Electronic Supplementary Information

Synthesis and characterization of TEMPO- and viologen-polymers for water-based redox-flow batteries

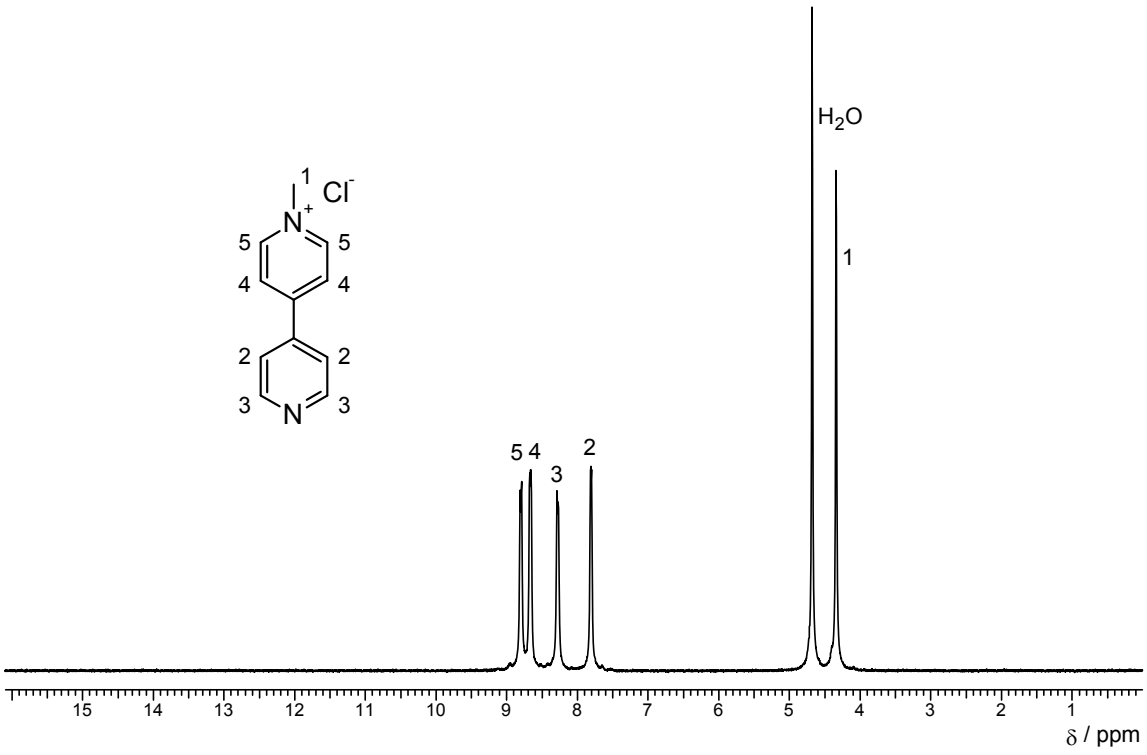
Tobias Janoschka,[a,b] Sabine Morgenstern,[a,b] Hannes Hiller,[a,b] Christian Friebe,[a,b] Konrad Wolkersdörfer,[a] Bernhard Häupler,[a,b] Martin D. Hager,[a,b] Ulrich S. Schubert[a,b]*

[a] Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstrasse 10, 07743 Jena, Germany.

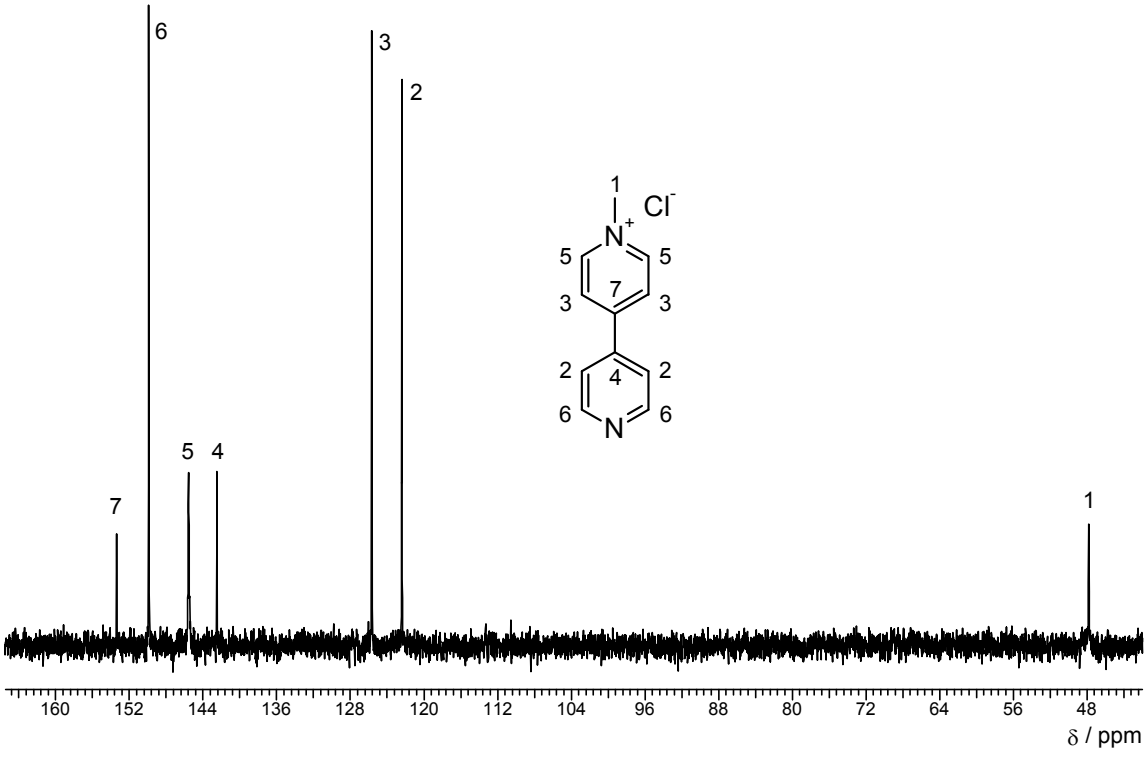
[b] Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany.

