Electronic Supplementary Material (ESI) for Polymer Chemistry.

Nucleophile-initiated anionic polymerization of zwitterionic monomers derived from vinylpyridines in aqueous media at ambient aerobic conditions

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Anionic polymerization, vinylpyridine, zwitterion, density functional calculations, nucleophilic addition, anti-biofouling

Contents: Polymerization and chain extension reactions, NMR & end group analysis and DFT results

Experimental

Free radical polymerization (FRP) of 4VPPS, SP1

4-Vinylpyridine propanesulfonate, 4VPPS (0.3 g, 1.32 mmol), 4,4'-azobis(4-cyanovaleric acid), ABCVA (7.3 mg, 0.026 mmol) and DMF (50 µl, as internal standard) were dissolved in 0.5M NaCl/water (1.5 ml) and purged with N_2 for 15 min. The mixture was heated on an oil bath at 70 ^oC under N_2 for required time. Time to time aliquots were collected for NMR analysis. Finally the polymer was precipitated out from water, washed with acetone and then dried in vacuum oven at 50 ^oC.

Results and Discussion

Table S1. FRP and nucleophile initiated polymerization of VP based monomers

Polymer code	Monomer	Initiator or Nucleophile[a]	Monomer : initiator/ Nucleophile	Solvent, Temperature (°C), atmosphere (state of polymerization)	Monomer conversion with time[b]			$M_{n,GPC}$, Da and (PDI) of final precipitated polymer[c]
					1 h	6h	23h	
SP1	4VPPS	ABCVA (FRP)	50:1	0.5M NaCl/water, 70 °C, N_2 (solution polymerization)	98.8	98.9	>99	N.A [f]
SP2	4VPPS	PMDETA	50:1	0.5M NaCl/water, 23 °C, Air (solution polymerization)	49.2	77.4	96.6	N.A.[f]
SP3	4VPPS	None	--	0.5M NaCl/water, 23 °C, Air	Nil	Nil	Nil[d]	--
SP4	4VP	DMAP	50:1	[e]MeOH-Water (1:1), 23 °C, Air	Nil	Nil	Nil	--
SP5	2VPPS	ABCVA (FRP)	50:1	Water, 70 °C, N_2 (solution polymerization)	30.0	65.5	83.1	11290 (1.43)
SP6	2VPPS	PMDETA	50:1	Water, 23 °C, Air (solution polymerization)	27.9	94.1	98.3	2400 (1.19)
SP7	2VPPS	TEA	20:1	MeOH (precipitation polymerization)	>98	--	--	5900 (1.58)
SP8	2VPPS	1VI	50:1	LiBr in MeOH (2M) (Hazy solution during polymerization)	30.2	96.2	>99	5700 (1.72) 10450[g]
SP9	2VPPS	NaOPh[i]	20:1	MeOH, 23 °C, Air (precipitation polymerization)	>99[h]	--	--	5280 (1.61)
SP10	2VPPS	$Ph_3P=O$[j]	20:1	MeOH, 23 °C, Air	Nil	Nil	Nil	--
SP11	P13 (150 mg)	APS (2 mg)	--	Water, 70 °C, N_2, 4h (solution polymerization)	-	-	-	10190 (1.68)

DMF was used as internal standard. N.A. = not available, Nil = no polymerization; ABCVA = 4,4'-azobis(4-cyanovaleric acid), FRP = free radical polymerization; PMDETA = *N,N,N',N'',N''*-pentamethyldiethylenetriamine; APS = Ammonium persulfate; [a] Nucleophiles were used as aqueous solution (0.1M) except ABCVA which was used as solid; [b] determined by ^{1}HNMR spectroscopy; [c] determined by aqueous GPC; [d] no polymerization observed in 7days.; [e] performed in MeOH-water mixture as 4VP was not fully miscible in water; [f] not soluble in GPC eluent ; [g] determined by NMR; [h] conversion in 5 min; [i] added as 0.2M MeOH solution; [j] added as 0.2M THF solution

Table S2. Evolution of molecular weight of poly(2VPPS) with time

Polymerization time (min)	Monomer conversion[a] (%)	Calculated M_n	GPC results[b]		
			M_n	M_p	PDI
5	21.0	2390	1930	2140	1.13
10	43.8	4980	2130	2420	1.23
15	57.9	6580	2240	2680	1.25
30	82.8	9410	2370	2730	1.27
45	89.8	10200	2390	3030	1.29
60	92.1	10450	2410	3080	1.29

Polymerization conditions: 2VPPS: NaOH = 50:1, in water, at 23 °C and under air atmosphere. [a] determined ^{1}HNMR spectroscopy; [b] determined by aqueous GPC using 0.1M $NaNO_3$ solution as eluent and PEO-PEG calibration.

