Supporting Information

Polyelectrolyte Complex Coacervation across a Broad Range of Charge Densities

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Materials and methods

Reagents were obtained from Sigma Aldrich unless otherwise noted. Ethylene oxide was obtained from Praxair, Inc (> 99%, lecture bottle). Tetrahydrofuran (THF, HPLC, inhibitor-free, Aldrich) used in polymerizations was dried and deoxygenated with a solvent purification system (MBraun SPS-800). All anionic glassware, metal needles, and stir bars were kept in a 130 °C oven. Custom-made anionic glassware was assembled while hot and immediately evacuated to ~5 mTorr. No open flames were used to dry glassware as customary in anionic polymerization due to safety restrictions at Argonne National Laboratory. Instead of a torch a heat gun was used.

Safety considerations: Di-*n*butylmagnesium and potassium *tert*-butoxide are pyrophoric reagents and must be handled under inert gas. Allyl glycidyl ether (AGE) is a sensitizer. Ethylene oxide (EO) is a highly toxic, flammable, and explosive gas that should only be handled by experts or under supervision. During transfer of EO into the reactor silver shield chemical resistant gloves and sleeves (Silver Shield) as well as a face shield were worn.

Experimental

Poly(allyl glycidyl ether) synthesis: Poly(allyl glycidyl ether) [PAGE] was synthesized via oxyanionic ring-opening polymerization, adapted from previously reported protocols.[1,2] Polymerizations were carried out on a 10-20 g scale of allyl glycidyl ether (AGE), a concentration of 10-20 wt% AGE in tetrahydrofuran, and with a target degree of polymerization (N_n) of 200. AGE was placed over calcium hydride (CaH_2) in a Schlenk flask with a stir bar, freeze-pump-thawed (FPT'ed) three times, backfilled with argon, and stored in a refrigerator until purification by distillation. A 250 mL custom anionic Schlenk flask containing a stir bar and a syringe port fitted with a septum and bush was connected to one side of a glass T (wrapped with heating tape) via a Swagelok ultra-Torr union fitting, the other side of the T was closed off with a small glass tube. The flask was evacuated while hot and backfilled with argon. Using a 6 mL disposable syringe and an 18-gauge metal needle, 3 mL of di-*n*butylmagnesium (*n*Bu_2Mg, 1M in heptane) were added to the 250 mL flask under argon and the solvent was evaporated under high vacuum and stirring. This was done overnight one day in advance or the same day of the polymerization by careful heat-gunning of the flask to drive solvent removal. A 1L, 5-port custom anionic polymerization reactor containing a stir bar coated in glass was assembled with a glass arm containing a syringe port and two Schlenk ports to connect the reactor to the manifold and to a pressure gauge. The reactor and glass arm were evacuated while hot and during distillation of AGE the reactor was cycled between vacuum and argon a minimum of 4 times. AGE on CaH_2 was removed from the refrigerator and allowed to come to rt. The small glass tube fixed to the glass T was replaced with the AGE flask. The AGE flask was briefly opened to high vacuum 3x to evacuate the atmosphere. The AGE flask was then placed into liquid nitrogen (LN_2) and AGE was FPT'ed 3x. The heating tape wrapped around the glass T was heated to 60 °C. The T was then closed off from the manifold and AGE was transferred from CaH_2 onto *n*Bu_2Mg under static vacuum by placing the AGE flask into a 100 °C water bath and aiding transfer into the receiving *n*Bu_2Mg flask in LN_2 by careful heat-gunning. Once a sufficient quantity of AGE was transferred, the AGE pot was closed and residual AGE in the system was driven into the receiving flask using a heat gun. The receiving flask was then closed, and AGE thawed under static vacuum. Liquid AGE on *n*Bu_2Mg was backfilled with argon and stirred at room temperature for 20-30 minutes. <u>AGE should not be left to stir on *n*Bu_2Mg for longer as this will lead to the formation of high molar mass PAGE</u>. AGE on CaH_2 was backfilled with argon and returned to the refrigerator. Another 250 mL flask with septum port was attached in its place and evacuated. The AGE/*n*Bu_2Mg flask atmosphere was evacuated quickly 3x and AGE was FPT'ed 3x. AGE was then transferred from *n*Bu_2Mg into the empty flask under static vacuum as described previously. Tetrahydrofuran (THF) was obtained using a hot burette from a solvent system. The burette was attached to the reactor under a stream of argon using a bush and a Chemraz® O-ring resistant to THF. The reactor was evacuated and then backfilled with argon to 3 psi. THF was drained into the reactor. Next, the appropriate volume of potassium *tert*-butoxide was added to the reactor using a de-gassed (3x), dry metal needle and a disposable syringe. The appropriate volume of AGE was added to the reactor in the same manner and the reactor was lowered into an oil bath that had been previously equilibrated to 45 °C. The clear, colorless solution was stirred for 36h during which it became amber in color. The heat was then turned off and ca. 20 mL methanol (MeOH) were FPT'ed 3x in a Schlenk flask with a septum port. The polymerization was quenched with 3 mL MeOH using a degassed needle and the solution stirred for 15 min prior to opening the reactor up to air. The crude reaction mixture was precipitated into cold (- 78 °C) hexanes under stirring, which afforded a viscous yellow liquid that collected at the bottom of the beaker. The hexanes were decanted, the residual polymer dissolved in methylene chloride, transferred to a flask, and dried under high vacuum at room temperature. PAGE was stored at -78 °C under argon to suppress cross-linking of the allyl groups. The purity and molar mass (M_n) were determined by ^1H NMR spectroscopy and the dispersity was determined using DMF SEC with a refractive index detector.

Copolymerization of ethylene oxide and allyl glycidyl ether: AGE was purified, and the polymerization reactor set up as described above. In a flask with two Schlenk ports and a glass-coated stir bar solvent was evaporated from 3 mL 1M *n*Bu_2Mg under high vacuum. EO was transferred from the tank into the Schlenk flask cooled in a dry ice bath under static high vacuum using a custom-made regulator. After a satisfactory amount of EO was transferred, the Schlenk flask was cooled in LN_2 while under dynamic high vacuum. The amount of EO transferred was calculated from the mass of the tank before and after transfer. The EO-containing Schlenk flask was closed, removed from the manifold, placed in a bucket of ice, and connected to the glass T. The other side of the T was connected to a dry burette. The system was evacuated, then EO sitting in ice was transferred into the burette cooled with LN_2 under static vacuum. The burette was closed, removed from the T, and placed in a bucket of ice. The reactor was equipped with the burette containing the solvent, aiming for a final concentration of 10-20 wt% AGE+EO in THF. The EO burette was connected to the reactor using a custom transfer tube, a bushing and a Chemraz® O-ring. The reactor was evacuated to 5-6 mTorr and backfilled to 3 psi with argon. Solvent was drained into the reactor, followed by addition of KO*t*Bu in THF. The transfer tube was cooled by sprinkling it with LN_2 and the EO burette was inverted while opening it at the same time. The burette was clamped open above the reactor and the appropriate amount of AGE was quickly added to the reactor using a syringe with a de-gassed needle. The reactor was then lowered into an oil bath previously equilibrated to 45 °C and the pressure was carefully monitored. The pressure was adjusted to 5-7 psi by pulling brief vacuum if necessary. Once the temperature and pressure had stabilized the reaction was left for the appropriate amount of time and quenched in the same way as described in the PAGE synthesis.

Thiol-ene click functionalizations: Typically, functionalizations were carried out on a 2-5g scale of PAGE or poly(EO-*co*-AGE). The polymer was combined in a round bottom flask with azobisisobutyronitrile (AIBN, 0.7 eq. relative to allyl groups) and either cysteamine hydrochloride (20 eq. relative to allyl groups) or sodium 3-mercapto-1-propanesulfonate (10 eq. relative to allyl groups) and dissolved in 3/1 DMF/H_2O. The solutions were de-gassed for 30 min, then lowered into an 80 °C bath and reacted for 16h. Conversion of the allyl groups was checked by ^1H NMR spectroscopy. It is imperative to ensure full conversion of the allyl groups as any residual double bonds will lead to cross-linking during lyophilization. If conversion was incomplete more AIBN was added, the reaction degassed, and reacted further at 80 °C. Upon complete conversion the reaction mixture was transferred into dialysis snakeskin tubing (3.5 kg/mol MWCO) and dialyzed against 4L MilliQ water under stirring. A total of 8 dialysis cycles were carried out, each cycle lasting between 4-12h. The purified polymer solution was then concentrated using Amicon-15 dialysis tubes with either 3 or 10 kg/mol MWCO, depending on the molar mass of the functionalized polymer. The concentrated solution was filtered and dried in Falcon tubes on a lyophilizer. The polyelectrolytes ranged from sticky oils at high EO fractions to fluffy solids at high AGE fractions.

Preparation of stock solutions and complexes: Stock solutions were prepared at a concentration of 50 mg/mL (co)polyelectrolyte in Falcon tubes using MilliQ water. (Co)polycation solutions were oxidized with 2 eq. H_2O_2 (30 wt%/v in water), vortexed, and heated at 37 °C for 30 min. A sodium chloride salt solution was prepared at a concentration of 5M with MilliQ water. Charge stoichiometric complexes at a final polyelectrolyte concentration of 10 mg/mL (unless otherwise noted) were prepared in the order of MilliQ water addition, sodium chloride stock solution (if adding salt), followed by addition of oxidized polycation stock solution, and finally addition of polyanion stock solution. The turbid suspensions were immediately vortexed for up to 30s.

Optical microscopy: 100 μL of turbid suspension were transferred into microscopy wells (96 wells, Costar, Corning Inc.) using a micropipette. The tray was sealed with a plastic coating to mediate evaporation. The complexes were imaged with a phase contrast optical microscope (Leica DMI 6000B) immediately and after a 24h period of equilibration.

Interaction parameters for simulation: The connectivity of copolymer chains is represented by FENE potential between boned beads:

$$U_{FENE} = -0.5KR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] \tag{S1}$$

where $K = 30\varepsilon/\sigma^2$ and $R_0 = 1.5\sigma$ (ε and σ are units for energy and length). All beads are interacting though shift and truncated LJ potential:

$$U_{LJ} = \begin{cases} 4\varepsilon_{LJ}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^{6}\right] & r \leq r_c \\ 0 & r > r_c \end{cases} \tag{S2}$$

For bonded beads, we use $\varepsilon_{LJ} = \varepsilon$ and $r_c = 2^{1/6}\sigma$ to balance the FENE potential. For non-bonded beads, we consider two cases. For one case, all beads have the same interactions: $\varepsilon_{LJ} = \varepsilon$ and $r_c = 2.5\sigma$. For the other case, $r_c = 2.5\sigma, \varepsilon_{p-p} = \varepsilon_{s-s} = \varepsilon$, and $\varepsilon_{s-p} = 1.5\varepsilon$. Namely, salt ions are more attractive to polymers. For both cases, all beads have same size σ. The temperature is maintained at Θ solvent condition $T = \frac{\varepsilon}{k_B} = T_\Theta = 3.18$. The electrostatic interactions in the system is given by:

$$\frac{U_{Coul}}{\varepsilon} = \frac{z_i z_j l_B}{r} \tag{S3}$$

where z_i is the valence of charge for i species and $z_i = 1 \; or -1$. l_B is the Bjerrum length and $l_B = \sigma$ for this work. The Coulomb interaction is solved by Particle-Particle Particle-Mesh method with the error for the long-range force is set to be within 10^{-4}.

(Co)polymer and (Co)polyelectrolyte Characterization Data

^{1}H and ^{13}C NMR spectral data. Spectra reported here were acquired either in $CDCl_3$ or D_2O and referenced to the internal standards tetramethylsilane (TMS) or 3-(trimethylsilyl) propionic-*2,2,3,3-d$_4$* acid, sodium salt, respectively. ^{1}H NMR spectra were acquired with a minimum of 16 scans and a relaxation delay (d1) of 10s.