Correspondence to: Ulrich S. Schubert (E-mail: *ulrich.schubert@uni-jena.de*)

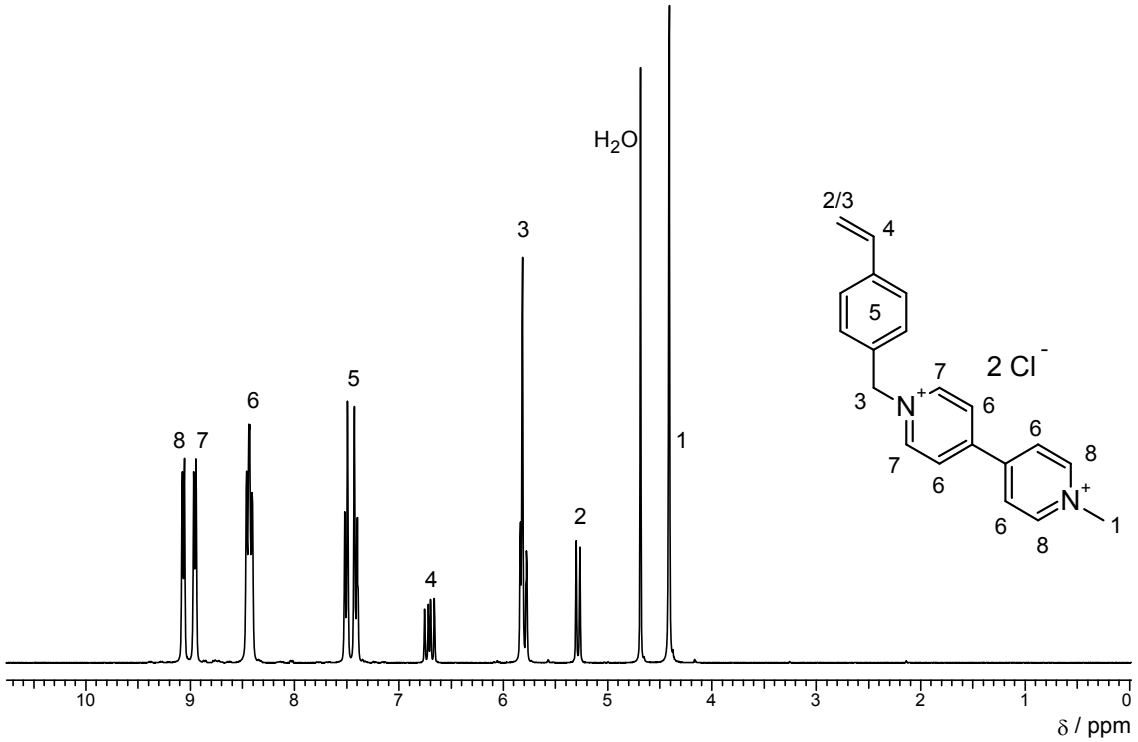
ESI Figure 1: ^{1}H NMR spectrum (300 MHz, D_2O): 1-methyl-[4,4'-bipyridine]-1-ium chloride (1a).



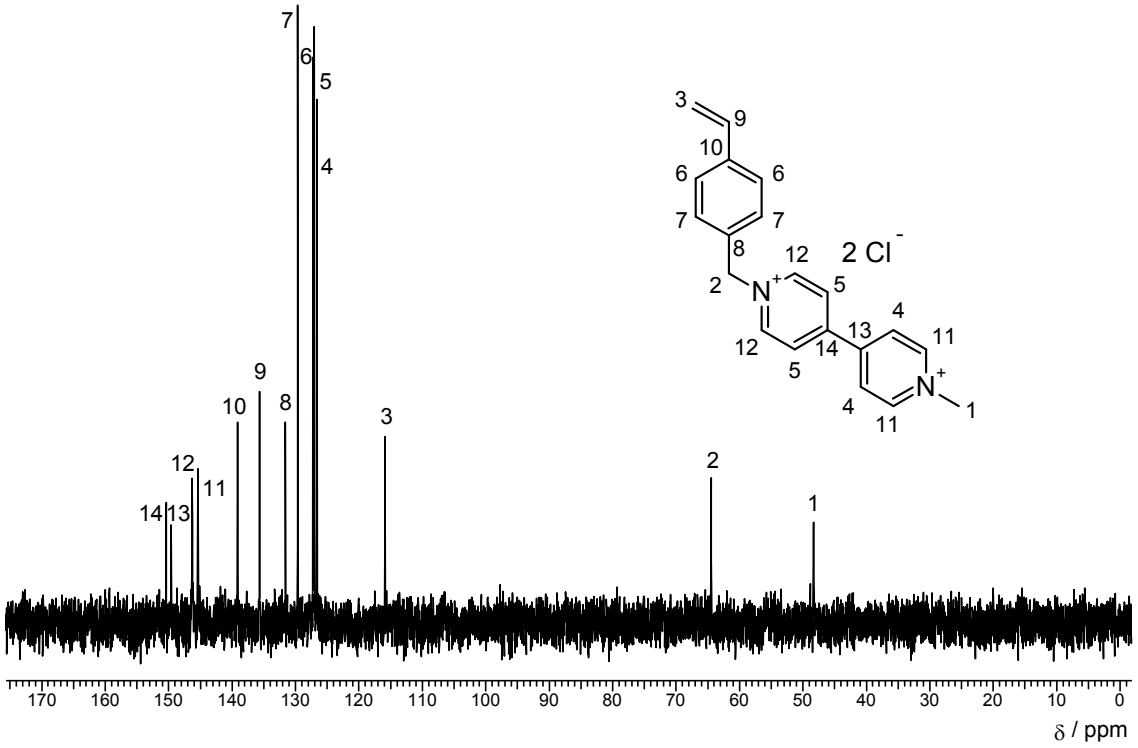
ESI Figure 2: ^{13}C NMR spectrum (75 MHz, D_2O): 1-methyl-[4,4'-bipyridine]-1-ium chloride (1a).



