogen atmosphere. The tubes were immersed in a thermostatic oil bath at 60 °C for 24 hours, then terminated by cooling the reaction mixture to –78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with toluene as an internal standard (e.g., 24 h, TBDMSVE/MA = >99/45%). The quenched reaction solutions were evaporated to dryness to give poly(MA-*co*-TBDMSVE) (M_n = 21 500, M_w/M_n = 2.94). The obtained polymer was purified by the dialysis in acetone, then evaporated for the ^{1}H NMR analysis.

Synthesis of RAFT Block Copolymers

The RAFT block copolymerization was carried out in a Schlenk flask equipped with a three-way stopcock. A typical procedure of the RAFT copolymerization for the block copolymer is given below. The RAFT polymerization of MA was first carried out in a Schlenk flask containing MA (2.69 ml, 30.0 mmol), CMDTTC (0.80 ml of 200 mM solution in toluene, 0.20 mmol), V-70 (0.015 g), and 1,2,3,4-tetrahydronaphthalene (0.10 ml) as an internal standard in toluene (total volume: 8.0 ml) at 20 °C. When the conversion of MA reached 38% (M_n = 7700, M_w/M_n = 1.11), PhMDO (2.17 ml, 15.0 mmol) was added to the polymerization mixture via dry syringe. After 24 h, the polymerization was terminated by cooling the reaction mixture to –78 °C. The monomer conversions were determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2,3,4-tetrahydronaphthalene as an internal standard (53% for PhMDO and 83% for MA). The quenched reaction solution was evaporated to dryness. The obtained polymer was purified by precipitation into methanol at –78 °C to give PMA-*b*-P(MA-*co*-PhMDO) (M_n = 17 300, M_w/M_n = 1.18, based on poly(methyl methacrylate) standard).

Deprotection of Acetal Groups

The acetal-containing copolymers were converted into polymers with diol units by the acetal deprotection under acidic conditions. A typical example is given below: the obtained PMA-*b*-P(MA-*co*-PhMDO) (0.89 g, M_n = 17 300, M_w/M_n = 1.18) was dissolved in THF (9.50 ml) and H_2O (0.40 mL), followed by the addition of 35–37.0% aq. HCl (1.91 ml of 1 M in water, 1.91 mmol) at 50 °C. After

stirring for 55 h, aq. conc. $NaHCO_3$ was added into the mixture until the solution turned basic. The solution was dialyzed in water, then freeze-dried to afford a polymer with diol units.

Deprotection of Silyl Group

The copolymer P(MA-*co*-TBDMSVE) were converted into polymers with hydroxyl groups by the silyl deprotection under acidic conditions. A typical example is given below: the obtained P(MA-*co*-TBDMSVE) (0.20 g, M_n = 21 500, M_w/M_n = 2.94) was dissolved in THF (2.8 ml) and H_2O (0.15 mL), followed by the addition of 35–37.0% aq. HCl (0.55 ml of 1 M solution in water, 0.55 mmol) at 40 °C. After stirring for 91 h, aq. conc. $NaHCO_3$ was added into the mixture until the solution turned basic. The solution was dialyzed in methanol, then evaporated to afford a polymer with hydroxyl groups.

Measurements

^{1}H NMR spectra were recorded on a JEOL ECZ-400S spectrometer, operating at 400 MHz, or a Bruker AVANCE III HD, operating at 500 MHz. ^{13}C NMR spectra were recorded on a JEOL ECZ-400S spectrometer, operating at 100 MHz. The number-average molecular weight and molecular weight distribution of the product polymers were determined by SEC in THF at 40 °C on two polystyrene gel columns [Tosoh Multipore H_{XL}-M (7.8 mm i.d. × 30 cm) × 2; flow rate 1.0 ml min^{-1}] or in DMF containing 100 mM LiCl at 40 °C on two hydrophilic polymer gel columns [Tosoh α-M + α-3000 (7.8 mm i.d. × 30 cm); flow rate 1.0 ml min^{-1}] connected to a JASCO PU-2085 or PU-2080 precision pump (for THF SEC or DMF SEC, respectively) and a JASCO RI-2031 detector. The columns were calibrated against standard polymethyl methacrylate (Agilent Technologies; M_p = 540–2 210 000, M_w/M_n = 1.02–1.14). Glass transition temperature of the polymers was recorded by DSC 250 differential scanning calorimeter (TA Instruments Inc.). Samples were first heated to >150 °C at 10 °C min^{-1}, equilibrated at this temperature for 5 min, and cooled to −100 °C at 10 °C min^{-1}. After being held at this temperature for 5 min, the samples were then reheated to >150 °C at 10 °C min^{-1}. All T_g values were obtained from the second scan after removing the thermal history. Thermogravimetric analysis (TGA) was performed on a TGA 55 system (TA Instruments Inc.). The samples were equilibrated at 100 °C for 10 min and heated to 500 °C at 20 °C min^{-1} under N_2 gas flow.

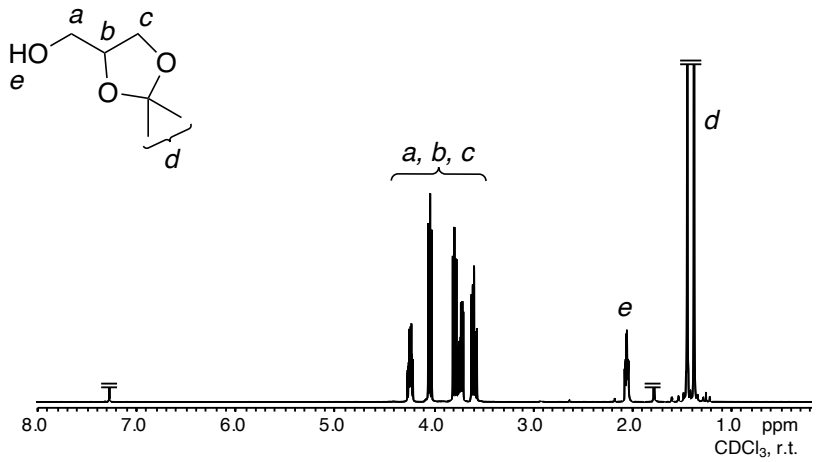

Figure S1. [1]H NMR spectrum of 1,2-isopropylidene glycerol.

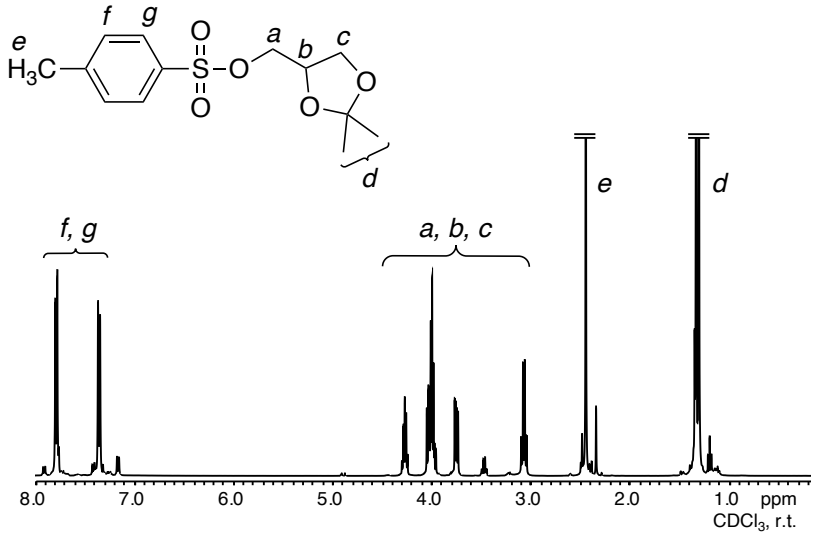

Figure S2. [1]H NMR spectrum of 2,2-dimethyl-4-tosyloxymethyl-1,3-dioxolane.

