

Supplementary information

Molecular Design of Chiral Quaternary Ammonium Polymers for Asymmetric Catalysis Application

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Materials and Measurements

All reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry Co., Ltd. at the highest available purity and used as is unless noted otherwise. Reactions were monitored by thin-layer chromatography (TLC) using Merck precoated silica-gel plates (Merck 5554, 60F254). Column chromatography was performed with a silica-gel column (Wakogel C-200, 100–200 mesh). Melting points were recorded using a Yanaco micro-melting apparatus and are uncorrected. ^1H (300 MHz) spectra were measured on a Varian Mercury 300 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. GC analyses were performed with a Shimadzu Capillary Gas Chromatograph 14B equipped with a capillary column (SPERCO β -DEX 325, 30 m \times 0.25 mm). HPLC analyses were performed with a JASCO HPLC system comprising a three-line degasser DG-980-50, an HPLC pump PV-980, and a CO-965 column oven equipped with a chiral column (CHIRALCEL OD or AD, Daicel); hexane/2-propanol was used as an eluent. A UV detector (JASCO UV-975 for JASCO HPLC system) was used for peak detection. Optical rotations were recorded with a JASCO DIP-149 digital polarimeter, using a 10-cm thermostated microcell. Intrinsic viscosity $[\eta]$ of each soluble sample was determined by viscosimetry, using a Ubbelohde viscometer at 40 °C in dimethyl sulfoxide (DMSO) solvent.

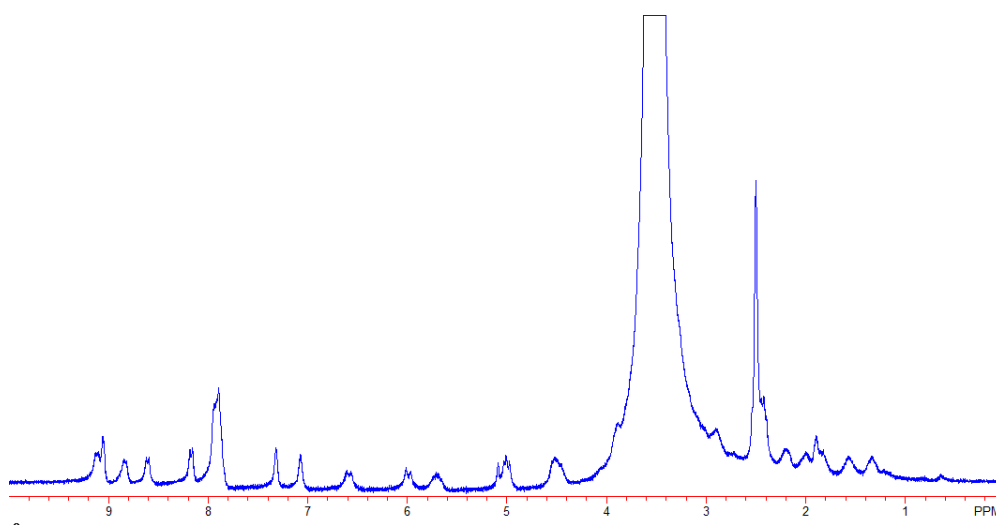
Preparation of ionic polymer **10H**

A solution of cinchona derived dimeric quaternary ammonium salt **6AH~6CH** (1 mmol,) in 10 mL CH_3OH and a solution of disulfonic acid-disodium salt **9** (1 mmol) in 8 mL water were mixed together and stirred vigorously at room temperature for 24 hours. Then it was filtered and washed with water and hexane to obtain the resulting ionic polymer **10H**. The

yield of the products was 75~90%. The intrinsic viscosity $[\eta]$ of the polymers in DMSO at 40 °C were in the range of 0.10~0.20.

Ionic polymer **10AaH**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.8, 147.9, 146.3, 144.5, 138.77, 138.75, 133.46, 133.43, 130.53, 130.09, 128.2, 125.1, 124.5, 121.0, 117.4, 68.3, 65.9, 61.6, 54.7, 52.37, 50.02, 37.9, 25.83, 35.25, 21.4 ppm. IR (KBr) ν 3232.11, 2944.77, 1662.34, 1509.99, 1453.10, 1029.80, 777.17, 754.03. From the chlorine analysis of **10AaH**, the molecular weight was estimated as follows. Molecular weight of the repeating unit of polymer **10AaH** ($\text{C}_{57}\text{H}_{62}\text{N}_4\text{O}_8\text{S}_2$) is 995.27. The molecular weight of the polymer for the compositional formula $(\text{C}_{57}\text{H}_{62}\text{N}_4\text{O}_8\text{S}_2)_n\text{ClNa}$ can be calculated as $995.27 \times n + 35.45 + 22.99$. Cl content in the polymer is found to be 0.46. From the following equation, $100 \times (35.45) \div (1079.35 \times n + 35.45 + 22.99) = 0.46$, n is calculated to be 10.1. Then the molecular weight of the polymer is estimated to be 10100. Anal. Calcd for $(\text{C}_{57}\text{H}_{62}\text{N}_4\text{O}_8\text{S}_2)_{10.1}\text{ClNa}$: C, 68.38; H, 6.24; N, 5.60, Cl, 0.35. Found: C, 67.75; H, 5.95; N, 5.45; Cl, 0.35.

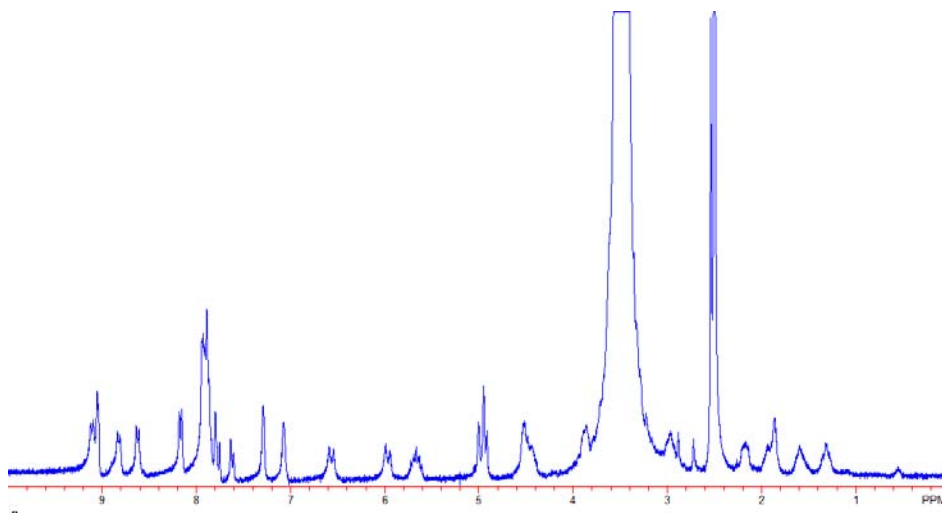


^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10AaH**

Ionic polymer **10AbH**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.2, 147.5, 146.2, 145.8, 138.72, 138.04, 133.05, 133.01, 132.6, 131.3, 129.6, 127.3, 126.96, 126.34, 124.68, 124.57, 124.43, 120.54, 120.51, 120.48, 116.3, 67.7, 65.7, 62.8, 55.4, 42.17, 42.16, 37.1, 26.8, 17.63 ppm. IR (KBr) ν 3407.60,

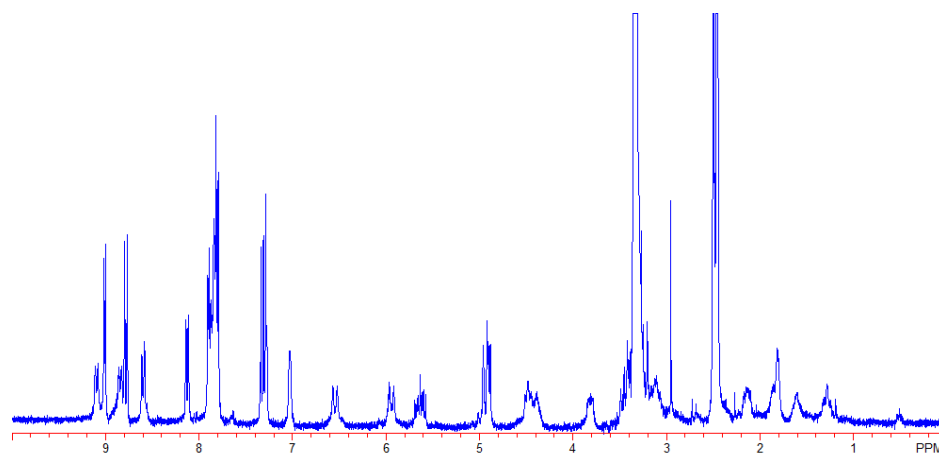
1637.27, 1590.02, 1508.06, 1191.79, 1102.12, 1025.94, 780.06, 697.14. From the chlorine analysis of **10AbH**, the molecular weight was estimated to be 7600. Anal. Calcd for $(C_{64}H_{62}N_4O_8S_2)_{7.0}ClNa$: C, 70.68; H, 5.75; N, 5.15, Cl, 0.46. Found: C, 70.25; H, 5.55; N, 5.05; Cl, 0.46.



1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10AbH**

Ionic polymer **10AdH**

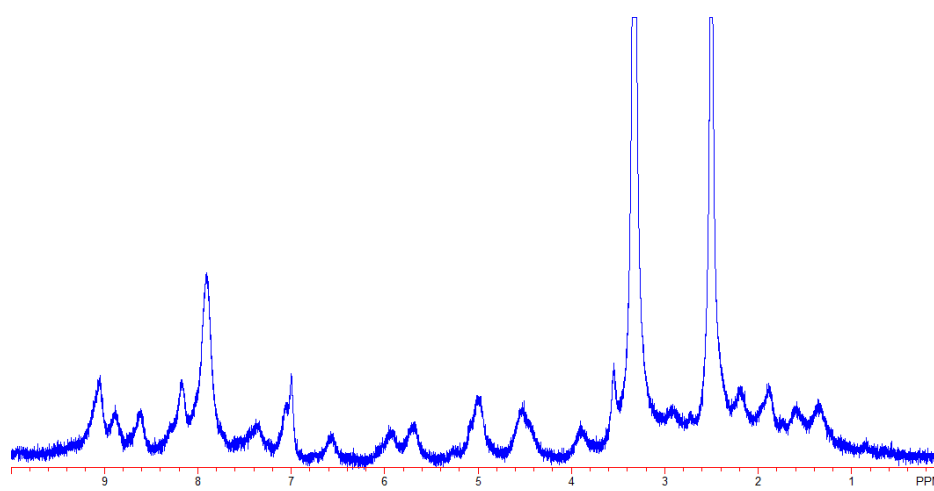
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.2, 147.6, 146.1, 143.7, 138.6, 133.06, 132.99, 129.60, 129.51, 129.06, 127.3, 126.97, 126.96, 126.33, 126.03, 124.62, 124.42, 124.00, 123.9, 120.4, 116.3, 67.8, 65.0, 60.5, 54.4, 42.16, 40.4, 37.1, 25.4, 21.6 ppm. $[\alpha]_D^{25} = -213.48$ (c 1.0, DMSO). IR (KBr) ν 3388.32, 1638.23, 1590.02, 1508.06, 1235.18, 1208.18, 1161.90, 1049.09, 1029.80, 780.06, 760.78, 611.32. From the chlorine analysis of **10AdH**, the molecular weight was estimated to be 8900. Anal. Calcd for $(C_{64}H_{62}N_4O_8S_2)_{8.2}ClNa$: C, 70.75; H, 5.75; N, 5.15, Cl, 0.40. Found: C, 68.76; H, 5.25; N, 5.02; Cl, 0.40.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10AdH**

Ionic polymer **10AeH**

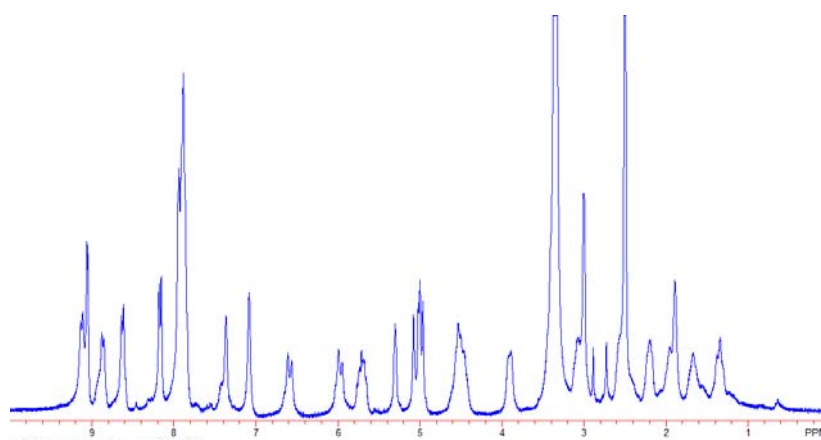
^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.3, 147.7, 145.9, 144.3, 138.5, 136.6, 133.06, 132.97, 129.2, 127.19, 127.12, 126.7, 124.61, 124.23, 120.43, 124.14, 116.58, 65.1, 62.7, 60.6, 59.5, 57.27, 54.6, 37.2, 25.2, 24.3, 21.3 ppm. $[\alpha]_{\text{D}}^{25} = -287.42$ (c 1.0, DMSO). IR (KBr) ν 3389.28, 1639.20, 1590.02, 1509.99, 1454.06, 1182.15, 1034.62, 1022.09, 779.10. From the chlorine analysis of **10AeH**, the molecular weight was estimated to be 7900. Anal. Calcd for $(\text{C}_{62}\text{H}_{64}\text{N}_4\text{O}_8\text{S}_2)_{7.4}\text{ClNa}$: C, 69.90; H, 6.60; N, 5.26, Cl, 0.45. Found: C, 68.73; H, 6.56; N, 5.10; Cl, 0.45.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10AeH**

