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Synthesis of polyvinylethylene glycols (PVEGs) via polyetherification of vinylethylene carbonate by synergistic catalysis

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1. Materials and methods

Materials

All the materials used in this study were purchased from commercial chemical suppliers (Sigma-Aldrich, Sinopharm Chemical reagent, Bidepharm, Titan, Macklin, and Meryer), unless otherwise stated. 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthalene (BINAP, 99%), 1,4-bis(diphenylphosphanyl)butane (DPPB, 98%, Jiangsu Sinocompund Catalysts), 1,3-bis(diphenylphosphanyl)propane (DPPP, 98%, Jiangsu Sinocompund Catalysts), (oxybis(2,1-phenylene))bis(diphenylphosphane) (DPEphos, 98%, Jiangsu Sinocompund Catalysts), tri(furan-2-yl)phosphane ($P(2\text{-furanyl})_3$, 98%, Jiangsu Sinocompund Catalysts), triphenylphosphine (PPh_3, 98%), tricyclohexylphosphane (PCy_3, 98%, Jiangsu Sinocompund Catalysts), triphenylphosphite ($P(OPh)_3$, 98%)

Methods

^1H, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer at 25° C. $CDCl_3$ (δ H = 7.26 ppm and δ C = 77.16 ppm) and DMSO-D_6 (δ H = 2.50ppm and δ C = 39.52 ppm) were used as internal standards. The number average (Mn), weight-average (Mw) molecular weights and corresponding molecular weight distribution (Mw/Mn, PDI) were measured through Gel Permeation Chromatography (GPC) by using an EcoSEC HLC-8320 series with THF as eluent at 25°C and a flow rate of 1.00 $mL \cdot min^{-1}$ with a refractive index (RI) detector. All calibrations were performed by using polystyrene (PS) standards (Sigma-Aldrich; Mp, 500−8000000). MALDI-TOF mass spectrometry (MS) measurements were performed by using (E)-2-(3-(4-(tert-butyl)phenyl)-2-methylallylidene)malononitrile (DCTB) as a matrix on a Bruker Autoflex Max instrument. Hydroxyl value was measured according to ASTM D4274 standard by phthalic anhydride-pyridine method. Thermogravimetric analysis (TGA) (TG 209 F3, NETZSCH) was employed under a nitrogen atmosphere from 50 to 800 °C with a heating rate of 10 $°C \cdot min^{-1}$. The storage/loss modulus and tan δ as a function of temperature were measured on a TA Instrument DMA Q850 with the tensile mode. Stress-strain curves were measured at room temperature using an INSTRON 3365 universal testing machine with a stretching speed of 50 mm·min^{-1}. For the tensile measurements, the specimens were cut into dog-bone shapes (width: 4 mm; gauge length: 20 mm; thickness 0.5mm).

2. General procedure for the synthesis of vinyl-functional polyvinylethylene glycols

Synthetic of P2: To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (114.1 mg, 1.0 mmol) and 1,4-phenylenedimethanol (13.8 mg, 0.10 mmol) were added. Then, $Pd_2(dba)_3{\cdot}CHCl_3$ (1.5 mg, 0.15 mol% for **1**), DPEphos ligand (1.6 mg, 0.3 mol% for **1**) were added. The reaction tube was sealed with rubber-septum, then evacuated and backfilled with nitrogen (this process was repeated a total of three times). Et_3B (3 μL of 1 mol·L^{-1} in THF solution, 0.3 mol% for **1**) and anhydrous THF (1 mL) were added sequentially via syringe. The resulting mixture was stirred at 10 °C for 2 h. The solvent was removed by rotary evaporation under vacuum. The remain catalysts were removed by short silica gel column to afford **P2** as a light-yellow oil (79.7 mg, 95% yield).

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.32 (4H, Ar*H*), 5.71 (1H, CH_2=C*H*), 5.33 (2H, C*H*$_2$=CH), 4.61/4.47 (4H, ArC*H*$_2$O), 3.99 (1H, OC*H*(CH=CH_2) CH_2O), 3.53 (2H, OCH(CH=CH_2) C*H*$_2$O) ppm. ^{13}C NMR (125MHz, $CDCl_3$): δ = 137.37 (Ar*C*), 135.77-134.99 (CH_2=*C*H), 127.77 (Ar*C*), 118.44-118.07 (*C*H$_2$=CH), 82.89/80.20/81.04/80.47/79.59 (O*C*H(CH=CH_2)CH_2), 71.90-71.24 (OCH(CH=CH2)*C*H$_2$O), 70.31 (Ar*C*H$_2$O), 65.33/65.16 (CH(CH=CH_2)*C*H$_2$OH) ppm.

Synthetic of P3: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (228.2 mg, 2.0 mmol), 1,4-phenylenedimethanol (13.8 mg, 0.10 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.1 mg, 0.15 mol% for **1**), DPEphos ligand (3.2 mg, 0.3 mol% for **1**), Et_3B (6μL of 1 mol·L^{-1} in THF solution, 0.3 mol% for **1**) were used. **P3** was obtained as light-yellow oil (144.9 mg, 94% yield).

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.31 (4H, Ar*H*), 5.72 (1H, CH_2=C*H*), 5.33 (2H, C*H*$_2$=CH), 4.60/4.49 (4H, ArC*H*$_2$O), 3.96 (1H, OC*H*(CH=CH_2)CH_2O), 3.54 (2H, OCH(CH=CH$_2$)C*H*$_2$O) ppm. ^{13}C NMR (125MHz, CDCl$_3$): δ = 137.82 (Ar*C*), 134.99-136.08 (CH$_2$=*C*H), 128.31 (Ar*C*), 118.47-118.08 (*C*H$_2$=CH), 82.97/82.23/80.78/79.38 (O*C*H(CH=CH$_2$)CH$_2$O), 71.62-71.20 (CH(CH=CH2)*C*H$_2$OCH), 70.36 (Ar*C*H$_2$O), 65.36/65.15 (CH(CH=CH$_2$)*C*H$_2$OH) ppm.

Synthetic of P4: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (456.4 mg, 4.0 mmol), 1,4-phenylenedimethanol (13.8 mg, 0.10 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (6.2 mg, 0.15 mol% for **1**), DPEphos ligand (6.4 mg, 0.3 mol% for **1**), Et$_3$B (12μL of 1 mol·L^{-1} in THF solution, 0.3 mol% for **1**) were used. **P4** was obtained as light-yellow oil (279.8 mg, 95% yield).

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.30 (4H, Ar*H*), 5.74 (1H, CH$_2$=C*H*), 5.21 (2H, C*H*$_2$=CH), 4.60/4.49 (4H, ArC*H*$_2$O), 3.95 (1H, OC*H*(CH=CH$_2$)CH$_2$O), 3.49 (2H, OCH(CH=CH$_2$)C*H*$_2$O) ppm. ^{13}C NMR (125MHz, CDCl$_3$): δ = 137.80 (Ar*C*), 136.07-134.43 (CH$_2$=*C*H), 127.61 (Ar*C*), 118.39-117.64 (*C*H$_2$=CH), 82.93/82.18/80.65/79.34 (O*C*H(CH=CH$_2$)CH$_2$O), 71.91-71.22 (CH(CH=CH2)*C*H$_2$OCH), 70.34 (Ar*C*H$_2$O), 65.31/65.11 (CH(CH=CH$_2$)*C*H$_2$OH) ppm.

Synthetic of P5: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (912.8 mg, 8.0 mmol), 1,4-phenylenedimethanol (13.8 mg, 0.10 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (12.4 mg, 0.15 mol% for **1**), DPEphos ligand (12.9 mg, 0.3 mol% for **1**), Et$_3$B (24μL of 1 mol·L^{-1} in THF solution, 0.3 mol% for **1**) were used. **P5** was obtained as light-yellow oil (534.9 mg, 93% yield).

^{1}H NMR (400MHz, CDCl$_3$): δ = 7.32 (4H, Ar*H*), 5.74 (1H, CH$_2$=C*H*), 5.21 (2H, C*H*$_2$=CH), 4.60/4.49 (4H, ArC*H*$_2$O), 3.93 (1H, OC*H*(CH=CH$_2$) CH$_2$O), 3.50 (2H, OCH(CH=CH$_2$) C*H*$_2$O) ppm. ^{13}C NMR (125MHz, CDCl$_3$): δ = 137.91 (Ar*C*), 136.17-134.96 (CH$_2$=*C*H), 127.60 (Ar*C*), 118.14-117.60 (*C*H$_2$=CH), 83.04/82.24/80.67/79.34 (O*C*H(CH=CH$_2$)CH$_2$O), 71.97-71.65 (CH(CH=CH2)*C*H$_2$OCH), 71.19 (Ar*C*H$_2$O), 65.39/65.20 (CH(CH=CH$_2$)*C*H$_2$OH) ppm.

Synthetic of P6: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (1825.6 mg, 16.0 mmol), 1,4-phenylenedimethanol (13.8 mg, 0.10mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (24.8 mg, 0.15 mol% for **1**), DPEphos ligand (25.8 mg, 0.3 mol% for

1), $\mathrm{Et_3B}$ (48 μL of 1 mol·L^{-1} in THF solution, 0.3 mol% for **1**) were used. **P6** was obtained as light-yellow oil (1045.7 mg, 92% yield).

^{1}H NMR (400MHz, $\mathrm{CDCl_3}$): δ = 7.30 (4H, $\mathrm{Ar}\mathit{H}$), 5.74 (1H, $\mathrm{CH_2{=}C}\mathit{H}$), 5.21 (2H, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH}$), 4.60/4.49 (4H, $\mathrm{ArC}\mathit{H}_2\mathrm{O}$), 3.91 (1H, $\mathrm{OC}\mathit{H}\mathrm{(CH{=}CH_2)\ CH_2O}$), 3.49 (2H, $\mathrm{OCH(CH{=}CH_2)\ C}\mathit{H}_2\mathrm{O}$) ppm. ^{13}C NMR (125MHz, $\mathrm{CDCl_3}$): δ = 137.53 ($\mathrm{Ar}\mathit{C}$), 136.18-134.97 ($\mathrm{CH_2{=}}\mathit{C}\mathrm{H}$), 127.65 ($\mathrm{Ar}\mathit{C}$), 118.53-117.58 ($\mathit{C}\mathrm{H_2{=}CH}$), 83.00/82.22/80.67/79.36 ($\mathrm{O}\mathit{C}\mathrm{H(CH{=}CH_2)CH_2O}$), 71.99-71.66 ($\mathrm{CH(CH{=}CH2)}\mathit{C}\mathrm{H_2OCH}$), 71.22 ($\mathrm{Ar}\mathit{C}\mathrm{H_2O}$), 65.38/65.17 ($\mathrm{CH(CH{=}CH_2)}\mathit{C}\mathrm{H_2OH}$) ppm.

Synthetic of P7: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (456.4 mg, 4.0 mmol), cyclohexane-1,4-diyldimethanol (14.4 mg, 0.10 mmol), $\mathrm{Pd_2(dba)_3{\cdot}CHCl_3}$ (6.2 mg, 0.15 mol% for **1**), DPEphos ligand (6.4 mg, 0.3 mol% for **1**), $\mathrm{Et_3B}$ (12 μL of 1 mol·L^{-1} in THF solution, 0.3 mol% for **1**) were used. **P7** was obtained as light-yellow oil (280.3 mg, 95% yield).

^{1}H NMR (400MHz, $\mathrm{CDCl_3}$): δ = 5.74 (1H, $\mathrm{CH_2{=}C}\mathit{H}$), 5.22 (2H, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH}$), 3.95 (1H, $\mathrm{OC}\mathit{H}\mathrm{(CH{=}CH_2)CH_2}$), 3.58-3.43 (H, $\mathrm{(CH_2)_2CC}\mathit{H}_2\mathrm{O}$ & $\mathrm{CH(CH{=}CH_2)\ C}\mathit{H}_2\mathrm{O}$), 1.81/1.50/1.35/0.91 (H, cyclohexane) ppm. ^{13}C NMR (125MHz, $\mathrm{CDCl_3}$): δ = 136.60-134.97 ($\mathrm{CH_2{=}}\mathit{C}\mathrm{H}$), 118.54-117.71 ($\mathit{C}\mathrm{H_2{=}CH}$), 83.02/82.25/80.66 ($\mathrm{O}\mathit{C}\mathrm{H(CH{=}CH_2)\ CH_2}$), 71.88-71.17 ($\mathrm{(CH_2)_2C}\mathit{C}\mathrm{H_2O}$ & $\mathrm{CH(CH{=}CH2)}\mathit{C}\mathrm{H_2O}$), 65.33/65.13 ($\mathrm{CH(CH{=}CH_2)}\mathit{C}\mathrm{H_2OH}$), 38.68/35.61 (cyclohexane, $\mathrm{(CH_2)_2}\mathit{C}$), 29.45/25.84 (cyclohexane, $\mathrm{(}\mathit{C}\mathrm{H_2)_2C}$) ppm.

Synthetic of P8: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (456.4 mg, 4.0 mmol), butane-1,4-diol (9.0 mg, 0.10 mmol), $\mathrm{Pd_2(dba)_3{\cdot}CHCl_3}$ (6.2 mg, 0.15 mol% for **1**), DPEphos ligand (6.4 mg, 0.3 mol% for **1**), $\mathrm{Et_3B}$ (12 μL of 1 mol·L^{-1} in THF solution, 0.3 mol% for **1**) were used. **P8** was obtained as light-yellow oil (269.4 mg, 93% yield).