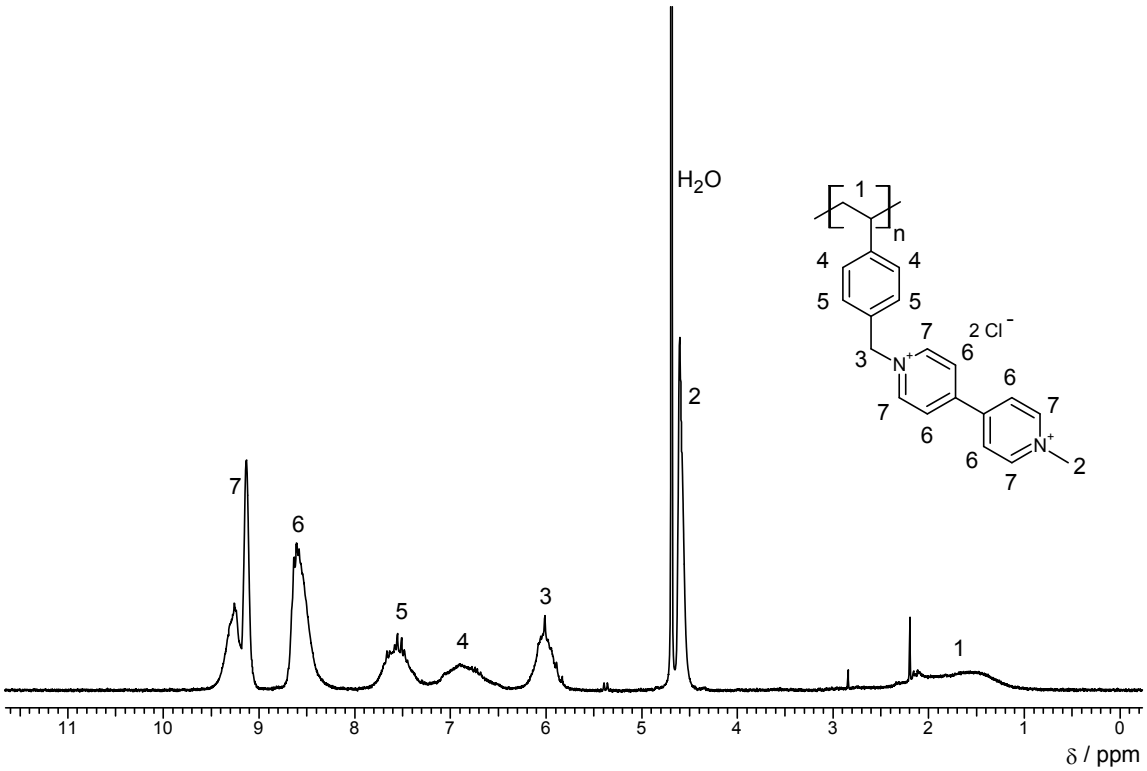
ESI Figure 3: ^{1}H NMR spectrum (300 MHz, D_2O): 1-Methyl-1'-(4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-diium dichloride (2).



