Electronic Supplementary Material (ESI) for Polymer Chemistry

Protecting-group-free synthesis of chain-end multifunctional polymers by combining ATRP with thiol-epoxy 'click' chemistry

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General Methods and Materials

All the chemicals and solvents were purchased from commercial sources and used as such without further purification except methyl methacrylate; it was passed through a small plug of basic alumina before use. Column chromatography was performed on silica gel (60 A°, 230-400 mesh). Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on AV500 (^{1}H: 500 MHz; ^{13}C: 125 MHz) spectrometer, using $CDCl_3$ as solvent with TMS as an internal standard. Mass spectra were recorded on Bruker Daltonics maXis instrument. Analytical GPC measurements were performed using a Viscotek GPC-system equipped with a pump and a degasser (GPC_{max} VE2001, flow rate 1.0 mL/min), a detector module (Viscotek 302 TDA) and three columns (2×PLGel Mix-C and 1×ViscoGEL GMHHRN 18055, 7.5 × 300 mm for each) using chloroform as an eluent. UV-visible spectra were recorded on JASCO V-670 UV-Vis-NIR spectrophotometer.

Synthesis of 1: To a stirring solution of glycidol (1.0 g, 13.50 mmol) in THF (15 mL) was added triethylamine (3.75 mL, 27.0 mmol) and stirring was continued for another 10 min, then 2-Bromo-2-methylpropionyl bromide (3.72 g, 16.2 mmol) in THF (15 mL) was added drop wise over a period of 15 minutes at 0 °C. The reaction mixture was then stirred for 2.5 hours at room temperature. After this time, the triethylamine salt was removed by filtration. The filtrate was concentrated under reduced pressure and the crude material obtained was dissolved in DCM (30 mL) and washed with water (20 mL), and saturated solution of $NaHCO_3$ (20 mL). The organic layer was dried over Na_2SO_4, and concentrated. The crude product was then purified by silica gel column chromatography using heptane:EtOAc solvent gradient (98:2 to 93:7) to afford 1.7 g of the product as a colourless liquid. (Yield = 56%). ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 4.49 (dd, J = 3.05, 12.3 Hz, 1H), 4.07 (dd, J = 5.96, 12.3 Hz, 1H), 3.26 (m, 1H), 2.86 (t, J = 4.61 Hz, 1H), 2.71 (dd, J = 2.63, 4.86 Hz, 1H), 1.95 (s, 6H); ^{13}C-NMR (δ, ppm, 125 MHz, $CDCl_3$): 171.61, 66.16, 55.48, 49.21, 44.62, 30.86; ESI-MS m/z = 245.86 $[M+Na]^+$ (calcd. 245.10 for $C_7H_{11}BrO_3Na$); IR (cm^{-1}): 3008, 2976, 2933, 1736, 1465, 1388, 1371, 1343, 1272, 1155, 1103, 1012, 987, 902, 841, 765, 643, 543, 474, 445, 405.

Synthesis of di-epoxide-OH (2b): To a stirring solution of trimethylolpropane diallyl ether (4.0 g, 18.6 mmol) in $CHCl_3$ (40 mL) was added a solution of *m*-chloroperoxybenzoicacid 70% (10.3 g, 59.7 mmol) in $CHCl_3$ (100 mL) at 0 °C over a period of 1 hour. The resulting reaction mixture was stirred at room temperature for 18 hours, and then filtered, and the organic filtrate was washed with 1 M NaOH (2 x 50 mL), water (50 mL), and brine (50mL). The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure to give a colorless liquid. This crude product was purified by silica gel column chromatography using DCM:MeOH mixture (99:1) to afford 3.7 g of product as a colourless viscous liquid. (Yield = 82%). ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 3.74 (m, 2H), 3.58 – 3.38 (m, 8H), 3.13 (m, 2H), 2.79 (t, J = 4.39 Hz, 2H), 2.70 (br s, 1H), 2.60 (m, 2H), 1.37 (q, J = 7.62 Hz 2H), 0.85 (t, J = 7.48 Hz, 3H); ^{13}C-NMR (δ, ppm, 125 MHz, $CDCl_3$): 73.86, 73.80, 73.77, 73.70, 72.19, 72.16, 71.97, 71.93, 66.94, 50.94, 50.90, 44.24, 43.17, 23.12, 7.72; ESI-MS m/z = 269.13 $[M+Na]^+$ (calcd. 269.30 for $C_{12}H_{22}O_5Na$); IR (cm^{-1}): 3485, 2905, 1471, 1339, 1251, 1095, 1042, 907, 841, 757, 628, 512.