^{1}H NMR (400MHz, $\mathrm{CDCl_3}$): δ = 5.74 (1H, $\mathrm{CH_2{=}C}\mathit{H}$), 5.21 (2H, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH}$), 3.93 (1H, $\mathrm{OC}\mathit{H}\mathrm{(CH{=}CH_2)CH_2O}$), 3.58-3.42 (H, $\mathrm{CH(CH{=}CH_2)C}\mathit{H}_2\mathrm{O}$ & $\mathrm{CH_2C}\mathit{H}_2\mathrm{OCH(CH{=}CH_2)}$), 1.62 (2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2OCH(CH{=}CH_2)}$) ppm. ^{13}C NMR (125MHz, $\mathrm{CDCl_3}$): δ = 136.51-135.17 ($\mathrm{CH_2{=}}\mathit{C}\mathrm{H}$), 118.16-117.66 ($\mathit{C}\mathrm{H_2{=}CH}$), 83.10/82.31/80.67/80.10 ($OCH(CH=CH_2)CH_2$), 71.96-71.63 ($OCH(CH=CH_2)CH_2O$), 68.85 ($CH_2CH_2OCH(CH=CH_2)$), 65.37 ($OCH(CH=CH_2)CH_2OH$), 29.67/26.57 ($CH_2CH_2OCH(CH=CH_2)$ ppm.

Synthetic of P9: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (456.4 mg, 4.0 mmol), 2,2'-oxybis(ethan-1-ol) (10.6 mg, 0.10 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (6.2 mg, 0.15 mol% for **1**), DPEphos ligand (6.4 mg, 0.3 mol% for **1**), Et_3B (12 µL of 1 $mol \cdot L^{-1}$ in THF solution, 0.3 mol% for **1**) were used. **P9** was obtained as light-yellow oil (262.2 mg, 90% yield).

^1H NMR (400MHz, $CDCl_3$): δ = 5.72 (1H, $CH_2=CH$), 5.21 (2H, $CH_2=CH$), 3.94 (1H, $OCH(CH=CH_2)CH_2O$), 3.58-3.43 (H, $CH(CH=CH_2)CH_2O$ & OCH_2CH_2OCH & OCH_2CH_2OCH) ppm. ^{13}C NMR (125MHz, $CDCl_3$): δ = 136.13-135.17 ($CH_2=CH$), 118.58-117.75 ($CH_2=CH$), 83.04/82.26/80.66 ($OCH(CH=CH_2)CH_2$), 71.96-71.63 ($CH(CH=CH_2)CH_2O$), 71.17 ($CH_2CH_2OCH(CH=CH_2)$), 70.59 ($CH_2CH_2OCH(CH=CH_2)$), 68.31/65.34 ($CH(CH=CH_2)CH_2OH$) ppm.

Synthetic of P10: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (456.4 mg, 4.0 mmol), tert-butyl bis(2-hydroxyethyl)carbamate (20.5 mg, 0.10mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (6.2 mg, 0.15 mol% for **1**), DPEphos ligand (6.4 mg, 0.3 mol% for **1**), Et_3B (12 µL of 1 $mol \cdot L^{-1}$ in THF solution, 0.3 mol% for **1**) were used. **P10** was obtained as light-yellow liquid (259.1 mg, 86% yield).

^1H NMR (400MHz, $CDCl_3$): δ = 5.74 (1H, $CH_2=CH$), 5.22 (2H, $CH_2=CH$), 3.93 (1H, $OCH(CH=CH_2)CH_2O$), 3.57-3.42 (H, $OCH(CH=CH_2)CH_2O$ & NCH_2CH_2OCH & NCH_2CH_2OCH), 1.43 (H, Boc) ppm. ^{13}C NMR (125MHz, $CDCl_3$): δ = 155.39 (Boc), 136.17-134.96 ($CH_2=CH$), 118.50-117.72 ($CH_2=CH$), 82.99/82.21/80.66/79.31 ($OCH(CH=CH_2)CH_2$), 79.31 (Boc), 71.95-71.19 ($CH(CH=CH_2)CH_2O$), 67.33 (NCH_2CH_2OCH), 65.36/65.15 ($CH(CH=CH_2)CH_2OH$), 53.43/47.97 (NCH_2CH_2OCH), 28.46 (Boc) ppm.

Synthetic of P11: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (456.4 mg, 4.0 mmol), 2-methylenepropane-1,3-diol (8.8 mg, 0.10mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (6.2 mg, 0.15 mol% for **1**), DPEphos ligand (6.4 mg, 0.3 mol% for **1**),

$\mathrm{Et_3B}$ (12 µL of 1 mol·$\mathrm{L^{-1}}$ in THF solution, 0.012 mmol, 0.3 mol% for **1**) were used. **P11** was obtained as light-yellow oil (275.0 mg, 95% yield).

^{1}H NMR (400MHz, $\mathrm{CDCl_3}$): δ = 5.74 (1H, $\mathrm{CH_2{=}C}\mathit{H}$), 5.22 (2H, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH}$), 4.06-3.94 (H, $\mathrm{CC}\mathit{H}_2\mathrm{OCH(CH{=}CH_2)}$ & $\mathrm{CH_2OC}\mathit{H}\mathrm{(CH{=}CH_2)CH_2}$), 3.57-3.42 (H, $\mathrm{CH(CH{=}CH_2)C}\mathit{H}_2\mathrm{O}$ & $\mathrm{C(C}\mathit{H}_2\mathrm{)CH_2O}$) ppm. ^{13}C NMR (125MHz, $\mathrm{CDCl_3}$): δ = 143.06 ($\mathit{C}\mathrm{(CH_2)\ CH_2}$), 136.06-134.98 ($\mathrm{CH_2{=}}\mathit{C}\mathrm{H}$), 118.50-117.56 ($\mathit{C}\mathrm{H_2{=}CH}$), 116.04 ($\mathrm{C(}\mathit{C}\mathrm{H_2)CH_2O}$), 82.98/82.21/80.65/79.31 ($\mathrm{O}\mathit{C}\mathrm{H(CH{=}CH_2)CH_2O}$), 71.96-71.19 ($\mathrm{OCH(CH{=}CH2)}\mathit{C}\mathrm{H_2O}$), 69.38 ($\mathrm{C(CH_2)}\mathit{C}\mathrm{H_2OCH}$), 65.33 ($\mathrm{CH(CH{=}CH_2)}\mathit{C}\mathrm{H_2OH}$) ppm.

Synthetic of P12: General procedure was followed. 4-Vinyl-1,3-dioxoian-2-one (VEC, **1**) (456.4 mg, 4.0 mmol), (Z)-but-2-ene-1,4-diol (8.8 mg, 0.10 mmol), $\mathrm{Pd_2(dba)_3{\cdot}CHCl_3}$ (6.2 mg, 0.15 mol% for **1**), DPEphos ligand (6.4 mg, 0.3 mol% for **1**), $\mathrm{Et_3B}$ (12 µL of 1 mol·$\mathrm{L^{-1}}$ in THF solution, 0.3 mol% for **1**) were used. **P12** was obtained as light-yellow oil (277.9 mg, 96% yield).

^{1}H NMR (400MHz, $\mathrm{CDCl_3}$): δ = 5.74 (H, $\mathrm{CH_2{=}C}\mathit{H}$ & $\mathrm{C}\mathit{H}\mathrm{CH_2OCH(CH{=}CH_2)}$), 5.22 (2H, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH}$), 4.08-3.93 (H, $\mathrm{CHC}\mathit{H}_2\mathrm{OCH(CH{=}CH_2)}$ & $\mathrm{CHCH_2OC}\mathit{H}\mathrm{(CH{=}CH_2)}$), 3.50 (2H, $\mathrm{CH(CH{=}CH_2)C}\mathit{H}_2\mathrm{O}$) ppm. ^{13}C NMR (125MHz, $\mathrm{CDCl_3}$): δ = 136.02-134.94 ($\mathrm{CH_2{=}}\mathit{C}\mathrm{H}$), 129.33 ($\mathit{C}\mathrm{HCH_2OCH(CH{=}CH_2)}$), 118.60-117.77 ($\mathit{C}\mathrm{H_2{=}CH}$), 83.05/82.28/80.66/79.59 ($\mathrm{O}\mathit{C}\mathrm{H(CH{=}CH_2)CH_2O}$), 71.87-71.16 ($\mathrm{OCH(CH{=}CH_2)}\mathit{C}\mathrm{H_2O}$), 65.35 ($\mathrm{CH}\mathit{C}\mathrm{H_2OCH(CH{=}CH_2)}$), 64.50 ($\mathrm{CH(CH{=}CH_2)}\mathit{C}\mathrm{H_2OH}$) ppm.

3. Typical synthesis of vinyl-functional thermoplastic polyurethane (VFTPU)

The polymer was synthesized by the traditional two-step solution polymerization. Briefly, the stoichiometry of **P4**/MDI/1,4-butanediol was 1:2:1. Before the reaction, **P4** (1.0089 g, 0.5 mmol) was evacuated at 70 °C for 2 h to remove moisture. MDI (0.2502 g, 1.0 mmol) was then added into the flask dropwise, followed by the addition of DBTDL (0.1304 g, 1 wt%) as a catalyst. THF was added once the viscosity of the reaction solution increased. The prepolymer reaction was carried out for 3 h at 70 °C. Afterward, 1,4-butanediol (0.0451 g, 0.5 mmol) as the chain extender was added into the solution and stirred for another 2h at 70°C under nitrogen protection. The resulting polymer was washed by methanol for further purification, then dried.

4. The procedure for thiol-ene click reaction

To test the reactivity of the allyl component toward 1-dodecanethiol, a model reaction was carried out. In order to ensure the complete reaction of vinyl-functional groups in PVEG **P4**, 1-dodecanethiol was added according to the stoichiometry 1:5 of vinyl/sulfhydryl (C=C/-SH). In a scintillation vial, 1-dodecanethiol (0.6072 g, 30 equiv), PVEG **P4** (0.2017 g, 1 equiv), and 2-Hydroxy-2-methylpropiophenone as a photoinitiator (0.0081 g, 1 wt%) were mixed well. Then, the samples were irradiated with UV lamps (365 nm, 300mW·cm^{-2}) for 60 seconds. Finally, the sample was removed by short silica gel column to afford thioether-functional polyglycol (TEFPG). The TEFPG were tested by ^{1}H NMR.

5. MALDI-TOF MS spectrum of vinyl-functional polyvinylethylene glycols (PVEG)

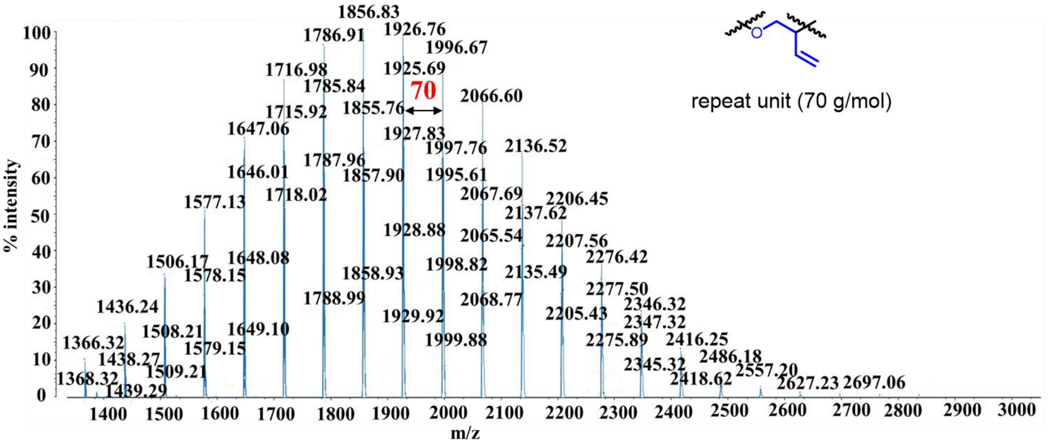


Figure S1. MALDI-TOF MS spectrum of PVEG (**P4**).

