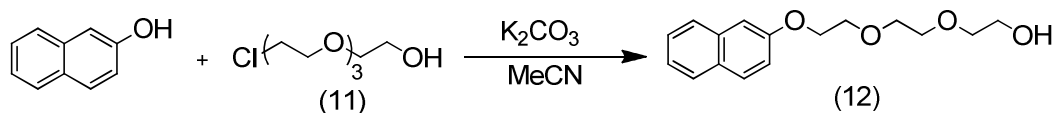


An Aqueous Supramolecular side-chain polymer: Designed for Molecular Loading

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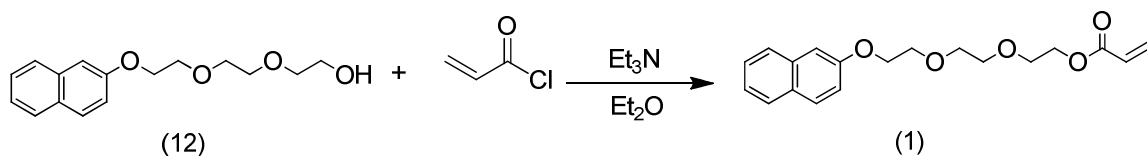
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All starting materials were purchased from Alfa Aesar and Sigma Aldrich and used as received unless stated otherwise. CB[8] was prepared according to literature procedure.^[1] ^1H and ^{13}C NMR spectra were recorded on Bruker DRX-400 (400 MHz) and Avance 500 BB-ATM (500 MHz) spectrometers, UV/visible spectra on a Varian Cary 4000 UV-Vis spectrophotometer. ATR FT-IR spectrum 100series FT-IR spectrometer equipped with a universal ATR sampling accessory. High-resolution mass spectra were recorded on a Bruker BioASpex II 4.7e FT-ICR mass spectrometer liquid chromatography-mass spectrometry Waters ZQ. Gel permeation chromatography (GPC) was carried out in dimethylformamide (DMF) on two Jordi 5 μm DVB columns connected in series with a SPD-M20A prominence diode array detector and Viscotak (both shimadzu) calibrated in relation to polystyrene standards. Samples were filtered over 0.45 μm PTFE filters before injection using a 0.75 ml/ min flow rate.



2-naphthol (8.6g, 0.06mol) was added into the solution of (9) (5.01g, 0.03mol) and potassium carbonate (8.20g, 0.06mol) in 150ml acetonitrile. The resulting solution was heated at reflux under N₂ for 36 hours. The solvent was removed under reduced pressure and the reaction mixture was loaded onto a column previously filled with SiO₂ and pre-eluted with hexane. The column was the washed with a 2:3 (vol / vol) hexane: ethyl acetate mixture. After removal of the solvent, (10) was obtained as light red oil 5.1g, yield 62%.

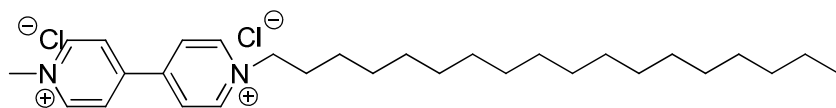
¹H NMR (500.05 MHz, CDCl₃, 298 K) δ = 7.70-7.75 (m, 3H); 7.42 (t, *J* = 6.9 Hz, 1H); 7.32 (t, *J* = 8.0 Hz, 1H); 7.17 (dd, *J* = 2.3, 2.5 Hz, 1H); 7.13 (d, *J* = 2.4 Hz, 1H); 4.23 (t, *J* = 4.6Hz, 2H); 3.91 (t, *J* = 3.4 Hz, 2H); 3.68-3.75 (m, 6H); 3.60 (m, 2H); 2.78 (s, 1H). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, 298 K) δ = 156.6 (1C, CO); 134.5 (1C, CH); 129.8 (1C, CH); 129.5 (1C, CH); 128.1 (1C, CH); 127.2 (1C, CH); 126.8 (1C, CH); 123.7 (1C, CH); 118.9 (1C, C); 106.7 (1C, C); 72.5 (1C, CH₂); 70.6 (1C, CH₂); 69.8 (1C, CH₂); 69.1 (1C, CH₂); 67.3 (1C, CH₂); 61.7 (1C, CH₂). Anal. Calcd. for C₁₆H₂₀O₄ C, 69.54; H, 7.30; Found: C, 69.34; H, 7.26.