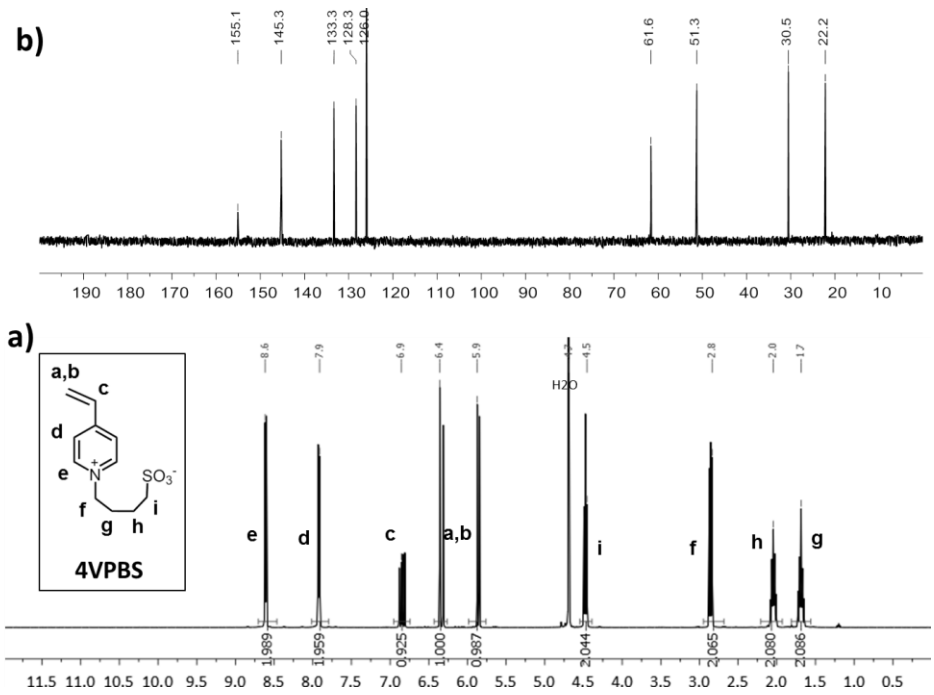


Figure S1. a) ^{1}H-NMR spectrum and b) ^{13}C-NMR spectrum (in D_2O) of 4VPBS

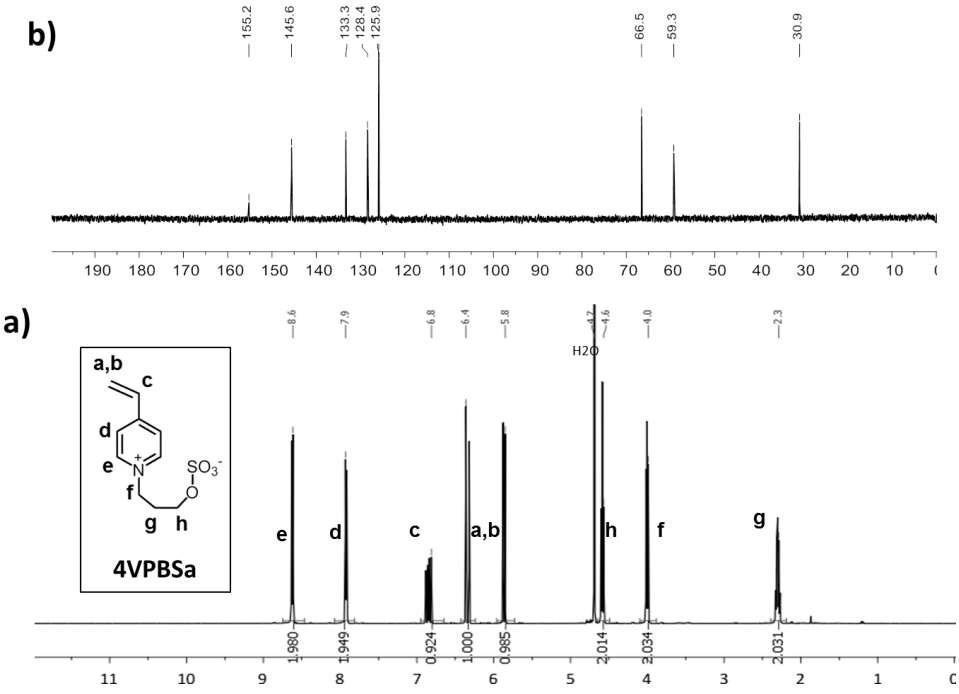


Figure S2. a) ^{1}H-NMR spectrum and b) ^{13}C-NMR spectrum (in D_2O) of 4VPPSa

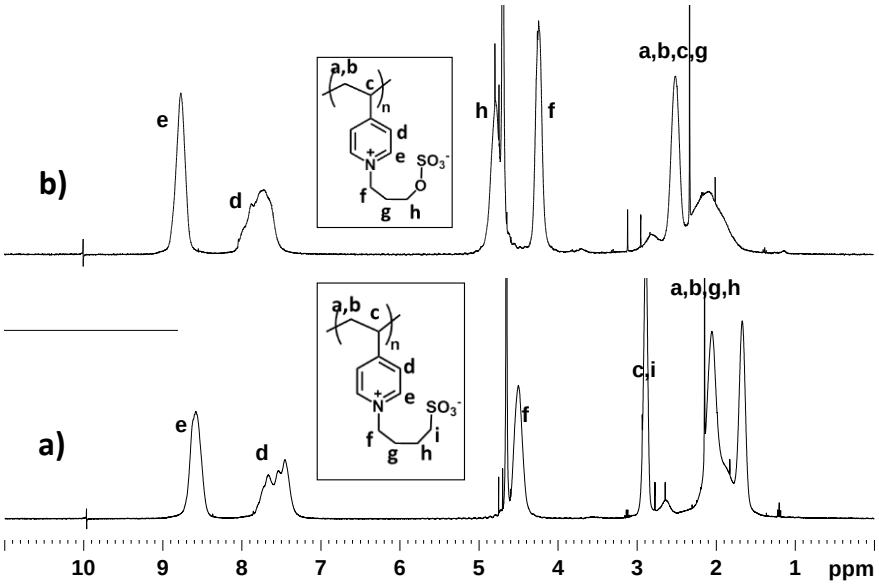


Figure S3. ^{1}H-NMR spectra (in 0.5M NaCl/D_2O) of a) poly(4VPBS) synthesized by using TEA (P7) and b) poly(4VPPSa) synthesized by using TEA (P8).

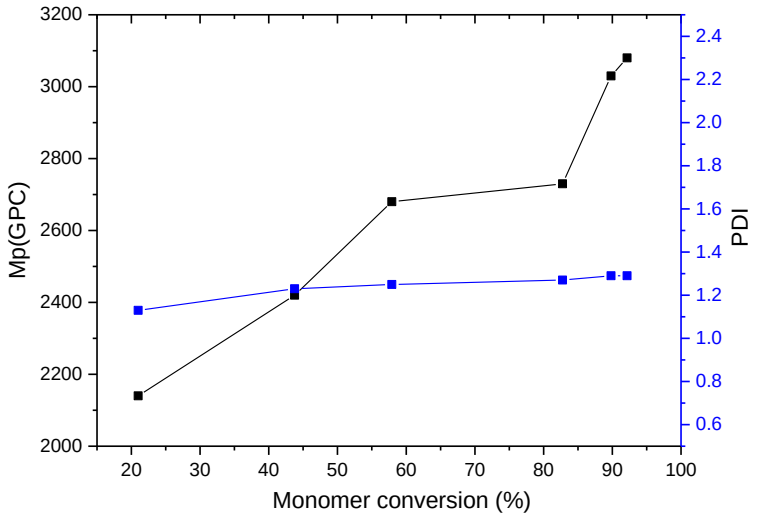


Figure S4. Evolution of molecular weight and PDI of poly(2VPPS) with monomer conversion

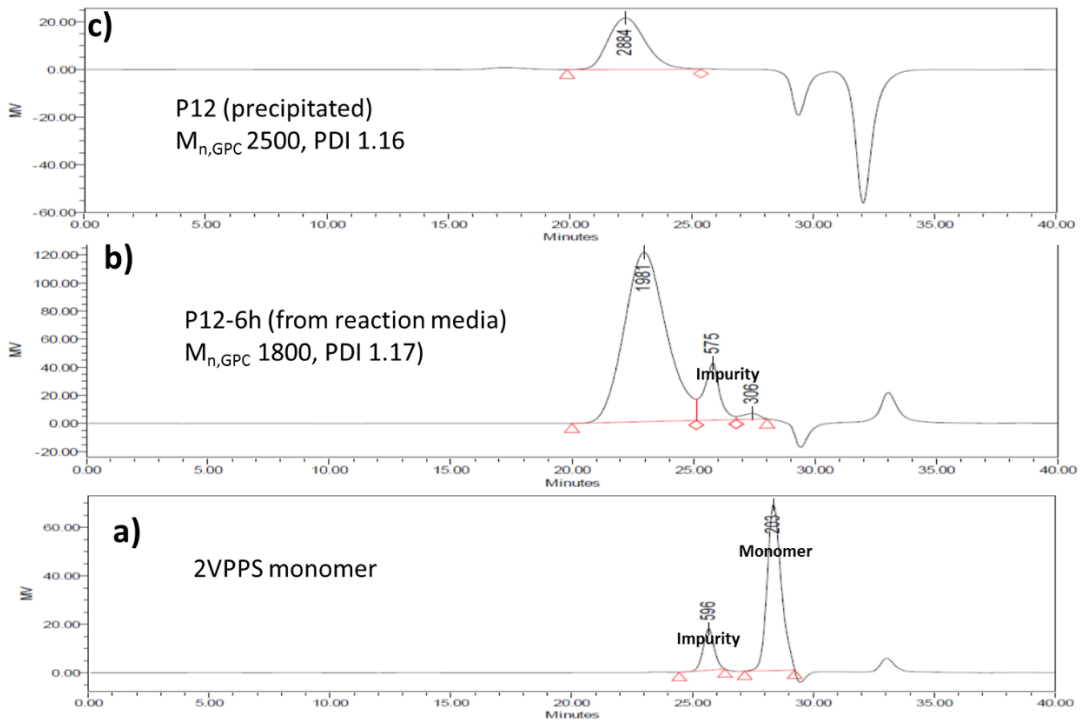
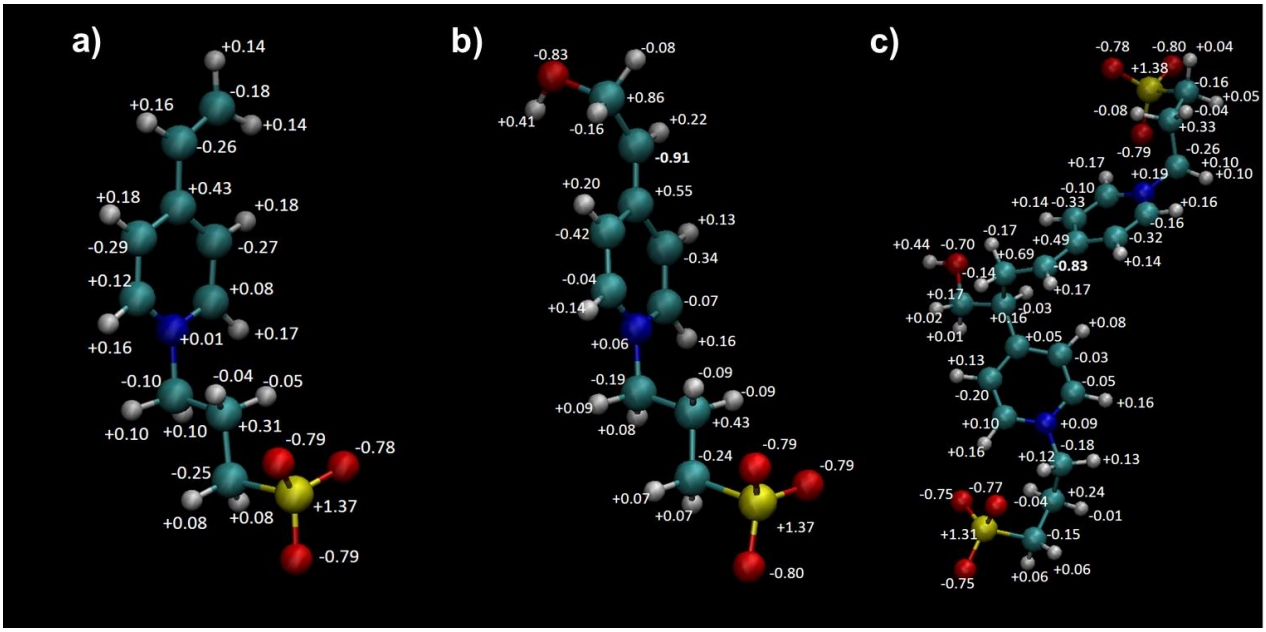
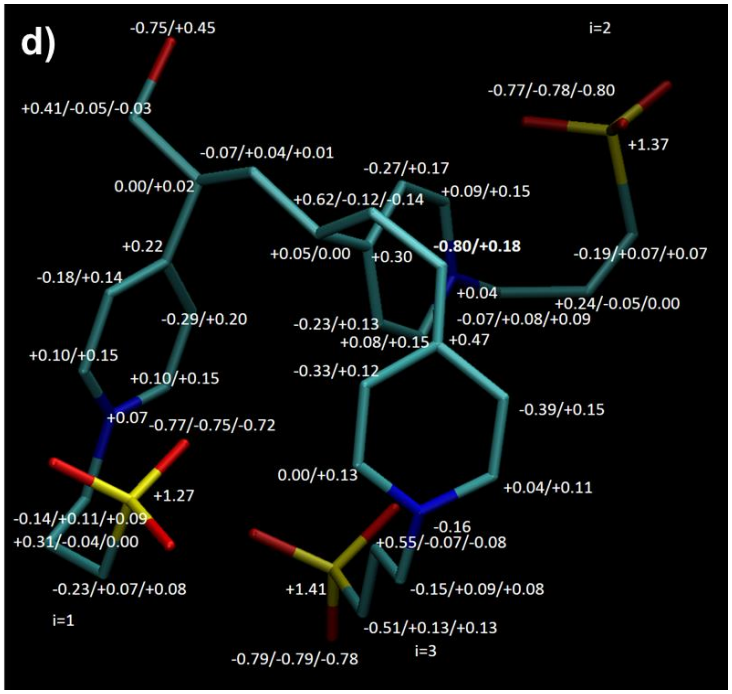
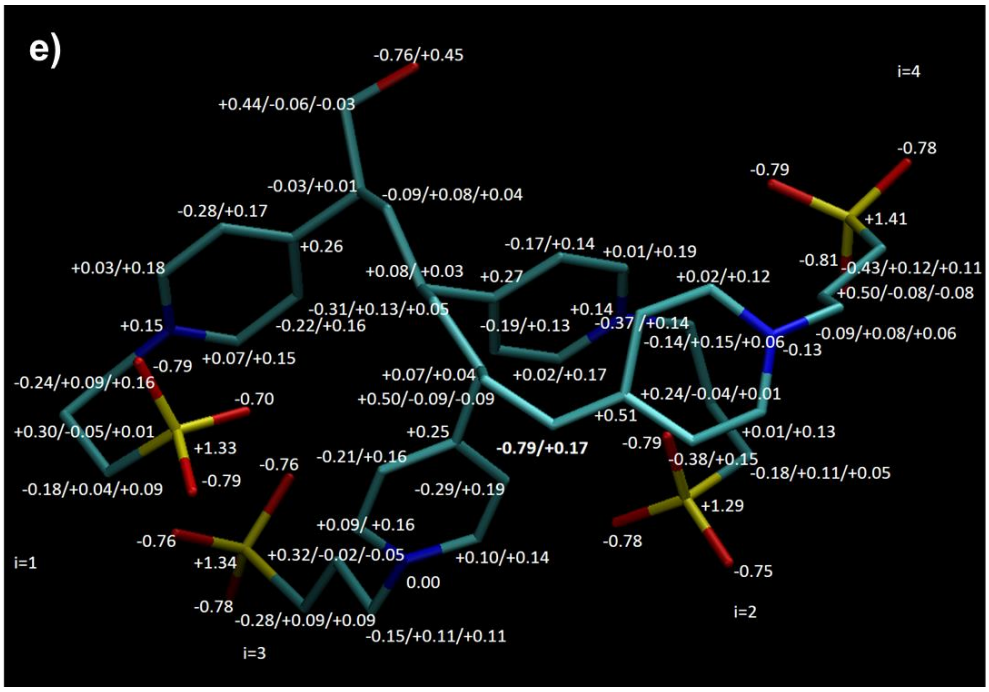