6. Copies of ^{1}H NMR and ^{13}C NMR spectrums and GPC chromatograms of PVEGs

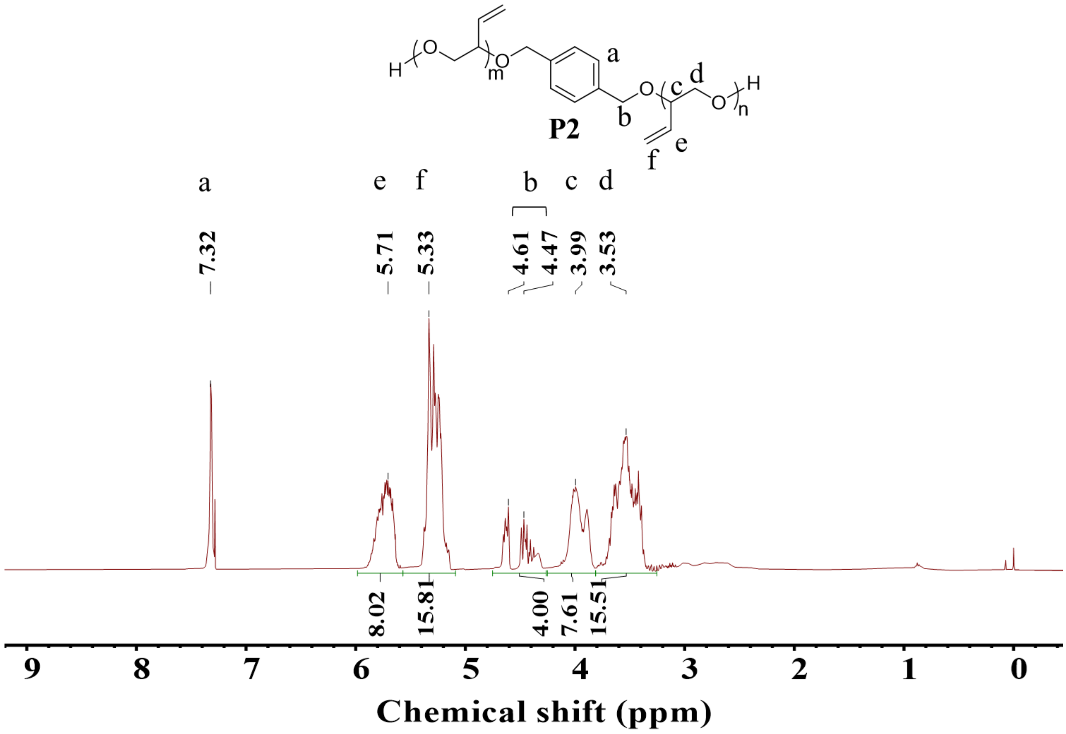


Figure S2. ^{1}H NMR spectrum of **P2** in $CDCl_3$ (400 MHz).

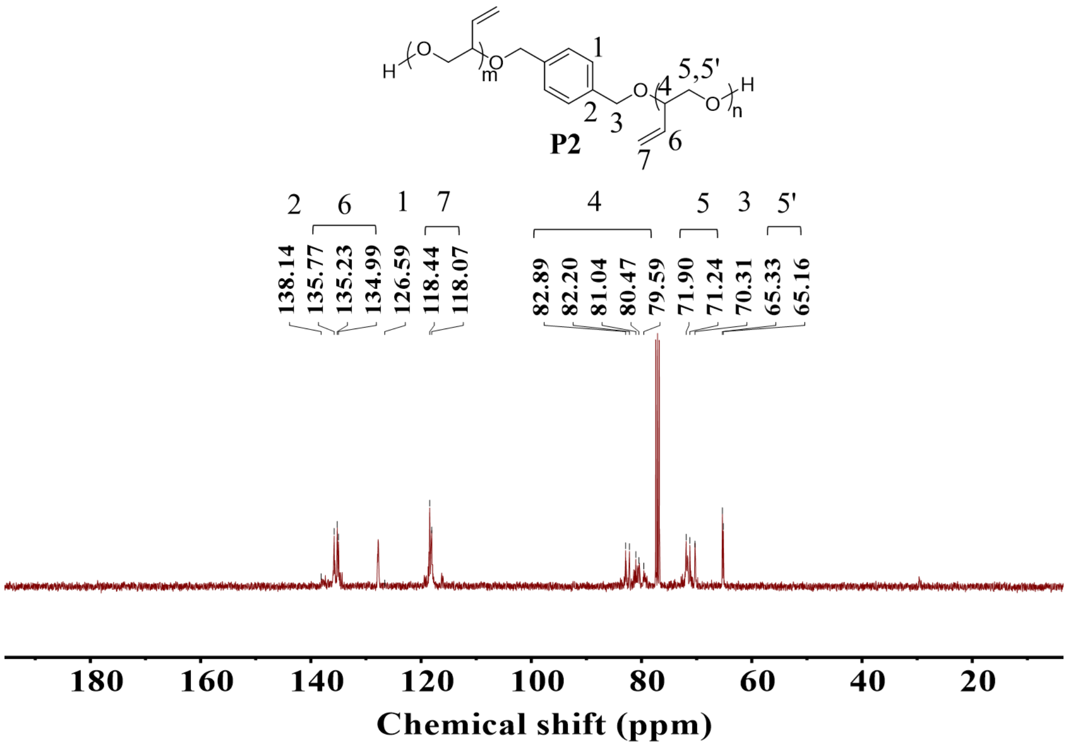


Figure S3. ^{13}C NMR spectrum of **P2** in $CDCl_3$ (125 MHz).

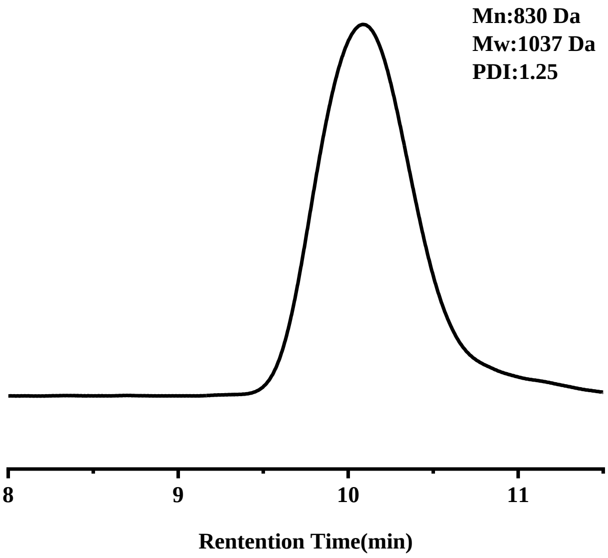


Figure S4. GPC chromatogram of **P2**.

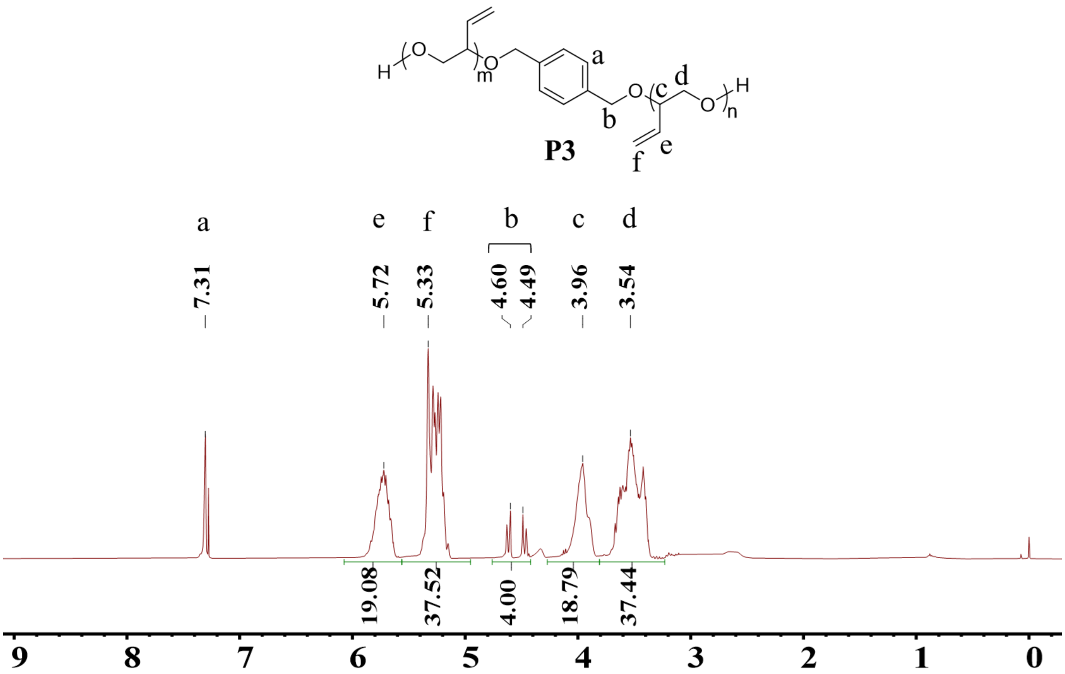


Figure S5. ^{1}H NMR spectrum of **P3** in $CDCl_3$ (400 MHz).

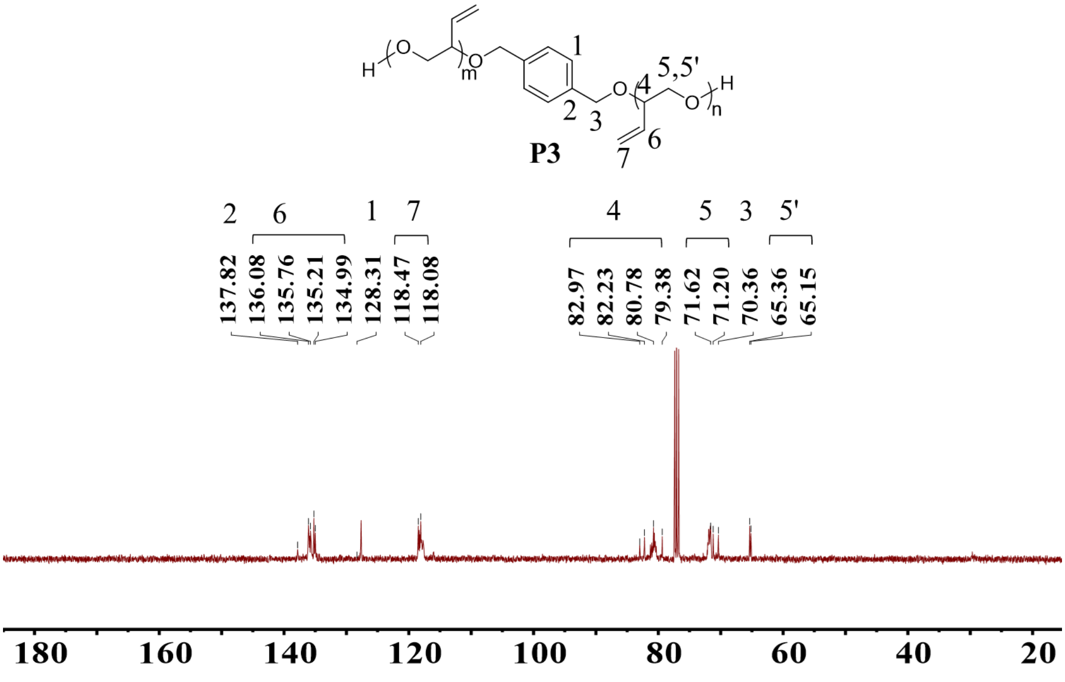


Figure S6. ^{13}C NMR spectrum of **P3** in $CDCl_3$ (125 MHz).

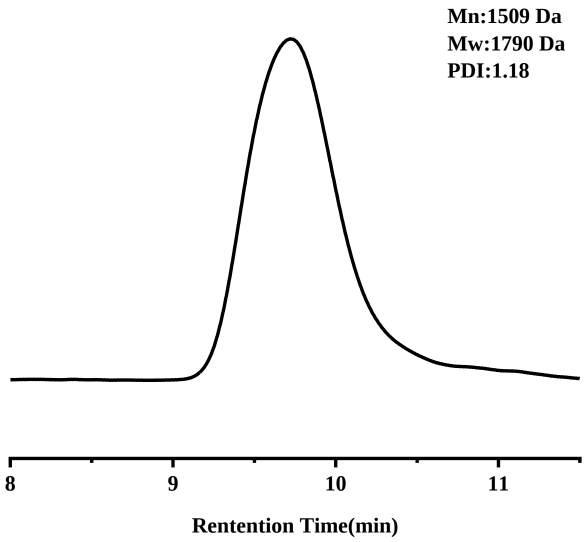


Figure S7. GPC chromatogram of **P3**.

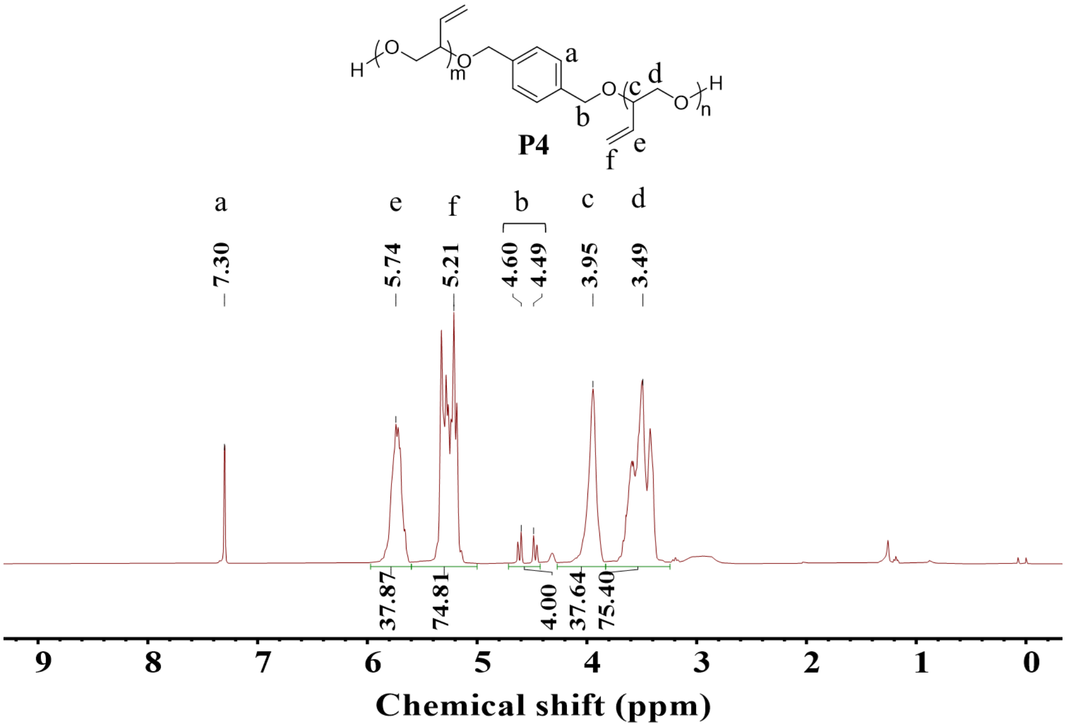


Figure S8. ^{1}H NMR spectrum of **P4** in $CDCl_3$ (400 MHz).