Synthesis of 2: To a stirring solution of di-epoxide-OH (1.7 g, 6.90 mmol) in THF (15 mL), was added triethylamine (2.2 mL, 15.8 mmol), and the stirring was continued for another 10 minutes, then 2-Bromo-2-methylpropionyl bromide (2.22 g, 9.66 mmol) in THF (10 mL) was added drop wise over a period of 15 minutes at 0 °C. The reaction mixture was then stirred for 8 hours at room temperature and then filtered to remove the triethylamine salt. The organic filtrate was reduced under low pressure, and the crude obtained was dissolved in DCM (30 mL), washed with water (20 mL), and saturated solution of $NaHCO_3$ (20 mL). The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography using DCM:MeOH mixture (99.5:0.5) to afford 1.58 g of **2** as a colourless viscous liquid. (Yield = 58%). ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 4.12 (s, 2H), 3.71 (dd, J = 2.89, 11.66 Hz, 2H), 3.40 (m, 6H), 3.12 (m, 2H), 2.77 (t, J = 4.62 Hz, 2H), 2.58 (dd, J = 2.79, 5.01 Hz, 2H), 1.93 (s, 6H), 1.49 (q, J = 7.70 Hz, 2H), 0.89 (t, J = 7.61 Hz, 3H); ^{13}C-NMR (δ, ppm, 125 MHz, $CDCl_3$): 171.52, 72.20, 72.18, 71.31, 66.27, 56.20, 51.00, 44.23, 43.02, 30.94, 22.96, 7.69; ESI-MS *m/z* = 417.08 $[M+Na]^+$ (calcd. 417.10 for $C_{16}H_{27}BrO_6Na$); IR (cm^{-1}): 2933, 1732, 1463, 1389, 1370, 1339, 1276, 1159, 1097, 1012, 985, 905, 842, 758, 643, 476.

Synthesis of tri-epoxide-OH (3b): To a stirring solution pentaerythritol triallyl ether (2.0 g, 7.80 mmol) in $CHCl_3$ (40 mL), was added a solution of *m*-chloroperoxybenzoicacid 70% (6.73 g, 39.01 mmol) in $CHCl_3$ (70 mL) at 0 °C over a period of 1 hour. The resulting reaction mixture was stirred at room temperature for 18 hours, then filtered, and the organic filtrate was washed with 1 M NaOH (2 x 50 mL), water (50 mL), and brine (50mL), and dried over Na_2SO_4, and concentrated under reduced pressure to give a colorless liquid. This crude product was purified by silica gel column chromatography using DCM:MeOH mixture (99:1) to afford 1.18 g of product as a colourless viscous liquid. (Yield = 50%). ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 3.72 (m, 5H), 3.54 (m, 6H), 3.39 (dd, J = 5.23, 11.33 Hz, 3H), 3.12 (m, 3H), 2.79 (t, J = 4.65 Hz, 3H), 2.71 (t, J = 6.35 Hz, 1H), 2.60 (dd, J = 2.71, 5.12 Hz, 3H); ^{13}C-NMR (δ, ppm, 125 MHz, $CDCl_3$): 72.17, 72.15, 72.12, 71.72, 71.66, 71.59, 65.35, 50.88, 45.46, 44.25; ESI-MS *m/z* = 327.14 $[M+Na]^+$ (calcd. 327.15 for $C_{14}H_{24}O_7Na$); IR (cm^{-1}): 3499, 2883, 1481, 1337, 1249, 1090, 1045, 903, 836, 757, 511.

Synthesis of 3: To a stirring solution of tri-epoxide-OH (1.0 g, 3.28 mmol) in THF (10 mL), was added triethylamine (1.04 mL, 7.55 mmol) and stirring was continued for another 10 min, then 2-Bromo-2-methylpropionyl bromide (1.05 g, 4.60 mmol) in THF (10 mL) was added

drop wise over a period of 15 minutes at 0 °C. The reaction mixture was then stirred for 8 hours at room temperature and then filtered to remove the triethylamine salt. The organic filtrate was reduced under low pressure and the crude obtained was dissolved in DCM (30 mL), washed with water (20 mL), and saturated solution of $NaHCO_3$ (20 mL). The organic layer was dried over Na_2SO_4, and concentrated. The crude product thus obtained was purified by silica gel column chromatography using DCM:MeOH mixture (99.5:0.5) to afford 0.707 g of **3** as a colourless viscous liquid. (Yield = 47%). ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 4.23 (s, 2H), 3.72 (dd, *J* = 2.90, 11.66 Hz, 3H), 3.54 (m, 6H), 3.37 (dd, *J* = 5.92, 11.72 Hz, 3H), 3.11 (m, 3H), 2.77 (t, *J* = 4.74 Hz, 3H), 2.58 (dd, *J* = 2.65, 5.06 Hz, 3H), 1.93 (s, 6H); ^{13}C-NMR (δ, ppm, 125 MHz, $CDCl_3$): 171.35, 72.30, 72.27, 72.24, 69.84, 64.96, 56.24, 50.91, 45.23, 44.25, 30.94; ESI-MS *m/z* = 470.13 $[M+NH_4]^+$ (calcd. 470.32 for $C_{18}H_{30}BrO_8N_3$); IR (cm^{-1}): 2930, 1732, 1479, 1463, 1387, 1371, 1341, 1273, 1162, 1094, 1011, 984, 904, 837, 758, 642, 474.

