Supporting Information

Catalyst-Free Aziridine-Based Step-Growth Polymerization: A Facile Approach to Optically Active Poly(Sulfonamide Amine)s and Poly(Sulfonamide Dithiocarbamate)s

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1 Experimental Section

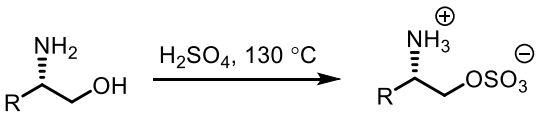
1.1 Materials

N,N′-Diethyl-1,6-diaminohexane (98%), *N,N′*-dimethyl-1,2-ethanediamine (98%), *N,N′*-dimethyl-1,3-propanediamine (98%), *N,N′*-bis(2-hydroxyethyl)ethylendiamine (98%), *p*-phenylenediamine (98%), (1R,2R)-(+)-1,2-diphenylethylenediamine (97%), 2-aminocyclohexanol (98%), 4,4'-bis(chlorosulfonyl)diphenyl ether (97%), *L*-phenylglycinol (98%), (S)-(+)-2-amino-1-propanol (98%), (S)-(+)-2-amino-3-methyl-1-butanol (97%), sulfuric acid (98%), sodium hydroxide (98%) were purchased commercially and used without further purification. Tetrahydrofuran (THF), toluene (Tol) were distilled from sodium benzophenone before use. Dichloromethane, acetonitrile, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), triethylamine (Et_3N), and carbon disulfide (98%) were dried over CaH_2 and distilled before use. 2-Methyl-1-tosylaziridine (TsMAz) was prepared according to the reported procedure.[1]

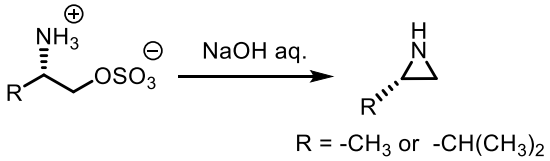
1.2 Characterizations

Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were recorded with a Bruker AVANCE III 400 spectrometer. Size exclusion chromatography (SEC) measurements were carried out in DMF with 0.01 M LiBr at 60 °C with the Agilent 1260 Infinity II instrument, equipped with two PLgel 10 μm MIXED-B columns and a differential refractive index (DRI) detector. The system was calibrated with poly(*γ*-benzyl-*L*-glutamate) standards at a flow rate of 1.0 mL/min. FT-IR spectra were obtained on a Thermo-Fisher Nicolet 6700 spectrometer. Thermal stabilities were evaluated by performing the thermogravimetric analysis (TGA) on an STA 449 F5 Jupiter instrument under dry nitrogen at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC3 calorimeter. Two scanning cycles of heating-cooling were performed in the temperature range from 25 to 250 °C with heating rates of 10 °C/min under nitrogen. T_g was determined from the second heating run. Scanning electron microscopy (SEM) was performed on a TESCAN CLARA scanning electron microscope with an Xplore30 energy dispersive spectroscopy (EDS). The electrospinning apparatus (ET-3556H) was purchased from Beijing Ucalery Technology Company, China.

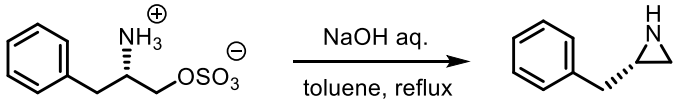
1.3 General Procedure for the Synthesis of Chiral Bis(*N*-sulfonyl aziridine)[2, 3]



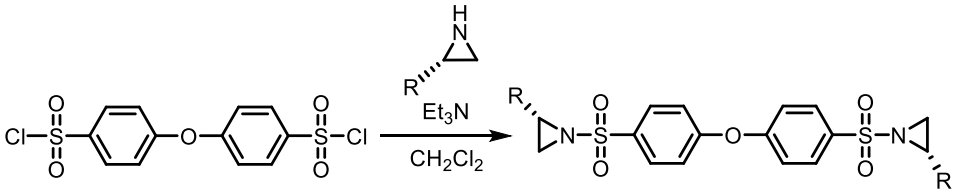
A cold mixture of sulfuric acid (98%, 10 g) and water (10 mL) was added to the chiral amino alcohol (100 mmol) in water (10 mL) at 0-5 °C. The mixture was heated to 110 °C for 3-4 h, and then water was carefully distilled off in vacuo to afford solid amino alcohol hydrogen sulfate.



For the synthesis of (S)-2-methylaziridine and (S)-2-isopropylaziridine: To the crude amino alcohol hydrogen sulfate was added NaOH aq. (50 mL, 25wt%), and the mixture was stirred at room temperature for 2 h, then distilled at 140 °C under atmospheric pressure. The distillate was saturated with NaOH pellets, and the upper organic layer was separated and used for the next step.



For the synthesis of (S)-2-benzylaziridine: Toluene (50 mL), and NaOH aq. (50 mL, 25wt%) were added to the crude amino alcohol hydrogen sulfate in sequence. The mixture was heated to reflux overnight. The organic phase was separated and dried over Na_2SO_4. After removal of the solvent, the residue was purified on a silica gel column with petroleum ether/EtOAc/Et_3N (5:1:1, v/v) as eluent to afford the product as a colorless oil.



1a: R = -CH_3
1b: R = -$CH(CH_3)_2$
1c: R = -$CH_2C_6H_5$

A solution of bis(chlorosulfonyl)diphenyl ether (10 mmol, 1.0 equiv) in anhydrous

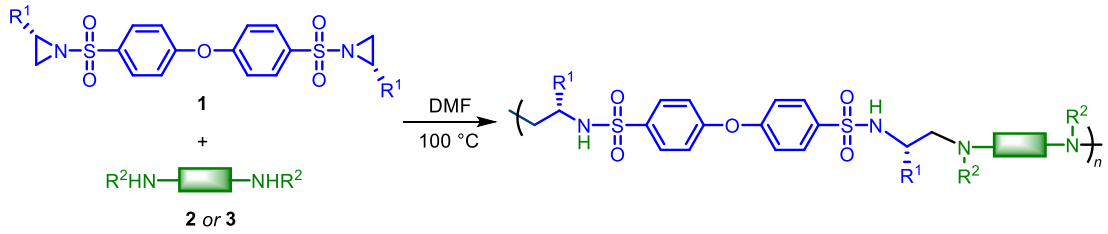
dichloromethane (10 mL) was added dropwise to a solution of aziridine (25 mmol, 2.5 equiv) and triethylamine (30 mmol, 3.0 equiv) dissolved in anhydrous dichloromethane (10 mL) at 0 °C under N_2. After the addition, the resulting mixture was allowed to warm to room temperature and stirred for 2~4 h. Then water (30 mL) was added to the mixture, and the mixture was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and dried with Na_2SO_4. After removing the solvent under reduced pressure, the crude product was obtained, which was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (4/1, v/v) to give the product as a white solid.

(2S,2'S)-1,1'-(oxybis(4,1-phenylenesulfonyl))bis(2-methylaziridine) **1a**. White solid; 68% yield; IR (neat): 3107, 2975, 1572, 1483, 1322, 1261, 1143, 1025, 982, 826, 704, 666, 567 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.30 (6H, d, *J* = 4.0 Hz), 2.07 (2H, d, *J* = 8.0 Hz), 2.66 (2H, d, *J* = 8.0 Hz), 2.86-2.93 (2H, m), 7.17 (4H, d, *J* = 8.0 Hz), 7.97 (4H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.0, 35.2, 36.3, 119.5, 130.5, 134.2, 160.1. HRMS (ESI+) calculated for $C_{18}H_{21}N_2O_5S_2^+$ (M^++H): 409.0892, found: 489.0887.

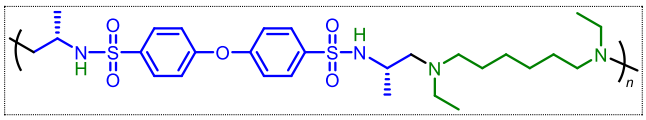
(2S,2'S)-1,1'-(oxybis(4,1-phenylenesulfonyl))bis(2-isopropylaziridine) **1b**. White solid; 81% yield; FT-IR (neat): 2975, 1591,1492, 1332, 1247, 1143, 977, 954, 898, 841, 732, 586 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.83 (6H, d, *J* = 4.0 Hz), 0.93 (6H, d, *J* = 4.0 Hz), 1.41-1.50 (2H, m), 2.16 (2H, d, *J* = 8.0 Hz), 2.54-2.58 (2H, m), 2.66 (2H, d, *J* = 4.0 Hz), 7.18 (4H, d, *J* = 12.0 Hz), 7.99 (4H, d, *J* = 12.0 Hz).^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 19.5, 30.1, 33.1, 46.4, 119.3, 130.6, 133.8, 160.0. HRMS (ESI+) calculated for $C_{22}H_{29}N_2O_5S_2^+$ (M^++H): 465.1518, found: 465.1507.

(2S,2'S)-1,1'-(oxybis(4,1-phenylenesulfonyl))bis(2-benzylaziridine) **1c**. White solid; 55% yield; FT-IR (neat): 3098, 1582,1488, 1313, 1233, 1157, 931, 846, 718, 576, 510 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.22 (2H, d, *J* = 8.0 Hz), 2.70 (2H, dd, *J* = 8.0, 12.0 Hz), 2.77 (2H, d, *J* = 8.0 Hz), 2.89 (2H, dd, *J* = 8.0, 16.0 Hz), 3.00-3.06 (2H, m), 7.03 (4H, d, *J* = 8.0 Hz), 7.06-7.10 (4H, m), 7.18-7.22 (6H, m), 7.82 (4H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 33.2, 37.6, 41.7, 119.2, 126.79, 128.6, 128.9, 130.5, 133.6, 137.1, 159.9. HRMS (ESI+) calculated for $C_{30}H_{29}N_2O_5S_2^+$ (M^++H): 561.1518, found: 561.1501.

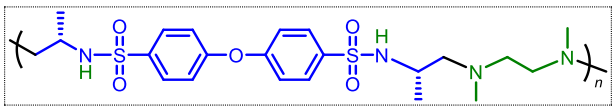
1.4 General Procedure for Polyaddition Between Bis(aziridine) and Diamine



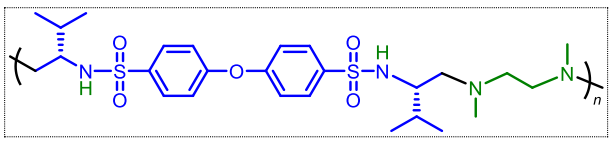
A flame-dried 10 mL Schlenk reaction tube, equipped with a stir bar, was charged with bis(*N*-sulfonyl aziridine) monomer (1.0 equiv), anhydrous DMF, and diamine (1.0 equiv) in sequence under N_2. Then the tube was sealed and immersed in a preheated oil bath (100 °C). After stirring for a specific time, the reaction mixture was added slowly to methanol. The precipitate was collected via centrifugation and dried at 40 °C under vacuum to give the desired polymer.



P1: FT-IR (neat): 3277, 2935, 1579, 1487, 1330, 1156, 1088, 870 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 0.79 (6H, t, J = 8.0 Hz), 0.94 (6H, d, J = 8.0 Hz), 1.04-2.37 (8H, m), 2.02-2.42 (10H, m), 2.97-3.18 (2H, m), 7.20 (4H, d, J = 8.0 Hz), 7.10-7.50 (2H, m), 7.84 (4H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 11.4, 19.4, 26.5, 26.8, 47.2, 45.0, 53.3, 59.4, 119.1, 129.1, 137.2, 158.5.

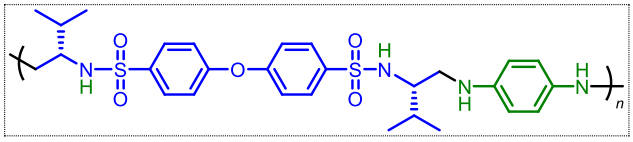


P2: FT-IR (neat): 3273, 2852, 1670, 1581, 1484, 1324, 1244, 1147, 994, 838 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11 (6H, d, J = 4.0 Hz), 2.06 (6H, s), 2.25-2.28 (2H, m), 2.29-2.44 (4H, m), 2.46-2.60 (2H, m), 3.16-3.33 (2H, m), 5.66-6.53 (2H, m), 7.11 (4H, d, J = 8.0 Hz), 7.93 (4H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 42.4, 47.5, 54.9, 62.2, 119.3, 129.9, 136.3, 159.4.

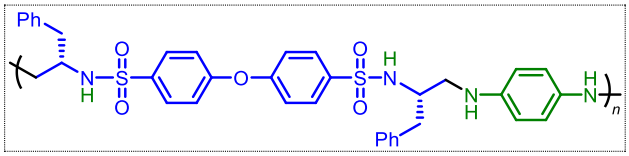


P3: FT-IR (neat): 3291, 2956, 1582, 1478, 1303, 1256, 1152, 1082, 1001, 945 cm^{-1}; ^1H

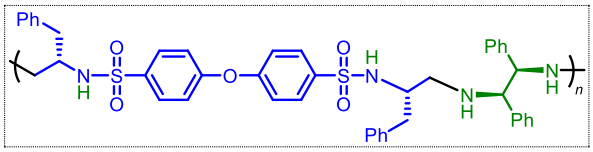
NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 0.72 (6H, d, J = 8.0 Hz), 0.75 (6H, d, J = 8.0 Hz), 1.68-1.93 (10H, m), 1.96-2.14 (4H, m), 2.14-2.29 (2H, m), 2.92-3.09 (2H, m), 7.16 (4H, d, J = 8.0 Hz), 7.25-7.36 (2H, m), 7.83 (4H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2, 18.0, 29.2, 42.1, 55.5, 56.4, 119.1, 129.8, 136.5, 159.3.



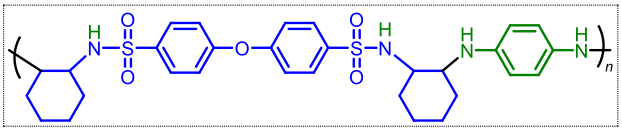
P4: FT-IR (neat): 3277, 2928, 1587, 1488, 1341, 1256, 1147,1096, 879, 694, 562 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 0.71 (6H, d, J = 8.0 Hz), 0.75 (6H, d, J = 8.0 Hz), 1.58-1.92 (2H, m), 2.58-2.97 (4H, m), 2.99-3.17 (2H, m), 4.22-4.83 (2H, br), 5.96-6.54 (4H, m), 7.14 (4H, d, J = 8.0 Hz), 7.47-7.58 (2H, m), 7.83 (4H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 16.7, 19.2, 45.8, 57.2, 119.0, 129.2, 137.4, 158.5.



P5: FT-IR (neat): 3291, 2932, 1577, 1488, 1322, 1238, 1157,1091, 864, 704, 567 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 2.52-2.64 (2H, m), 2.75-3.06 (6H, m), 3.38-3.55 (2H, m), 4.75 (2H, br), 6.06-6.45 (4H, m), 6.83-7.26 (14H, m), 7.59 (4H, d, J = 8.0 Hz), 7.75-7.89 (2H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 38.3, 48.3, 54,6, 113.6, 115.5, z118.9, 126.0, 128.0, 128.7, 129.2, 136.7, 138.3, 139.6, 158.2.

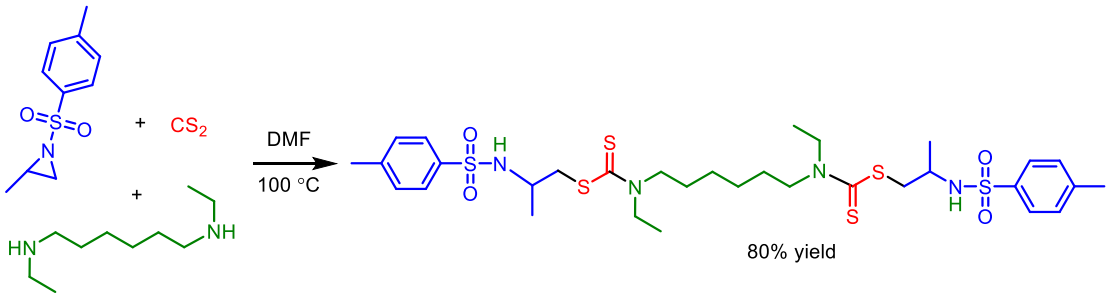


P6: FT-IR (neat): 3287, 3046, 2900, 1587, 1502, 1327, 1247, 1143, 1082, 958 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 2.08-2.30 (4H, m), 2.39-2.47 (2H, m), 2.62-2.85 (2H, m), 2.90-3.03 (2H, m), 3.42-3.51 (2H, m), 6.83-6.97 (8H, m), 6.99-7.15 (18H, m), 7.54 (4H, d, J = 8.0 Hz), 7.57-7.71 (2H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 38.2, 50.1, 55.3, 68.3, 118.2, 125.9, 126.5, 127.6, 127.9, 128.0, 128.6, 129.3, 137.1, 138.4, 141.5, 158.0.



P13: FT-IR (neat): 3560, 3291, 2914, 1644, 1572, 1483, 1318, 1238, 1147, 1087 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 1.0-1.30 (8H, m), 1.42-1.68 (6H, m), 1.84-2.07 (2H, m), 2.79-3.11 (4H, m), 3.98-4.36 (2H, m), 6.13-6.53 (4H, m), 7.21 (4H, d, *J* = 8.0 Hz), 7.62-7.75 (2H, m), 7.87 (4H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 22.5, 23.0, 30.2, 30.5, 54.7, 55.7, 114.4, 119.1, 129.1, 137.4, 139.3, 158.4.

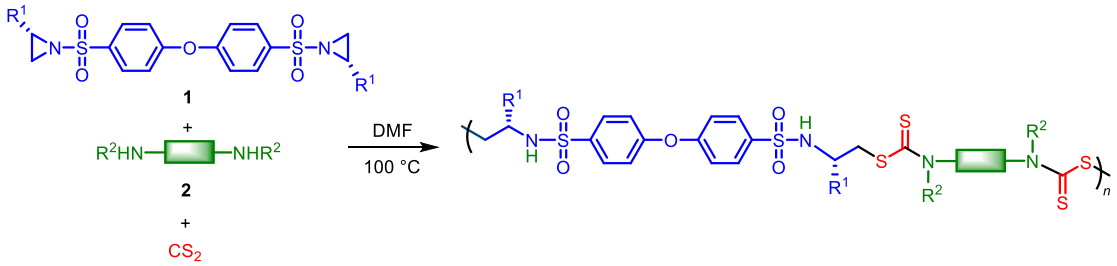
1.5 Procedure for the Synthesis of *β*-Sulfonamido Dithiocarbamates[4]



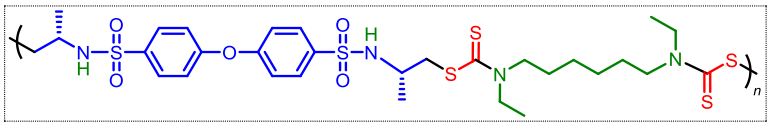
A flame-dried 10 mL Schlenk reaction tube, equipped with a stir bar, was charged with *N,N′*-diethyl-1,6-diaminohexane (0.5 mmol, 104 μL, 1.0 equiv), and anhydrous DMF (2.5 mL) under N_2. The mixture was cooled to 0 °C, and carbon disulfide (2.0 mmol, 120 μL, 4.0 equiv) was then added. After stirring for 2 h at 0 °C, TsMAz (1.0 mmol, 0.221 g, 2.0 equiv) was added to the mixture. The tube was then immersed in a preheated oil bath (100 °C). After stirring for 6 h, the crude product was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (4/1, v/v) to give the product as a light yellow solid (0.298 g, 80% yield).

Bis(2-((4-methylphenyl)sulfonamido)propyl) hexane-1,6-diylbis(ethylcarbamo dithioate). ^1H NMR (400 MHz, ($CDCl_3$, TMS): δ 1.0-1.31 (14H, m), 1.34-1.48 (5H, m), 1.51-1.87 (6H, m), 2.31-2.51 (6H, s), 3.23-3.43 (2H, m), 3.45-3.70 (8H, m), 3.78-4.13 (4H, m), 5.49-5.78 (2H, m), 7.25 (4H, d, *J* = 8.0 Hz), 7.73 (4H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 12.5, 21.7, 22.3, 22.5, 25.7, 26.1, 25.7, 26.1, 26.35, 26.44, 26.5, 26.6, 27.0, 42.2, 42.3, 42.5, 47.7, 50.1, 50.75, 50.83, 50.87, 50.9, 51.0, 52.4, 55.3, 55.4, 68.1, 127.2, 129.6, 138.2, 143.0, 195.6, 195.8. HRMS (ESI+) calculated for $C_{32}H_{51}N_4O_4S_6^+$ (M^++H): 747.2235, found: 747.2239.

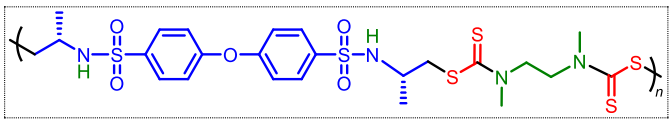
1.6 General Procedure for Polyaddition Between Bis(aziridine) and Bis(dialkyldithiocarbamate)



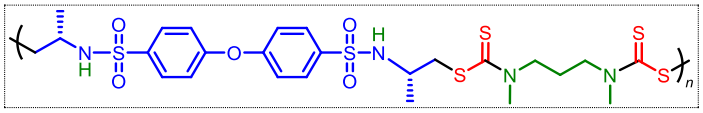
A flame-dried 10 mL Schlenk reaction tube, equipped with a stir bar, was charged with diamine (1.0 equiv) and anhydrous DMF. The mixture was cooled to 0 °C, and carbon disulfide (3.0 equiv) was then added. After stirring for 2 h at 0 °C, a solution of bis(aziridine) in DMF was added to the mixture. The tube was immersed in a preheated oil bath (100 °C). After stirring for a specific time, the reaction mixture was added slowly to methanol. The precipitate was collected via centrifugation and dried at 40 °C under vacuum to give the desired polymer.



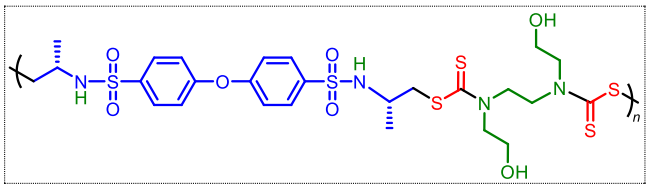
P7: FT-IR (neat): 3268, 2923, 1582, 1478, 1416, 1318, 1238, 1147, 1096 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 1.06 (6H, d, J = 4.0 Hz), 1.09-1.19 (6H, m), 1.21-1.36 (4H, m), 1.49-1.72 (4H, m), 3.09-3.30 (4H, m), 3.42-3.52 (2H, m), 3.52-3.73 (4H, m), 3.74-4.05 (4H, m), 7.22 (2H, d, J = 8.0 Hz), 7.82 (2H, d, J = 8.0 Hz), 7.79-7.89 (2H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 11.2, 12.3, 20.92, 21.0, 21.01, 25.7, 25.8, 25.9, 26.7, 42.5, 42.6, 42.7, 47.0, 48.7, 49.6, 51.6, 54.1, 119.1, 129.13, 137.1, 158.5, 193.7, 193.8, 193.8.



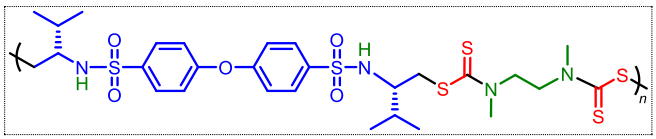
P8: FT-IR (neat): 3272, 2956, 1582, 1492, 1421, 1403, 1308, 1233, 1138, 982 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 0.99-1.14 (6H, m), 3.13-3.29 (8H, m), 3.36-3.40 (2H, m), 3.42-3.55 (2H, m), 3.84-4.44 (4H, m), 7.21 (4H, d, J = 8.0 Hz), 7.82 (4H, d, J = 8.0 Hz), 7.85-7.90 (2H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 20.8, 20.9, 42.7, 42.9, 43.0, 43.8, 48.9, 50.1, 50.2, 50.3, 52.4, 53.1, 119.0, 129.2, 137.1, 158.5, 196.40, 196.44.



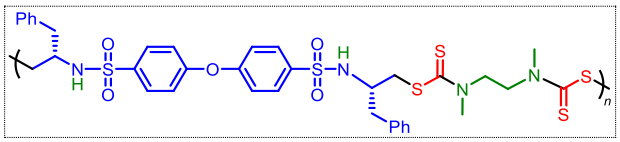
P9: FT-IR (neat): 3263, 2951, 1577, 1483, 1384, 1318, 1242, 1152, 1091, 977, 831, 685, 567 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 0.89-1.11 (6H, m), 1.83-2.02 (2H, m), 3.01-3.31 (8H, m), 3.32-3.41 (2H, m), 3.61-3.81 (2H, m), 3.85-4.18 (2H, m), 7.21 (4H, d, J = 8.0 Hz), 7.82 (4H, d, J = 8.0 Hz), 7.70-7.89 (2H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 20.9, 21.1, 23.5, 24.1, 30.5, 42.6, 42.8, 43.0, 43.3, 43.4, 48.6, 48.7, 51.1, 51.4, 53.5, 53.8, 119.2, 129.2, 137.1, 158.6, 194.4, 194.6, 195.4, 195.7.



P10: FT-IR (neat): 3514, 3253, 2908, 1572, 1490, 1401, 1311, 1235, 1154, 979 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 0.91-1.09 (6H, m), 3.09-3.36 (4H, m), 3.46-3.54 (2H, m), 3.61-3.88 (6H, m), 3.91-4.39 (4H, m), 4.81-5.16 (2H, m), 7.22 (4H, d, J = 8.0 Hz), 7.82 (4H, d, J = 8.0 Hz), 7.79-7.89 (2H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 20.7, 20.8, 36.9, 42.8, 43.1, 43.2, 48.7, 49.5, 50.3, 51.2, 52.1, 55.1, 55.3, 57.2, 57.6, 57.9, 58.0, 58.2, 119.3, 129.2, 137.2, 158.6, 195.9, 196.4, 196.7.