A solution of (12) (5.00g, 18.09mmol) and Et₃N (4.54 ml, 32.57 mmol) in Et₂O (150

ml) was cooled to -20 °C and a solution of acryloyl chloride (2.20ml, 27.14mmol) in Et₂O (5 ml) was added dropwise over ca. 1 h. The mixture was then stirred at ambient temperature overnight. The triethylammonium chloride salt was filtered off and the volatiles removed under reduced pressure. The crude product was therefore purified by flash chromatography (CC, SiO₂, Hexane/Ethyl acetate (4:1, v/v). The relevant fractions were collected, combined and concentrated to dryness under reduced pressure. Obtained 5.28g (89%) as yellowish oil.

¹H NMR (500.05 MHz, CDCl₃, 298 K) δ = δ = 7.70-7.76 (m, 3H); 7.44 (t, *J* = 6.9 Hz, 1H); 7.32 (t, *J* = 7.0 Hz, 1H); 7.15-7.18 (m, 2H); 6.38-6.39 (dd, *J* = 1.6 Hz; *J* = 1.4 Hz, 1H); 6.14-6.18 (m, 1H); 5.7-5.8 (dd, *J* = 1.4Hz; *J* = 1.7 Hz, 1H); 4.32 (m, 2H); 4.24 (m, 2H); 3.91 (m, 2H); 3.75 (m, 4H), 3.70 (m, 2H). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, 298 K) δ = 167.8 (1C, CO); 157.2 (1C, C); 136.6 (1C, CCH₃); 134.9 (1C, CH); 129.8 (1C, CH); 128.0 (1C, CH); 127.2 (1C, CH); 126.8 (1C, C); 126.1 (1C, CH); 124.1 (1C, CH₂); 119.4 (1C, CH); 107.2 (1C, CH); 71.3 (1C, CH₂); 71.1 (1C, CH₂); 70.2 (1C, CH₂); 69.6 (1C, CH₂); 69.4 (1C, CH₂); 67.8 (1C, CH₂); 64.3 (1C, CH₂);
 Anal. Calcd. for C₂₀H₂₄O₅ C, 73.15; H, 7.37; Found: C, 73.19; H, 7.33.



1-Octadecyl-1'-methyl-4,4'-bipyridinium bromide iodide **6**: A 50 mL RBF flask was charged with 1-methyl-4,4'-bipyridinium iodide (0.6 g, 2 mmol), 1-bromooctadecane (10 mmol) and acetonitrile (20 mL). The reaction mixture was heated at reflux for 48 h. A red precipitate was collected and recrystallized from ethanol/water. ¹H NMR

(D₂O): $\delta = 9.05$ (d, 2H), 9.00 (d, 2H), 8.5 (m, 4H), 4.65 (t, 2H), 4.45 (s, 3H), 2.05 (q, 2H), 1.32 (d, 2H), 1.20 (m, 28H), 0.80 (t, 3H) ppm.

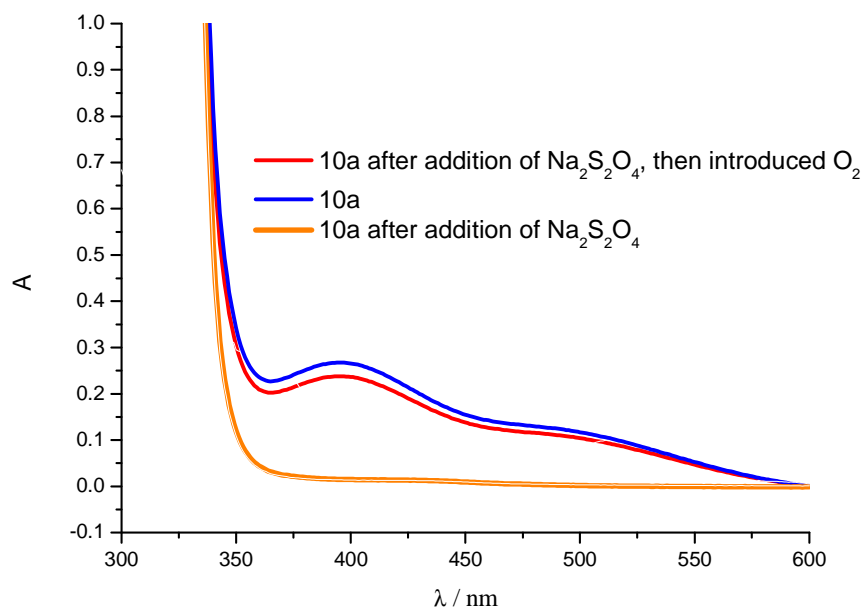


Fig. 1. UV/vis spectra in water of **10a** (blue), and **10a** after addition of Na₂S₂O₄ (yellow), and **10a** after addition of Na₂S₂O₄ then introduced oxygen into the solution (red), respectively (each at 1.0 mmol). The complex is disassembled upon adding a reductant Na₂S₂O₄ and reassembled upon introducing oxygen.