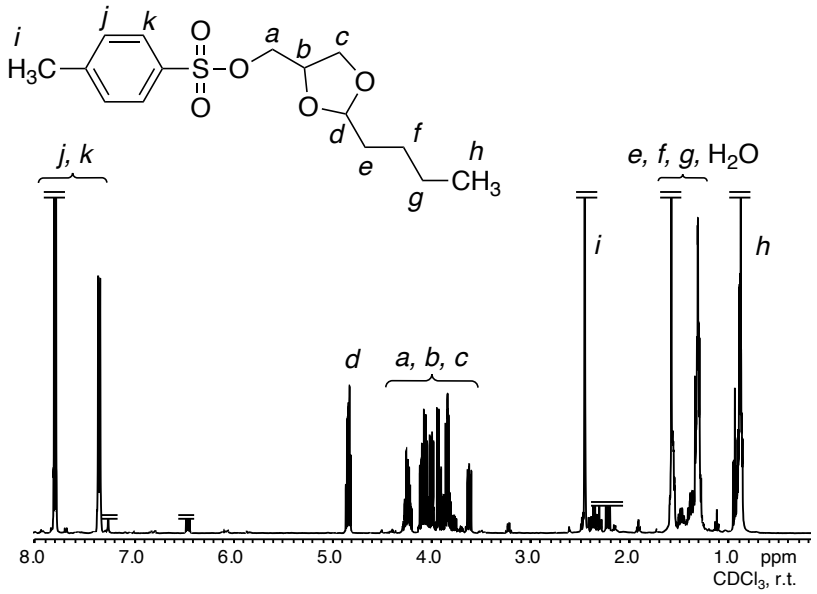

Figure S3. [1]H NMR spectrum of 2-butyl-4-tosyloxymethyl-1,3-dioxolane.

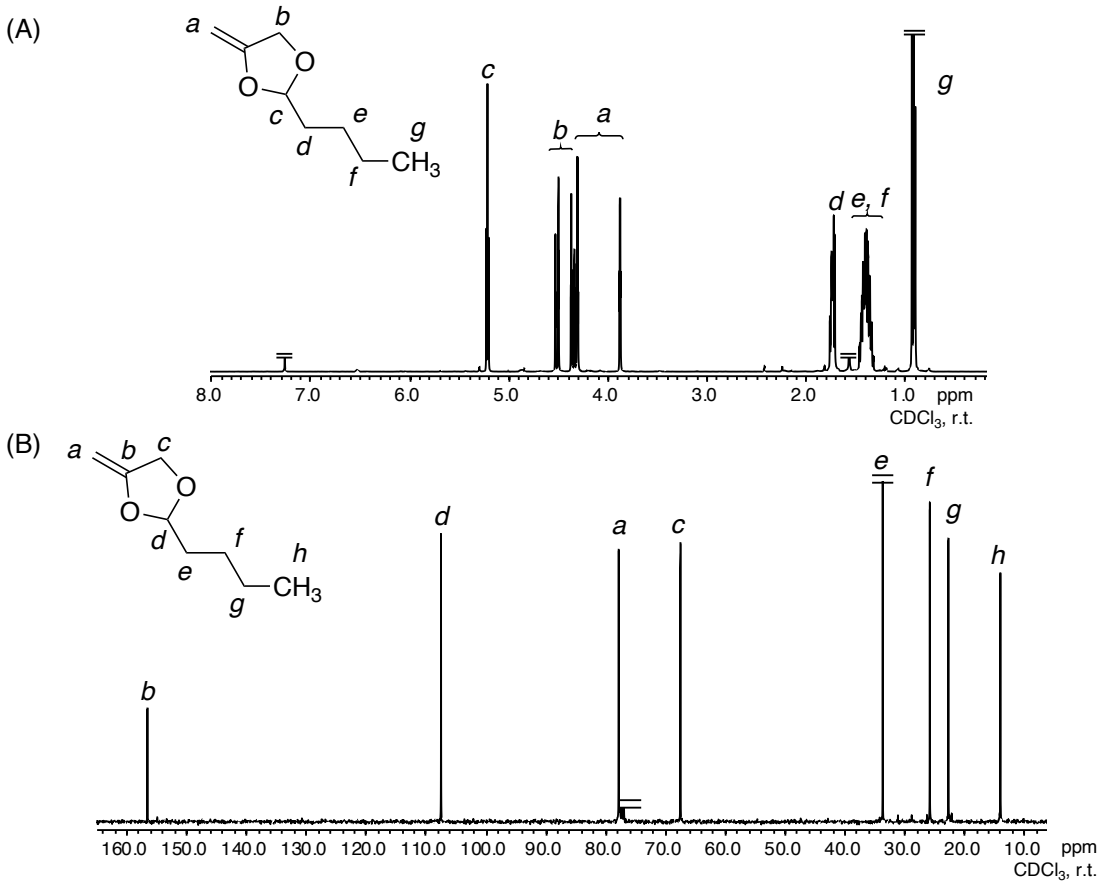

Figure S4. [1]H NMR (A) and [13]C NMR (B) spectra of 2-butyl-4-methylene-1,3-dioxolane (BuMDO).

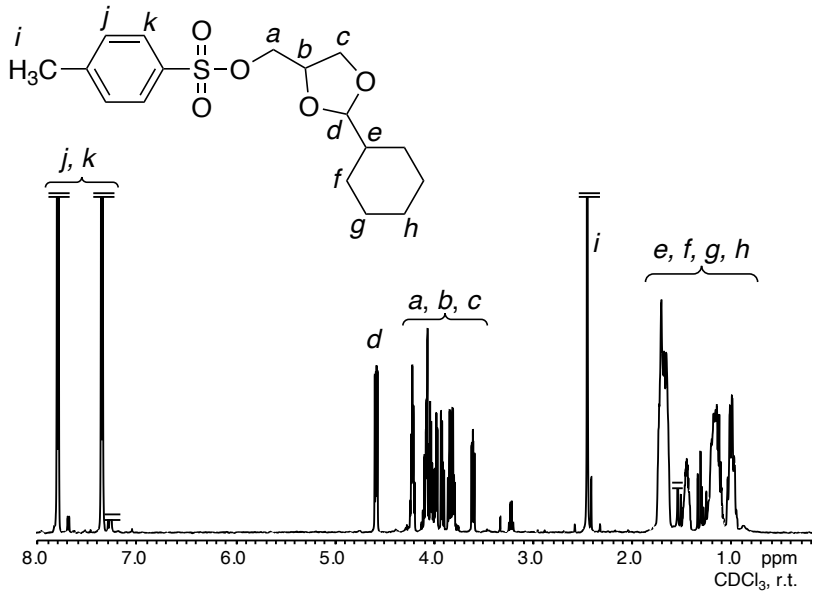

Figure S5. [1]H NMR spectrum of 2-cyclohexyl-4-tosyloxymethyl-1,3-dioxolane.

