Orthogonal Modification of Norbornene-Functional Degradable Polymers

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Supporting Information

Materials

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was dried over CaH_2, distilled and stored under inert atmosphere. Benzyl alcohol was dried and stored over 3 Å molecular sieves. 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea was synthesized as reported[1] and dried over CaH_2 in dry THF. Monomer **4** was dried over 3 Å molecular sieves in dry CH_2Cl_2. Benzyl azide[2] and triethylene glycol monomethyl ether azide[3] were synthesized according to methods reported in the literature. $CDCl_3$ was dried over 3 Å molecular sieves, distilled and degassed before use. CH_2Cl_2 and THF were purified over Innovative Technology SPS alumina solvent columns and degassed before use. All other solvents and chemicals were obtained from Sigma-Aldrich or Fischer Scientific and used as received.

General Considerations

Ring-opening polymerizations were performed under inert atmosphere in a glovebox. Thiol-ene reactions were performed in a Metalight QX1 lightbox. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 or AC-400 spectrometer at 298 K. Chemical shifts are reported as δ in parts per million (ppm) and referenced to the chemical shift of the residual solvent resonances ($CHCl_3$: ^1H δ = 7.26 ppm; ^{13}C δ = 77.16 ppm). Mass spectra were recorded on a Bruker HCT+ ESI spectrometer. Elemental analysis was performed in duplicate by Warwick Analytical Services. Size exclusion chromatography (SEC) was conducted on a system composed of a Varian 390-LC-Multi detector suite fitted with

differential refractive index, light scattering, and ultraviolet detectors equipped with a guard column (Varian Polymer Laboratories PLGel 5 μM, 50 × 7.5 mm) and two mixed D columns (Varian Polymer Laboratories PLGel 5 μM, 300 × 7.5 mm). The mobile phase was THF with 2% TEA at a flow rate of 1.0 mL min^{-1}. SEC samples were calibrated against Varian Polymer Laboratories Easi-Vials linear poly(styrene) standards (162-2.4 × 10^5 g mol^{-1}) using Cirrus v3.3 software. MALDI-ToF (matrix-assisted laser desorption ionization – time of flight) spectra were recorded using a Bruker Daltronics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with a positive ion ToF detection performed using an accelerating voltage of 25 kV. Samples were spotted onto a Bruker ground steel MALDI-ToF analytical plate through application of a small portion of a solution containing trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) as a matrix (20 μL of a 10 mg mL^{-1} solution in THF), sodium trifluoroacetate as a cationization agent (5 μL of a 10 mg mL^{-1} solution in THF), and analyte (5 μL of a 10 mg mL^{-1} solution in THF) followed by solvent evaporation. The samples were measured in reflectron ion mode and calibrated by comparison to 2 x 10^3 poly(ethylene oxide) standards. UV-Vis spectra were recorded using a Perkin-Elmer UV-Vis Spectrometer (Lambda 35). Lower critical solution temperature (LCST) measurements were analyzed using a Perkin-Elmer UV-Vis Spectrometer (Lambda 35) equipped with a Peltier temperature controller at 500 nm with a heating/cooling rate of 1 ^oC min^{-1}.

Experimental Procedures

Synthesis of acetonide-protected 2,2-bis(hydroxymethyl)propionic acid (1)

Acetonide-protected 2,2-bis(hydroxymethyl)propionic acid (**1**) was prepared according to the literature procedure.[4] 2,2-Bis(hydroxymethyl)propionic acid (10.0 g, 76.1 mmol), 2,2-dimethoxypropane (14.0 mL, 114 mmol) and *p*-toluenesulfonic acid (0.724 g, 3.80 mmol) were dissolved in acetone (70 mL). The solution was stirred at room temperature. After 2 h

ammonium hydroxide was added until the reaction mixture was neutralised and the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and washed with water (2 × 50 mL) and the organic layer dried over $MgSO_4$. CH_2Cl_2 was removed under reduced pressure to yield a white solid (8.24 g, 47.3 mmol, 62%). Characterisation data were in accordance with that previously reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.54 (br S, 1H, COO*H*), 4.17 (d, 2H, C(CH_3)C*H*$_2$O, *J* = 11.8 Hz), 3.64 (d, 2H, C(CH_3)C*H*$_2$O, *J* = 11.8 Hz), 1.43 (s, 3H, C(C*H*$_3$)$_2$), 1.39 (s, 3H, C(C*H*$_3$)), 1.16 (s, 3H, C(C*H*$_3$)CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 179.9, 98.4, 66.3, 42.0, 25.4, 22.1, 18.6.

Synthesis of norbornene-functionalized acetonide protected bis-MPA (2)

N-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (15.4 g, 80.5 mmol) was added to a solution of **1** (13.4 g, 76.7 mmol) and 4-(dimethylamino)pyridine (0.468 g, 3.83 mmol) in dry CH_2Cl_2 (300 mL) at 0 ^{o}C. The solution was allowed to warm to room temperature and stirred for 30 min before the addition of 5-norbornene-2-methanol (a mixture of *endo* and *exo* isomers) (10.0 g, 80.5 mmol). Following stirring of the solution for a further 48 h under nitrogen, the reaction mixture was washed with water (3 × 250 mL) and brine (1 × 250 mL) and the organic layer was dried over $MgSO_4$. CH_2Cl_2 was removed under reduced pressure and the crude product was purified by column chromatography (silica, ethyl acetate: petroleum ether (1:4)) to yield a colourless oil (14.5 g, 51.6 mmol, 67%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *endo* isomer δ = 6.15 (m, 1H, C*H*=CHCH$_{bridgehead}$($CH_{2\text{-}bridge}$)CH(CH_2)CH_2O), 5.94 (m, 1H, CH=C*H*CH$_{bridgehead}$($CH_{2\text{-}bridge}$)CH(CH_2)CH_2O), 4.19 (d, 2H, C(CH_3)C*H*$_2$O, *J* = 11.8 Hz), 3.91 (m, 1H, C*H*$_2$OC(O)C(CH_3)), 3.73 (m, 1H, C*H*$_2$OC(O)C(CH_3)), 3.64 (d, 2H, C(CH_3)C*H*$_2$O, *J* = 11.8 Hz), 2.88 (m, 2H, CH$_{bridgehead}$$CH_{2\text{-}bridge}$C*H*$_{bridgehead}$CH($CH_2$)$CH_2$O), 2.81, (m, 1H, C*H*$_{bridgehead}$$CH_2$-