Epoxy functionalized polymer 4: Atom transfer radical polymerization (ATRP) initiator **1** (0.08 g, 0.358 mmol), methyl methacrylate (6.1 g, 60.97 mmol), PMDETA (0.08 g, 0.466 mmol), and anisole (7.0 mL) were taken in a schlenk tube and degassed by two freeze-pump-thaw cycles. Cu(I)Br (0.056 g, 0.394 mmol) was added and the resulting reaction mixture was degassed again by one freeze-pump-thaw cycle. The reaction mixture was then stirred under nitrogen atmosphere in a pre-heated oil bath at 35 °C for 80 minutes. After this time, the reaction vessel was opened to air, cooled to room temperature, and precipitated into 400 mL of methanol. The precipitated polymer was isolated by filtration and purified by passing through a small plug of silica gel using DCM (200 mL) as eluent. The collected fractions were concentrated and precipitated into 400 mL of methanol. The polymer precipitate was collected by filtration and dried to give 1.63 g of the product as a white powder. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 4.37 (d, *J* = 12.39 Hz, 1H), 3.84 – 3.35 (br s, backbone, -OCH_3), 3.20 (m, 1H), 2.84 (t, *J* = 4.52 Hz, 1H), 2.64 (m, 1H), 2.07 – 0.85 (br m, backbone); GPC ($CHCl_3$): M_n = 12100, M_w = 18900, PDI (M_w/ M_n) = 1.5; IR (cm^{-1}): 2994, 2943, 1722, 1453, 1382, 1241, 1142, 982, 836, 751.

Epoxy functionalized polymer 5: ATRP initiator **2** (0.08 g, 0.202 mmol), methyl methacrylate (6.07 g, 60.71 mmol), PMDETA (0.045 g, 0.263 mmol), and anisole (2.0 mL) were taken in a schlenk tube and degassed by two freeze-pump-thaw cycles. Cu(I)Br (0.031 g, 0.222 mmol) was added and the resulting reaction mixture was degassed again by freeze-

pump-thaw cycle. The reaction mixture was then stirred under nitrogen atmosphere in a pre-heated oil bath at 35 °C for 80 minutes. After this time the reaction vessel was opened to air, cooled to room temperature, and precipitated into 400 mL of methanol. The polymer precipitate was isolated by filtration and then purified by passing through a small plug of silica gel using DCM (200 mL) as eluent. The collected fractions were concentrated and precipitated into 400 mL of methanol. The polymer was collected by filtration and dried to give 1.5 g of the product as a white powder. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 4.0 (m, 2H), 3.84 – 3.36 (br m, backbone, -OCH_3), 3.12 (m, 2H), 2.78 (t, J = 4.64 Hz, 2H), 2.59 (m, 2H), 2.07 – 0.85 (br m, backbone); GPC ($CHCl_3$): M_n = 22100, M_w = 33700, PDI (M_w/ M_n) = 1.5; IR (cm^{-1}): 2990, 2952, 1727, 1453, 1387, 1246, 1147, 977, 836, 746.

Epoxy functionalized polymer 6: ATRP initiator **3** (0.08 g, 0.176 mmol), methyl methacrylate (6.0 g, 60.0 mmol), PMDETA (0.039 g, 0.229 mmol), and anisole (2.0 mL) were taken in a schlenk tube and degassed by two freeze-pump-thaw cycles. Cu(I)Br (0.027 g, 0.194 mmol) was added and the resulting reaction mixture was degassed again by one freeze-pump-thaw cycle. The reaction mixture was then stirred under nitrogen atmosphere in a pre-heated oil bath at 35 °C for 80 minutes. After this time the reaction vessel was opened to air, cooled to room temperature, and precipitated into 400 mL of methanol. The polymer precipitate was then isolated by filtration and purified by passing through a small plug of silica gel using DCM (200 mL) as eluent. The collected fractions were concentrated and precipitated into 400 mL of methanol. The resulting precipitate was filtered and dried to give 1.5 g of the product as a white powder. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 4.09 (m, 3H), 3.84 – 3.37 (br m, backbone, -OCH_3), 3.11 (m, 3H), 2.78 (t, J = 4.93 Hz, 3H), 2.59 (m, 3H), 2.07 – 0.85 (br m, backbone), GPC ($CHCl_3$): M_n = 17300, M_w = 25500, PDI (M_w/ M_n) = 1.4; IR (cm^{-1}): 2994, 2948, 1722, 1455, 1389, 1244, 1161, 977, 841, 751.

Thiol functionalized polymer 7: To a stirring solution of polymer **4** (0.6 g, 0.06 mmol) and 1-thionaphthol (0.038 g, 0.24 mmol) in THF (6.0 mL), was added LiOH (0.0015 g, 0.036 mmol) in 0.3 mL of water at 0 °C. The resulting reaction mixture was stirred for 16 hours at ambient temperature. THF was evaporated and the crude polymer was dissolved in DCM (20 mL) and washed with water (2 x 10 mL). The organic layer was dried, concentrated, and the solid obtained was dissolved in a minimum quantity of DCM and precipitated into MeOH (150 mL), then filtered and dried to give 0.550 g of the product. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 8.44 (d, J = 8.49 Hz, 1H), 7.88 (d, J = 7.80 Hz, 1H), 7.80 (d, J = 8.14 Hz, 1H), 7.69

(d, *J* = 7.21 Hz, 1H), 7.58 (m, 2H), 7.43 (t, *J* = 7.61 Hz, 1H), 4.15 (m, 2H), 3.94 (m, 1H), 3.84 – 3.35 (br s, backbone -OCH_3), 3.12 (m, 2H), 2.07 – 0.85 (br m, backbone); IR (cm^{-1}): 2994, 2943, 1722, 1453, 1382, 1241, 1142, 982, 836, 751.