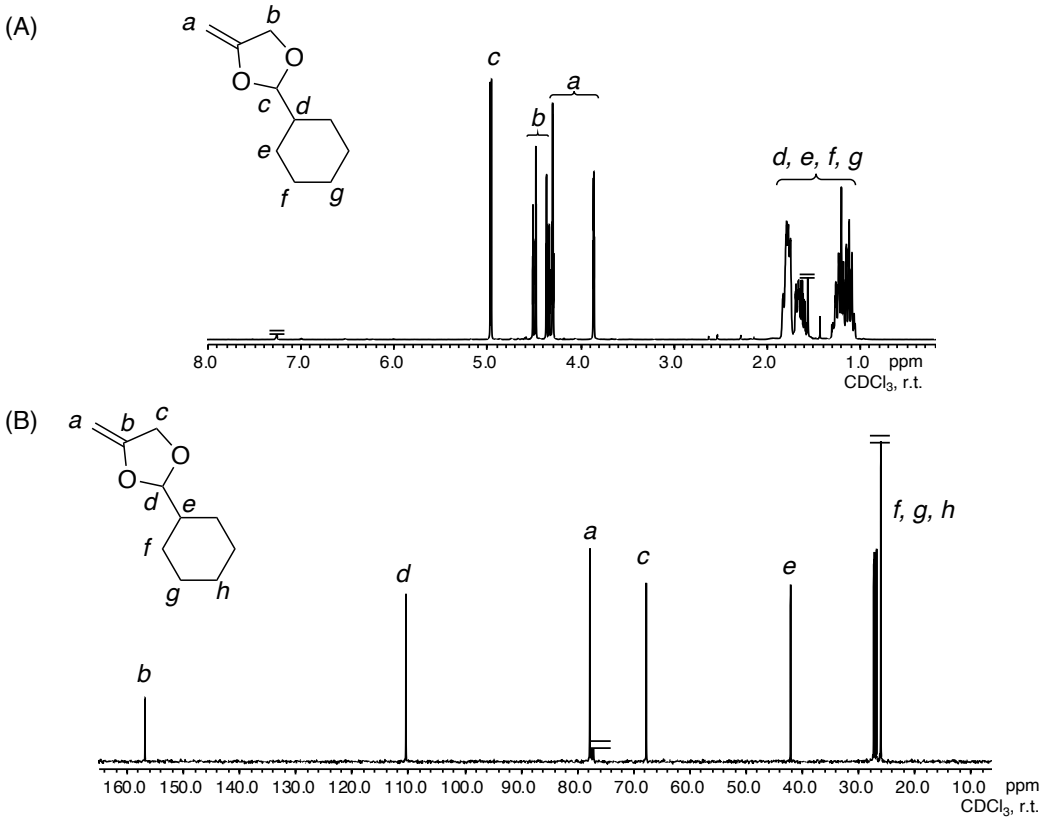

Figure S6. [1]H NMR (A) and [13]C NMR (B) spectra of 2-cyclohexyl-4-methylene-1,3-dioxolane (CyMDO).

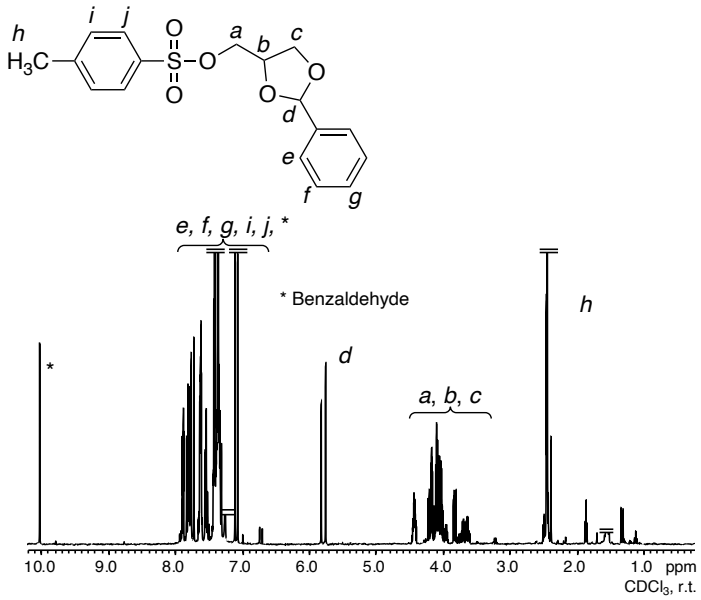

Figure S7. ^{1}H NMR spectrum of 2-phenyl-4-tosyloxymethyl-1,3-dioxolane.

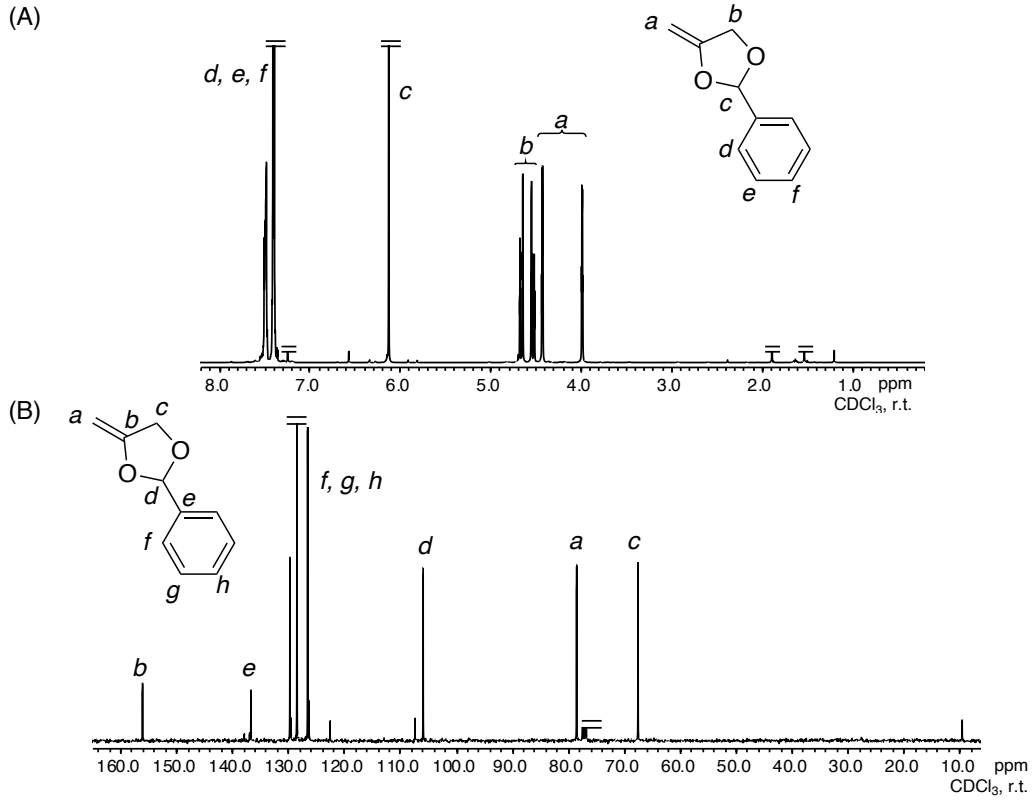

Figure S8. ^{1}H NMR (A) and ^{13}C NMR (B) spectra of 4-methylene-2-phenyl-1,3-dioxolane (PhMDO).

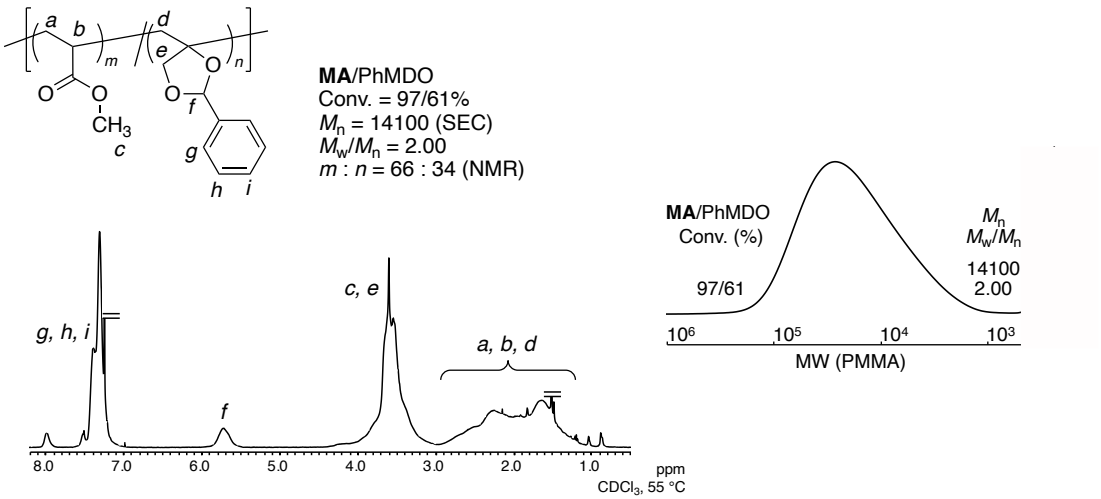

Figure S9. [1]H NMR spectrum and SEC curve of random copolymer obtained from the radical copolymerization of PhMDO and MA.