DMF SEC data. Samples were eluted at a flow rate of 0.3 mL/min in a 0.01 M solution of sodium bromide in DMF at 50 °C using a Tosoh EcoSEC with Tosoh SuperAW3000, SuperAW4000, and a guard column. Analyte was detected using a refractive index detector.

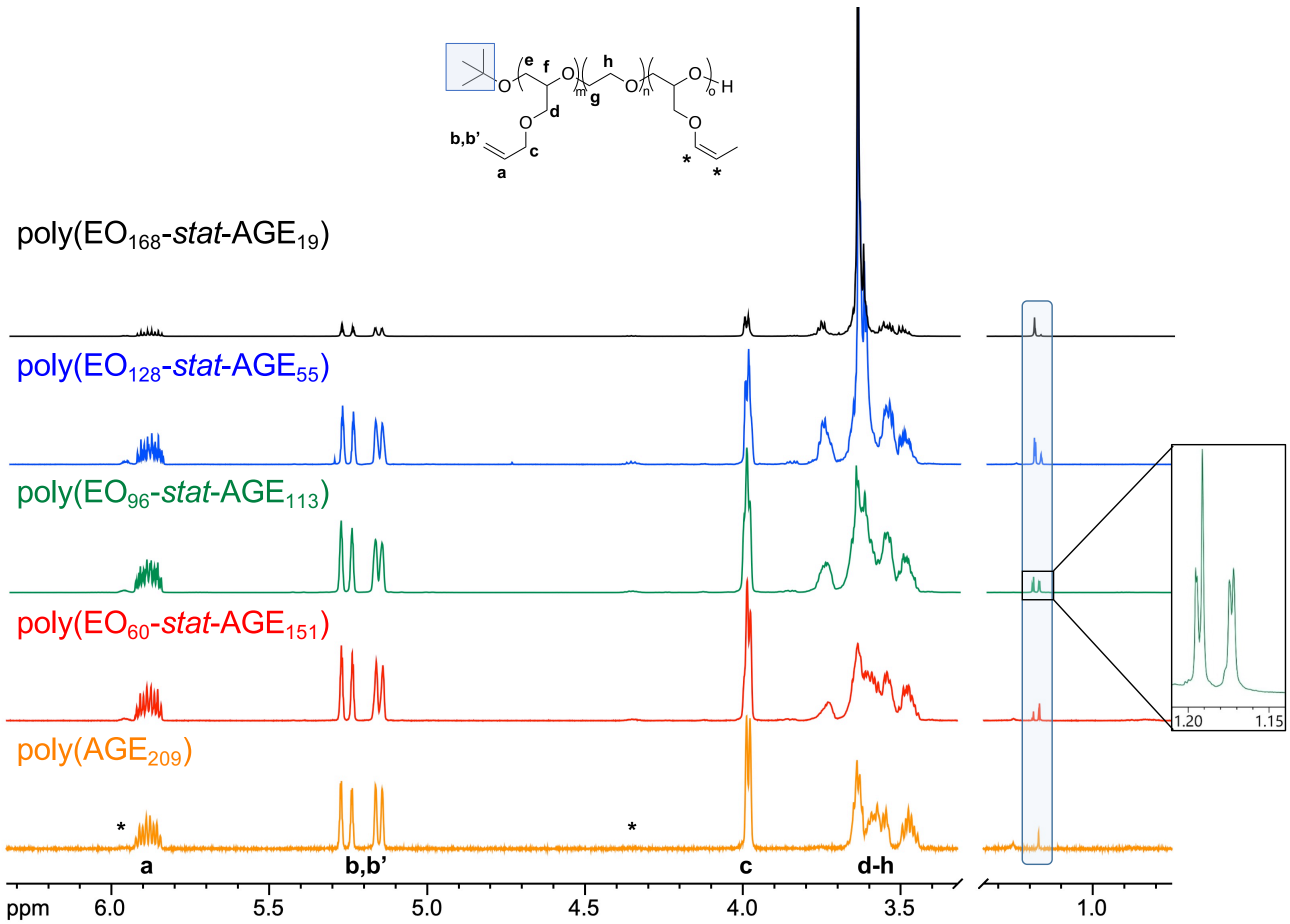

Figure S1. Overlaid ^{1}H NMR spectra ($CDCl_3$) of poly(EO-*stat*-AGE) copolymers synthesized to produce the homologous copolyelectrolytes studied in this work. The end group signal derived from *tert*-butoxide is magnified for a copolymer with 54% AGE and it can be seen that 4 distinct signals arise from the possible ultimate-penultimate monomer combinations: EO-EO, EO-AGE, AGE-EO, and AGE-AGE, in line with what has been reported previously. The relative intensities of these signals change with composition. Minor signals (*) are attributed to AGE olefins that have isomerized to the internal *cis*-alkene. The fraction of isomerized alkene units are as follows: poly(AGE_{209}) → 3.6%, poly(EO_{60}-*stat*-AGE_{151}) → 4%, poly(EO_{96}-*stat*-AGE_{113}) → 4%, poly(EO_{128}-*stat*-AGE_{55}) → 6.4%, poly(EO_{168}-*stat*-AGE_{19}) → 0.6%.

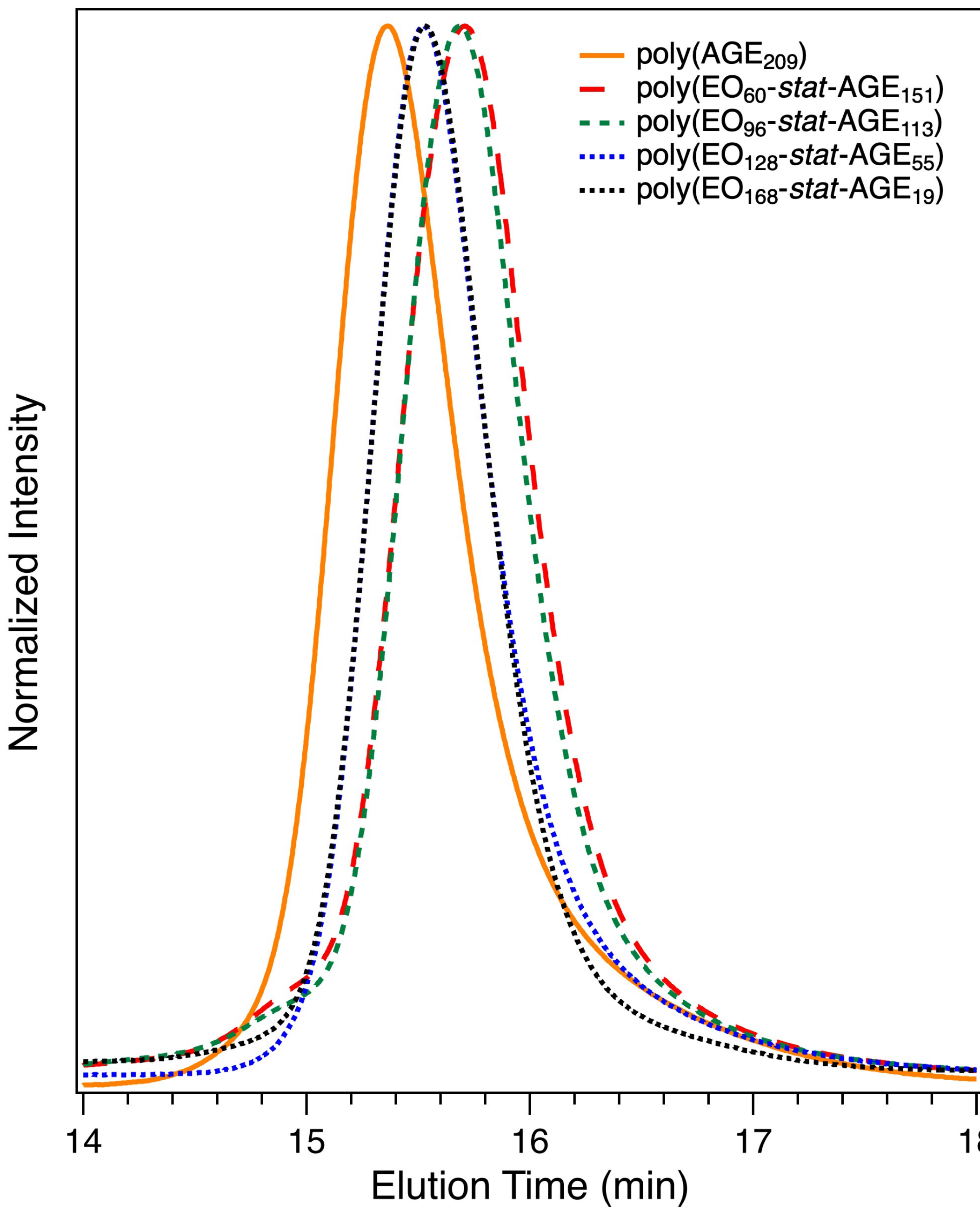

Figure S2. Overlaid DMF SEC traces of neutral (co)polymers from **Figure S1** and **Table 1** in the main text.

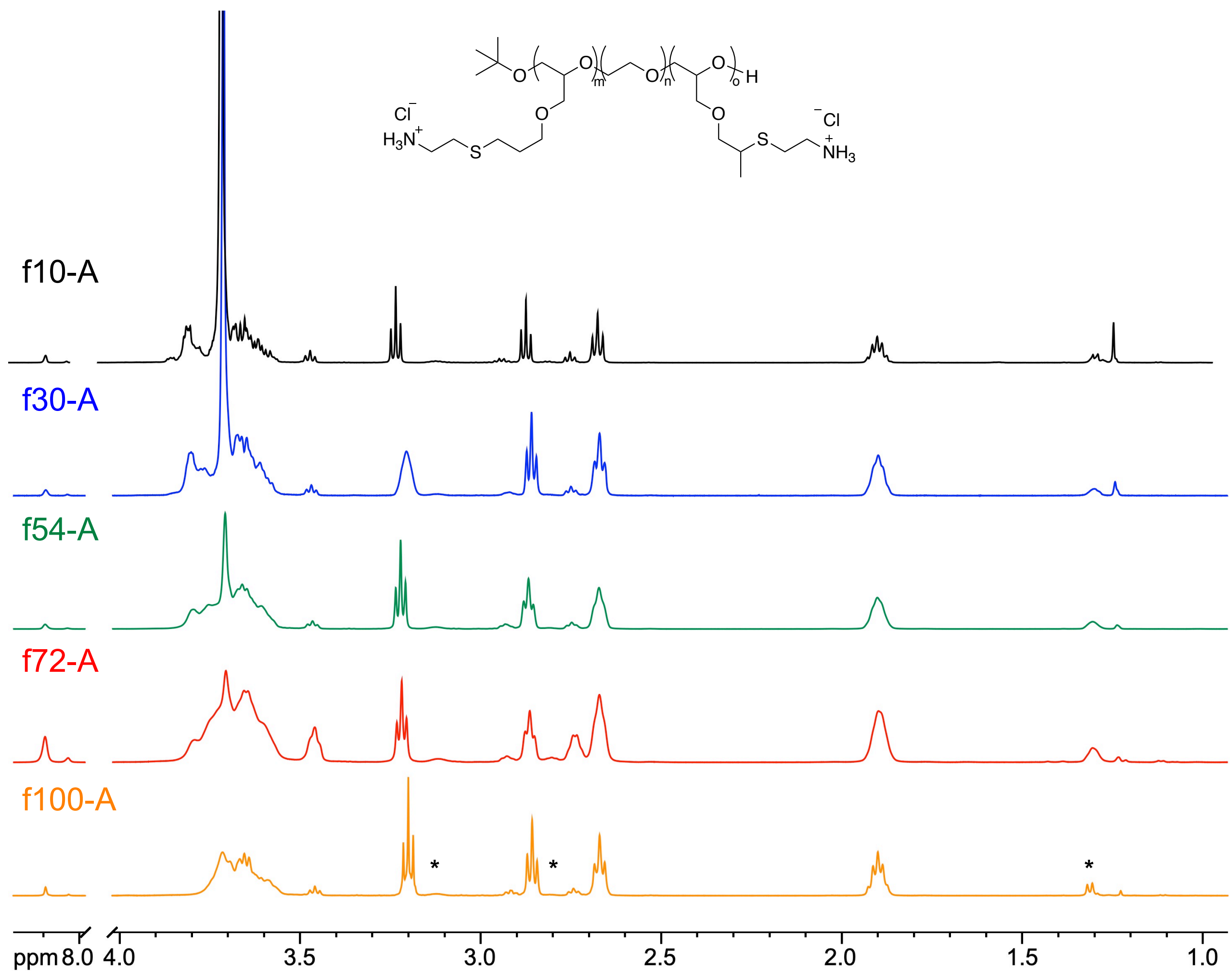

Figure S3. Overlaid [1]H NMR spectra of (co)polycations derived from the neutral (co)polymers in Figure S1. Minor signals (*) are attributed to products of thiol-ene click with isomerized AGE olefins.