Ionic polymer **10AfH**

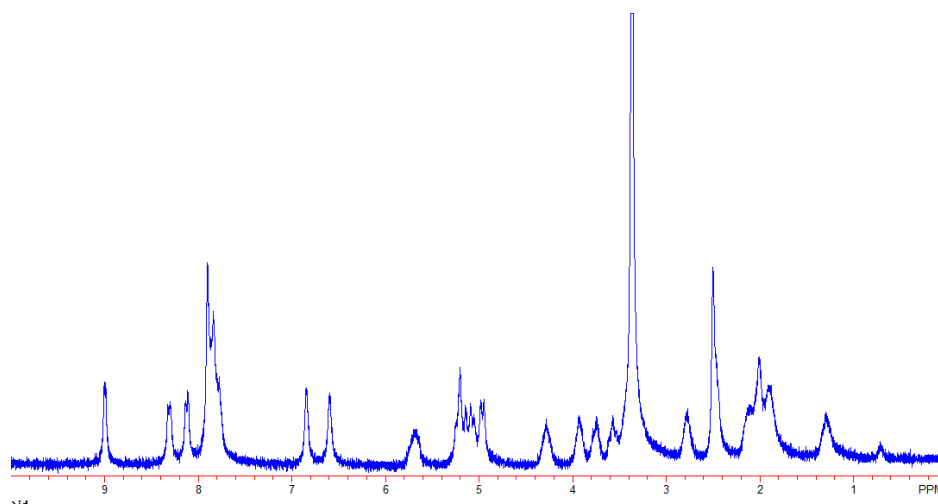
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.4, 147.7, 145.8, 138.57, 138.02, 133.1, 129.85, 129.61, 127.17, 127.10, 126.63, 126.31, 125.8, 124.57, 124.25, 120.4, 116.6, 67.9, 65.0, 60.7, 55.4, 54.5, 51.4, 37.2, 25.4, 24.63, 216 ppm. $[\alpha]_D^{25} = -326.38$ (c 1.0, DMSO). IR (KBr) ν 3232.11, 2952.48, 1654.62, 1590.99, 1509.99, 1453.10, 1186.97, 1029.80, 779.10, 618.07. From the chlorine analysis of **10AfH**, the molecular weight was estimated to be 8400. Anal. Calcd for $(\text{C}_{58}\text{H}_{62}\text{N}_4\text{O}_8\text{S}_2)_{8.3}\text{ClNa}$: C, 68.68; H, 6.16; N, 5.52, Cl, 0.42. Found: C, 68.50; H, 6.08; N, 5.20; Cl, 0.42.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10AfH**

Ionic polymer **10BaH**

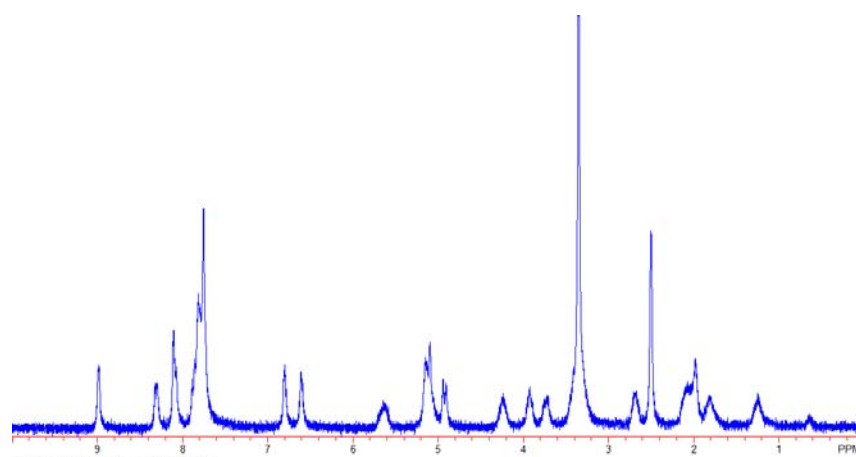
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.2, 147.6, 145.4, 138.3, 134.1, 129.88, 129.79, 129.50, 127.4, 124.3, 123.7, 120.1, 116.2, 67.7, 64.2, 62.1, 59.1, 50.77, 50.54, 36.7, 26.0, 24.1, 21.41, 21.18 ppm. $[\alpha]_D^{25} = -8.75$ (c 1.0, DMSO). IR (KBr) ν 3151.11, 2948.63, 1934.25, 1849.40, 1721.16, 1665.23, 1590.99, 1507.10, 1455.99, 1389.46, 1159.01, 1094.40, 1029.80, 923.74, 855.28, 779.10, 758.85. From the bromine analysis of **10BaH**, the molecular weight was estimated to be 9800. Anal. Calcd for $(\text{C}_{49}\text{H}_{58}\text{N}_4\text{O}_8\text{S}_2)_{10.8}\text{BrNa}$: C, 65.06; H, 6.46; N, 6.19, Br, 0.82. Found: C, 64.76; H, 6.58; N, 5.97; Br, 0.82.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10BaH**

Ionic polymer **10BbH**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.1, 147.4, 145.30, 145.27, 138.1, 134.1, 133.0, 131.1, 129.73, 129.64, 129.27, 127.79, 127.46, 125.0, 124.59, 124.13, 123.41, 120.0, 116.3, 67.5, 64.5, 62.2, 59.3, 50.7, 36.7, 25.9, 24.2, 21.3, ppm. $[\alpha]_{\text{D}}^{25} = -11.48$ (c 1.0, DMSO). IR (KBr) ν 3260.07, 2121.31, 1639.20, 1590.99, 1509.99, 1462.74, 1317.14, 1218.79, 1103.08, 1026.91, 945.91, 855.28, 777.17, 758.85, 700.03. From the bromine analysis of **10BbH**, the molecular weight was estimated to be 9100. Anal. Calcd for $(\text{C}_{56}\text{H}_{58}\text{N}_4\text{O}_8\text{S}_2)_{9.2}\text{BrNa}$: C, 67.91; H, 5.90; N, 5.66, Br, 0.88. Found: C, 64.93; H, 6.04; N, 5.36; Br, 0.88.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10BbH**

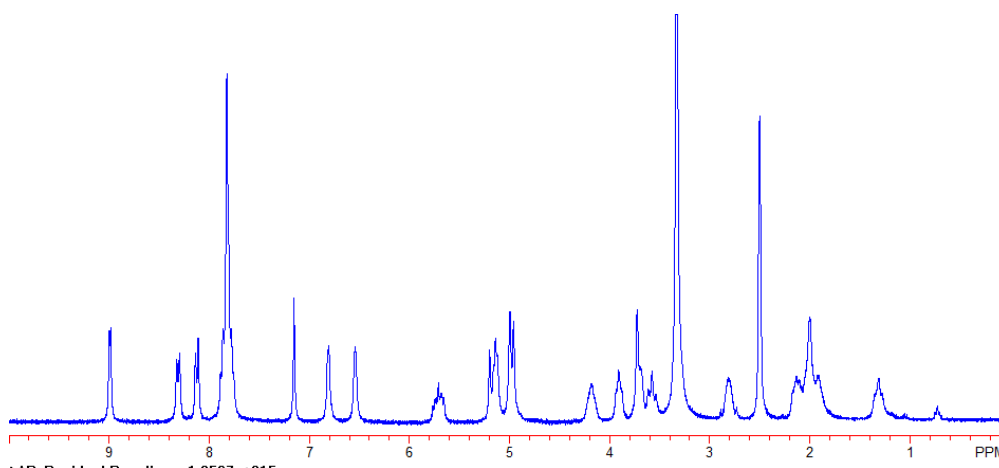
Ionic polymer **10BdH**

Due to the low solubility NMR spectra were not recorded. IR (KBr) ν 3208.97, 3083.62, 3029.62, 3007.44, 2955.38, 2878.24, 1929.43, 1714.41, 1640.16, 1589.06, 1508.06, 1464.67,

1321.00, 1237.11, 1216.86, 1127.19, 1059.69, 1031.73, 778.14, 765.60, 612.29. From the bromine analysis of **10BdH**, the molecular weight was estimated to be 12000. Anal. Calcd for $(C_{56}H_{58}N_4O_8S_2)_{12.1}BrNa$: C, 68.10; H, 5.92; N, 5.67, Br, 0.67. Found: C, 67.62; H, 6.02; N, 5.33; Br, 0.67.

Ionic polymer **10BeH**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.3, 147.6, 145.5, 138.4, 134.1, 133.0, 129.89, 129.73, 129.62, 129.55, 127.42, 124.39, 123.8, 120.1, 116.3, 67.7, 64.2, 62.1, 59.2, 57.4, 50.4, 36.7, 26.0, 24.1, 21.1, ppm. $[\alpha]_D^{25} = -8.55$ (c 1.0, DMSO). IR (KBr) ν 3228.25, 1639.20, 1589.06, 1509.99, 1461.78, 1218.79, 1178.29, 1130.08, 1935.59, 1021.12, 777.17, 605.54. From the bromine analysis of **10BeH**, the molecular weight was estimated to be 7300. Anal. Calcd for $(C_{54}H_{60}N_4O_8S_2)_{7.5}BrNa$: C, 66.80; H, 6.23; N, 5.77, Br, 1.10. Found: C, 66.54; H, 5.88; N, 5.45; Br, 1.10.

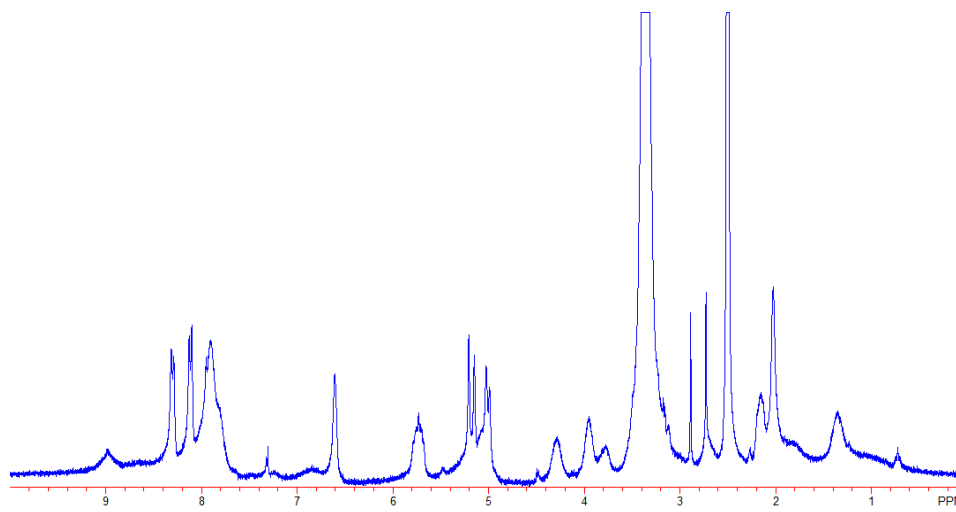


1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10BeH**

Ionic polymer **10BfH**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.2, 147.6, 145.3, 138.3, 134.1, 129.88, 129.79, 129.48, 127.32, 126.42, 124.3, 123.8, 123.8, 120.1, 116.2, 67.5, 64.2, 62.87, 62.04, 59.1, 50.6, 36.3, 25.9, 24.1, 21.2 ppm. IR (KBr) ν 3223.43, 1642.09, 1589.06, 1572.66, 1509.03, 1461.78, 1124.30, 1061.62, 1034.62, 929.52, 823.46, 777.17, 755.96. From the bromine analysis of **10BfH**, the molecular weight was estimated to be 9000. Anal. Calcd for

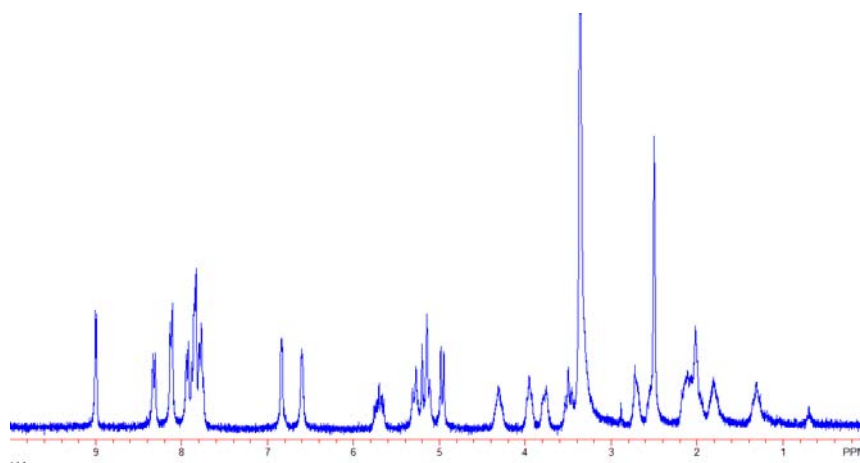
(C₅₀H₅₈N₄O₈S₂)_{9.8}BrNa: C, 65.44; H, 6.37; N, 6.11, Br, 0.89. Found: C, 63.23; H, 6.27; N, 5.85; Br, 0.89.