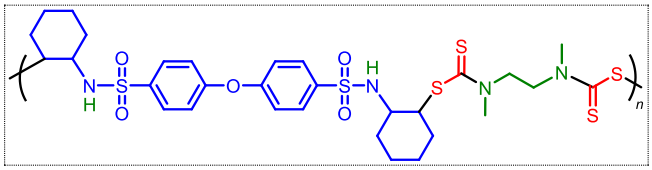


P11: FT-IR (neat): 3272, 2965, 1663, 1577, 1483, 1398, 1313, 1251, 1157, 1150, 987 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 0.63-0.97 (12H, m), 1.68-1.90 (2H, m), 2.82-3.20 (6H, m), 3.25-3.42 (4H, m), 3.72-4.57 (4H, m), 7.17 (4H, d, J = 8.0 Hz), 7.80 (4H, d, J = 8.0 Hz), 7.64-7.95 (2H, m); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 17.3, 17.4, 17.7, 17.8, 18.5, 18.7, 18.9, 30.5, 31.1, 31.2, 31.5, 31.8, 40.3, 43.7, 43.9, 50.2, 52.3, 53.0, 57.2, 57.4, 119.0, 129.2, 137.6, 158.5, 195.5, 195.7, 196.5, 196.9.



P12: FT-IR (neat): 3282, 2982, 1663, 1582, 1488, 1370, 1322, 1242, 1143, 1077, 987 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, TMS): δ 2.53-2.88 (4H, m), 2.91-3.22 (6H, m),

3.22-3.38 (4H, m), 3.57-3.73 (2H, m), 3.78-4.38 (4H, m), 6.88-7.29 (14H, m), 7.67 (4H, d, J = 8.0 Hz), 7.86-8.00 (2H, m). ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 30.5, 40.4, 40.7, 40.8, 41.1, 41.3, 41.4, 43.7, 44.0, ,43.8, 43.9, , 50.3, 51.0, 52.4, 53.1, 53.9, 119.0, 126.4, 129.0, 129.5, 136.9, 137.0, 137.3, 158.3, 195.2, 195.3, 196.3, 196.7.



P14: FT-IR (neat): 3272, 2923, 1658, 1582, 1492, 1379, 1322, 1251, 1157, 1068, 958 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.01-1.83 (14H, m), 1.89-2.29 (4H, m), 2.97-3.30 (6H, m), 3.34-3.53 (1H, m), 3.72-4.48 (5H, m), 6.08-6.57 (2H, m), 6.88-7.17 (4H, m), 7.64-8.04 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 26.6, 29.8, 32.6, 32.8, 35.9, 36.1, 36.3, 36.4, 41.1 ,41.2, 44.9, 52.8, 53.0, 54.5, 54.8,59.1, 59.2, 59.4, 59.7, 59.8, 77.4, 118.9, 119.1, 129.4, 128.6, 137.4, 137.8, 159.1, 159.3, 198.8, 199.0.

1.7 Antimicrobial Assay

1) Medium preparation. 2.5 g of LB broth medium and 100 mL of distilled water was mixed in a 250 mL bottle. The mixture was then sterilized in a high-pressure steam sterilizer at 121°C for 15 min.

2) Bacterial suspension preparation. 3 mL of LB liquid medium was added to the bacterial culture tube, followed by the addition of *S. aureus* or *E. coli* colony. The culture solution was shaken for 15 h (37 °C, 200 rpm).

3) Colony counting assay. The polymer films were sterilized in a high-pressure steam sterilizer at 121°C for 20 min before use.

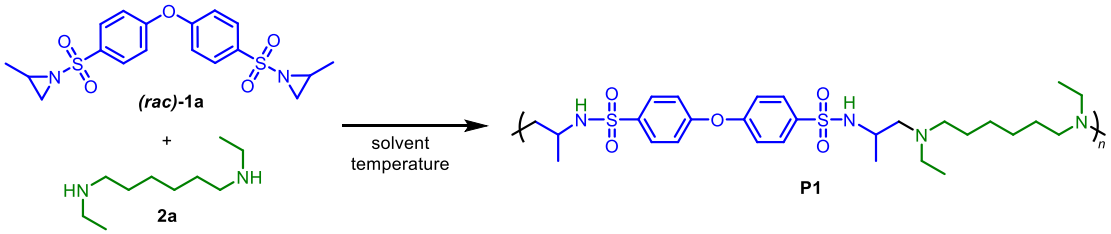
The antibacterial activity of the polymer film was quantitatively evaluated using the viable cell count method. *S. aureus* or *E. coli* bacterial solution was diluted with LB liquid medium to 10^6 CFU/mL. In the petri dish, 8 μL of the diluted bacterial solution was added to the surface of the polymer film, and no polymer sample was used for the blank control. After being cultivated at 37 °C for 4 h, the samples were immersed in 1.5 mL of PBS buffer and ultrasonicated for 3 min to release the adherent bacteria into PBS solution. Then the bacteria suspension was diluted 10 and 100 times, and 100 μL of each dilution was dispersed onto an agar plate. Survival colonies on agar plate were counted after incubation at 37 °C for 18 h. Each assay was performed in 3 replicates. The bacterial reduction(%) was calculated according to the following equation:

$$R = (1\text{-}A/B) \times 100\%$$

where R is the bacterial reduction (%), A and B are the number of live bacterial cells in the flask of treated and control samples, respectively.

2. Supporting Tables, Figures, and Schemes

Table S1. Screening of the Polyaddition between Racemic Bis(aziridine) 1a and Diamine 2a



entry[a]	solvent	temperature (°C)	time (h)	$M_{n,SEC}$[b] (kDa)	$Đ$[b]
1	DMSO	100	16.5	30.3	1.41
2	DMF	100	16.5	36.5	1.49
3	toluene	100	< 3	gel	-
4	THF	55	< 3	gel	-

[a]Reaction conditions: **(*rac*)-1a** (0.2 mmol, 1.0 equiv, 0.2 M), **2a** (1.0 equiv). [b]Determined by SEC in DMF at 60 °C (poly(*γ*-benzyl-*L*-glutamate) standards calibration).

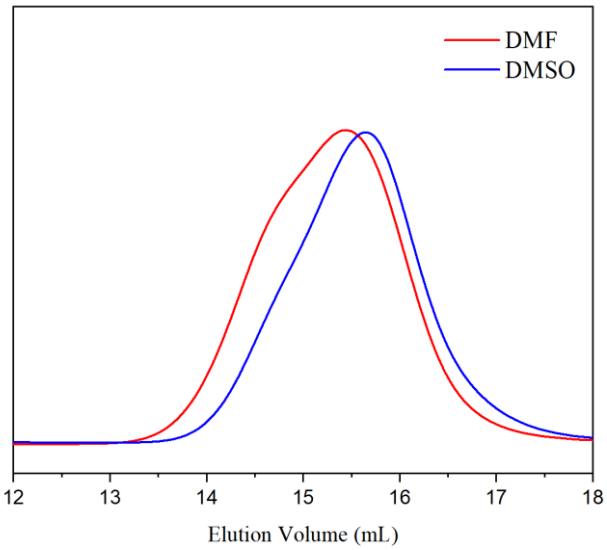
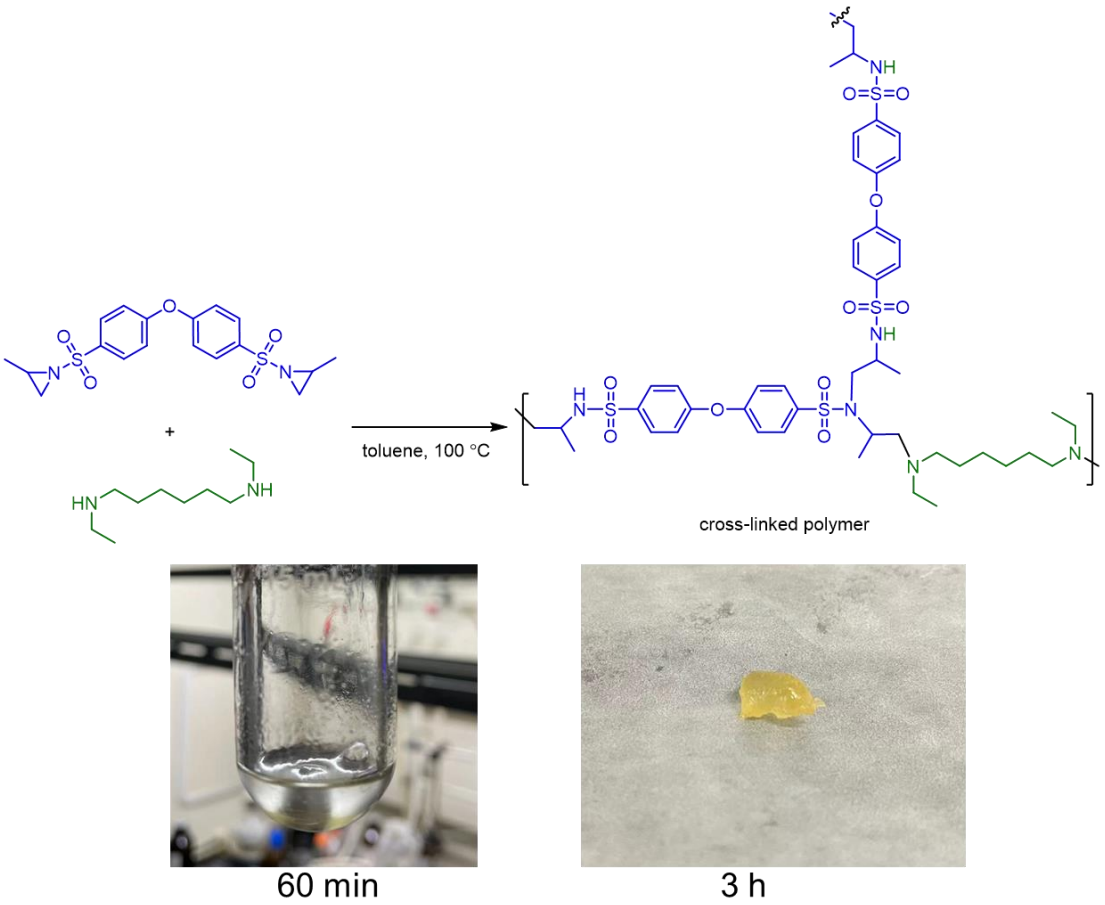


Fig. S1 SEC (DMF, 60 °C, poly(*γ*-benzyl-*L*-glutamate) standards) traces of polymers synthesized in DMF and DMSO (entries 1 & 2, Table S1).



Scheme S1. Polymerization of **(*rac*)-1a** and **2a** in toluene at 100 °C (Photos of the reaction mixture in 60 min, and the gel formed in 3 h).

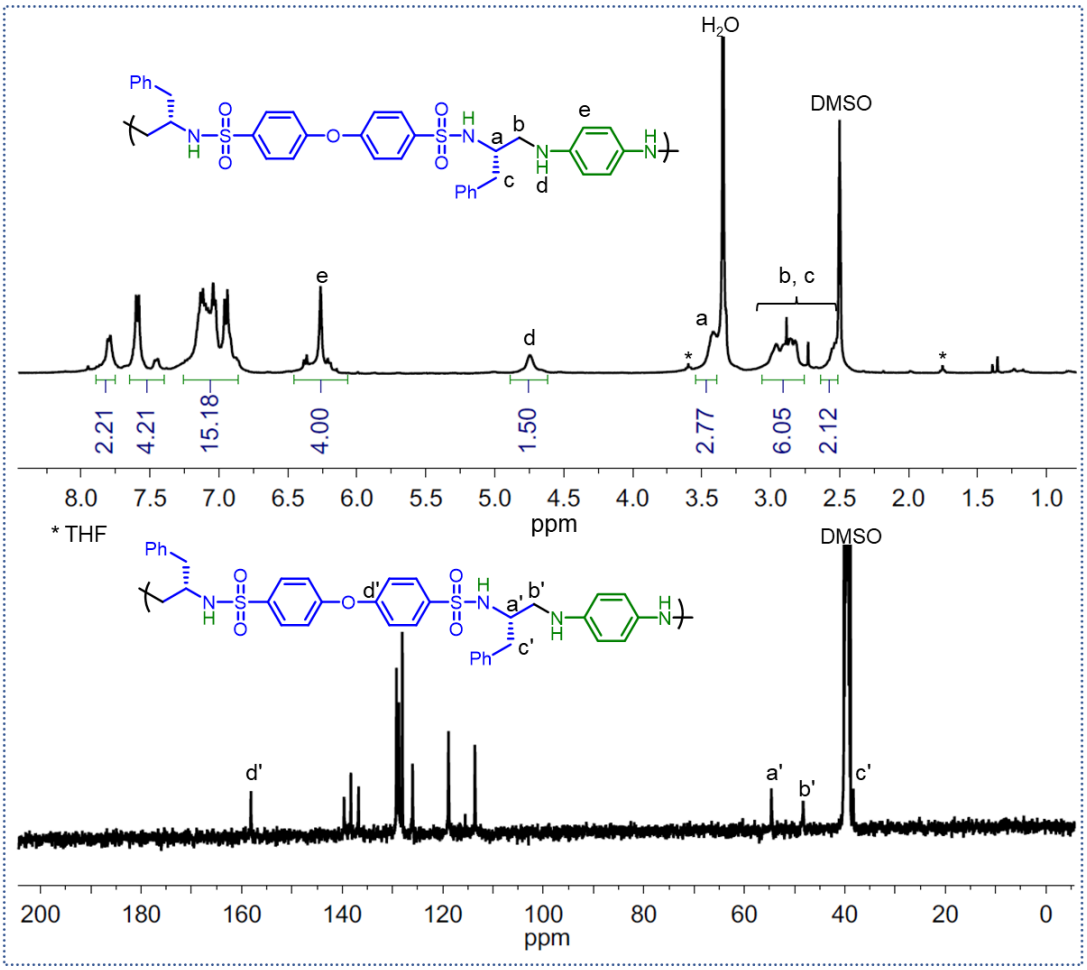


Fig. S2 ^{1}H (400 MHz, DMSO-d_6, 25 °C) and ^{13}C (100 MHz, DMSO-d_6, 25 °C) NMR spectra of the synthesized **P5**.

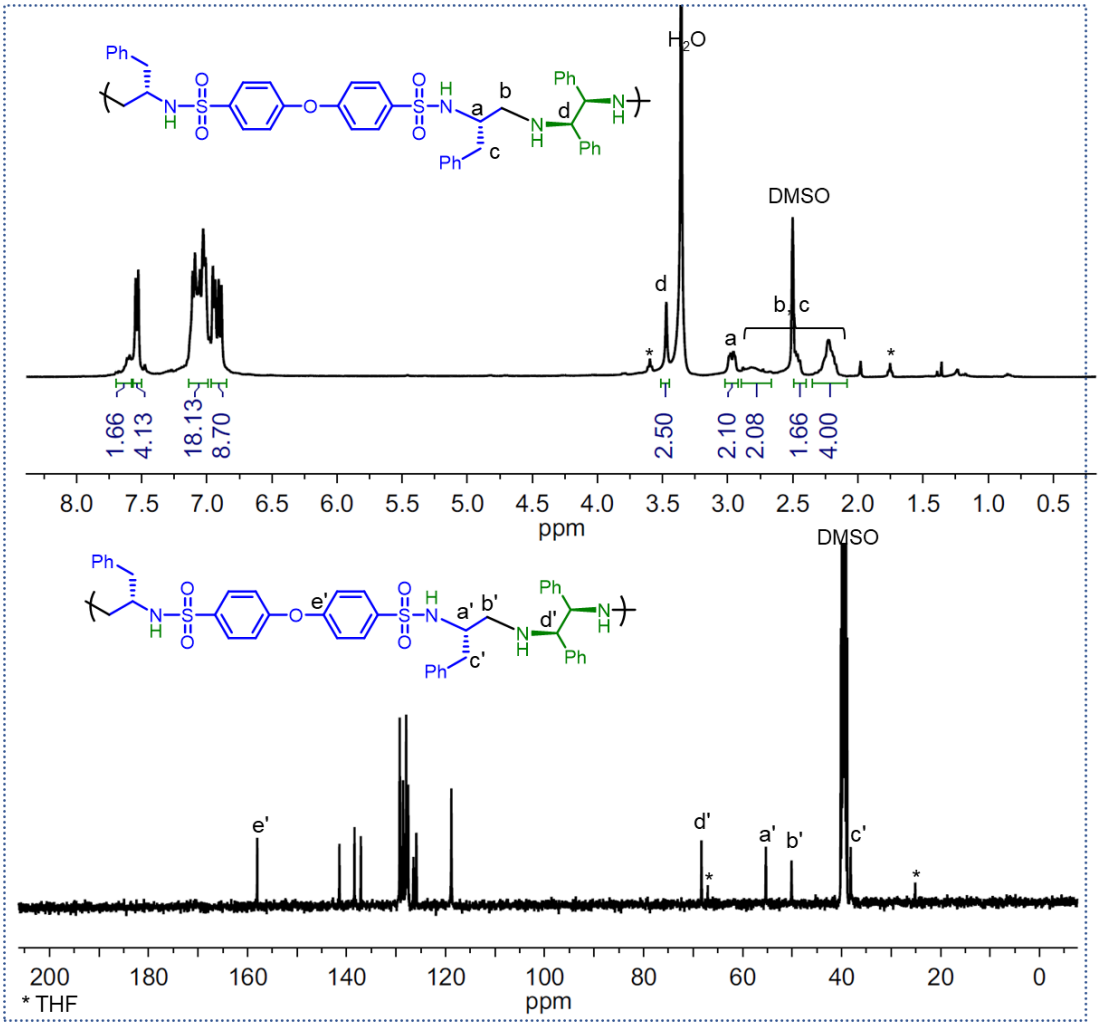
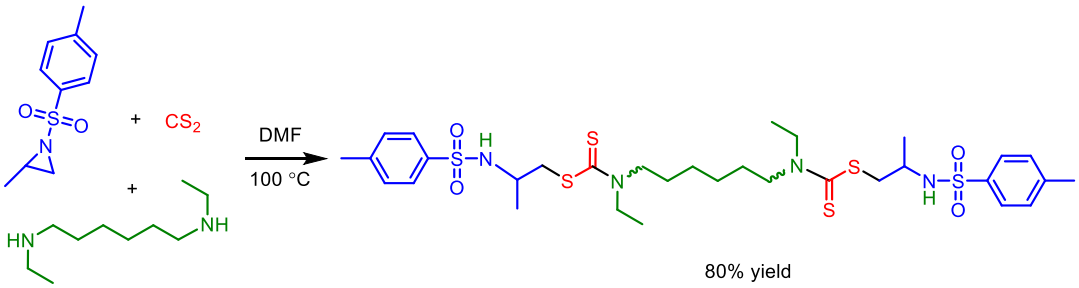


Fig. S3 ^{1}H (400 MHz, DMSO-d_6, 25 °C) and ^{13}C (100 MHz, DMSO-d_6, 25 °C) NMR spectra of the synthesized **P6**.



Scheme S2. The model reaction of TSMAz, CS_2, and *N,N′*-diethyl-1,6-diaminohexane (2.1:4.0/1.0) for the synthesis of *β*-sulfonamido dithiocarbamates.

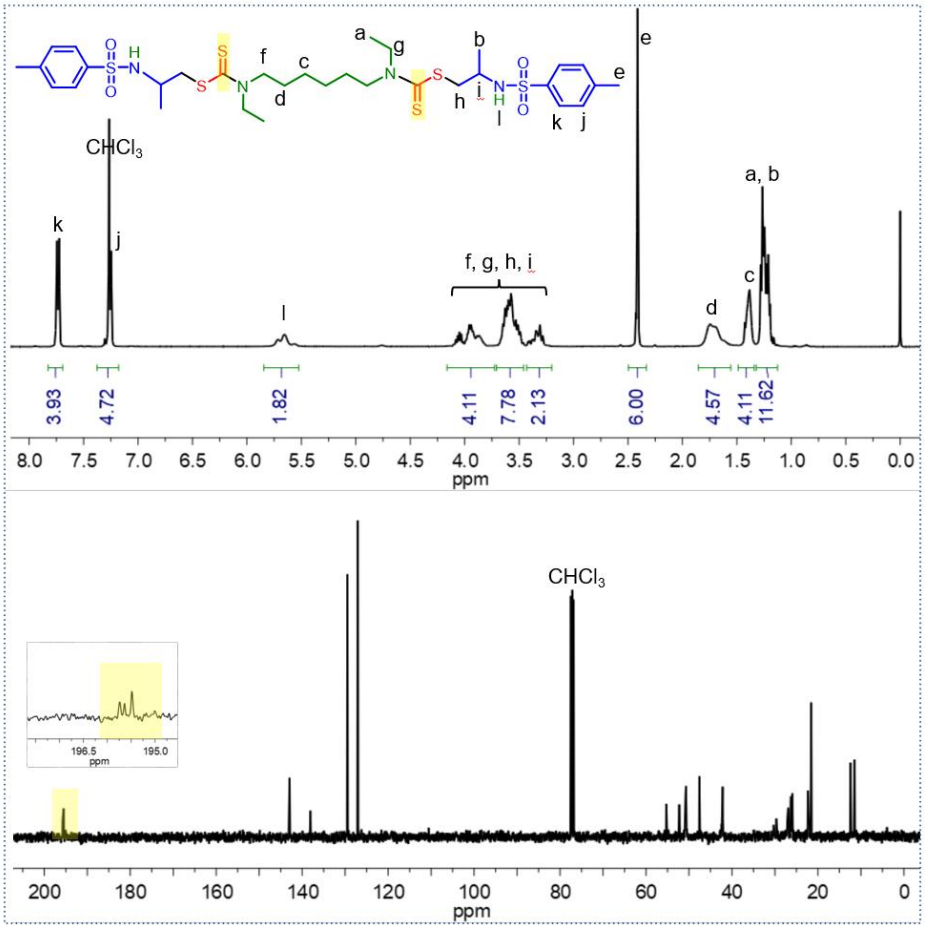


Fig. S4 ^{1}H (400 MHz, $CDCl_3$, 25 °C) and ^{13}C (100 MHz, $CDCl_3$, 25 °C) spectra of the synthesized *β*-sulfonamido dithiocarbamates.

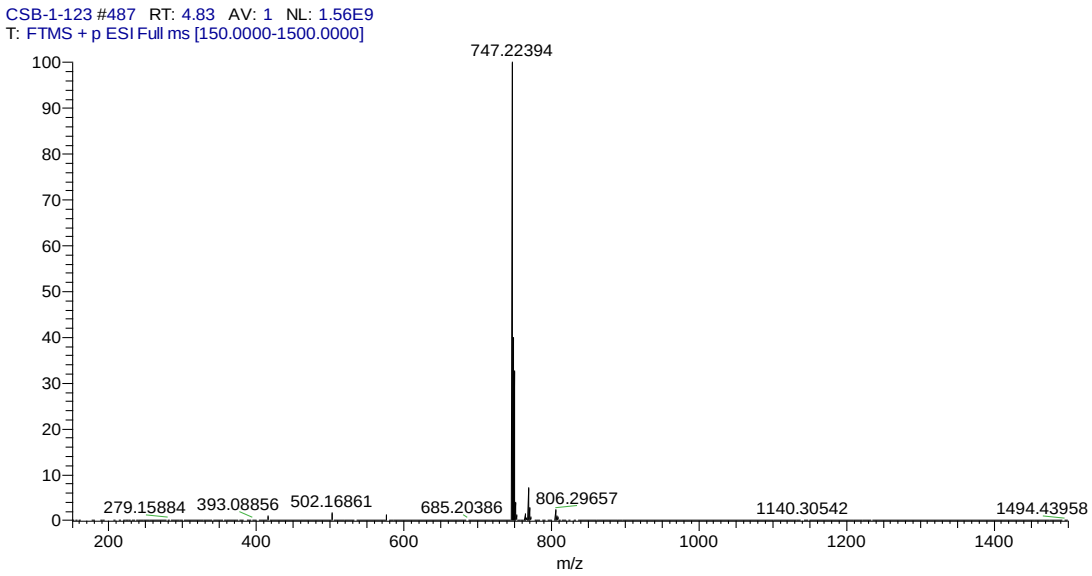
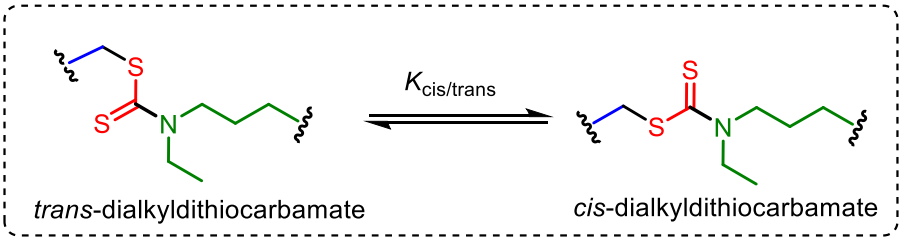
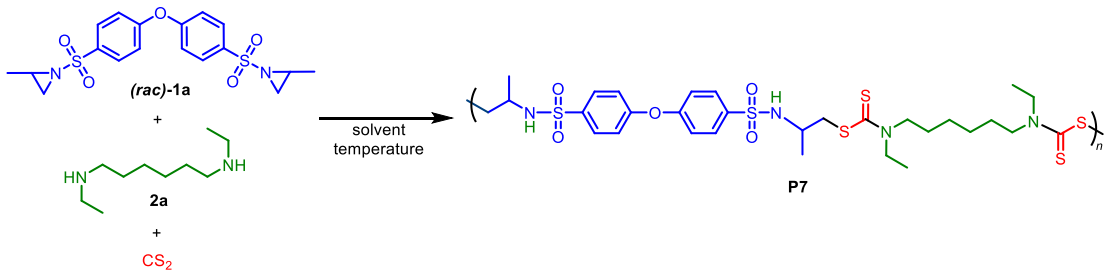


Fig. S5 HR-MS spectrum of the synthesized *β*-sulfonamido dithiocarbamates (calculated for $C_{32}H_{51}N_4O_4S_6^+$ (M^++H): 747.2235, found: 747.2239).



Scheme S3. The *E*- and *Z*-rotamers for dithiocarbamates.