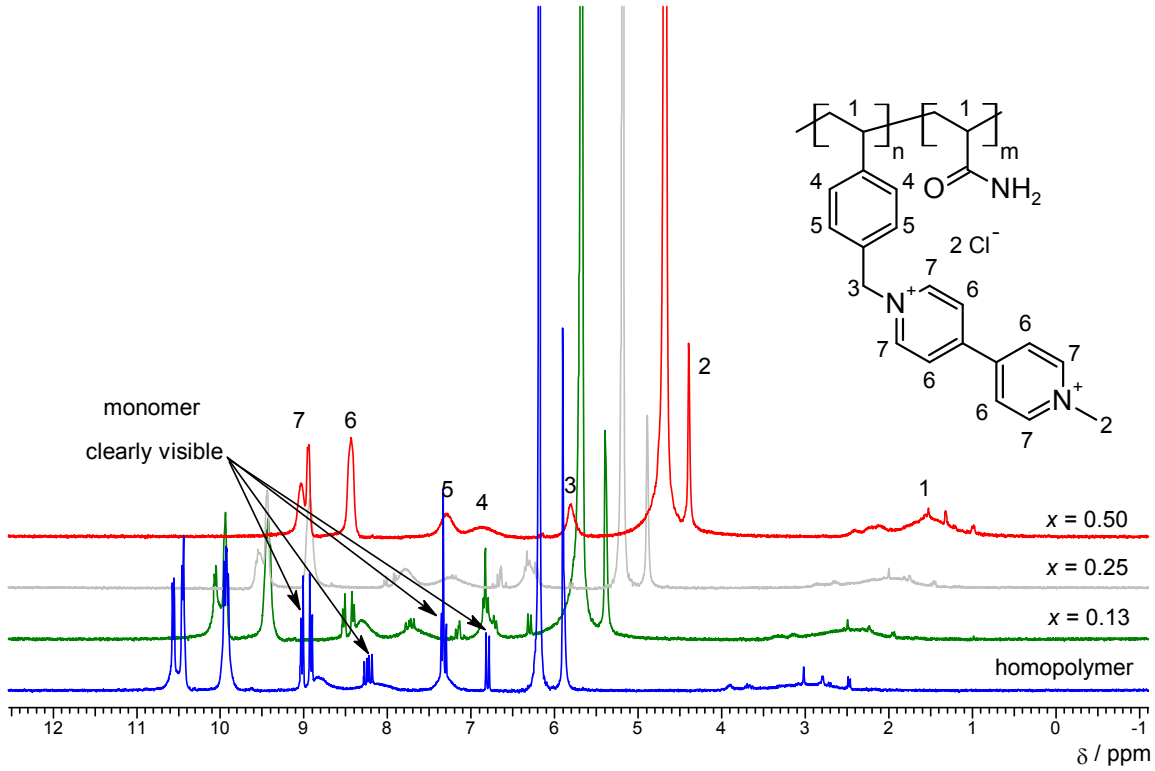
ESI Figure 4: ^{13}C NMR spectrum (75 MHz, D_2O): 1-Methyl-1'-(4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-diium dichloride (2).



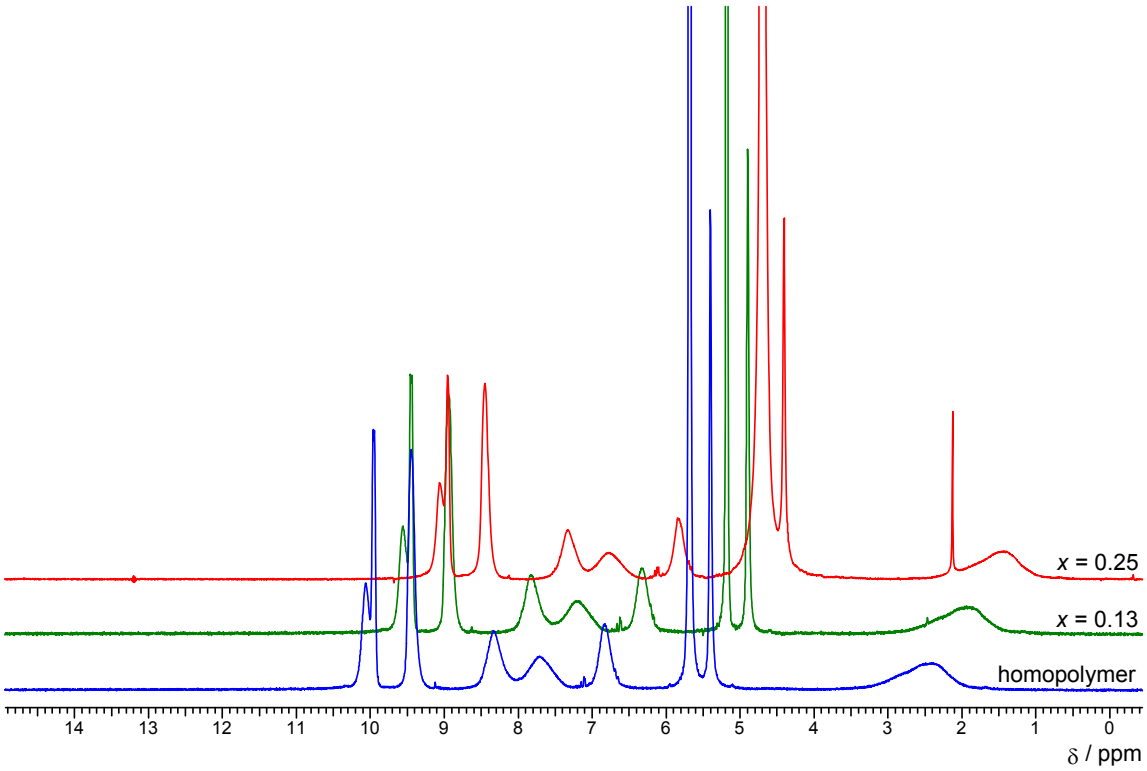
ESI Figure 5: Representative ^{1}H NMR spectrum (300 MHz, D_2O): poly(1-methyl-1'-(4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-diium dichloride) (P2a), prepared with 7 mol-% thioacetic acid.