Figure S5. GPC chromatogram (using 0.1M $NaNO_3/D_2O$ eluent) of a) 2VPPS, b) polymer produced analyzed using reaction media after 6h of reaction and c) final precipitated poly(2VPPS)s (**P12**)


a)
+0.14
-0.18
+0.16
+0.14
-0.26
+0.18
+0.43
+0.18
-0.29
-0.27
+0.12
+0.08
+0.16
+0.01
+0.17
-0.10
-0.04
-0.05
+0.10
+0.10
+0.31
-0.79
-0.78
-0.25
+1.37
+0.08
+0.08
-0.79
b)
-0.83
-0.08
+0.86
+0.41
-0.16
+0.22
-0.91
+0.20
+0.55
+0.13
-0.42
-0.34
-0.04
-0.07
+0.14
+0.06
+0.16
-0.19
-0.09
-0.09
+0.09
+0.08
+0.43
-0.24
-0.79
-0.79
+0.07
+0.07
+1.37
-0.80
c)
-0.78
-0.80
+0.04
+1.38
-0.16
+0.05
-0.08
-0.04
+0.33
-0.79
-0.26
+0.17
+0.10
+0.19
+0.10
-0.10
+0.14
-0.33
+0.16
-0.16
-0.17
+0.49
-0.32
+0.44
-0.70
+0.69
-0.83
+0.14
-0.14
+0.17
+0.17
+0.02
+0.16
-0.03
+0.01
+0.05
+0.08
+0.13
-0.03
-0.20
-0.05
+0.16
+0.10
+0.09
+0.16
-0.18
+0.12
+0.13
-0.75
-0.77
-0.04
+0.24
-0.01
+1.31
-0.15
-0.75
+0.06
+0.06


d)
-0.75/+0.45
i=2
-0.77/-0.78/-0.80
+0.41/-0.05/-0.03
+1.37
-0.07/+0.04/+0.01
-0.27/+0.17
0.00/+0.02
+0.62/-0.12/-0.14
+0.09/+0.15
+0.22
+0.05/0.00
+0.30
-0.80/+0.18
-0.19/+0.07/+0.07
-0.18/+0.14
+0.04
+0.24/-0.05/0.00
-0.29/+0.20
-0.23/+0.13
-0.07/+0.08/+0.09
+0.08/+0.15
+0.47
+0.10/+0.15
-0.33/+0.12
+0.10/+0.15
-0.39/+0.15
+0.07
-0.77/-0.75/-0.72
0.00/+0.13
+0.04/+0.11
+1.27
-0.14/+0.11/+0.09
-0.16
+0.31/-0.04/0.00
+0.55/-0.07/-0.08
-0.23/+0.07/+0.08
+1.41
-0.15/+0.09/+0.08
i=1
-0.51/+0.13/+0.13
-0.79/-0.79/-0.78
i=3



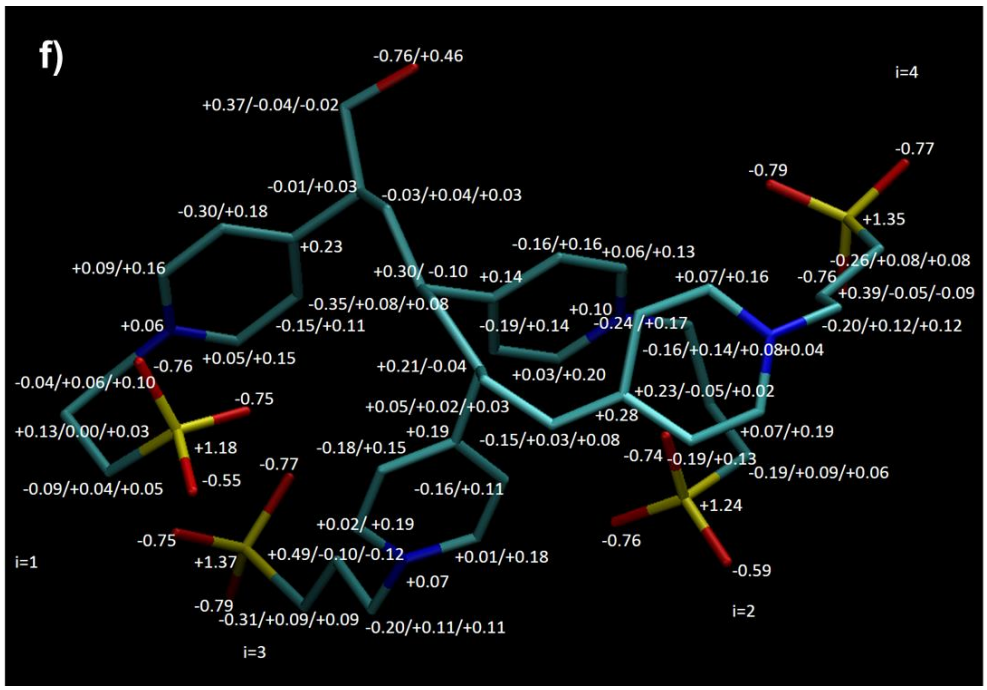


Figure S6. Detailed charge distribution during NaOH initiated polymerization of a) monomer (4VPPS), propagating species of b) monomer anion, c) dimer anion, d) trimer anion, e) tetramer anion and the f) H^+ terminated tetramer obtained from DFT calculations. In d)-f) hydrogens are not displayer for clarity. In these cases the first number corresponds to the charge on the atom to which hydrogen is bonded and the following numbers in the same line are the charges of the hydrogens.