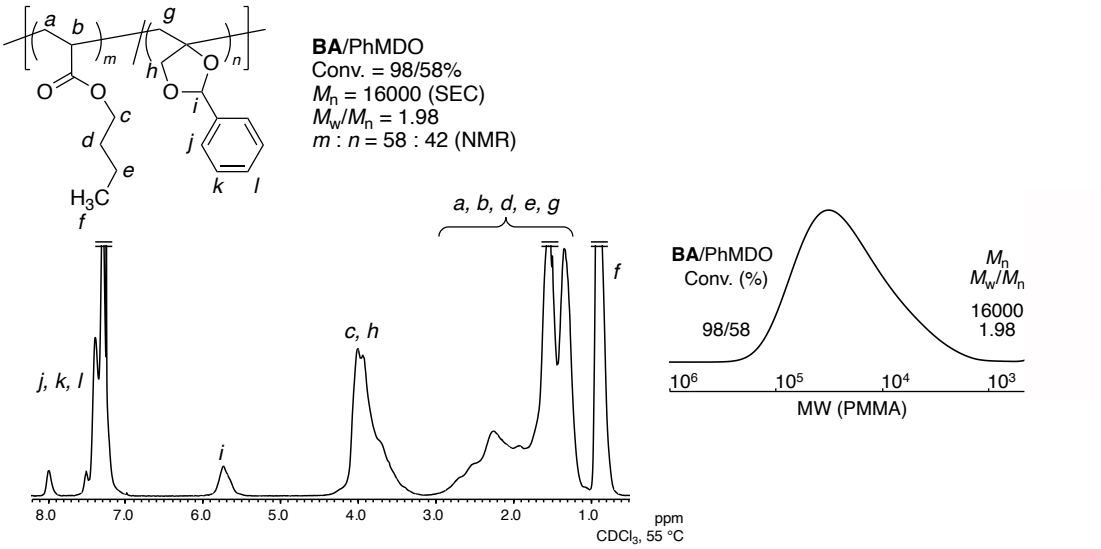

Figure S10. [1]H NMR spectrum and SEC curve of random copolymer obtained from the radical copolymerization of PhMDO and BA.

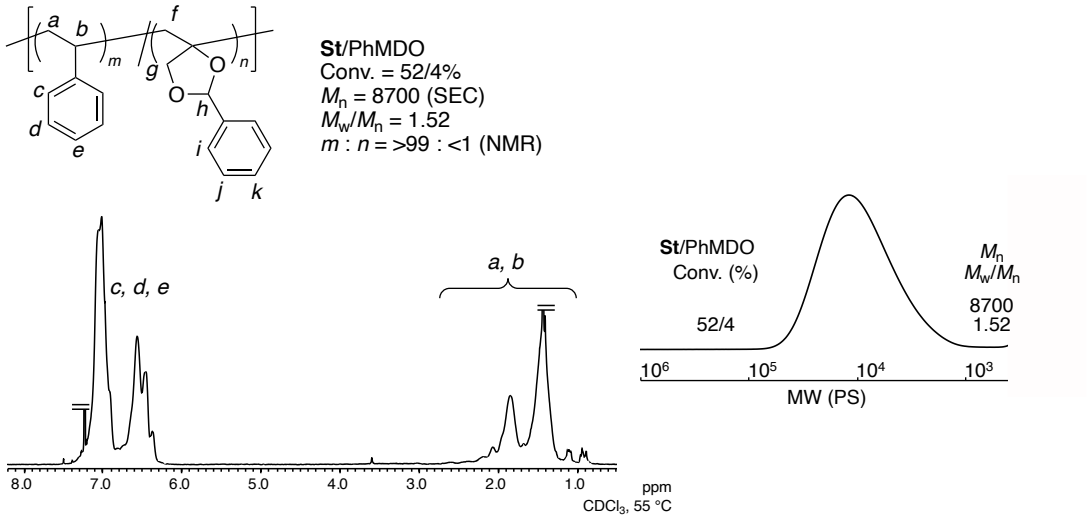

Figure S11. ^{1}H NMR spectrum and SEC curve of random copolymer obtained from the radical copolymerization of PhMDO and St.

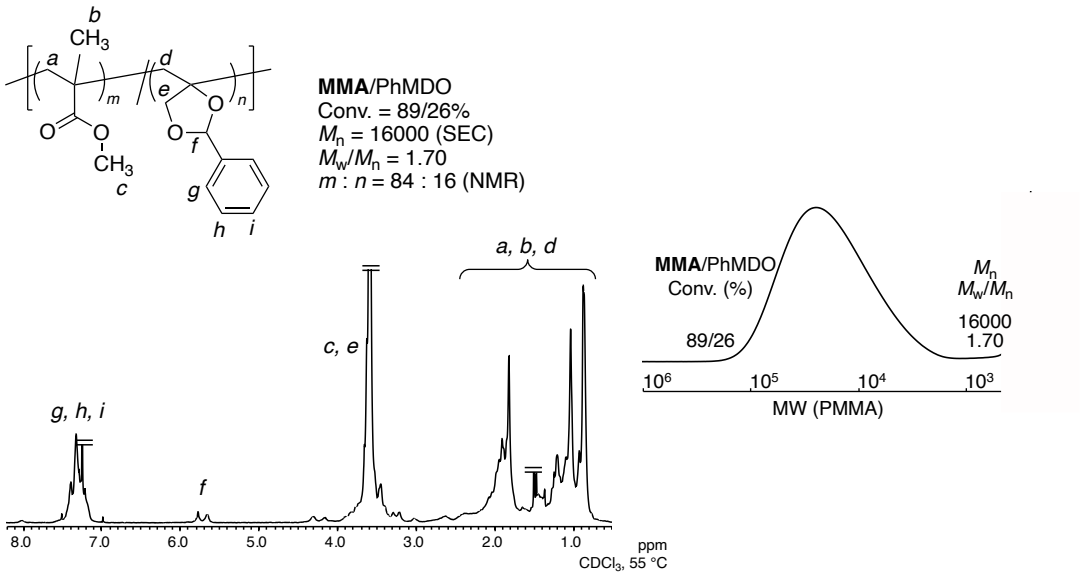

Figure S12. ^{1}H NMR spectrum and SEC curve of random copolymer obtained from the radical copolymerization of PhMDO and MMA.

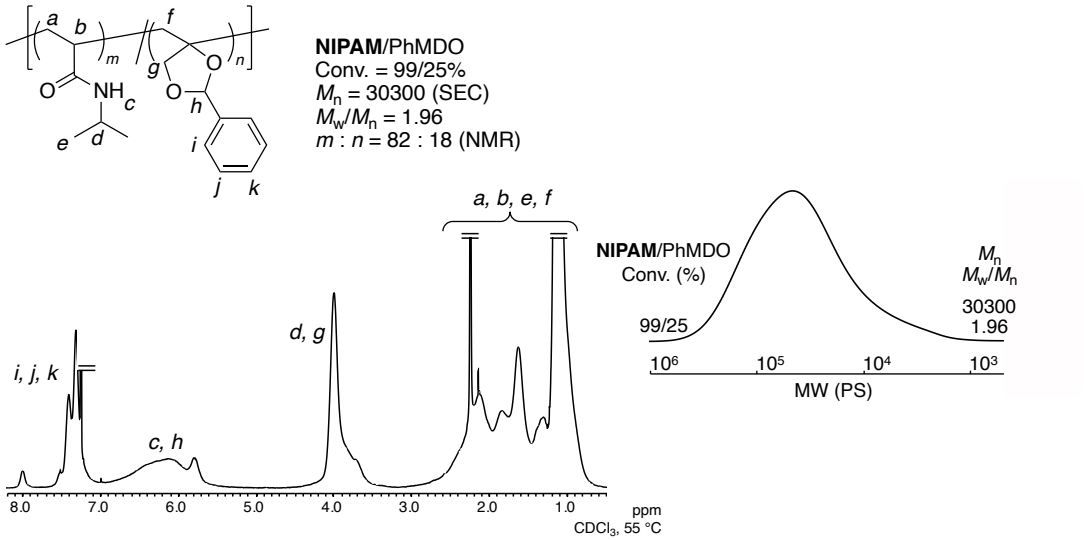

Figure S13. ^{1}H NMR spectrum and SEC curve of random copolymer obtained from the radical copolymerization of PhMDO and NIPAM.