¹H NMR (d⁶-DMSO, 300 MHz) spectrum of **10BfH**

Ionic polymer **10CaH**

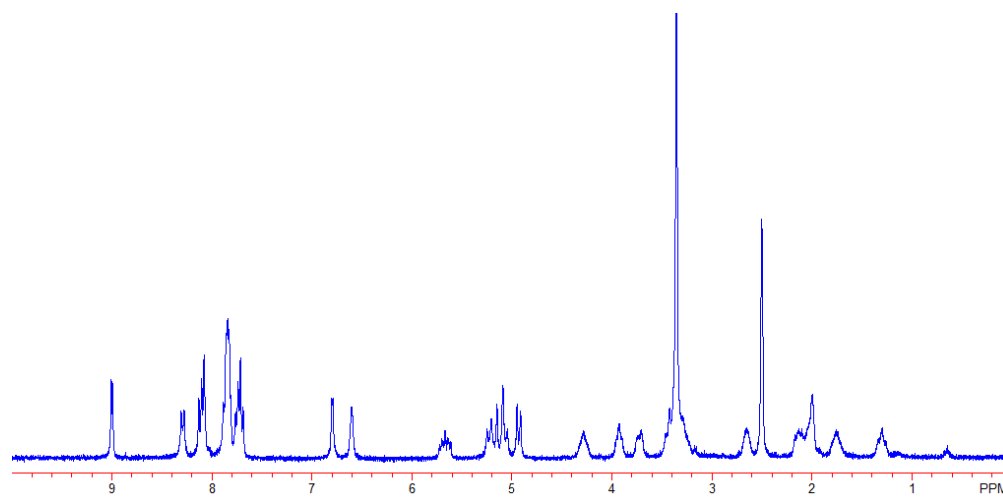
¹³C NMR (d⁶-DMSO, 75 MHz) δ 150.3, 147.6, 145.4, 139.0, 138.2, 135.4, 129.875, 129.58, 129.57, 128.7, 127.5, 124.4, 123.8, 120.24, 116.4, 67.7, 64.3, 62.3, 50.7, 50.54, 36.8, 25.9, 24.28, 24.25, 21.43, 21.23 ppm. [α]_D²⁵ = -189.89 (c 1.0, DMSO). IR (KBr) ν 3428.61, 3215.72, 2955.38, 1935.22, 1866.76, 1639.20, 1591.95, 1507.10, 1459.85, 1163.83, 1117.55, 1064.51, 1029.80, 931.45, 778.14, 762.71. From the bromine analysis of **10CaH**, the molecular weight was estimated to be 9900. Anal. Calcd for (C₄₉H₅₈N₄O₈S₂)_{11.0}BrNa: C, 65.07; H, 6.46; N, 6.19, Br, 0.80. Found: C, 64.78; H, 6.65; N, 5.95; Br, 0.80.



¹H NMR (d⁶-DMSO, 300 MHz) spectrum of **10CaH**

Ionic polymer **10CbH**

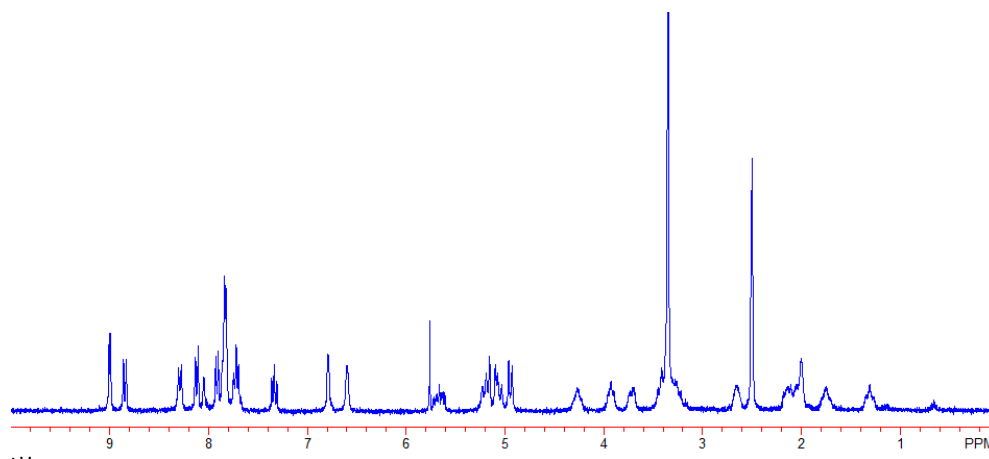
^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.4, 147.6, 145.42, 145.37, 139.1, 138.1, 135.3, 132.9, 131.26, 129.93, 129.91, 129.61, 128.7, 127.56, 127.49, 124.80, 124.59, 124.40, 123.6, 120.2, 116.4, 67.8, 64.5, 62.5, 59.4, 50.8, 36.9, 25.9, 24.3, 21.2, ppm. $[\alpha]_{\text{D}}^{25} = -161.04$ (c 1.0, DMSO). IR (KBr) ν 3390.24, 2951.52, 1639.20, 1590.99, 1509.03, 1461.78, 1217.83, 1102.12, 1026.91, 777.17, 699.07, 574.68. From the bromine analysis of **10CbH**, the molecular weight was estimated to be 12600. Anal. Calcd for $(\text{C}_{56}\text{H}_{58}\text{N}_4\text{O}_8\text{S}_2)_{12.8}\text{BrNa}$: C, 68.13; H, 5.92; N, 5.67, Br, 0.63. Found: C, 68.02; H, 6.05; N, 5.56; Br, 0.63.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10CbH**

Ionic polymer **10CdH**

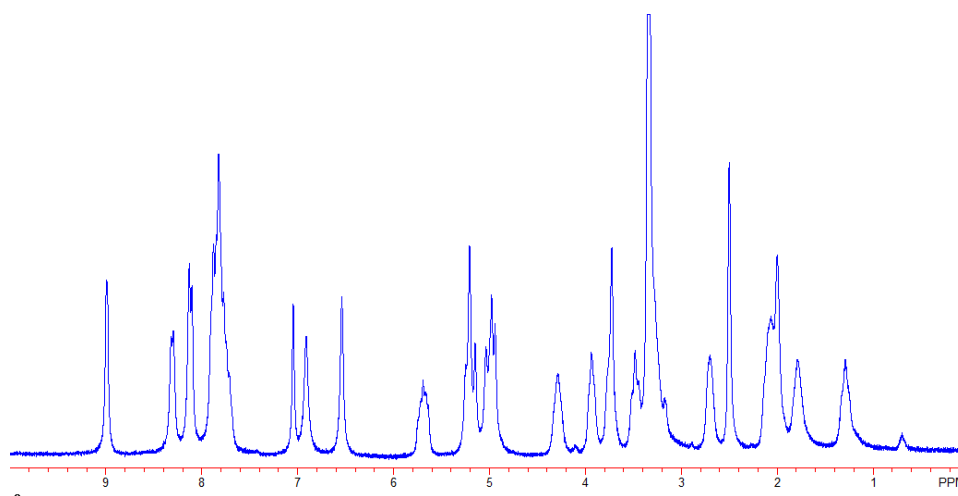
^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.2, 147.5, 145.5, 143.3, 139.0, 138.1, 135.2, 129.75, 129.63, 129.55, 129.20, 128.6, 127.51, 127.48, 124.37, 124.11, 123.61, 123.59, 120.2, 116.4, 67.8, 64.4, 62.5, 59.3, 50.8, 36.8, 25.9, 24.6, 21.1, ppm. $[\alpha]_{\text{D}}^{25} = -159.378$ (c 1.0, DMSO). IR (KBr) ν 3233.07, 2951.52, 1638.23, 1590.02, 1509.03, 1460.81, 1239.04, 1185.04, 1030.77, 797.42, 777.17, 763.67, 610.36, 563.11, 523.58. From the bromine analysis of **10CdH**, the molecular weight was estimated to be 11600. Anal. Calcd for $(\text{C}_{56}\text{H}_{58}\text{N}_4\text{O}_8\text{S}_2)_{11.7}\text{BrNa}$: C, 68.08; H, 5.92; N, 5.67, Br, 0.69. Found: C, 67.72; H, 5.85; N, 5.38; Br, 0.69.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10CdH**

Ionic polymer **10CeH**

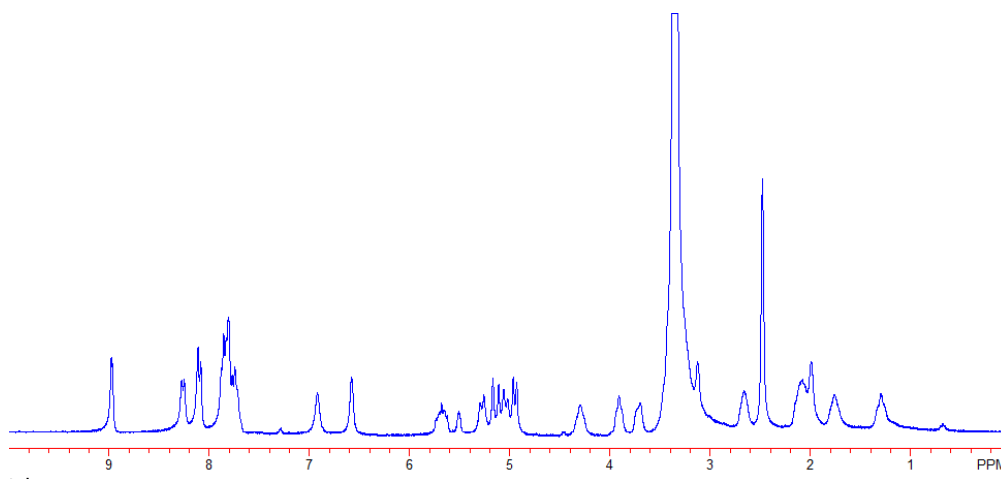
^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.3, 147.6, 145.4, 139.2, 138.2, 135.3, 132.9, 129.87, 129.57, 129.44, 128.6, 127.5, 124.4, 123.80, 123.78, 120.2, 116.3, 67.7, 64.4, 62.3, 59.3, 57.3, 50.7, 36.8, 25.9, 24.3, 21.1, ppm. $[\alpha]_{\text{D}}^{25} = -176.90$ (c 1.0, DMSO). IR (KBr) ν 3209.93, 1702.84, 1639.20, 1590.02, 1509.03, 1460.81, 1421.28, 1215.90, 1168.65, 1130.08, 1035.59, 1021.12, 801.28, 776.21, 755.96, 633.50, 607.47, 552.51, 521.65. From the bromine analysis of **10CeH**, the molecular weight was estimated to be 12500. Anal. Calcd for $(\text{C}_{54}\text{H}_{60}\text{N}_4\text{O}_8\text{S}_2)_{13}\text{BrNa}$: C, 67.02; H, 6.27; N, 5.81, Br, 0.64. Found: C, 66.25; H, 6.27; N, 5.79; Br, 0.64.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10CeH**

Ionic polymer **10CfH**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.3, 147.6, 145.4, 139.2, 138.1, 135.2, 129.87, 129.52, 129.45, 128.6, 127.4, 126.8, 124.4, 123.7, 120.2, 116.4, 67.8, 64.2, 62.2, 59.2, 55.3, 50.6, 36.9, 25.9, 24.2, 21.1 ppm. $[\alpha]_{\text{D}}^{25} = -181.55$ (c 1.0, DMSO). IR (KBr) ν 3210.90, 1639.20, 1590.99, 1509.03, 1459.85, 1210.11, 1030.77, 801.28, 777.17, 758.85. From the bromine analysis of **10CfH**, the molecular weight was estimated to be 11500. Anal. Calcd for $(\text{C}_{50}\text{H}_{58}\text{N}_4\text{O}_8\text{S}_2)_{12.6}\text{BrNa}$: C, 65.61; H, 6.39; N, 6.12, Br, 0.69. Found: C, 65.32; H, 6.18; N, 5.99; Br, 0.69.



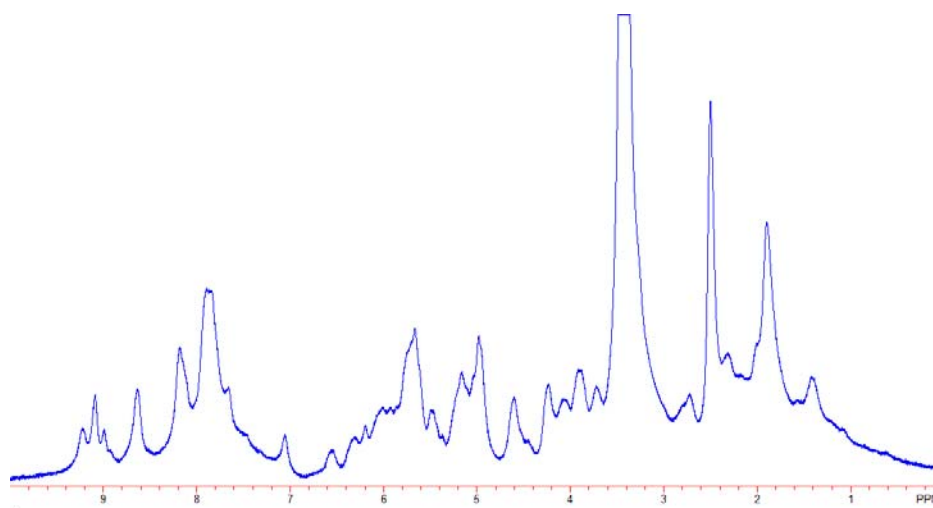
^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10CfH**

Synthesis of ionic polymer **10Allyl**

A solution of cinchona derived dimeric quaternary ammonium salt **6AAllyl**~**6CAllyl** (1 mmol) in 10 mL CH_3OH and a solution of disulfonic acid-disodium salt **9** (1 mmol) in 8 mL water were mixed together and stirred vigorously at room temperature for 24 hours. After completion of reaction the volume of solvent was reduced by rota evaporator and then 10 mL DCM and 5 mL water was added to the reaction mixture. Then it was extracted with DCM (3X20 mL) and the amount of DCM was reduced by rotavaporator and recrystallized in methanol-ether system to get the ionic polymer **10Allyl**. The yield of the products was 70~90%. The intrinsic viscosity $[\eta]$ of the polymers in DMSO at 40 °C were in the range (0.10~0.20).

