Supporting Information

Lower critical solution temperature in polyelectrolyte complex coacervates

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MATERIALS AND SAMPLE PREPARATION

Sodium poly(styrene sulfonate) (NaPSS) and poly(diallyl dimethyl ammonium chloride) (PDADMAC) were purchased from Sigma Aldrich, Inc. Aqueous polyelectrolyte solutions were prepared using two different salts, either NaCl (Sigma Aldrich, Inc.) or KBr (Sigma Aldrich, Inc.). The first set of samples used NaPSS and PDADMAC with NaCl. The second set used KBr with potassium-poly(styrene sulfonate) (KPSS) and poly(diallyl dimethyl ammonium bromide) (PDADMAB).

KPSS and PDADMAB samples with alternate counterions were prepared by ion-exchange. The solution of PDADMAB is obtained by ion-exchange of a 2 % w/v PDADMAC solution through Br- resin (Br- exchanged DOWEX® MR-3 from Sigma Aldrich, Inc.). The KPSS is obtained from 2 % w/v NaPSS by ion-exchange to the acid form with a H+ resin (Dowex® 650C from Aldrich Chemical Company, Inc.), then titrated with KOH until the end point. The solutions of PDADMAB and KPSS are then dialyzed against deionized water and freeze-dried to obtain dry powders.

Stock solutions of 5 mol/L KBr and 0.5 mol/L polymer solution are used for sample preparation. All samples are prepared at room temperature in 1.6 mL centrifuge cuvettes by mixing anionic and cationic polyelectrolytes solutions at 1:1 charge stoichiometric ratio. The salt concentrations of the component solutions are adjusted separately before mixing. The initial polymer concentration is kept fixed at 0.3 mol/L. A set of samples with an identical composition is prepared for different temperature studies at a fixed salt concentration.

All samples are kept in a bath at temperature ≈ 2 °C for 1 h. Samples are then vortex mixed for 15 s immediately after taking out of the bath and then replaced back to the bath for another 2 min. This procedure is repeated for 5 to 7 times. This results in uniform solutions for $C_{KBr} \geq 2.0$ mol/L. However, samples with $C_{KBr} = 1.75$ mol/L always remain phase separated even at 2 °C. All samples are subsequently stored at 5 °C for 24 hr before performing further measurements.

RHEOLOGY

Small amplitude oscillatory rheological measurements are performed on Ares G2 stain-controlled rheometer using cone – plate geometry with a cone radius of 25 mm and a cone angle of 1 °. The surfaces of the geometry are sand-blasted to a roughness value of approximately 2 μm to avoid slippage of the sample. After transferring the required amount of the dense phase from the bottom of the sample cuvette a small amount of silicone oil of viscosity 4.6 mPa·s was applied to the rim of the cone fixture to avoid evaporation of water. Frequency sweep measurements are performed in the frequency range of 0.2 rad/s to 200 rad/s and at strain amplitude of 3 % at 30 °C as shown in Figure S1. The applied strain is much smaller compared to the extent of the linear viscoelastic regime. The samples were thermally equilibrated at 30 °C for 15 min before performing measurements. All rheological data are acquired using TRIOS v4 software of TA instruments.

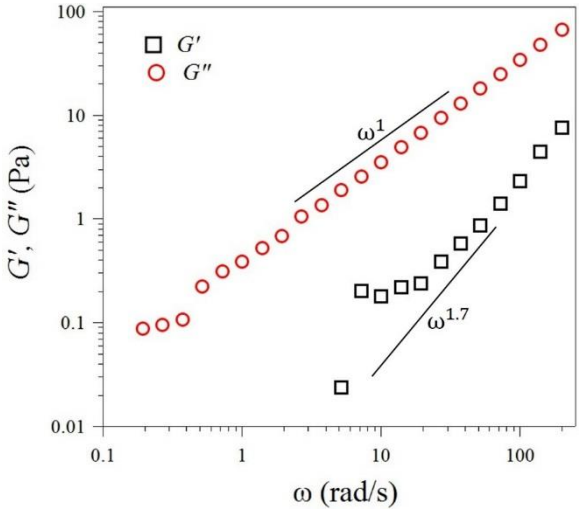

Figure S1: Variation of the elastic moduli G' (squares) and viscous moduli G'' (circles) of dense phase as functions of angular frequency ω at applied strain amplitude of 3% at 30 °C. The dense phase behaves like a viscoelastic liquid ($G'' > G'$) and exhibits terminal-like relaxation behavior leading to $G' \sim \omega^{1.7}$ and $G'' \sim \omega^{1}$.