Thiol functionalized polymer 8: To a stirring solution of polymer **5** (0.6 g, 0.04 mmol) and 1-thionaphtol (0.044 g, 0.28 mmol) in THF (6.0 mL), was added LiOH (0.0015 g, 0.036 mmol) in 0.3 mL of water. The resulting reaction mixture was stirred for 16 hours at ambient temperature. THF was evaporated and crude polymer was dissolved in DCM (20 mL), and washed with water (2 x 10 mL). Organic layer was dried, concentrated and polymer obtained was dissolved in minimum quantity of DCM and precipitated into MeOH (150 mL). Polymer was filtered, washed, and dried to give 0.53 g of polymer. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 8.40 (d, *J* = 7.91 Hz, 2H), 7.84 (d, *J* = 7.91 Hz, 2H), 7.74 (d, *J* = 8.47 Hz, 2H), 7.63 (d, *J* = 7.06 Hz, 2H), 7.53 (m, 4H), 7.39 (t, *J* = 7.91 Hz, 2H), 3.84 – 3.29 (br m, backbone -OCH_3), 3.10 (m, 4H), 2.07 – 0.64 (br m, backbone); IR (cm^{-1}): 2990, 2952, 1727, 1453, 1387, 1246, 1147, 977, 836, 746.

Thiol functionalized polymer 9: To a stirring solution of polymer **6** (0.4 g, 0.019 mmol) and 1-thionaphtol (0.030 g, 0.190 mmol) in THF (4.0 mL), was added LiOH (0.00095 g, 0.022 mmol) in 0.2 mL of water at 0 °C. The resulting reaction mixture was stirred for 16 hours at ambient temperature. THF was evaporated and crude polymer was dissolved in DCM (20 mL), and washed with water (2 x 10 mL). Organic layer was dried, concentrated and polymer obtained was dissolve in minimum quantity of DCM and precipitated into MeOH (100 mL). Polymer was filtered, washed, and dried to give 0.35 g of polymer. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 8.40 (d, *J* = 8.32 Hz, 3H), 7.83 (d, *J* = 7.82 Hz, 3H), 7.73 (d, *J* = 8.32 Hz, 3H), 7.62 (d, *J* = 7.07 Hz, 3H), 7.52 (m, 6H), 7.39 (t, *J* = 7.91 Hz, 3H), 3.93 – 3.35 (br m, backbone -OCH_3), 3.06 (d, *J* = 6.30 Hz, 6H), 2.08 – 0.66 (br m, backbone); IR (cm^{-1}): 2994, 2948, 1722, 1455, 1389, 1244, 1161, 977, 841, 751.

Bifunctional polymer 10: To a stirring solution of polymer **7** (0.1 g) in pyridine (1.3 mL), was added *p*-toluoyl chloride (0.1 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour and then at room temperature for 16 hours. Pyridine was removed under reduced pressure. The crude polymer was dissolved in DCM (10 mL) and washed with water (10 mL), saturated solution of $NaHCO_3$ (10 mL), and 0.5 M HCl solution (10 mL). The organic layer was dried, concentrated, and the crude solid thus obtained was dissolved in a minimum

quantity of DCM and then precipitated into MeOH (50 mL). The polymer precipitate thus obtained was filtered, washed with MeOH, and dried to give 0.09 g of the product. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 8.41 (d, J = 8.29 Hz, 1H), 7.79 (m, 5H), 7.53 (m, 2H), 7.41 (t, J = 7.80 Hz, 1H), 7.20 (d, J = 7.31 Hz, 2H), 5.40 (q, J = 5.36 Hz, 1H), 4.38 (m, 2H), 3.85 – 3.35 (br s, backbone -OCH_3), 2.42 (s, 3H), 2.07 – 0.63 (br m, backbone); IR (cm^{-1}): 2994, 2943, 1722, 1453, 1382, 1241, 1142, 982, 836, 751.

Bifunctional polymer 11: To a stirring solution of polymer **8** (0.070 g) in pyridine (1 mL), was added *p*-toluoyl chloride (0.1 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour and then at room temperature for 16 hours. Pyridine was removed under reduced pressure and the crude polymer thus obtained was dissolved in DCM (10 mL) and washed with water (10 mL), saturated solution of $NaHCO_3$ (10 mL), and 0.5 M HCl solution (10 mL). The organic layer was dried, concentrated, and the crude solid thus obtained was dissolved in a minimum amount of DCM and precipitated into MeOH (50 mL). The precipitate was collected by filtration and washed with MeOH, and dried to give 0.06 g of the product. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 8.38 (d, J = 8.0 Hz, 2H), 7.77 (m, 6H), 7.68 (m, 4H), 7.48 (m, 4H), 7.36 (t, J = 7.71 Hz, 2H), 7.14 (d, J = 8.0 Hz, 4H), 5.27 (q, J = 5.14 Hz, 2H), 3.84 – 3.35 (br m, backbone -OCH_3), 3.28 (m, 10H), 2.36 (s, 6H), 2.07 – 0.63 (br m, backbone); IR (cm^{-1}): 2990, 2952, 1727, 1453, 1387, 1246, 1147, 977, 836, 746.