Ionic polymer **10AaAllyl**

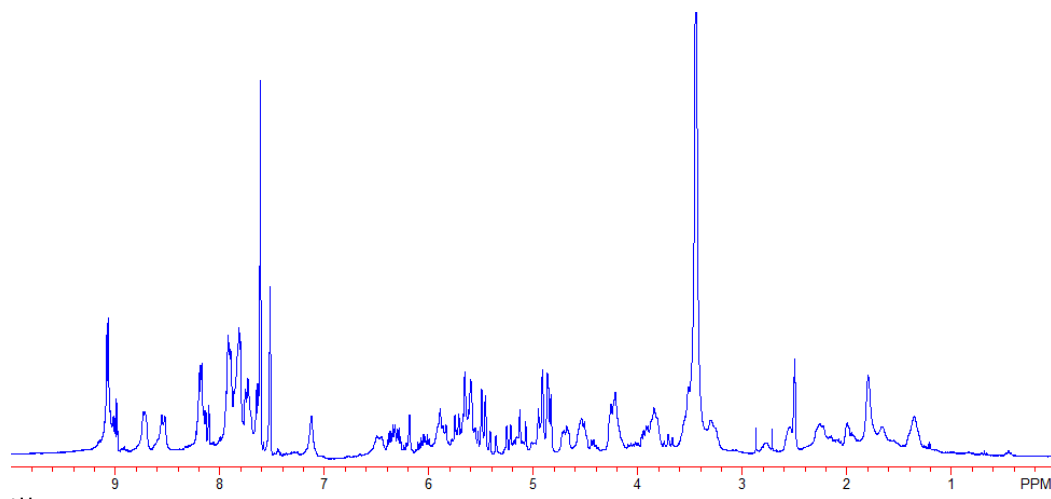
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.3, 148.0, 141.3, 140.9, 138.4, 137.8, 134.1, 132.94, 129.7, 127.4, 126.2, 125.3, 124.4, 124.4, 123.5, 119.7, 117.5, 116.7, 72.1, 69.2, 65.9, 62.4, 60.1, 52.4, 50.8, 37.3, 36.8, 26.2, 24.6, 21.4 ppm. IR (KBr) ν 3449.06, 3074.94, 2948.63, 1642.09, 1588.09, 1508.06, 1459.85, 1240.00, 1222.65, 1192.76, 1068.37, 1042.34, 774.28, 758.85. From the chlorine analysis of **10AaAllyl**, the molecular weight was estimated to be 12400. Anal. Calcd for $(\text{C}_{63}\text{H}_{70}\text{N}_4\text{O}_8\text{S}_2)_{11.5}\text{ClNa}$: C, 70.03; H, 6.53; N, 5.19, Cl, 0.29. Found: C, 68.89; H, 6.02; N, 4.93; Cl, 0.29.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10AaAllyl**

Ionic polymer **10AbAllyl**

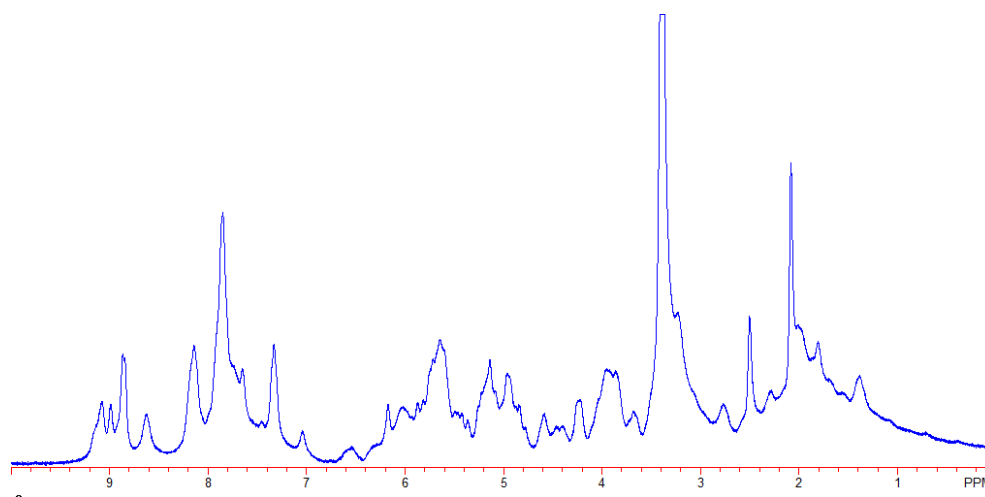
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.2, 148.17, 147.99, 145.3, 141.27, 141.04, 138.3, 137.8, 134.1, 133.1, 132.8, 132.3, 130.6, 129.7, 127.3, 126.9, 125.4, 124.23, 124.15, 119.7, 117.2, 116.3, 71.9, 69.2, 67.4, 62.5, 54.6, 51.6, 37.2, 24.58, 24.20, 21.9 ppm. $[\alpha]_{\text{D}}^{25} = -201.53$ (c 1.0, DMSO). IR (KBr) ν 3400.85, 3074.94, 2946.70, 1643.05, 1589.06, 1598.06, 1457.92, 1192.76, 1100.19, 1025.94, 775.24, 758.85, 696.18. From the chlorine analysis of **10AbAllyl**, the molecular weight was estimated to be 10000. Anal. Calcd for $(\text{C}_{70}\text{H}_{70}\text{N}_4\text{O}_8\text{S}_2)_{8.6}\text{ClNa}$: C, 72.09; H, 6.05; N, 4.80, Cl, 0.35. Found: C, 71.02; H, 6.12; N, 4.56; Cl, 0.35.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10AbAllyl**

Ionic polymer **10AdAllyl**

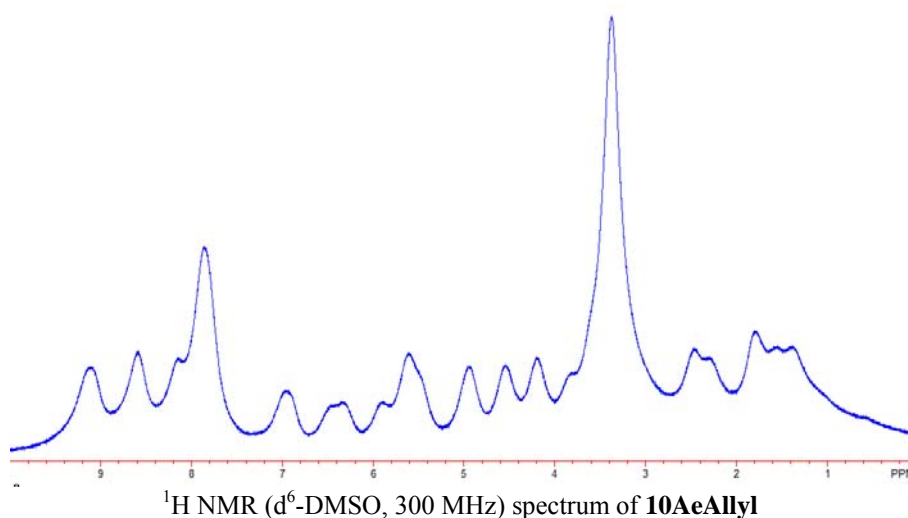
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.2, 148.15, 147.99, 141.3, 140.9, 138.4, 137.8, 136.8, 134.11, 134.07, 133.3, 132.9, 129.8, 127.4, 126.2, 125.29, 125.06, 124.4, 123.6, 119.7, 117.5, 116.7, 69.3, 66.0, 62.4, 60.1, 59.2, 46.3, 37.2, 26.1, 24.4, 21.8 ppm. IR (KBr) ν 3420.14, 3077.83, 2943.80, 1644.02, 1589.06, 1508.06, 1457.92, 1238.08, 1202.40, 1030.77, 996.05, 929.52, 796.46, 761.74, 610.36. From the chlorine analysis of **10AdAllyl**, the molecular weight was estimated to be 10700. Anal. Calcd for $(\text{C}_{70}\text{H}_{70}\text{N}_4\text{O}_8\text{S}_2)_{9.2}\text{ClNa}$: C, 72.12; H, 6.05; N, 4.81, Cl, 0.33. Found: C, 71.50; H, 6.16; N, 4.44; Cl, 0.33.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10AdAllyl**

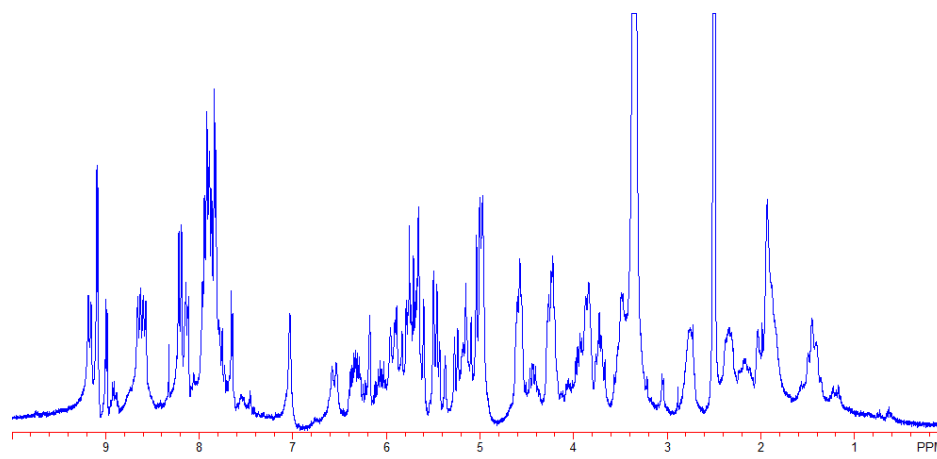
Ionic polymer **10AeAllyl**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.4, 148.2, 140.9, 138.4, 134.2, 133.33, 133.07, 133.00, 129.96, 129.85, 129.35, 127.46, 127.15, 126.5, 125.74, 125.38, 124.4, 120.2, 117.0, 70.7, 69.4, 67.5, 60.7, 58.6, 57.3, 54.6, 36.9, 25.4, 24.3, 21.9 ppm. $[\alpha]_D^{25} = -319.19$ (c 1.0, DMSO). IR (KBr) ν 3400.85, 3075.90, 2950.55, 1643.05, 1588.09, 1509.03, 1453.10, 1215.90, 1180.22, 1131.05, 1068.37, 1034.62, 920.84, 776.21, 758.85, 605.54. From the chlorine analysis of **10AeAllyl**, the molecular weight was estimated to be 11800. Anal. Calcd for $(\text{C}_{68}\text{H}_{72}\text{N}_4\text{O}_8\text{S}_2)_{10.3}\text{ClNa}$: C, 71.45; H, 6.35; N, 4.90, Cl, 0.30. Found: C, 70.59; H, 6.26; N, 4.54; Cl, 0.30.