$_{bridge}CH_{bridgehead}CH(CH_2)CH_2O$), 2.42 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.83 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.44 (m, 1H, $CH_{2\text{-}bridge}$), 1.42 (s, 3H, $C(CH_3)_2$), 1.39 (s, 3H, $C(CH_3)_2$), 1.25 (m, 1H, $CH_{2\text{-}bridge}$), 1.19 (s, 3H, $C(CH_3)$), 0.56 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$); *exo* isomer δ = 6.08 (m, 2H, CH=CH), 4.21 (m, 1H, $CH_2OC(O)C(CH_3)$), 4.19 (d, 2H, $C(CH_3)CH_2O$, J = 11.8 Hz), 4.05 (m, 1H, $CH_2OC(O)C(CH_3)$), 3.64 (d, 2H, $C(CH_3)CH_2O$, J = 11.8 Hz), 2.83 (m, 1H, $CH_{bridgehead}CH_{2\text{-}bridge}CH_{bridgehead}CH(CH_2)CH_2O$), 2.69 (m, 1H, $CH_{bridgehead}CH_{2\text{-}bridge}CH_{bridgehead}CH(CH_2)CH_2O$), 1.75 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.42 (s, 3H, $C(CH_3)_2$), 1.39 (s, 3H, $C(CH_3)_2$), 1.35 (m, 2H, $CH_{2\text{-}bridge}$), 1.35 (s, 3H, $C(CH_3)$), 1.27 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.18 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): both isomers δ = 174.3, 174.1, 137.6, 137.0, 136.2, 132.2, 98.1, 68.9, 68.2, 66.1, 49.4, 45.0, 43.9, 43.6, 42.2, 41.9, 41.9, 41.6, 38.1, 37.8, 29.5, 28.8, 24.6, 24.5, 23.0, 22.9, 18.8. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.5; H, 8.6%. Found: C, 68.1; H, 8.6%. MS (ESI +ve): m/z 303 $[M+Na]^+$.

Synthesis of norbornene functionalized diol (3)

Dowex 50W-X2 acidic resin (5.0 g) was added to a stirred solution of **2** (14.5 g, 46.4 mmol) in MeOH (200 mL). After stirring at room temperature for 16 h, the resin was removed by filtration before concentration of the solution *in vacuo* to yield **3** as a white solid (12.7 g, 52.7 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *endo* isomer δ = 6.17 (m, 1H, CH=CH$CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 5.94 (m, 1H, CH=CH$CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 3.96 (m, 1H, $CH_2OC(O)C(CH_3)$), 3.92 (d, 2H, $C(CH_3)CH_2O$, J = 11.2 Hz), 3.78 (m, 1H, $CH_2OC(O)C(CH_3)$), 3.72 (d, 2H, $C(CH_3)CH_2O$, J = 11.2 Hz), 2.88 (m, 2H, $CH_{bridgehead}CH_{2\text{-}bridge}CH_{bridgehead}CH(CH_2)CH_2O$), 2.83 (m, 1H, $CH_{bridgehead}CH_{2\text{-}bridge}CH_{bridgehead}CH(CH_2)CH_2O$) 2.44 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 2.40 (br s, 2H, OH), 1.85 (m, 1H,

$CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.46 (m, 1H, $CH_{2\text{-}bridge}$), 1.27 (m, 1H, $CH_{2\text{-}bridge}$), 1.07 (s, 3H, $C(CH_3)$), 0.58 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$); *exo* isomer δ = 6.09 (m, 2H, CH=CH), 3.93 (d, 2H, $C(CH_3)CH_2O$, J = 11.2 Hz), 4.22 (m, 1H, $CH_2OC(O)C(CH_3)$), 3.73 (d, 2H, $C(CH_3)CH_2O$, J = 11.2 Hz), 4.10 (m, 1H, $CH_2OC(O)C(CH_3)$), 2.85 (m, 1H, $CH_{bridgehead}CH_{2\text{-}bridge}CH_{bridgehead}CH(CH_2)CH_2O$), 2.70 (m, 1H, $CH_{bridgehead}CH_{2\text{-}bridge}CH_{bridgehead}CH(CH_2)CH_2O$), 2.40 (br s, 2H, OH), 1.77 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.35 (m, 1H, $CH_{2\text{-}bridge}$), 1.30 (m, 1H, $CH_{2\text{-}bridge}$), 1.28 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.18 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.08 (s, 3H, $C(CH_3)$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): both isomers δ = 176.1, 176.0, 137.8, 137.1, 136.2, 132.2, 69.2, 68.5, 68.3, 68.3, 49.5, 49.3, 45.1, 44.0, 43.7, 42.3, 41.7, 42.3, 41.7, 38.1, 37.8, 29.6, 28.9, 17.3. Anal. Calcd for $C_{13}H_{20}O_4$: C, 65.0; H, 8.4%. Found: C, 64.9; H, 8.4%. MS (ESI +ve): m/z 263 $[M+Na]^+$.

Synthesis of norbornene functionalized carbonate monomer (4)

A solution of triphosgene (9.26 g, 31.2 mmol) in dry CH_2Cl_2 (100 mL) was added in stepwise portions over 30 minutes to a solution of **3** (12.5 g, 52.0 mmol) and pyridine (25.0 mL, 0.312 mol) in dry CH_2Cl_2 (150 mL) at -78 ^{o}C under nitrogen. The reaction was stirred for 1 h at -78 ^{o}C and for a further 2 h at room temperature before being washed with saturated aqueous NH_4Cl solution (200 mL), 1 M HCl (3 × 150 mL) and saturated aqueous $NaHCO_3$ solution (150 mL). The organic layer was dried over $MgSO_4$ and reduced under vacuum to yield a white solid that was recrystallized from cyclohexane to yield **4** as a white crystalline solid (10.2 g, 38.5 mmol, 74%.)