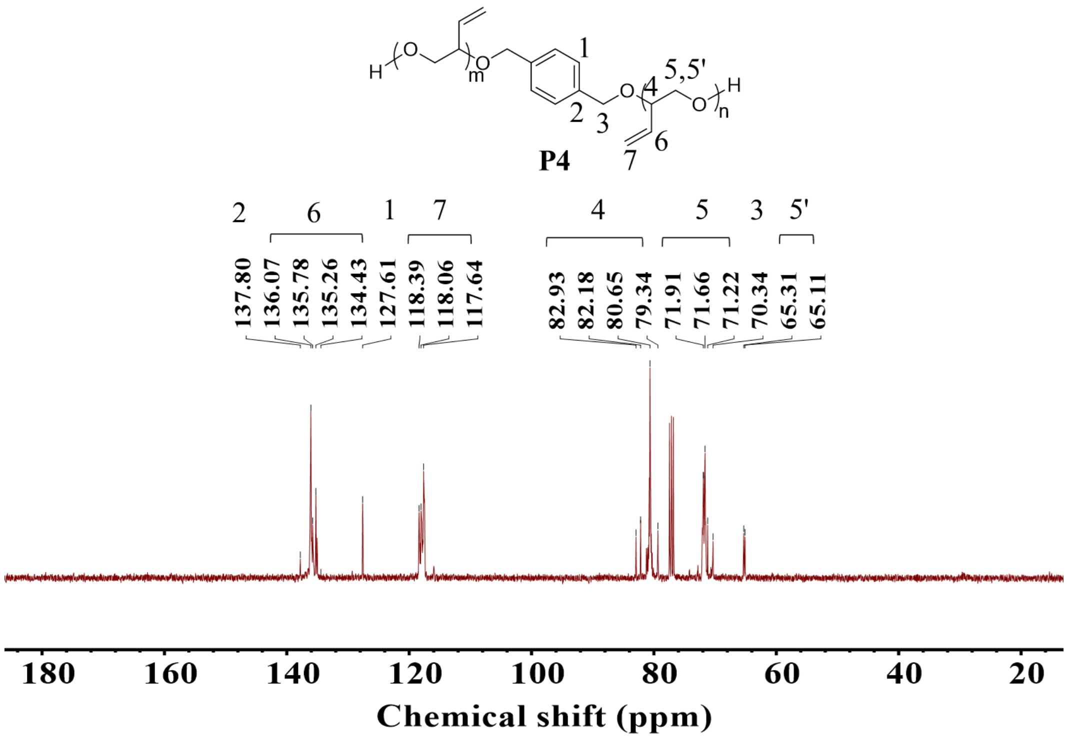


Figure S9. ^{13}C NMR spectrum of **P4** in $CDCl_3$ (125 MHz).

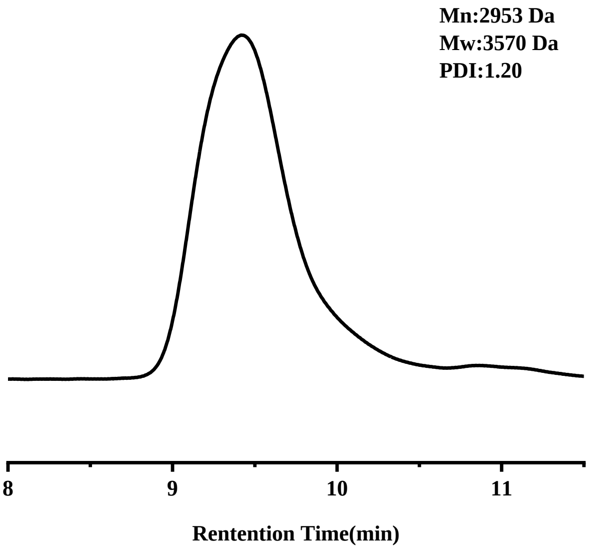


Figure S10. GPC chromatogram of **P4**.

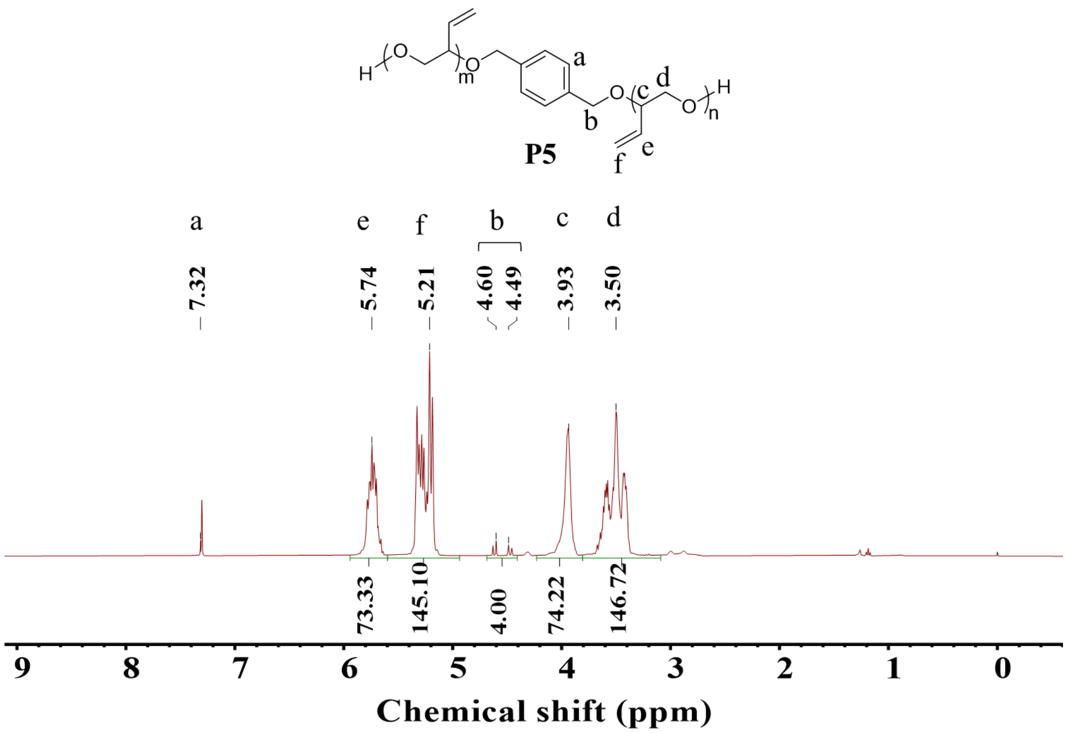


Figure S11. ^{1}H NMR spectrum of **P5** in $CDCl_3$ (400 MHz).

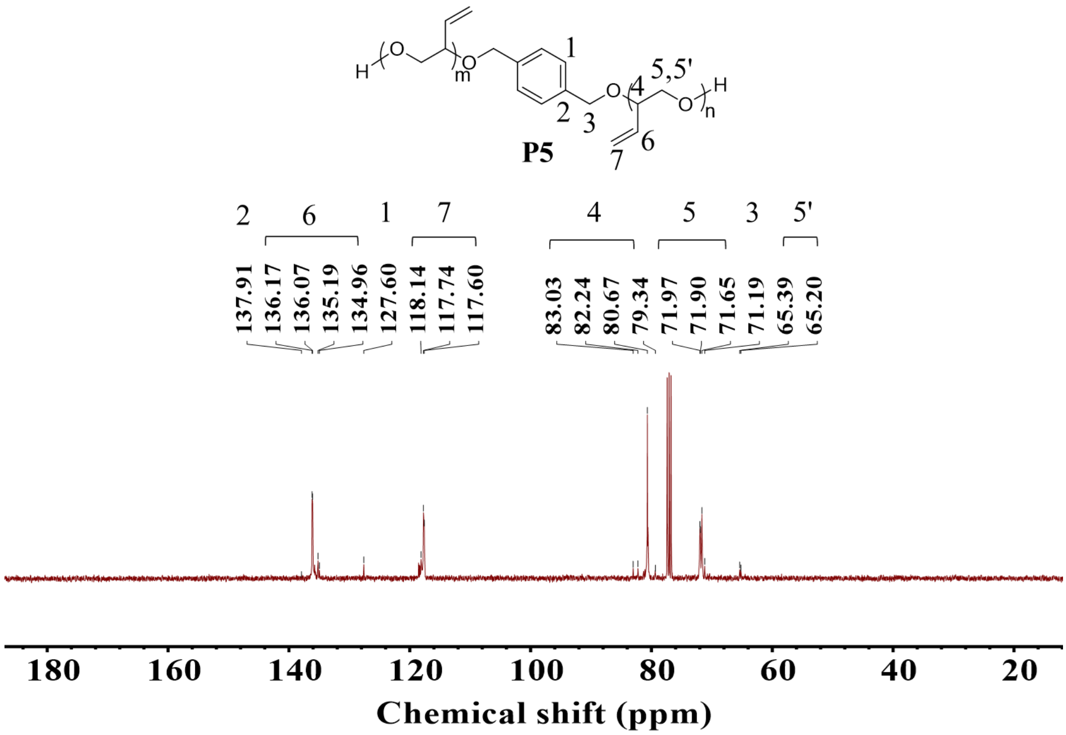


Figure S12. ^{13}C NMR spectrum of **P5** in $CDCl_3$ (125 MHz).

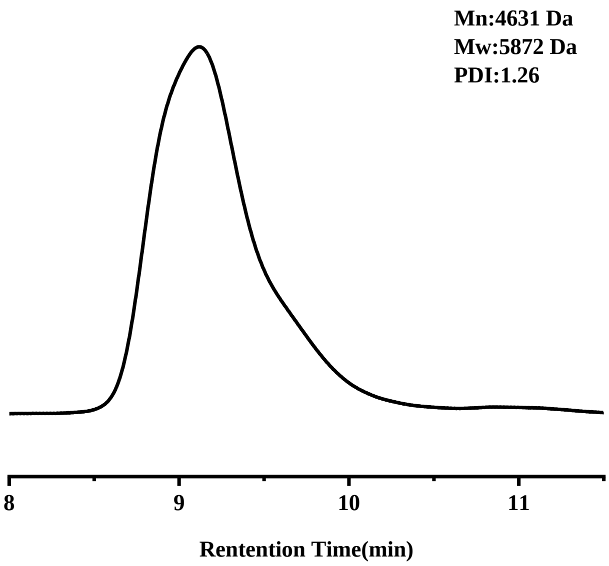


Figure S13. GPC chromatogram of **P5**.

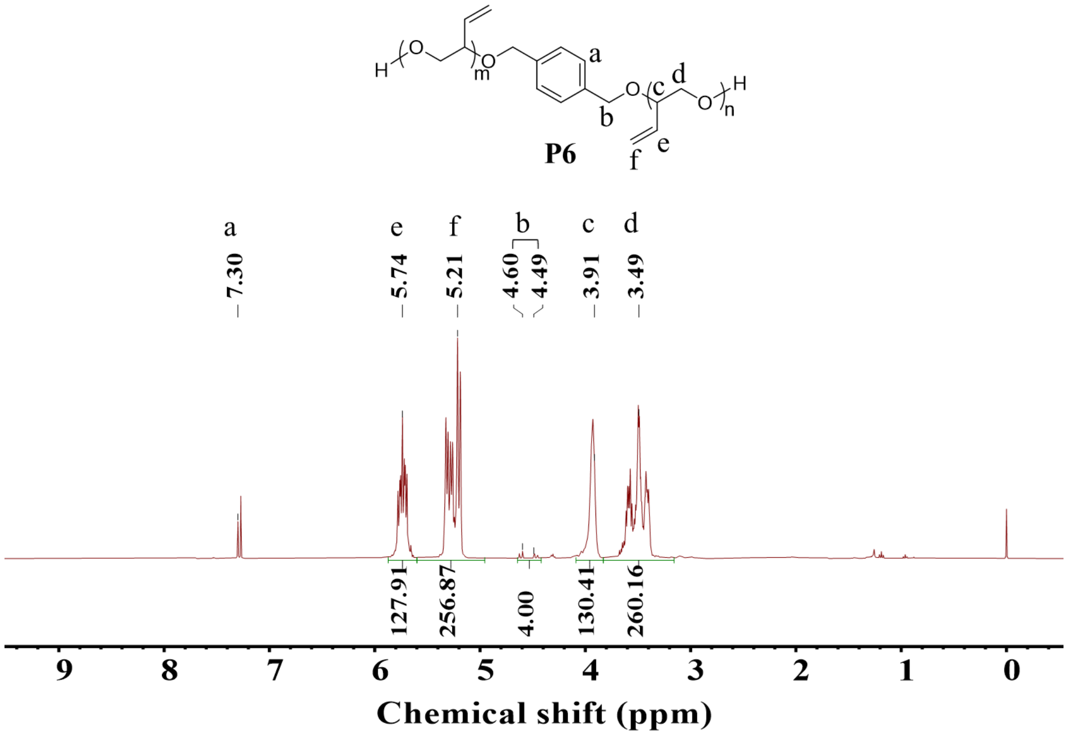


Figure S14. ^{1}H NMR spectrum of **P6** in $CDCl_3$ (400 MHz).