Table S2. Screening of Polyaddition Between Racemic Bisaziridine 1a, Diamine 2a, and CS_2



entry[a]	solvent	temperature	time (h)	$M_{n,SEC}$[b] (kDa)	$Đ$[b]
1	CH_3CN	80	3	33.8	1.68
2	DMF	80	3	25.5	1.68
3	DMSO	80	3	14.9	1.39
4	Tol	80	3	24.4	1.57
5	THF	55	3	20.1	1.97
6	DMF	60	3	20.0	1.61
7	DMF	100	3	28.5	2.02

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv, 0.2 M), **1b** (1.0 equiv). [b] Determined by SEC in DMF at 60 °C (poly(γ-benzyl-*L*-glutamate) standards calibration).

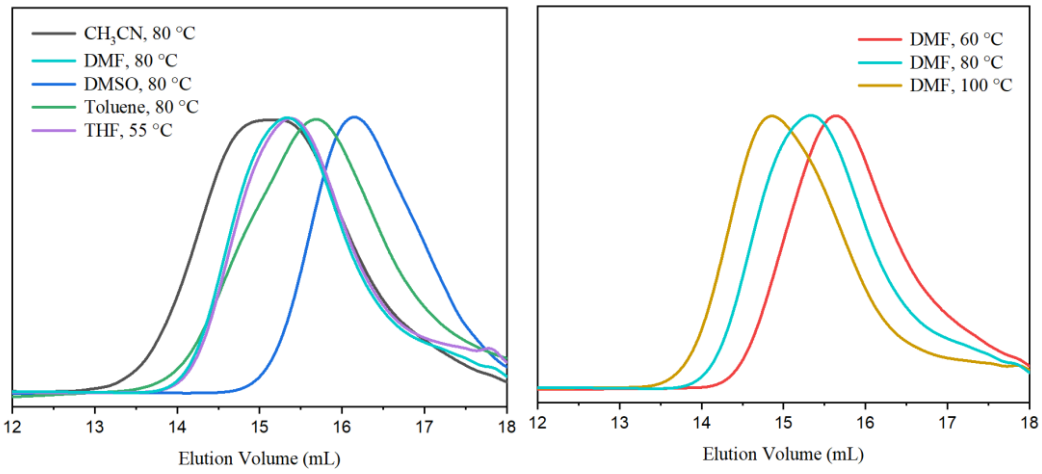
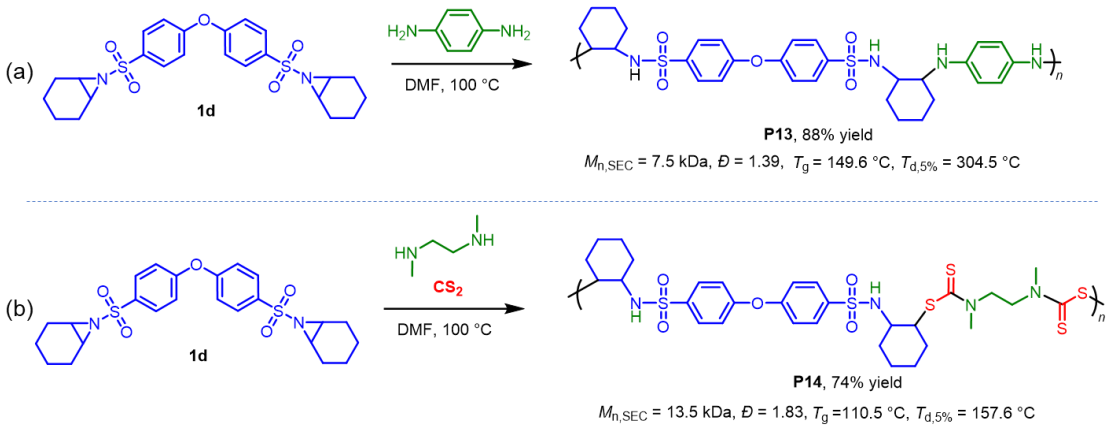


Fig. S6 SEC (DMF, 60 °C, poly(γ-benzyl-*L*-glutamate) standards) traces of polymers synthesized in Table S2.



Scheme S4. Synthesis of **P13** and **P14** from bis(*N*-sulfonyl aziridine) **1d**.

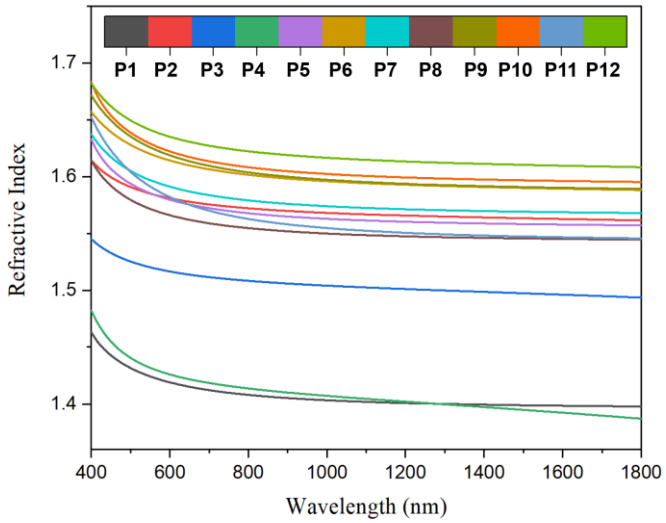


Fig. S7 Refractive indexes of **P1**-**P12**.

Table S3. Refractive index (n_{633}), Abbé number (υ_D), modified Abbé number (υ'_D), optical dispersions (D and D') and thickness of thin films of polymers **P1**-**P14**.[a]

polymer	n_{633}	υ_D	D	υ'_D	D'	thickness (nm)
P1	1.416	21.480	0.0466	106.3	0.00941	18.81
P2	1.579	37.852	0.0264	132.2	0.00757	82.79
P3	1.515	37.866	0.0264	78.0	0.0128	42.71
P4	1.423	18.933	0.0528	33.3	0.0301	79.58
P5	1.577	26.643	0.0376	143.4	0.00697	32.00
P6	1.611	28.856	0.0347	114.1	0.00876	515.17
P7	1.588	27.574	0.0363	139.4	0.00717	46.18
P8	1.563	27.161	0.0368	146.5	0.00682	35.46
P9	1.615	24.074	0.0415	108.5	0.00922	640.6
P10	1.619	24.494	0.0408	124.6	0.00803	61.32
P11	1.577	17.043	0.0587	88.0	0.0114	181.87
P12	1.632	28.551	0.0350	112.1	0.00892	268.64
P13	1.574	19.078	0.0524	52.6	0.0190	77.01
P14	1.467	11.199	0.0893	22.5	0.0444	86.04

[a]Abbreviation: n = refractive index, v_D = Abbé number = $(n_{589} - 1)/ (n_{486} - n_{656})$, υ'_D = $(n_{1319} - 1)/(n_{1060} - n_{1550})$, $D' = 1/v'_D$.

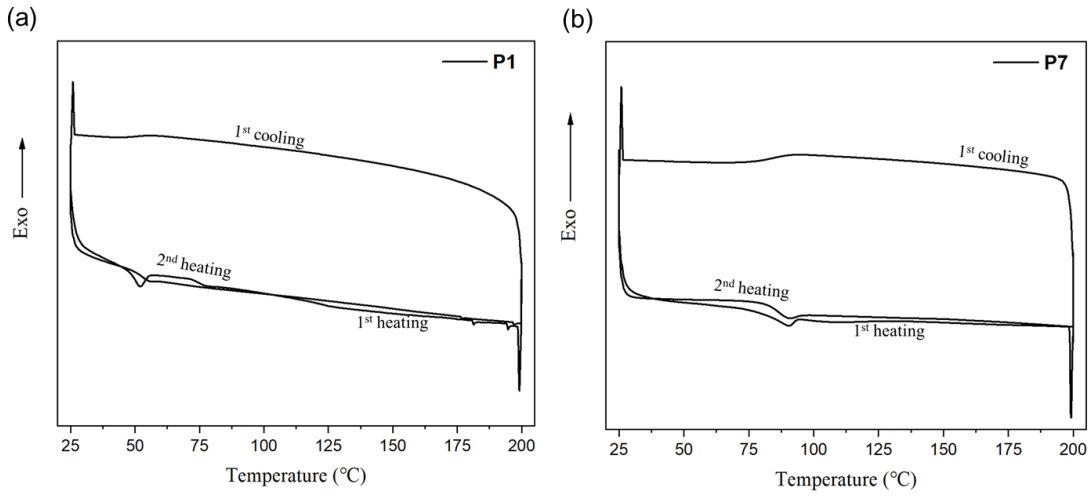


Fig. S8 The complete DSC curves of **P1** and **P7**.

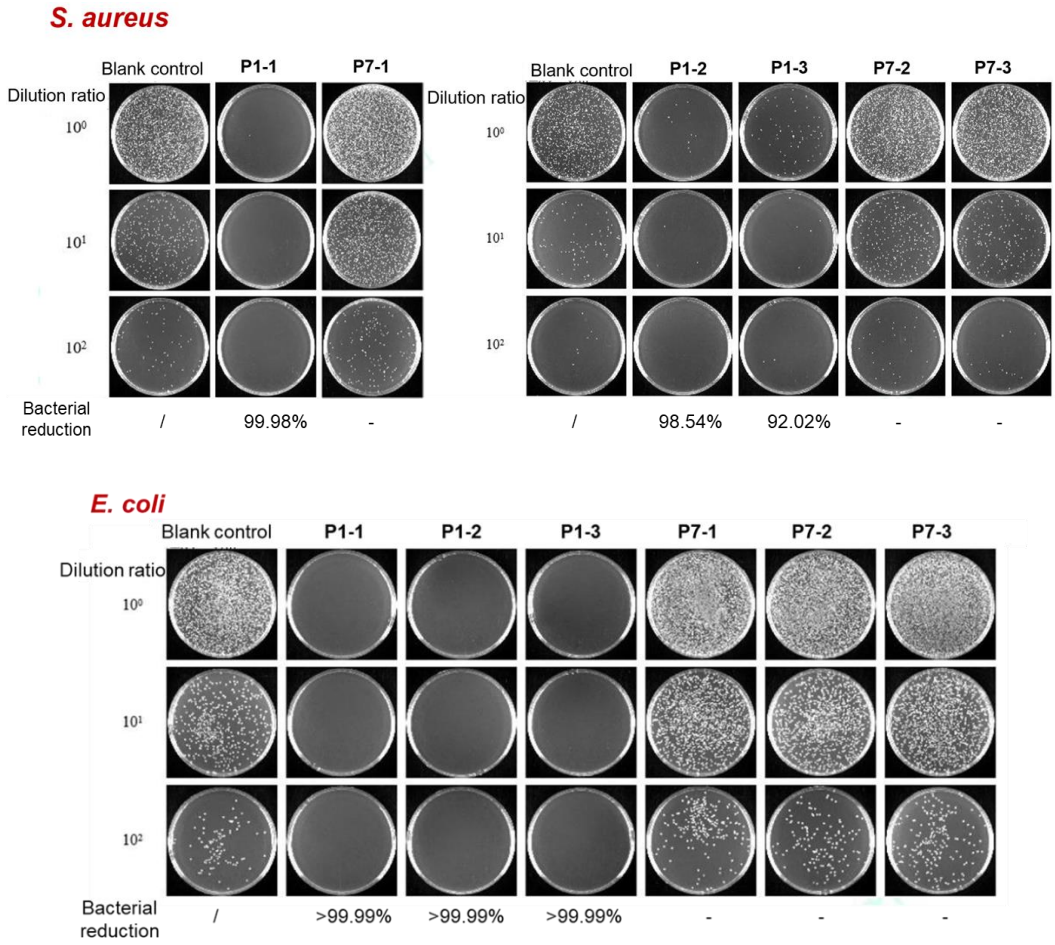


Fig. S9 Photographs of the *S. aureus* and *E. coli* colonies (**P1** and **P7** films, each assay was performed in 3 replicates).

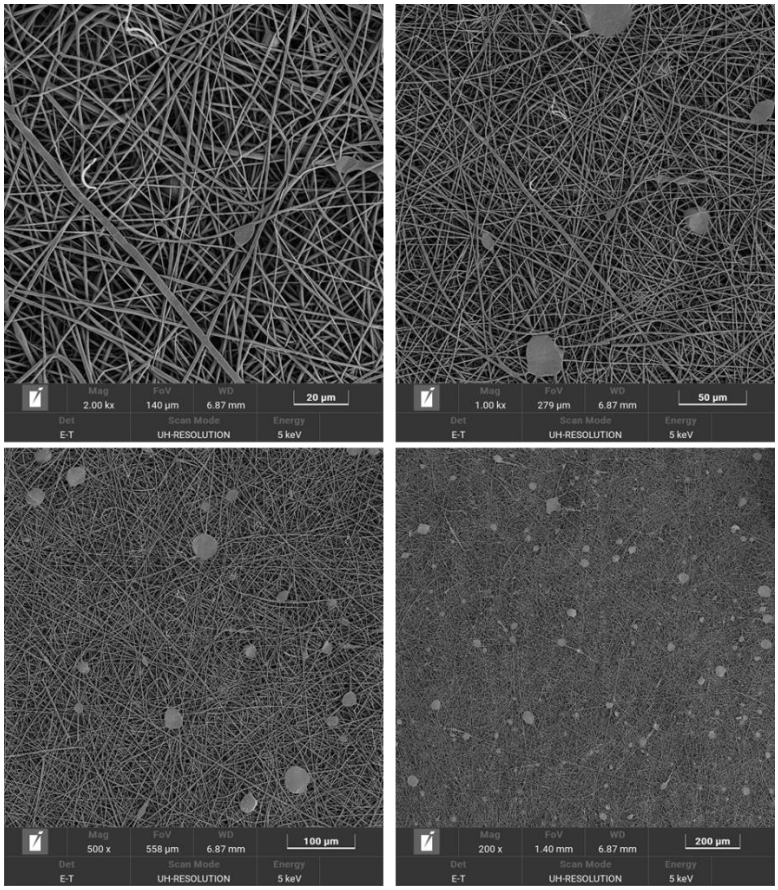
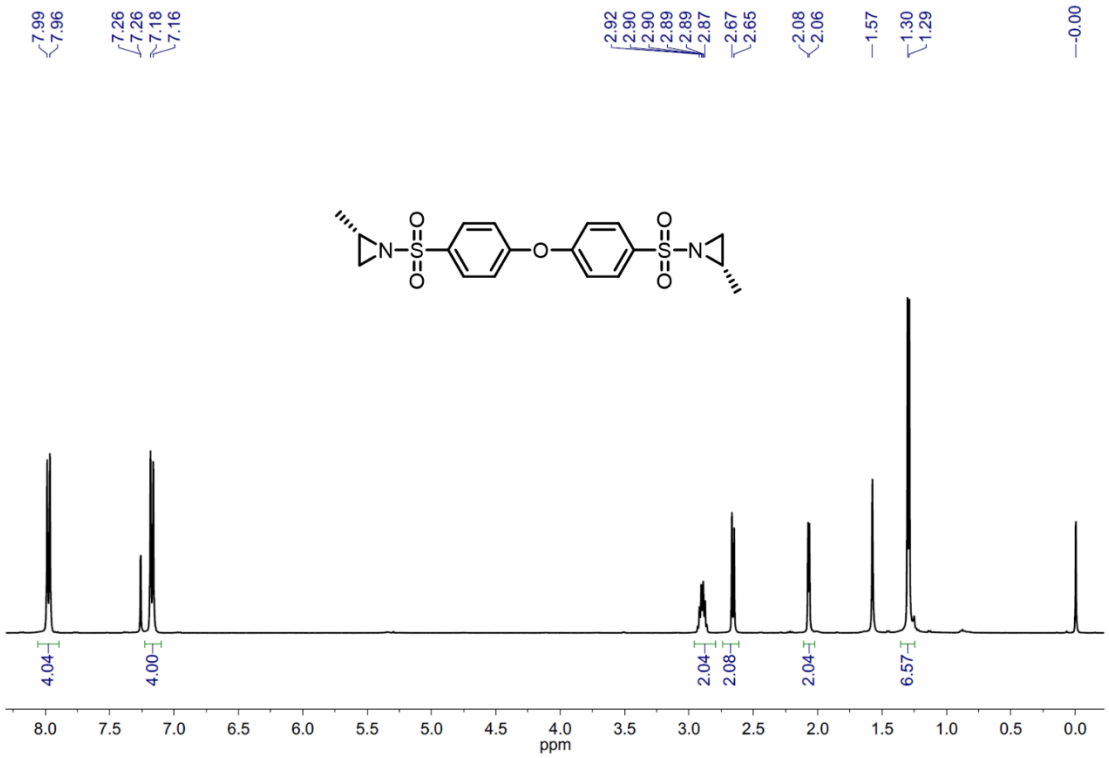
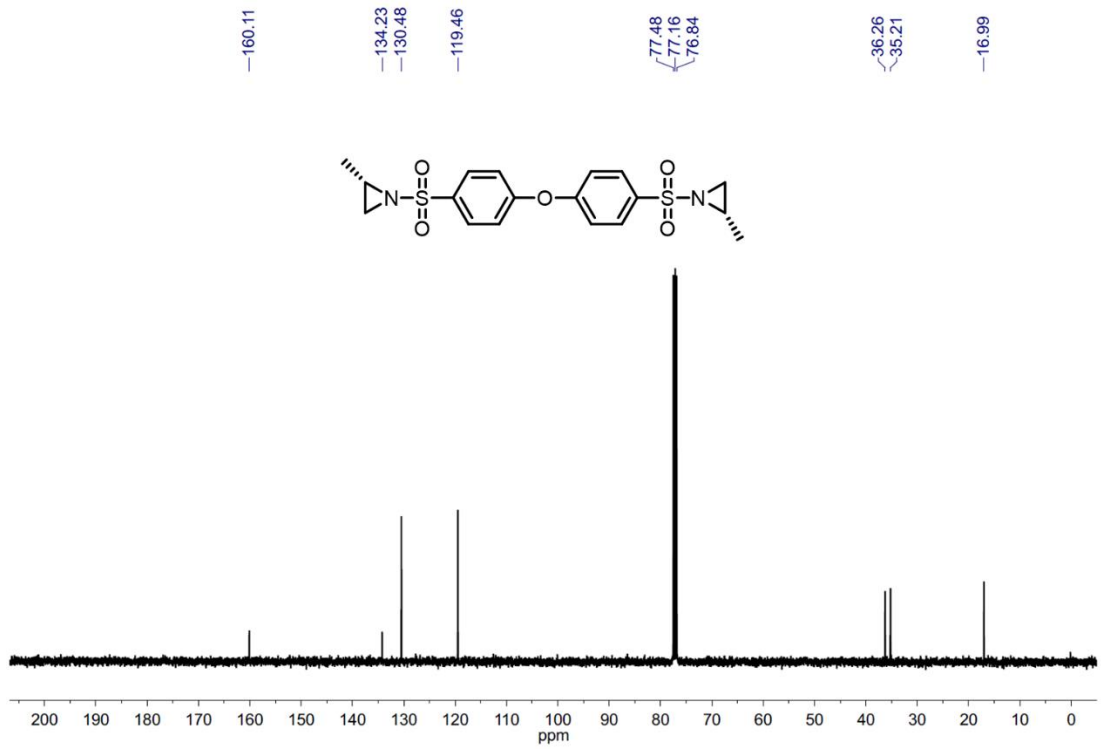
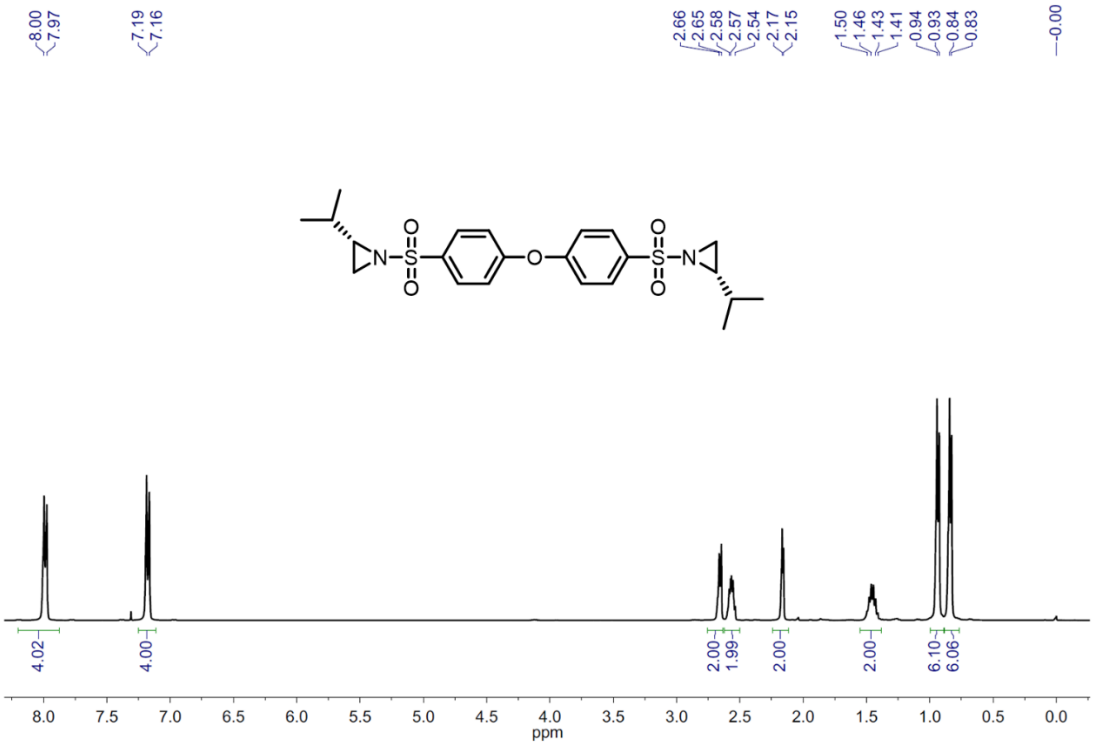


Fig. S10 SEM images of electrospun mats prepared from solutions containing **P1**.