CONFOCAL MICROSCOPY

A Leica TCS SP5 II fluorescent laser scanning microscope equipped with 20X air-objective was used to image coacervate samples with an excitation wavelength of 542 nm. Samples are loaded in a $5\ mm \times 150\ nm$ sealed channel constructed using microscopy glass slides, glass cover slip and double-sided tape. To perform fluorescent imaging of coacervate samples, a small amount of Rhodamine-B dye was added to the polyelectrolyte solution before mixing during the sample preparation described earlier. The Rhodamine-B dye appear to adsorb to the polyelectrolyte, which provides the contrast between polymer-rich and polymer-poor domain under laser light excitation.

TURBIDITY DATA

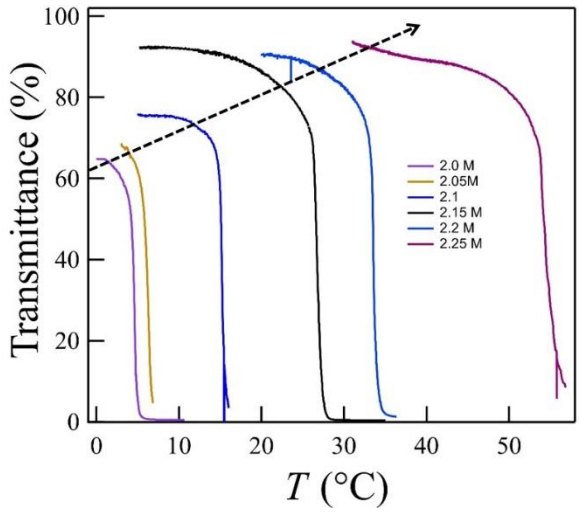

Figure S2: Temperature dependence of transmittance at 632 nm measured at heating rate of 0.2 °C/min for KPSS/PDADMAB aqueous mixture prepared at an initial polymer concentration $C_{pi} = 0.3$ mol/L and at varying C_{KBr}.

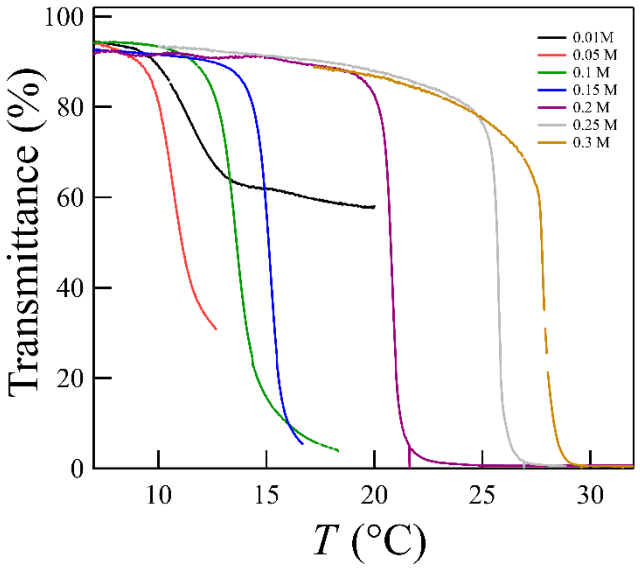

Figure S3: Temperature dependence of transmittance at 632 nm, measured at heating rate of 0.2 C/min for KPSS/PDADMAB aqueous mixture prepared at $C_{KBr} = 2.15$ mol/L and at varying initial polymer concentrations C_{pi} in the range 0.01 mol/L to 0.3 mol/L.