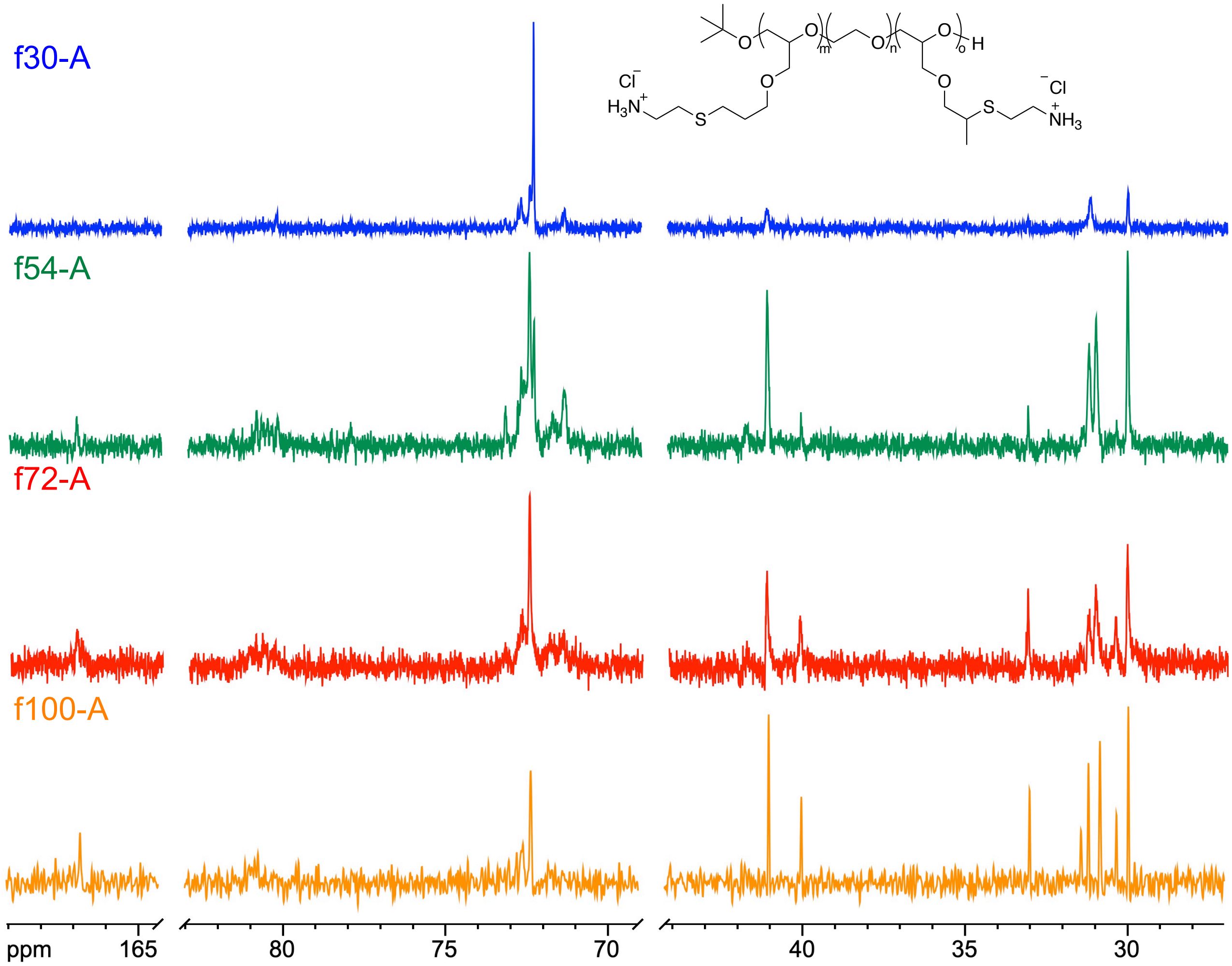

Figure S4. Overlaid [13]C NMR spectra (D_2O) of (co)polycations derived from the neutral (co)polymers in Figure S1.

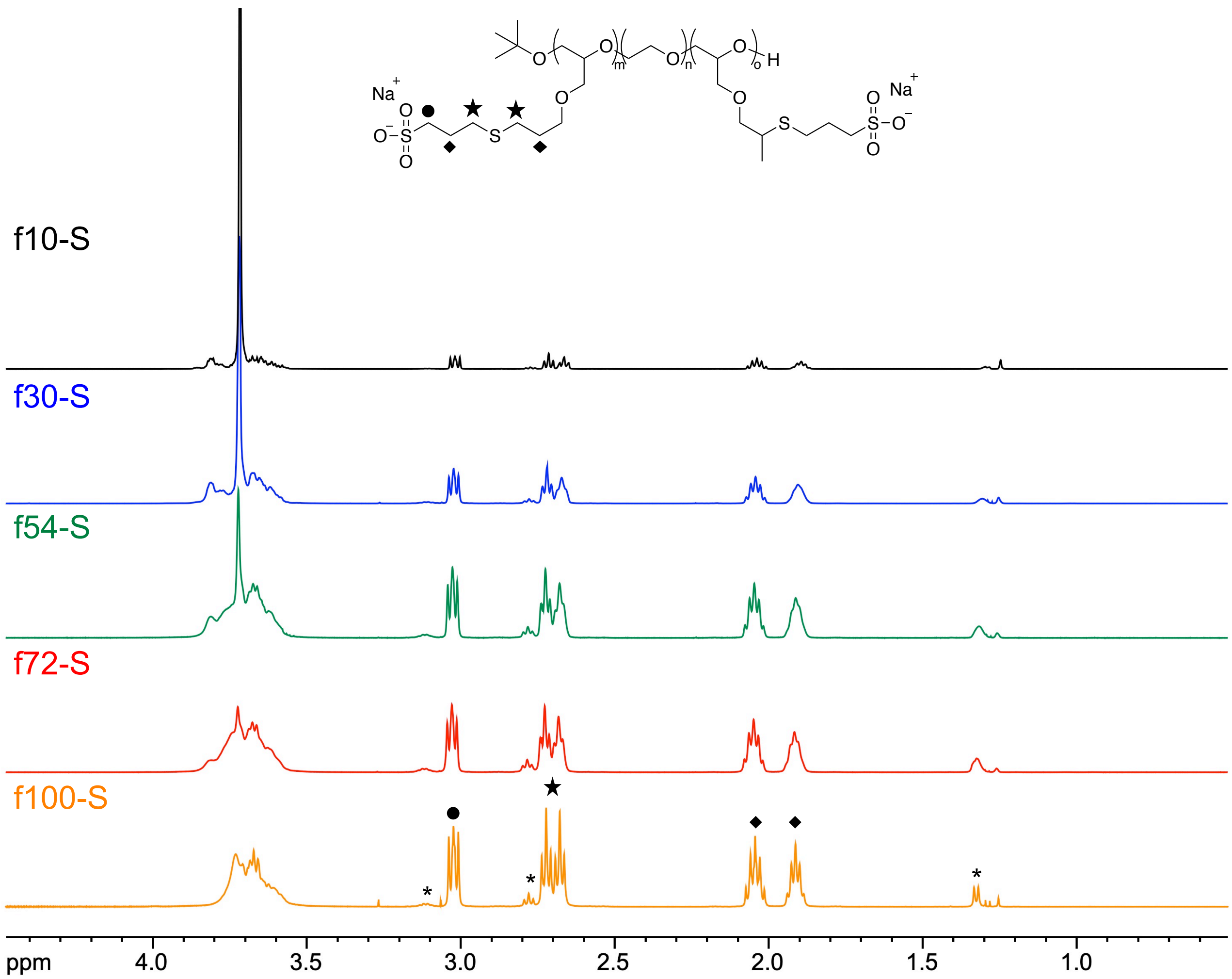

Figure S5. Overlaid [1]H NMR spectra (D_2O) of (co)polyanions derived from the neutral (co)polymers in Figure S1. Minor signals (*) are attributed to products of thiol-ene click with isomerized AGE olefins.

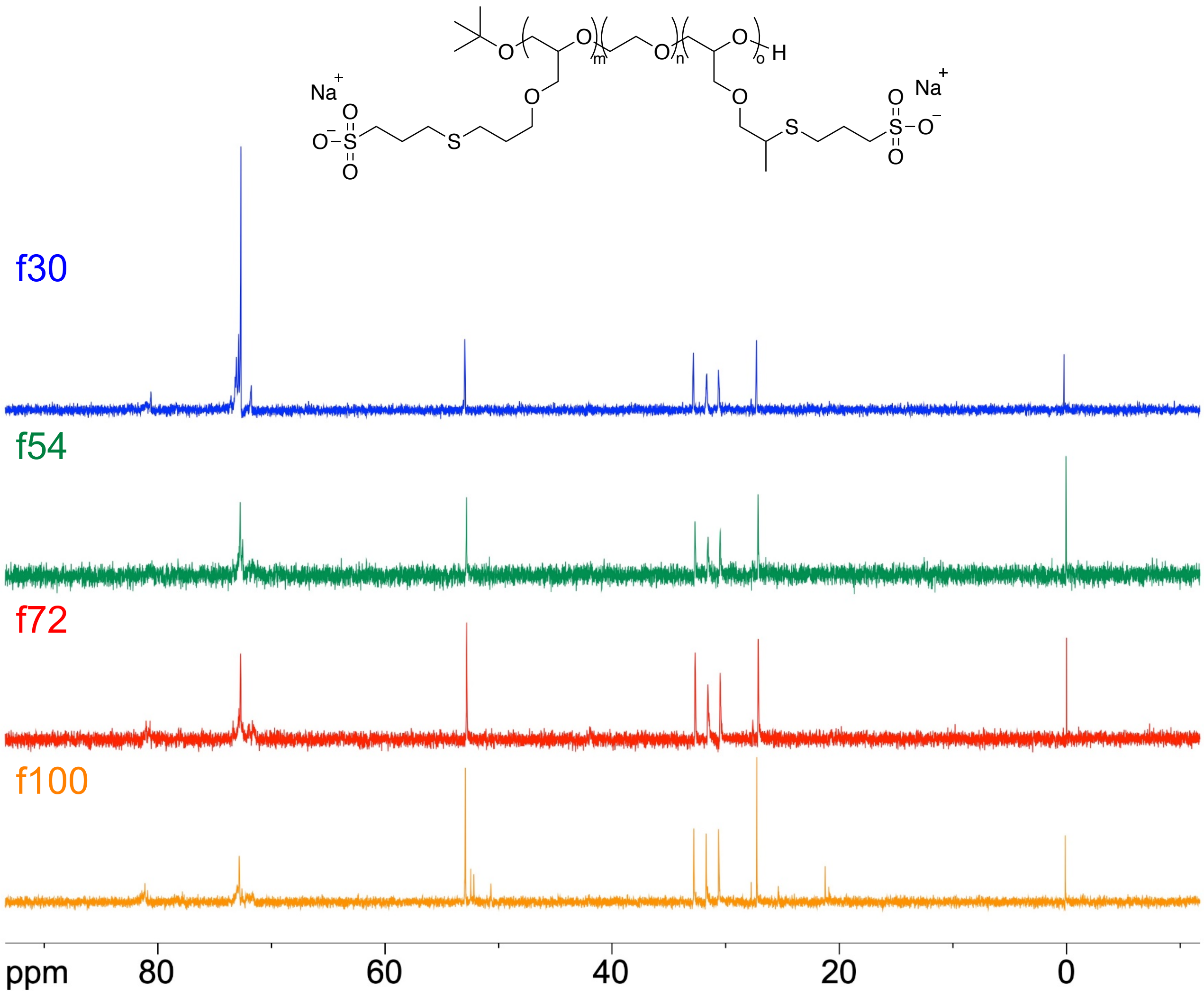

Figure S6. Overlaid ^{13}C NMR spectra (D_2O) of (co)polyanions derived from the neutral (co)polymers in Figure S1.