3. Spectroscopic NMR Data



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1.43
1.41
0.94
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4.00
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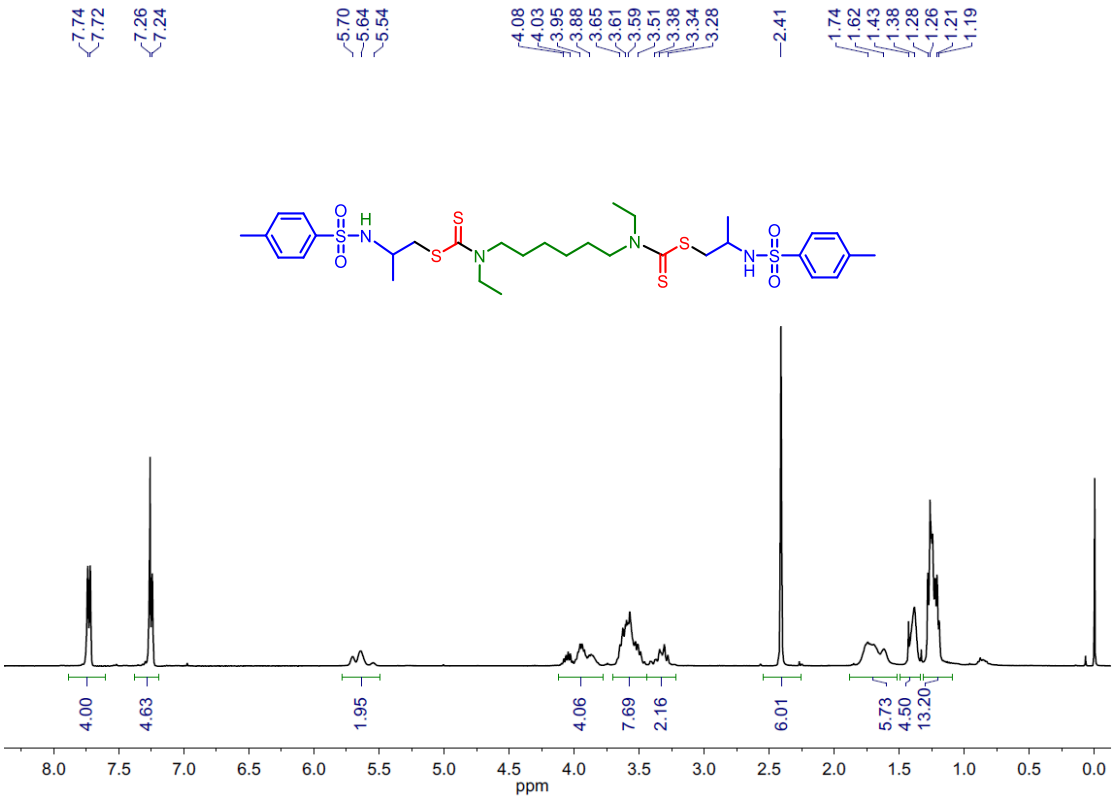
2.00
2.00
6.10
6.06
ppm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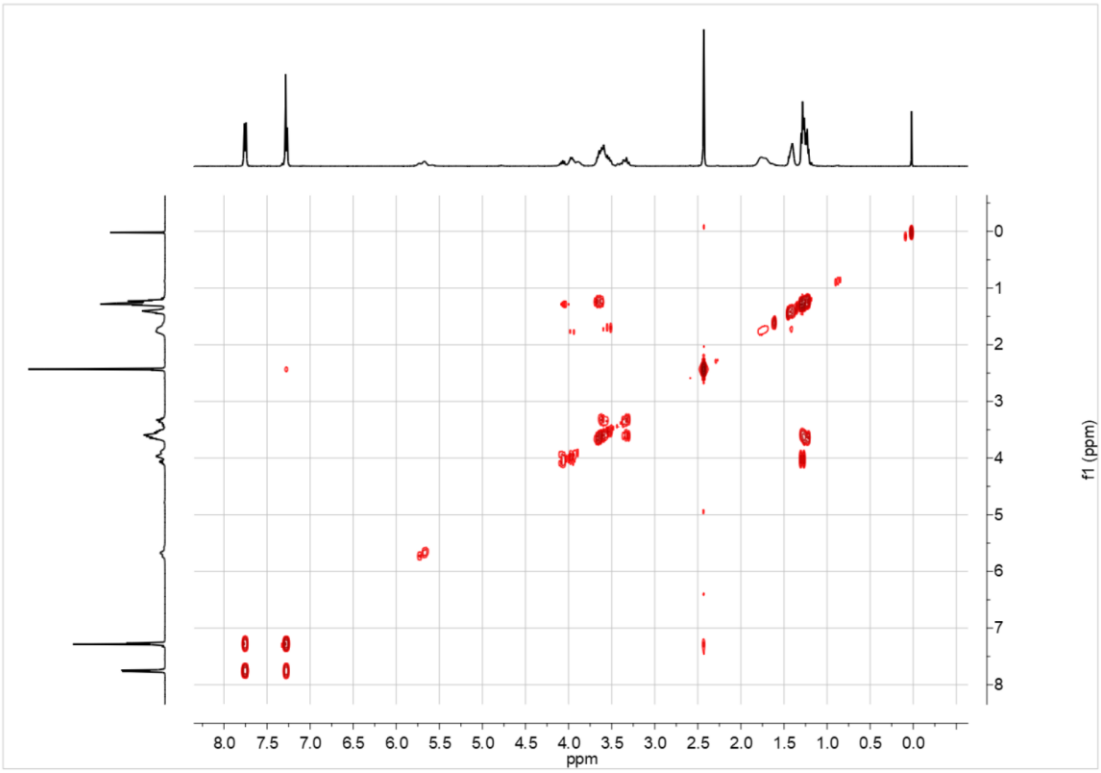
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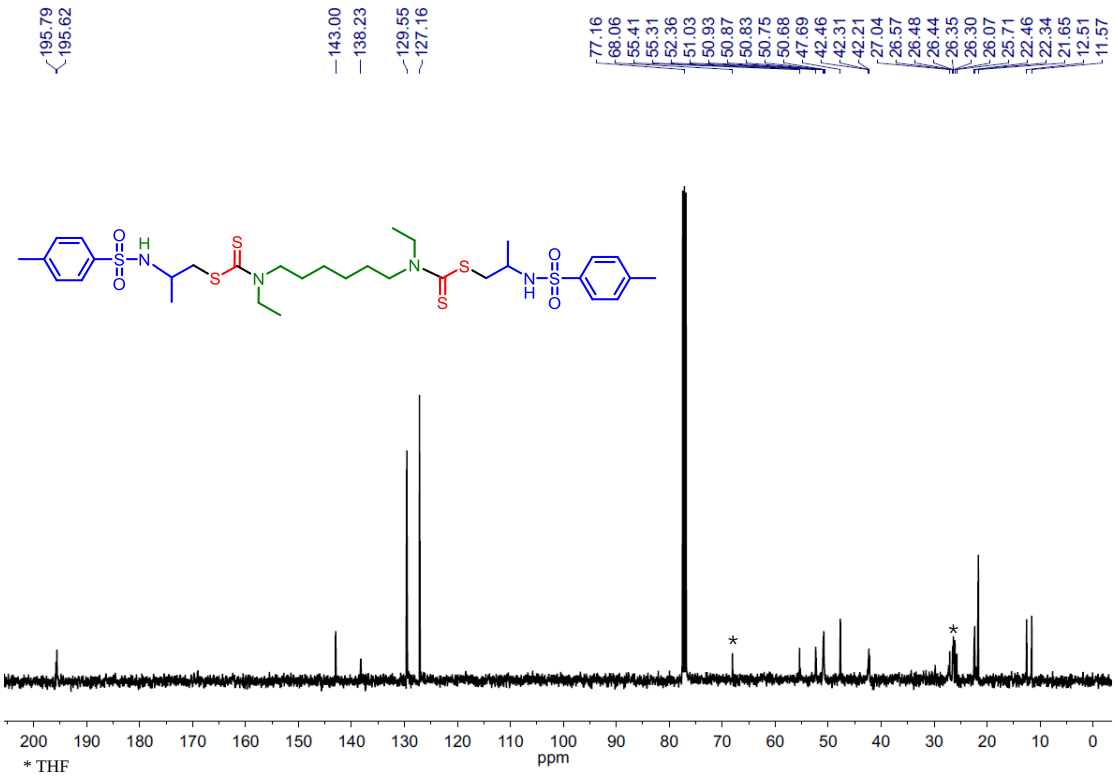
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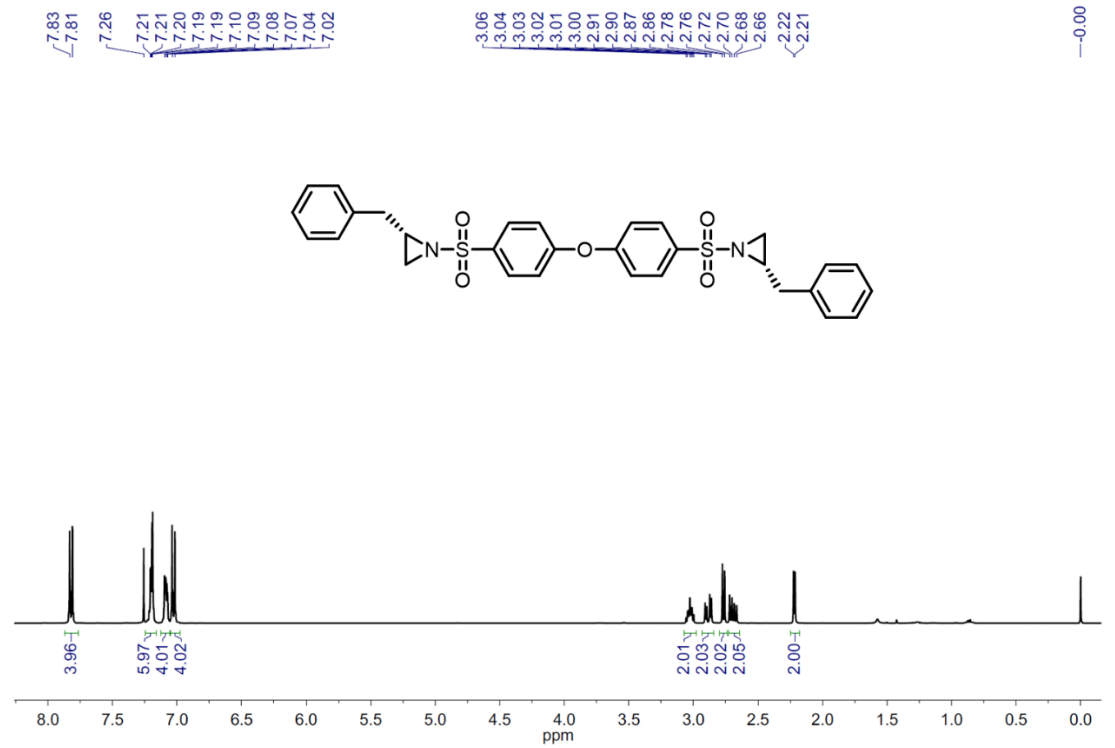
ppm
* THF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7.04
7.02
3.06
3.04
3.03
3.02
3.01
3.00
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2.90
2.87
2.86
2.78
2.76
2.72
2.70
2.68
2.66
2.22
2.21
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3.96
5.97
4.01
4.02
2.01
2.03
2.02
2.05
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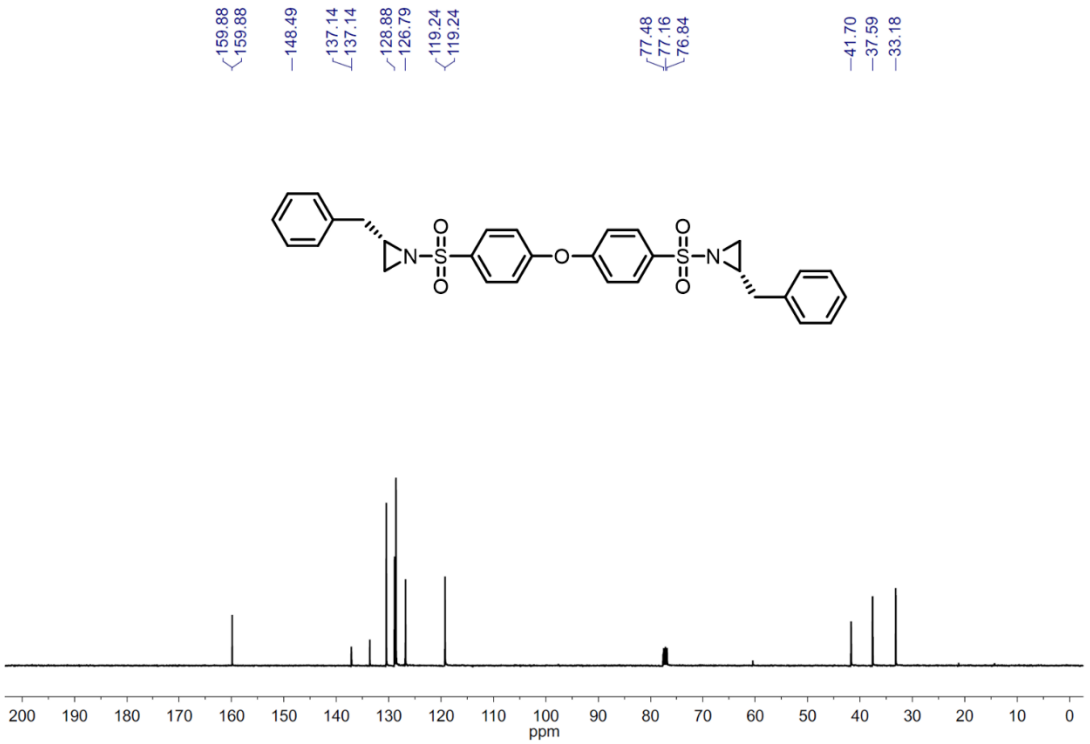
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77.16
76.84
41.70
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O
N
O
O
S
O
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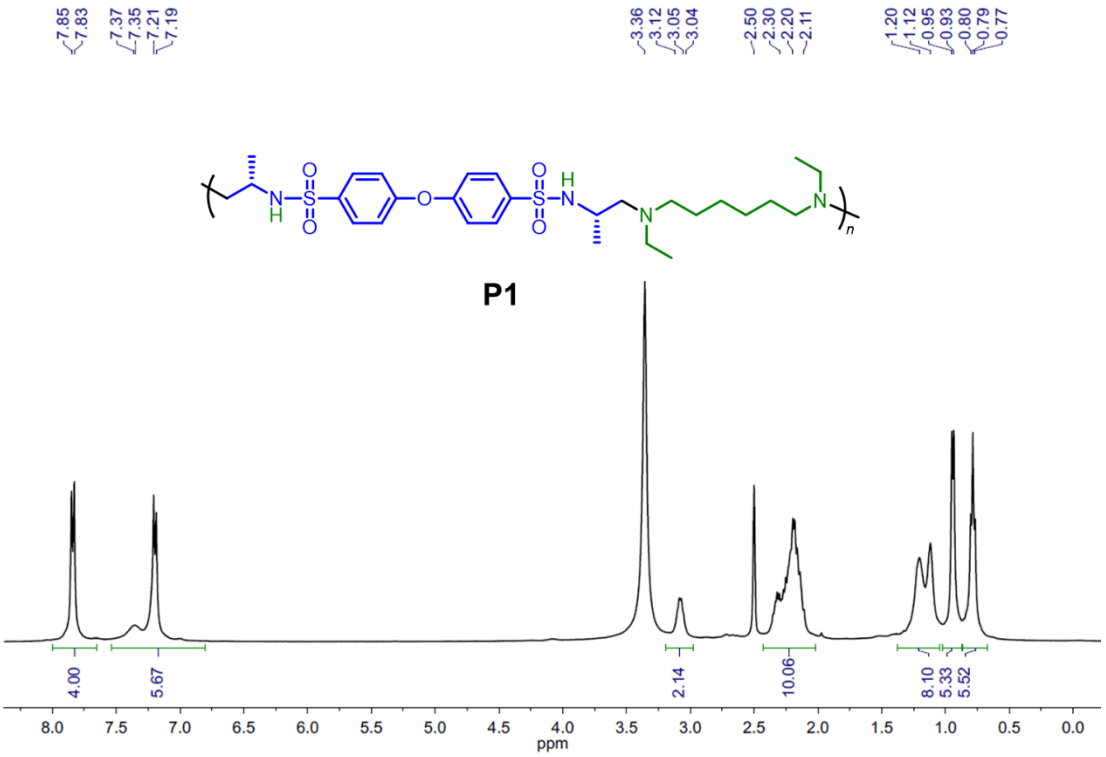
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2.20
2.11
1.20
1.12
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0.93
0.80
0.79
0.77
P1
4.00
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2.14
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8.10
5.33
5.52
8.0
7.5
7.0
6.5
6.0
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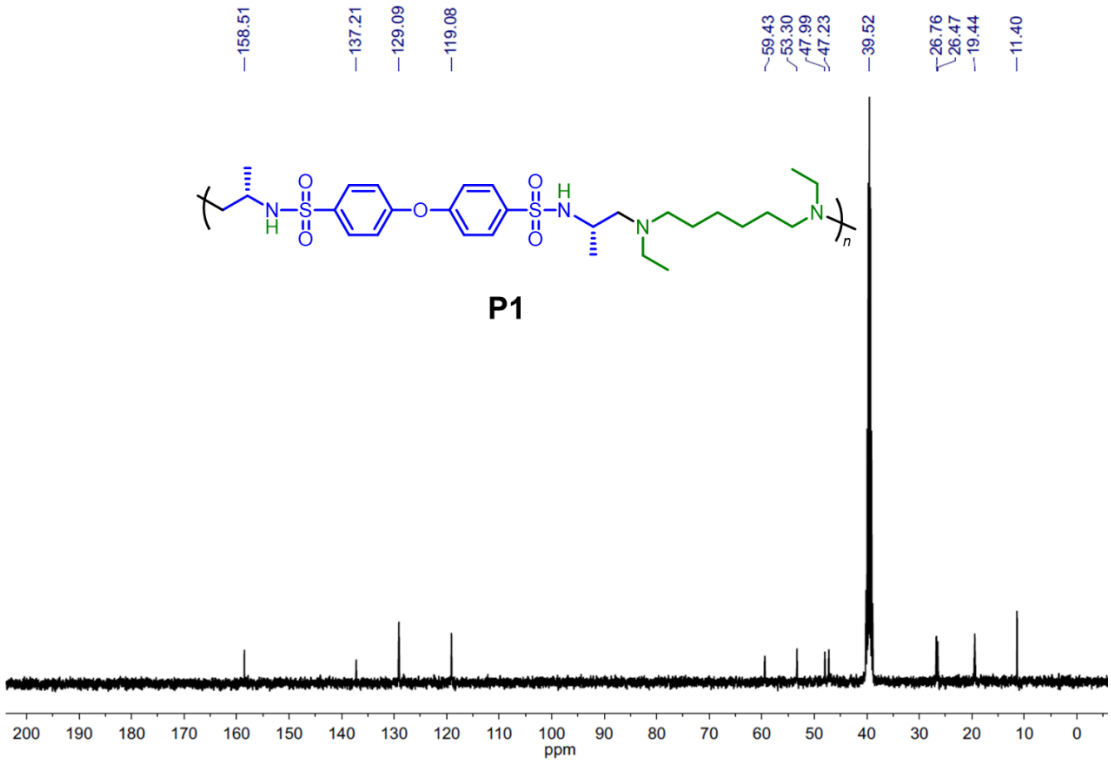
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26.47
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11.40
P1
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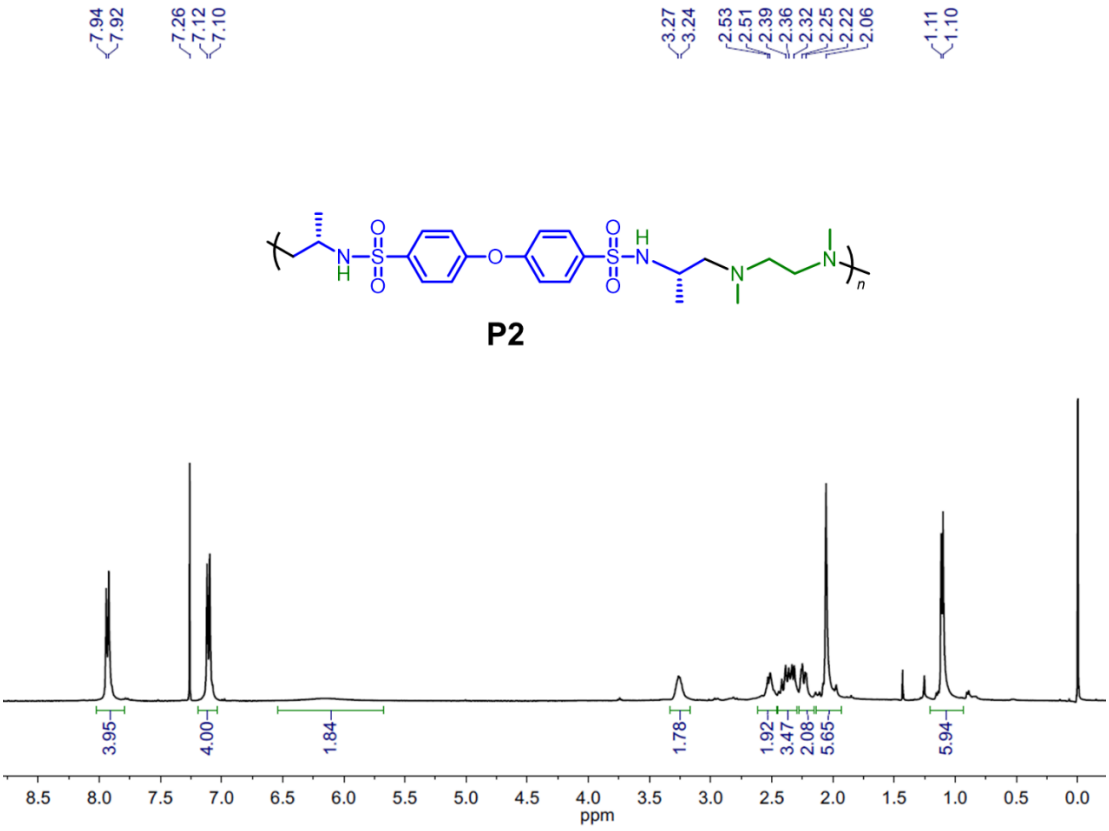
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2.25
2.22
2.06
1.11
1.10
P2
3.95
4.00
1.84
1.78
1.92
3.47
2.08
5.65
5.94
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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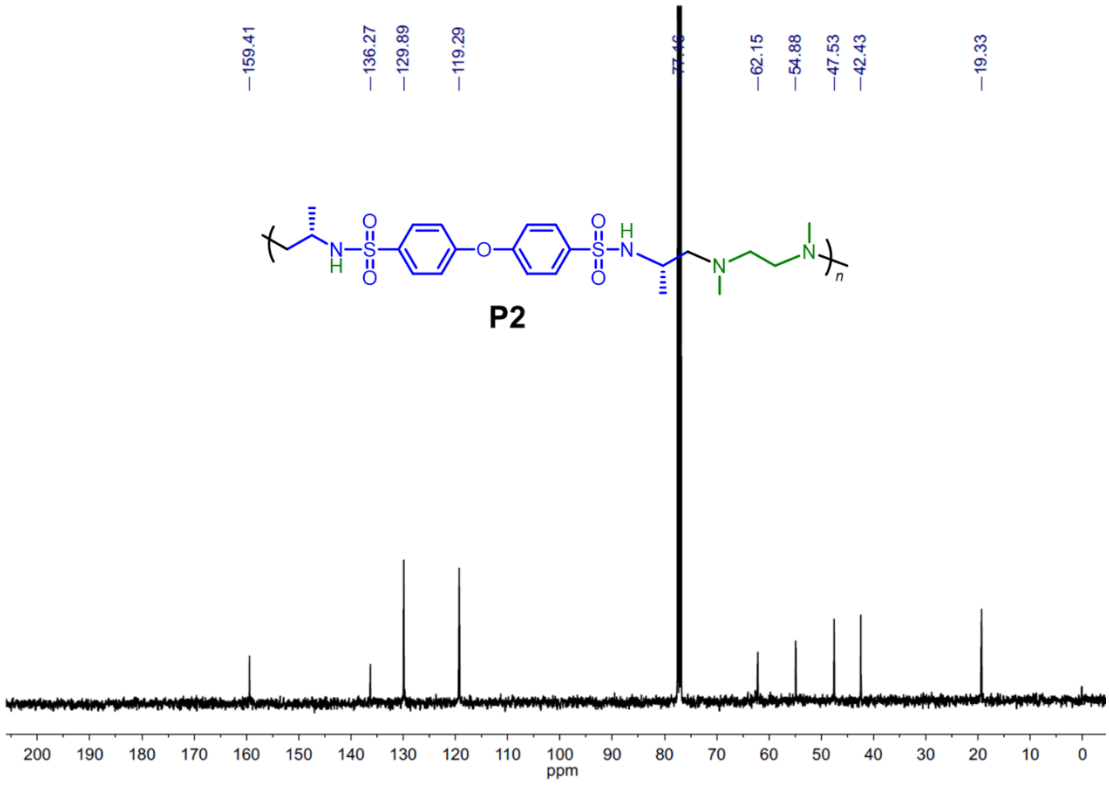
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P2
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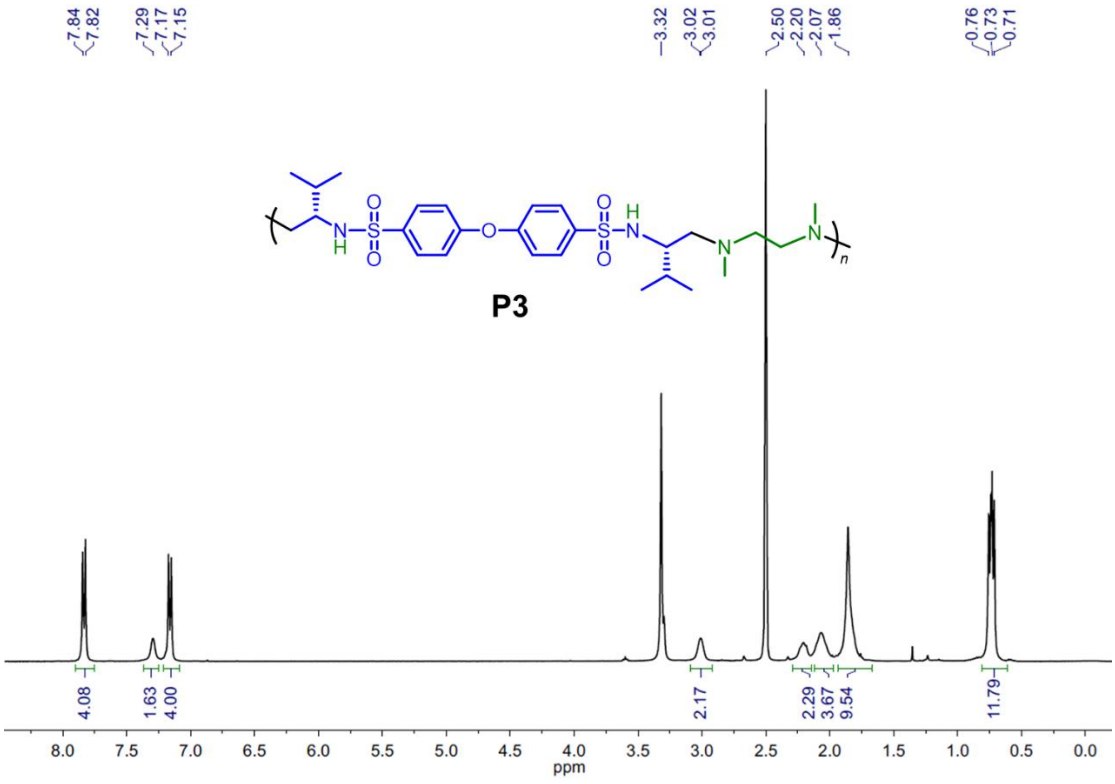
ppm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0.73
0.71
P3
4.08
1.63
4.00
2.17
2.29
3.67
9.54
11.79
8.0
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7.0
6.5
6.0
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1.5
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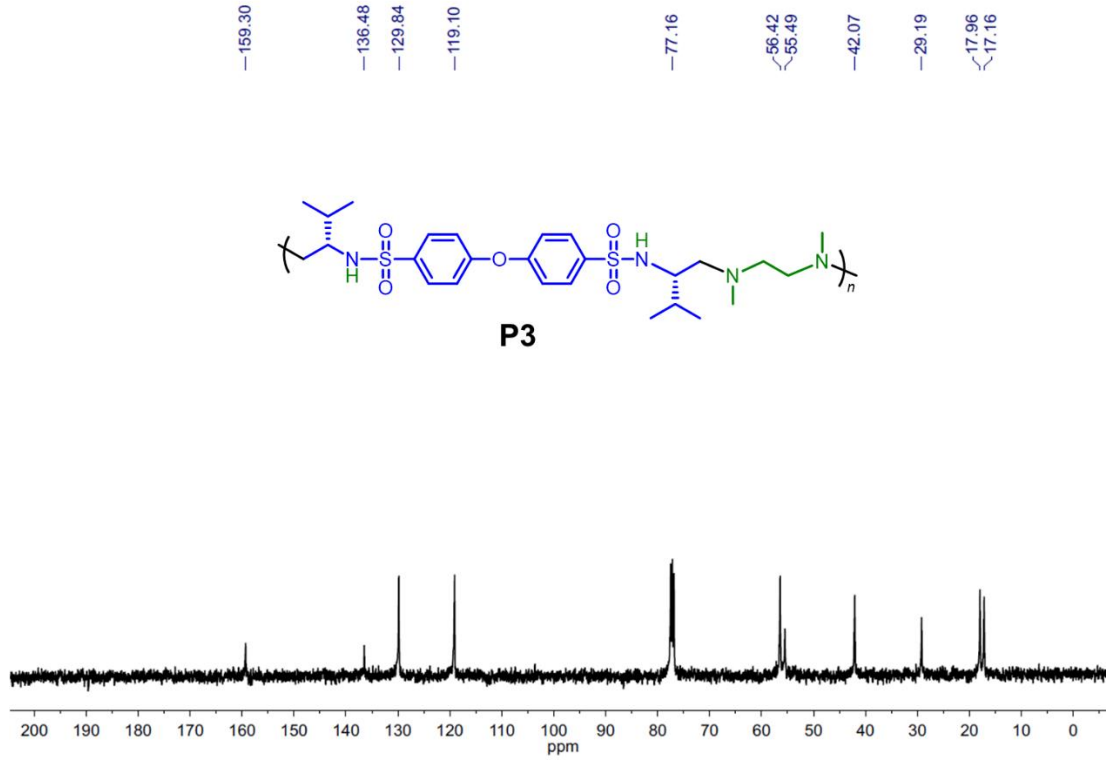