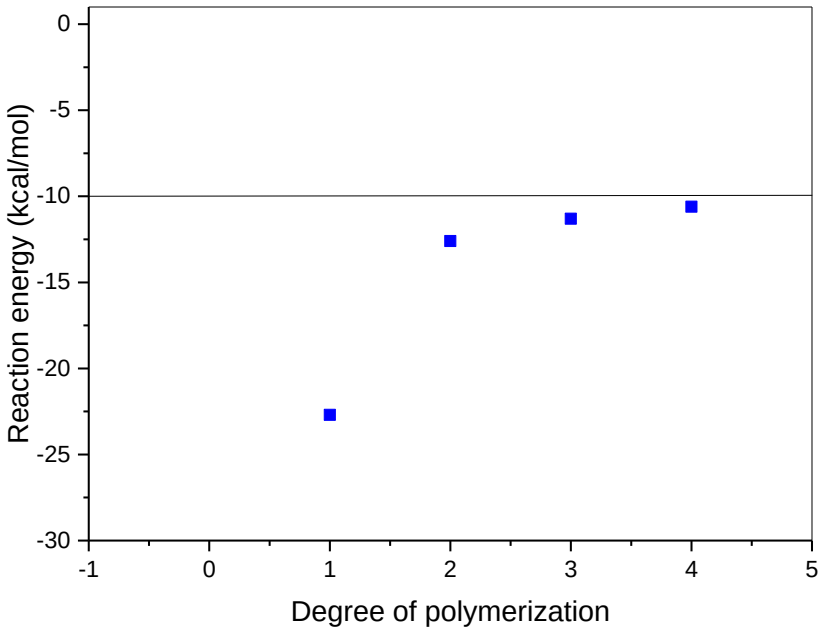


Figure S7. Reaction energy of NaOH initiated polymerization of 4VPPS obtained from DFT calculations. The reaction energy at *n*=1 corresponds to the activation of the neutral monomer by OH^-. A convergence of the reaction energy for large *n* can be estimated to be about -10 kcal/mol.

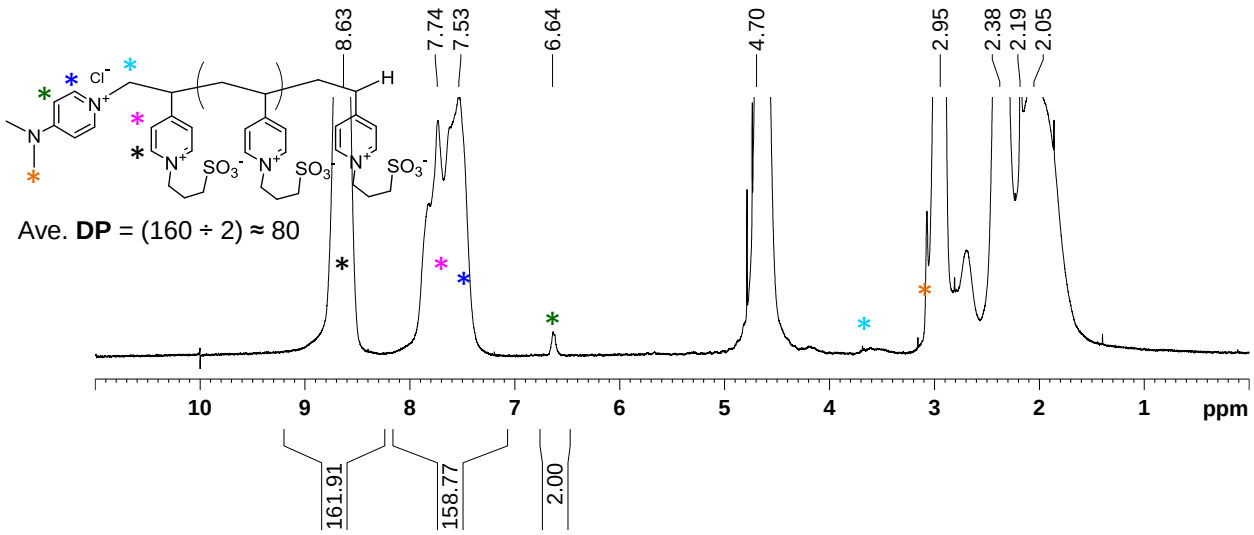


Figure S8. ^{1}H-NMR spectrum and end group analysis of P4.

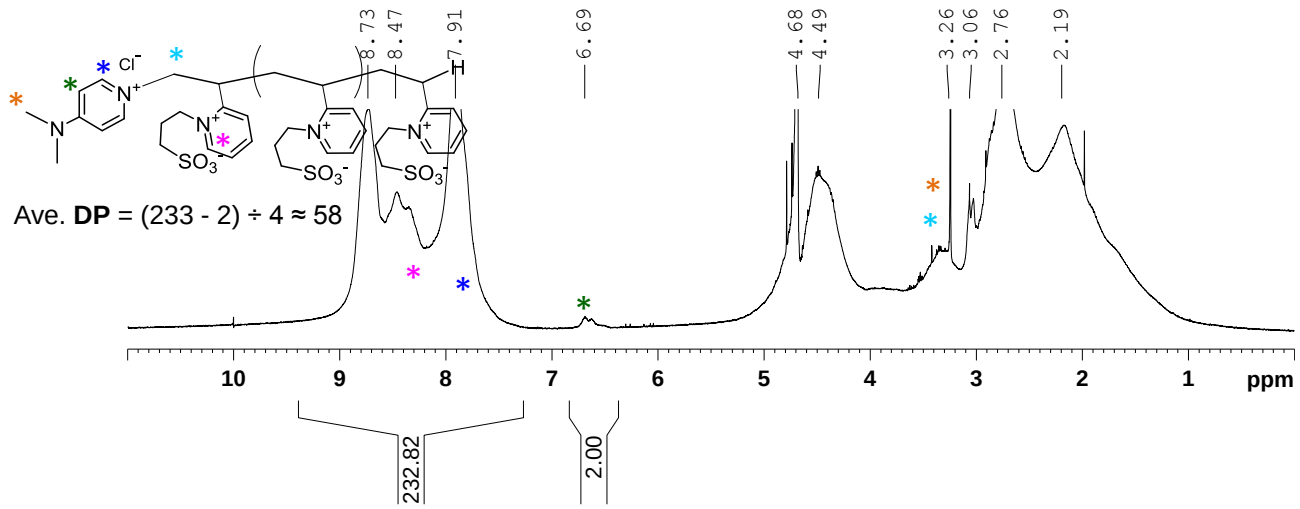


Figure S9. ^{1}H-NMR spectrum and end group analysis of P11.

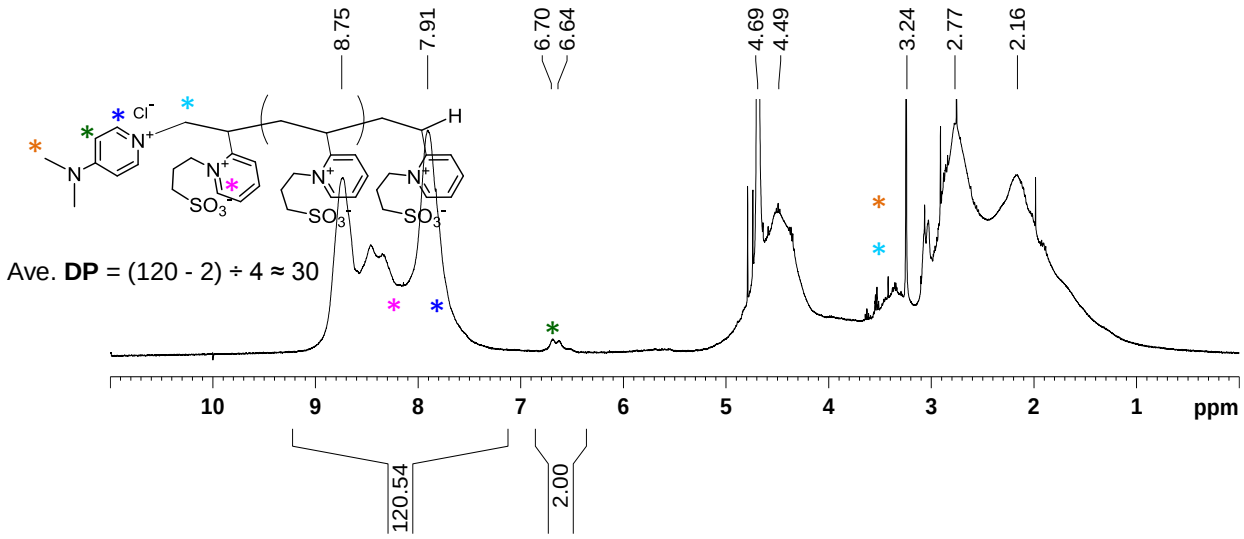


Figure S10. ^{1}H-NMR spectrum and end group analysis of P12.