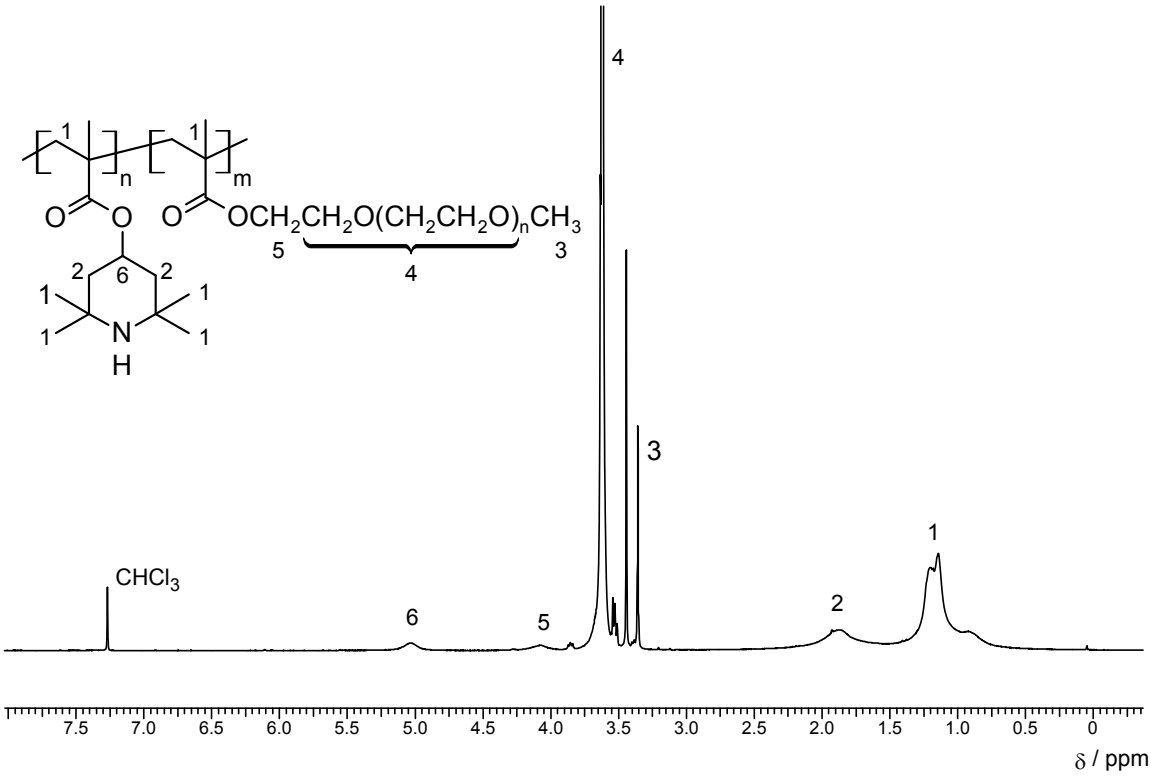
ESI Figure 6: ^{1}H NMR spectrum (300 MHz, D_2O) of poly(1-methyl-1'-(4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-diium dichloride-*co*-acrylamide) (P2b) prepared using 4,4′-azo*bis*(4-cyanovaleric acid) at different mole fractions of acrylamide comomoner, 16 h reaction time.



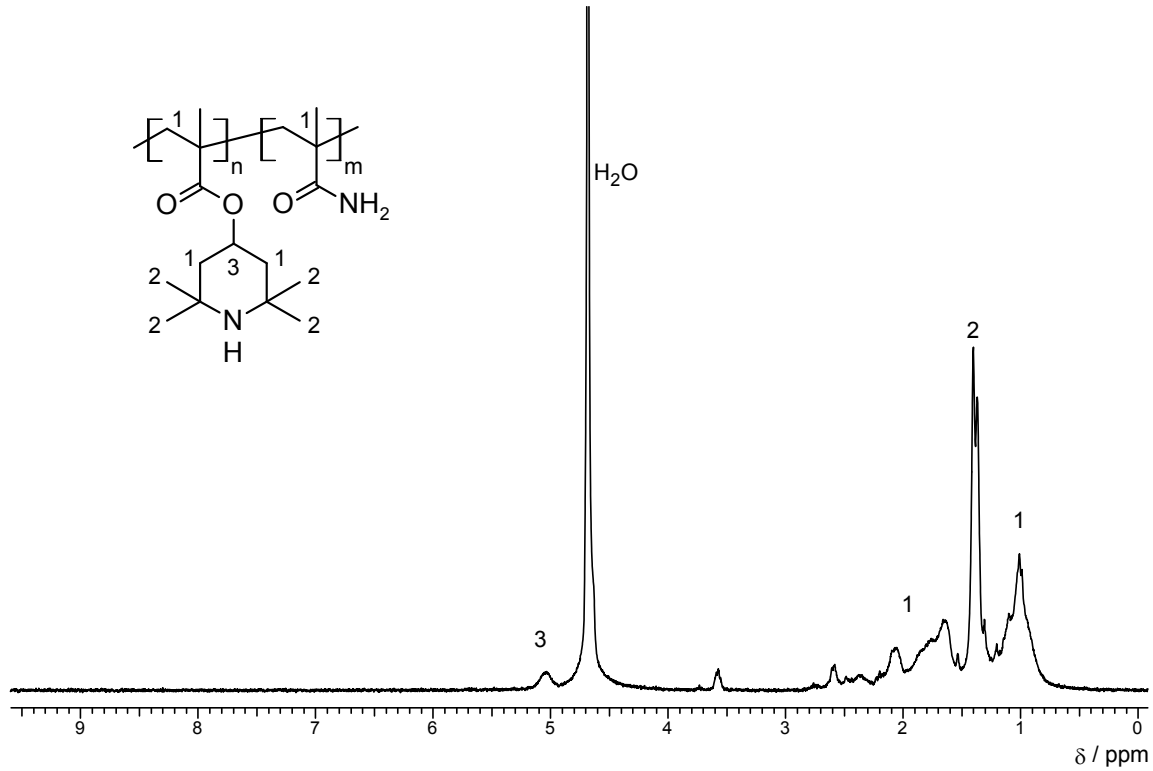
ESI Figure 7: ^{1}H NMR spectrum (300 MHz, D_2O) of poly(1-methyl-1'-(4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-diium dichloride-*co*-acrylamide) (P2b) prepared using potassium peroxodisulfate at different mole fractions of acrylamide comomoner, 1 h reaction time.