^{1}H NMR (400 MHz, $CDCl_3$, ppm): *endo* isomer δ = 6.18 (m, 1H, CH=CH$CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 5.93 (m, 1H, CH=CH$CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 4.70 (d, 2H, $C(CH_3)CH_2O$, J = 10.9 Hz), 4.20 (d, 2H, $C(CH_3)CH_2O$, J = 10.9 Hz), 3.97 (m, 1H, $CH_2OC(O)C(CH_3)$), 3.82 (m, 1H, $CH_2OC(O)C(CH_3)$), 2.86 (m, 2H, $CH_{bridgehead}$), 2.42 (m,

1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.86 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.48 (m, 1H, $CH_{2\text{-}bridge}$), 1.33 (s, 3H, $C(CH_3)$), 1.27 (m, 1H, $CH_{2\text{-}bridge}$), 0.57 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$); *exo* isomer δ = 6.09 (m, 2H, CH=CH), 4.71 (d, 2H, $C(CH_3)CH_2O$, J = 10.9 Hz), 4.26 (m, 1H, $CH_2OC(O)C(CH_3)$), 4.21 (d, 2H, $C(CH_3)CH_2O$, J = 10.9 Hz), 4.12 (m, 1H, $CH_2OC(O)C(CH_3)$), 2.84 (m, 1H, $CH_{bridgehead}CH_{2\text{-}bridge}CH_{bridgehead}CH(CH_2)CH_2O$), 2.66 (m, 1H, $CH_{bridgehead}CH_{2\text{-}bridge}CH_{bridgehead}CH(CH_2)CH_2O$), 1.76 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.39 (m, 1H, $CH_{2\text{-}bridge}$), 1.35 (s, 3H, $C(CH_3)$), 1.32 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$), 1.30 (m, 1H, $CH_{2\text{-}bridge}$), 1.17 (m, 1H, $CH_{bridgehead}(CH_{2\text{-}bridge})CH(CH_2)CH_2O$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): both isomers δ = 171.2, 171.1, 147.6, 137.8, 137.0, 136.0 131.9, 73.0, 70.2, 69.5, 49.4, 45.0, 43.8, 43.5, 42.1, 41.5, 40.2, 37.9, 37.6, 29.4, 28.7, 17.4. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.8%. Found: C, 62.85.; H, 6.8%. MS (ESI +ve): m/z 289 $[M+Na]^+$.

General procedure for ring-opening polymerizations

Benzyl alcohol, DBU (1 mol% to monomer), and 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (5 mol% to monomer) were dissolved in dry $CDCl_3$ or dry CH_2Cl_2. **4** was dissolved separately in the same solvent and added to the initiator/catalyst solution. After the desired amount of time the polymerization was quenched by the addition of acidic amberlyst 15 resin. The resin was removed by filtration and the solvent removed under reduced pressure. The residual monomer and catalyst were removed by column chromatography (silica, ethyl acetate (30%)/ hexane (70%), then 100% ethyl acetate).

General procedure for post-polymerization modifications *via* the 1,3-dipolar cycloaddition of norbornenes and azides

Benzyl azide (10 eq. per Nb moiety) was added to a solution of norbornene-functional poly(carbonate) in 1,4-dioxane ($[Nb]_0$ = 0.04 M) and stirred at 90 ^oC for 14 h. The solvent

was then removed *in vacuo,* the residue dissolved in the minimum amount of $CHCl_3$ and precipitated into cold methanol.

General procedure for post-polymerization modifications *via* the inverse electron demand Diels-Alder reaction between norbornenes and tetrazines

3,6-Di-2-pyridyl-1,2,4,5-tetrazine (1 eq. per Nb moiety) was added to a solution of norbornene-functional poly(carbonate) in 1,4-dioxane ($[Nb]_0$ = 0.04 M) and stirred at room temperature for 10 h. The solvent was then removed *in vacuo,* the residue dissolved in the minimum amount of $CHCl_3$ and precipitated into hexane.

General procedure for post-polymerization modifications *via* the radical addition of thiols to norbornenes

1-dodecanethiol (1.3 eq. per Nb moiety) and 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (0.015 eq. per Nb moiety) were added to a solution of norbornene-functional poly(carbonate) in 1,4-dioxane ([Nb] = 0.04 M) and irradiated with UV light for 1.5 h. The solvent was then removed *in vacuo,* the residue dissolved in the minimum amount of $CHCl_3$ and precipitated into cold methanol.

One-pot three-step modification of norbornene-functional poly(carbonate)

Triethyleneglycol monomethyl ether azide (10 eq. per Nb moiety) was added to a solution of norbornene-functional poly(carbonate) in 1,4-dioxane ($[Nb]_0$ = 0.04 M) and stirred at 90 ^{o}C for 1 h. The reaction was cooled to room temperature before the addition of 3,6-di-2-pyridyl-1,2,4,5-tetrazine (0.5 eq. per remaining Nb moiety) and stirred for 4 h. Finally, 1-dodecanthiol (2 eq. per remaining Nb moiety) and 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (0.015 eq.) were added and the reaction mixture irradiated for 2 h

with UV light. The solvent was then removed *in vacuo,* the residue dissolved in the minimum amount of $CHCl_3$ and precipitated into hexane.

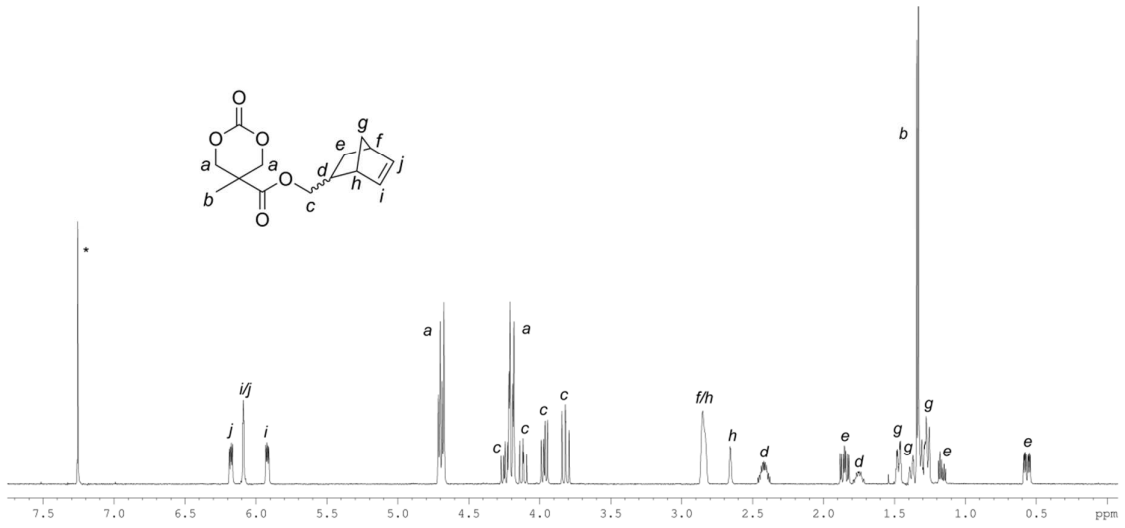

Figure S1. ^{1}H NMR spectrum of norbornene-functional carbonate monomer **4** in $CDCl_3$ (400 MHz, 298 K) (*$CHCl_3$).