Bifunctional polymer 12: To a stirring solution of polymer **9** (0.070 g) in pyridine (1 mL), was added *p*-toluoyl chloride (0.15 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour and then at room temperature for 16 hours. Pyridine was removed under reduced pressure and the crude solid thus obtained was dissolved in DCM (10 mL) and washed with water (10 mL), saturated solution of $NaHCO_3$ (10 mL), and 0.5 M HCl solution (10 mL). The organic layer was dried, concentrated, and the obtained crude solid was dissolved in a minimum amount of DCM and precipitated into MeOH (50 mL). The precipitate obtained was collected by filtration, washed with MeOH, and dried to give 0.062 g of the product polymer. ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): ^{1}H-NMR (δ, ppm, 500 MHz, $CDCl_3$): 8.36 (d, J = 8.0 Hz, 3H), 7.76 (m, 9H), 7.66 (m, 6H), 7.46 (m, 6H), 7.34 (t, J = 7.62 Hz, 3H), 7.11 (d, J = 7.62 Hz, 6H), 5.24 (q, J = 5.21 Hz, 3H), 3.92 – 3.31 (br m, backbone -OCH_3), 3.24 (m, 10H), 2.33 (s, 9H), 2.07 – 0.64 (br m, backbone); IR (cm^{-1}): 2994, 2948, 1722, 1455, 1389, 1244, 1161, 977, 841, 751.

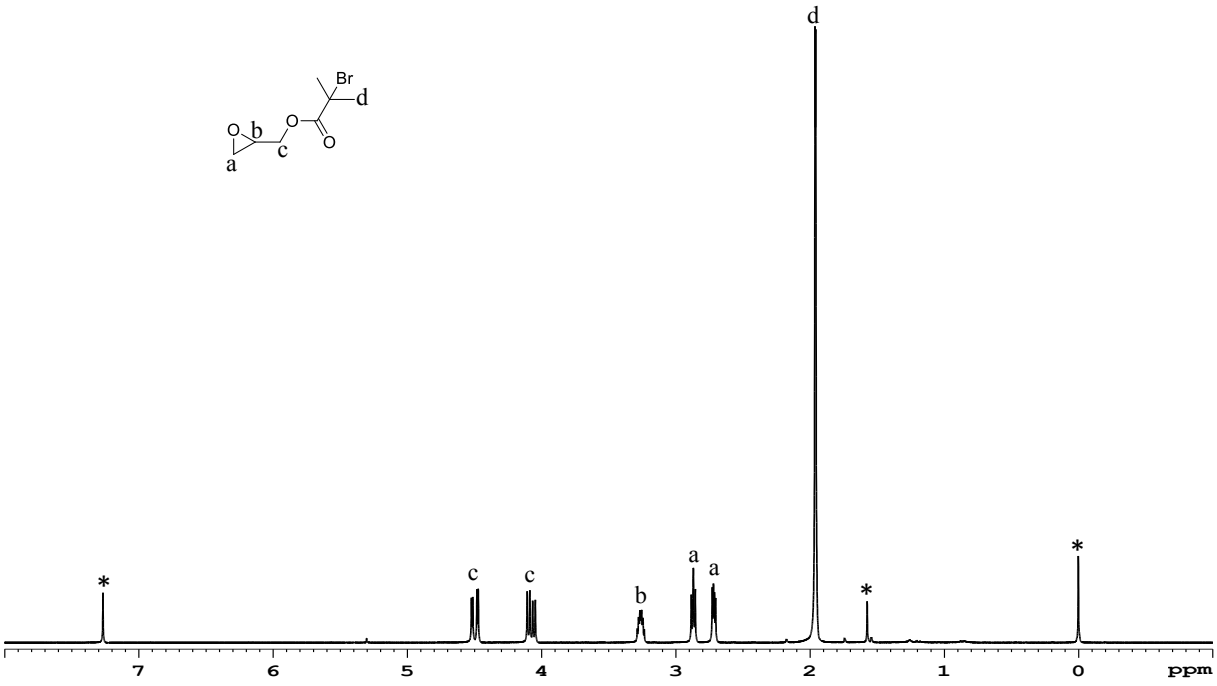

Figure S1. Chemical structure and ^{1}H NMR spectrum of **1** in $CDCl_3$. TMS, water, and $CHCl_3$ signals are shown with an asterisk.