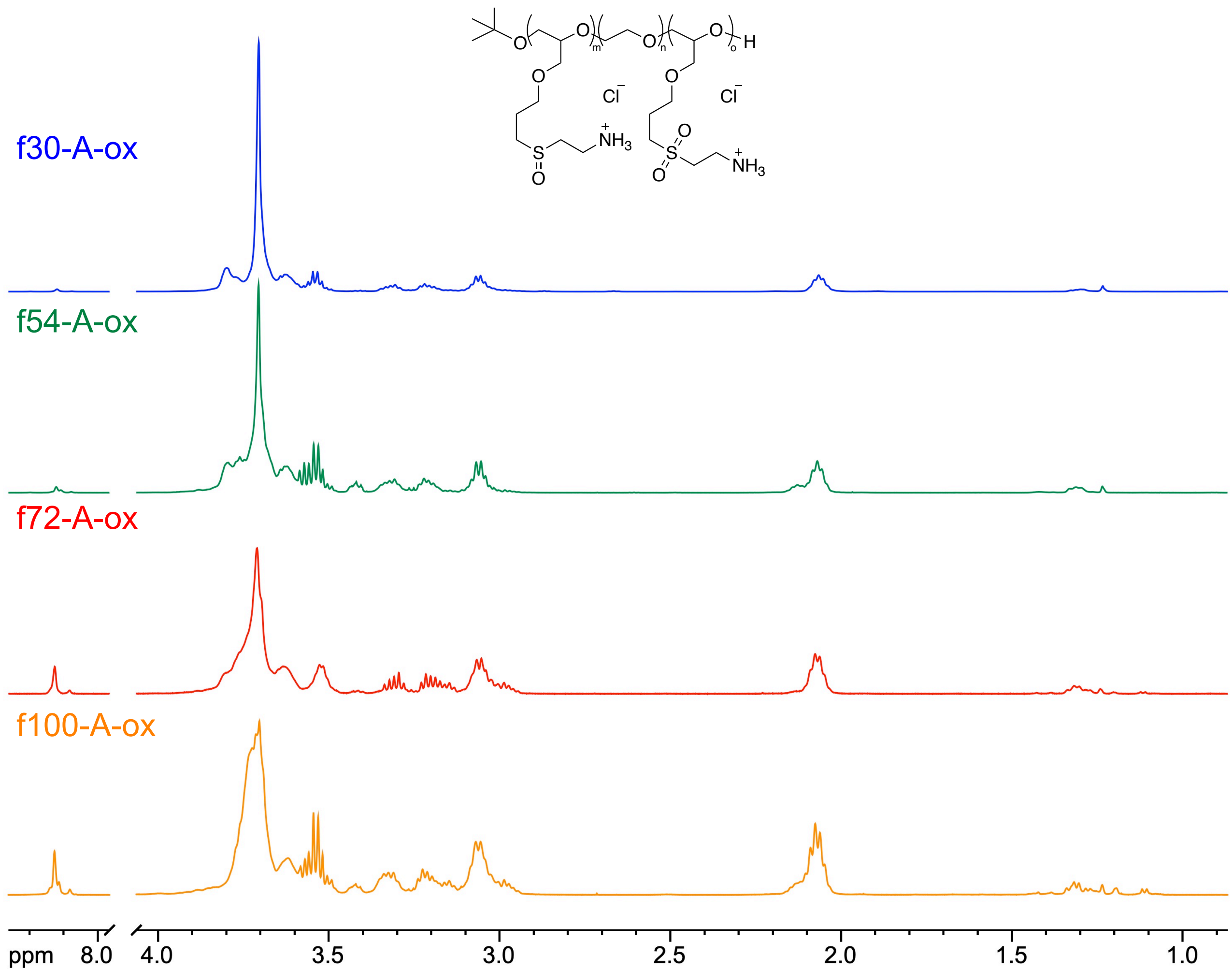

Figure S7. Overlaid [1]H NMR spectra (D_2O) of (co)polycations after oxidation with 2 eq. H_2O_2 relative to moles of sulfur in Figure S3.

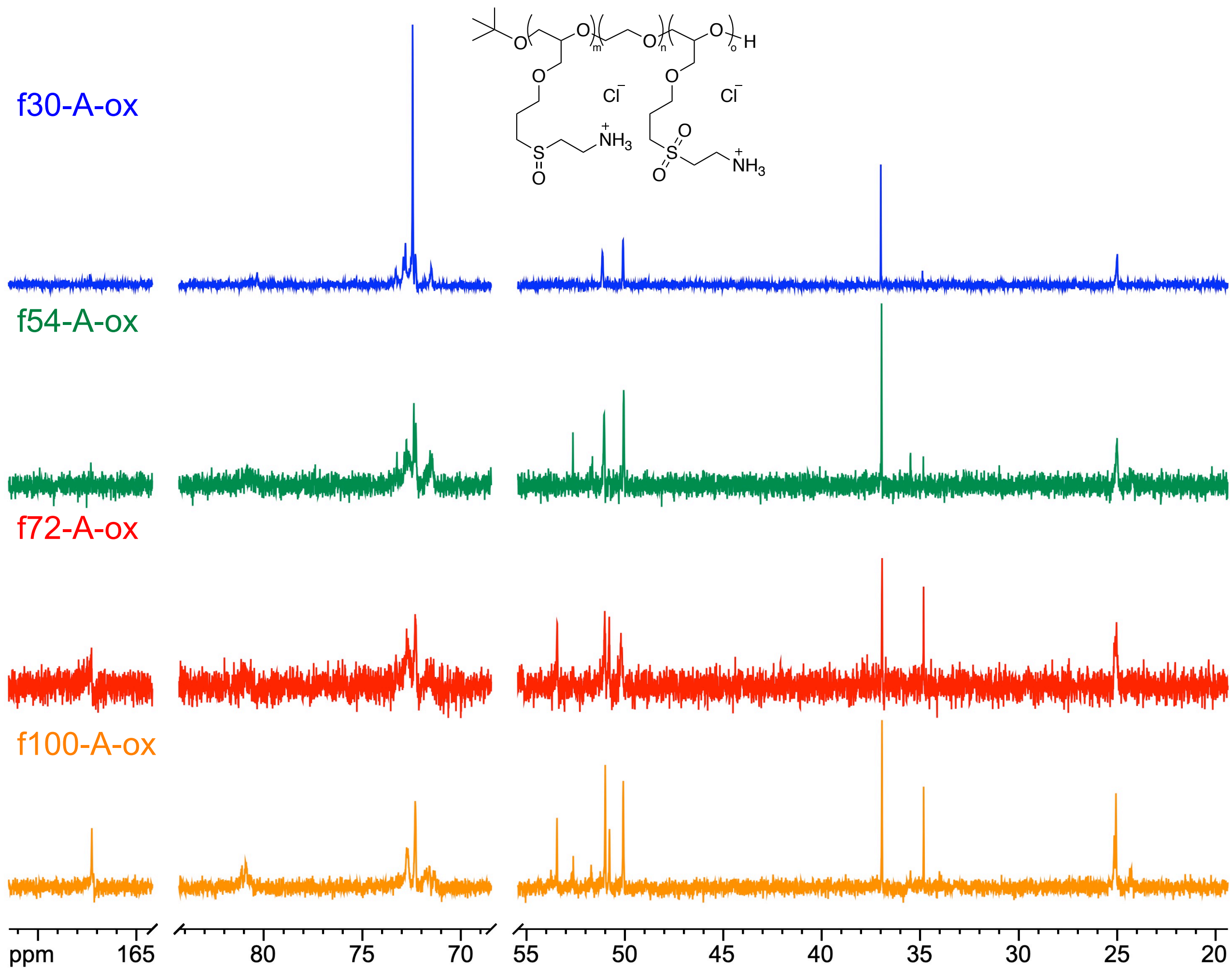

Figure S8. Overlaid [13]C NMR spectra (D_2O) of (co)polycations after oxidation with 2 eq. H_2O_2 relative to moles of sulfur in Figure S3.

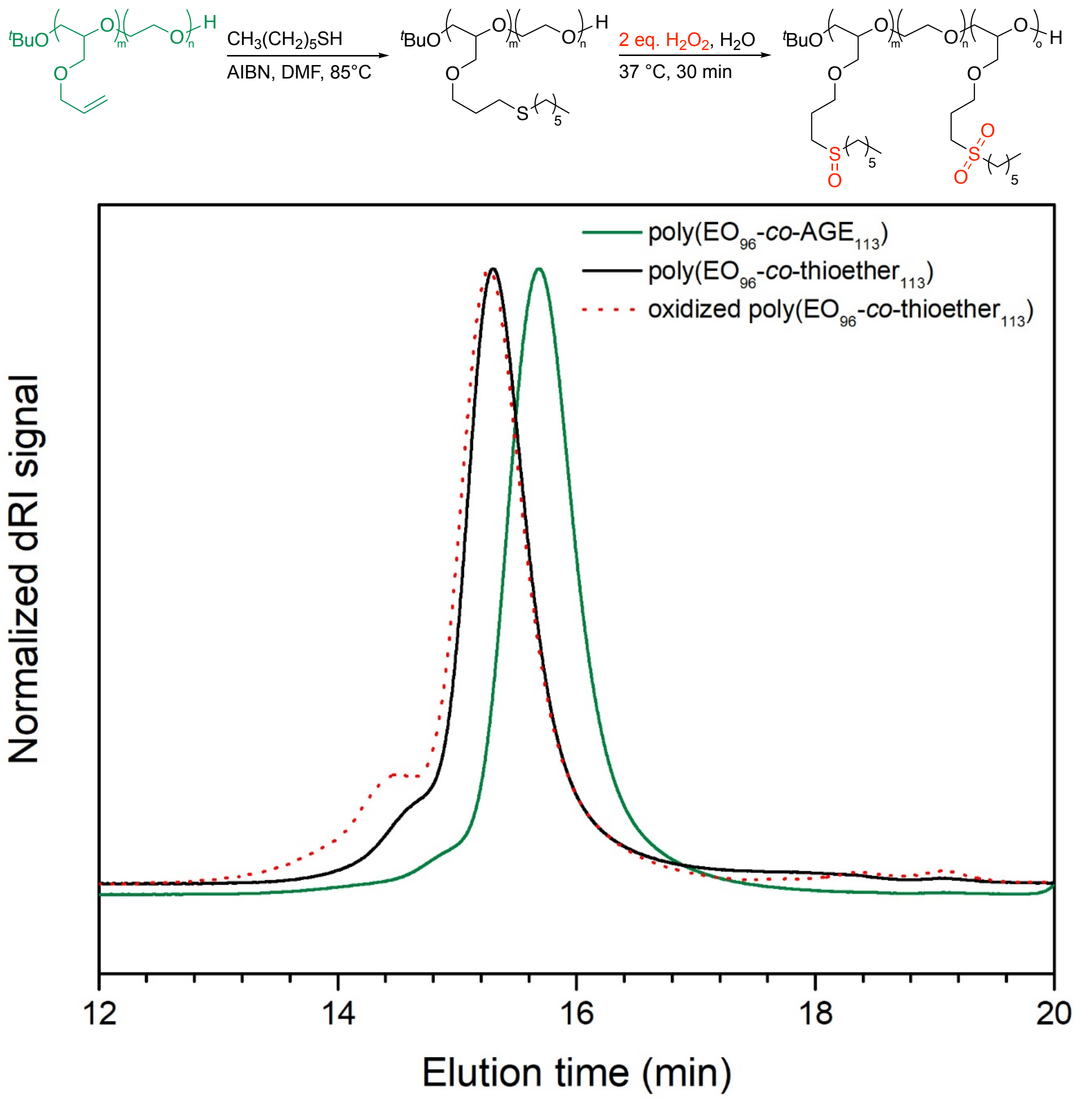

Figure S9. DMF SEC traces of poly(EO-*stat*-AGE) with f_{AGE} = 0.54 prior to postpolymerization modification, after thiol-ene click reaction with hexanethiol, and after oxidation with 2 eq. H_2O_2. A shift to lower elution time is observed upon polymer functionalization with hexanethiol, indicating an increase in the hydrodynamic radius of the functionalized polymer in DMF. The elution trace does not change appreciably after copolymer oxidation; most importantly, no multimodal distributions and/or shift to higher elution times are observed. This supports that no polyether backbone cleavage occurred with H_2O_2 treatment.