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55.49
42.07
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17.96
17.16
P3
200
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140
130
120
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90
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60
50
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20
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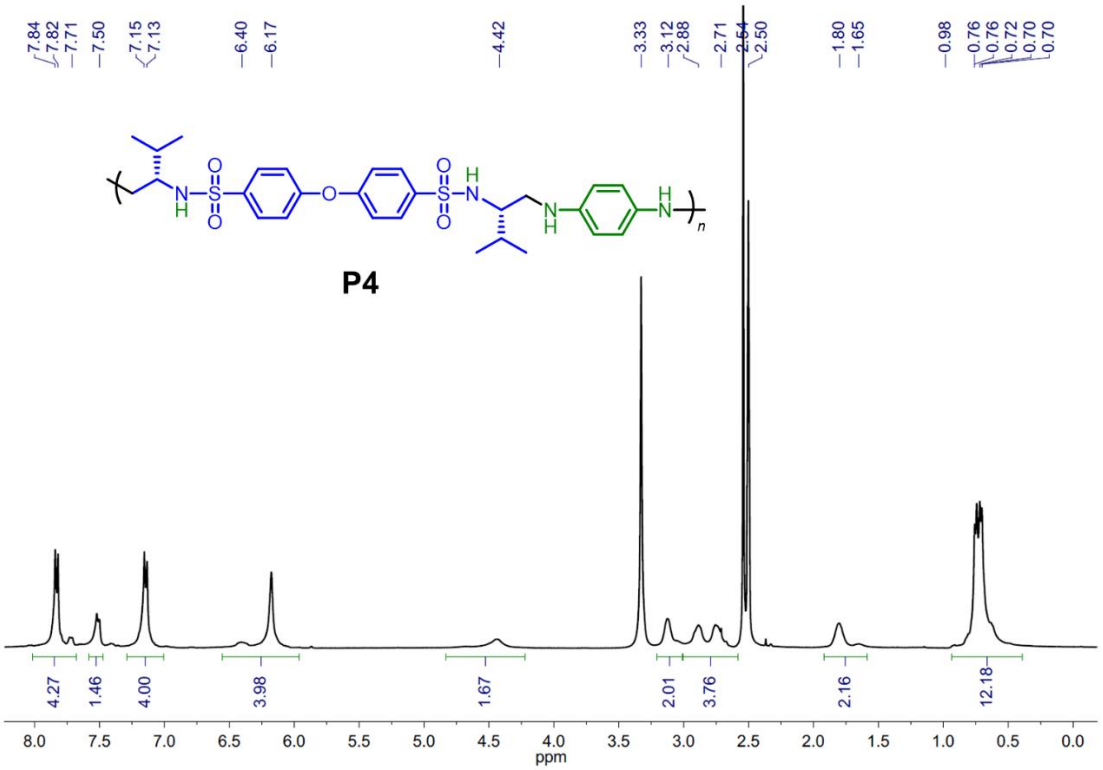
ppm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3.12
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2.50
1.80
1.65
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0.76
0.76
0.72
0.70
0.70
P4
4.27
1.46
4.00
3.98
1.67
2.01
3.76
2.16
12.18
8.0
7.5
7.0
6.5
6.0
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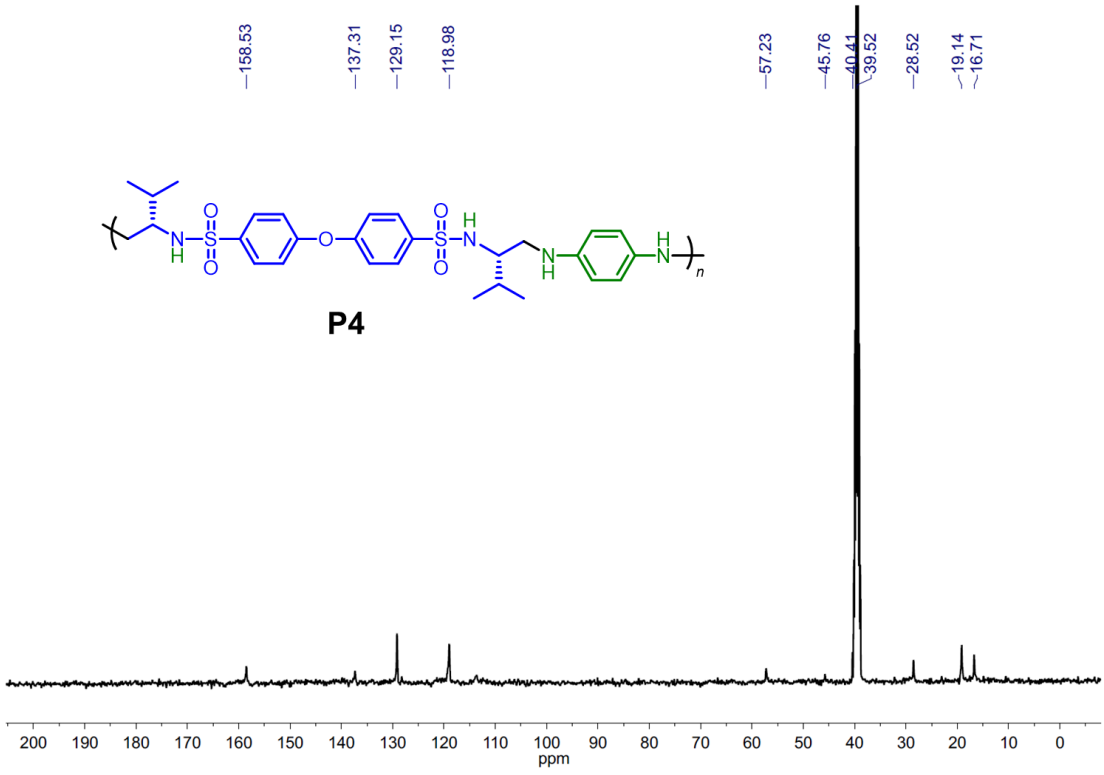
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19.14
16.71
P4
200
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140
130
120
110
100
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60
50
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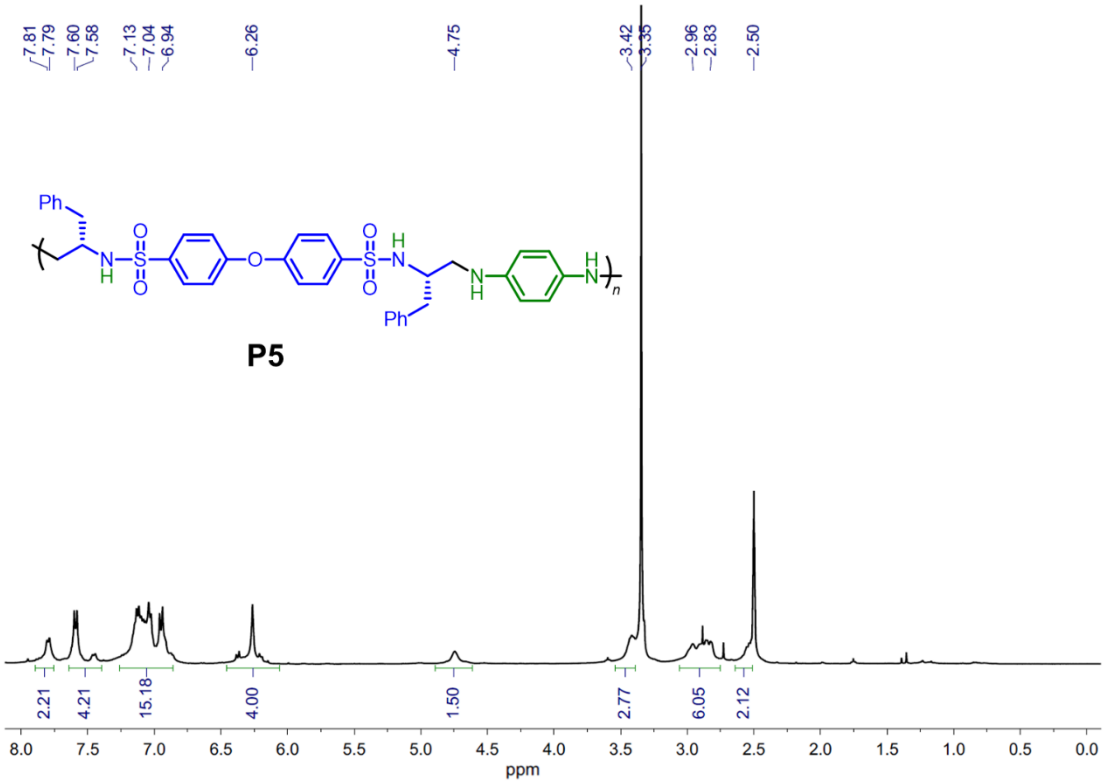
30
20
10
0
ppm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3.35
2.96
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Ph
P5
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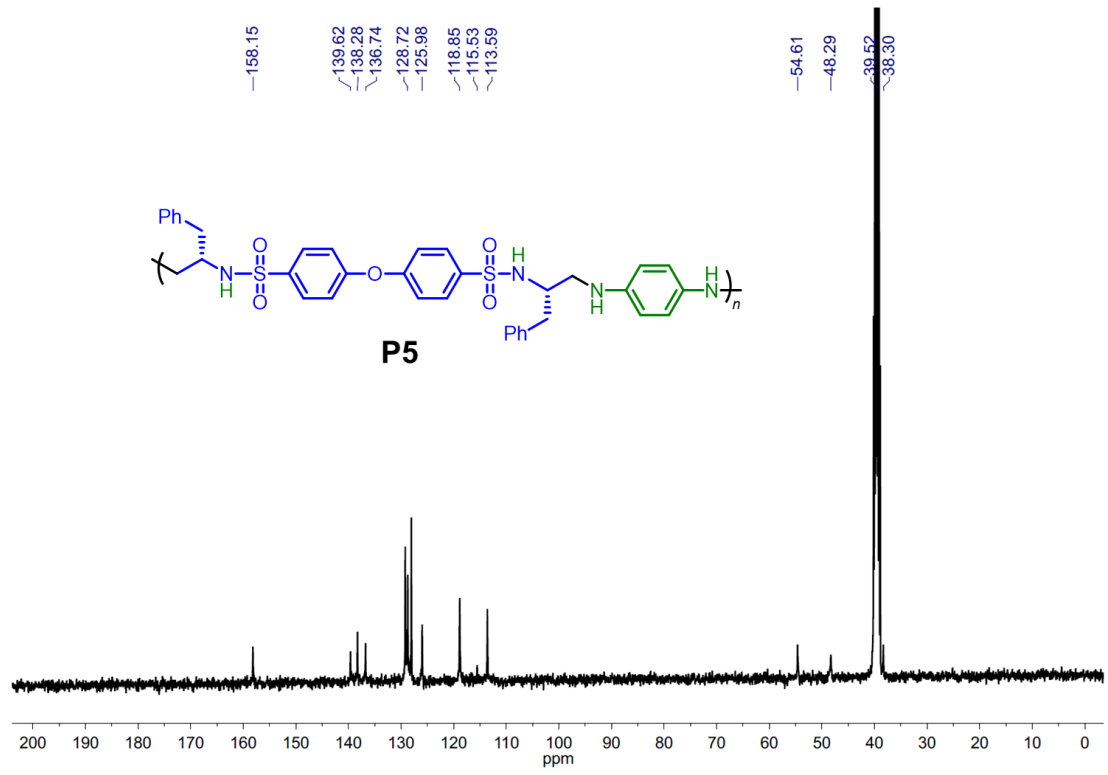
6.05
2.12
ppm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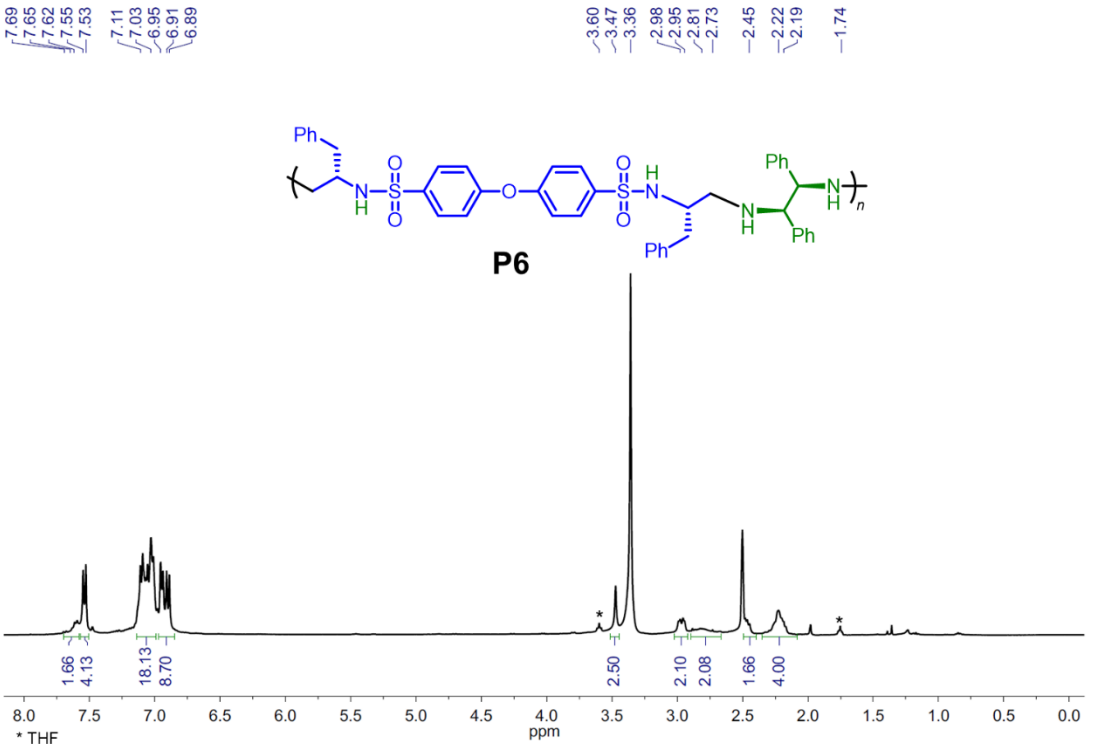
Ph
P5
ppm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2.95
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2.45
2.22
2.19
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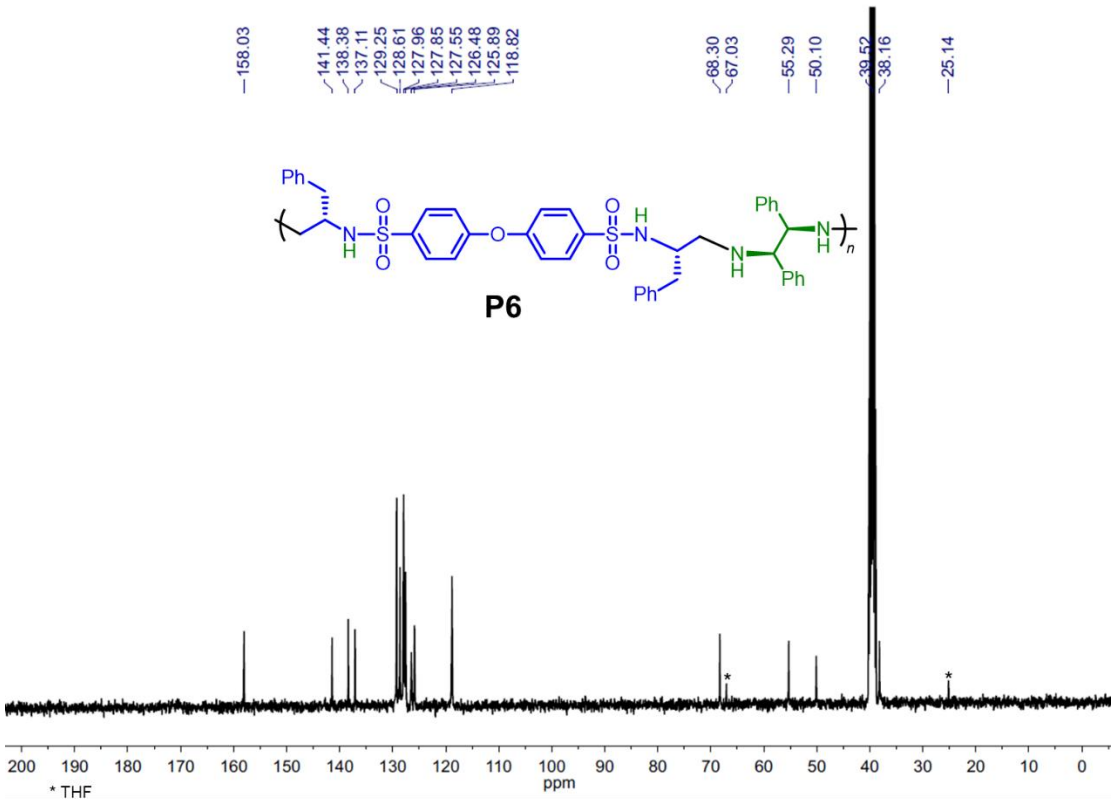
* THF
ppm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38.16
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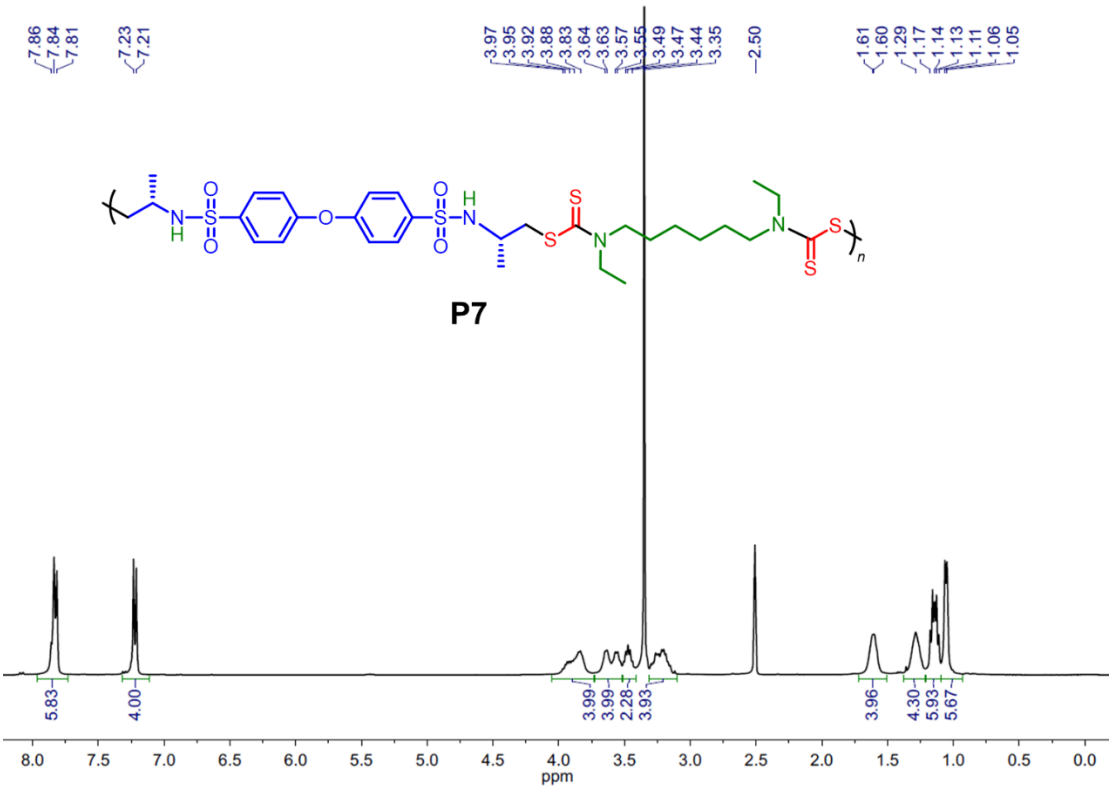
P6
* THF
ppm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3.49
3.47
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3.35
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1.61
1.60
1.29
1.17
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1.13
1.11
1.06
1.05
P7
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6.5
6.0
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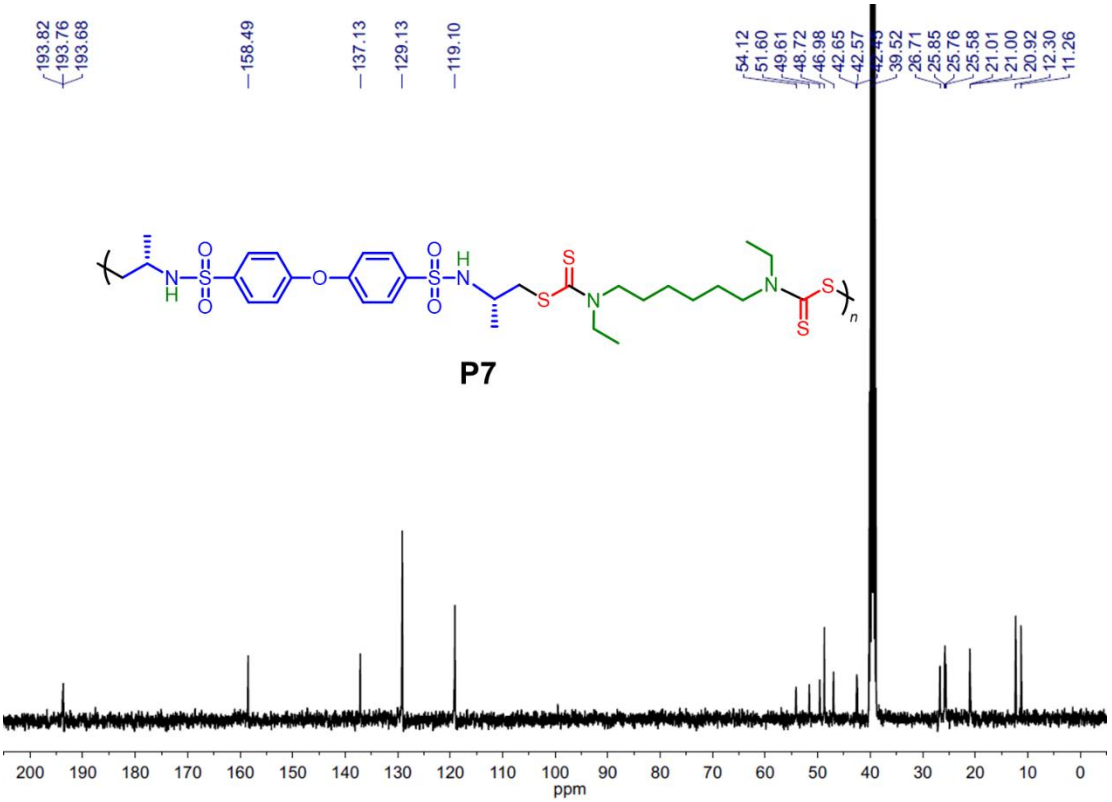
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21.00
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12.30
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P7