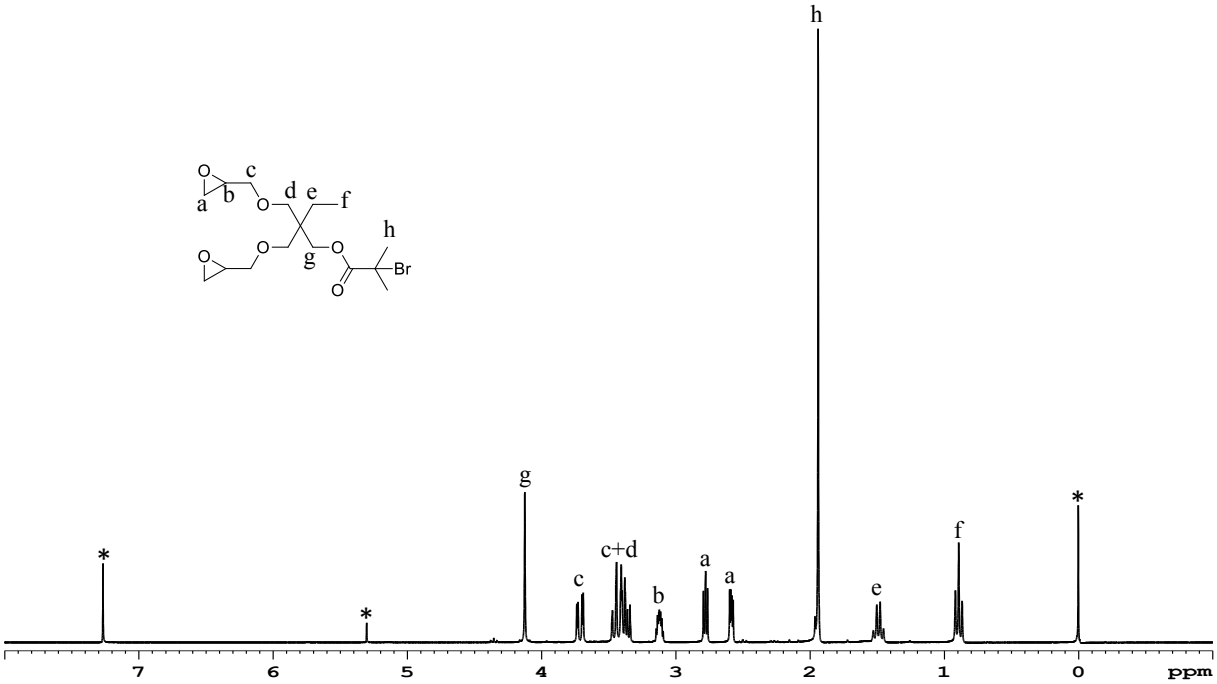

Figure S2. Chemical structure and ^{1}H NMR spectrum of **2** in $CDCl_3$. TMS, DCM, and $CHCl_3$ signals are shown with an asterisk.

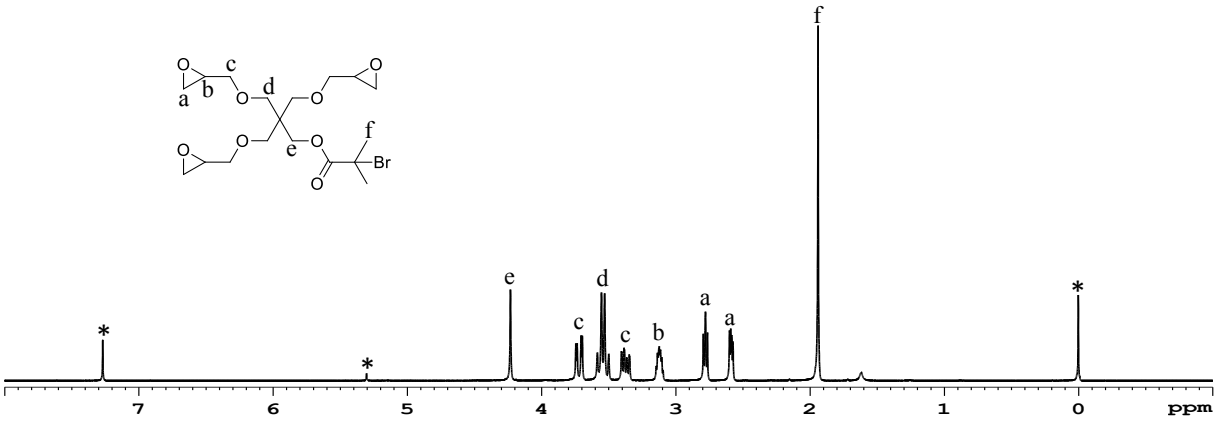

Figure S3. Chemical structure and ^{1}H NMR spectrum of **3** in $CDCl_3$. TMS, DCM, and $CHCl_3$ signals are shown with an asterisk.

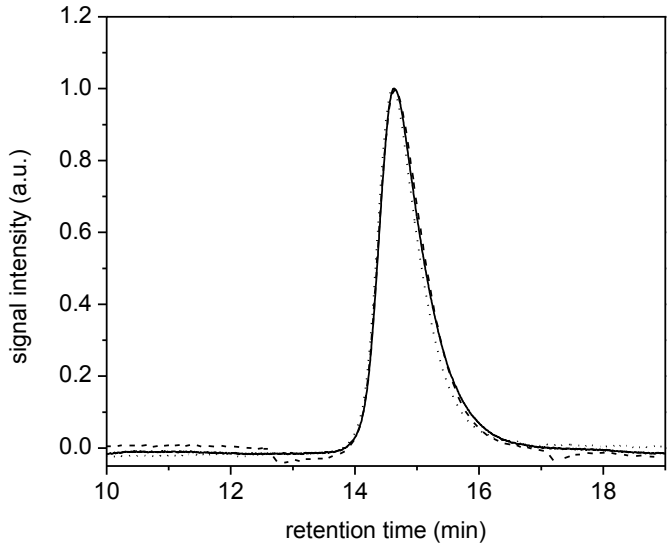

Figure S4. GPC chromatograms of polymer **4** (solid line), **7** (dash line), and **10** (dot line).