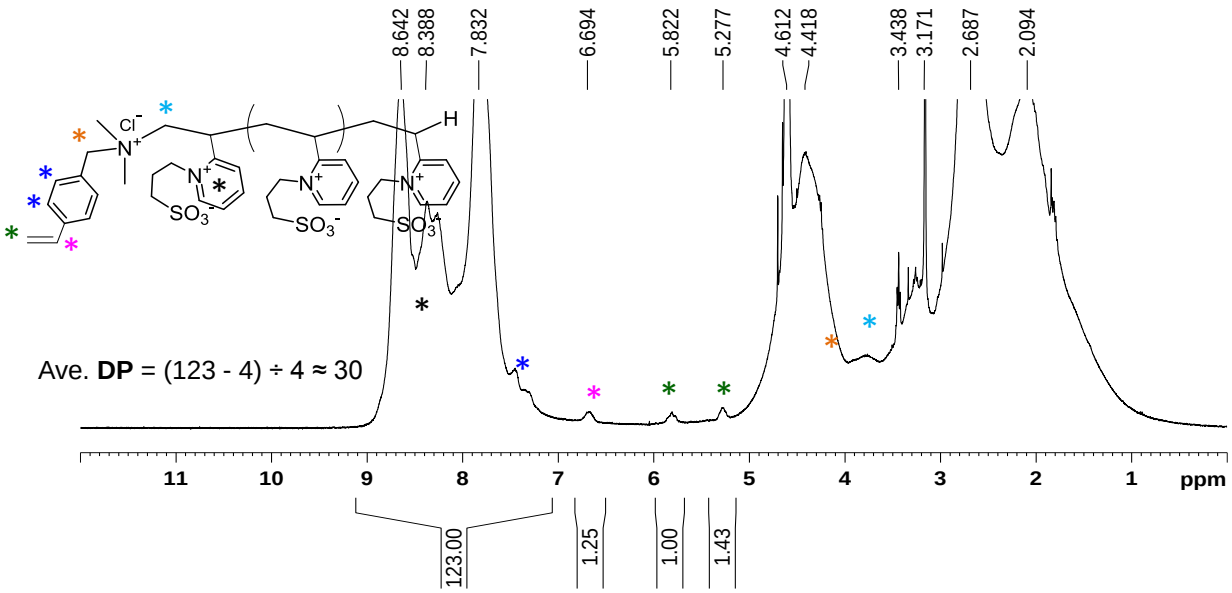


Figure S11. [1]H-NMR spectrum and end group analysis of P13.

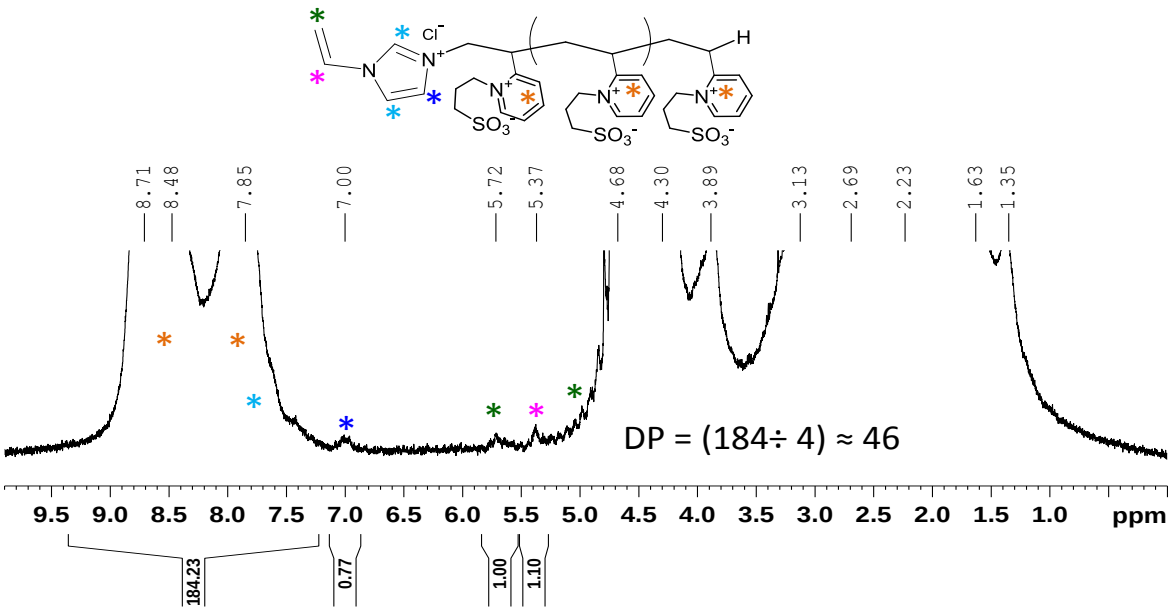


Figure S12. [1]H-NMR spectrum and end group analysis of SP7.

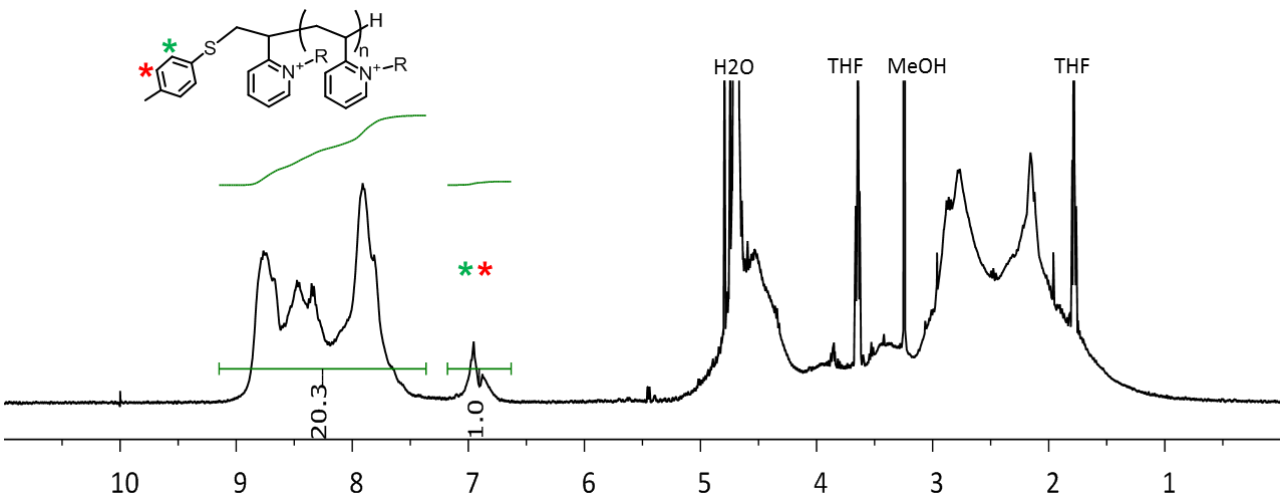
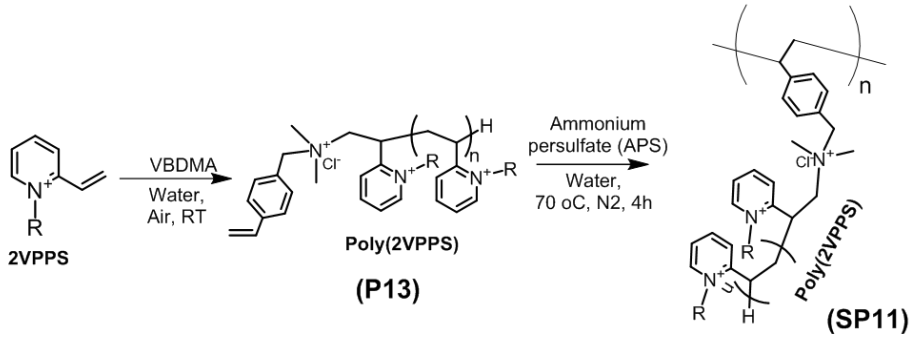


Figure S13. ^{1}H NMR spectrum and end group analysis of P19.



Scheme S1. Synthesis of comb type plymer from poly(2VPPS)-VBDMA macromonomer, P13 via FRP.