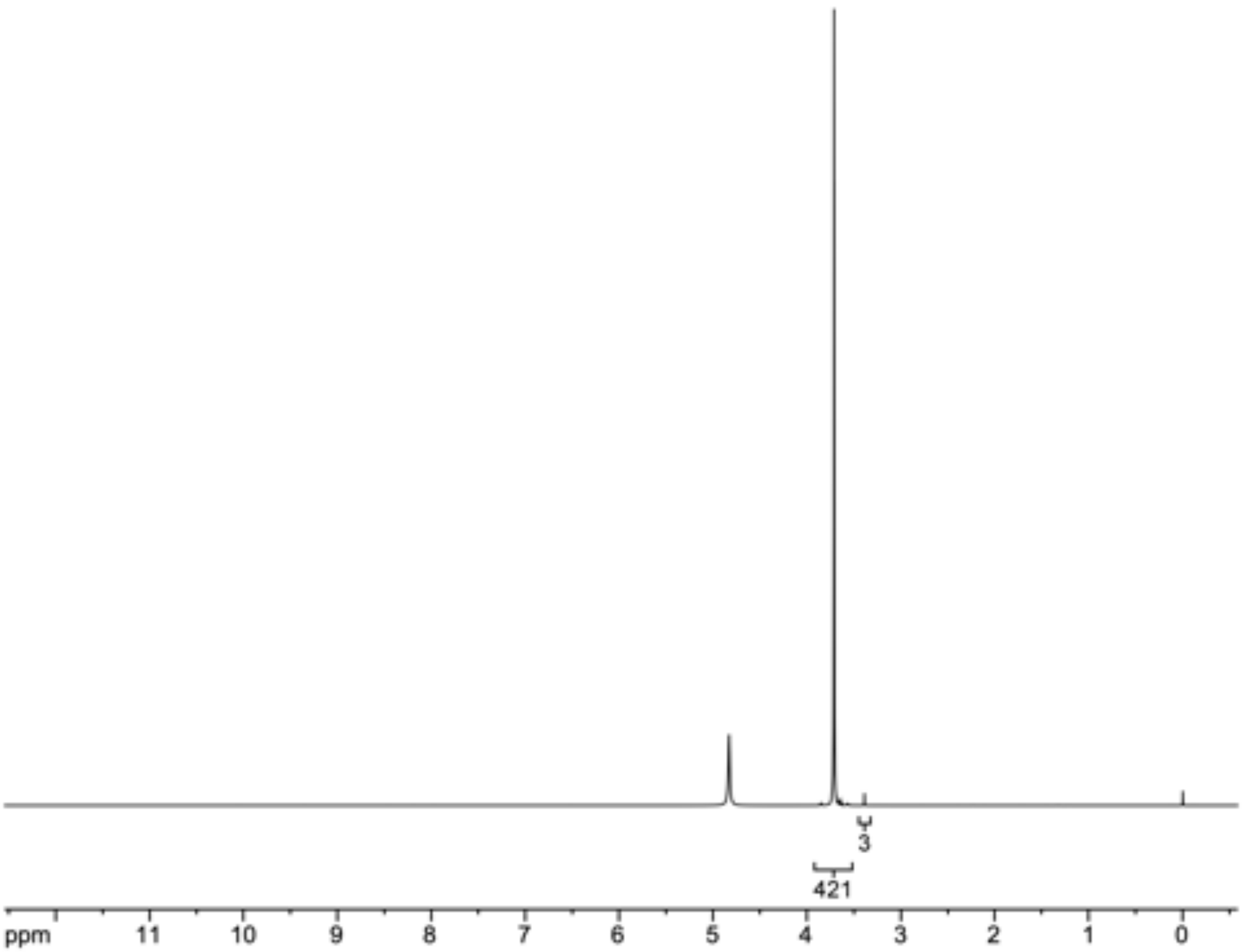

Figure S10. [1]H NMR spectrum (D_2O) of polyethylene oxide methyl ether (M_n ~ 4.6 kg/mol) after treatment with H_2O_2. Analogous to polycation oxidation reactions, 1 mL of a 50 mg/mL solution of PEO in MilliQ water was treated with 40 μL of 30 wt.%/v H_2O_2 (this volume was based on what is added to oxidize 1 mL of f = 1 polycation with 2 eq. H_2O_2 relative to thioether sidechains), incubated at 37 °C for 30 min, lyophilized, and analyzed to check for potential side reactions of the PEO backbone with H_2O_2. As can be seen, no structural changes are evident from the spectrum.

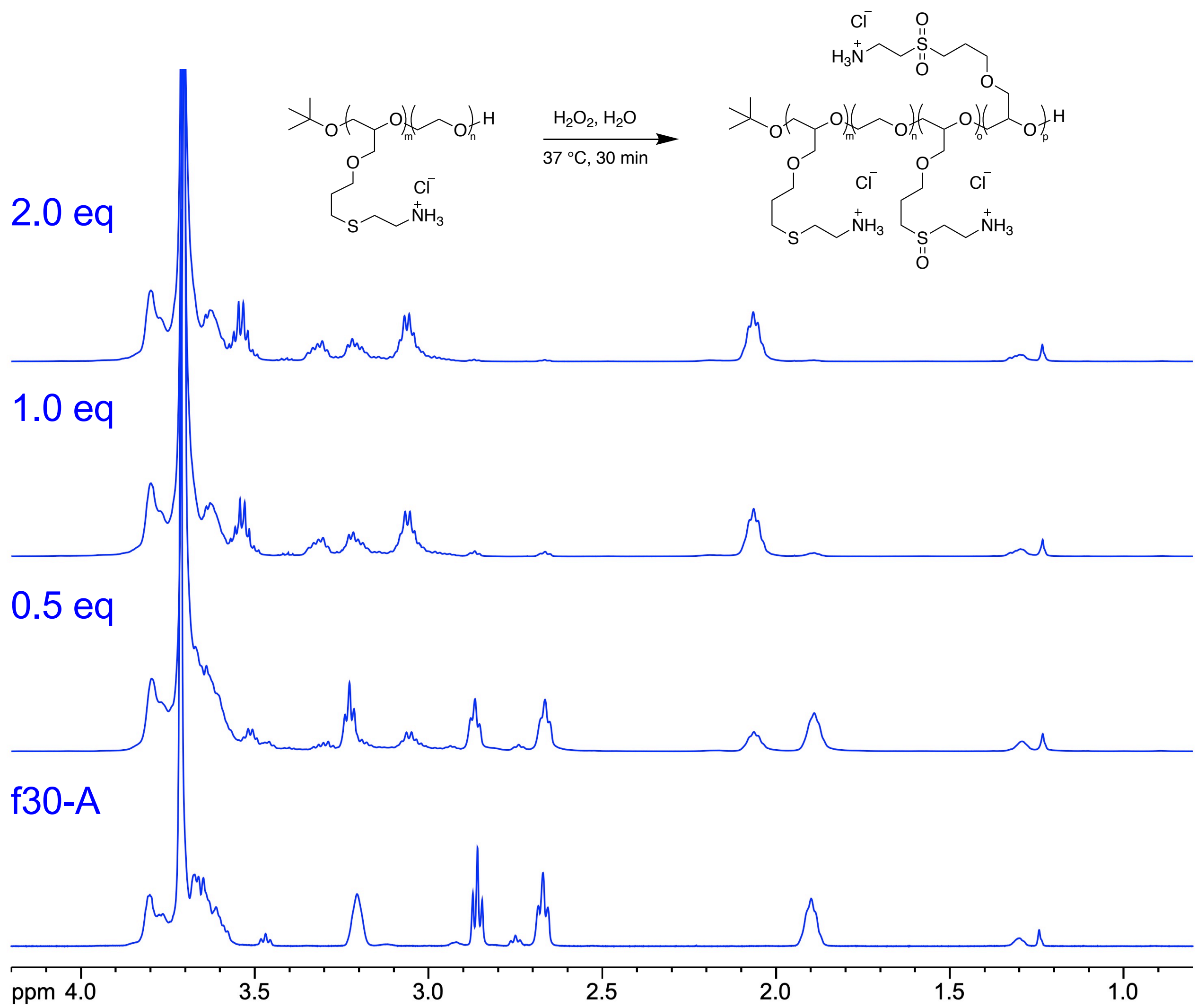

Figure S11. Overlaid [1]H NMR spectra of (co)polycations with $f = 0.30$ oxidized with 0–2 eq. H_2O_2 relative to moles of sulfur. As can be seen, thioethers have been completely transformed to sulfoxide and sulfonium moieties at 2 eq. of H_2O_2. Based on model studies by Xia and coworkers, a ratio of ~1/1 sulfoxide/sulfonium functionalized monomers was estimated.