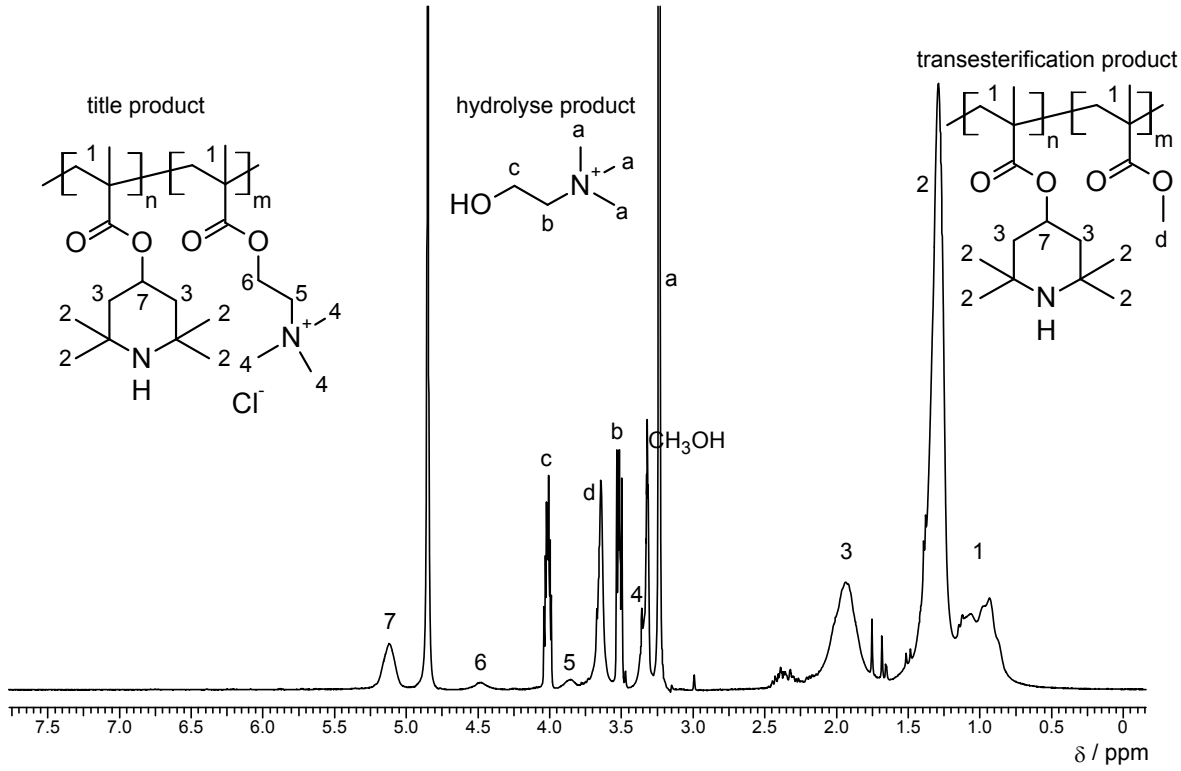
ESI Figure 8: Representative ^{1}H NMR spectrum (300 MHz, $CDCl_3$): Poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate-co-poly(ethylene glycol) methyl ether methacrylate) (P3b), x_{4b} = 0.33.



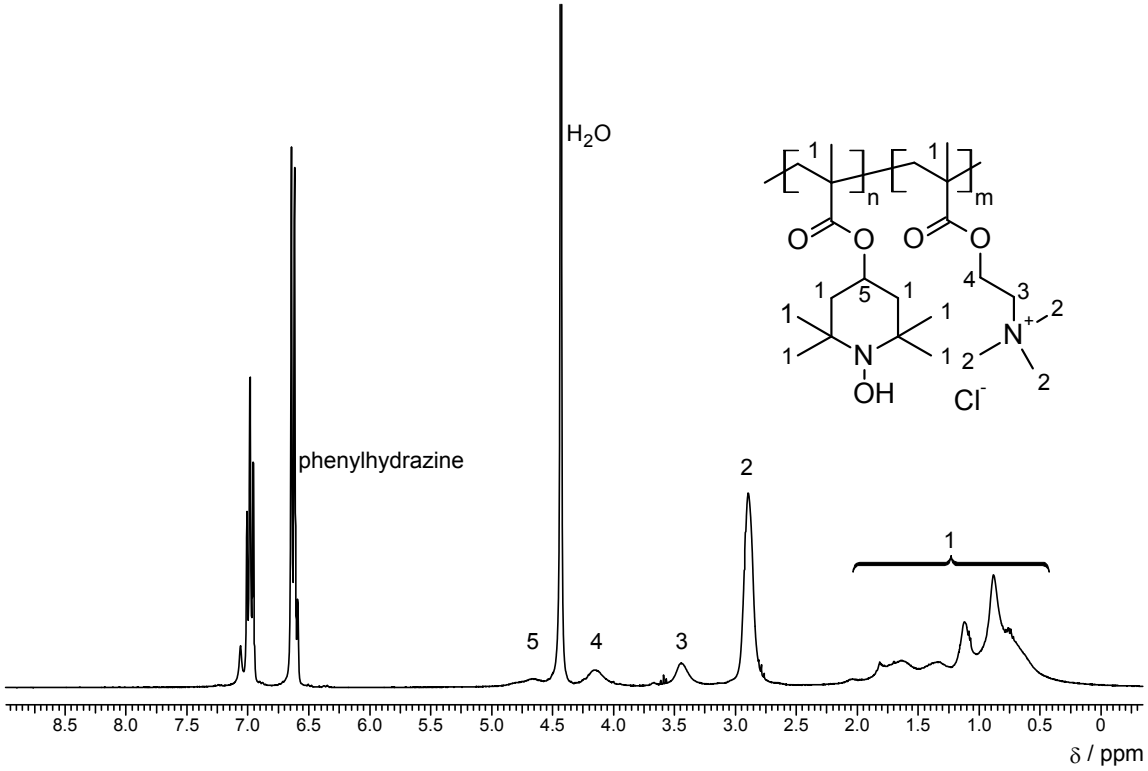
ESI Figure 9: Representative ^{1}H NMR spectrum (300 MHz, D_2O): Poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate-*co*-methacrylamide) (P3d), x_{4d} = 0.67 prepared with 8% 2-mercaptoethanole.