Ionic polymer **10AfAllyl**

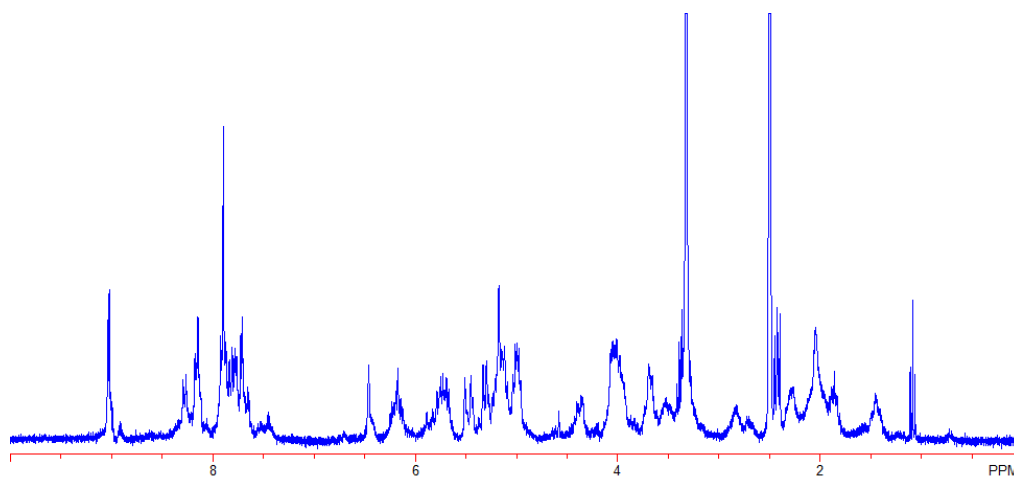
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.2, 148.16, 147.99, 141.3, 140.9, 138.4, 137.8, 134.1, 133.3, 132.9, 129.7, 127.3, 126.2, 125.3, 124.4, 123.5, 119.7, 116.7, 69.3, 67.4, 65.9, 62.4, 60.0, 59.2, 46.3, 37.2, 26.1, 24.4, 21.8 ppm. IR (KBr) ν 3380.60, 3074.94, 2935.13, 1717.30, 1644.98, 1588.09, 1508.06, 1452.14, 1068.37, 1029.80, 995.09, 920.84, 775.24, 757.89. From the chlorine analysis of **10AfAllyl**, the molecular weight was estimated to be 8900. Anal. Calcd for $(\text{C}_{64}\text{H}_{70}\text{N}_4\text{O}_8\text{S}_2)_{8.1}\text{ClNa}$: C, 70.23; H, 6.45; N, 5.12, Cl, 0.40. Found: C, 69.56; H, 6.55; N, 4.87; Cl, 0.40.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10AfAllyl**

Ionic polymer **10BaAllyl**

^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.4, 148.1, 141.5, 137.9, 134.35, 134.18, 129.9, 127.6, 126.2, 125.2, 123.6, 119.8, 117.93, 117.80, 116.8, 72.2, 69.4, 67.7, 66.1, 62.6, 60.3, 52.5, 50.7, 37.3, 26.2, 24.7, 20.7 ppm. $[\alpha]_{\text{D}}^{25} = -81.51$ (c 1.0, DMSO). IR (KBr) ν 3401.82, 3073.01, 2944.77, 2119.39, 1642.09, 1569.06, 1508.06, 1459.85, 1185.04, 1068.37, 1029.80, 758.85. From the bromine analysis of **10BaAllyl**, the molecular weight was estimated to be 11600. Anal. Calcd for $(\text{C}_{55}\text{H}_{66}\text{N}_4\text{O}_8\text{S}_2)_{11.8}\text{BrNa}$: C, 67.13; H, 6.76; N, 5.69, Br, 0.69. Found: C, 66.31; H, 6.81; N, 5.34; Br, 0.69.

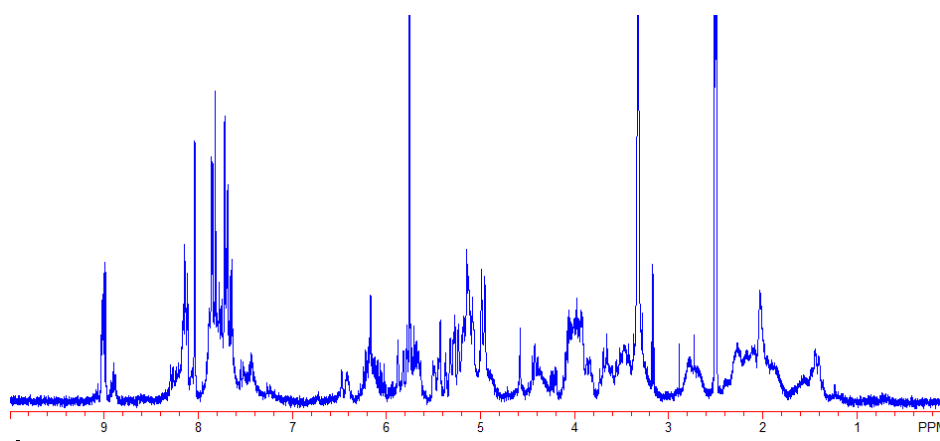


^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10BaAllyl**

Ionic polymer **10BbAllyl**

^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.3, 148.0, 1451.9, 141.3, 137.8, 134.33, 134.23, 134.09, 132.6, 131.3, 129.97, 129.71, 127.35, 127.24, 126.1, 125.1, 124.60, 124.53, 119.7, 117.6,

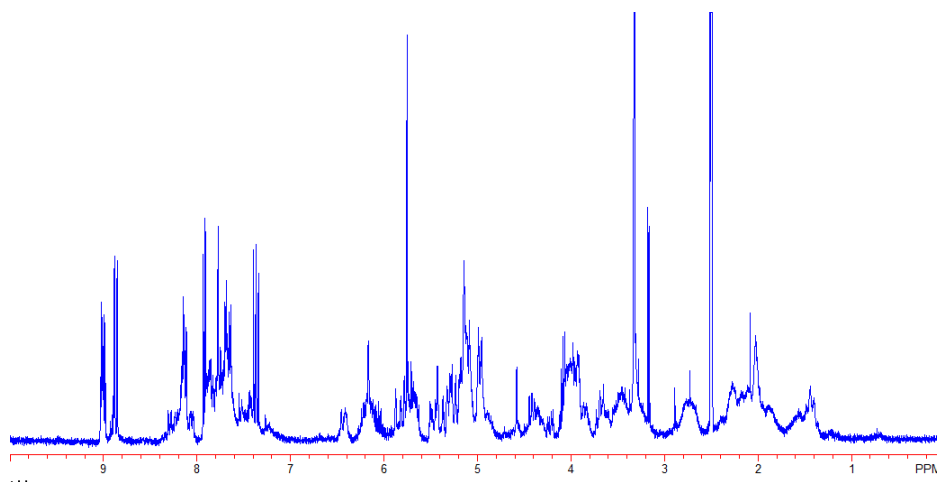
116.7, 72.1, 69.3, 66.0, 62.5, 59.0, 52.4, 37.2, 26.1, 24.6, 20.6 ppm. $[\alpha]_D^{25} = -49.38$ (*c* 1.0, DMSO). IR (KBr) ν 3418.21, 3072.05, 2941.88, 2119.39, 1941.97, 1643.05, 1589.06, 1508.06, 1460.81, 1196.61, 1101.15, 1026.91, 758.85, 696.18. From the bromine analysis of **10BbAllyl**, the molecular weight was estimated to be 11600. Anal. Calcd for $(C_{62}H_{66}N_4O_8S_2)_{10.9}BrNa$: C, 69.67; H, 6.22; N, 5.24, Br, 0.69. Found: C, 68.05; H, 6.11; N, 5.10; Br, 0.69.



1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10BbAllyl**

Ionic polymer **10BdAllyl**

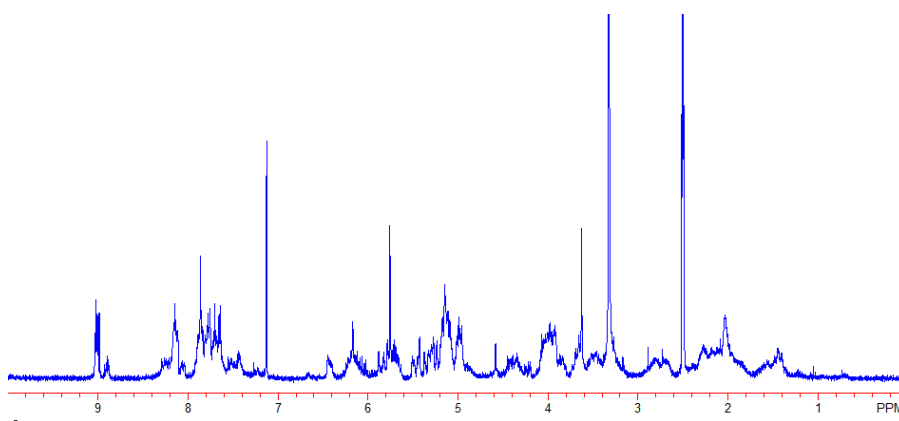
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.3, 148.03, 148.02, 143.8, 141.3, 137.8, 134.1, 129.97, 129.74, 129.63, 129.16, 129.71, 127.4, 126.1, 125.1, 124.2, 123.95, 123.48, 119.7, 117.7, 116.7, 72.1, 69.4, 67.6, 62.6, 59.1, 51.0, 37.3, 26.0, 24.6, 20.6 ppm. $[\alpha]_D^{25} = -68.24$ (*c* 1.0, DMSO). IR (KBr) ν 3412.42, 3073.98, 2937.05, 2119.39, 1942.93, 1844.58, 1641.13, 1589.06, 1508.06, 1460.81, 1238.08, 1202.40, 1030.77, 760.78, 610.36. From the bromine analysis of **10BdAllyl**, the molecular weight was estimated to be 13600. Anal. Calcd for $(C_{62}H_{66}N_4O_8S_2)_{12.7}BrNa$: C, 69.76; H, 6.23; N, 5.25, Br, 0.59. Found: C, 68.85; H, 6.33; N, 5.16; Br, 0.59.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10BdAllyl**

Ionic polymer **10BeAllyl**

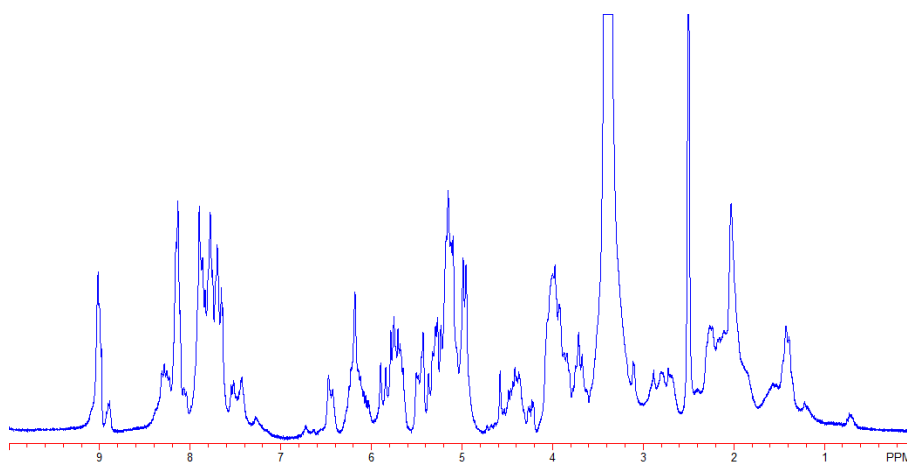
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.3, 148.0, 141.30, 141.29, 140.6, 137.9, 134.2, 133.2, 129.6, 127.2, 126.2, 129.71, 125.04, 125.01, 119.7, 117.5, 116.56, 116.06, 72.1, 69.3, 66.0, 63.3, 62.4, 58.9, 52.2, 37.2, 28.9, 26.2, 20.9 ppm. $[\alpha]_{\text{D}}^{25} = -67.27$ (c 1.0, DMSO). IR (KBr) ν 3402.78, 3071.08, 2943.80, 2119.39, 1942.93, 1641.13, 1589.06, 1509.03, 1460.81, 1215.90, 1185.04, 1132.97, 1035.59, 1022.09, 758.85, 607.47. From the bromine analysis of **10BeAllyl**, the molecular weight was estimated to be 12600. Anal. Calcd for $(\text{C}_{60}\text{H}_{68}\text{N}_4\text{O}_8\text{S}_2)_{12.0}\text{BrNa}$: C, 68.90; H, 6.55; N, 5.36, Br, 0.64. Found: C, 67.36; H, 6.45; N, 5.14; Br, 0.64.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10BeAllyl**

Ionic polymer **10BfAllyl**

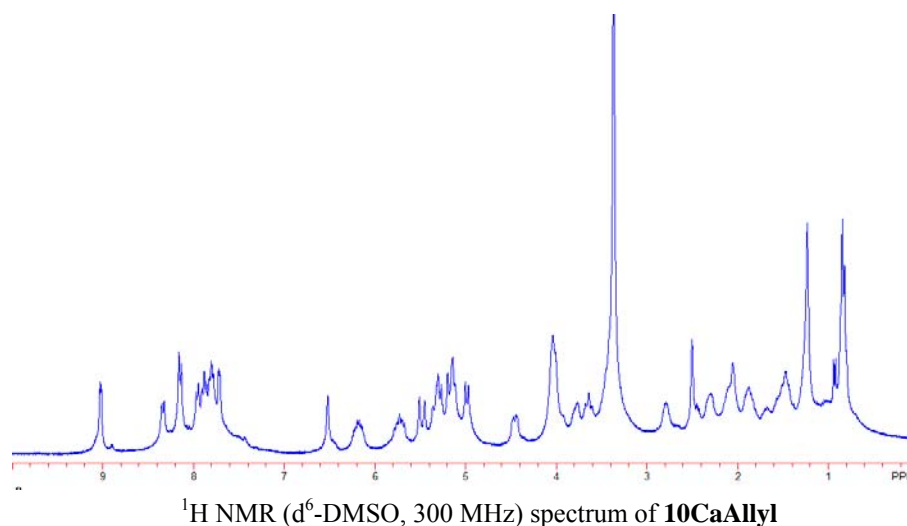
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.3, 148.0, 141.30, 137.87, 137.86, 134.15, 134.07, 129.7, 127.54, 127.31, 126.21, 125.0, 123.0, 119.7, 116.2, 72.0, 69.2, 67.6, 65.8, 62.4, 58.8, 50.7, 37.2, 26.1, 24.4, 20.9 ppm. $[\alpha]_D^{25} = -63.97$ (c 1.0, DMSO). IR (KBr) ν 3389.28, 3071.08, 2940.91, 2118.42, 1642.09, 1588.09, 1508.06, 1459.85, 1422.24, 1068.37, 997.02, 925.66, 774.28, 757.89. From the bromine analysis of **10BfAllyl**, the molecular weight was estimated to be 11400. Anal. Calcd for $(\text{C}_{56}\text{H}_{68}\text{N}_4\text{O}_8\text{S}_2)_{11.4}\text{BrNa}$: C, 67.37; H, 6.87; N, 5.61, Br, 0.70. Found: C, 66.71; H, 6.63; N, 5.35; Br, 0.70.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **10BfAllyl**