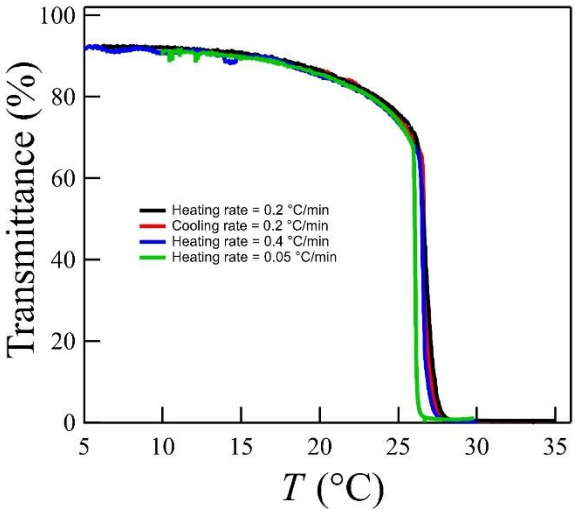

Figure S4: Temperature dependence of transmittance at 632 nm, measured at varying temperature ramping conditions (see legends) for KPSS/PDADMAB aqueous mixture prepared at $C_{KBr} = 2.15$ mol/L and $C_{pi} = 0.3$ mol/L.

COEXISTENCE CURVE

Concentrations of PSS in the supernatant and coacervate phases were estimated by UV-Vis absorption spectroscopy with a Varian Carry 500 spectrometer. UV-VIS absorption calibration curves for aqueous solution of KPSS were prepared using a a stock solution of KPSS with initial $C_{PSS} = 15$ mmol/L and salt concentration $C_{KBr} = 2.5$ mol/L. This solution was diluted stepwise using 2.5 ml/L KBr solution to prepare KPSS solutions in the concentration range 0.1 mmol/L to 5 mmol/L. The UV-Vis absorption spectra measured at room temperature for different C_{PSS} are shown in Figure S5a. All spectra exhibit a characteristic absorption peak for PSS at λ = 261 nm. The calibration curve (Figure S5b) provides the extinction coefficient a =0.622 (mmol/L)$^{-1}$ for PSS in water.

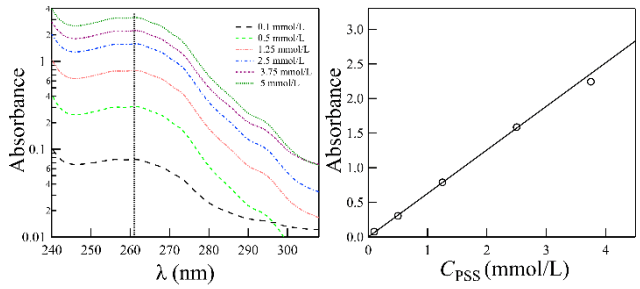

Figure S5: (a) UV-VIS absorption spectra measured at varying concentrations of PSS (MW = 200,000) dissolved in 2.5 mol/L KBr solutions at T=20 °C. Absorption of light by quartz-cuvette wall and background solution is subtracted by measuring baseline for a pure 2.5 M KBr solution. The vertical dotted line indicates the PSS absorbance peak. (b) Absorbance at peak (λ = 261 nm) versus PSS concentration. A linear fit (solid line) gives an extinction coefficient of a = 0.768 (mmol/L)$^{-1}$.

To measure C_{PSS} in coexisting phases at varying temperatures, the previously prepared samples are vortex mixed at ≈ (2 to 3) °C and subsequently thermally equilibrated at desired measurement temperature for at least three hours. Next, samples cuvettes are spun at RCF = 10,000g m/S^2 for 15 min on a temperature-controlled centrifuge machine set to the desired temperature.

Immediately after centrifugation, known volumes of supernatant and coacervate are carefully collected from the coexisting phases using precision micropipette and subsequently diluted by a 2.5 mol/L KBr solution. These diluted mixtures are vortexed for 1 min and stored at room temperature for 24 h before measurements.

UV-VIS measurements are performed at room temperature on a single-beam setup. Initial measurement is performed for the baseline at 2.5 mol/L KBr background and subsequently measured for the diluted samples prepared at different temperatures using the method described above. The peak absorbance at λ = 261 nm is used to determine the PSS concentration as $C_{PSS} = \beta A/a$. Here, β is dilution factor, A is absorbance at 261 nm and a is the extinction coefficient. Details of these quantities at C_{pi} =0.3 mol/L, and C_{KBr} =1.75 mol/L, 2 mol/L and 2.05 mol/L are shown in Table S1-S3. Errors in C_{pss} are estimated from the uncertainty in the sample volumes from the micropipette.