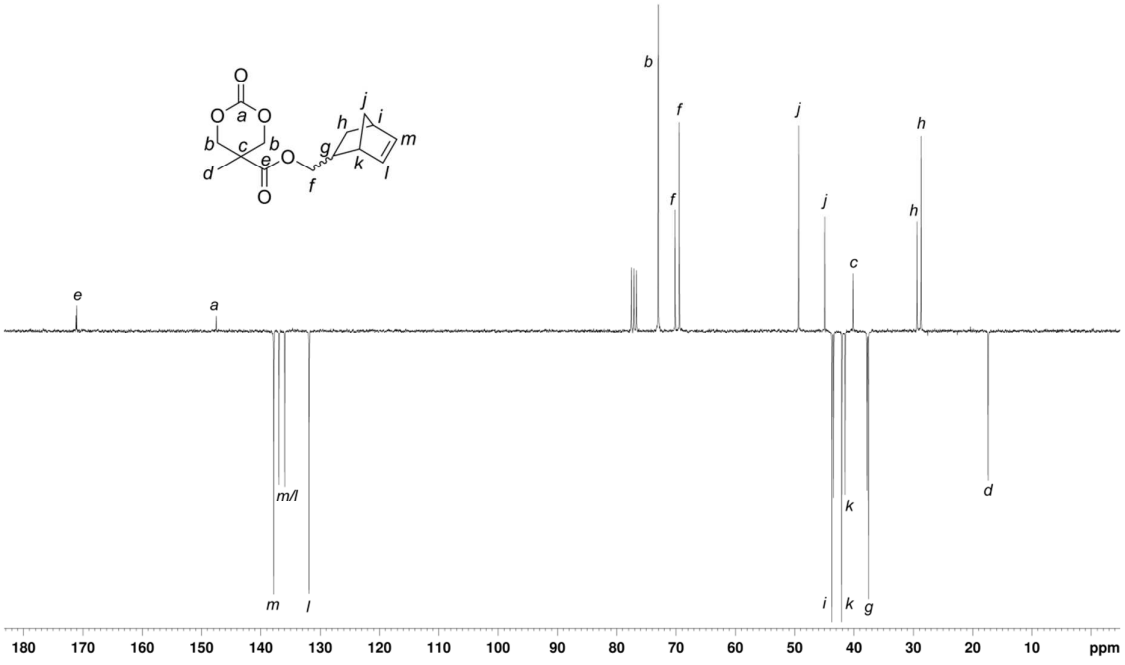

Figure S2. ^{13}C NMR spectrum of norbornene-functional carbonate monomer **4** in $CDCl_3$ (100 MHz, 298 K).

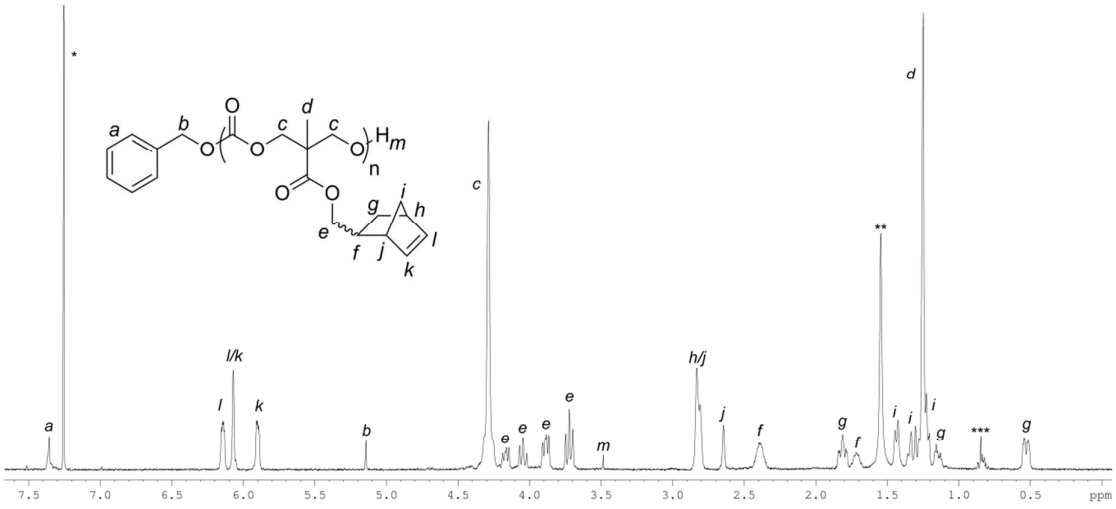

Figure S3. ^{1}H NMR spectrum of norbornene-functional poly(carbonate) in $CDCl_3$ (400 MHz, 298 K) (*$CHCl_3$, **H_2O, ***hexane).