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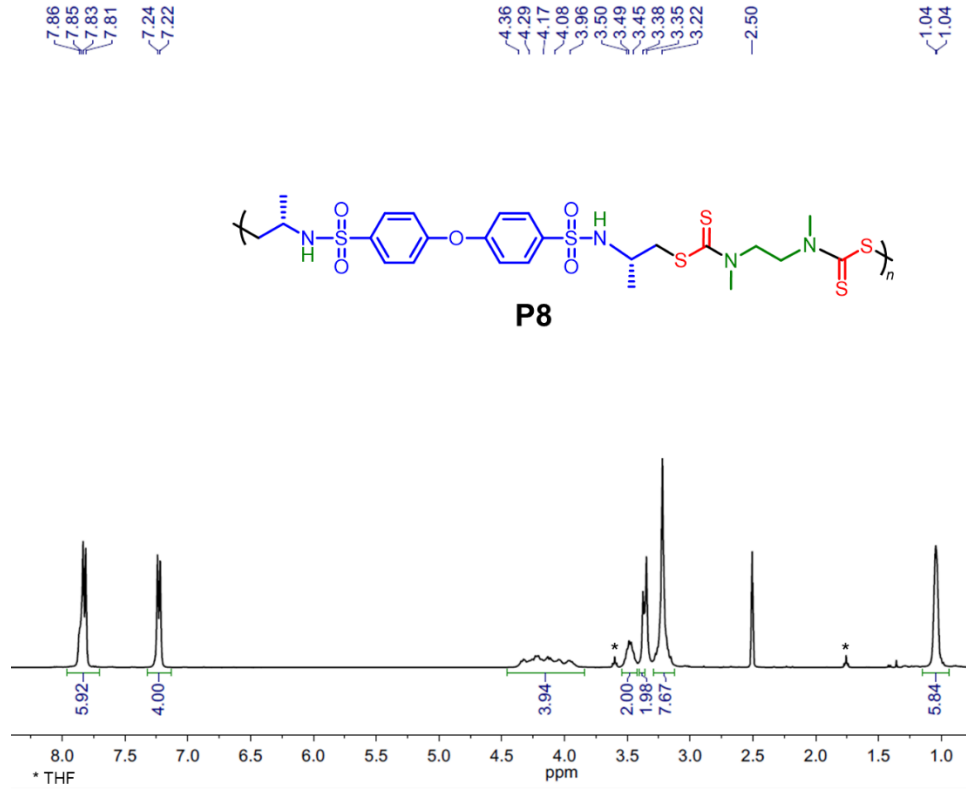
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3.22
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* THF
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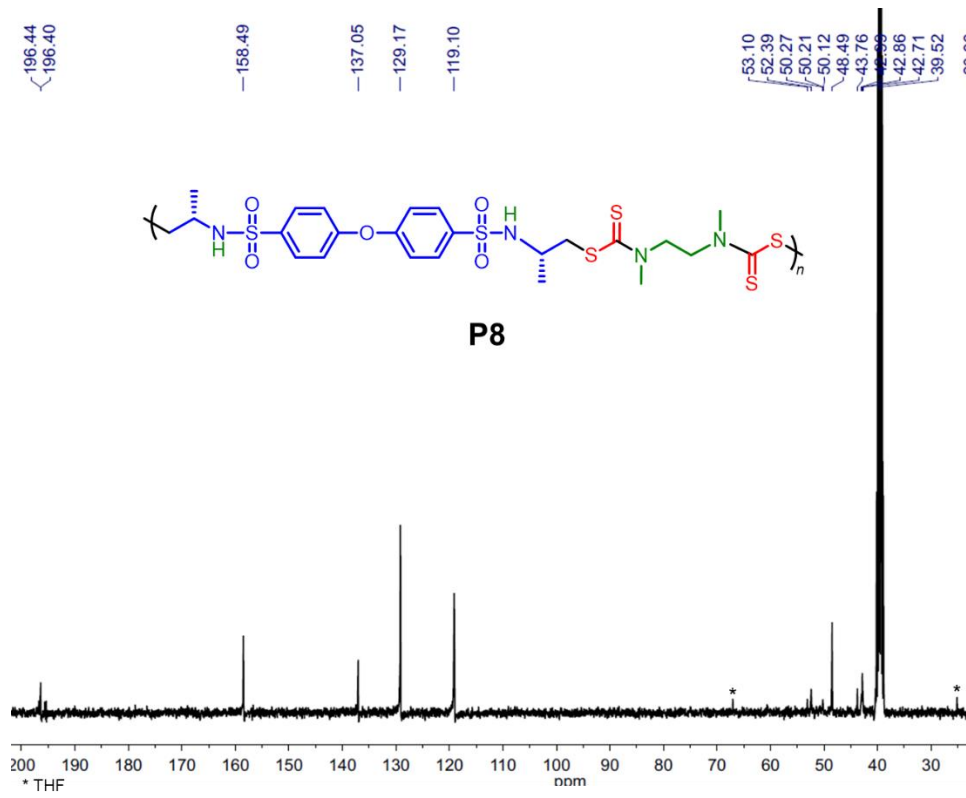
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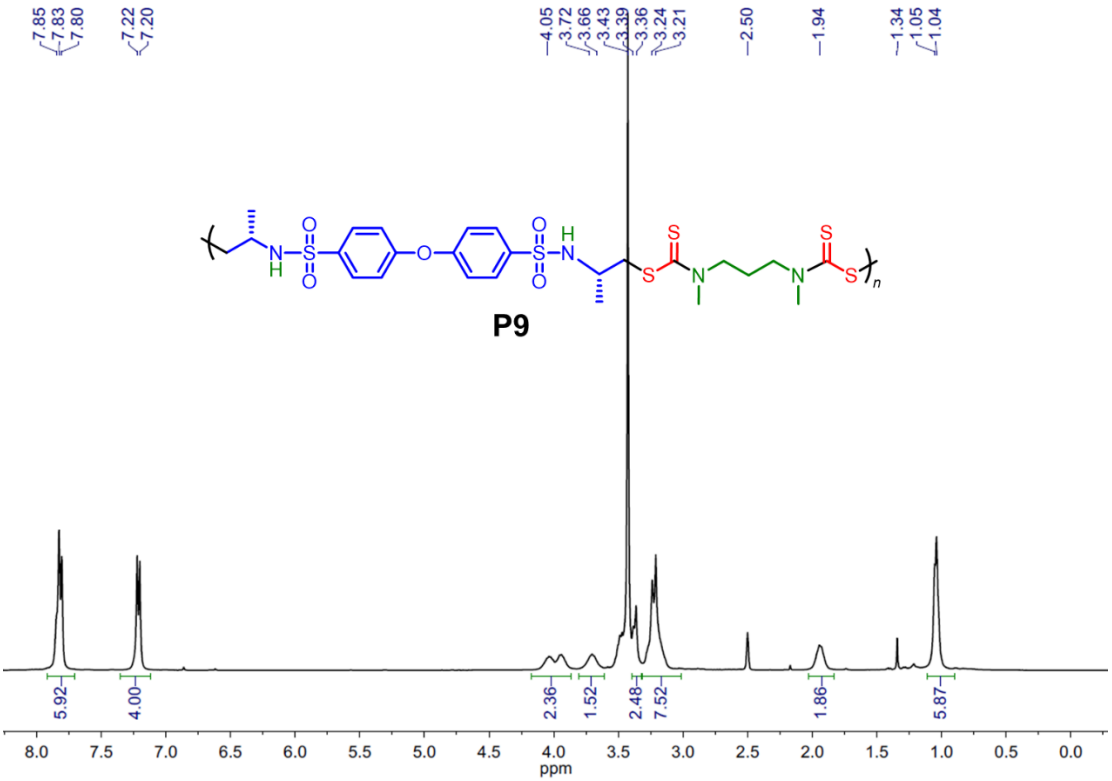
* THF
ppm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1.94
1.34
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1.04
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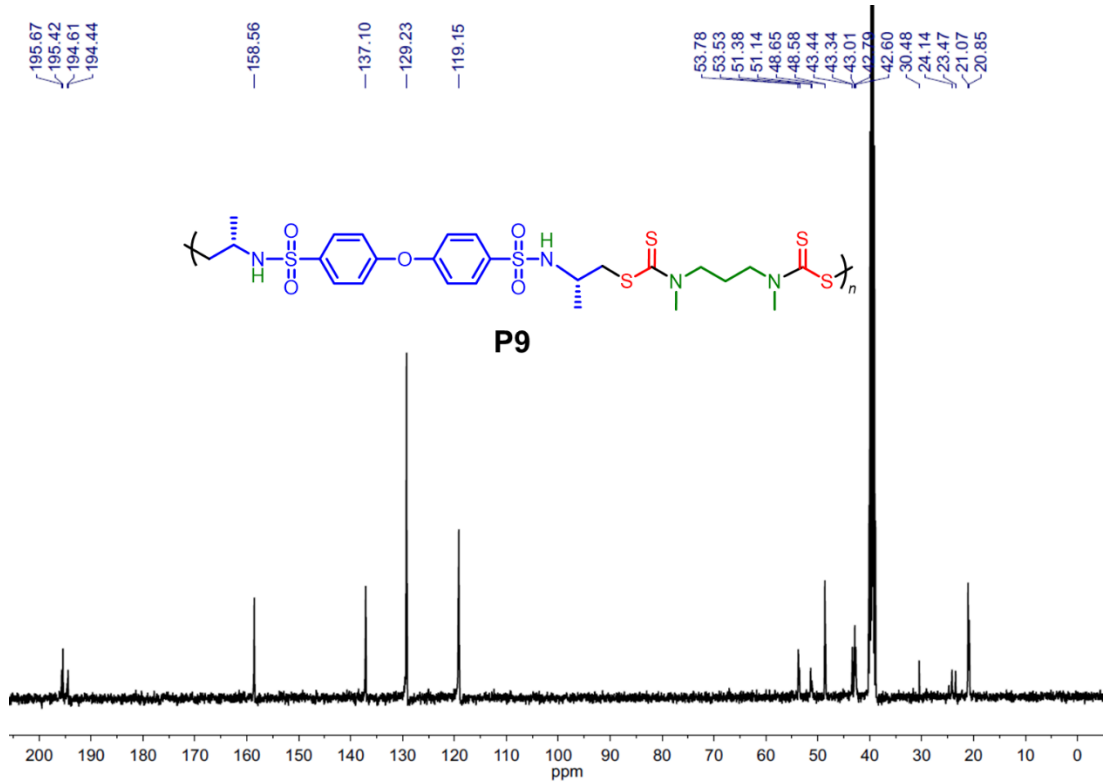
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24.14
23.47
21.07
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P9
200
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60
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30
20
10
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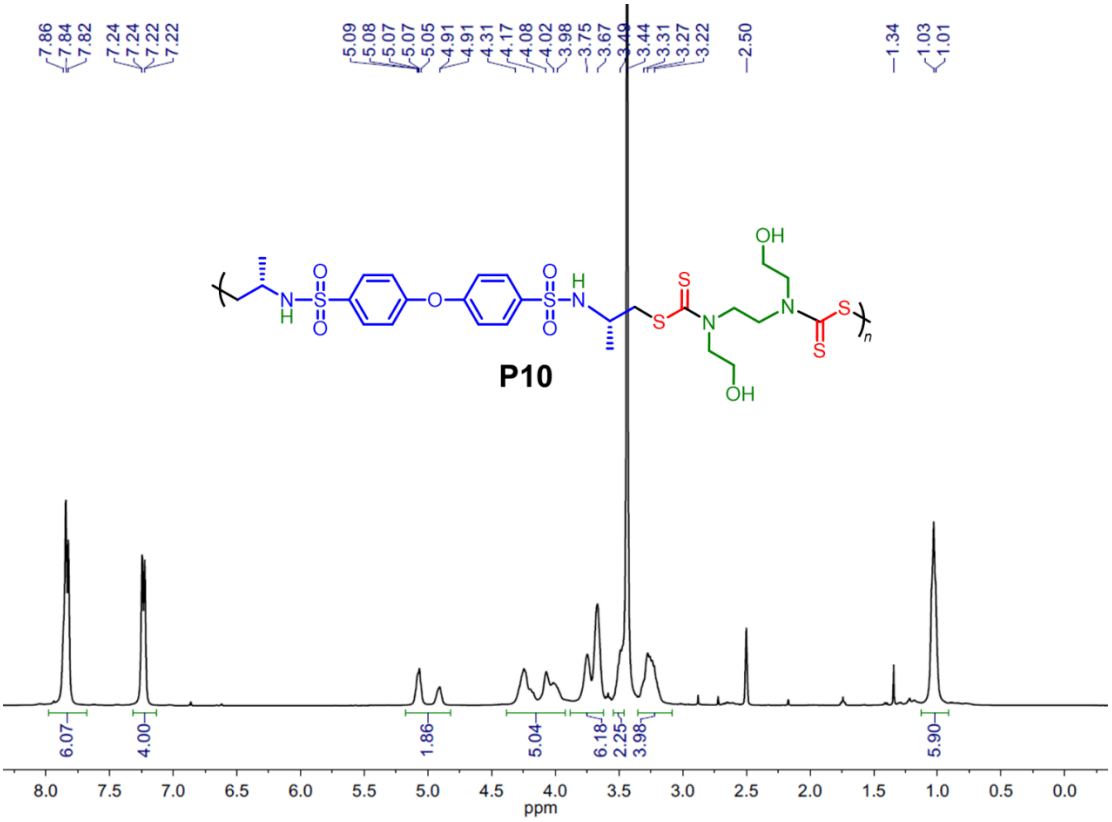
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OH
OH
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5.90
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6.0
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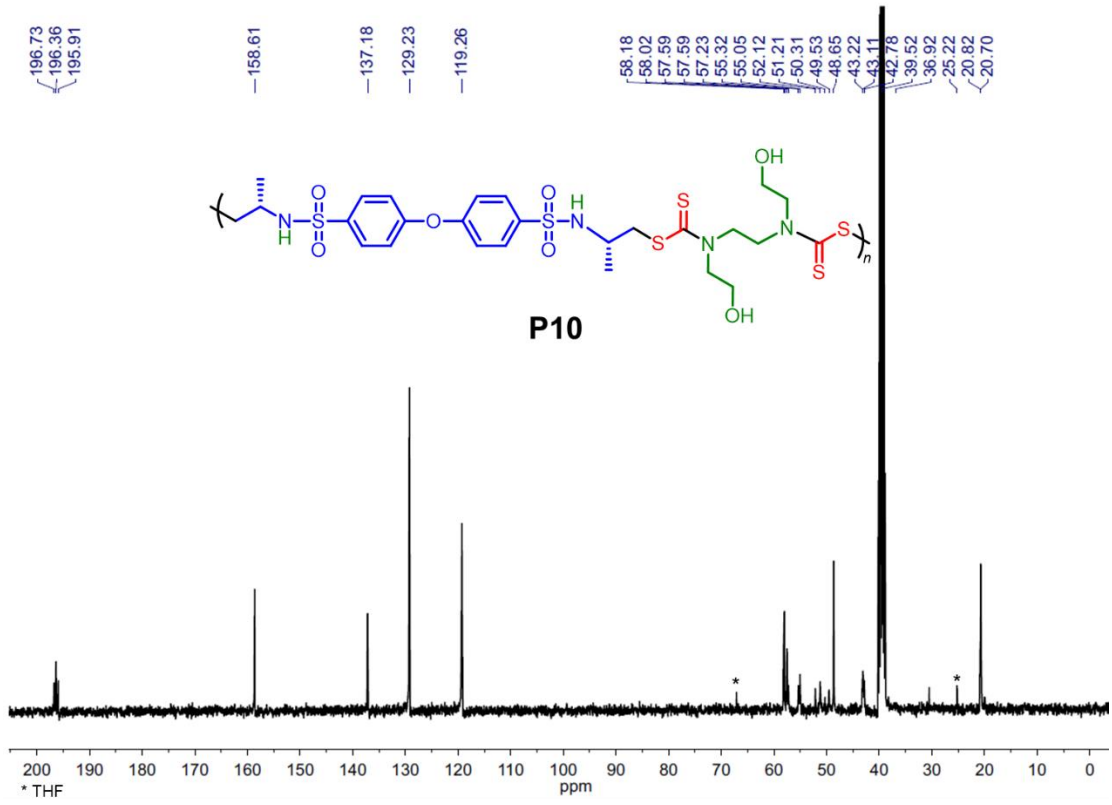
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48.65
43.22
43.11
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36.92
25.22
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20.70
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OH
P10
*
*
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180
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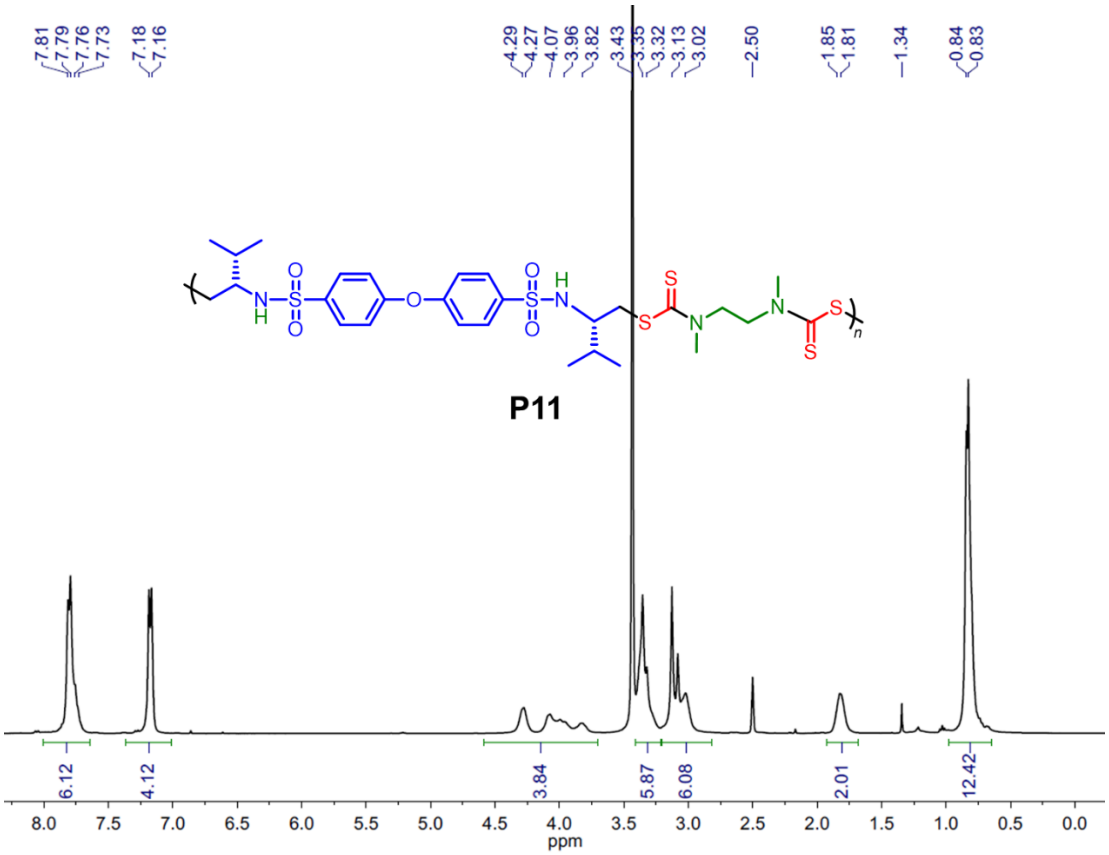
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3.32
3.13
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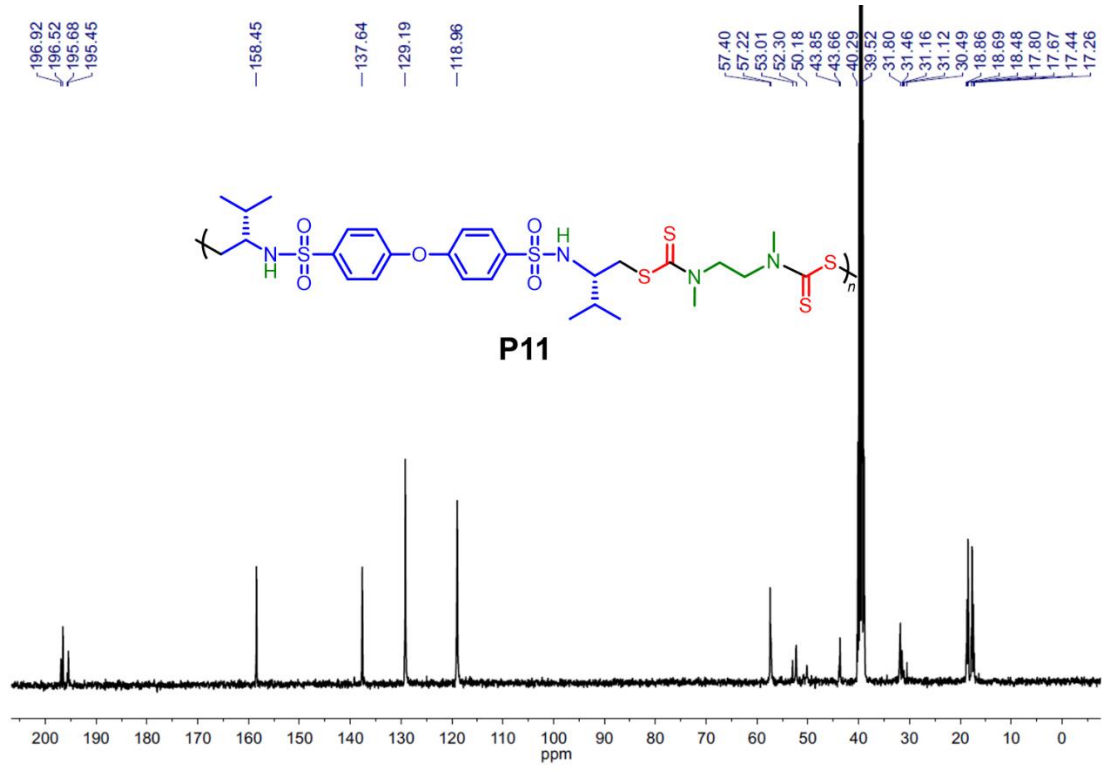
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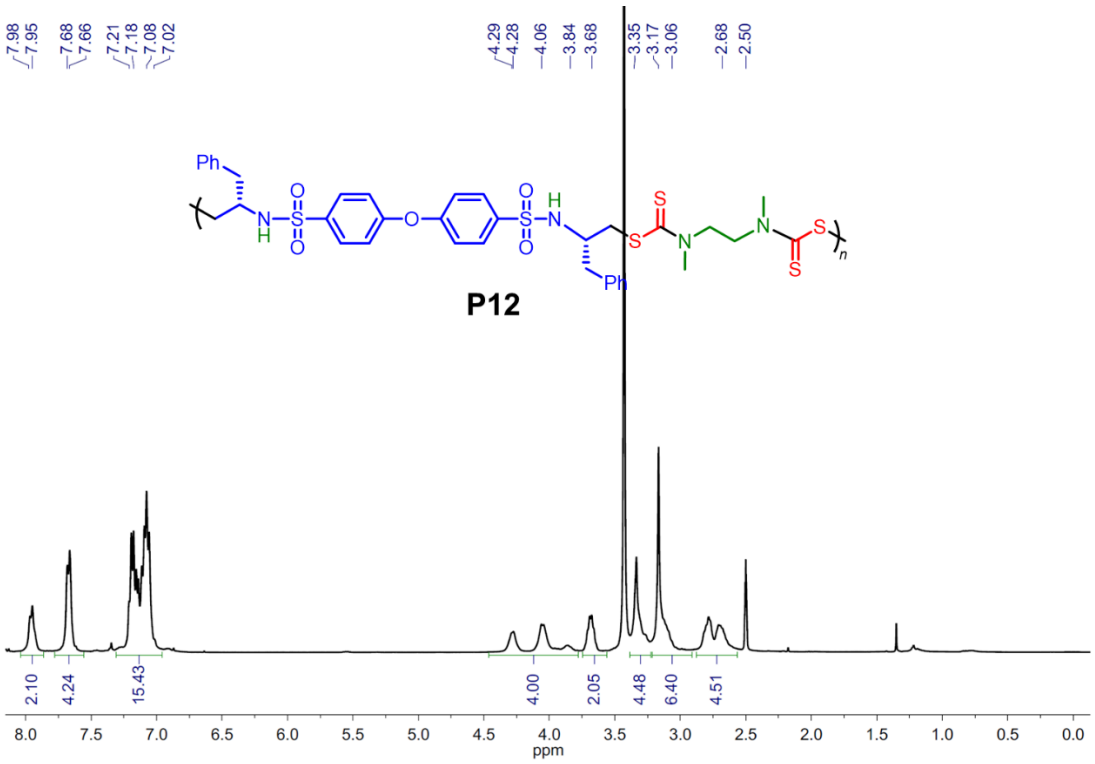
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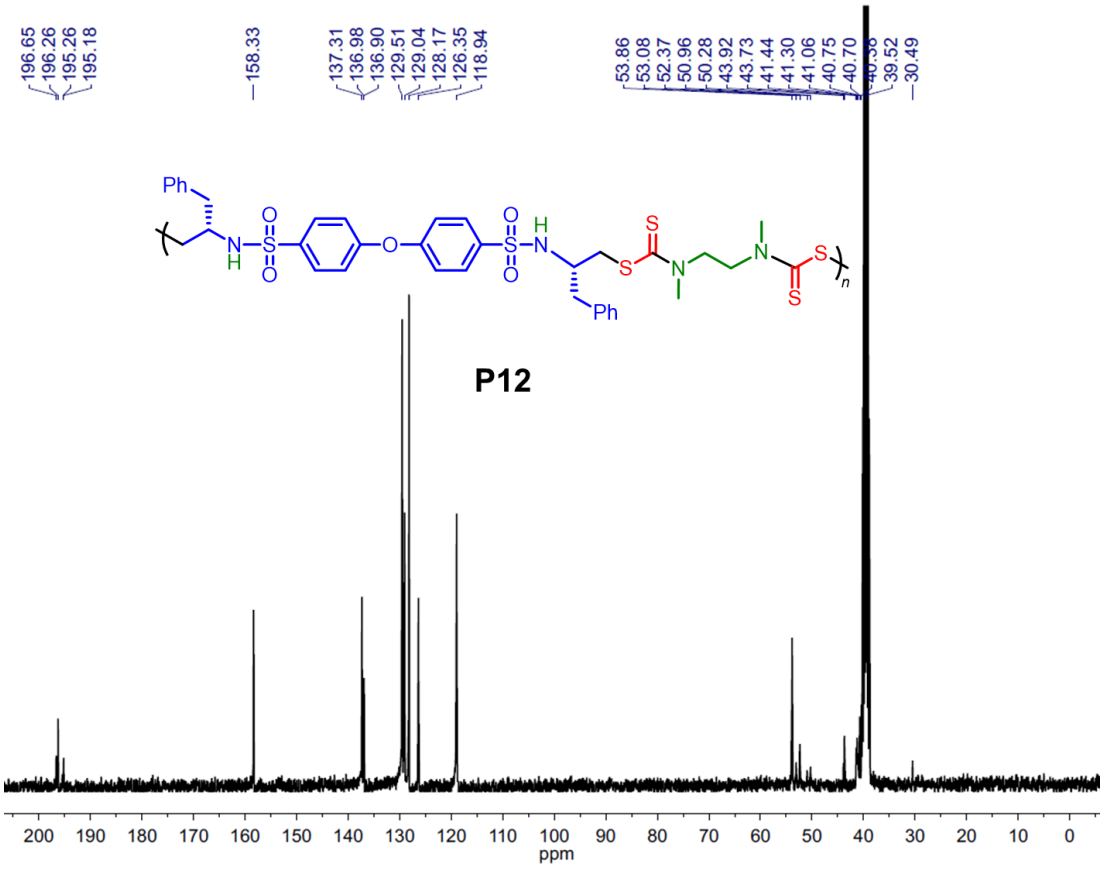
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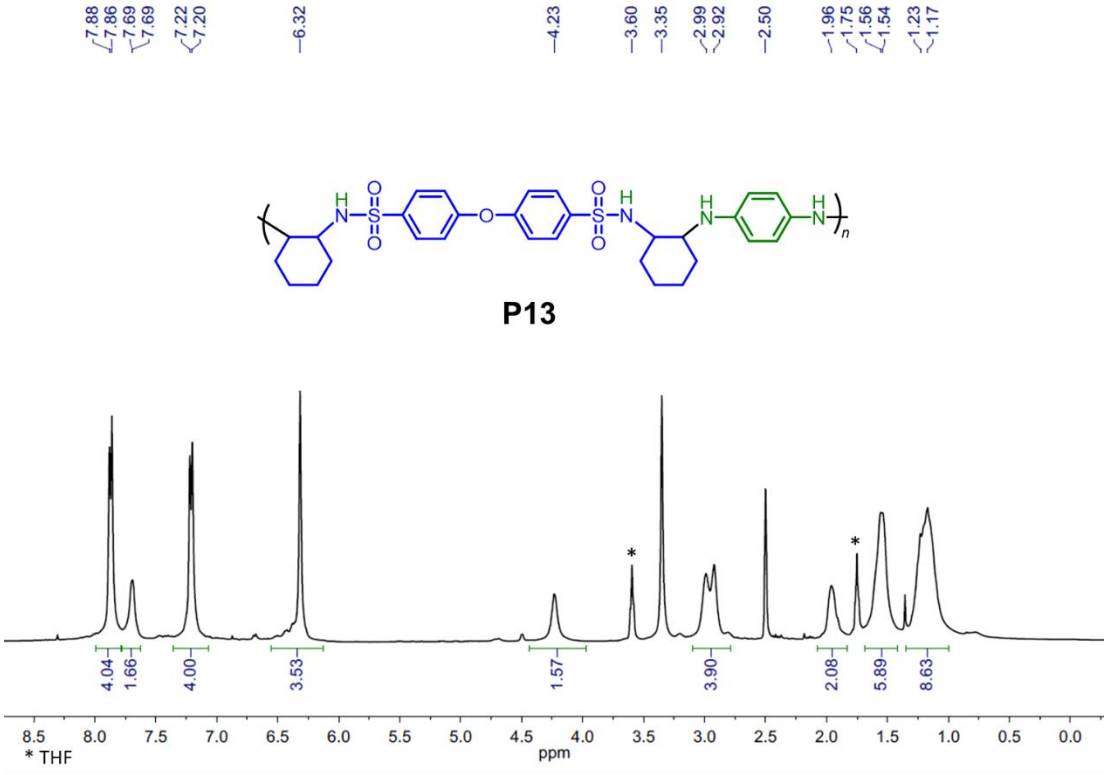
Ph
P12
ppm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1.75
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1.23
1.17
P13
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3.90
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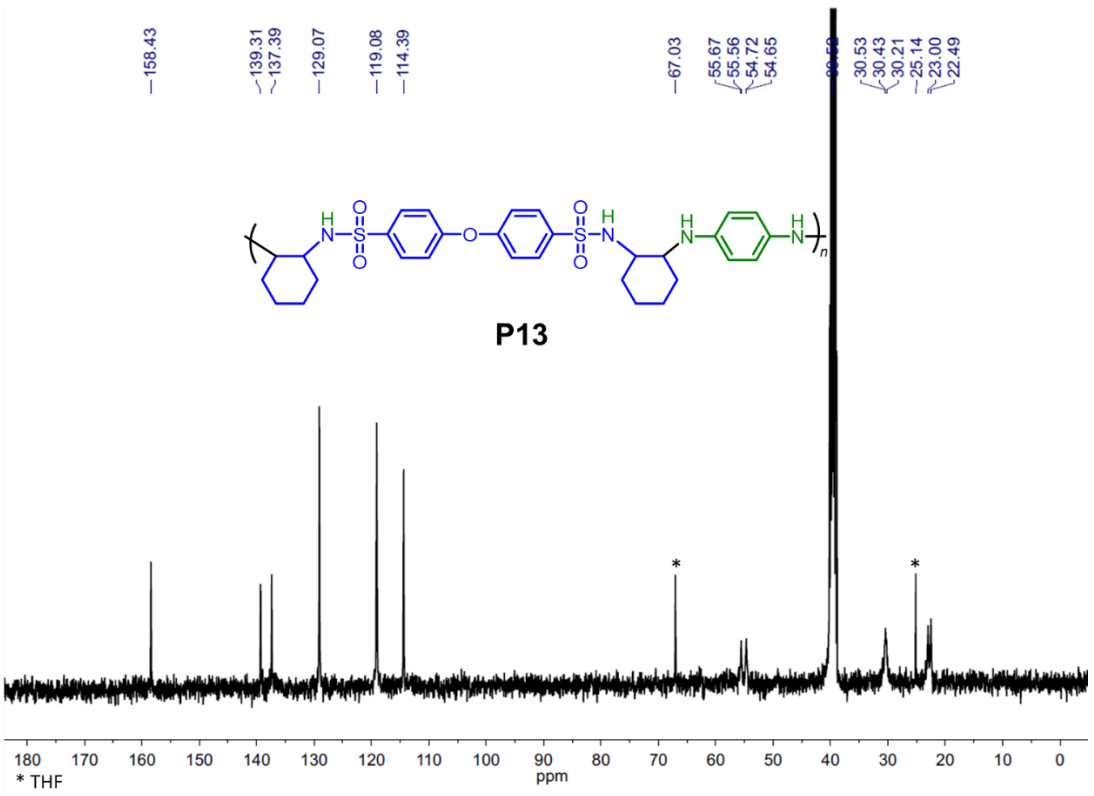
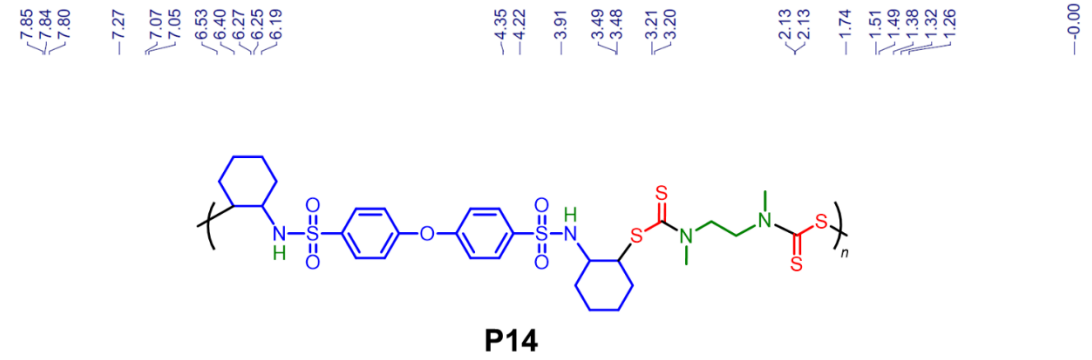
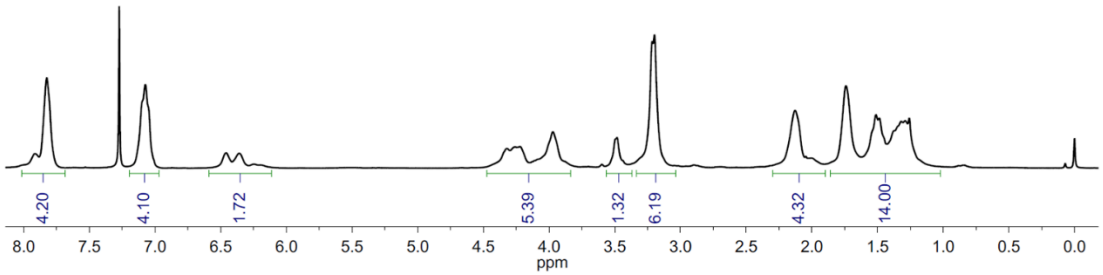
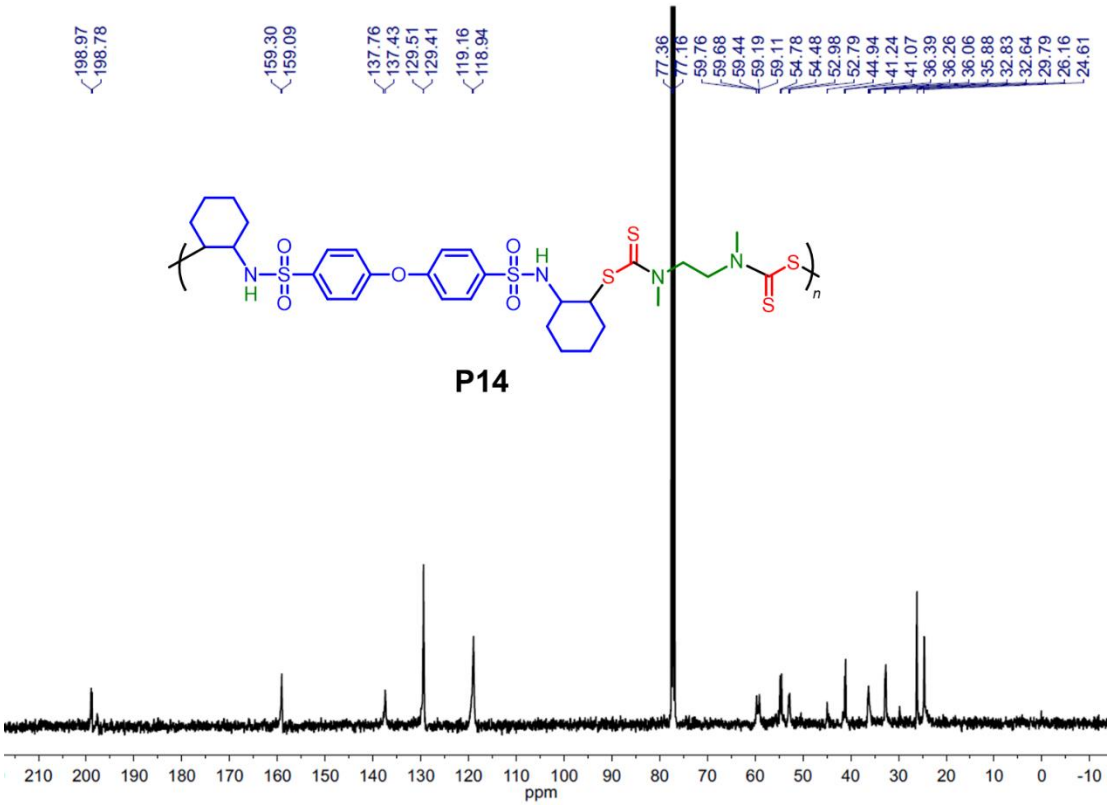
8.63
* THF
ppm