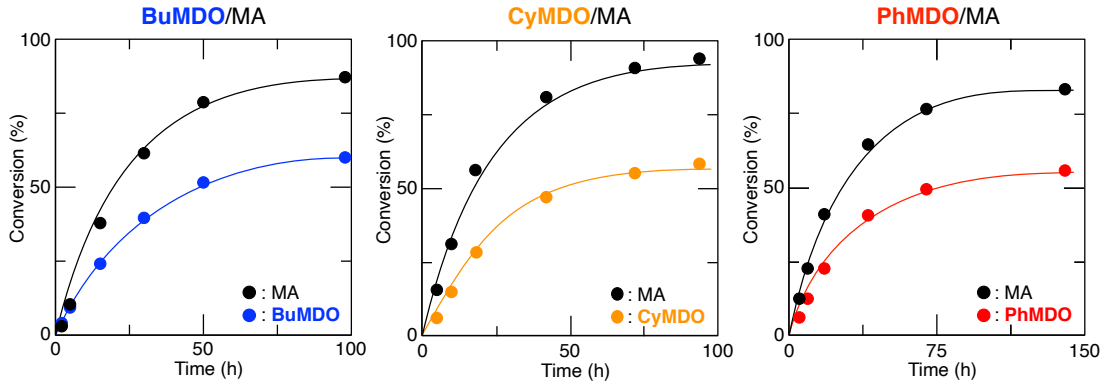

Figure S14. Time-conversion for the RAFT copolymerization of glycerol-derived cyclic vinyl ethers and MA: $[VE]_0/[MA]_0/[CPBD]_0/[AIBN]_0$ = 1500/1500/20/5.0 mM in toluene at 60 °C.

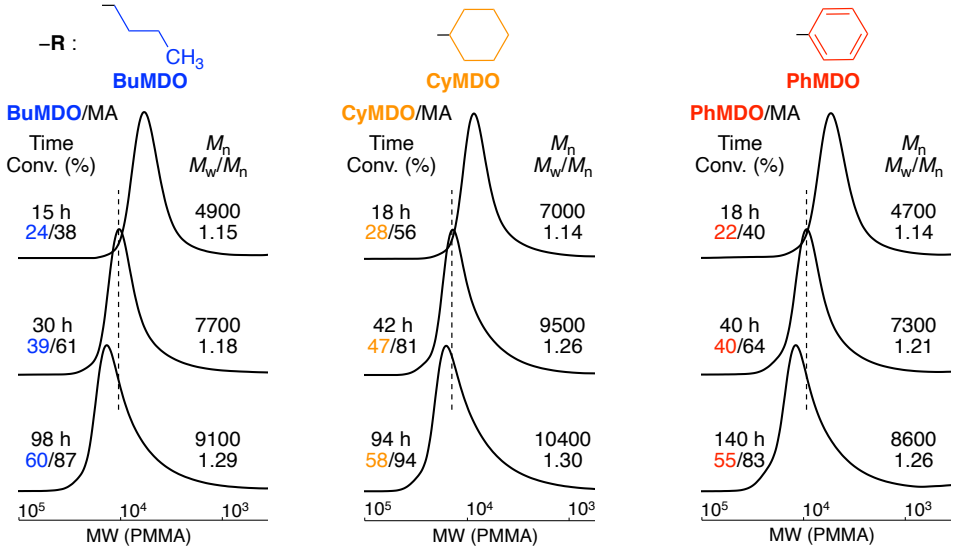

Figure S15. SEC curves for the RAFT copolymerization of glycerol-derived cyclic vinyl ethers and MA: $[VE]_0/[MA]_0/[CPBD]_0/[AIBN]_0$ = 1500/1500/20/5.0 mM in toluene at 60 °C.

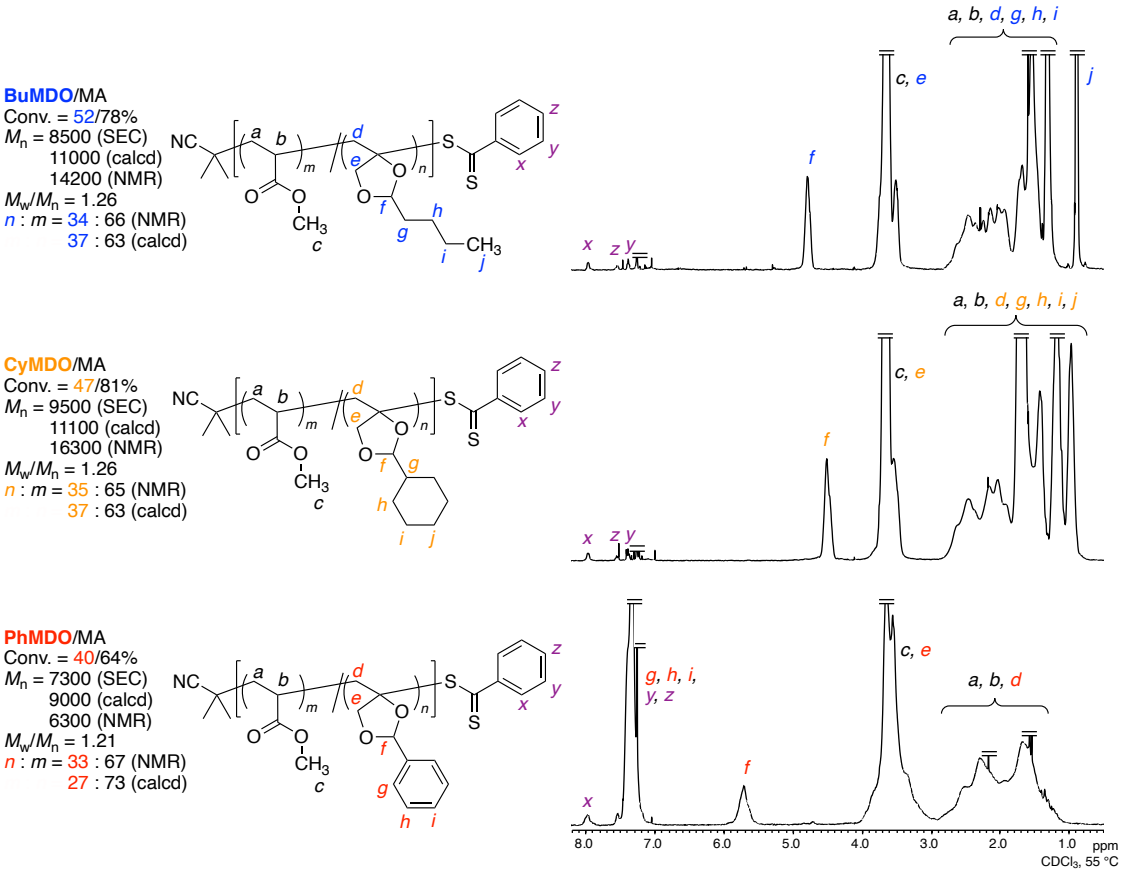

Figure S16. ^{1}H NMR spectra of random copolymers obtained from the RAFT copolymerization of vinyl ethers and MA: $[VE]_0/[MA]_0/[CPBD]_0/[AIBN]_0$ = 1500/1500/20/5.0 mM in toluene at 60 °C.

Table S1. RAFT copolymerization of glycerol-derived cyclic-vinyl ethers and MA[a].

Entry	M_1	$[M_1]_0/[MA]_0$	Time (h)	Conv. (%)[b] M_1/MA	M_n (SEC)[c]	M_w/M_n[c]	M_n (calcd)	M_n (NMR)	M_1/MA (mol%)[d]
1	BuMDO	1000/2000	30	52/68	9200	1.26	9600	12500	25/75
2	BuMDO	1500/1500	50	52/78	8500	1.26	11000	14200	34/66
3	BuMDO	2000/1000	50	38/84	6600	1.31	9100	12800	40/60
4	CyMDO	1000/2000	40	51/69	9900	1.21	10200	14400	27/73
5	CyMDO	1500/1500	42	47/81	9500	1.26	11100	16300	37/63
6	CyMDO	2000/1000	40	43/87	7500	1.25	11000	16200	50/50
7	PhMDO	1000/2000	70	53/76	10900	1.24	11800	8100	27/73
8	PhMDO	1500/1500	69	46/79	8500	1.26	10900	5800	35/65
9[e]	PhMDO	1500/3000	39	68/85	18800	1.17	19500	19900	32/68

[a]The polymerization conditions: $[CPBD]_0/[AIBN]_0$ = 20/5 mM in toluene at 60 °C. [b]Determined by ^{1}H NMR of the reaction mixture. [c]Determined by SEC. [d]Determined by ^{1}H NMR of the obtained polymer. [e]Polymerization condition: $[CMDTTC]_0/[V\text{-}70]_0$ = 20/5 mM in toluene at 20 °C.