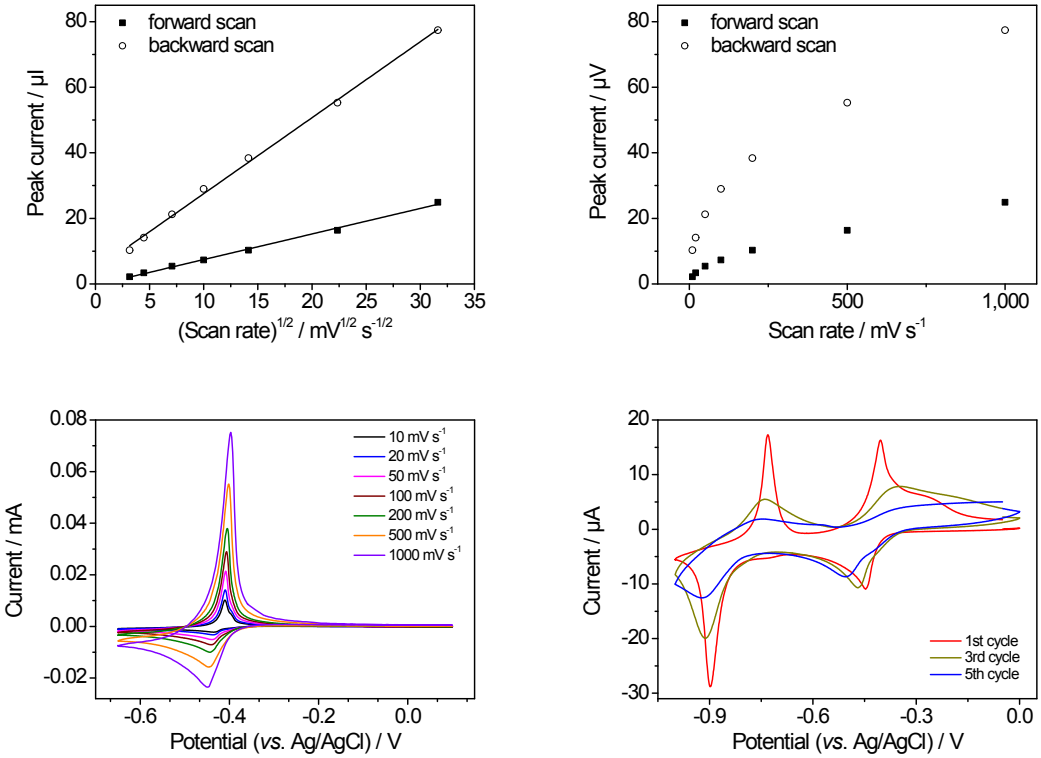
ESI Figure 10: ^{1}H NMR spectrum (300 MHz, methanol-d_4) of poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate-*co*-2-(methacryloyloxy)-*N,N,N*-trimethylethane ammonium chloride) (P3e) showing the partial hydrolysis of the ester in monomer 4e (x_{4e} = 0.5), occurring if the reaction mixture is not neutralized with HCl prior to polymerization.



ESI Figure 11: Representative ^{1}H NMR spectrum (300 MHz, D_2O): Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-*co*-2-(methacryloyloxy)-*N,N,N*-trimethylethane ammonium chloride) (P4e), prepared with 8 mol-% 2-mercaptoethanole, quenched with phenyl hydrazine.

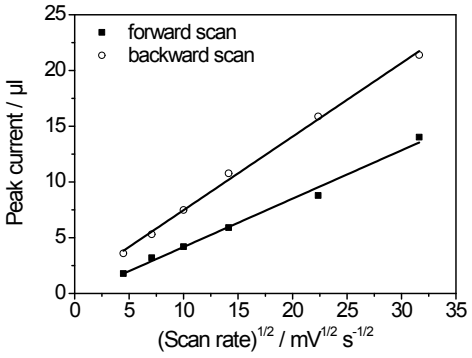


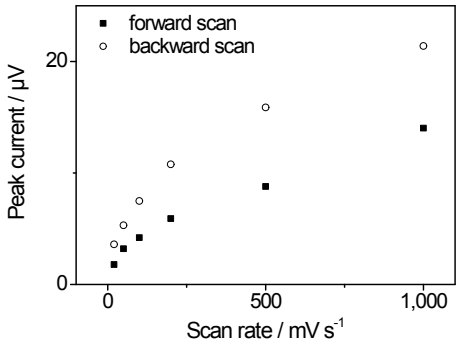
ESI Figure 12: Poly(1-methyl-1'-(4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-diium dichloride) (P2a), prepared with 7 mol-% thioacetic acid.