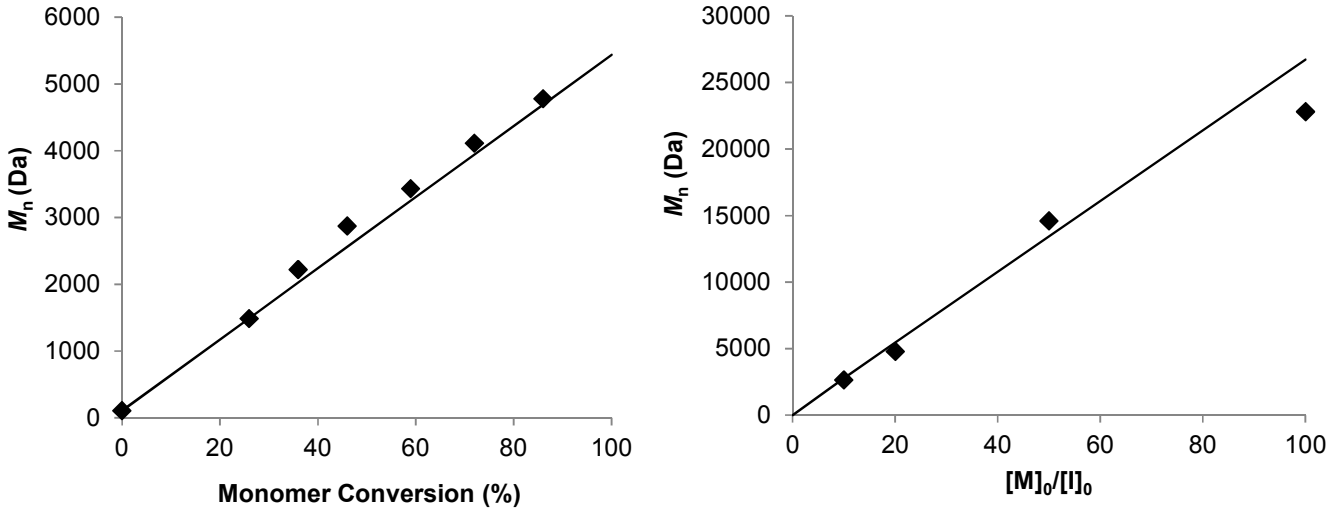

Figure S4. (Left) Plot of M_n(SEC) vs. monomer conversion for the ROP of **4**, line represents theoretical values of M_n ($[M]_0/[I]_0$ = 20, $[\mathbf{4}]_0$ = 0.5 M, using benzyl alcohol as an initiator). (Right) Plot of M_n(SEC) vs. $[M]_0/[I]_0$ for the ROP of **4**, line represents theoretical values of M_n ($[\mathbf{4}]_0$ = 0.5 M, using benzyl alcohol as an initiator).

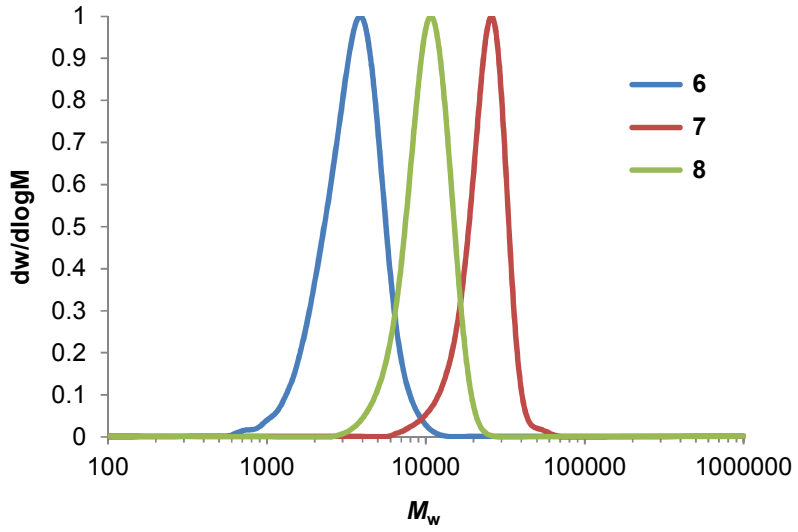

Figure S5. SEC traces of norbornene-functional poly(carbonate)s **6** (M_n = 2.8 kDa, $Đ_M$ = 1.21), **7** (M_n = 24.5 kDa, $Đ_M$ = 1.11) and **8** (M_n = 9.5 kDa, $Đ_M$ = 1.12).

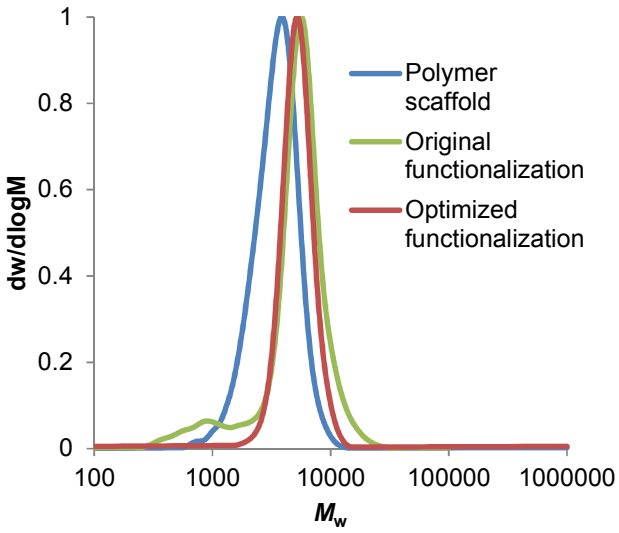

Figure S6. SEC trace showing degradation of norbornene-functional poly(carbonate) after modification with benzyl azide *via* prolonged heating (36 h) at 90 °C, as well as the precursor polymer scaffold (**6**) and polymer after functionalization with optimum conditions.

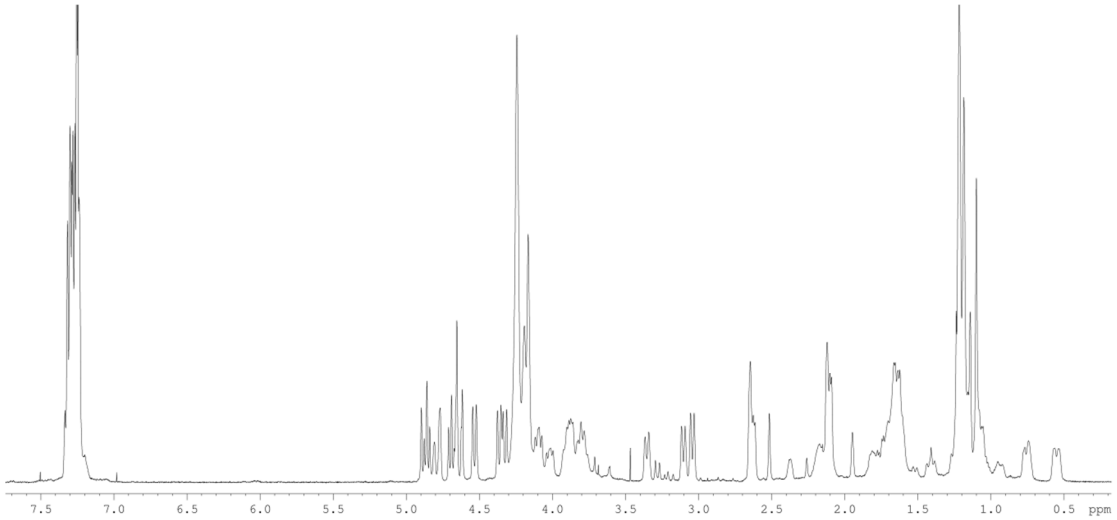

Figure S7. ^{1}H NMR spectrum of norbornene-functional poly(carbonate) after the post-polymerization 1,3-dipolar cycloaddition of benzyl azide (**7a)** in $CDCl_3$ (400 MHz, 298 K).