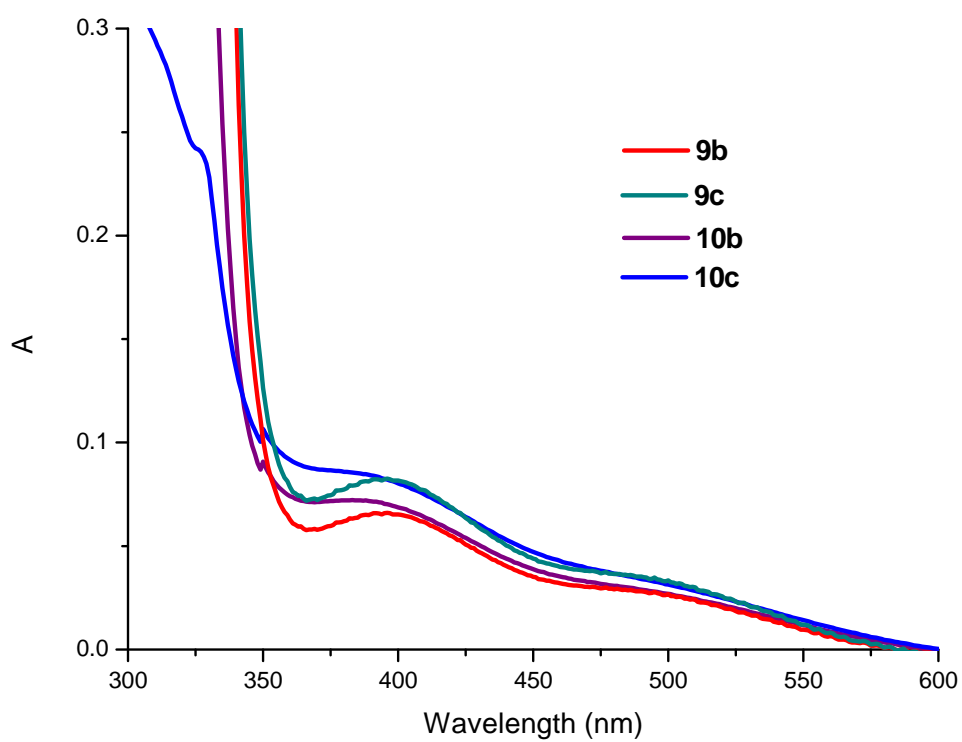


Fig. 2. UV/vis spectra in water of **9b**, **9c**, **10b**, and **10c**, respectively (each at 1.0 mmol).