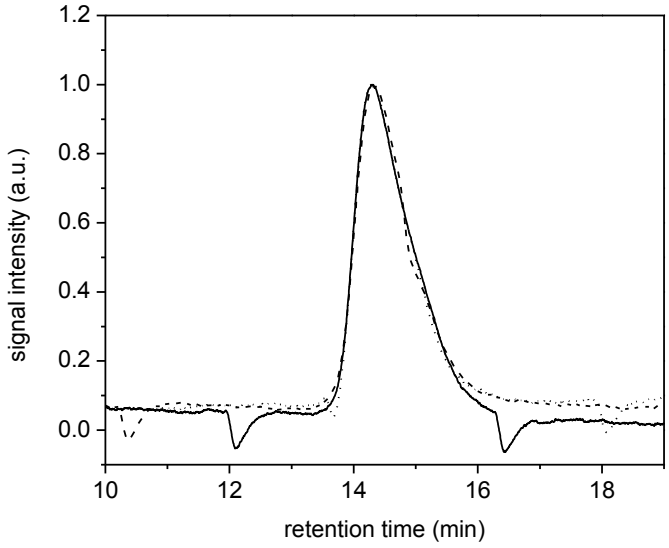

Figure S5. GPC chromatograms of polymer **5** (solid line), **8** (dash line), and **11** (dot line).

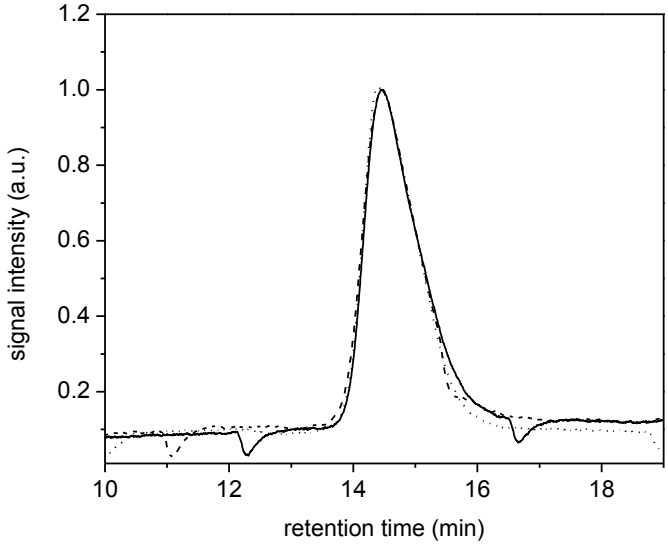

Figure S6. GPC chromatograms of polymer **6** (solid line), **9** (dash line), and **12** (dot line).

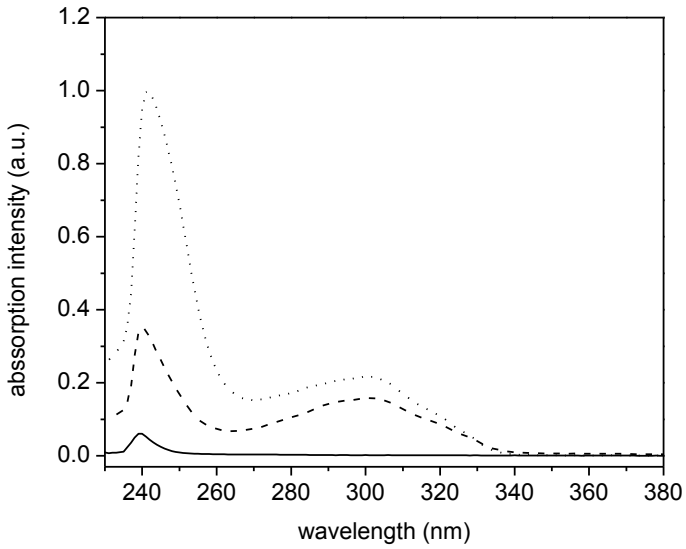

Figure S7. UV-Vis spectra of polymers **4** (solid line), **7** (dash line), and **10** (dot line).