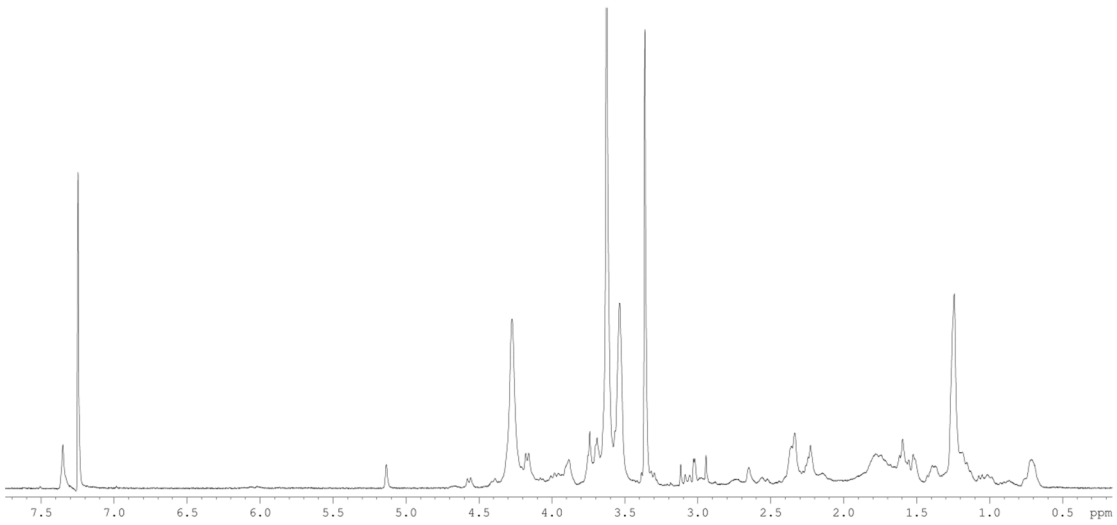

Figure S8. ^{1}H NMR spectrum of norbornene-functional poly(carbonate) after the post-polymerization 1,3-dipolar cycloaddition of TEG azide (**6b**) in $CDCl_3$ (400 MHz, 298 K).

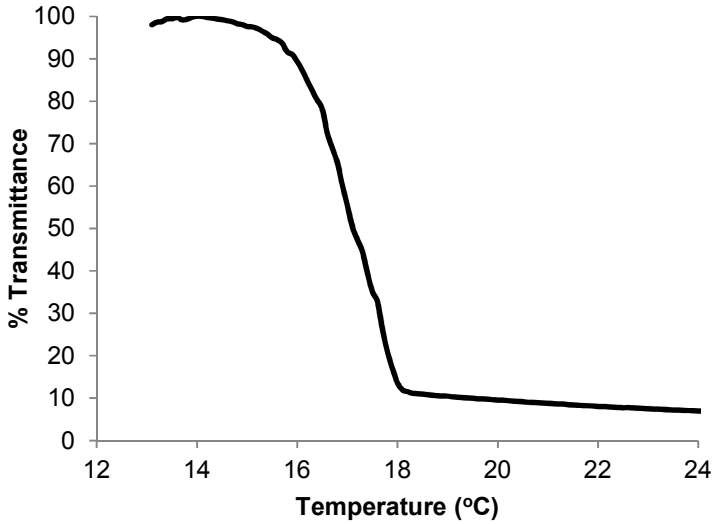

Figure S9. Percentage transmittance *versus* temperature plot for norbornene-functional poly(carbonate) after the post-polymerization 1,3-dipolar cycloaddition of TEG azide (**6b**) at 1mg mL^{-1} in nanopure water (heating rate 1 ^{o}C min^{-1}).

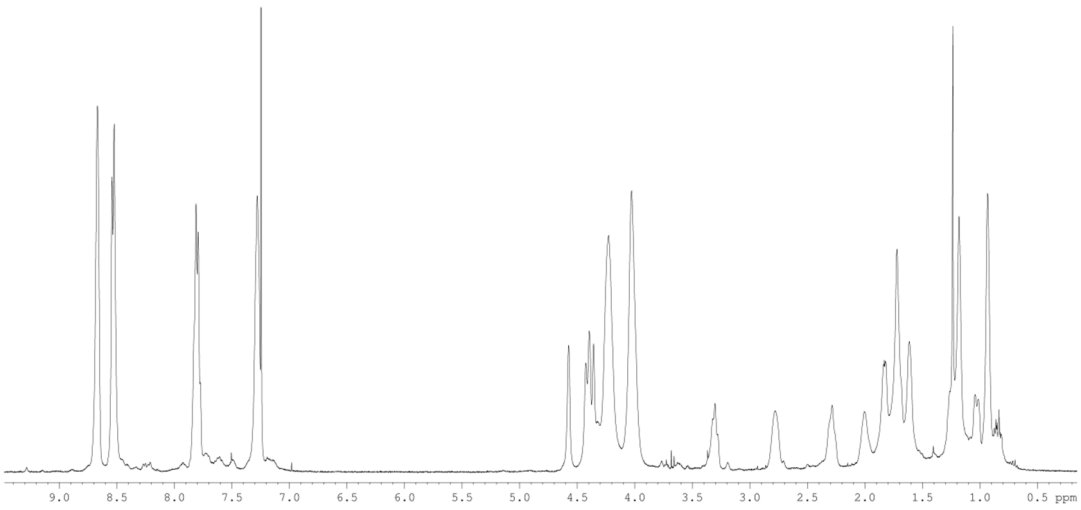

Figure S10. ^{1}H NMR spectrum of norbornene-functional poly(carbonate) after the post-polymerization DA_{inv} with dipyridyltetrazine (**7c**) in $CDCl_3$ (400 MHz, 298 K).