Table S2. Monomer reactivity ratios of cyclic vinyl ethers and MA.

Entry	M_1	M_2	Finemann-Ross[a]		Kelen-Tüdõs[a]		Meyer-Lowry[b,c]	
			r_1	r_2	r_1	r_2	r_1	r_2
1	BuMDO	MA	−0.01	1.04	−0.02	0.98	0.01	0.99
2	CyMDO	MA	–0.01	1.05	−0.02	1.00	0.02	1.10
3	PhMDO	MA	0.05	0.86	0.02	0.79	0.001	1.15

[a]Polymerization condition: $[M_1]_0 + [M_2]_0$ = 2.0 M, $[AIBN]_0$ = 20 mM in toluene at 60 °C for 10 minutes. [b]Polymerization condition: $[M_1]_0/[M_2]_0/[CPBD]_0/[AIBN]_0$ = 1000/2000/20/5 mM in toluene at 60 °C. [c]r_1 and r_2 were optimized to fit the data.

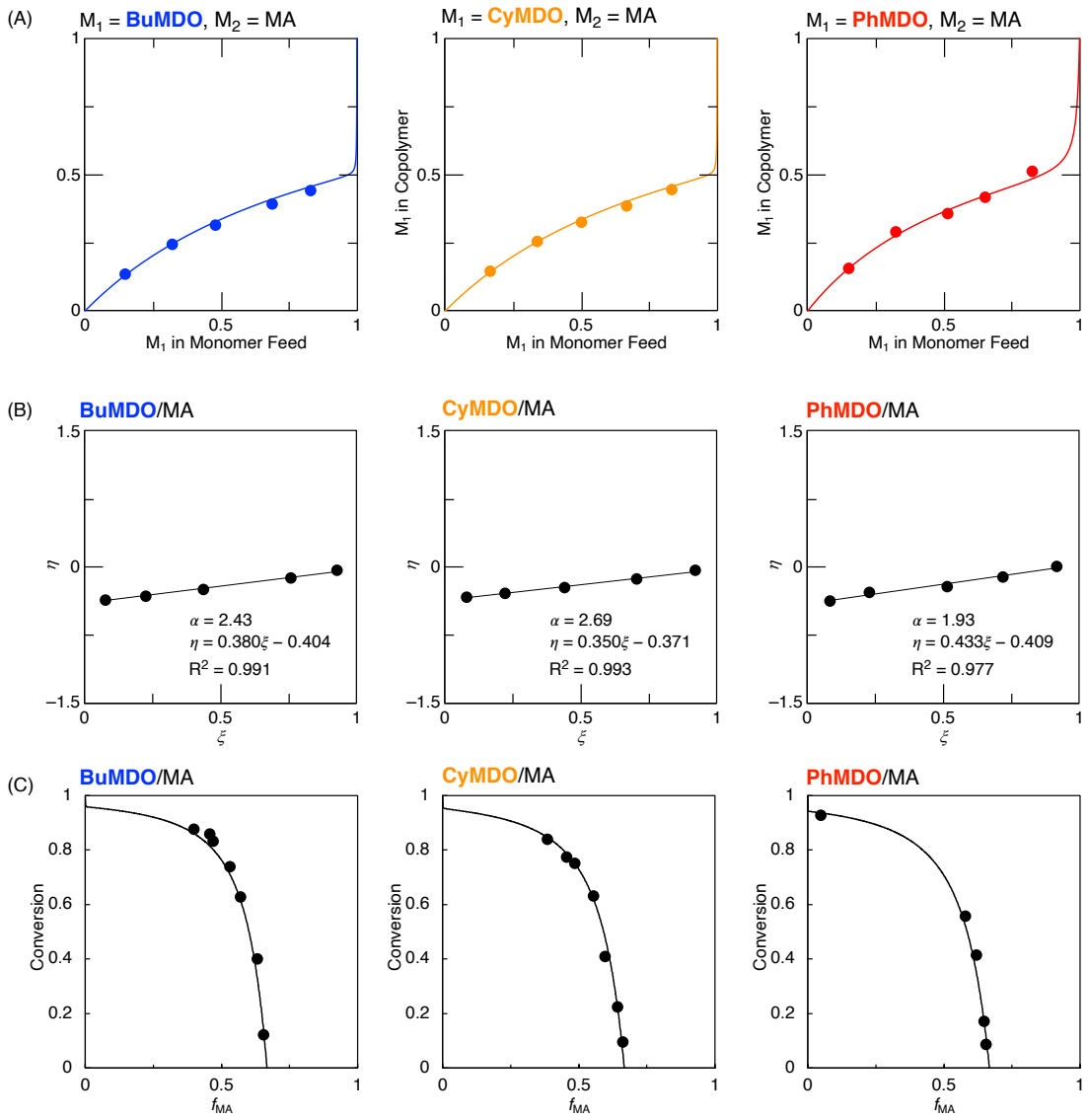

Figure S17. Copolymer composition curves for the radical copolymerization (A), Kelen–Tüdõs plots (B) and Meyer-Lowry plots[2] (C) for determining monomer reactivity ratio of cyclic vinyl ethers as M_1 and MA as M_2.

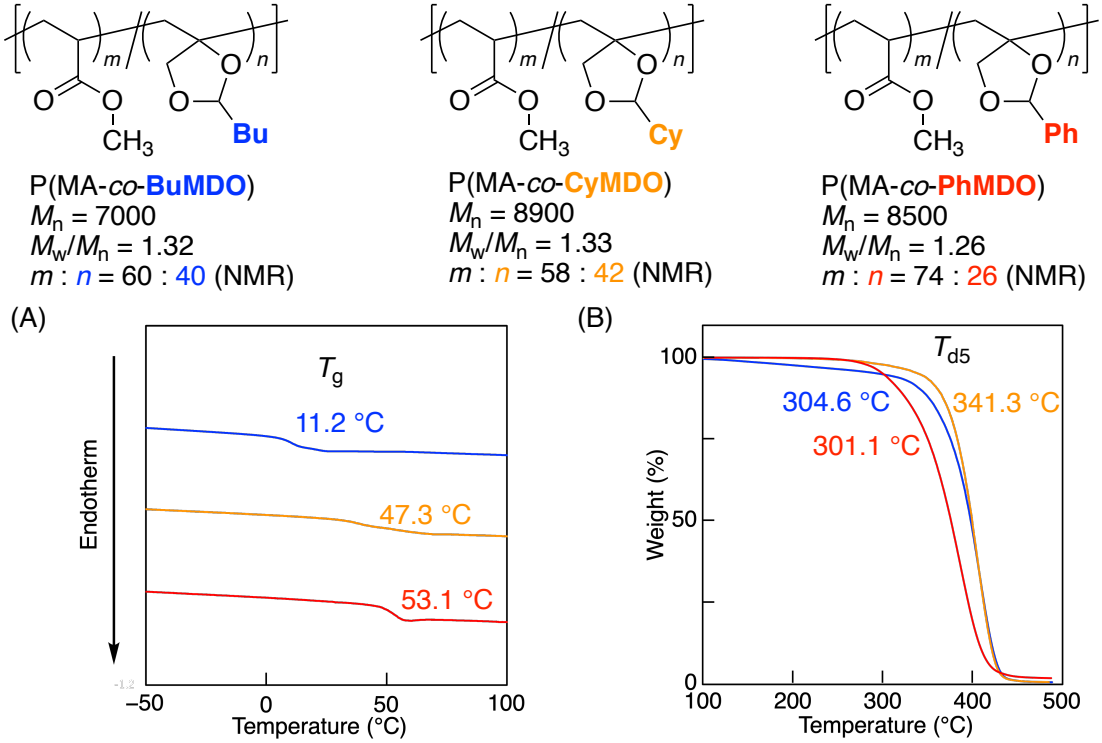

Figure S18. Differential scanning calorimetry (DSC) curves (A) and thermogravimetric analysis (TGA) curves (B) of the copolymers obtained in the RAFT copolymerization of cyclic vinyl ethers with MA.