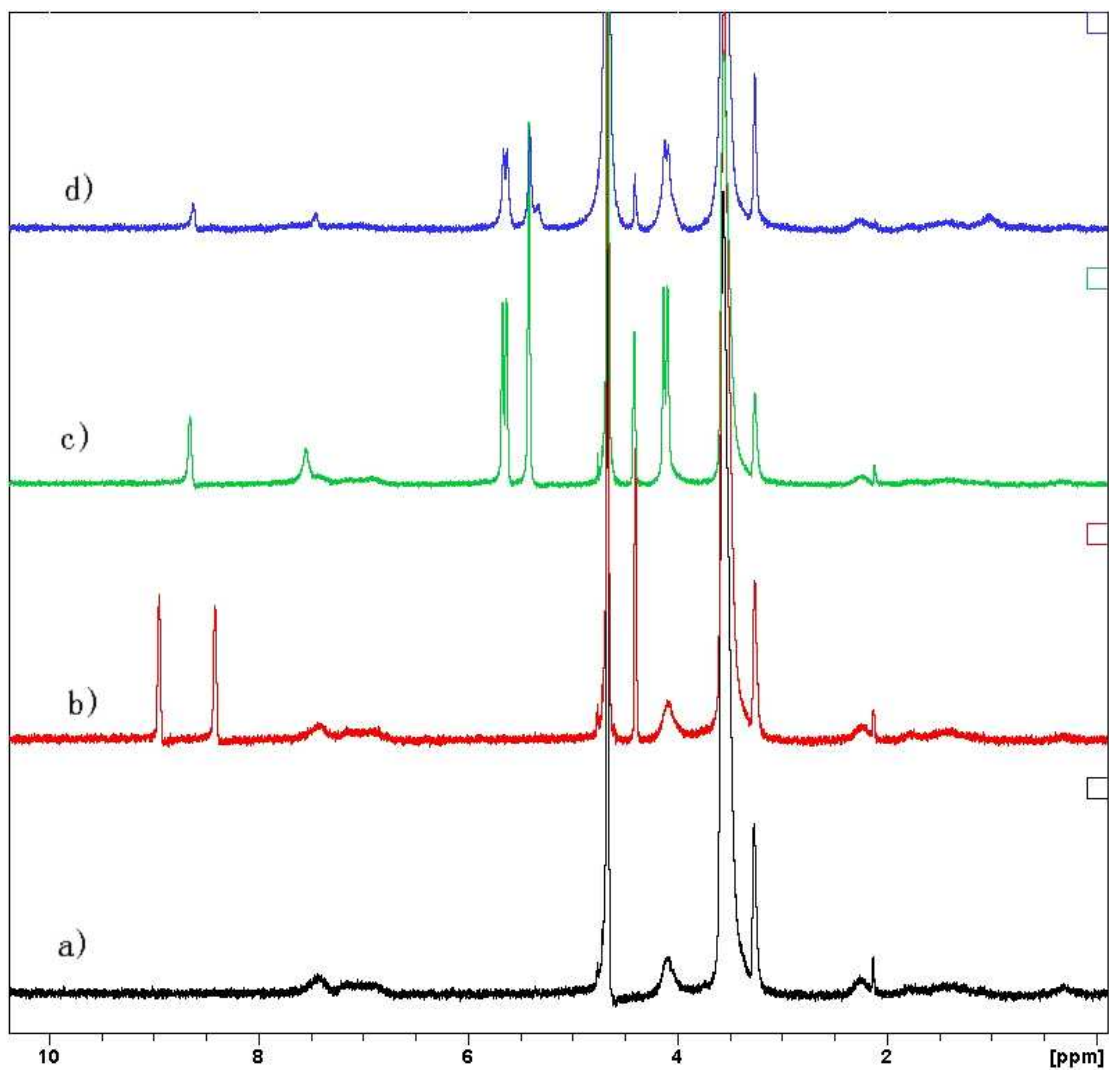


Fig. 3. ¹H NMR spectra in D₂O: a) **4b**, b) **4b** and **5**, c) **9b**, d) **10b**. Each at 1 mmol.