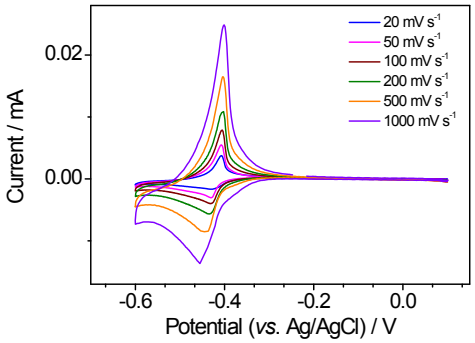


Scan rate (mV s^{-1})	$I_{forward\ scan}$ (µA)	$I_{backward\ scan}$ (µA)
1000	24.9	77.4
500	16.4	55.3
200	10.3	38.4
100	7.3	28.9
50	5.4	21.2
20	3.4	14.1
10	2.2	10.3

ESI Figure 13: Poly(1-methyl-1'-(4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-diium dichloride) (P2a), prepared without thioacetic acid.

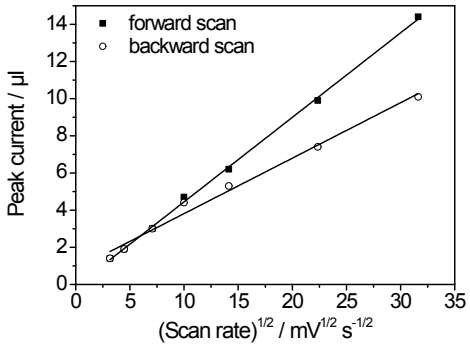


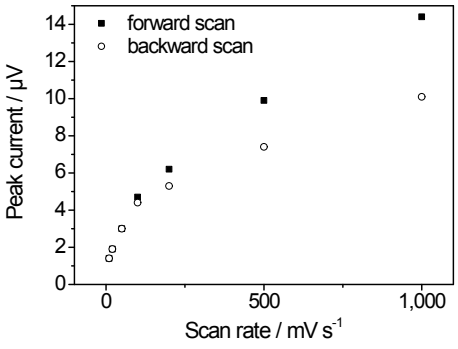


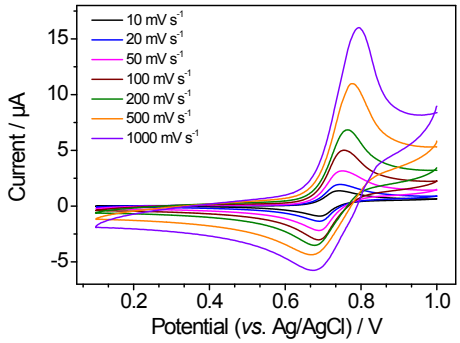


Scan rate (mV s^{-1})	$I_{forward\ scan}$ (µA)	$I_{backward\ scan}$ (µA)
1000	14.0	21.4
500	8.8	15.9
200	5.9	10.8
100	4.2	7.5
50	3.2	5.3
20	1.78	3.6

ESI Figure 14: Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-*co*-2-(methacryloyloxy)-*N,N,N*-trimethylethane ammonium chloride) (P4e), prepared with 1 mol-% 2-mercaptoethanole.

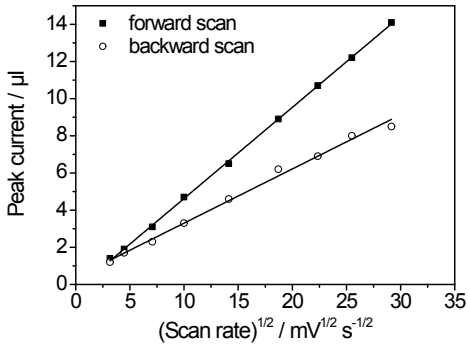


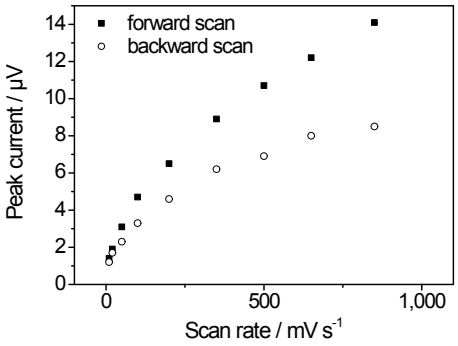


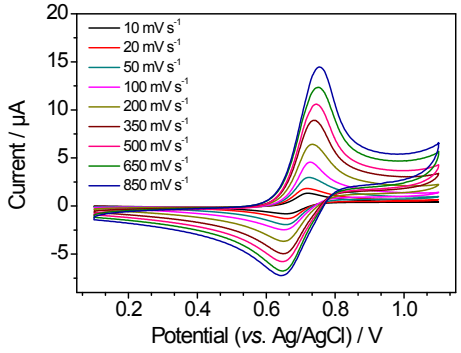


Scan rate (mV s^{-1})	$I_{forward\ scan}$ (µA)	$I_{backward\ scan}$ (µA)
1000	14.4	10.1
500	9.9	7.4
200	6.2	5.3
100	4.7	4.4
50	3	3
20	1.9	1.9
10	1.4	1.4

ESI Figure 15: Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-*co*-2-(methacryloyloxy)-*N,N,N*-trimethylethane ammonium chloride) (P4e), prepared with 8 mol-% 2-mercaptoethanole.







Scan rate (mV s^{-1})	$I_{forward\ scan}$ (µA)	$I_{backward\ scan}$ (µA)
850	14.1	8.5
650	12.2	8.0
500	10.7	6.9
350	8.9	6.2
200	6.5	4.6
100	4.7	3.3
50	3.1	2.3
20	1.9	1.7
10	1.4	1.2