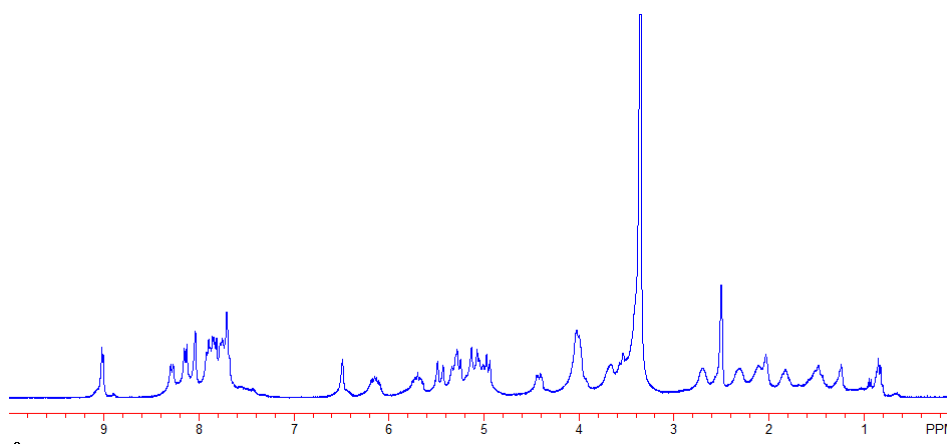
Ionic polymer **10CaAllyl**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.1, 148.0, 141.39, 141.31, 138.74, 138.00, 134.55, 134.11, 128.50, 128.47, 125.09, 125.07, 120.7, 119.86, 119.58, 117.70, 117.16, 71.9, 67.7, 63.0, 59.8, 50.98, 50.67, 36.7, 31.1, 26.3, 25.7, 24.8, 22.0 ppm. $[\alpha]_D^{25} = -105.84$ (c 1.0, DMSO). IR (KBr) ν 3403.74, 3073.01, 2950.55, 1933.29, 1641.13, 1589.06, 1508.06, 1459.85, 1167.69, 1068.37, 1030.77, 999.91, 926.63, 806.10, 775.24, 757.89. From the bromine analysis of **10CaAllyl**, the molecular weight was estimated to be 11500. Anal. Calcd for $(\text{C}_{55}\text{H}_{66}\text{N}_4\text{O}_8\text{S}_2)_{11.7}\text{BrNa}$: C, 67.13; H, 6.76; N, 5.69, Br, 0.69. Found: C, 66.04; H, 6.63; N, 5.45; Br, 0.69.



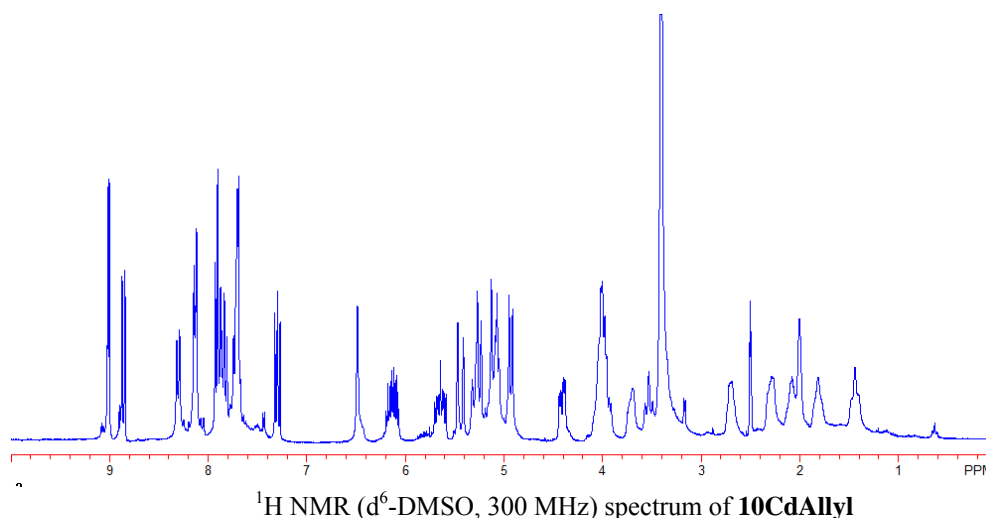
Ionic polymer **10CbAllyl**

¹³C NMR (d⁶-DMSO, 75 MHz) δ 150.45, 150.16, 148.0, 145.76, 145.74, 141.40, 141.38, 137.8, 134.1, 132.7, 131.25, 131.23, 128.52, 128.51, 127.52, 127.06, 126.99, 125.11, 125.09, 124.7, 123.4, 119.9, 116.6, 71.9, 67.9, 63.3, 59.2, 51.35, 51.03, 36.7, 26.3, 25.7, 21.2 ppm. $[\alpha]_D^{25} = -104.95$ (*c* 1.0, DMSO). IR (KBr) ν 3413.39, 3073.01, 2950.55, 1642.09, 1589.06, 1508.06, 1460.81, 1197.58, 1102.12, 1068.37, 697.14. From the bromine analysis of **10CbAllyl**, the molecular weight was estimated to be 12900. Anal. Calcd for (C₆₂H₆₆N₄O₈S₂)_{12.1}BrNa: C, 69.74; H, 6.23; N, 5.25, Br, 0.62. Found: C, 69.03; H, 6.81; N, 5.13; Br, 0.62.



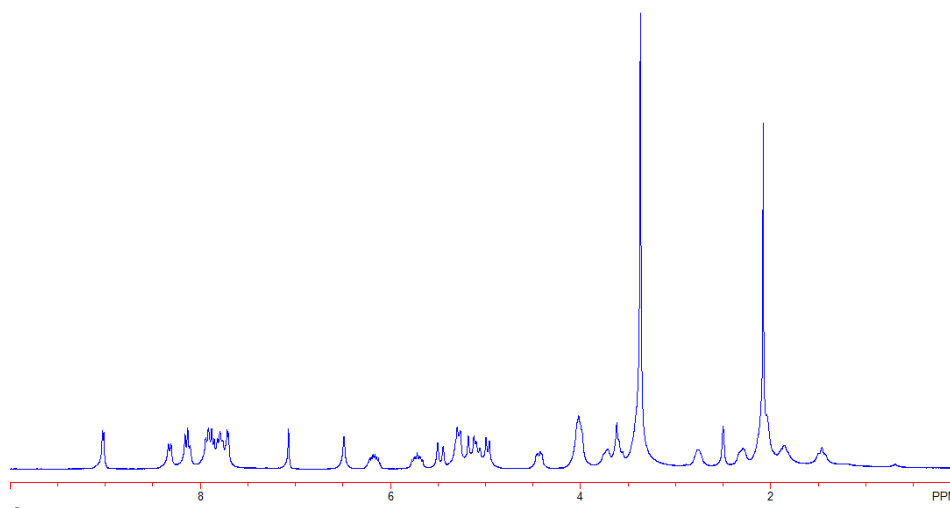
Ionic polymer **10CdAllyl**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.3, 148.0, 143.7, 141.3, 138.9, 137.8, 135.4, 134.2, 129.95, 129.70, 129.57, 129.09, 128.4, 127.6, 125.05, 125.03, 124.1, 123.83, 123.57, 119.6, 117.6, 116.6, 72.0, 69.3, 68.0, 63.1, 59.0, 50.9, 36.8, 26.0, 24.2, 20.8 ppm. $[\alpha]_{\text{D}}^{25} = -102.94$ (c 1.0, DMSO). IR (KBr) ν 3412.42, 3074.94, 2946.70, 1943.89, 1640.16, 1589.06, 1508.06, 1459.85, 1238.08, 1202.40, 1030.77, 796.46, 760.78, 610.36. From the bromine analysis of **10CdAllyl**, the molecular weight was estimated to be 11300. Anal. Calcd for $(\text{C}_{62}\text{H}_{66}\text{N}_4\text{O}_8\text{S}_2)_{10.6}\text{BrNa}$: C, 69.66; H, 6.22; N, 5.25; Br, 0.71. Found: C, 68.73; H, 6.38; N, 5.09; Br, 0.71.



Ionic polymer **10CeAllyl**

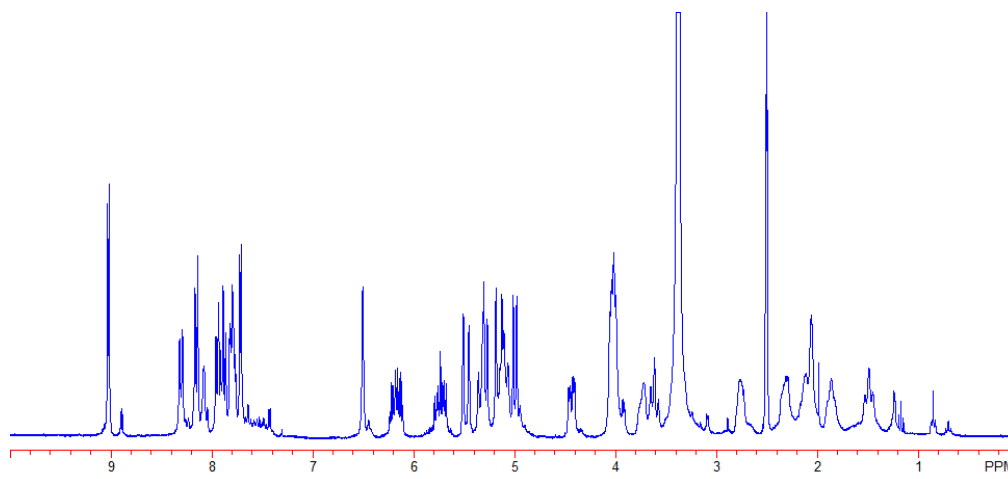
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.47, 150.17, 148.06, 148.04, 141.4, 138.1, 134.50, 134.16, 133.1, 129.6, 128.5, 127.92, 127.09, 128.4, 127.6, 125.1, 124.2, 123.6, 119.7, 117.8, 116.6, 71.9, 68.1, 63.1, 59.0, 57.4, 50.9, 36.8, 26.3, 25.8, 24.3, 21.3 ppm. $[\alpha]_{\text{D}}^{25} = -128.61$ (c 1.0, DMSO). IR (KBr) ν 3411.46, 3073.98, 2947.66, 1641.13, 1589.06, 1509.03, 1459.85, 1213.97, 1186.01, 1133.94, 1068.37, 1035.59, 1022.09, 928.56, 776.21, 757.89, 607.47. From the bromine analysis of **10CeAllyl**, the molecular weight was estimated to be 11500. Anal. Calcd for $(\text{C}_{60}\text{H}_{68}\text{N}_4\text{O}_8\text{S}_2)_{11.0}\text{BrNa}$: C, 68.85; H, 6.55; N, 5.35; Br, 0.69. Found: C, 68.19; H, 6.49; N, 5.16; Br, 0.69.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10CeAllyl**

Ionic polymer **10CfAllyl**

^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.3, 148.0, 141.3, 137.9, 135.5, 134.31, 134.28, 129.93, 129.90, 129.69, 129.50, 128.4, 127.6, 125.0, 123.8, 119.6, 117.7, 116.5, 72.0, 69.4, 67.8, 62.95, 62.84, 58.8, 50.9, 36.7, 26.0, 24.2, 20.9 ppm. $[\alpha]_{\text{D}}^{25} = -119.44$ (c 1.0, DMSO). IR (KBr) ν 3392.17, 3071.08, 2943.80, 1640.16, 1589.06, 1508.06, 1458.89, 1068.37, 997.02, 923.74, 805.13, 775.24, 756.92. From the bromine analysis of **10CfAllyl**, the molecular weight was estimated to be 9800. Anal. Calcd for $(\text{C}_{56}\text{H}_{68}\text{N}_4\text{O}_8\text{S}_2)_{9.8}\text{BrNa}$: C, 67.27; H, 6.86; N, 5.60; Br, 0.81. Found: C, 66.81; H, 6.78; N, 5.72; Br, 0.81.