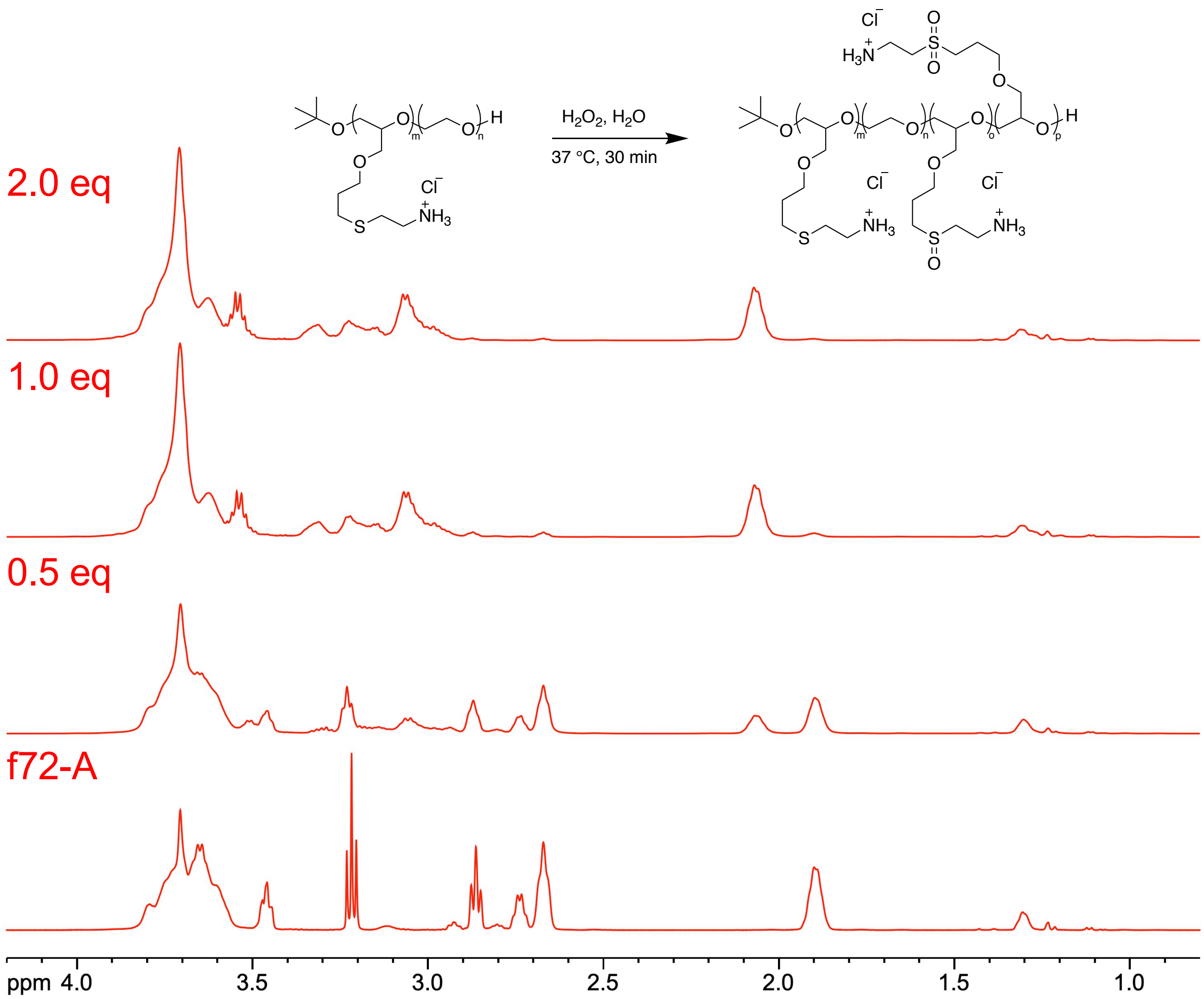

Figure S12. Overlaid [1]H NMR spectra of (co)polycations with f = 0.72 oxidized with 0–2 eq. H_2O_2 relative to moles of sulfur. As can be seen, thioethers have been completely transformed to sulfoxide and sulfonium moieties at 2 eq. of H_2O_2. Based on model studies by Xia and coworkers, a ratio of ~1/1 sulfoxide/sulfonium functionalized monomers was estimated.

Thermogravimetric Analysis

All samples were prepared in 1.5 mL centrifuge tubes on 1.5 mL scale as described in the experimental section above. The tubes were then centrifuged at 17,000x*g* for 20 min, at which point two transparent homogenous phases were observed (*c.f.* **Figure 3**). Supernatant and coacervate were separated by decanting the supernatant into a separate tube. A micropipette was used to transfer aliquots of supernatant and coacervate phases into tared aluminum pans, which were then transferred to a furnace, and subjected to the heating program outlined in the experimental section of the main text. Salt concentrations indicated as 0* refer to samples prepared at 0M exogenous NaCl and washed twice with pH ~ 3-4 MilliQ water to wash out small ions.

Table S1. Control experiments probing the nature of the residue after the 600 °C isotherm.

f value	[NaCl] (M)	Sample mass (mg)	Theoretical NaCl (mg)	Residual mass (mg)	Average (mg)	STDEV (mg)
0.300	0.050	49.610	0.146	0.160	0.170	0.010
		49.69		0.170		
		49.16		0.180		
0.540	0.300	49.690	0.877	0.890	0.903	0.012
		49.8		0.910		
		50.38		0.910		
0.720	0.500	49.920	1.461	1.460	1.487	0.038
		50.08		1.470		
		51.43		1.530		
1.000	0.500	49.450	1.461	1.420	1.430	0.010
		49.09		1.430		
		50.1		1.440		

Data presented here were obtained from samples that were not centrifuged and thus not macrophase separated.

Table S2. Data obtained from thermogravimetric analysis for **poly(Am)/poly(Sulf)**.

[NaCl] (M)	Macrophase	Amount of copolyelectrolyte (%)	Amount of NaCl (%)	Mass sample (mg)
0	Supernatant	0.0205	0.1024	48.82
		0.0000	0.1025	48.8
		0.0000	0.1228	48.87
	Complex	47.1322	0.0499	20.05
		47.0771	0.1244	16.08
		45.0698	0.0465	21.5
0.1	Supernatant	0.0203	0.6904	49.25
		0.0406	0.6706	49.21
		0.0810	0.6479	49.39
	Complex	44.0252	0.4492	11.13
		43.8312	0.3788	18.48
		41.0985	0.3788	15.84
0.2	Supernatant	0.0521	1.2513	57.54
		0.0604	1.2075	49.69
		0.0604	1.1888	49.63
	Complex	43.5159	1.0086	13.88
		45.1431	0.8447	21.31
		47.1193	0.8916	14.58
0.4	Supernatant	0.0992	2.3422	50.38
		0.1405	2.3088	49.81
		0.0800	2.5815	49.97
	Complex	47.7719	1.5333	20.87
		42.4815	1.5683	21.68
		46.4571	1.4917	18.77
0.6	Supernatant	0.0601	3.5063	49.91
		0.0998	3.4916	50.12
		0.0798	3.2535	50.1
	Complex	44.1386	2.7527	21.07
		41.1888	2.0092	23.89
		43.6979	2.2243	21.58
0.8	Supernatant	0.0800	4.6028	49.97
		0.0396	3.4619	50.55
		0.0592	5.2133	50.64
	Complex	42.6608	2.7494	22.55
		39.5380	3.0797	22.08
		40.3280	2.9016	23.78
1.00	Supernatant	0.1985	5.6184	50.37
		0.1581	5.6533	50.59
		0.1787	5.6405	50.35
	Complex	38.6107	3.5614	28.36
		37.3050	3.5816	28.2
		37.8378	3.5802	28.49
2	Supernatant	0.4588	10.7054	52.3100
		0.0953	5.2220	52.4700
		0.1913	7.4995	52.2700
	Complex	30.1459	7.3582	30.8500
		29.2191	7.5461	34.1900
		29.4618	7.4913	31.7700
3	Supernatant	0.3221	13.3142	55.8800
		0.3380	15.3709	56.2100
		0.3605	15.5732	55.4800
	Complex	28.7852	10.7901	28.7300
		26.7627	11.2511	33.3300
		24.6996	11.6382	31.6200
4	Supernatant	0.2804	20.3610	57.0700
		0.2432	20.3440	57.5600
		0.2945	20.3707	57.7300
	Complex	27.8407	14.4383	30.8900
		32.4992	13.2905	29.5700
		30.2784	13.8255	31.9700

Table S3. Data obtained from thermogravimetric analysis for **poly(Am$_{ox}$)/poly(Sulf)**.

[NaCl] (M)	Macrophase	(Co)polyelectrolyte (wt %)	NaCl (wt %)	Mass sample (mg)
0*	Supernatant	0.0000	0.0202	49.61
		0.0000	0.0202	49.6
		0.0000	0.0000	49.56
	Complex	39.0499	0.0699	28.63
		39.7880	0.0707	28.3
		41.4532	0.0765	26.15
0	Supernatant	0.0000	0.1010	29.69
		0.0201	0.1005	49.76
		0.0000	0.1006	29.81
	Complex	37.3399	0.1130	26.54
		37.9522	0.1447	27.64
		38.1022	0.1103	27.19
0.1	Supernatant	0.0604	0.6444	49.66
		0.0402	0.6833	49.76
		0.0402	0.6836	49.74
	Complex	35.9933	0.6010	29.95
		36.1389	0.7348	29.94
		36.0993	0.6534	30.61
0.2	Supernatant	0.0611	1.2414	49.14
		0.0605	1.2495	49.62
		0.0713	1.2354	42.09
	Complex	33.5699	1.1535	33.81
		33.0240	1.1377	33.4
		33.3130	1.1887	32.81
0.3	Supernatant	0.0600	1.8207	49.98
		0.0396	1.8214	50.51
		0.0402	1.8069	49.81
	Complex	31.6971	1.6269	35.65
		31.4698	1.6231	33.27
		32.1138	1.5921	29.52
0.4	Supernatant	0.1784	2.2742	44.85
		0.1590	2.3062	50.3
		0.1786	2.2628	50.38
	Complex	29.5434	2.1470	33.07
		29.4819	2.1244	38.6
		29.8038	2.0693	37.21
0.5	Supernatant	0.1580	2.9034	50.63
		0.1190	2.9167	50.4
		0.0993	2.9400	50.34
	Complex	26.9472	2.5795	39.93
		25.4688	2.5893	44.8
		27.1040	2.5990	40.4
0.6	Supernatant	0.1395	3.5273	50.18
		0.0985	3.5074	50.75
		0.1370	3.5029	51.1
	Complex	24.0577	3.1116	39.53
		23.6005	3.0746	47.16
		23.6037	3.0831	39.57
0.7	Supernatant	0.2763	3.9866	50.67
		0.2949	3.9520	50.86
		0.3355	3.9274	50.67
	Complex	19.9577	3.6402	47.25
		19.3774	3.6425	47.22
		20.5626	3.5887	41.24
0.8	Supernatant	0.5087	4.5979	51.11
		0.4715	4.5972	50.9
		0.5109	4.5589	50.89
	Complex	15.7080	4.1759	36.16
		15.7550	4.2450	35.1
		16.0817	4.2622	27.92

0* refers to coacervate samples prepared at 0M exogenous NaCl and washed 2x with pH ~ 3-4 MilliQ water to wash out as many small ions as possible.

Table S4. Data obtained from thermogravimetric analysis for **poly(Am$_{ox}$-*stat*-EO)/poly(Sulf-*stat*-EO)** with f = 0.72.

[NaCl] (M)	Macrophase	(Co)polyelectrolyte (wt %)	NaCl (wt %)	Mass sample (mg)
0*	Supernatant	0.0204	0.0000	48.92
		0.0000	0.0204	49.01
		0.0000	0.0203	49.21
	Complex	35.1858	0.0341	29.33
		34.3228	0.0309	32.34
		33.8393	0.0595	33.6
0	Supernatant	0.0202	0.1008	49.58
		0.0000	0.1010	49.51
		0.0200	0.1002	49.89
	Complex	33.2491	0.2212	31.64
		33.1733	0.2259	35.42
		33.9230	0.2173	32.22
0.1	Supernatant	0.0405	0.6483	49.36
		0.0694	0.6595	28.81
		0.0601	0.6811	49.92
	Complex	30.7850	0.7909	34.14
		30.4777	0.8006	37.47
		30.8797	0.8079	33.42
0.2	Supernatant	0.1199	1.1788	50.05
		0.1016	1.2398	49.2
		0.1207	1.2068	49.72
	Complex	28.9294	1.2908	39.51
		28.8186	1.3247	36.99
		29.0666	1.3727	29.14
0.3	Supernatant	0.1188	1.7815	50.52
		0.0993	1.8279	50.33
		0.1590	1.7286	50.33
	Complex	26.1111	1.7460	37.8
		25.4766	1.7331	40.39
		26.0582	1.7262	42.29
0.4	Supernatant	0.1986	2.3034	50.36
		0.1647	2.4382	30.35
		0.1967	2.2624	50.83
	Complex	21.5054	2.2317	49.29
		21.6507	2.2679	42.77
		22.0424	2.2321	35.84
0.5	Supernatant	0.2552	2.9643	50.94
		0.2764	2.8820	50.66
		0.2577	2.9534	50.45
	Complex	18.4620	2.7142	35.37
		17.5670	2.7214	49.24
		18.3211	2.7447	43.72
0.55	Supernatant	0.5324	3.2144	50.71
		0.4521	3.2042	50.87
		0.5077	3.2416	51.21
	Complex	16.2725	2.9565	42.28
		16.1526	2.9535	38.26
		15.3669	2.9916	39.11
0.6	Supernatant	0.6815	3.4852	51.36
		0.6876	3.4774	50.9
		0.7060	3.4713	50.99
	Complex	13.2813	3.2670	14.08
		13.2085	3.2528	20.29
		14.2520	3.2563	21.19
0.625	Supernatant	0.8862	3.6432	50.78
		0.8864	3.6439	50.77
		0.8670	3.6847	50.75
	Complex	7.2464	3.8647	2.07
		6.4159	3.5398	4.52
		7.7778	3.7778	4.5

Table S5. Data obtained from thermogravimetric analysis for **poly(Am$_{ox}$-*stat*-EO)/poly(Sulf-*stat*-EO)** with f = 0.54.