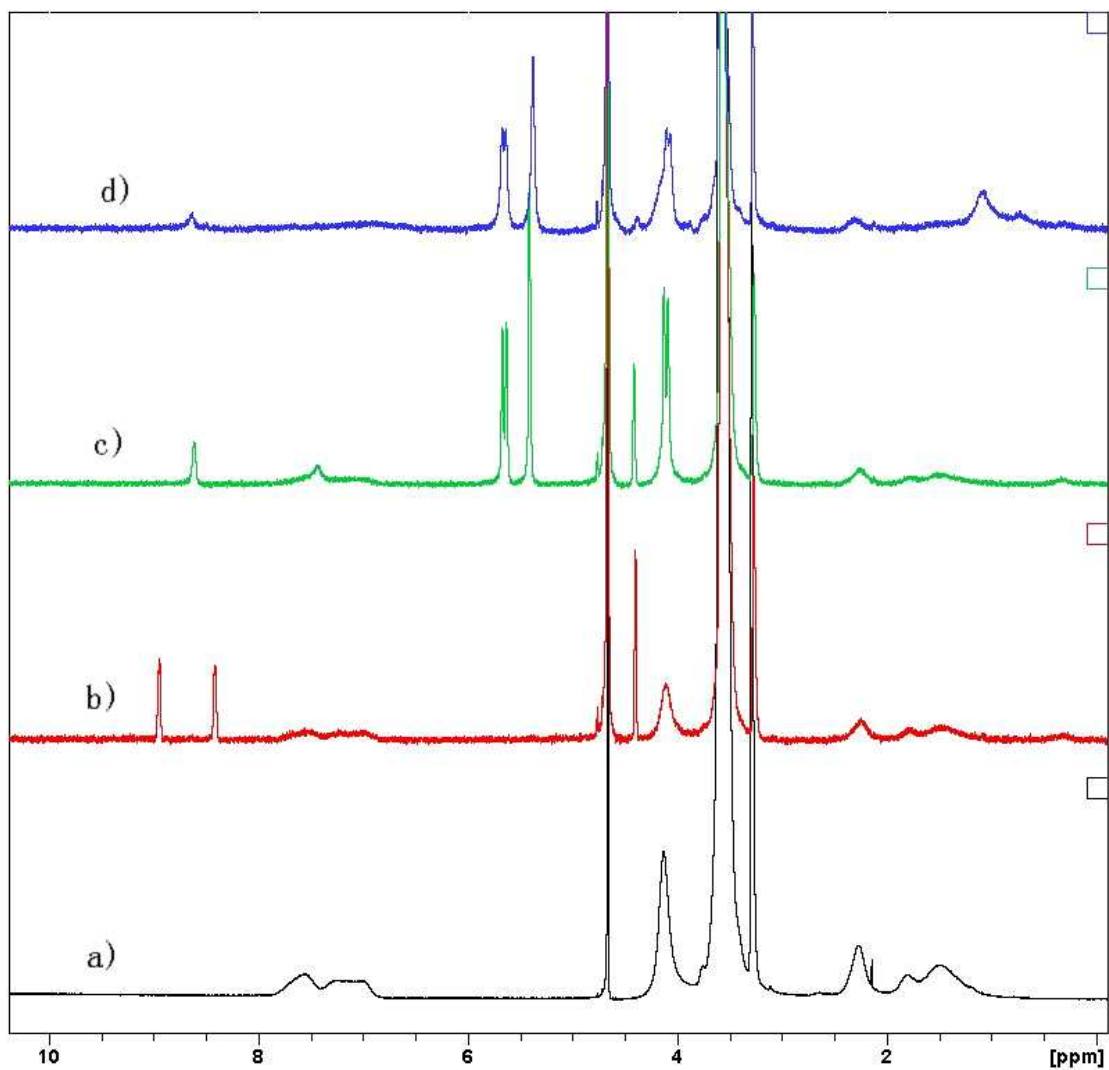


Fig. 4. ¹H NMR spectra in D₂O: a) **4c**, b) **4c** and **5**, c) **9c**, d) **10c**. Each at 1 mmol.