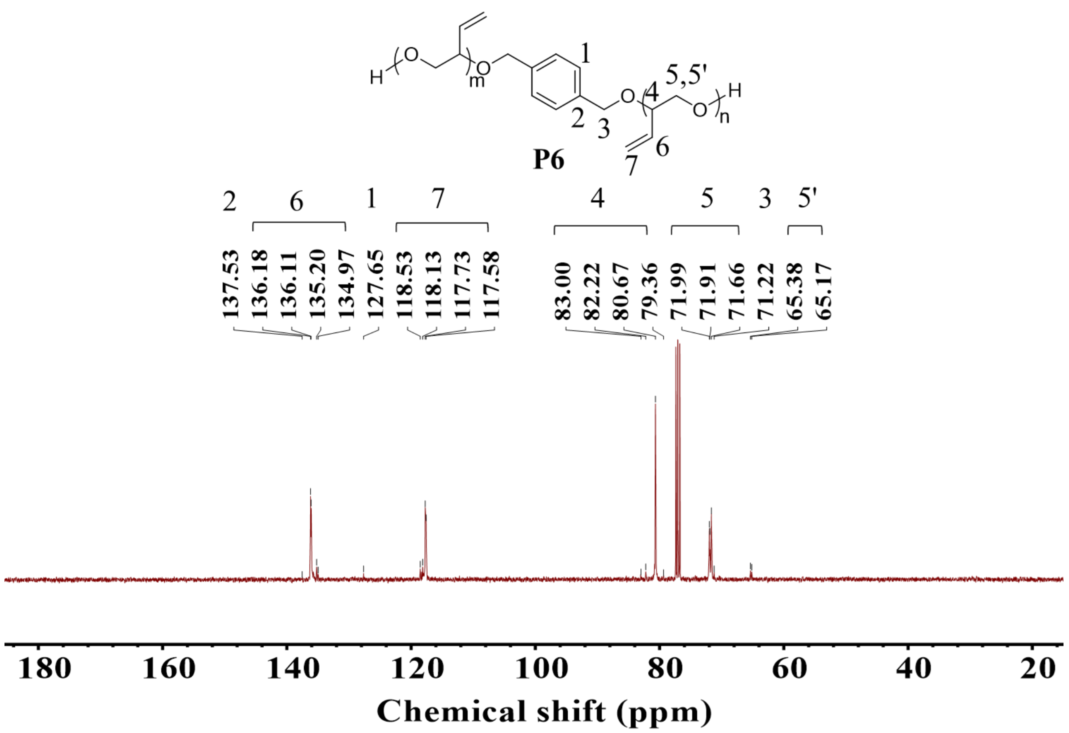


Figure S15. ^{13}C NMR spectrum of **P6** in $CDCl_3$ (125 MHz).

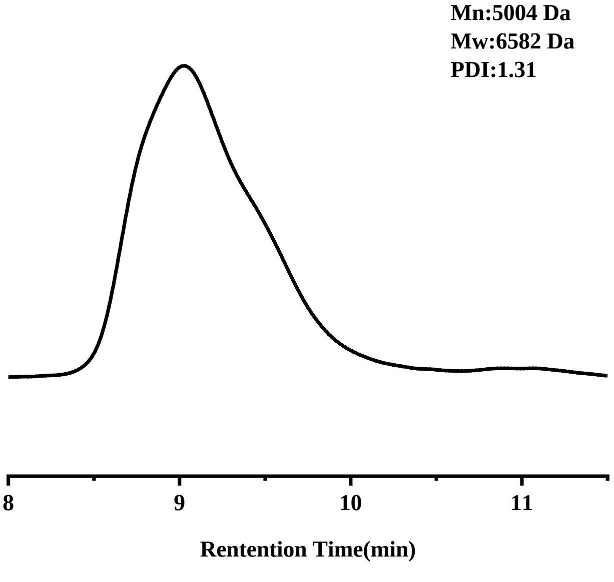


Figure S16. GPC chromatogram of **P6**.

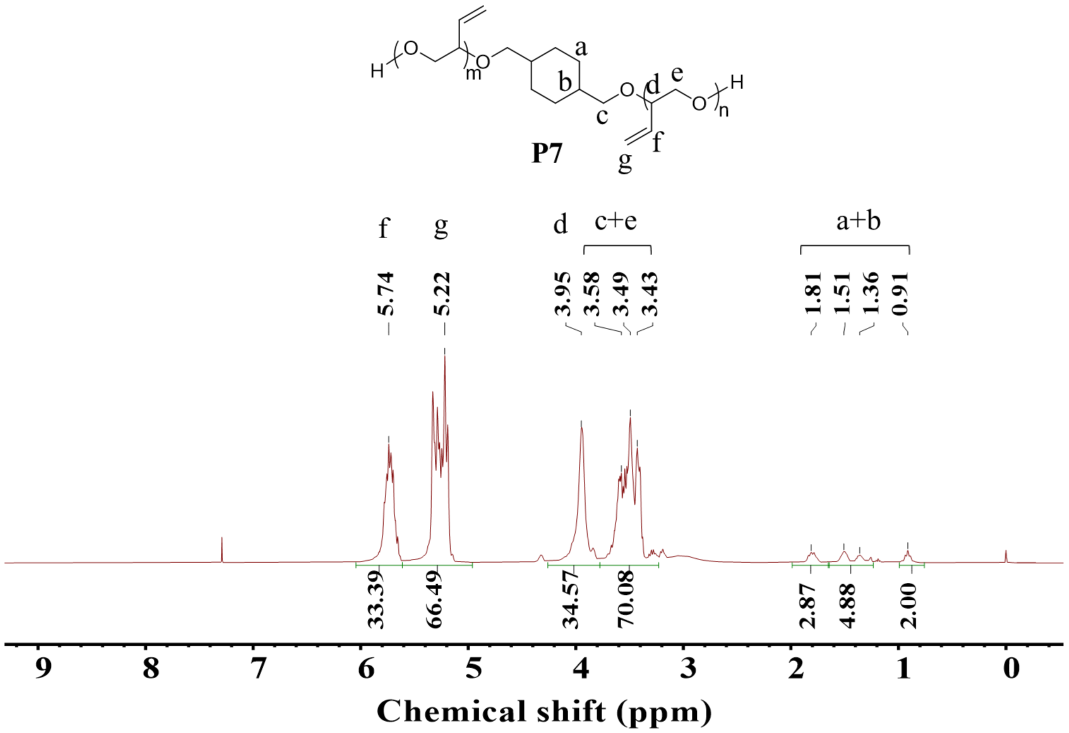


Figure S17. ^{1}H NMR spectrum of **P7** in $CDCl_3$ (400 MHz).

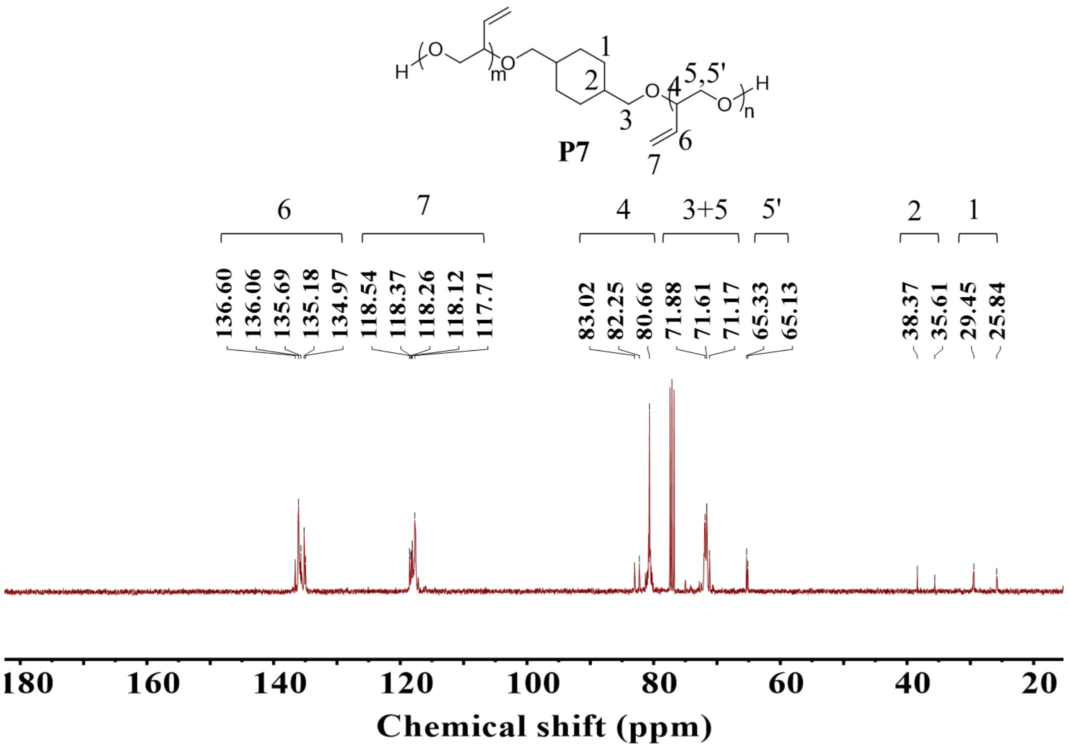


Figure S18. ^{13}C NMR spectrum of **P7** in $CDCl_3$ (125 MHz).

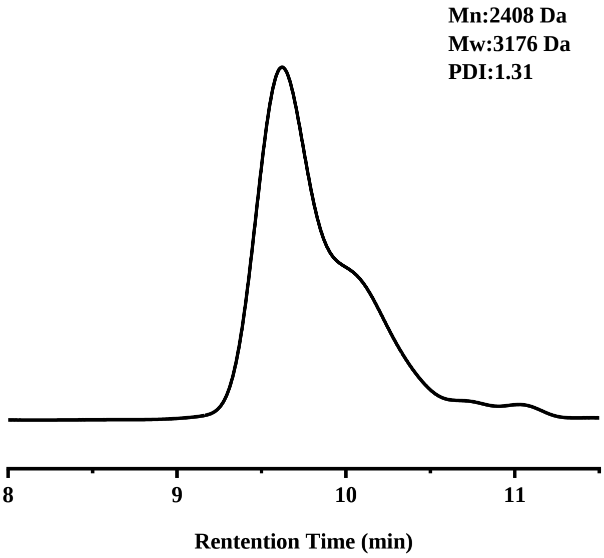


Figure S19. GPC chromatogram of **P7**.

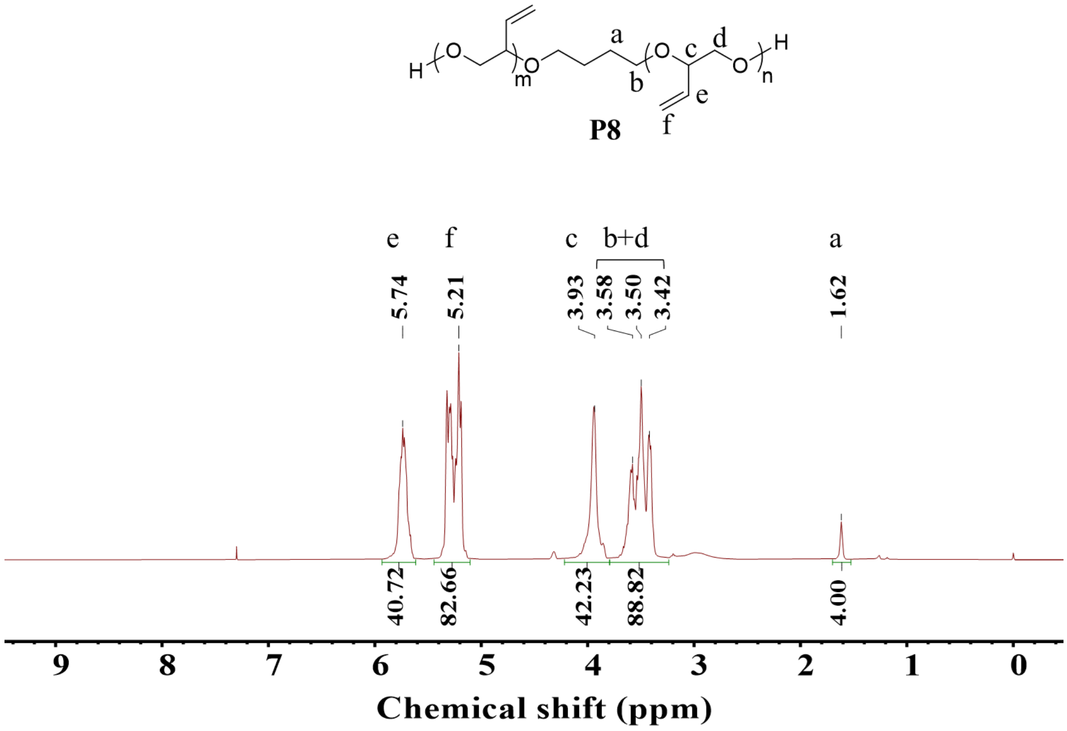


Figure S20. ^{1}H NMR spectrum of **P8** in $CDCl_3$ (400 MHz).