158.43
139.31
137.39
129.07
119.08
114.39
67.03
55.67
55.56
54.72
54.65
30.53
30.43
30.21
25.14
23.00
22.49
P13
* THF
ppm


7.85
7.84
7.80
7.27
7.07
7.05
6.53
6.40
6.27
6.25
6.19
4.35
4.22
3.91
3.49
3.48
3.21
3.20
2.13
2.13
1.74
1.51
1.49
1.38
1.32
1.26
0.00

P14


4.20
4.10
1.72
5.39
1.32
6.19
4.32
14.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

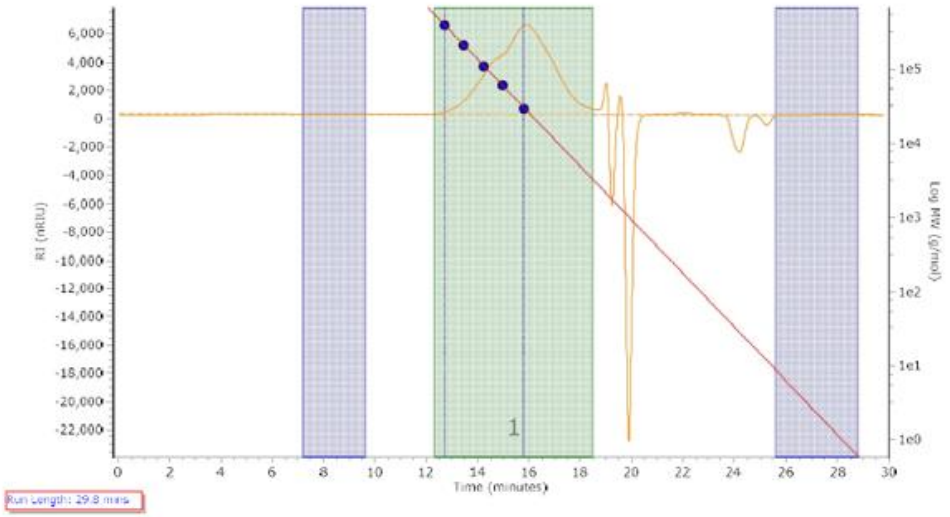

198.97
198.78
159.30
159.09
137.76
137.43
129.51
129.41
119.16
118.94
77.36
77.16
59.76
59.68
59.44
59.19
59.11
54.78
54.48
52.98
52.79
44.94
41.24
41.07
36.39
36.26
36.06
35.88
32.83
32.64
29.79
26.16
24.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