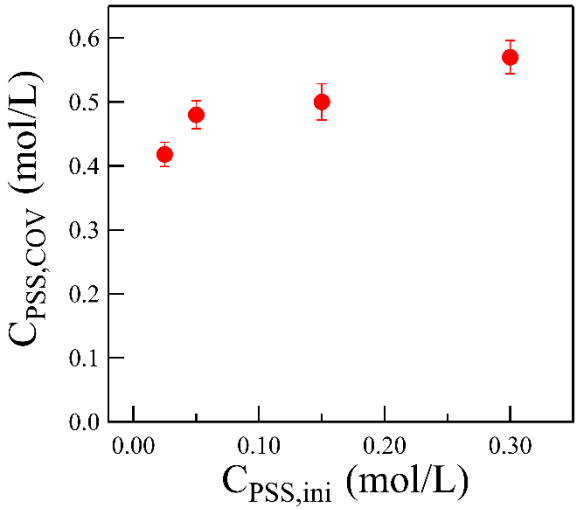

Figure S6: Effect if initial polymer concentration on the coacervate concentration for phase separation at 30 °C and C_{KBr} = 2.0 mol/L.

USANS

Ultra-small angle neutron scattering were performed on the BT5 double-crystal diffractometer using 0.24 nm wavelength (λ) neutrons with Δλ/λ = 6 %.[34] The Q-range of 0.0003 nm^{-1} to 0.01 nm^{-1} provides sensitivity to micron scale fluctuations. The samples thermostatically controlled in Hellma cuvettes had the upper dilute phase masked by cadmium to measure only the dense coacervate phase. The smeared data were analyzed by models smeared by the resolution of the instrument.

The temperature of the sample was controlled using a circulating bath at 0.1 °C resolution. The data were reduced to absolute scale and analyzed by available Igor Pro software routines.[1] The USANS data are fitted to the empirical Guinier–Porod empirical model[2] given by

$$I(Q) = G\ exp\left(\frac{-Q^2R_g^2}{3}\right) \text{ for } Q \le Q_1$$

$$I(Q) = \frac{D}{Q^d} \text{ for } Q \ge Q_1$$

Where Q is the scattering vector, $I(Q)$ is the scattered intensity, R_g is the radius of gyration, d is the Porod exponent, G and D are the Guinier and the Porod scale factors, respectively. These relations assume that the derivative $(dI(Q)/dQ)$ is continuous at $q = q_1$.