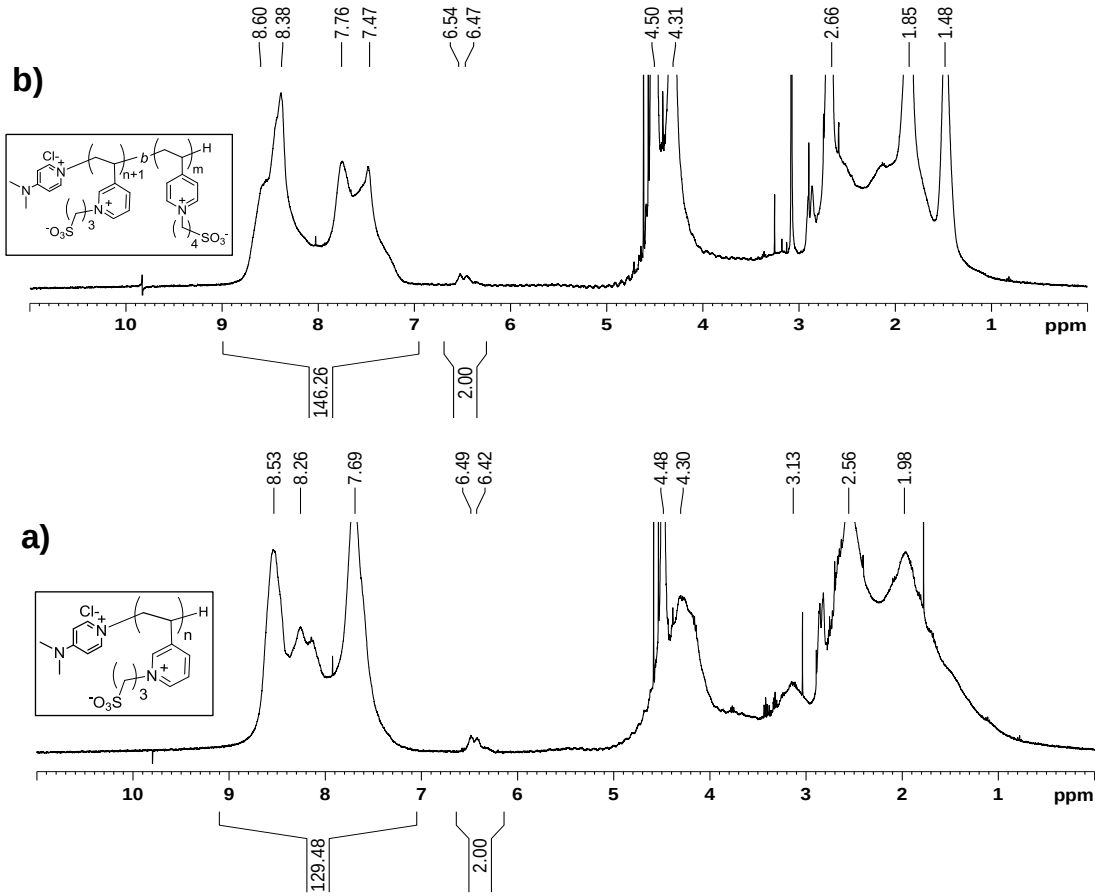


Figure S14. ^{1}H NMR spectra of a) poly(2VPPS), P21a and b) poly(2VPPS)-*b*-poly(4VPBS), P21b.

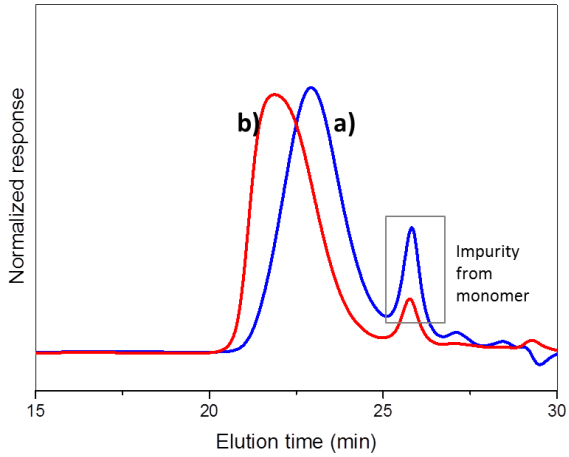


Figure S15. Overlay GPC chromatogram (using reaction aliquots) of chain extension reactions a) poly(2VPPS), P22a and b) poly(2VPPS)-*b*-poly(4VPPS), P22b.

Methodology for density functional theory (DFT) calculations

Quantum chemical calculation were carried out with the Gaussian09 code.[1] All structures were fully optimized using density functional theory (DFT) with the hybrid functional B3LYP[2,3] in combination with the triple-zeta Pople basis set 6-311++G(d,p).[4] Several starting geometries were considered and only optimized structures with lowest energy are reported. All geometries were optimized within a water solvent that was described as a solvent continuum with the PCM method as implemented in Gaussian09.[5] That optimized geometries were indeed minima of the potential energy surface was confirmed by finding that all molecular vibrational frequencies were positive. The electron charge distributions of the optimized structures were quantified by deriving atomic partial charges derived from the molecular electrostatic potential (ESP charges) using the CHELPG scheme.[6]

Polymerization energies (ΔE_i) were determined for polymerization initiation with hydroxyl as follows:

$$\Delta E_1 = E_{P1} - (E_M + E_{OH^-}) \quad \text{for i=1} \qquad (1)$$

$$\Delta E_i = E_{Pi} - (E_{P(i-1)} + E_M) \quad \text{for i}\neq 1 \qquad (2)$$

In equations 1-2 E_M, E_{OH^-} and E_{Pi} are the potential energies of the monomer, hydroxyl and the polymer chain with a degree of polymerization of i, respectively. The monomer is of neutral charge, whereas all polymer chains carry a charge of -1.

The termination energy ΔE_T of the polymerization was estimated as follows:

$$\Delta E_T = E_T - (E_{P4} + E_{H^+}) \qquad (3)$$

In eq 3 E_T is the energy of the protonated tetramer and E_{H^+} is the energy of a solvated proton. For E_{H^+} we used an experimentally determined value because its calculation is challenging and would require the consideration of a variety of larger water clusters. Instead, we used a value of -264.23 kcal/mol taken from ref. 7.

DFT result details

Several starting structures were considered for geometry optimizations. Additional to different initial orientations of the side chains, isotactic and syndiotactic structures were considered. Calculations strongly suggest that syndiotactic polymers are most favorable. In case of the tetramer the energy of the most stable syndiotactic configuration was found to be 9.1 kcal/mol lower than the most stable isotactic structure.

In case of the trimer and tetramer the polymers fold into a compact structure in which the electrostatic attraction between the negatively charged SO_3^- groups and positively charged rings of the side chains is maximized and the mutual ring-ring and SO_3^--SO_3^- repulsions are minimized. This is achieved by orienting the side chains in such a way that the sulfonates are found in the proximity of the rings, while neighboring sulfonates point into opposite directions, which is also facilitated by the syndiotactic polymer organization. The resulting structures are shown in Figure 3g.

Polymerization energies for a degree of polymerization from *n*=1-4 are shown in Figure S9. The initiation with hydroxyl releases energy of 22.7 kcal/mol. Adding further monomers to the polymer is also exothermic and reaches a value of -10.6 kcal/mol to form a tetramer. From these values it is possible to extrapolate an estimated polymerization energy of about -10 kcal/mol for long polymer chains.

The stabilization of the polymer structure through favorable electrostatic interactions also contributes to the exothermic polymerization energies shown in Figure S9. The polymerization reaction should be facilitated by favorable electrostatic interactions of the added monomer with the neighboring polymer units.

The calculated atomic partial charges were aggregated into charges of various polymer moieties as shown in Figures 3b)-f). As expected from a polymeric chain reaction, the negative charge from the hydroxyl initiator propagates throughout the polymerization to the last added polymer unit. Moreover, the charge distribution of the last added unit is markedly different from the other units and is characterized by a decrease of the ring charge from +0.6-0.7e to about +0.2e. The unsaturated carbon of the last unit, which will form a bond to a monomer in the next step of the polymerization, indeed accumulates a large negative charge of -0.6-0.7e on the –CH group with -0.8e on the carbon alone, thereby facilitating polymerization. Overall, the found charge distributions in Figures 3b)-f) describe a resonance hybrid of the dormant and actice resonance structure shown in Figure 3a), hence confirming the proposed reaction mechanism.

Optimized structures, determined with B3LYP/6-311++G(d,p) and PCM water solvent, given as list of atom numbers and Cartesian coordinates and together with their potential energy:

Monomer (4VPPS)

Energy: -1067.67202 au

6	-1.897650	-1.437511	0.241129
1	-1.327229	-2.295729	0.566656
7	-1.305309	-0.627042	-0.663240
6	0.083090	-0.910229	-1.116577
6	-1.956870	0.468071	-1.123324
1	-1.430223	1.072331	-1.848446
6	-3.222791	0.777908	-0.687366
1	-3.696819	1.660738	-1.091990
6	-3.870974	-0.043022	0.253925
6	-5.218070	0.214725	0.766777
6	-3.164880	-1.169829	0.707909
1	-3.604837	-1.846541	1.428215
6	1.114914	-0.189299	-0.243236
1	0.215506	-1.990922	-1.080075
1	0.150656	-0.596967	-2.157913
1	0.959154	0.890381	-0.308247
1	0.978253	-0.483273	0.800197
6	2.531940	-0.535120	-0.692589
16	3.811164	0.300786	0.303059
1	2.735989	-1.603422	-0.598343
1	2.716738	-0.231780	-1.724814
8	3.600658	1.765108	0.100716
8	3.581871	-0.129393	1.714439
8	5.108419	-0.185203	-0.252436
6	-5.998456	1.248214	0.431807
1	-5.586651	-0.514698	1.481164
1	-5.696811	2.014516	-0.272730
1	-6.984285	1.354529	0.867572

Activated monomer anion (HO-4VPPS anion)

Energy: -1143.66753 au

6	-1.547361	-0.456747	-1.070275
1	-1.080902	-1.139323	-1.769131
7	-0.796488	0.645947	-0.729679
6	0.582499	0.799049	-1.203019
6	-1.344748	1.549293	0.157515
1	-0.723416	2.401914	0.399838
6	-2.581644	1.388596	0.681980
1	-2.954179	2.144333	1.363398
6	-3.423372	0.243796	0.357317
6	-4.669165	0.091633	0.905123
6	-2.792485	-0.675038	-0.582540
1	-3.314594	-1.558891	-0.924050
6	1.615025	0.172651	-0.254459
1	0.647595	0.342958	-2.193277
1	0.777148	1.867008	-1.326161
1	1.524426	0.632639	0.733200
1	1.403190	-0.893933	-0.142011
6	3.033189	0.364899	-0.783590
16	4.317706	-0.325842	0.308458
1	3.175564	-0.126864	-1.748363
1	3.283808	1.422427	-0.892531