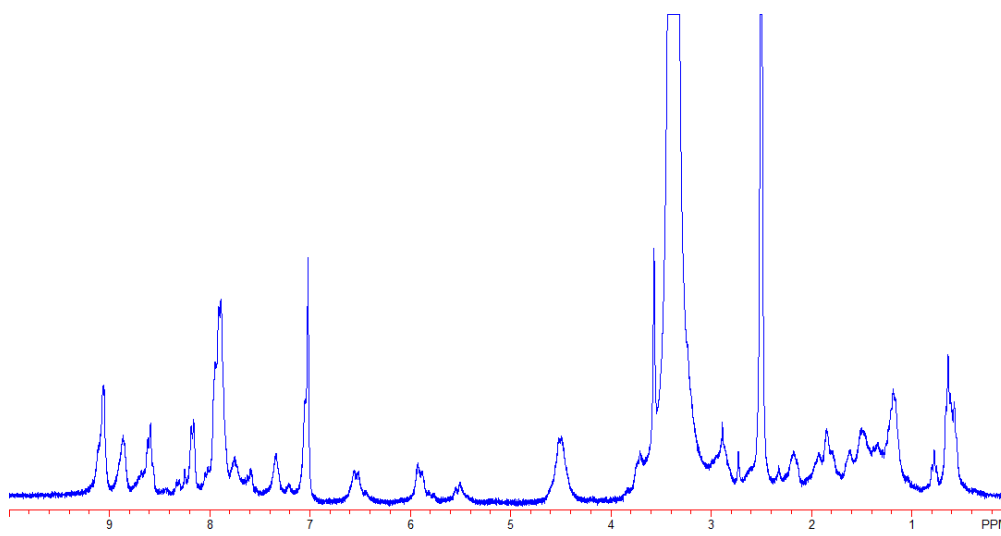
^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **10CfAllyl**

Synthesis of ionic polymers derived from dihydrocinchonidine **13H**, **13Allyl**

A solution of 10,11-dihydrocinchonidine derived dimeric quaternary ammonium salt **12AH~12CH**, **12AAllyl~12CAllyl** (1 mmol,) in 10 mL CH₃OH and a solution of disulfonic acid-disodium salt **9** (1 mmol) in 8 mL water were mixed together and stirred vigorously at room temperature for 24 hours. After completion of reaction the volume of solvent was reduced by rota evaporator and then 10 mL DCM and 5 mL water was added to the reaction mixture. Then it was extracted with DCM (3X20 mL) and the amount of DCM was reduced by rotavaporator and recrystallized in methanol-ether system to get the ionic polymer **12H**, **12Allyl**. The yield of the products was 70~90%. The intrinsic viscosity $[\eta]$ of the polymers in DMSO at 40 °C were in the range (0.10~0.20).

Ionic polymer **13AeH**

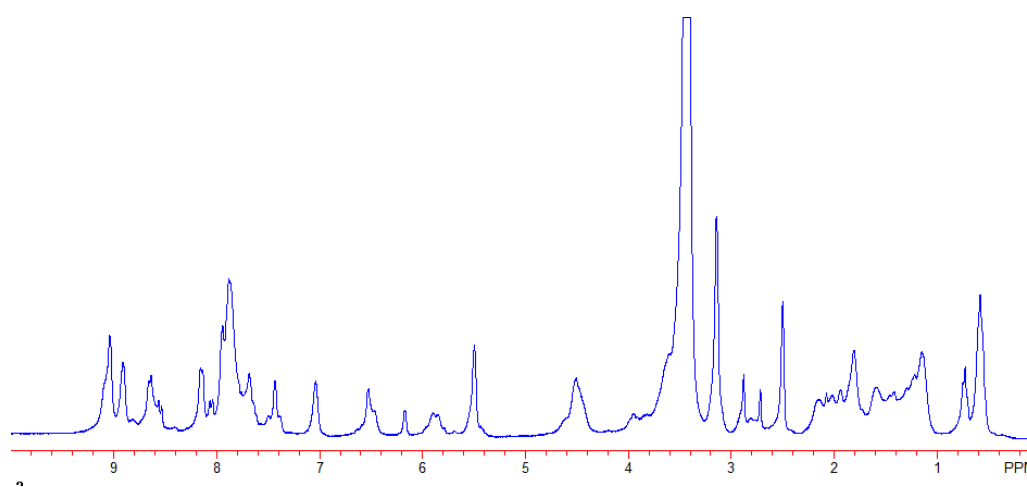
¹³C NMR (d⁶-DMSO, 75 MHz) δ 150.4, 147.8, 146.0, 133.1, 129.89, 129.64, 127.59, 127.17, 125.87, 125.21, 124.82, 124.43, 123.90, 120.68, 119.26, 67.7, 65.5, 60.1, 57.4, 56.1, 51.6, 35.6, 26.2, 25.9, 24.5, 11.77, 11.57 ppm. $[\alpha]_D^{25} = -209.59$ (*c* 1.0, DMSO). IR (KBr) ν 3389.28, 2958.27, 2875.34, 1661.37, 1590.99, 1509.99, 1457.92, 1214.93, 1180.22, 1129.12, 1034.62, 1021.12, 781.03, 758.85, 606.50. From the chlorine analysis of **13AeH**, the molecular weight was estimated to be 8500. Anal. Calcd for (C₆₂H₆₈N₄O₈S₂)_{11.0}BrNa: C, 68.85; H, 6.55; N, 5.35; Br, 0.69. Found: C, 68.19; H, 6.49; N, 5.16; Br, 0.69.



¹H NMR (d⁶-DMSO, 300 MHz) spectrum of **13AeOH**

Ionic polymer **13AfH**

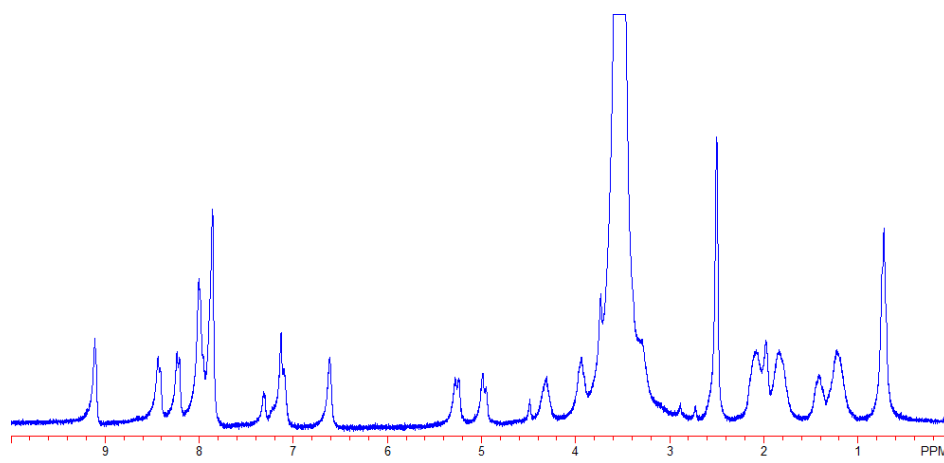
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.3, 147.7, 145.9, 133.0, 129.83, 129.55, 127.23, 127.04, 126.9, 124.66, 124.45, 124.35, 120.5, 118.9, 67.4, 65.1, 62.8, 59.5, 55.3, 42.8, 35.86, 35.21,, 25.70, 25.45, 24.2, 11.4 ppm. $[\alpha]_{\text{D}}^{25} = -237.45$ (c 1.0, DMSO). IR (KBr) ν 3219.58, 2957.30, 1661.37, 1590.02, 1509.03, 1457.92, 1186.97, 1123.33, 1030.77, 780.06, 618.07. From the chlorine analysis of **13AfH**, the molecular weight was estimated to be 9000. Anal. Calcd for $(\text{C}_{58}\text{H}_{66}\text{N}_4\text{O}_8\text{S}_2)_{8.8}\text{BrNa}$: C, 68.44; H, 6.53; N, 5.50; Cl, 0.40. Found: C, 68.22; H, 6.35; N, 5.40; Br, 0.40.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **13AfH**

Ionic polymer **13BeH**

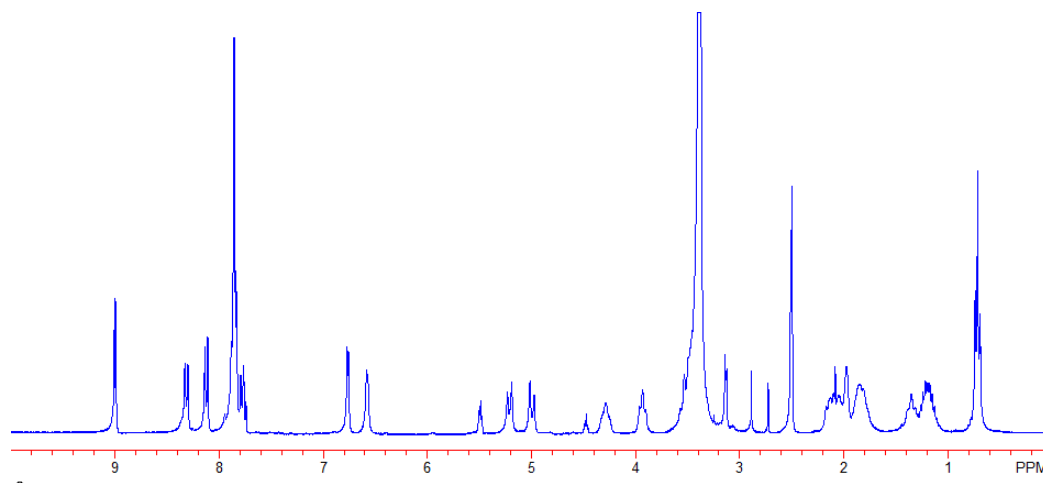
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.6, 148.6, 144.3, 134.7, 131.9, 130.41, 130.20, 129.1, 128.7, 127.3, 125.28, 125.05, 121.2, 68.1, 64.9, 62.54, 62.35, 57.8, 51.1, 35.6, 26.3,, 25.3, 24.2, 21.4, 12.0 ppm. $[\alpha]_{\text{D}}^{25} = -109.86$ (c 1.0, DMSO). IR (KBr) ν 3202.22, 2959.23, 2091.42, 1636.30, 1599.66, 1544.70, 1509.99, 1460.81, 1219.76, 1168.65, 1129.12, 1035.59, 857.20, 778.14, 606.50. From the bromine analysis of **13BeH**, the molecular weight was estimated to be 8800. Anal. Calcd for $(\text{C}_{54}\text{H}_{64}\text{N}_4\text{O}_8\text{S}_2)_{9.0}\text{BrNa}$: C, 66.68; H, 6.63; N, 5.76; Br, 0.91. Found: C, 67.12; H, 6.68; N, 5.59; Br, 0.91.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **13BeH**

Ionic polymer **13BfH**

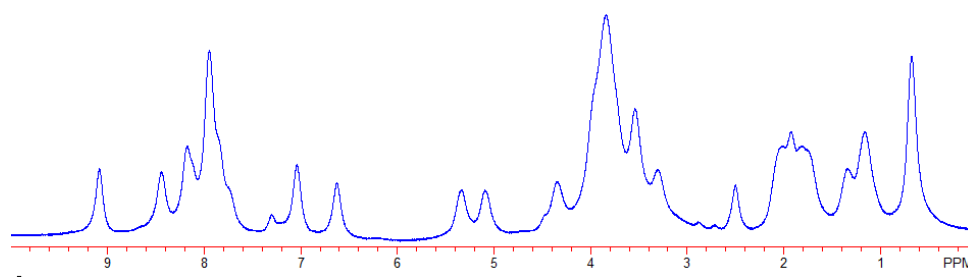
^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.3, 149.1, 147.6, 145.4, 134.1, 129.84, 129.51, 127.4, 126.9, 124.4, 123.8, 120.2, 67.6, 64.2, 62.8, 61.7, 55.4, 50.6, 35.0, 25.7, 24.7, 23.6, 20.8, 11.5 ppm. $[\alpha]_{\text{D}}^{25} = -94.71 (c\ 1.0, \text{DMSO})$. IR (KBr) ν 3234.04, 2958.27, 1654.62, 1590.02, 1509.99, 1460.81, 1207.22, 1125.26, 1056.80, 1032.69, 778.14. From the bromine analysis of **13BfH**, the molecular weight was estimated to be 6600. Anal. Calcd for $(\text{C}_{50}\text{H}_{62}\text{N}_4\text{O}_8\text{S}_2)_{7.1}\text{BrNa}$: C, 64.88; H, 6.75; N, 6.05; Br, 1.22. Found: C, 64.32; H, 6.40; N, 5.95; Br, 1.22.



^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **13BfH**

Ionic polymer **13CeH**

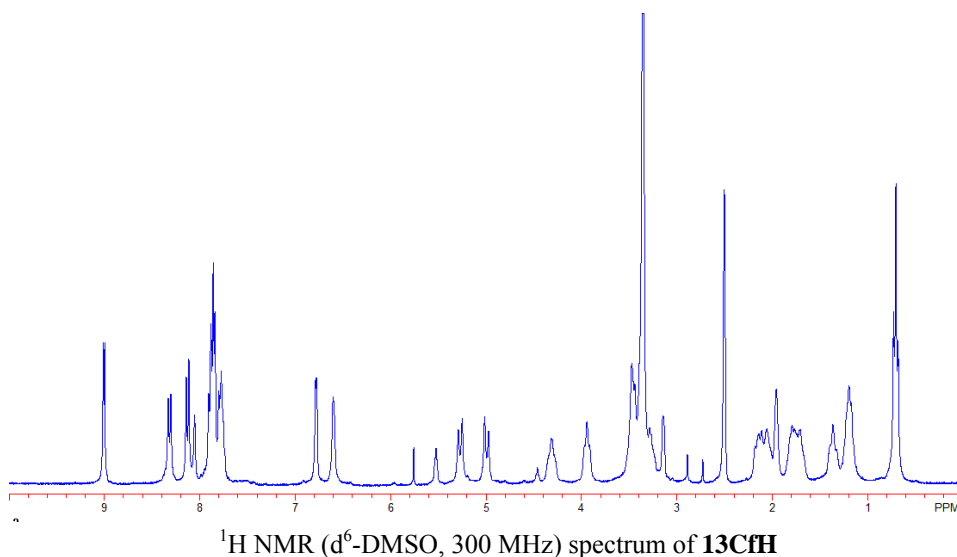
^{13}C NMR (d^6 -DMSO, 75 MHz) δ 148.94, 147.98, 145.3, 139.1, 135.13, 135.11, 130.6, 129.4, 128.66, 128.06, 126.4, 124.56, 124.12, 124.16, 120.5, 67.6, 64.3, 62.2, 61.4, 50.51, 50.49, 35.2, 25.7, 24.90, 24.17, 20.9, 11.3 ppm. $[\alpha]_{\text{D}}^{25} = -121.57$ (c 1.0, DMSO). IR (KBr) ν 3203.18, 2959.23, 2875.34, 1651.73, 1590.99, 1509.03, 1458.89, 1217.83, 1036.55, 777.17, 755.96. From the bromine analysis of **13CeH**, the molecular weight was estimated to be 11700. Anal. Calcd for $(\text{C}_{50}\text{H}_{62}\text{N}_4\text{O}_8\text{S}_2)_{12.7}\text{BrNa}$: C, 65.33; H, 6.80; N, 6.09; Br, 0.68. Found: C, 64.96; H, 6.85; N, 5.95; Br, 0.68.