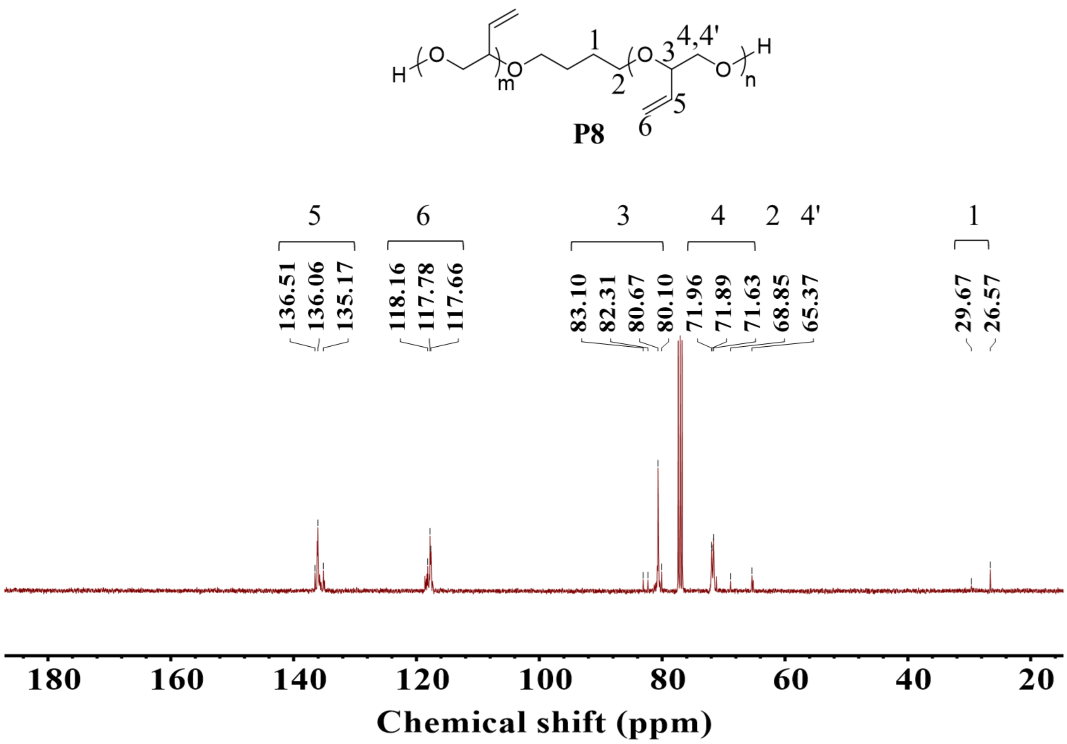


Figure S21. ^{13}C NMR spectrum of **P8** in $CDCl_3$ (125 MHz).

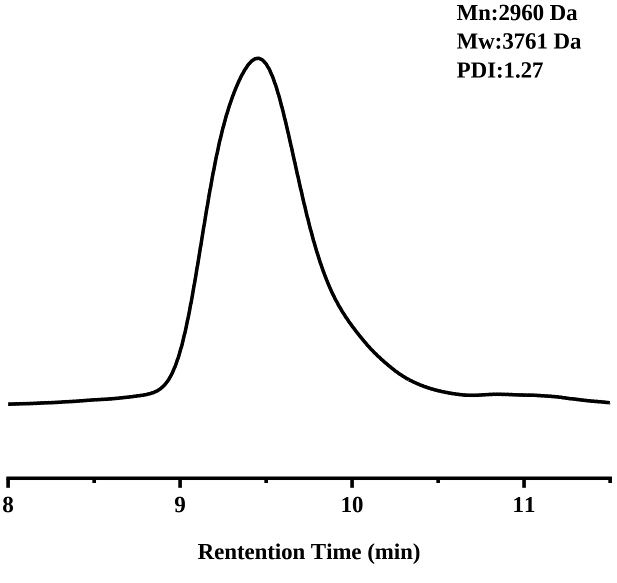


Figure S22. GPC chromatogram of **P8**.

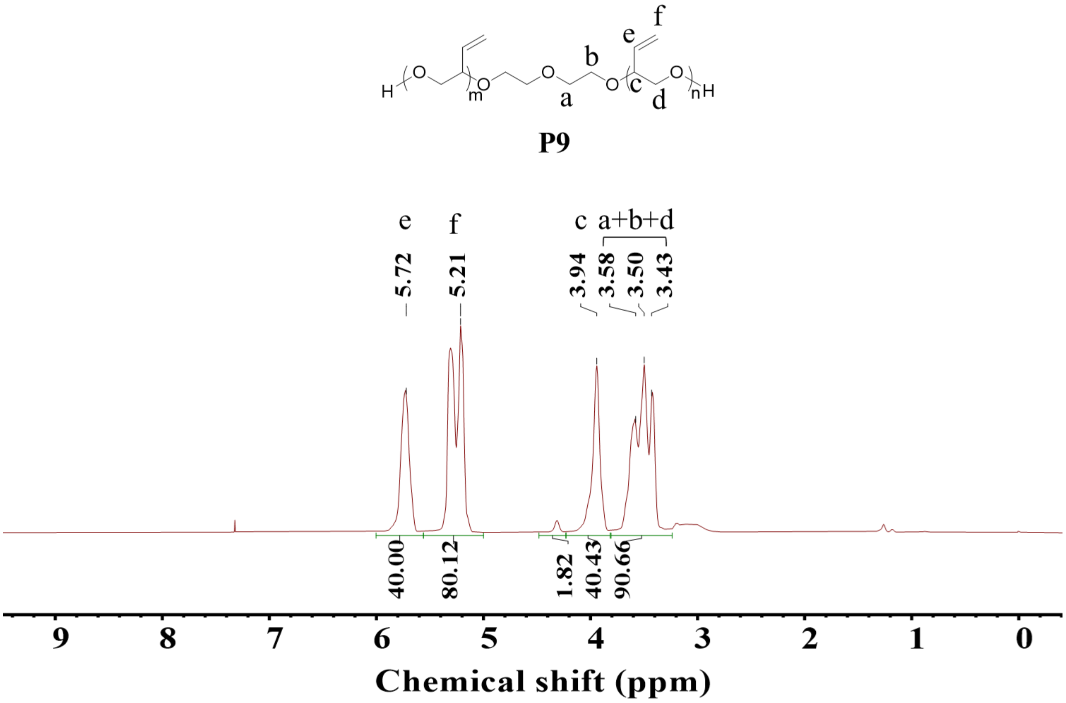


Figure S23. ^{1}H NMR spectrum of **P9** in $CDCl_3$ (400 MHz).

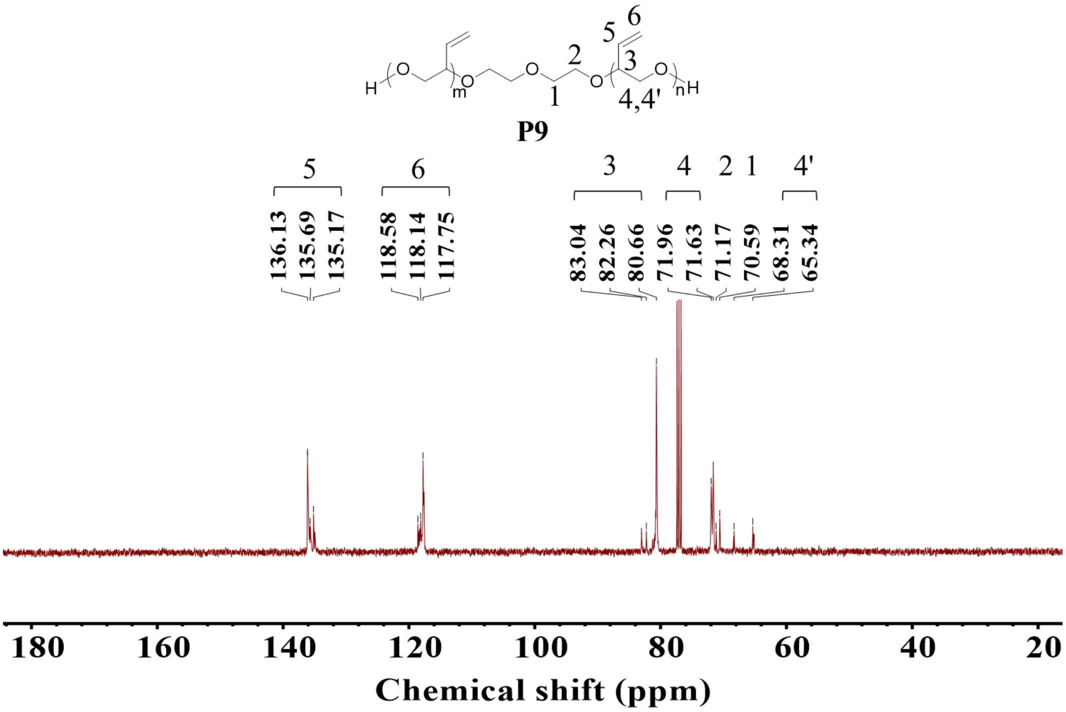


Figure S24. ^{13}C NMR spectrum of **P9** in $CDCl_3$ (125 MHz).

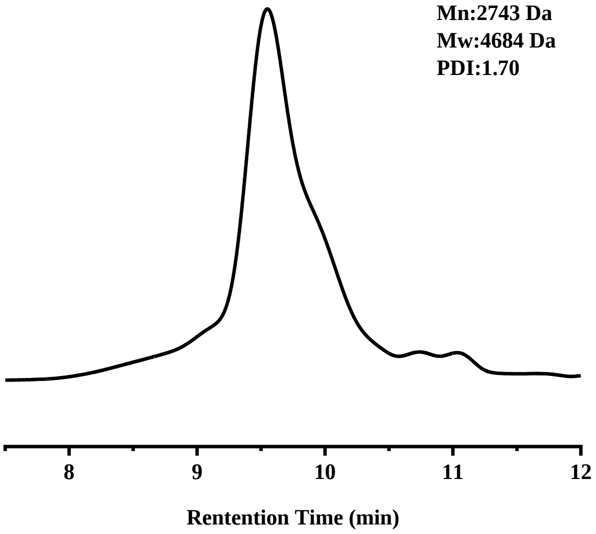


Figure S25. GPC chromatogram of **P9**.

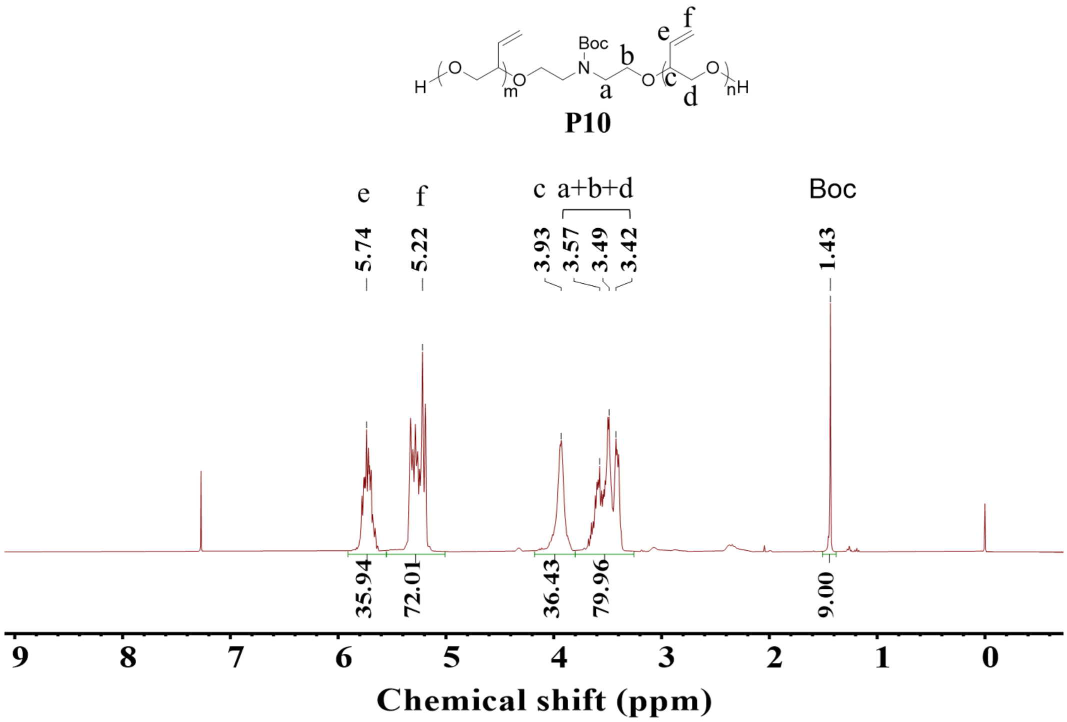


Figure S26. ^{1}H NMR spectrum of **P10** in $CDCl_3$ (400 MHz).