P14

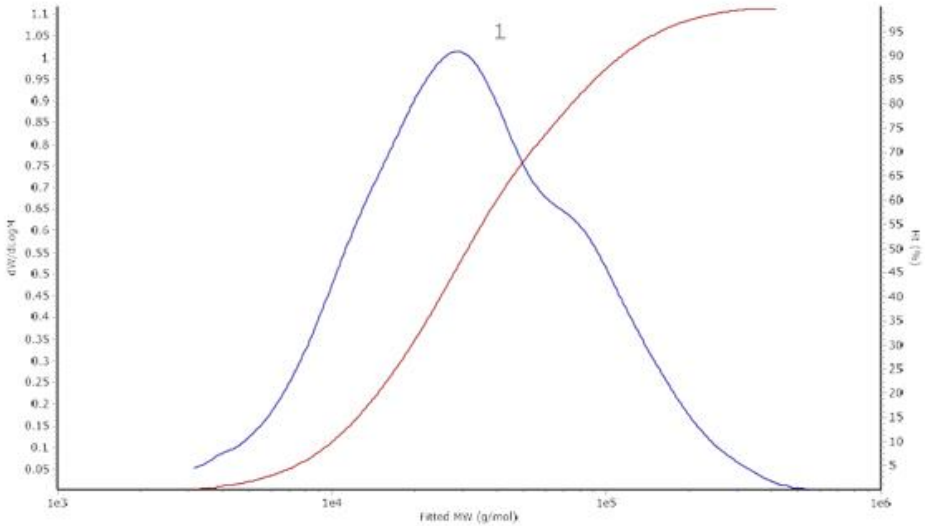
4. Full SEC (DMF, 60 °C) Traces

P1

Chromatogram Plot

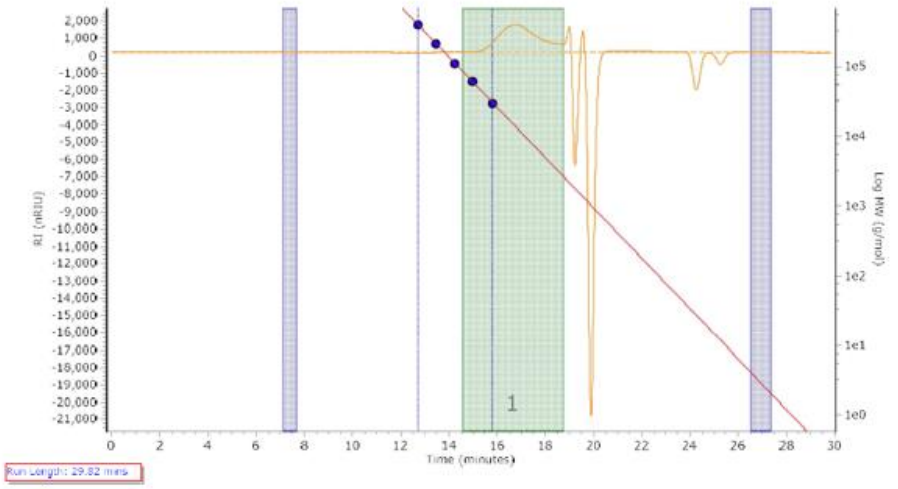


Distribution Plot

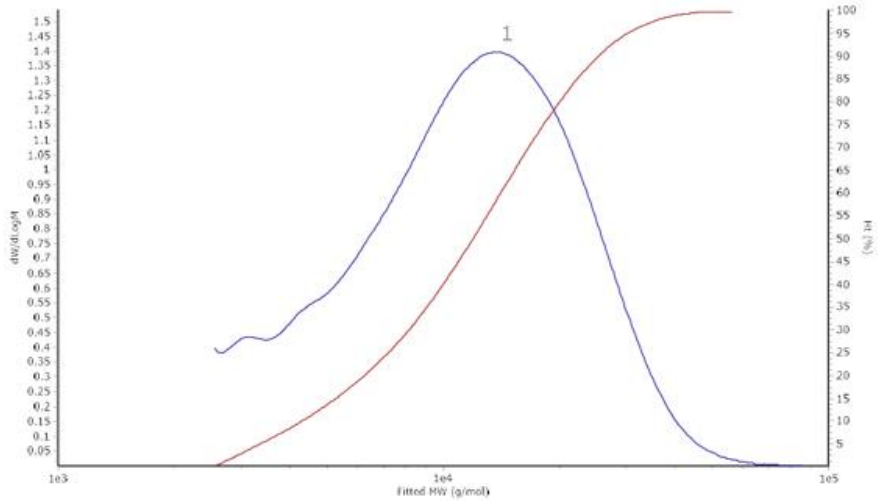


P2

Chromatogram Plot

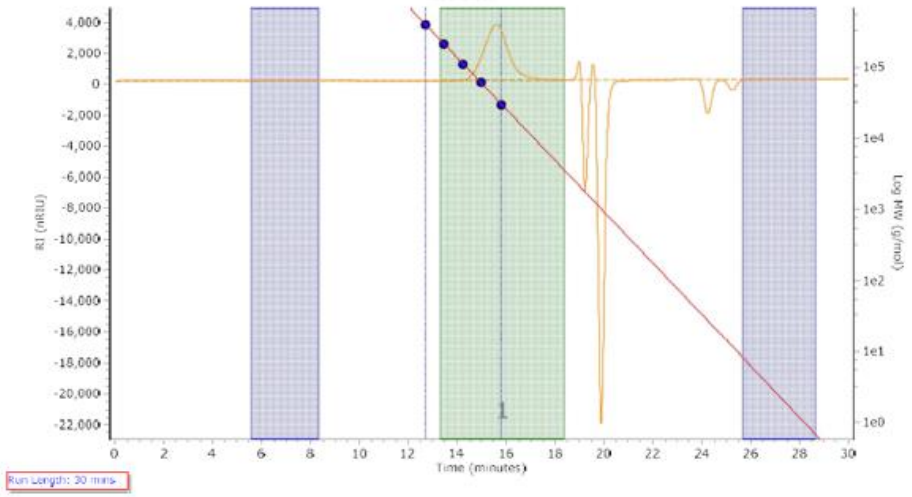


Distribution Plot

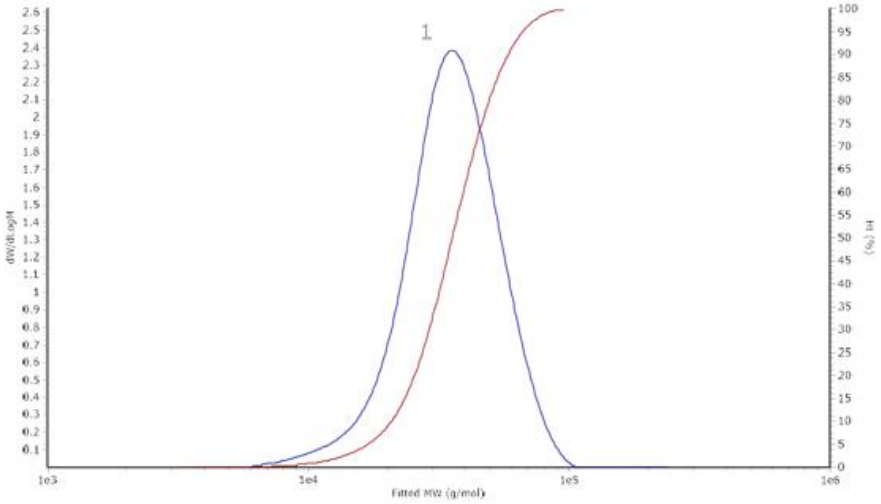


P3

Chromatogram Plot

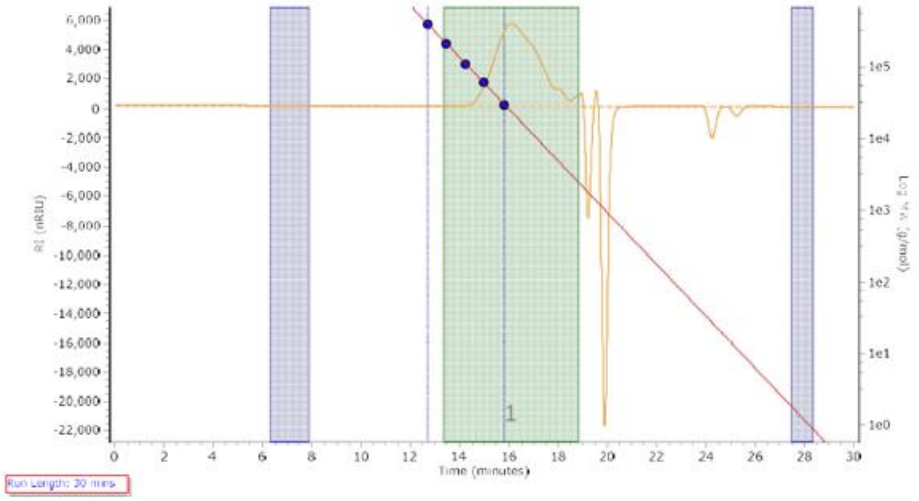


Distribution Plot

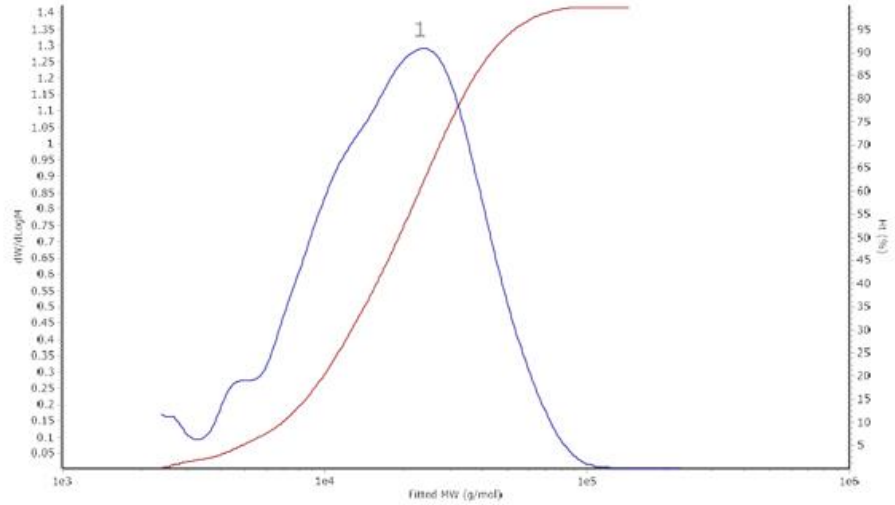


P4

Chromatogram Plot

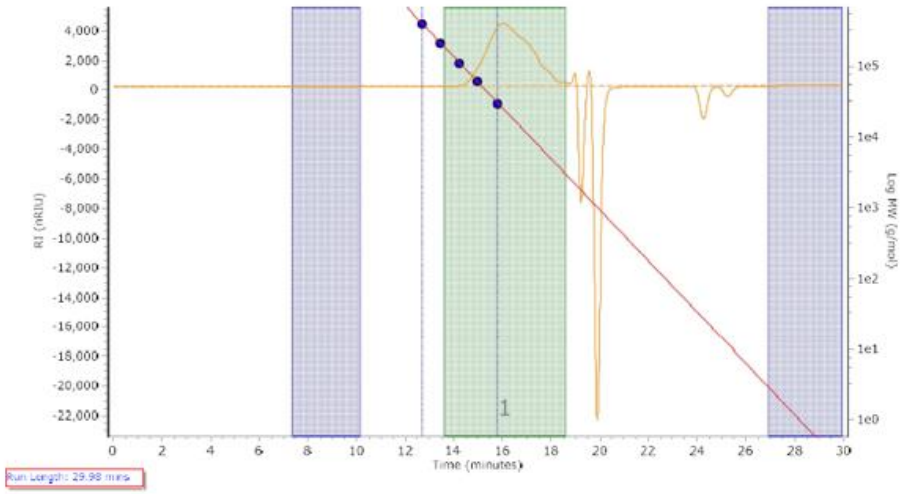


Distribution Plot

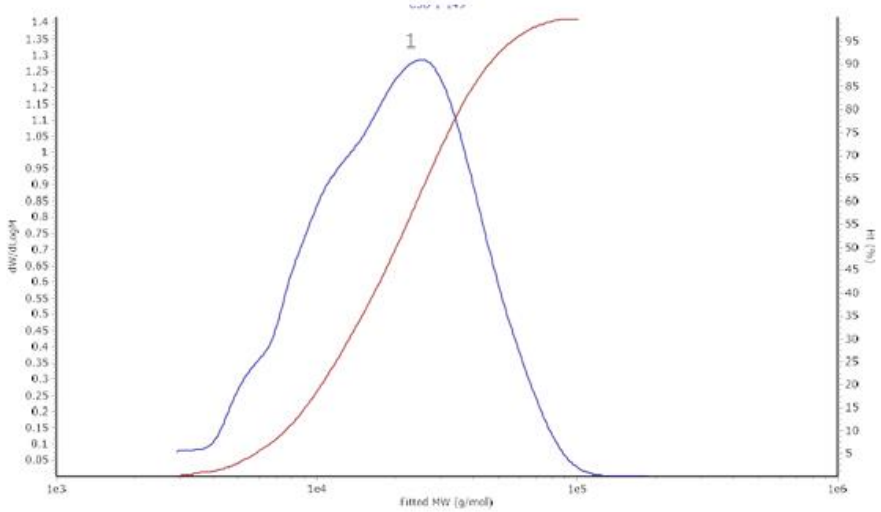


P5

Chromatogram Plot

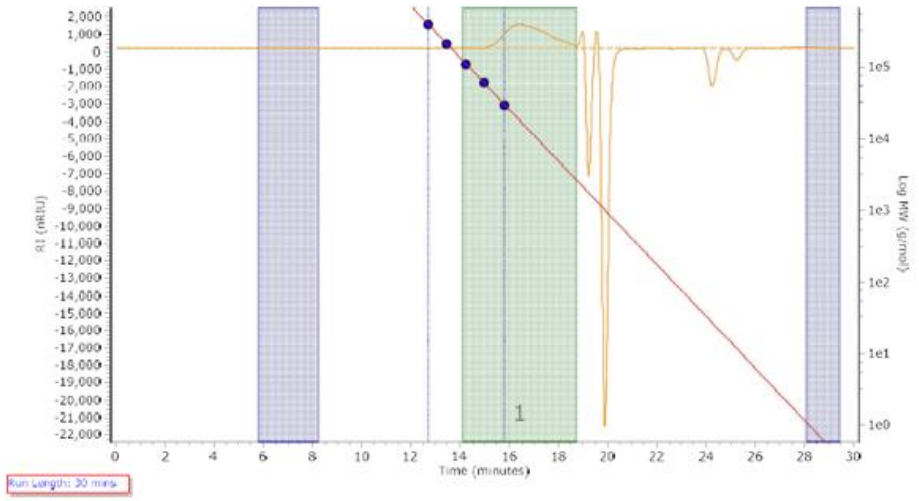


Distribution Plot

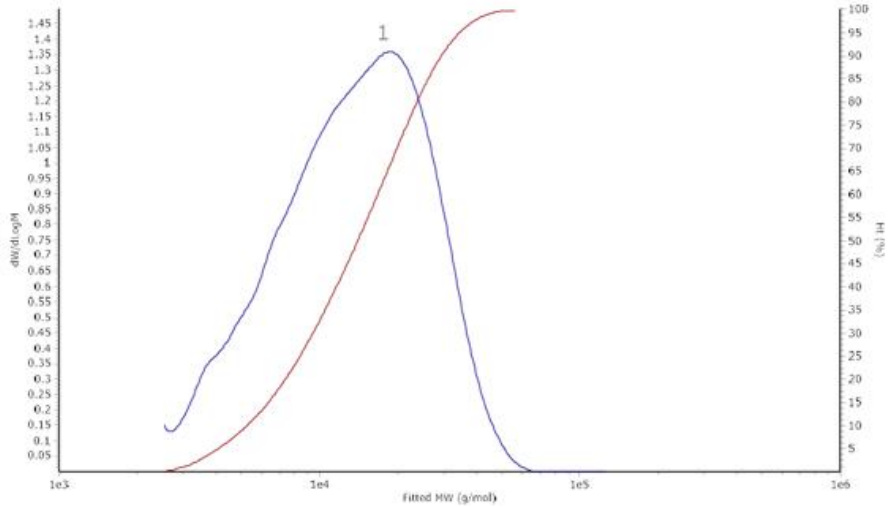


P6

Chromatogram Plot

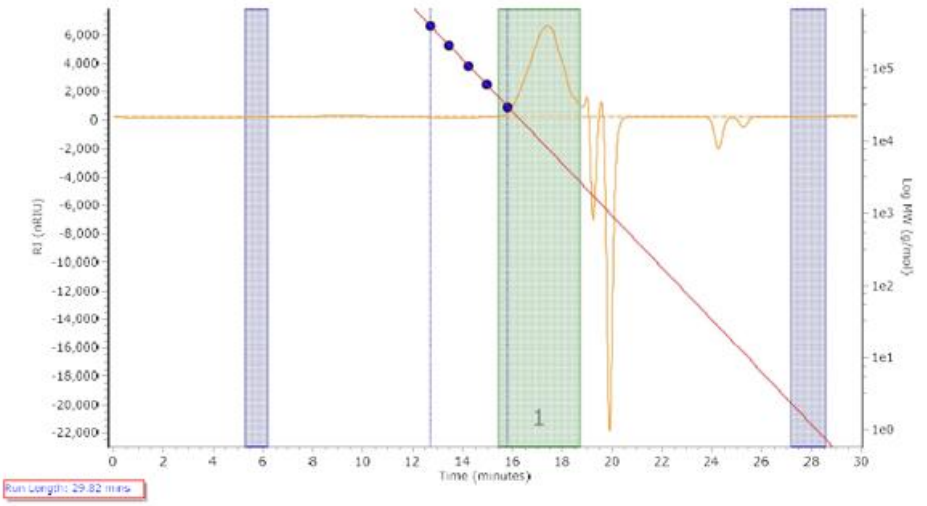


Distribution Plot

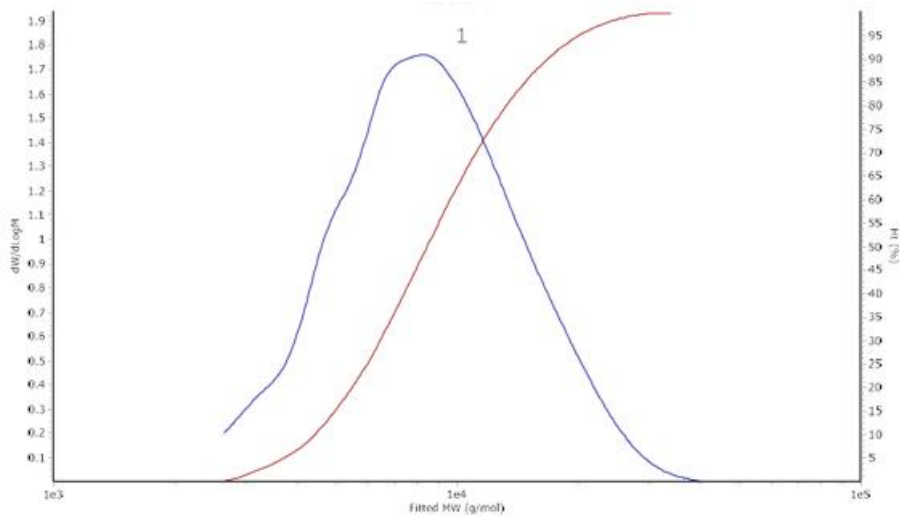


P7

Chromatogram Plot

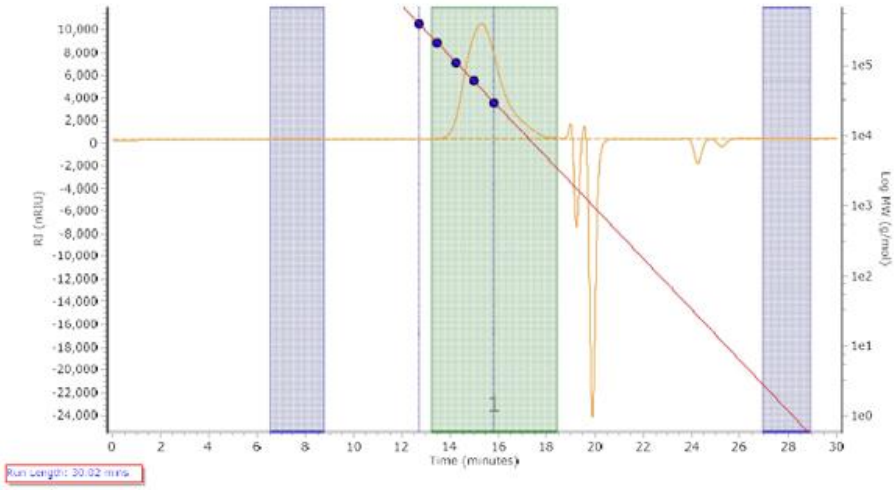


Distribution Plot

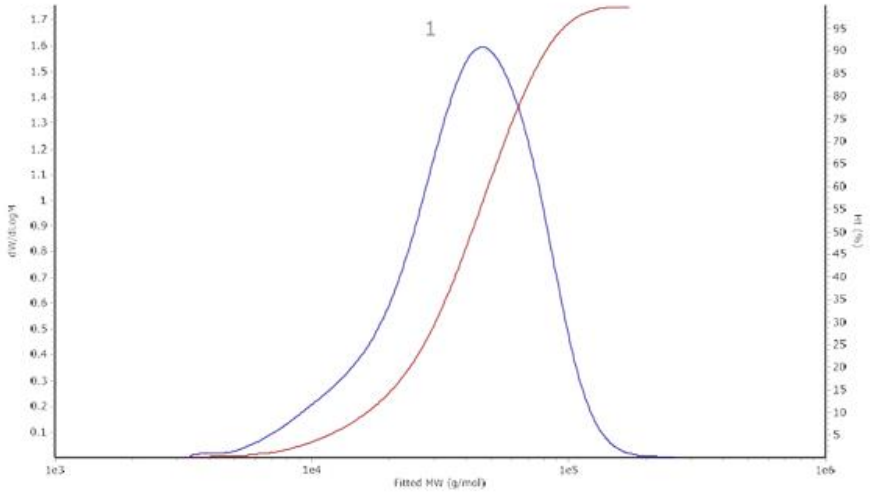


P8

Chromatogram Plot

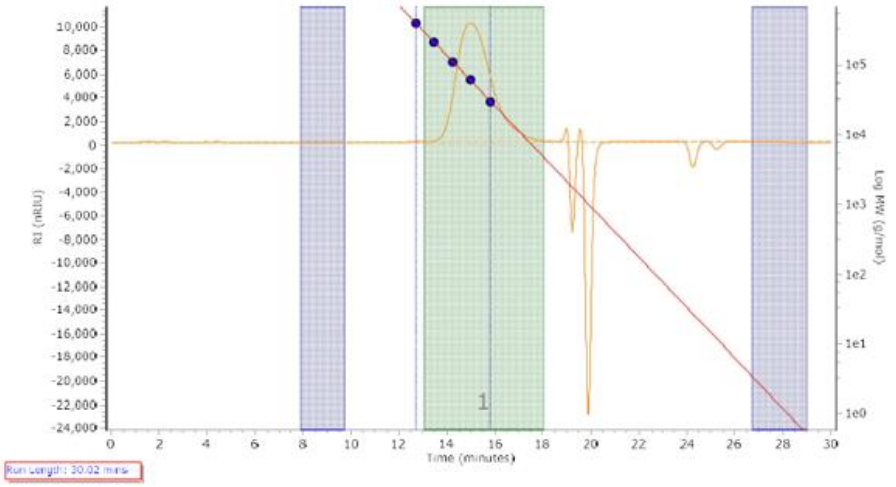


Distribution Plot

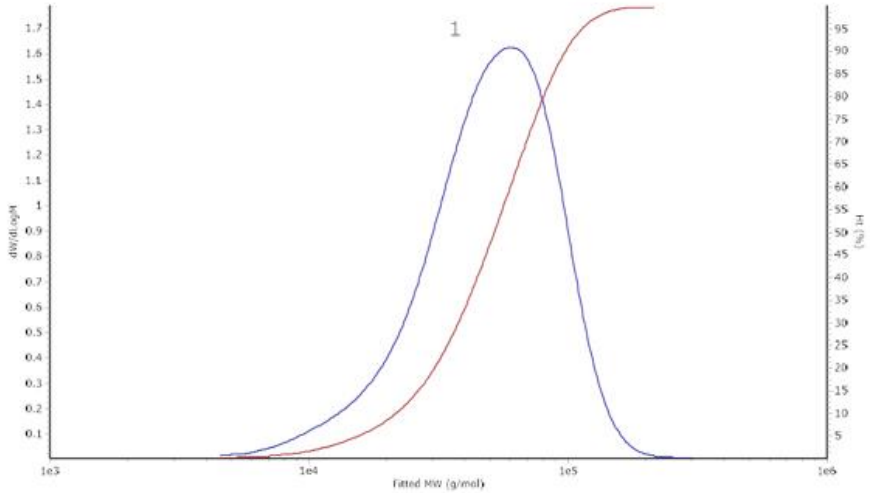


P9

Chromatogram Plot

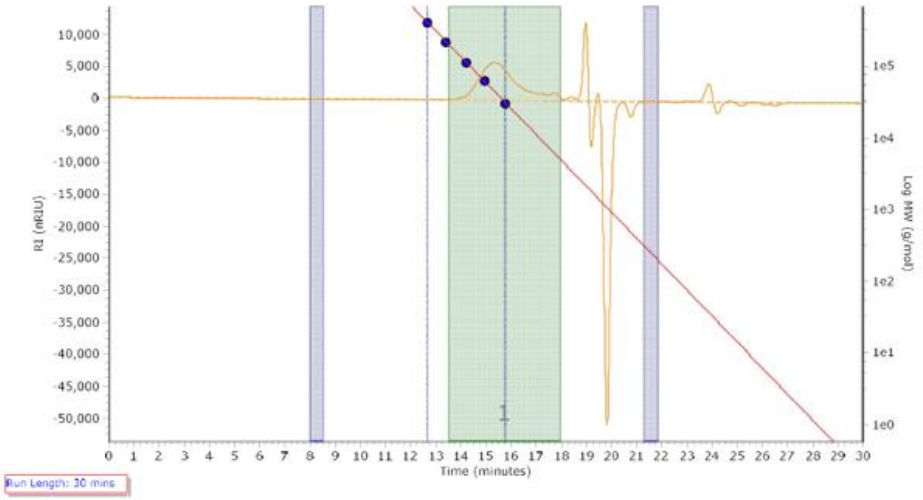


Distribution Plot

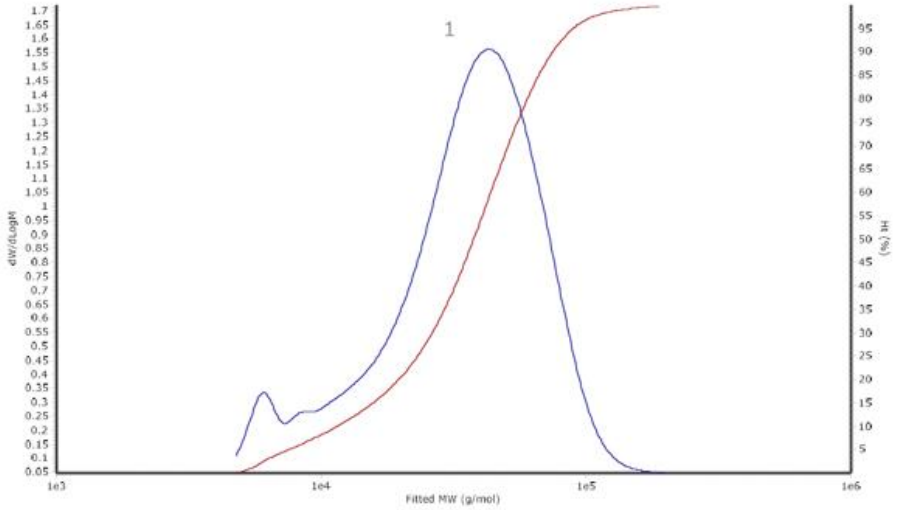


Chromatogram Plot

P10

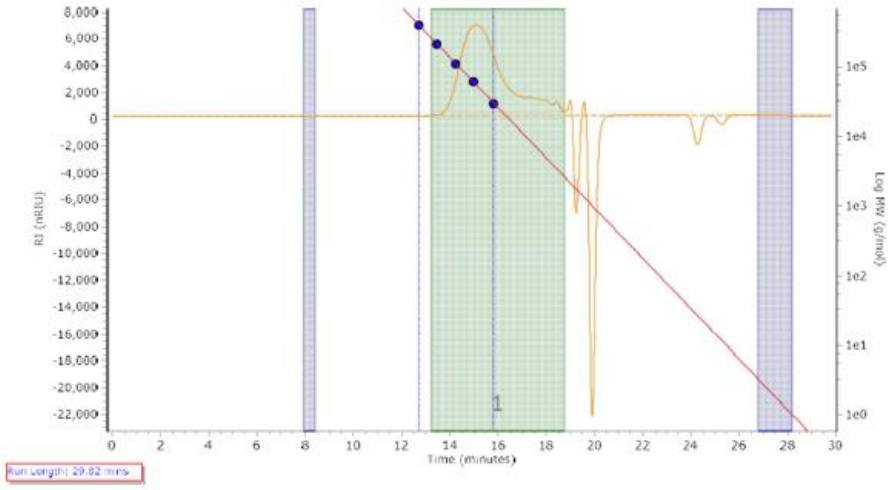


Distribution Plot

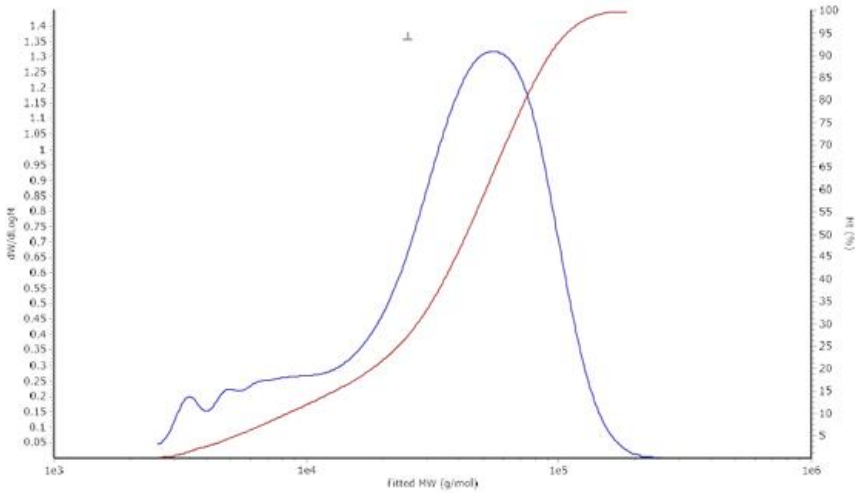


Chromatogram Plot

P11

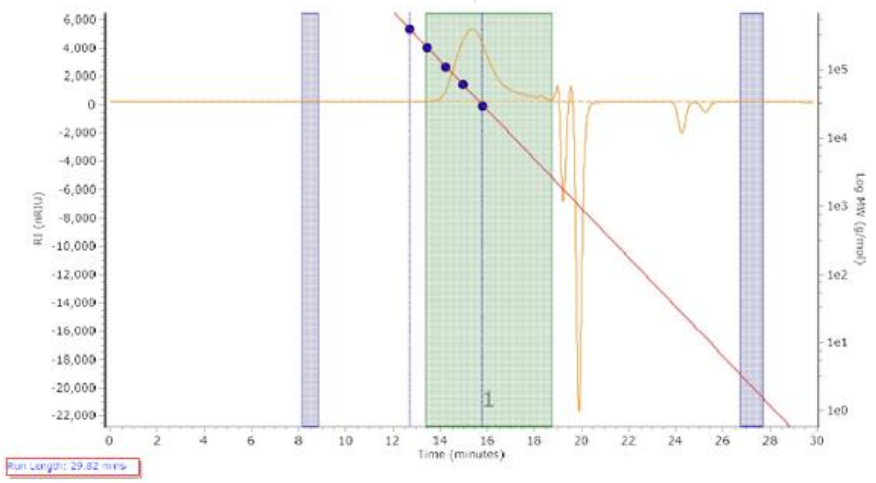


Distribution Plot

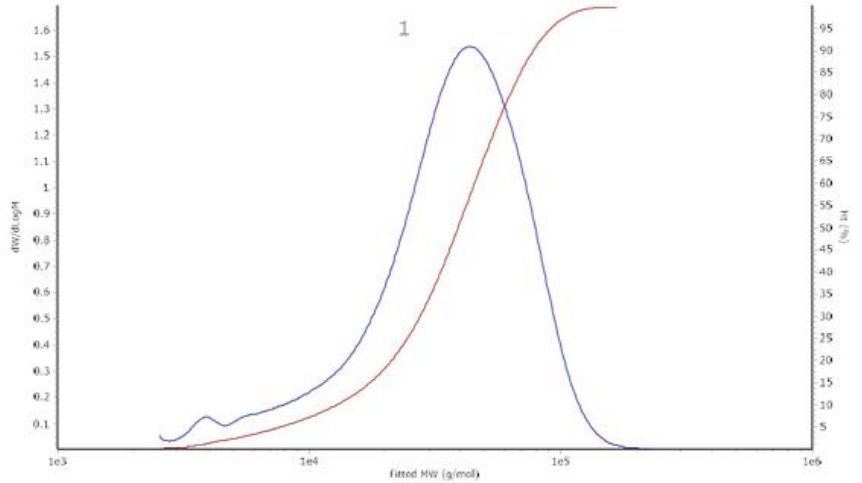


Chromatogram Plot

P12

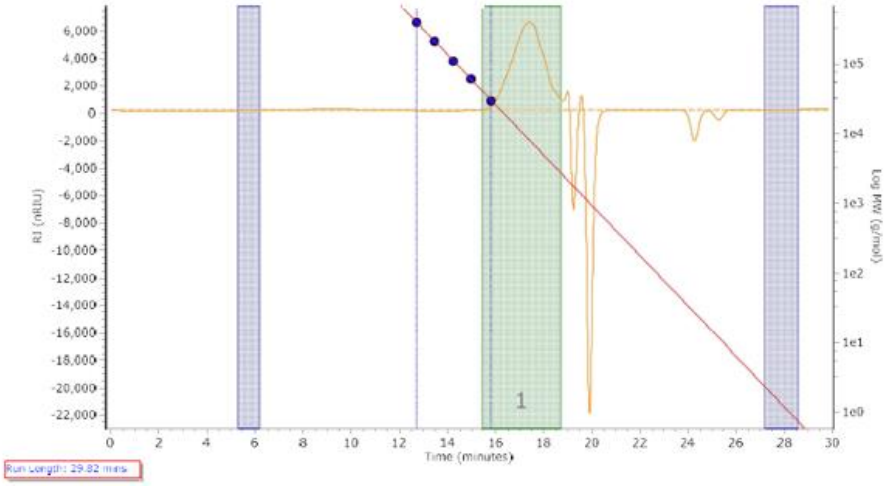


Distribution Plot

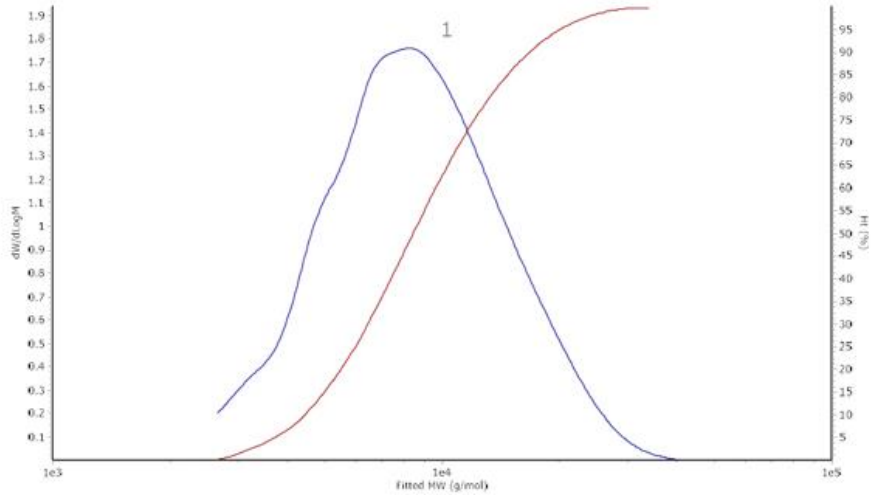


Chromatogram Plot

P13

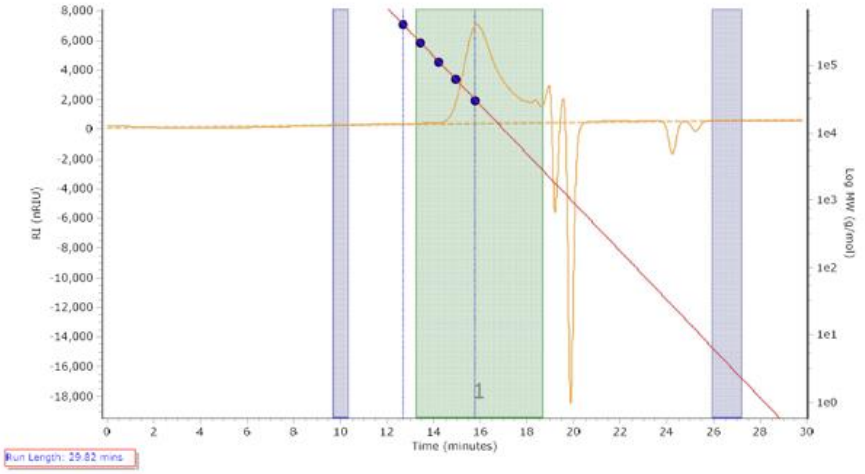


Distribution Plot

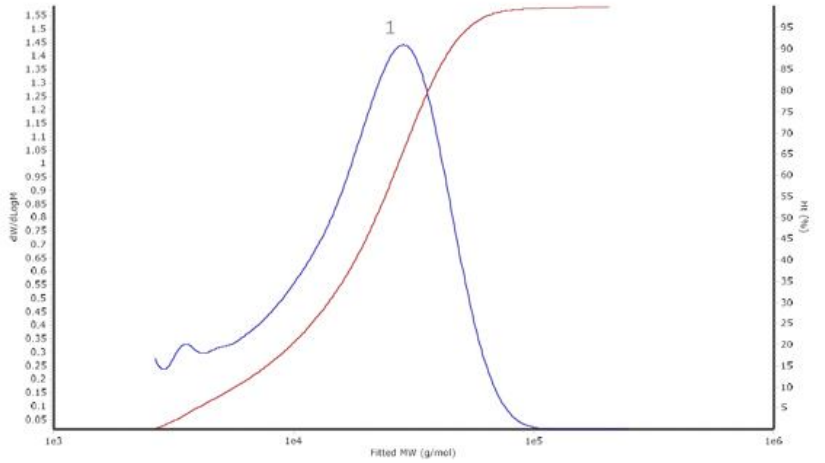


P14

Chromatogram Plot



Distribution Plot



5. References

(1) Shintani, R.; Ikehata, K.; Hayashi, T. Synthesis of Nine-Membered Azlactones by Palladium-Catalyzed Ring-Expansion of *γ*-Methylidene-*δ*-valerolactones with Aziridines. *J. Org. Chem.* **2011**, *76*, 4776-4780.

(2) Zhang, W.; Wang, B.; Chen, N.; Du, D.-M.; Xu, J. Expeditious and practical synthesis of various substituted taurines from amino alcohols. *Synthesis* **2008**, 197-200.

(3) Li, X.; Chen, N.; Xu, J. An Improved and Mild Wenker Synthesis of Aziridines. *Synthesis* **2010**, 3423-3428.

(4) Alagiri, K.; Prabhu, K. R. Catalyst-Free Regio- and Stereospecific Synthesis of β-Sulfonamido Dithiocarbamates: Efficient Ring-Opening Reactions of *N*-Tosyl Aziridines by Dialkyldithiocarbamates. *Eur. J. Chem.* **2011**, *17*, 6922-6925.