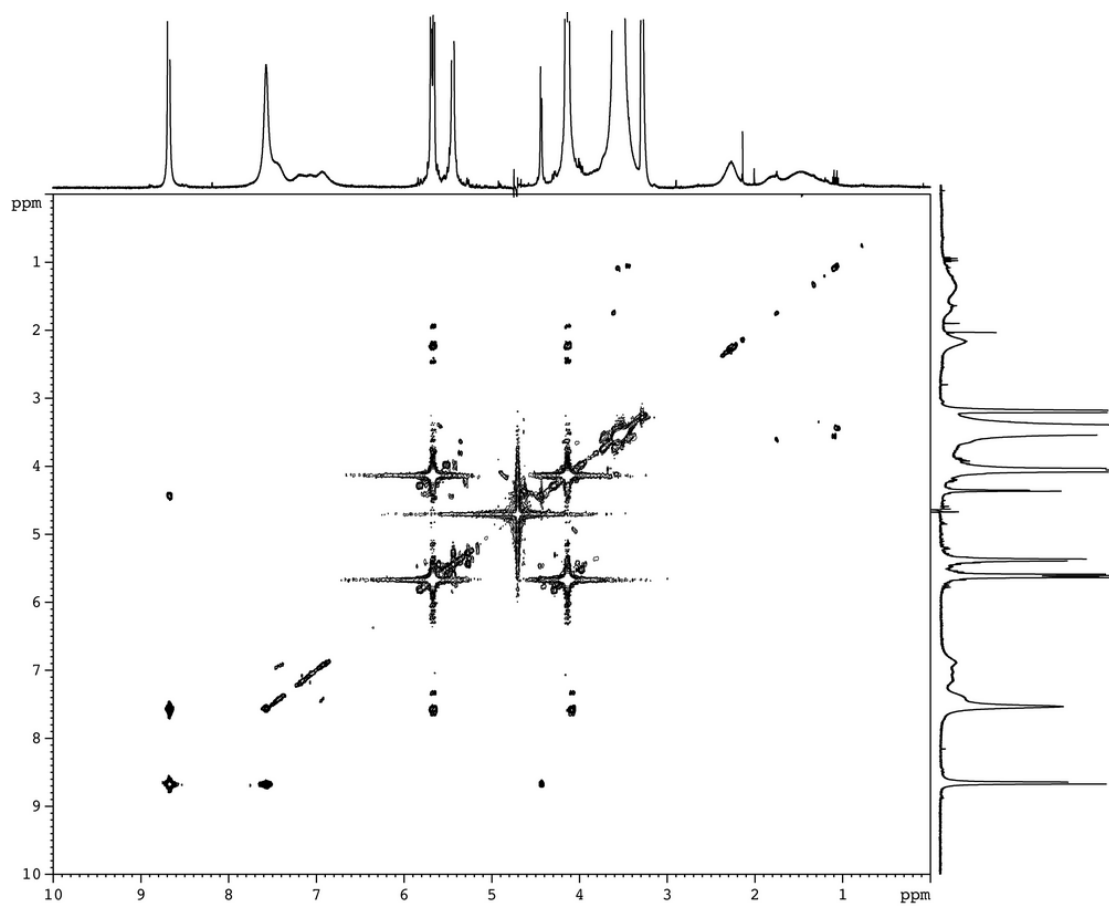


Fig. 5. Two-dimensional-COSY NMR spectrum of the copolymer complex **9a** in D₂O.

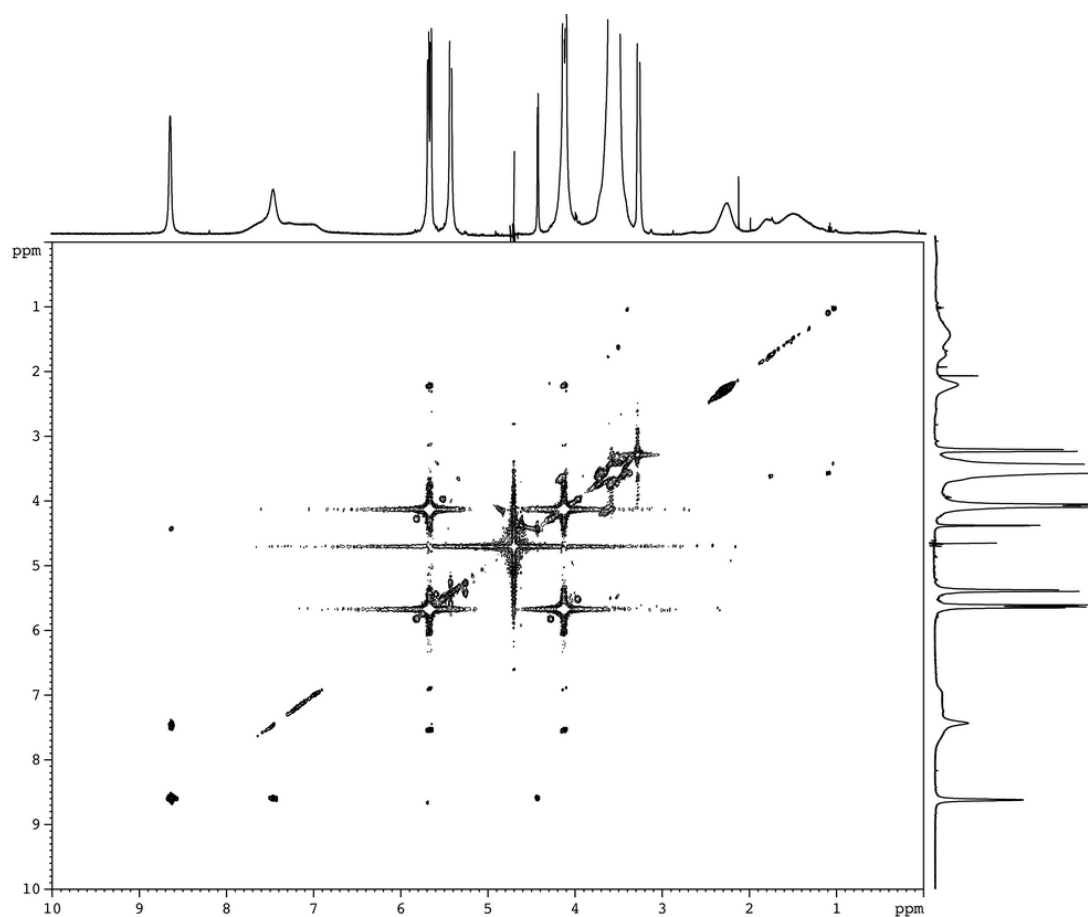


Fig. 6. Two-dimensional-COSY NMR spectrum of the copolymer complex **9b** in D₂O.

- [1] J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2000**, *122*, 540.