^1H NMR (d^6 -DMSO, 300 MHz) spectrum of **13CeH**

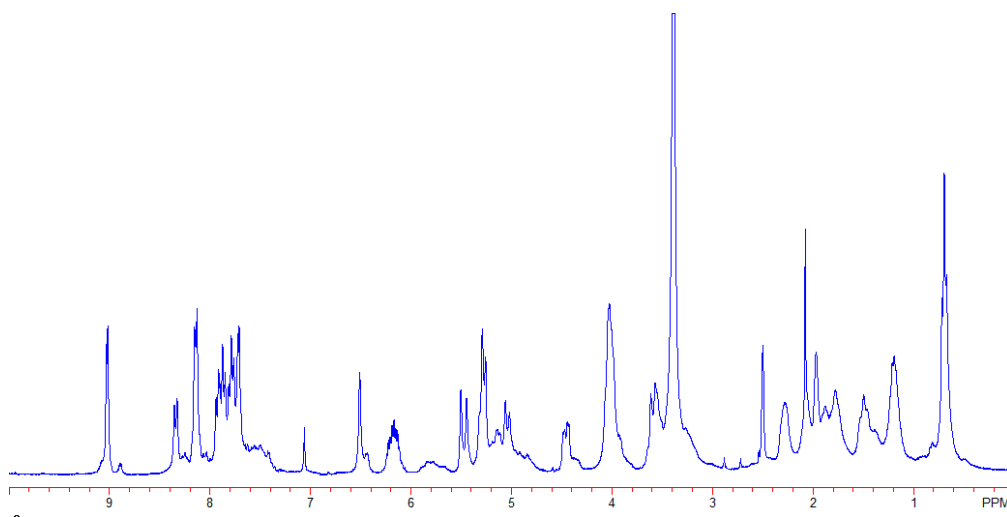
Ionic polymer **13CfH**

^{13}C NMR (d^6 -DMSO, 75 MHz) δ 150.2, 147.6, 145.4, 139.1, 135.1, 129.86, 129.46, 128.7, 127.4, 126.8, 124.4, 123.76, 123.74, 120.3, 67.6, 64.2, 62.3, 61.4, 50.5, 50.49, 35.2, 25.7, 24.88, 24.21, 20.8, 11.3 ppm. $[\alpha]_{\text{D}}^{25} = -136.56$ (c 1.0, DMSO). IR (KBr) ν 3208.97, 2957.30, 1651.73, 1590.02, 1509.03, 1458.89, 1187.94, 1166.72, 1119.47, 1030.77, 803.21, 778.14, 755.96. From the bromine analysis of **13CfH**, the molecular weight was estimated to be 8800. Anal. Calcd for $(\text{C}_{50}\text{H}_{62}\text{N}_4\text{O}_8\text{S}_2)_{9.9}\text{BrNa}$: C, 65.16; H, 6.78; N, 6.08; Br, 0.88. Found: C, 64.56; H, 6.70; N, 5.97; Br, 0.88.



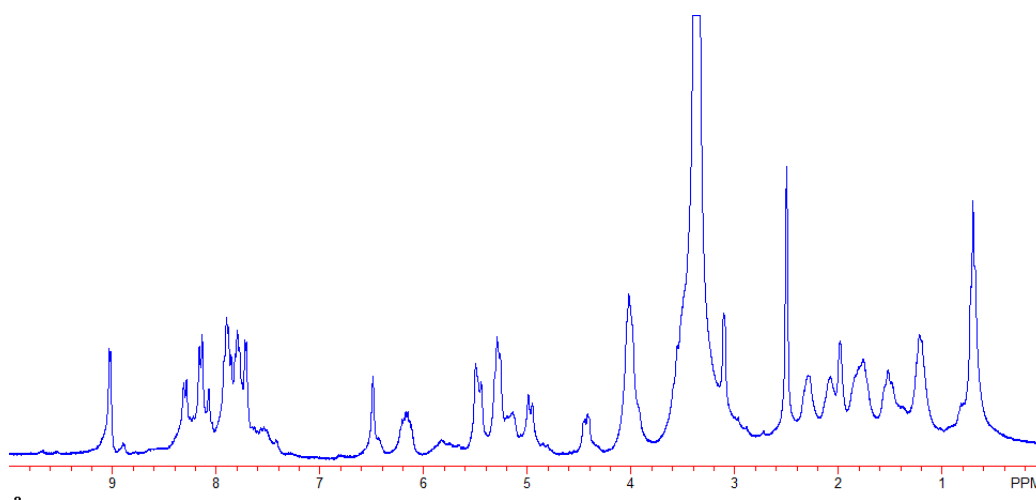
Ionic polymer **13CeAllyl**

¹³C NMR (d⁶-DMSO, 75 MHz) δ 150.2, 148.0, 141.4, 135.4, 134.3, 129.92, 129.66, 129.64, 129.53, 129.45, 128.5, 127.6, 125.1, 123.8, 119.69, 119.67, 117.5, 72.0, 69.2, 67.8, 63.1, 60.9, 50.8, 34.9, 25.4, 24.83, 24.41, 20.6, 14.8, 11.1 ppm. $[\alpha]_D^{25} = -81.21$ (*c* 1.0, DMSO). IR (KBr) ν 3395.07, 2957.30, 2874.38, 1645.95, 1589.06, 1508.06, 1458.89, 1213.97, 1128.15, 1069.33, 1033.66, 756.92. From the bromine analysis of **13CeAllyl**, the molecular weight was estimated to be 12000. Anal. Calcd for (C₆₀H₇₂N₄O₈S₂)_{11.4}BrNa: C, 68.61; H, 6.91; N, 5.33; Br, 0.67. Found: C, 67.98; H, 6.88; N, 5.26; Br, 0.67.



Ionic polymer **13CfAllyl**

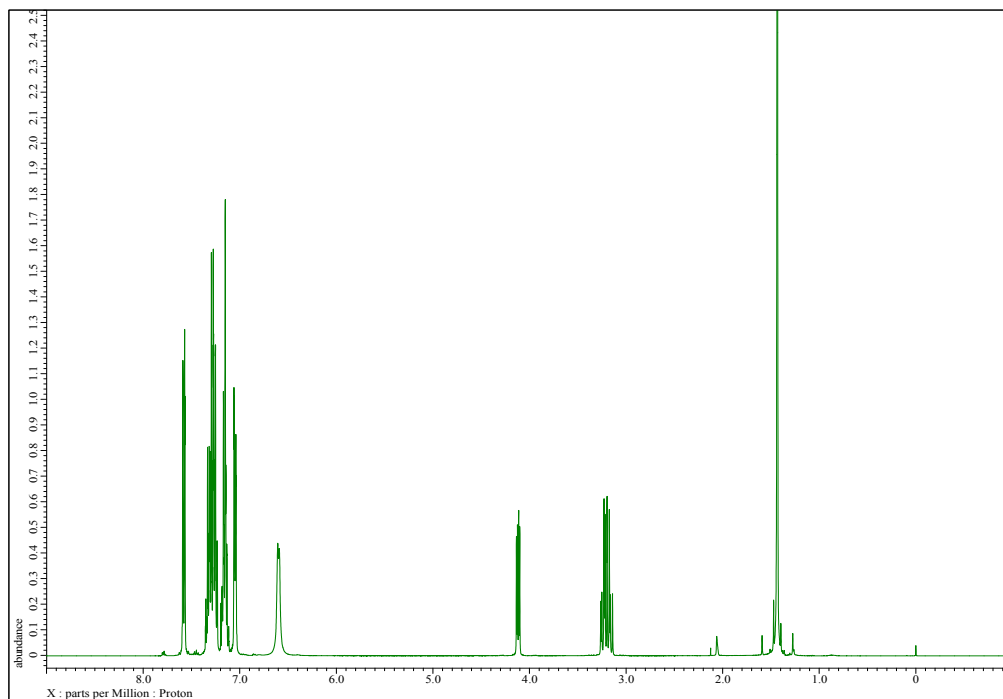
^{13}C NMR ($\text{d}^6\text{-DMSO}$, 75 MHz) δ 150.3, 148.0, 141.4, 139.3, 135.4, 134.4, 129.89, 129.70, 129.45, 128.48, 127.6, 126.8, 125.1, 124.0, 119.7, 117.6, 72.0, 69.3, 67.7, 63.1, 60.95, 55.4, 50.8, 34.9, 25.4, 24.88, 24.45, 20.8, 11.1 ppm. $[\alpha]_{\text{D}}^{25} = -90.23$ (c 1.0, DMSO). IR (KBr) ν 3410.49, 2957.30, 2874.38, 1645.95, 1589.06, 1508.06, 1458.89, 1189.86, 1125.26, 1069.33, 1030.77, 757.89. From the bromine analysis of **13CfAllyl**, the molecular weight was estimated to be 8800. Anal. Calcd for $(\text{C}_{56}\text{H}_{70}\text{N}_4\text{O}_8\text{S}_2)_{8.8}\text{BrNa}$: C, 67.06; H, 7.03; N, 5.59; Br, 0.91. Found: C, 66.68; H, 7.18; N, 5.35; Br, 0.91.



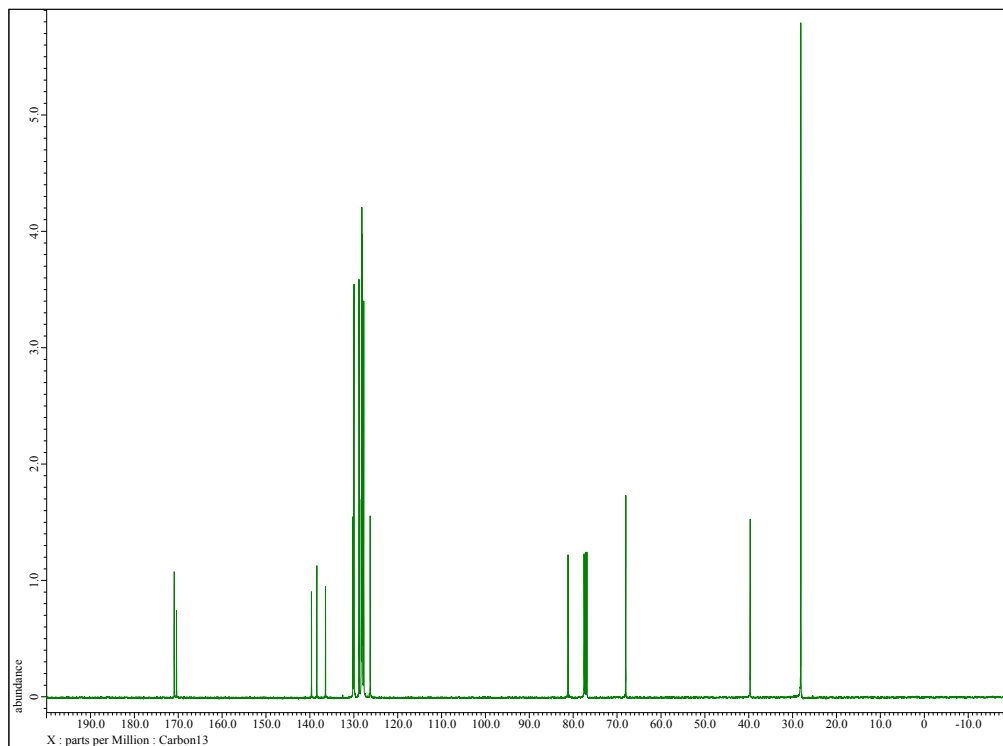
^1H NMR ($\text{d}^6\text{-DMSO}$, 300 MHz) spectrum of **13CfAllyl**

Characterization for compound **15** synthesized using polymeric catalyst

^1H NMR (CDCl_3 , 400 MHz) δ 7.59~7.57 (m, 2H), 7.35~7.23 (m, 6H), 7.20~7.12 (m, 3H), 7.06~7.04 (m, 2H), 6.60 (d, $J = 6$ Hz, 2H), 4.14~4.10 (m, 1H), 3.26~3.14 (m, 2H), 1.43 (s, 9H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz) δ 170.92, 170.39, 139.6, 138.4, 136.4, 130.19, 130.00, 128.80, 128.30, 128.17, 128.14, 128.03, 127.7, 126.3, 81.2, 68.0, 39.7, 28.1 ppm.



^1H NMR (CDCl_3 , 400 MHz) spectrum of **15**



^{13}C NMR (CDCl_3 , 100 MHz) spectrum of **15**