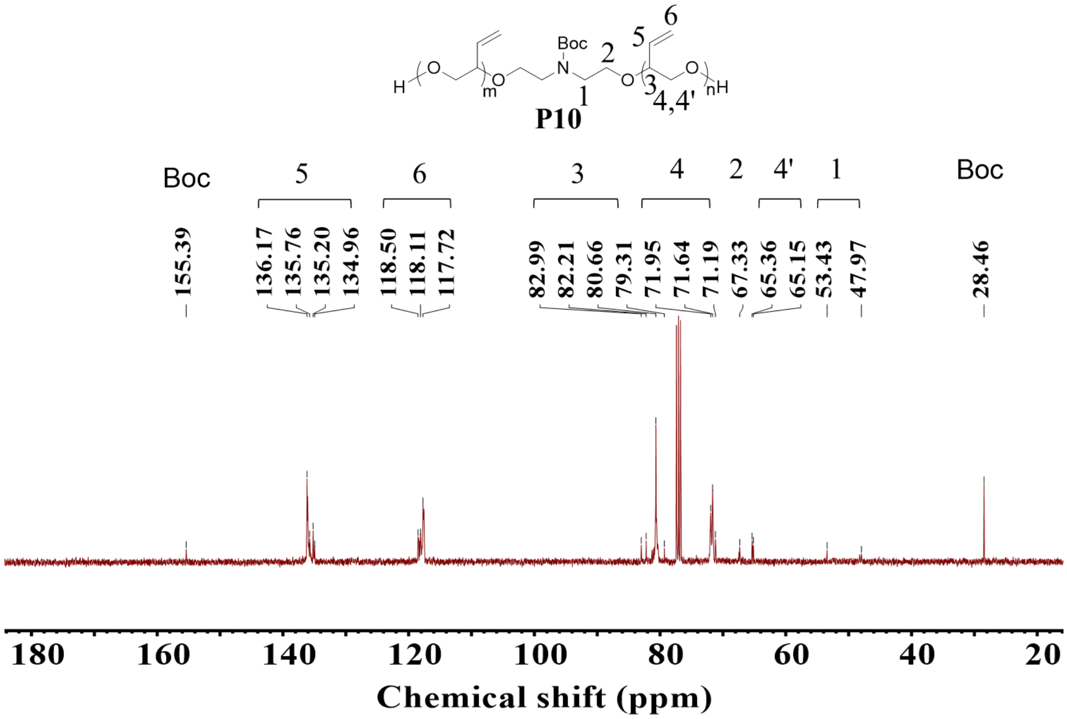


Figure S27. ^{13}C NMR spectrum of **P10** in $CDCl_3$ (125 MHz).

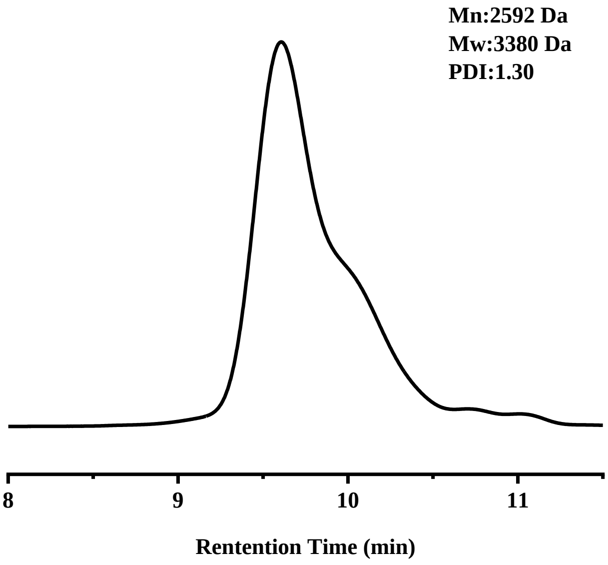


Figure S28. GPC chromatogram of **P10**.

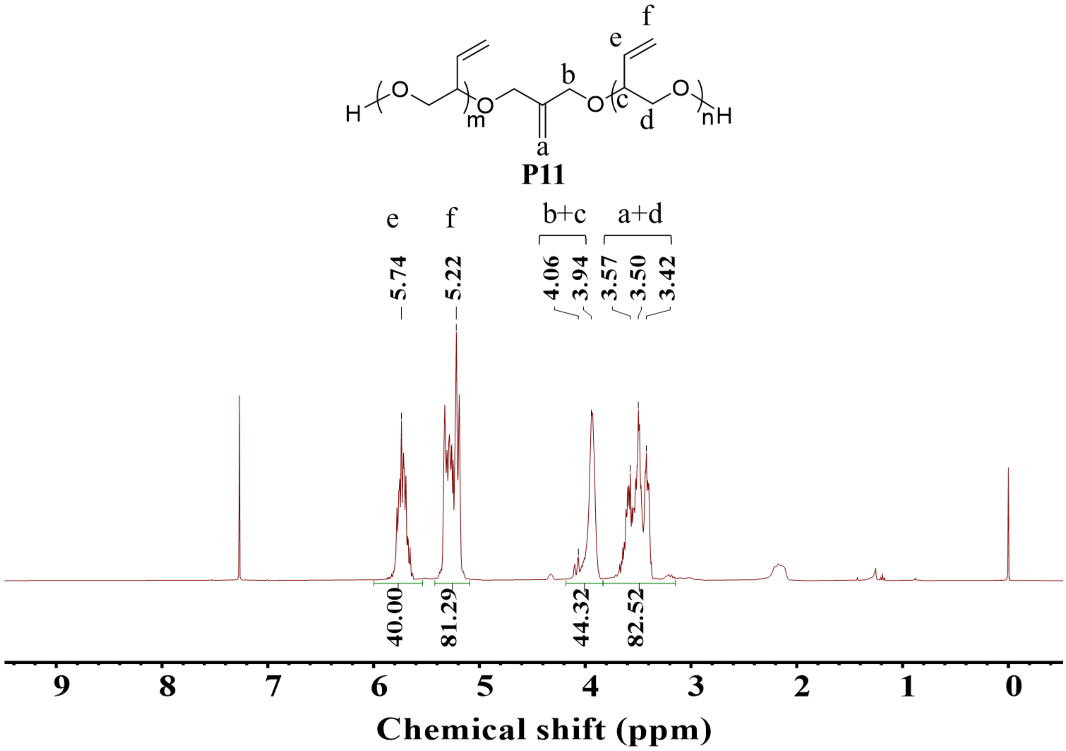


Figure S29. ^{1}H NMR spectrum of **P11** in $CDCl_3$ (400 MHz).

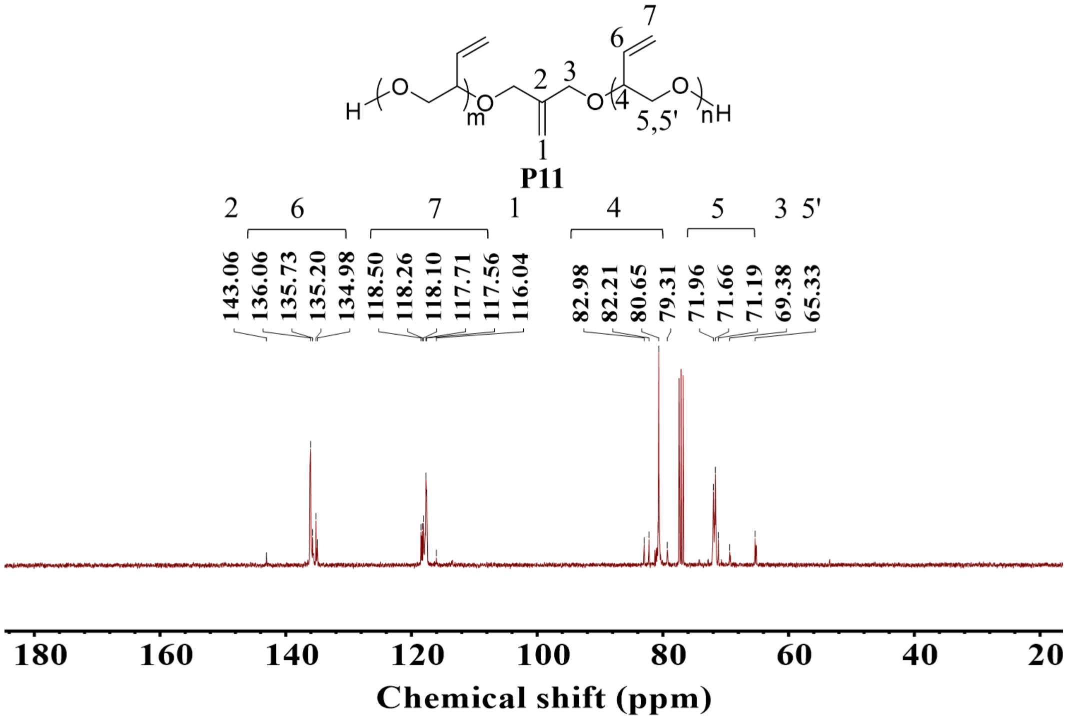


Figure S30. ^{13}C NMR spectrum of **P11** in $CDCl_3$ (125 MHz).

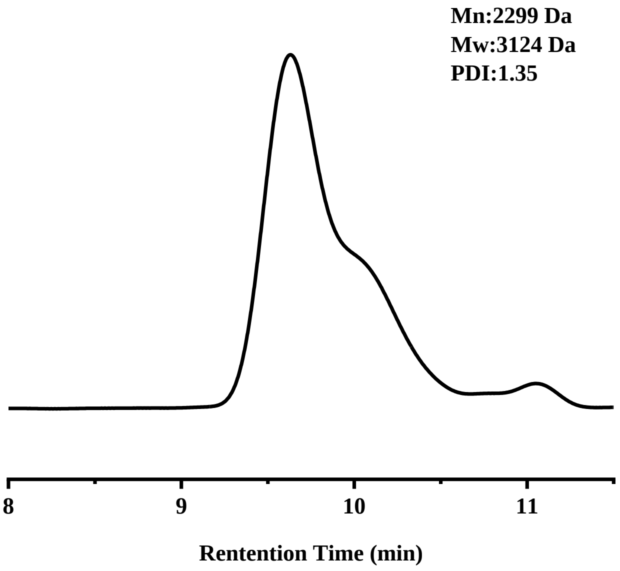


Figure S31. GPC chromatogram of **P11**.

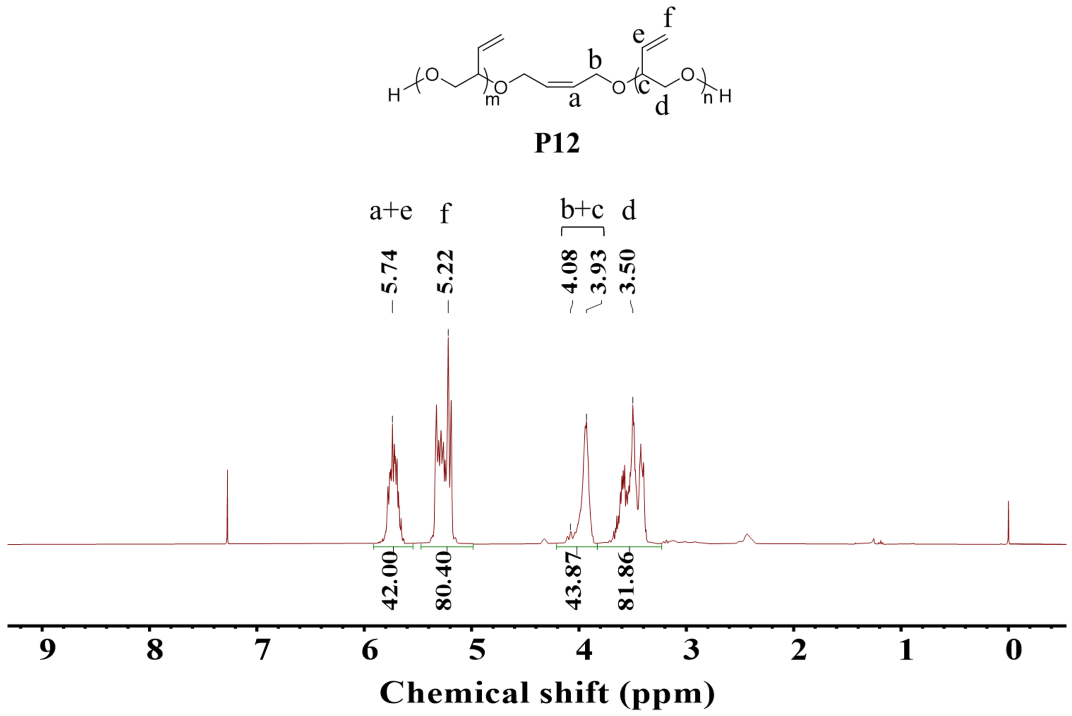


Figure S32. ^{1}H NMR spectrum of **P12** in $CDCl_3$ (400 MHz).