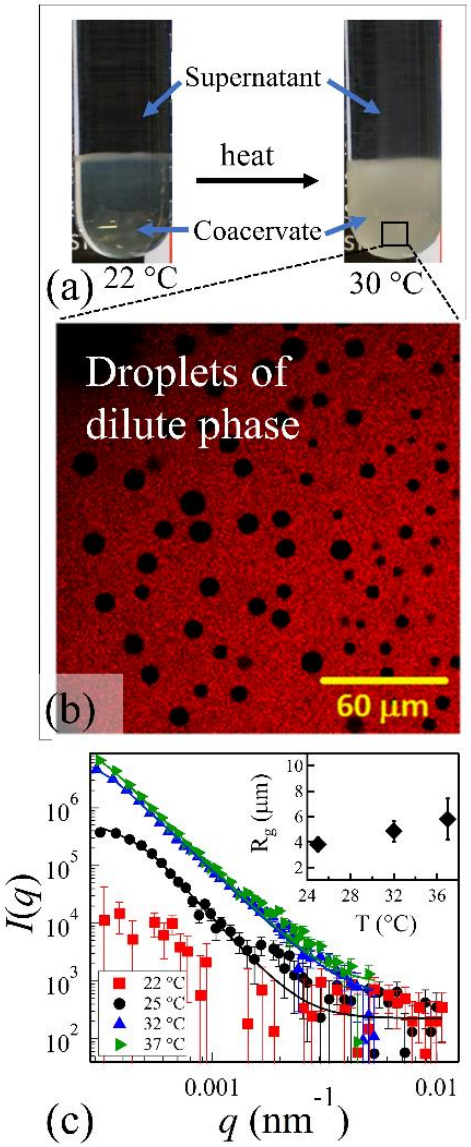

Figure S7: NaPSS/PDADMAC complex prepared at C_{NaCl} = 4.15 mol/L and C_{pi} = 0.3 mol/L (a) Photos showing *T*-induced clear-to-cloudy transition of coacervate (b) Confocal micrograph of microscopic droplets of dilute phase within the coacervate domain that causes turbidity at T = 30 °C and (c) USANS from the dense polymer-rich phase. Uncertainties (error bars) in the radius of gyration are estimated by one standard deviation of the mean by least-squares minimization of fits to USANS data. While error bars are shown, they may be smaller than the symbols used.

The effects of the lower critical solution temperature are also observed by a change in temperature of a phase separated solution. This causes the translucent coacervate to become turbid. To illustrate the generality, a phase separated NaPSS and PDADMAC at C_{NaCl} = 4.15 mol/L (Figure S7a) was prepared at 22 °C. The clear coacervate becomes turbid due to the formation of micron size polymer-poor droplets (Figure S7b). Ultra-small angle neutron scattering (USANS) of the polymer-rich phase shows the emergence of these domains (Figure S7c). At 22 °C, the USANS signal is very low, but an increase in scattering is observed upon heating. The average radius of gyration (R_g) of the droplets was estimated by the Guinier-Porod model as shown in the inset. The R_g of the dilute droplets at 25 °C is 3.8 ± 1.0 µm, higher temperatures lead to larger uncertainty due to a less defined Guinier region. The response of the coacervate is not simply a movement of the meniscus, but through a spontaneous formation of droplets. As the temperature is increased, the system tries to achieve new equilibrium concentrations for the two coexisting phases. It appears this occurs via nucleation and growth of an excess dilute phase that are kinetically trapped by the viscoelastic coacervate.

REFERENCES

(1) Kline, S. R. Reduction and Analysis of SANS and USANS Data Using IGOR Pro. *J. Appl. Crystallogr.* **2006**, *39* (6), 895–900.

(2) Hammouda, B. A New Guinier–Porod Model. *J. Appl. Crystallogr.* **2010**, *43* (4), 716–719.

Table S1a: UV-Vis data for concentration of PSS in supernatant phase at varying temperatures for sample prepared at C_{pi} =0.3 mol/L and C_{KBr} =1.75 mol/L

T (°C)	Supernatant volume (µl)	Added 2.5 mol/L KBr volume (µl)	Dilution factor (β)	Absorption (A)	$C_{PSS,\,SUP}$ (mol/L)
5	40	2400	61	0.09304	0.0086 ±0.0002
10	40	2400	61	0.08736	0.0084 ± 0.0002
15	40	2400	61	0.08571	0.0070 ± 0.0002
20	40	2400	61	0.07148	0.0068± 0.0002
25	40	2400	61	0.06899	0.0065 ± 0.0002
30	40	2400	61	0.06600	0.0059± 0.0001
35	40	2400	61	0.06008	0.0056 ± 0.0001
40	40	2400	61	0.05737	0.0056 ± 0.0001
50	40	2400	61	0.05423	0.0053 ± 0.0001

Table S1b: UV-Vis data for concentration of PSS in dense coacervate phase at varying temperatures for sample prepared at C_{pi} =0.3 mol/L and C_{KBr} =1.75 mol/L

T (°C)	Coacervate volume (µL)	Added 2.5 mol/L KBr volume (µL)	β_1	Volume diluted (µL)	Added 2.5 mol/L KBr volume (µL)	β_2	($\beta=\beta_1\times\beta 2$)	Absorption (A)	$C_{PSS,COV}$ (mol/L)
10	15	2600	174.3	1520	1000	1.66	289.03	1.25847	0.58 ± 0.02
15	15	2600	174.3	1520	1000	1.66	289.03	1.26998	0.59± 0.02
20	15	2600	174.3	1520	1000	1.66	289.03	1.26384	0.59 ± 0.02
25	15	2600	174.3	1520	1000	1.66	289.03	1.39980	0.65± 0.02
30	15	2600	174.3	1520	1000	1.66	289.03	1.31783	0.61 ± 0.02
35	15	2600	174.3	1520	1000	1.66	289.03	1.27064	0.59 ± 0.02
40	15	2600	174.3	1520	1000	1.66	289.03	1.40713	0.65 ± 0.02
50	15	2600	174.3	1520	1000	1.66	289.03	1.50027	0.70 ± 0.02