8	4.190691	0.394611	1.611446
8	4.028905	-1.787295	0.424742
8	5.609889	-0.043716	-0.386532
6	-5.616079	-1.023126	0.629257
1	-5.019328	0.864636	1.584849
1	-5.109621	-1.887829	0.188679
1	-6.106178	-1.363377	1.545281
8	-6.728828	-0.639639	-0.237508
1	-6.351809	-0.135590	-0.968337

Dimer anion (HO-4VPPS-4VPPS anion)

Energy: -2211.35971 au

6	-2.660779	-1.191483	-0.542097
1	-2.540616	-2.232327	-0.810057
7	-3.931369	-0.766725	-0.354108
6	-5.079246	-1.707204	-0.498615
6	-4.178806	0.523225	-0.016193
1	-5.230459	0.805168	0.083013
6	-3.130247	1.409764	0.144379
1	-3.379455	2.424832	0.423681
6	-1.801514	1.008534	-0.042708
6	-0.620438	1.894482	0.190856
6	-1.591092	-0.338662	-0.398173
1	-0.589921	-0.712785	-0.560076
6	-5.989219	-1.354189	-1.698309
1	-4.651804	-2.705234	-0.592485
1	-5.649061	-1.649619	0.432826
1	-5.754014	-0.345530	-2.043814
1	-5.778870	-2.032784	-2.531794
6	-7.484470	-1.394475	-1.368726
16	-7.940113	-0.223177	-0.019952
1	-8.067158	-1.097630	-2.241805
1	-7.820196	-2.380913	-1.041720
8	-7.427279	-0.881670	1.219714
8	-7.161125	1.014431	-0.354602
8	-9.403682	-0.082579	-0.099489
6	-0.915762	3.382990	-0.006379
1	0.154964	1.624631	-0.533186
1	-1.478507	3.539135	-0.936718
1	-1.518128	3.769535	0.827951
8	0.340259	4.054627	-0.066157
1	0.190935	5.002730	-0.121686
6	-0.005641	1.626004	1.629067
1	0.799478	2.360361	1.725303
1	-0.771091	1.900491	2.363344
6	0.484632	0.237619	1.890320
1	-0.146570	-0.409729	2.491726
7	4.100535	-1.416583	0.448992
6	1.671778	-0.272825	1.430546
6	5.378787	-1.963704	-0.034139
6	3.249445	-2.144297	1.241624
1	3.565381	-3.157528	1.457605
6	2.087637	-1.634384	1.719697
1	1.459162	-2.263525	2.339693
6	2.626499	0.457996	0.612523
1	2.447597	1.493313	0.352289
6	3.775417	-0.110967	0.161948
1	4.510295	0.415370	-0.441479
1	5.275025	-3.051405	-0.072899
1	5.521115	-1.589520	-1.047506

6	6.591782	-1.547465	0.823516
1	6.370298	-0.607685	1.337185
1	6.774285	-2.295909	1.603676
6	7.852515	-1.339459	-0.019289
1	8.749544	-1.326387	0.601080
1	7.972992	-2.106060	-0.789478
16	7.839614	0.290087	-0.885316
8	9.027240	0.249173	-1.769022
8	6.529628	0.308163	-1.617157
8	7.900076	1.286929	0.215009

Trimer anion (HO-4VPPS-4VPPS-4VPPS anion)

Energy: -3279.04979 au

6	3.967281	-1.371386	-2.163942
1	4.082188	-0.578663	-2.886220
7	5.075052	-1.743439	-1.493821
6	6.394932	-1.116494	-1.807130
6	5.008194	-2.721280	-0.562268
1	5.932215	-2.982771	-0.067389
6	3.818513	-3.352595	-0.278873
1	3.820914	-4.126899	0.476122
6	2.648946	-2.999558	-0.969787
6	1.332501	-3.704417	-0.719332
6	2.754992	-1.989590	-1.928066
1	1.892721	-1.667121	-2.496250
6	7.068583	-0.379953	-0.642750
1	7.038195	-1.930858	-2.141754
1	6.231868	-0.451502	-2.653265
1	7.008337	-0.970454	0.274321
1	8.130252	-0.342628	-0.904125
6	6.638596	1.060961	-0.362364
16	5.012657	1.278320	0.434558
1	7.348973	1.517041	0.328829
1	6.611063	1.663874	-1.272247
8	3.991286	0.988119	-0.617220
8	4.977561	0.303514	1.565266
8	4.987619	2.701307	0.885211
6	1.441000	-5.168872	-1.184477
1	0.578896	-3.234976	-1.358424
1	1.854205	-5.202218	-2.198587
1	2.110888	-5.729381	-0.521379
8	0.128204	-5.731474	-1.162441
1	0.188642	-6.656103	-1.426149
6	0.868847	-3.619495	0.752237
1	0.035635	-4.314502	0.878376
1	1.666872	-3.981680	1.408161
6	0.452324	-2.214771	1.237769
1	1.258614	-1.514431	1.008078
7	-3.046389	-0.649829	-0.697110
6	-0.784835	-1.690457	0.537029
6	-4.282786	-0.100472	-1.314049
6	-1.896940	0.057392	-0.714260
1	-1.924671	1.026966	-1.204744
6	-0.762577	-0.450684	-0.111055
1	0.143053	0.140254	-0.136943
6	-1.998541	-2.394341	0.527339
1	-2.096178	-3.360483	1.003967
6	-3.107107	-1.859901	-0.091111
1	-4.071028	-2.353472	-0.125630
1	-3.972414	0.604336	-2.083200

1	-4.787938	-0.940526	-1.785020
6	-5.200275	0.567520	-0.272333
1	-5.023279	0.137348	0.716714
1	-4.953768	1.628923	-0.196002
6	-6.682820	0.418893	-0.624591
1	-7.287351	1.157981	-0.098381
1	-6.867429	0.522657	-1.695543
16	-7.370988	-1.200543	-0.131219
8	-8.746739	-1.238371	-0.705361
8	-6.461114	-2.236597	-0.717606
8	-7.356454	-1.212271	1.361718
6	-0.692137	2.618218	3.389510
1	-1.372382	3.426706	3.628607
7	0.444355	2.992630	2.683069
6	0.355651	4.128836	1.753666
6	1.395071	2.013837	2.445751
1	2.310526	2.359947	1.979244
6	1.204193	0.715769	2.772660
1	2.015090	0.021818	2.591593
6	-0.064051	0.249063	3.330103
6	-0.454997	-1.052048	3.393661
6	-0.933178	1.342454	3.757740
1	-1.828075	1.124046	4.329317
6	-0.207404	3.660646	0.401231
1	-0.287054	4.884912	2.209939
1	1.350937	4.564260	1.636485
1	0.521378	2.990312	-0.062984
1	-1.110895	3.075933	0.589828
6	-0.546580	4.787251	-0.565388
16	-1.051872	4.141878	-2.198496
1	-1.383490	5.391850	-0.210277
1	0.303357	5.443863	-0.763352
8	0.178412	3.563123	-2.817309
8	-2.098761	3.102137	-1.933499
8	-1.581776	5.319856	-2.947062
6	0.273123	-2.231188	2.797705
1	-1.430047	-1.258033	3.825845
1	1.282812	-2.346646	3.212915
1	-0.266519	-3.144454	3.065730

Tetramer anion (HO-4VPPS-4VPPS-4VPPS-4VPPS anion)

Energy: -4346.73869 au

6	-4.585554	0.053210	2.185857
1	-4.907919	1.059756	1.937807
7	-5.488828	-0.938997	2.060656
6	-6.895628	-0.608830	1.673757
6	-5.138619	-2.214029	2.329692
1	-5.910658	-2.961987	2.226303
6	-3.855501	-2.536421	2.713384
1	-3.626609	-3.577473	2.896993
6	-2.889080	-1.531045	2.861620
6	-1.466790	-1.842532	3.281537
6	-3.296405	-0.220377	2.602525
1	-2.611856	0.609770	2.714509
6	-7.504260	-1.449886	0.547513
1	-7.490083	-0.736971	2.579692
1	-6.903116	0.444396	1.396544
1	-7.385917	-2.522305	0.722799
1	-8.578936	-1.262667	0.632096
6	-7.117207	-1.088525	-0.890558
16	-5.605598	-1.870447	-1.533496