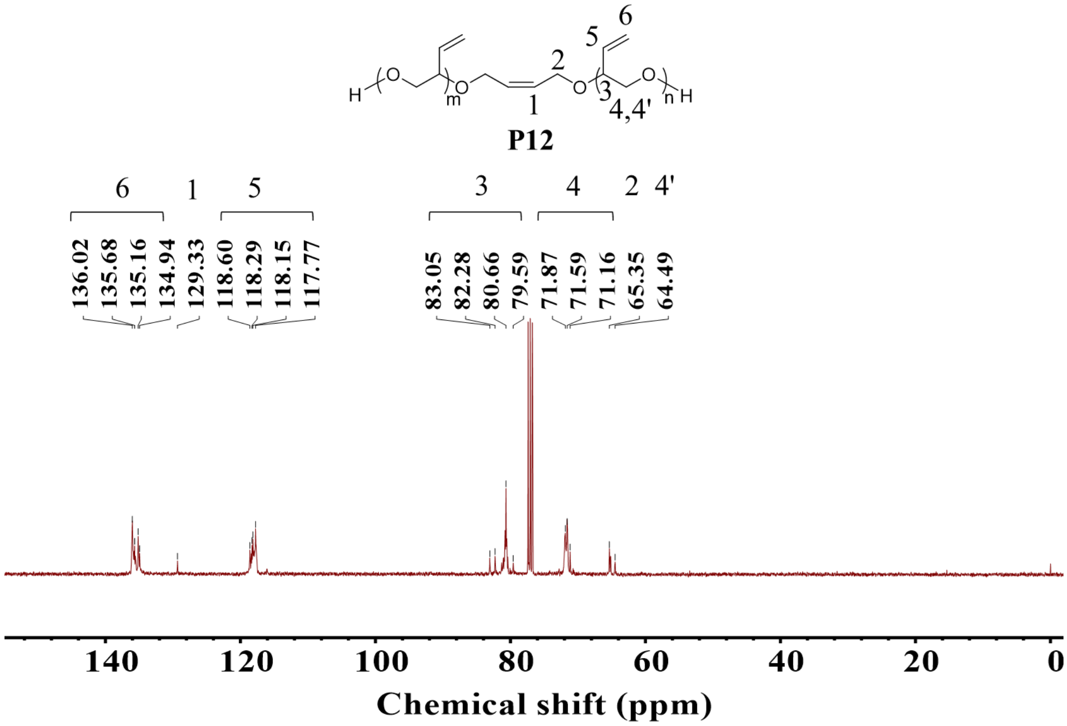


Figure S33. ^{13}C NMR spectrum of **P12** in $CDCl_3$ (125 MHz).

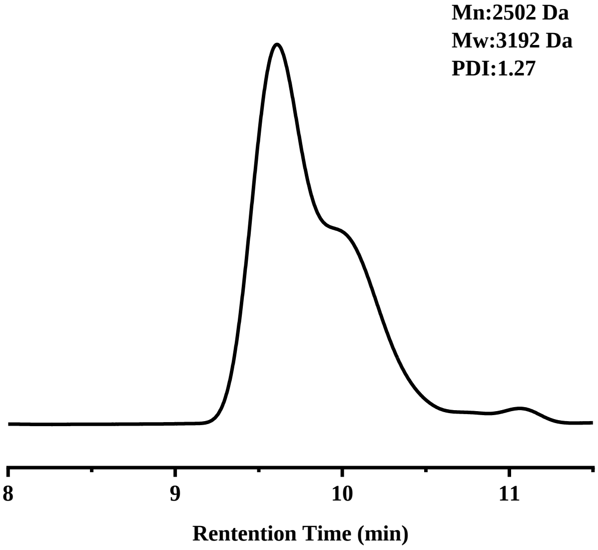


Figure S34. GPC chromatogram of **P12**.

7. Characterization of vinyl-functional thermoplastic polyurethane (VFTPU)

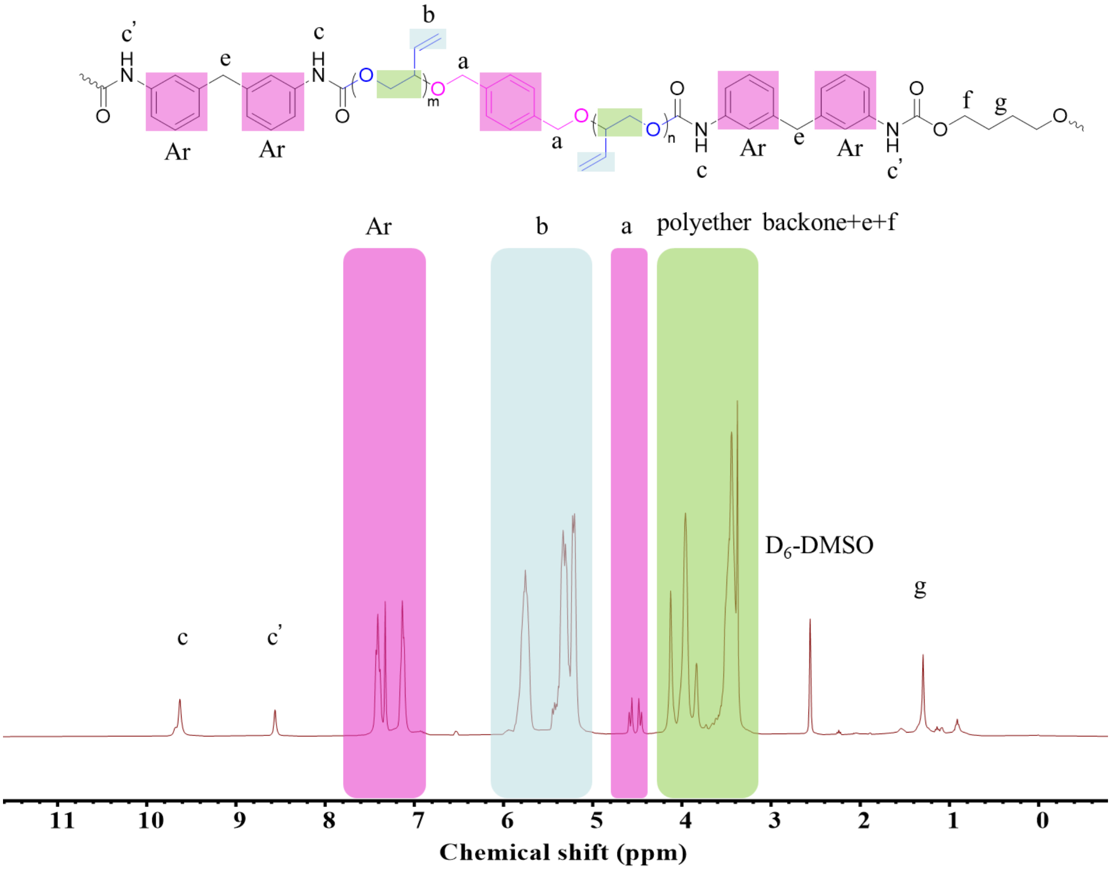


Figure S35. ^{1}H NMR spectrum (D$_6$-DMSO, 400 MHz) of VFTPU

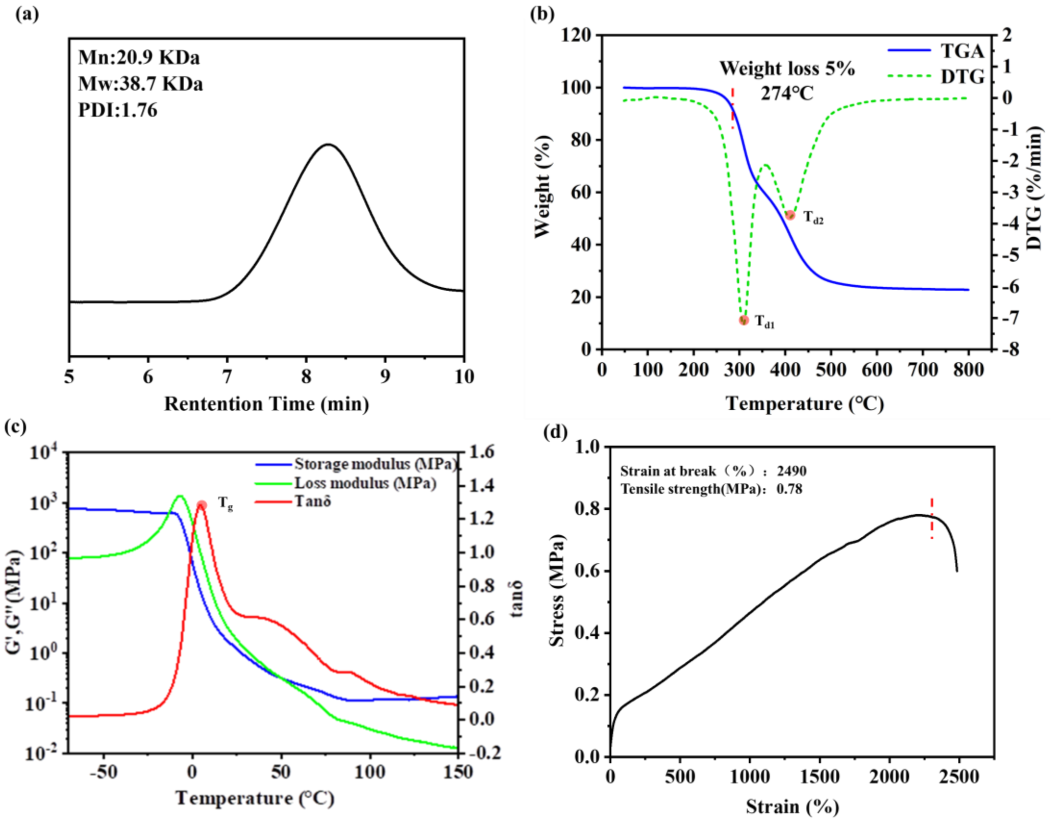


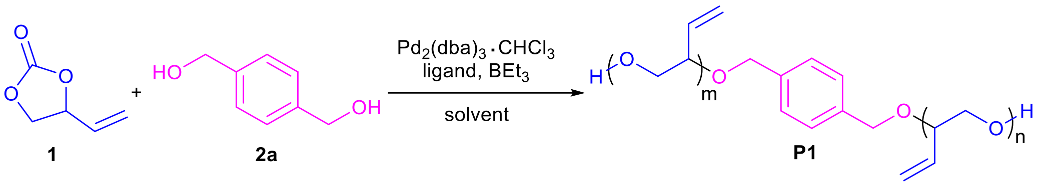
Figure S36. GPC chromatogram (a), thermogravimetric curve (b), dynamic mechanical analysis curve (c), and stress-strain curves (d) of VFTPU.

Table S1. Physical properties of VFTPU.

sample	T_{d1}[a] (°C)	T_{d2}[a] (°C)	Tg [b] (°C)
VFTPU	310	420	4.5

[a] measured by thermogravimetric analysis (TGA); [b] measured by dynamic mechanical analysis.

8. Optimization of the detailed polymerization conditions[a]



entry	ligand	solvent	Temp. (°C)/time (h)	Yield (%)[b]
1	PPh_3	THF	20/24	0
2	PCy_3	THF	20/24	0
3	$P(OPh)_3$	THF	20/24	0
4	P(2-furanyl)$_3$	THF	20/12	81
5	dppp	THF	20/12	5
6	dppb	THF	20/12	20
7	BINAP	THF	20/12	80
8	DPEphos	THF	20/2	86
9	DPEphos	1,4-dioxane	20/2	61
10	DPEphos	MTBE	20/2	75
11	DPEphos	toluene	20/2	78
12	DPEphos	CH_2Cl_2	20/2	73
13	DPEphos	CH_3CN	20/2	76
14	DPEphos	THF	10/2	95
15	DPEphos	THF	30/2	89
16	DPEphos	THF	50/2	91
17	DPEphos	THF	70/2	92
18[c]	DPEphos	THF	10/2	95
19[d]	DPEphos	THF	10/12	91
20[e]	DPEphos	THF	10/24	45

[a] Reaction conditions: **1** (1.0 mmol, 10 equiv.), **2a** (0.1 mmol, 1 equiv.), $Pd_2(dba)_3 \cdot CHCl_3$ (0.2 mol% for **1**), ligand (0.8 mol% for monophosphines; 0.4 mol% for bisphosphines), BEt_3 (0.4 mol% for 1), solvent (1.0 mL). [b] Isolated yields. [c] The reaction carried out using $Pd_2(dba)_3 \cdot CHCl_3$ (0.15 mol% for **1**), DPEphos (0.3 mol% for **1**) and BEt_3 (0.3 mol% for **1**) under otherwise identical conditions. [d] The reaction carried out using $Pd_2(dba)_3 \cdot CHCl_3$ (0.1 mol% for **1**), DPEphos (0.2 mol% for **1**) and BEt_3 (0.2 mol% for **1**) under otherwise identical conditions. [e] The reaction carried out using $Pd_2(dba)_3 \cdot CHCl_3$ (0.05 mol% for **1**), DPEphos (0.1 mol% for **1**) and BEt_3 (0.1 mol% for **1**) under otherwise identical conditions. BINAP, 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthalene; dppb, 1,4-bis(diphenylphosphanyl)butane; dppp, 1,3-bis(diphenylphosphanyl)propane; MTBE, methyl tert-butyl ether.