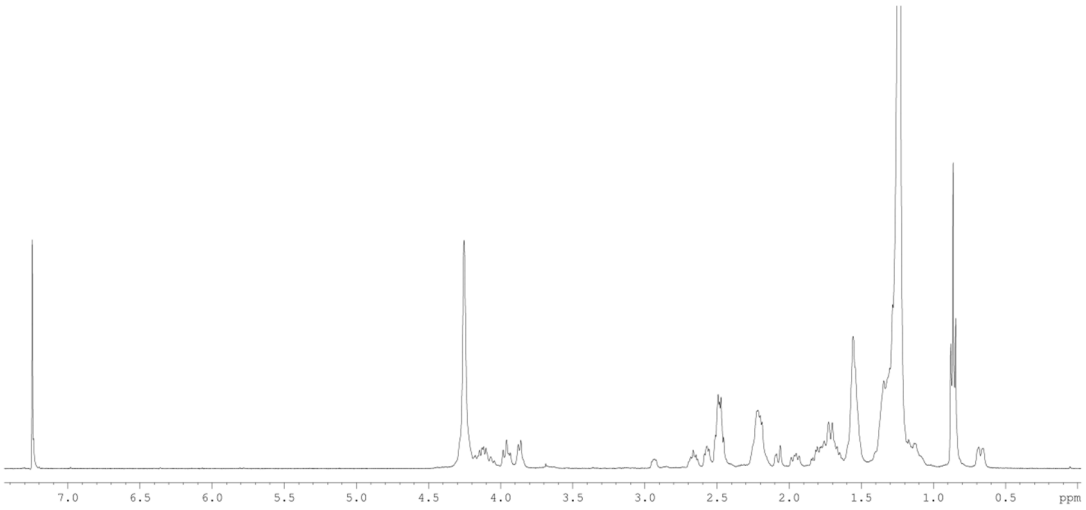

Figure S11. ^{1}H NMR spectrum of norbornene-functional poly(carbonate) after the post-polymerization radical thiol addition of 1-dodecanethiol (**7d**) in $CDCl_3$ (400 MHz, 298 K).

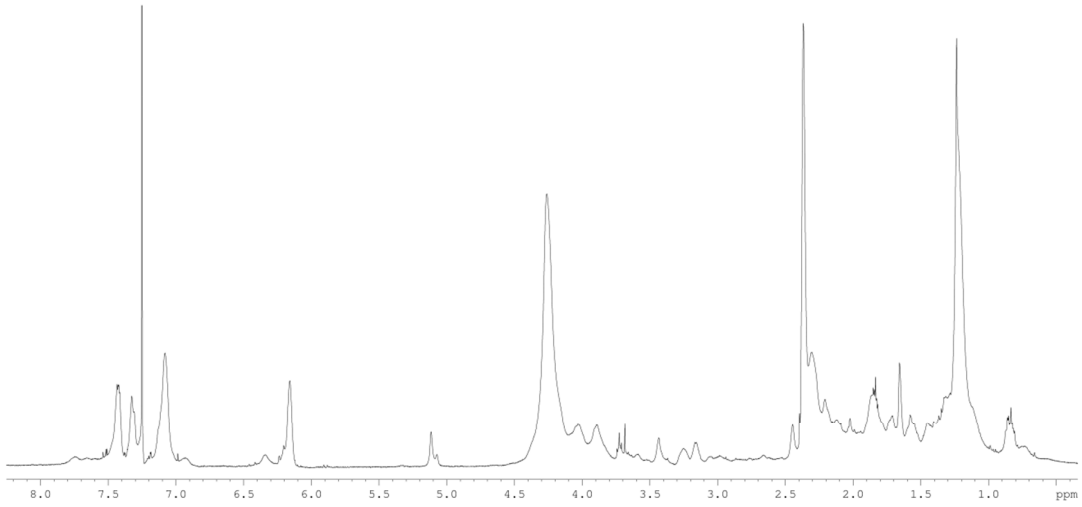

Figure S12. ^{1}H NMR spectrum of norbornene-functional poly(carbonate) after the post-polymerization radical thiol addition of 7-mercapto-4-methylcoumarin (**6e**) in $CDCl_3$ (400 MHz, 298 K).

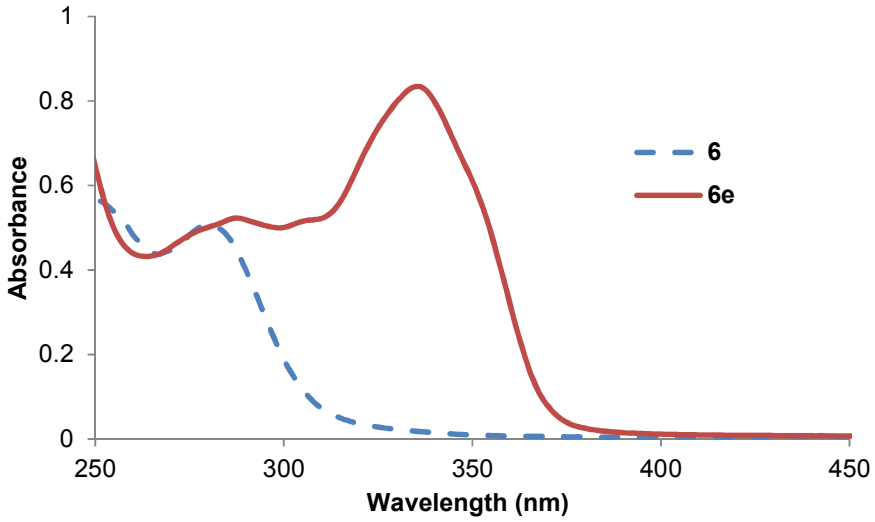

Figure S13. UV-Vis spectrum of norbornene-functional poly(carbonate) before (**6**) and after the post-polymerization radical thiol addition of 7-mercapto-4-methylcoumarin (**6e**).