[NaCl] (M)	Macrophase	(Co)polyelectrolyte (wt %)	NaCl (wt %)	Mass sample (mg)
0*	Supernatant	0.0204	0.0204	48.92
		0.0203	0.0203	49.23
		0.0000	0.0204	49.11
	Complex	32.8650	0.1004	19.93
		32.7310	0.1033	19.37
		32.2737	0.0000	33.03
0	Supernatant	0.2459	0.0820	48.8
		0.2248	0.1022	48.94
		0.2457	0.0819	48.84
	Complex	30.4173	0.2562	27.32
		30.1455	0.2772	28.86
		29.9588	0.2745	29.14
0.05	Supernatant	0.2016	0.3528	19.84
		0.1527	0.3055	19.64
		0.1540	0.3593	19.48
	Complex	26.9231	0.6811	24.96
		26.2638	0.6319	25.32
		26.3471	0.7132	25.24
0.1	Supernatant	0.1518	0.6579	19.76
		0.1529	0.6626	19.62
		0.2030	0.6599	19.7
	Complex	24.7270	0.9521	35.71
		24.2440	0.9577	39.68
		24.5810	0.9703	34.01
0.15	Supernatant	0.1011	1.0111	19.78
		0.1503	1.0020	19.96
		0.1001	1.0010	19.98
	Complex	22.8528	1.2414	39.47
		22.4422	1.2901	33.33
		23.1451	1.2625	45.15
0.2	Supernatant	0.1558	1.2461	19.26
		0.2013	1.3085	19.87
		0.1505	1.3039	19.94
	Complex	22.0819	1.5159	39.58
		21.4109	1.4604	40.4
		21.8588	1.4538	38.52
0.25	Supernatant	0.3024	1.5625	19.84
		0.3110	1.5034	19.29
		0.2996	1.5477	20.03
	Complex	19.9954	1.6605	43.36
		19.5816	1.6527	47.8
		19.9274	1.6465	41.3
0.3	Supernatant	0.3471	1.8840	20.17
		0.4431	1.7725	20.31
		0.3467	1.8326	20.19
	Complex	17.1115	1.8390	44.59
		18.6245	1.8707	36.35
		17.4837	1.8509	39.98
0.35	Supernatant	0.4871	2.0458	20.53
		0.5478	1.9920	20.08
		0.4955	2.0317	20.18
	Complex	15.7231	2.0928	37.27
		15.2490	2.0945	39.15
		16.0563	2.0701	37.68
0.4	Supernatant	0.6914	2.4198	20.25
		0.7171	2.3705	50.2
		0.6398	2.3622	20.32
	Complex	14.2224	2.3130	20.32
		14.1202	2.3896	13.81
		13.1179	2.4081	15.78
0.425	Supernatant	0.7886	2.5628	20.29
		0.7890	2.5641	20.28
		0.7825	2.6084	50.38
	Complex	13.3224	2.4671	12.16
		12.3755	2.7027	12.85
		12.8519	2.5704	8.17

Table S6. Data obtained from thermogravimetric analysis for **poly(Am$_{ox}$-*stat*-EO)/poly(Sulf-*stat*-EO)** with f = 0.30.

[NaCl] (M)	Macrophase	(Co)polyelectrolyte (wt %)	NaCl (wt %)	Mass sample (mg)
0*	Supernatant	0.0406	0.0609	49.29
		0.0405	0.0203	49.33
		0.0608	0.0203	49.35
	Complex	17.9590	0.0402	49.78
		18.6141	0.0426	46.9
		18.6489	0.0202	49.44
0	Supernatant	0.1406	0.0803	49.79
		0.1615	0.0807	49.55
		0.1803	0.0601	49.92
	Complex	15.9252	0.1886	63.61
		16.7305	0.1613	49.61
		15.6612	0.1523	65.64
0.025	Supernatant	0.2190	0.2190	50.22
		0.2204	0.2004	49.91
		0.2017	0.2219	49.57
	Complex	13.1124	0.3012	49.8
		13.6907	0.2989	50.18
		13.7488	0.2967	50.55
0.04	Supernatant	0.3226	0.3024	49.6
		0.2814	0.3215	49.76
		0.3200	0.3200	50
	Complex	12.5755	0.4024	49.7
		12.6101	0.4003	49.96
		12.2924	0.4253	49.38
0.05	Supernatant	0.4218	0.3414	49.79
		0.4586	0.3390	50.15
		0.4641	0.3430	49.56
	Complex	9.4998	0.5478	69.37
		11.6804	0.4721	57.19
		11.7614	0.4720	52.97
0.06	Supernatant	0.5787	0.3991	50.11
		0.6383	0.4189	50.13
		0.5810	0.4408	49.91
	Complex	10.0261	0.4977	42.19
		10.2170	0.5294	37.78
		10.1138	0.4915	38.66

Optical Microscopy

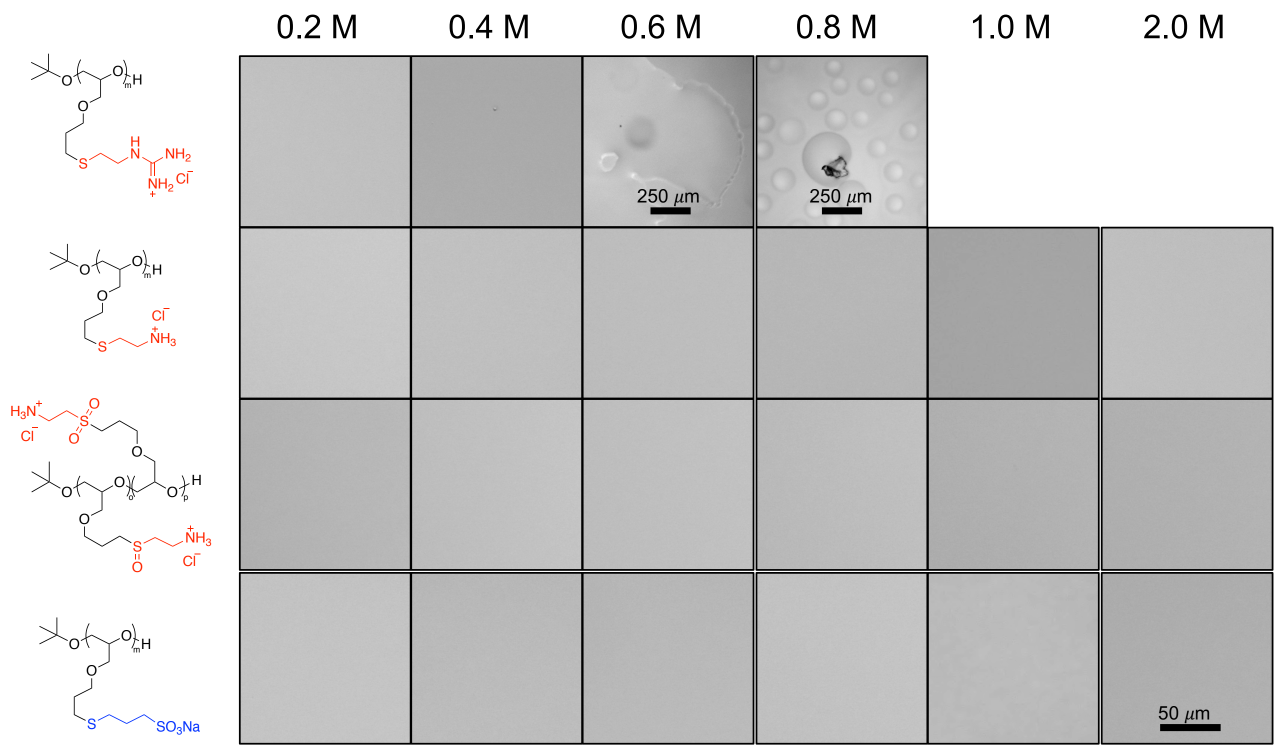

Figure S13. Solubility studies of fully charged (f = 1) (co)polycations and (co)polyanions in aqueous sodium chloride solutions of variable ionic strength. As can be seen, all copolyelectrolytes exhibited good solubility up to 2M NaCl except for **poly(Guan)/poly(Sulf)** (top row), where samples became visibly cloudy at 0.4M exogenous NaCl and large droplets that quickly coalesced to form a macrophase were observed.

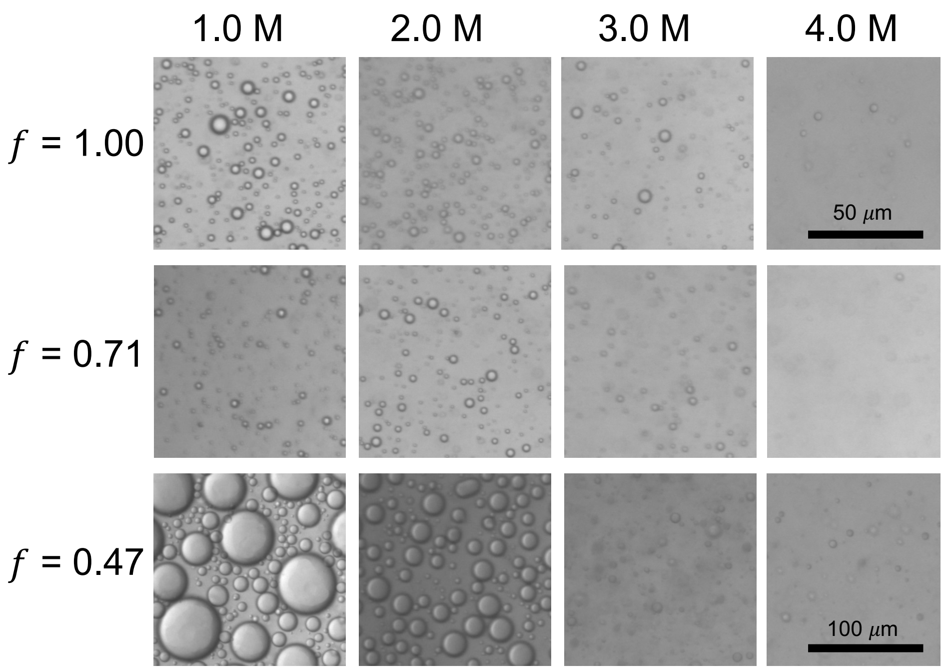

Figure S14. Polyelectrolyte complex coacervates formed from **poly(Guan-*stat*-EO)/poly(Sulf-*stat*-EO)** with increasing concentrations of exogenous NaH_2PO_4. At high [NaH_2PO_4] coacervates could be re-transitioned into a single-phase regime. Coacervates droplets displayed here were formed with [polymer] = 10 mg/mL and imaged immediately after mixing. No coacervate droplets were observed for f = 0.1 and 0.3 at 0M exogenous salt or above.