1	-7.901223	-1.428959	-1.569049
1	-6.984979	-0.012247	-1.015079
8	-4.461287	-1.290682	-0.771277
8	-5.774581	-3.339257	-1.314213
8	-5.570619	-1.496607	-2.982792
6	-1.448849	-2.643690	4.595792
1	-0.971837	-0.892170	3.500603
1	-2.101284	-2.158641	5.329904
1	-1.815433	-3.663783	4.431021
8	-0.100665	-2.670831	5.069507
1	-0.077412	-3.172223	5.891811
6	-0.685929	-2.580308	2.165373
1	0.217360	-3.006607	2.607815
1	-1.288104	-3.420260	1.806282
6	-0.303951	-1.709881	0.937908
1	-1.195070	-1.156326	0.627621
7	2.635196	1.263251	1.953682
6	0.751342	-0.676893	1.293967
6	3.639638	2.295697	2.356742
6	1.338265	1.602765	1.823960
1	1.083773	2.638027	1.996846
6	0.390870	0.661871	1.485382
1	-0.632709	0.988281	1.360253
6	2.105268	-0.997236	1.457448
1	2.465860	-2.009437	1.329370
6	3.027504	-0.016711	1.770773
1	4.090444	-0.206175	1.879242
1	3.393373	2.575810	3.382497
1	4.607790	1.798098	2.359746
6	3.671769	3.548442	1.480310
1	2.679419	3.996591	1.386965
1	4.263070	4.270658	2.051610
6	4.330261	3.426783	0.103974
1	4.610424	4.421076	-0.247963
1	5.228797	2.806880	0.134794
16	3.286343	2.771887	-1.239224
8	4.075908	3.034349	-2.480828
8	3.099507	1.312389	-0.968177
8	2.002759	3.536907	-1.179547
6	-0.848061	1.515565	-2.188947
1	-0.617694	2.569744	-2.120502
7	-2.113673	1.191932	-2.537111
6	-3.152617	2.252768	-2.632312
6	-2.477503	-0.105129	-2.669227
1	-3.506147	-0.304596	-2.946861
6	-1.578685	-1.114652	-2.400281
1	-1.922047	-2.135979	-2.493496
6	-0.284166	-0.814996	-1.957636
6	0.666393	-1.892607	-1.490631
6	0.080193	0.537368	-1.902019
1	1.075881	0.840094	-1.593813
6	-3.967486	2.300523	-1.332199
1	-2.639985	3.194601	-2.824869
1	-3.778387	2.021173	-3.494025
1	-4.490324	1.349049	-1.207484
1	-3.283964	2.408933	-0.486778
6	-4.961549	3.458360	-1.330888
16	-6.140917	3.360491	0.060044
1	-4.461844	4.423626	-1.232674
1	-5.580862	3.474397	-2.229768
8	-7.077166	2.241482	-0.263777

8	-5.320452	3.080559	1.281091
8	-6.806304	4.695127	0.094287
6	0.110576	-2.620420	-0.241588
1	1.596407	-1.397035	-1.204193
1	-0.761975	-3.221829	-0.515333
1	0.875565	-3.328690	0.092131
6	5.803752	-1.698197	-3.324464
1	6.588880	-1.146489	-3.826257
7	6.172747	-2.301890	-2.133080
6	7.331003	-1.829678	-1.365827
6	5.221705	-3.062648	-1.481886
1	5.567401	-3.569767	-0.589192
6	3.950997	-3.179333	-1.923413
1	3.283626	-3.820832	-1.364125
6	3.478703	-2.468895	-3.110172
6	2.168851	-2.401321	-3.482025
6	4.554224	-1.796551	-3.833551
1	4.342578	-1.318180	-4.782910
6	6.937190	-0.687621	-0.410852
1	7.727903	-2.678640	-0.802330
1	8.103227	-1.513468	-2.069426
1	6.733304	0.217509	-0.988788
1	6.006851	-0.966160	0.090629
6	7.993236	-0.405992	0.651538
16	7.425635	0.808042	1.889209
1	8.241737	-1.304673	1.220734
1	8.912894	0.008626	0.234236
8	7.242901	2.097493	1.158155
8	6.136209	0.272934	2.437742
8	8.510238	0.861479	2.913905
6	1.041698	-2.909899	-2.626242
1	1.911240	-1.836250	-4.373424
1	0.157603	-3.128392	-3.231542
1	1.310284	-3.854544	-2.143130

Protonated tetramer (HO-4VPPS-4VPPS-4VPPS-H)

Energy: -4347.21409 au

6	-4.513555	1.132787	2.055153
1	-4.719836	2.023617	1.465956
7	-5.518370	0.237993	2.175186
6	-6.865934	0.581920	1.622698
6	-5.312539	-0.938624	2.804945
1	-6.153758	-1.611899	2.864617
6	-4.075385	-1.261056	3.319959
1	-3.959292	-2.228622	3.789289
6	-3.008205	-0.357451	3.217995
6	-1.623704	-0.685539	3.741692
6	-3.271202	0.865401	2.595535
1	-2.499562	1.616930	2.496306
6	-7.476497	-0.424618	0.645670
1	-7.525618	0.717775	2.481068
1	-6.743365	1.542344	1.126735
1	-7.641866	-1.399873	1.107588
1	-8.470811	-0.021594	0.430371
6	-6.750716	-0.577044	-0.692685
16	-5.348336	-1.755017	-0.701623
1	-7.429849	-0.970946	-1.449344
1	-6.352100	0.376729	-1.042359
8	-4.151831	-1.009316	-0.207394
8	-5.742801	-2.884570	0.188332

8	-5.198847	-2.167276	-2.134075
6	-1.697017	-1.005292	5.246490
1	-1.013653	0.217877	3.651689
1	-2.222253	-0.193946	5.761847
1	-2.253070	-1.934833	5.416512
8	-0.362671	-1.126082	5.740245
1	-0.401957	-1.221354	6.698509
6	-0.920636	-1.833873	2.970858
1	0.014684	-2.046473	3.493067
1	-1.532471	-2.738767	3.043326
6	-0.610196	-1.591767	1.466735
1	-1.562948	-1.446961	0.950131
7	1.622488	2.055735	0.969567
6	0.200704	-0.322284	1.278385
6	2.374083	3.337552	0.806881
6	0.344340	1.975956	0.541893
1	-0.094670	2.867261	0.113465
6	-0.369442	0.804262	0.670224
1	-1.389215	0.785161	0.312475
6	1.516480	-0.193494	1.734941
1	2.027426	-1.008054	2.231555
6	2.207177	0.989512	1.553608
1	3.228260	1.116258	1.884862
1	1.765526	4.105837	1.283461
1	3.300176	3.227029	1.368308
6	2.659047	3.757616	-0.641565
1	1.750213	3.720582	-1.246967
1	2.930114	4.815083	-0.572977
6	3.799896	3.034609	-1.366259
1	4.228304	3.675023	-2.138533
1	4.593851	2.739608	-0.678107
16	3.299654	1.530910	-2.264584
8	4.494041	1.144074	-3.080742
8	2.968495	0.503849	-1.226053
8	2.118136	1.909350	-3.094527
6	-0.377632	-0.288095	-3.033631
1	-0.029637	0.624940	-3.498203
7	-1.684826	-0.610768	-3.189734
6	-2.636462	0.435530	-3.664159
6	-2.177205	-1.744549	-2.646532
1	-3.238396	-1.946479	-2.768943
6	-1.378389	-2.549295	-1.854870
1	-1.836468	-3.416190	-1.397936
6	-0.068568	-2.167539	-1.558728
6	0.755166	-2.856744	-0.488359
6	0.442803	-1.045054	-2.226798
1	1.449721	-0.682844	-2.034240
6	-2.931648	1.353215	-2.467752
1	-2.169193	0.973402	-4.488998
1	-3.522176	-0.078577	-4.032687
1	-3.415861	0.764623	-1.684015
1	-1.974152	1.691998	-2.067051
6	-3.771687	2.580975	-2.787987
16	-4.009129	3.606828	-1.282609
1	-3.290810	3.242003	-3.511229
1	-4.772064	2.326712	-3.142157
8	-5.006314	2.887259	-0.422611
8	-2.665783	3.702048	-0.630705
8	-4.511228	4.918102	-1.771959
6	0.060735	-2.882819	0.902936
1	1.675297	-2.276301	-0.381300

1	-0.712926	-3.657233	0.893034
1	0.815630	-3.220599	1.619778
6	4.818838	-1.777657	-2.191720
1	5.007965	-0.804195	-2.640659
7	5.621872	-2.172112	-1.185439
6	6.658713	-1.236553	-0.672221
6	5.392494	-3.339503	-0.530701
1	6.094527	-3.601961	0.248242
6	4.300312	-4.114981	-0.838832
1	4.136555	-5.027062	-0.279762
6	3.404784	-3.700142	-1.840823
6	2.109588	-4.425021	-2.084030
1	2.307165	-5.487657	-2.254050
6	3.726482	-2.544227	-2.548933
1	3.091427	-2.184221	-3.347140
6	6.076245	-0.433626	0.494734
1	7.525683	-1.829010	-0.380016
1	6.945355	-0.590139	-1.500076
1	5.217491	0.136342	0.130832
1	5.708009	-1.118130	1.261918
6	7.106521	0.506417	1.108832
16	6.344861	1.640143	2.327943
1	7.886954	-0.036128	1.644782
1	7.569752	1.154968	0.363086
8	5.566657	2.642743	1.532937
8	5.469520	0.800026	3.201603
8	7.485163	2.248423	3.064997
6	1.146042	-4.304213	-0.880921
1	1.642359	-4.039301	-2.993128
1	0.249401	-4.888253	-1.108176
1	1.601885	-4.773435	-0.004163

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Author Contributions

SJ conceived, designed, performed experiments and prepared the manuscript. MK performed DFT calculations and AP was involved with technical discussion and manuscript preparation. All authors discussed the results and commented on the manuscript.