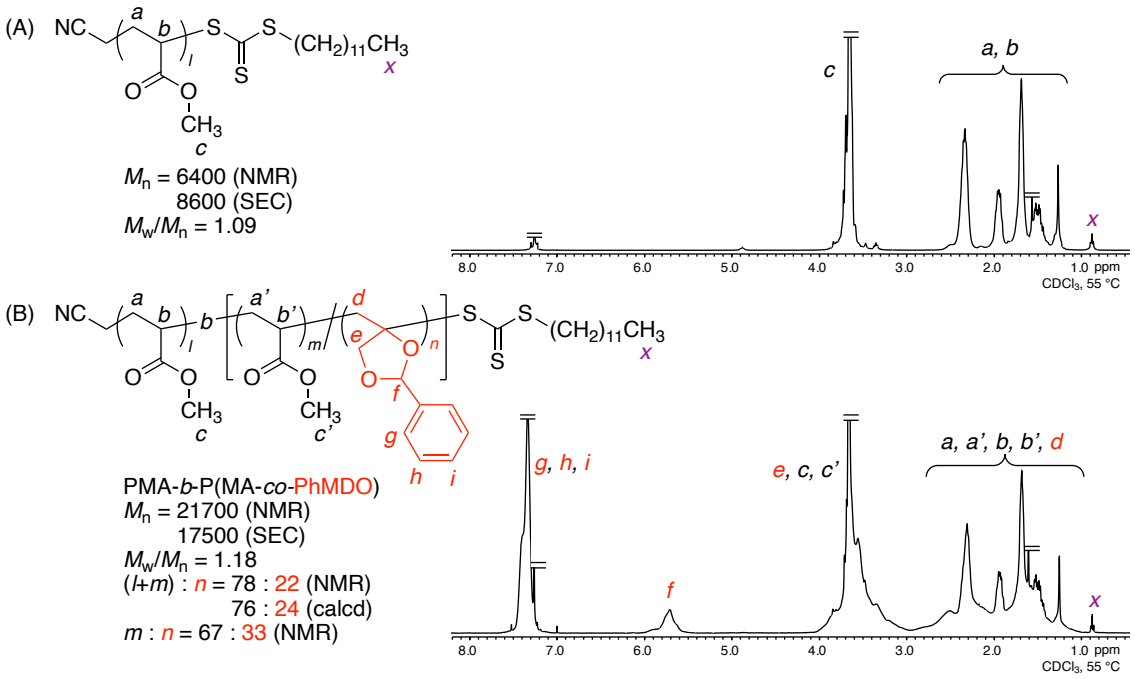

Figure S19. ^{1}H NMR spectra of PMA (A) and the continuing PMA-*b*-P(MA-*co*-PhMDO) (B) obtained from the RAFT block copolymerization of vinyl ethers and MA. $[MA]_0/[CMDTTC]_0/[V\text{-}70]_0$ = 3750/25/6.25 mM; $[PhMDO]_{add}$ = 1500 mM in toluene at 20 °C.

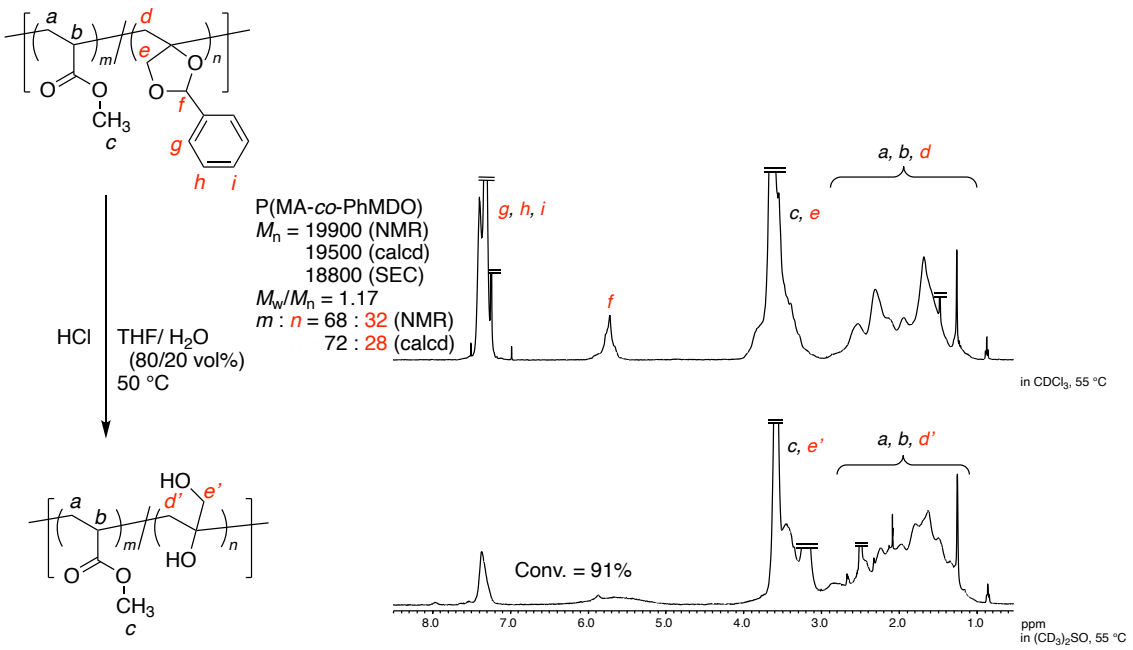

Figure S20. ^{1}H NMR spectra of random copolymer P(MA-*co*-PhMDO) before and after acetal deprotection.

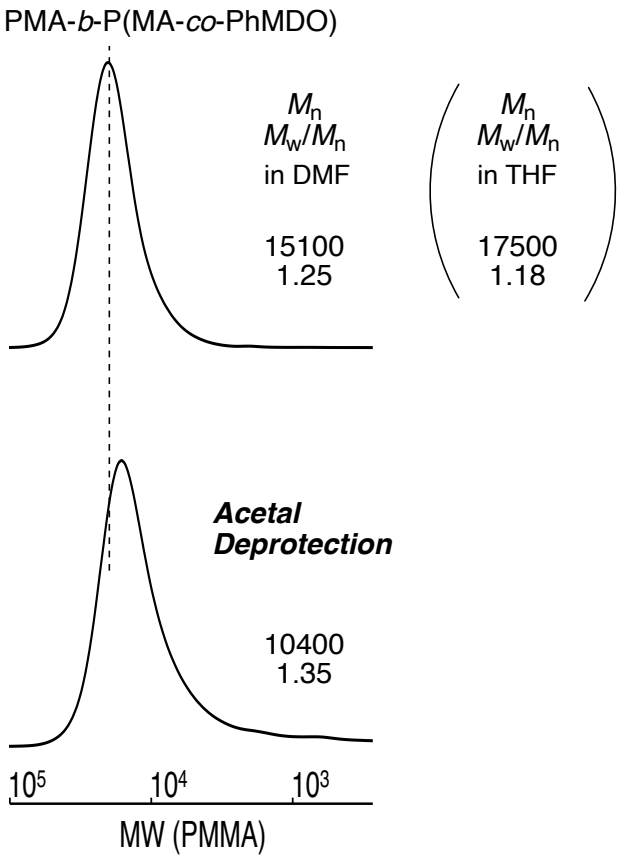

Figure S21. SEC curves (in DMF containing LiBr as the eluent) of block copolymer PMA-*b*-P(MA-*co*-PhMDO) (A) before and (B) after acetal deprotection.

Table S3. Solubility of polymers before (entry 1 and 5) and after deprotection (entries 2–4 and 6–7)[a].