Binodal Phase Diagrams

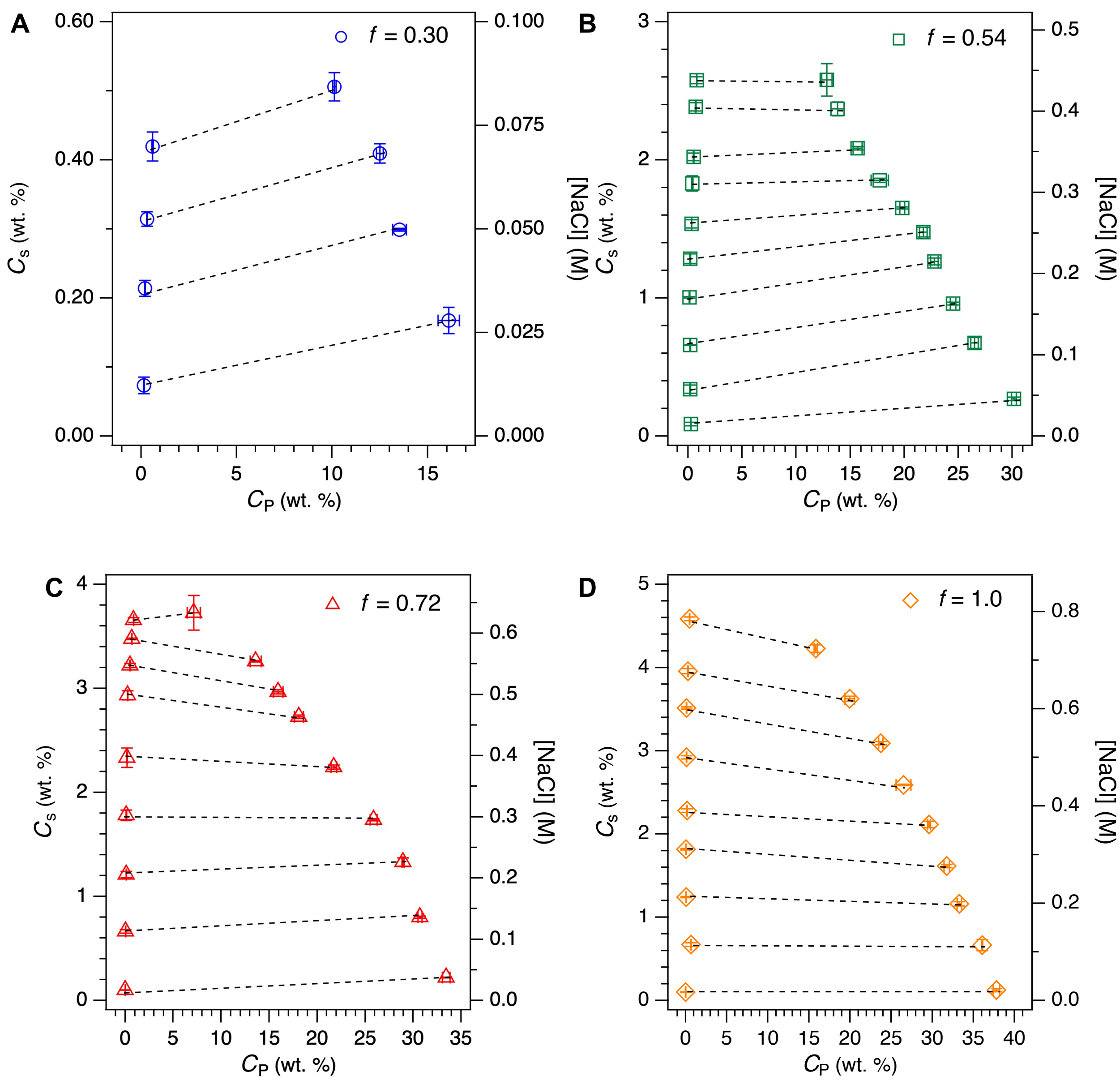

Figure S15. Binodal phase diagrams with tie lines for complexes of **poly(Sulf-*stat*-EO)/poly(Am$_{ox}$-stat-EO)** with f = 0.30, 0.54, 0.72, and 1.0, plotted from the data displayed in the corresponding **Tables S3-6**. Data obtained from washing out counterions were omitted in these plots.

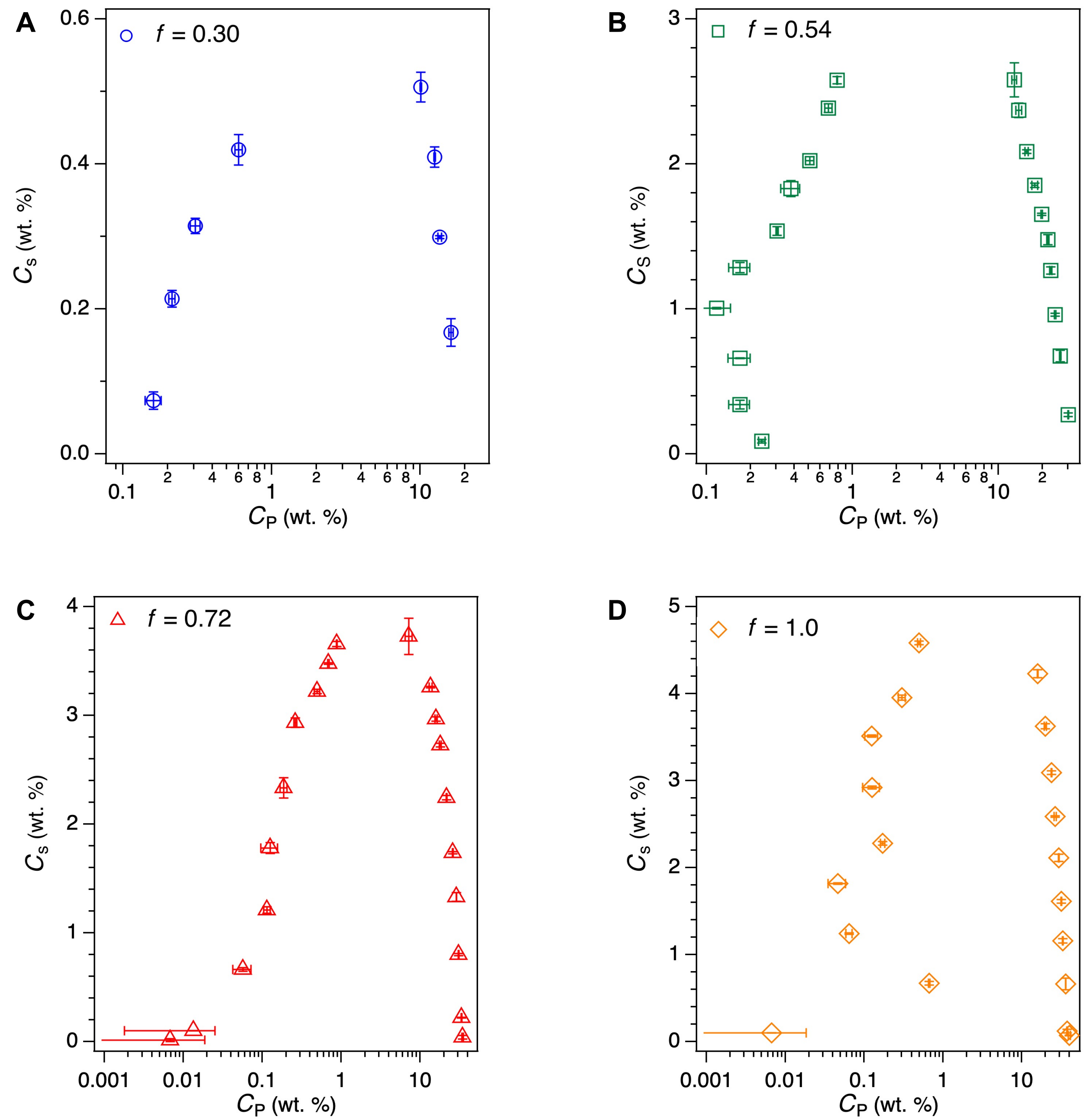

Figure S16. Binodal phase diagrams for complexes of **poly(Sulf-*stat*-EO)/poly(Am$_{ox}$-stat-EO)** with f = 0.30, 0.54, 0.72, and 1.0, plotted from the data displayed in the corresponding **Tables S3-6**. Here, (co)PE concentration on the abscissa has been depicted on a logarithmic scale to allow for visualization of the supernatant composition. Data obtained from washing out counterions were omitted in these plots.

In initial studies, the pH of stock solutions was not adjusted with 1M hydrochloric acid. The pH of sample supernatants was measured as pH = 6.5 when stock solutions were prepared with MilliQ water. The adjustment of (co)polycation solutions to pH = 3–4 (this can also be accomplished by dialysis against MilliQ water adjusted to pH = 3–4) was important in the purification as high charge density (f = 0.72 and 1.00) (co)polycations were not fully ionized at pH = 6.5, which led to backpressure when solutions were filtered through 0.22 μm polysulfone syringe filters prior to lyophilization. With regards to the impact of pH on phase behavior, it can be seen that a higher fraction of (co)polyelectrolytes partitioned into the supernatant phase at no or low exogenous [NaCl] for f = 0.72 and 1.00; the corresponding coacervates are therefore less dense and have lower salt stabilities than their acidified versions (*c.f.* **Figure 4**). The impact of pH on phase behavior was negligible for polyelectrolyte complex coacervates formed with polyelectrolytes of f = 0.30 and 0.54. This is in line with expectations; high charge densities significantly impact the pK_a values of ionizable moieties.

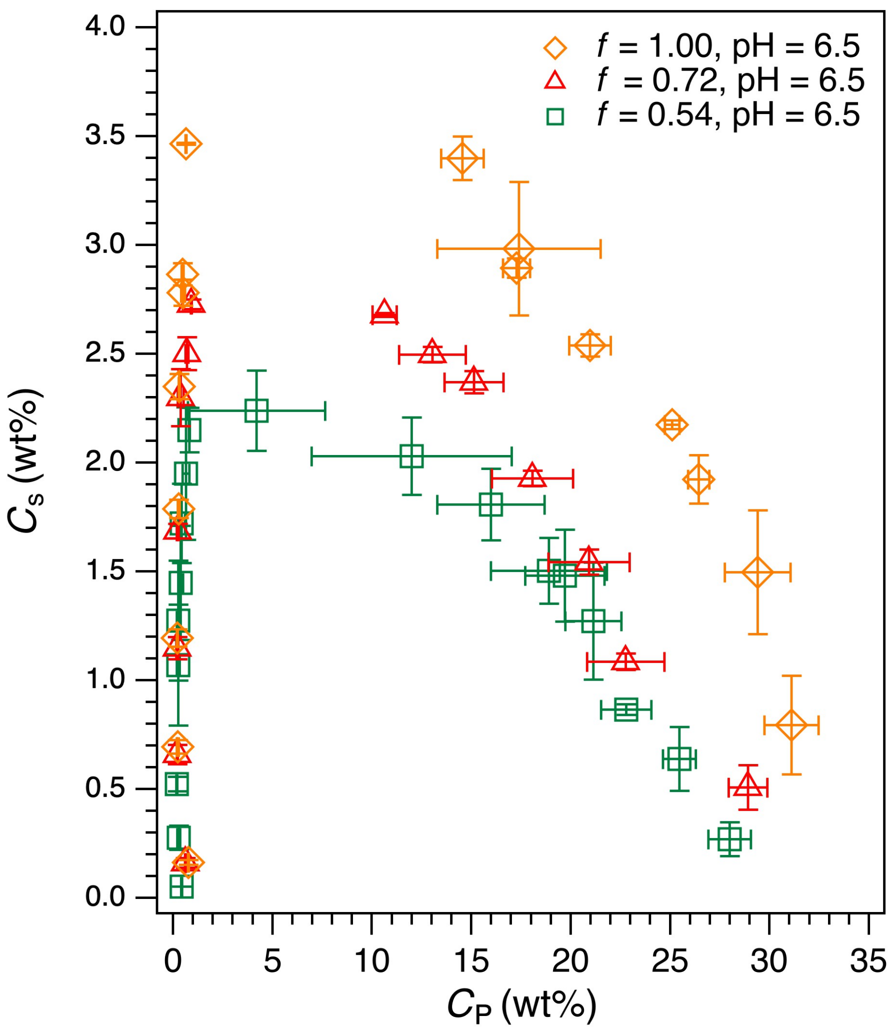

Figure S17. Binodal phase diagrams of **poly(Am$_{ox}$-*stat*-EO)/poly(Sulf-*stat*-EO)** with f = 0.54–1.00 obtained with solutions at pH = 6.5.