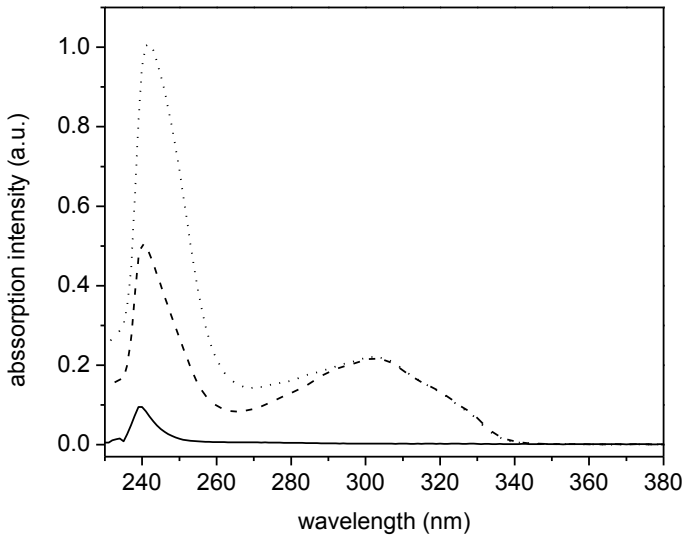

Figure S8. UV-Vis spectra of polymers **5** (solid line), **8** (dash line), and **11** (dot line).

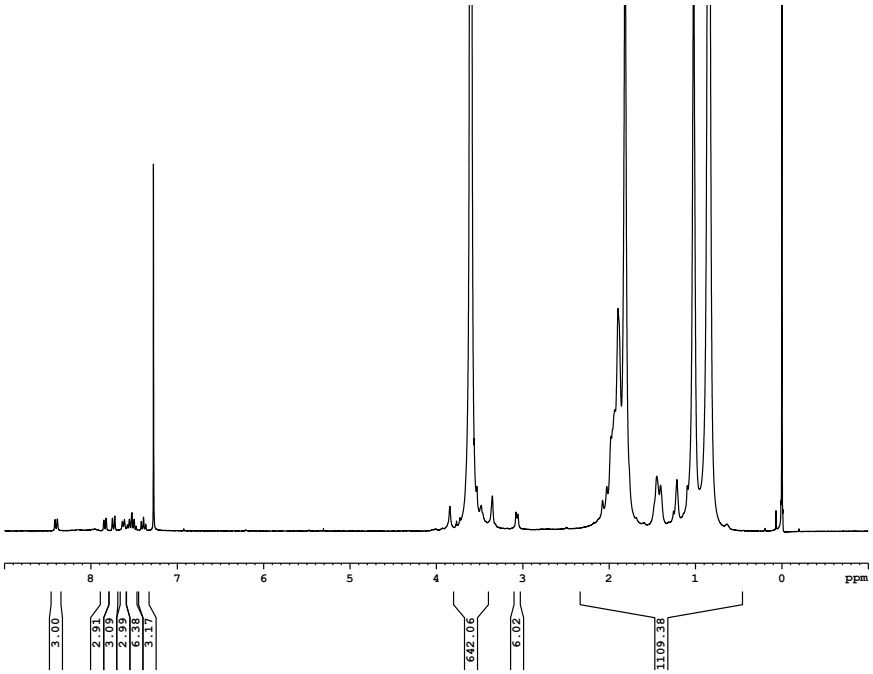

Figure S9. ^{1}H NMR of polymer **9**.

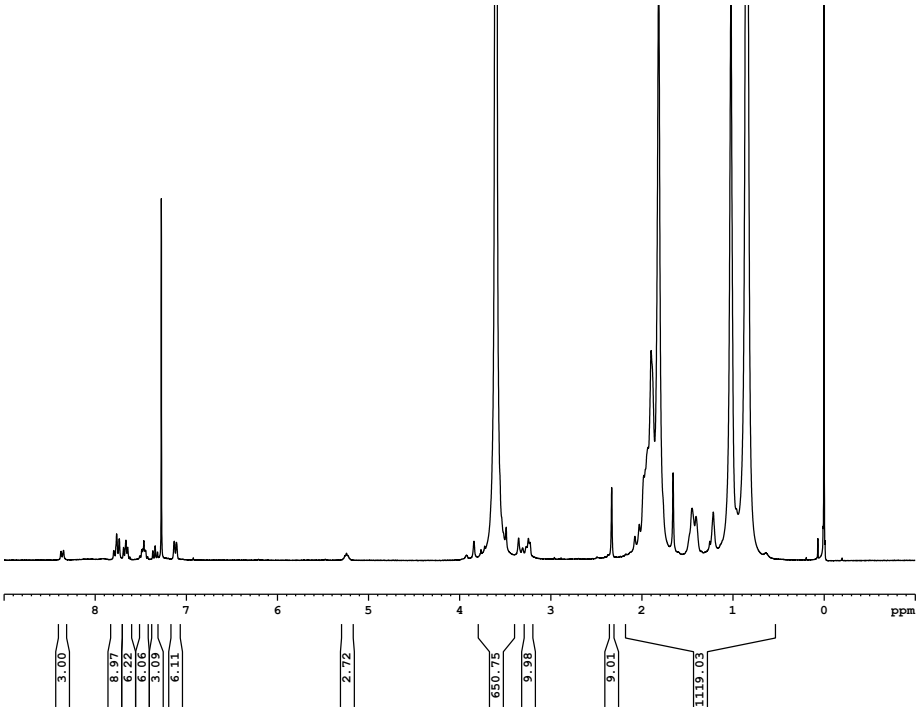

Figure S10. ^{1}H NMR of polymer **12**.