Entry		*l*:*m*:*n*	M_n[b]	Solvents				
				H_2O	Methanol	THF	Acetone	Chloroform
1	PMA-*b*-P(MA-*co*-PhMDO)	34:44:22	17300	×	×	○	○	○
2	Deprotected PMA-*b*-P(MA-*co*-PhMDO)[c]	34:44:22	17300[d]	○	○	Δ[e]	×	×
3	Deprotected P(MA-*co*-PhMDO)[c]	0:68:32	19900[d]	○	—[f]	×	×	×
4	Deprotected P(MA-*co*-PhMDO)[c]	0:86:14	12000[d]	○	○	×	×	×
5	P(MA-*co*-TBDMSVE)	0:68:32	21500[d]	×	×	○	○	○
6	Deprotected P(MA-*co*-TBDMSVE)	0:68:32	21500[d]	Δ	○	Δ	×	×
7	Deprotected P(MA-*co*-TBDMSVE)	0:77:23	30100[d]	Δ	○	Δ	×	×

[a]Each test (○: soluble, Δ: partially soluble, ×: insoluble) was conducted in 1 wt% solution at 23 °C. [b]The number-average molecular weight (M_n) was determined by size-exclusion chromatography in THF (poly(methyl methacrylate) standard). [c]Conversions of the deprotection were 84% (for entry 2), 91% (for entry 3), 79% (for entry 4), 98% (for entry 6), and 97% (for entry 7), respectively. [d]M_n of the original copolymer before acetal deprotection. [e]Partially soluble at 60 °C. [f]Not tested.

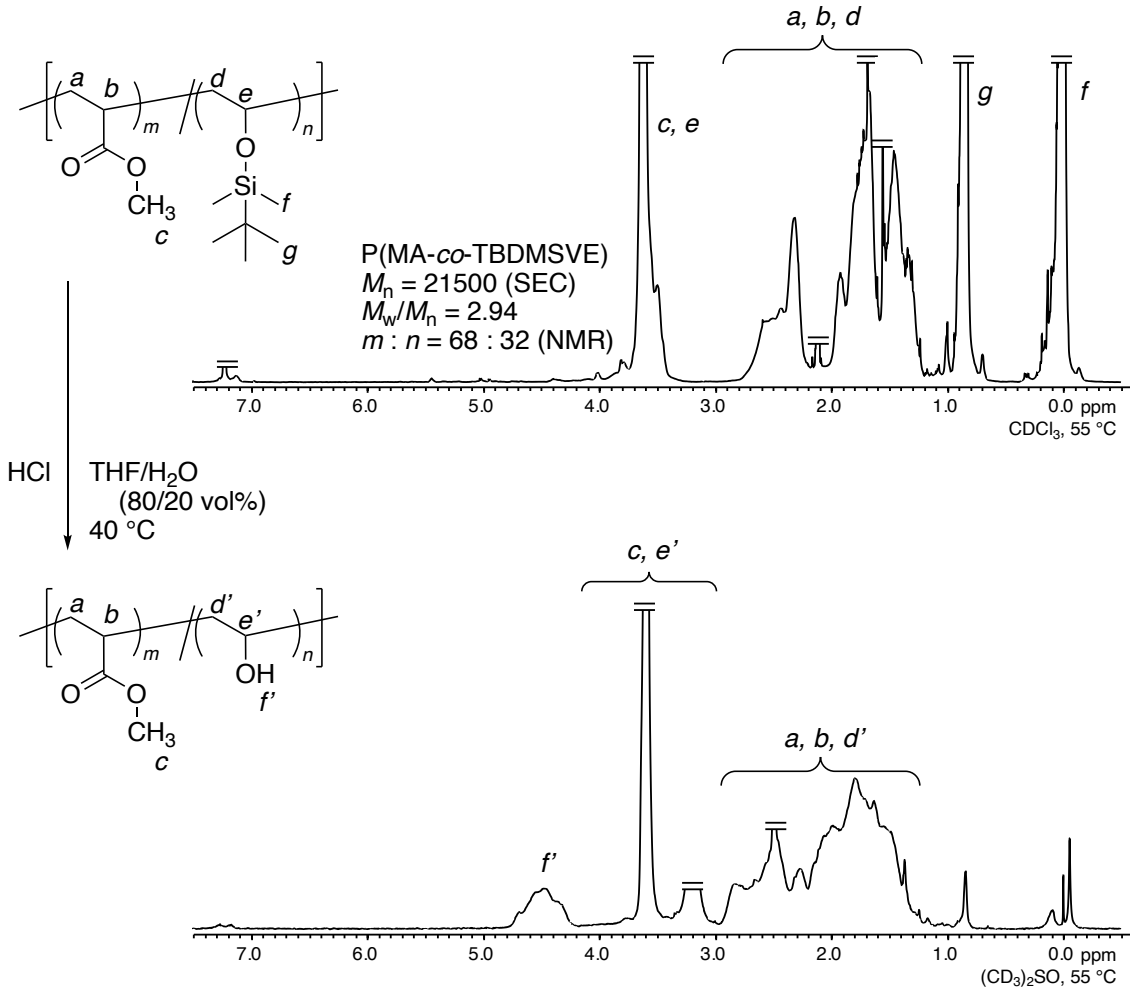

Figure S22. ^{1}H NMR spectra of random copolymer P(MA-*co*-TBDMSVE) before and after silyl deprotection (98% deprotection).

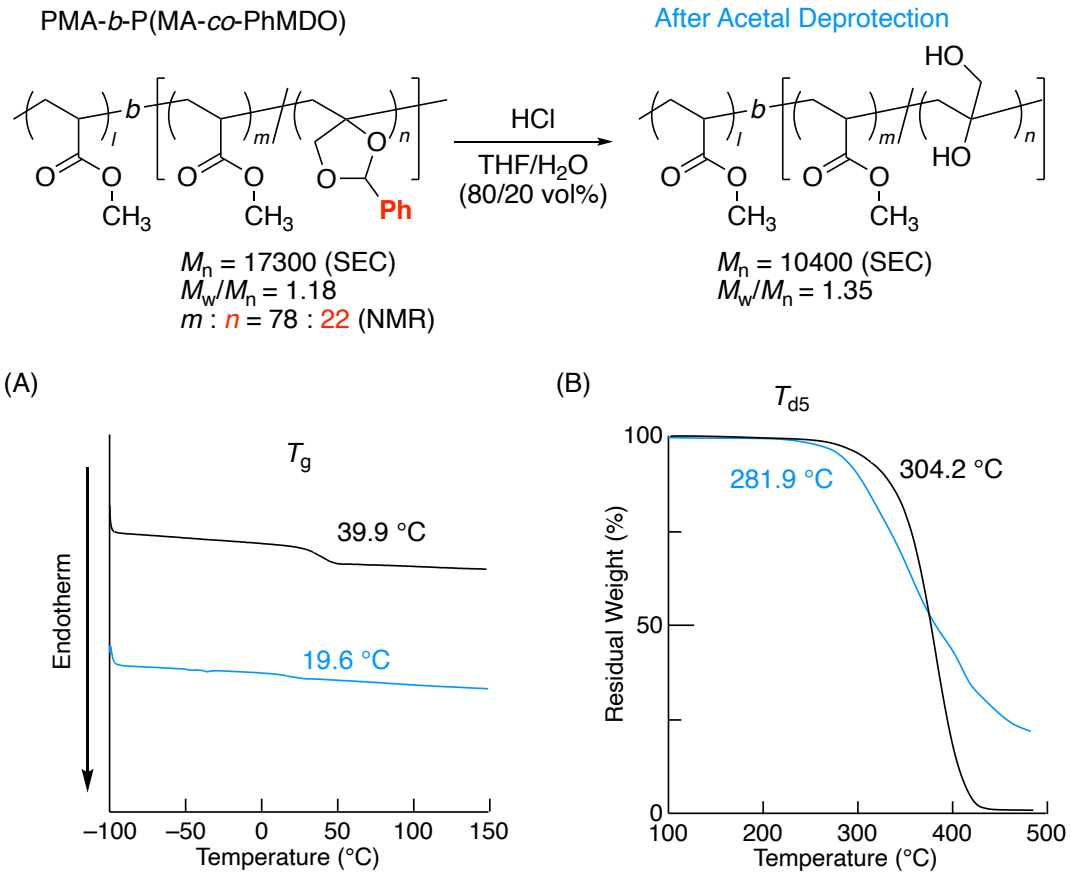

Figure S23. DSC curves (A) and TGA curves (B) of PMA-*b*-P(MA-*co*-PhMDO) (black lines) and the copolymer obtained after acetal deprotection (blue lines).

References

1 M. E. Jung, R. B. Blum, *Tetrahedron Lett.* 1977, **18**, 3791.

2 N. A. Lynd, R. C. Ferrier Jr. and B. S. Beckingham, *Macromolecules* 2019, **52**, 2277–2285.