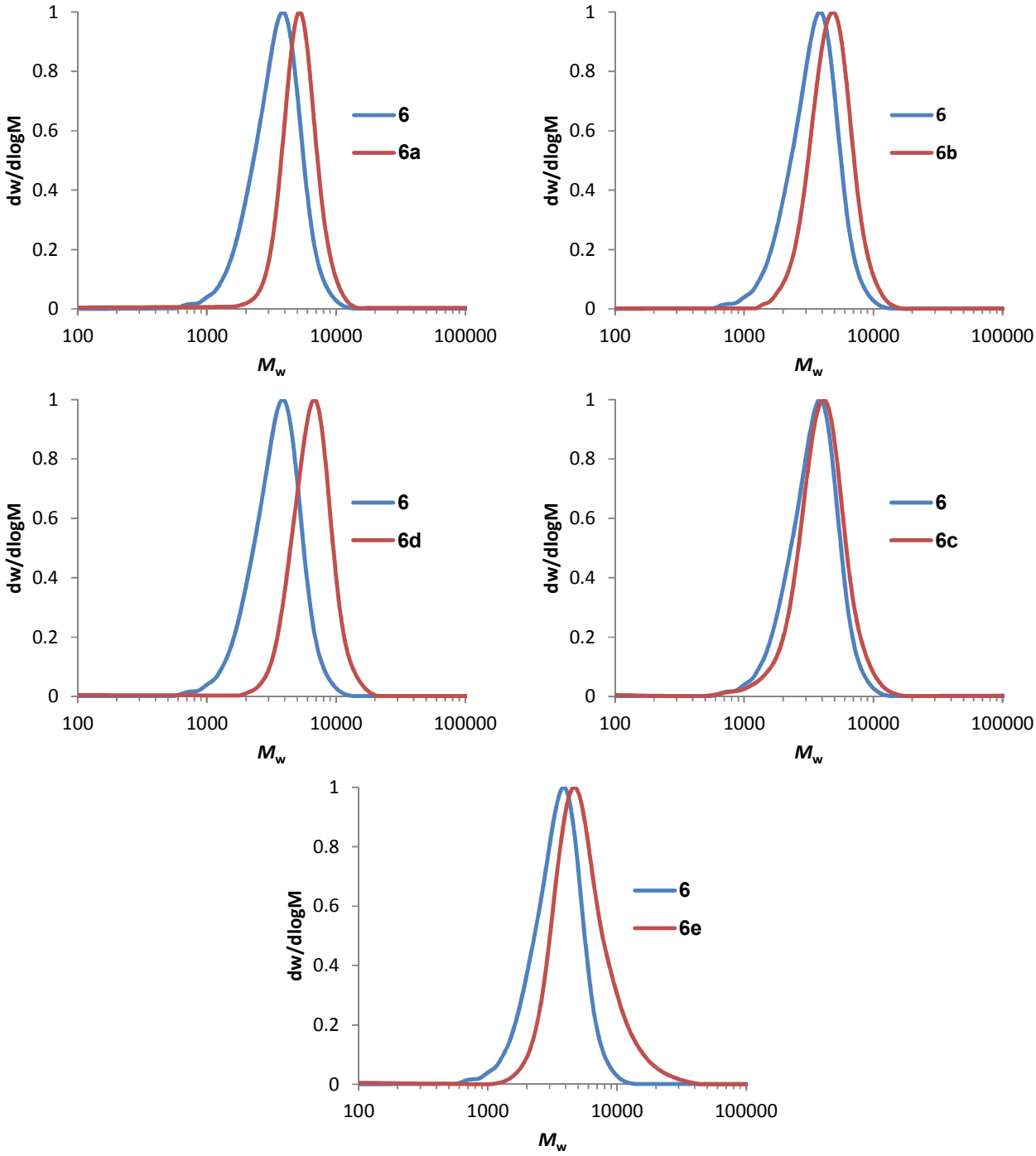

Figure S14. SEC traces of norbornene-functional poly(carbonate) before (**6**, M_n = 2.8 kDa, $Đ_M$ = 1.21) and after post-polymerization modification (**6a,** M_n = 4.9 kDa, $Đ_M$ = 1.10, **6b**, M_n = 4.4 kDa, $Đ_M$ = 1.14, **6c**, M_n = 3.5 kDa, $Đ_M$ = 1.23, **6d**, M_n = 6.0 kDa, $Đ_M$ = 1.13 and **6e**, M_n = 4.7 kDa, $Đ_M$ = 1.30).

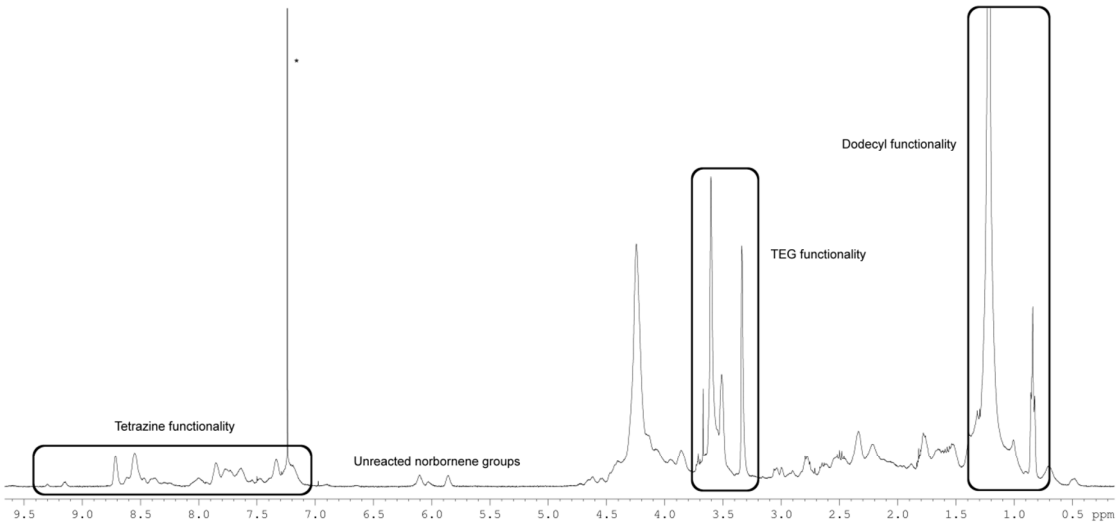

Figure S15. ^{1}H NMR spectrum of multi-functionalized poly(carbonate) after one-pot three-step modification of norbornene-functional poly(carbonate) **8** in $CDCl_3$ (400 MHz, 298 K) (*$CHCl_3$).

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