Table S2a: UV-Vis data for concentration of PSS in supernatant phase at varying temperatures for sample prepared at C_{pi} =0.3 mol/L and C_{KBr} =2.0 mol/L

T (°C)	Supernatant volume (µl)	Added 2.5 mol/L KBr volume (µl)	Dilution factor (β)	Absorption (A)	$C_{PSS,SUP}$ (mol/L)
5	40	2400	61	0.80255	0.079 ± 0.004
10	40	2400	61	0.54785	0.054 ± 0.003
15	40	2400	61	0.44569	0.044 ± 0.002
20	40	2400	61	0.25309	0.025 ± 0.001
25	40	2400	61	0.28826	0.028 ± 0.001
30	40	2400	61	0.32080	0.031 ± 0.001
35	40	2400	61	0.23386	0.023 ± 0.001
40	40	2400	61	0.19716	0.019 ± 0.001
50	40	2400	61	0.17150	0.017 ± 0.001

Table S2b: UV-Vis data for concentration of PSS in dense coacervate phase at varying temperatures for sample prepared at C_{pi} =0.3 mol/L and C_{KBr} =2.0 mol/L

T (°C)	Coacervate volume (µl)	Added 2.5 mol/L KBr volume (µl)	β_1	Volume diluted (µL)	Added 2.5 mol/L KBr volume (µl)	β_2	($\beta=\beta_1\times\beta 2$)	Absorption (A)	$C_{PSS,COV}$ (mol/L)
5	20	500	26	100	2200	23	598	0.17163	0.17 ± 0.01
5	20	500	26	400	2200	6.5	169	0.60939	0.17 ± 0.01
10	20	500	26	400	2200	6.5	169	1.23244	0.33 ± 0.02
15	20	500	26	200	2200	12	312	0.73798	0.37 ± 0.02
20	20	500	26	200	2200	12	312	0.83535	0.42 ± 0.02
25	20	500	26	200	2200	12	312	0.96671	0.49 ± 0.03
30	20	500	26	200	2200	12	312	0.98775	0.50 ± 0.03
35	20	500	26	200	2200	12	312	0.94908	0.48 ± 0.03
40	20	500	26	200	2200	12	312	0.97322	0.49 ± 0.03
50	20	500	26	200	2200	12	312	1.18619	0.60 ± 0.03

Table S3a: UV-Vis data for concentration of PSS in supernatant phase at varying temperatures for sample prepared at C_{pi} =0.3 mol/L and C_{KBr} =2.05 mol/L

T (°C)	Supernatant volume (µl)	Added 2.5 mol/L KBr volume (µl)	Dilution factor (β)	Absorption (A)	$C_{PSS,SUP}$ (mol/L)
10	20	2400	121.0	0.401927	0.078 ± 0.002
15	20	2400	121.0	0.344346	0.067 ± 0.001
20	20	2400	121.0	0.233526	0.045 ± 0.001
25	20	2400	121.0	0.265565	0.052 ± 0.001
30	20	2400	121.0	0.217625	0.042 ± 0.001
35	20	2400	121.0	0.167371	0.032 ± 0.001
40	20	2400	121.0	0.124628	0.024 ± 0.0005
50	20	2400	121.0	0.132197	0.025 ± 0.0006

Table S3b: UV-Vis data for concentration of PSS in dense coacervate phase at varying temperatures for sample prepared at C_{pi} =0.3 mol/L and C_{KBr} =2.05 mol/L

T (°C)	Coacervate volume (µl)	Added 2.5 mol/L KBr volume (µl)	β_1	Volume diluted (µL)	Added 2.5 mol/L KBr volume (µl)	β_2	($\beta=\beta_1\times\beta 2$)	Absorption (A)	$C_{PSS,cov}$ (mol/L)
10	50	500	11.0	20	2200	111	1221.0	0.08572	0.17 ± 0.02
15	65	500	8.7	50	2200	45	391.2	0.29012	0.18 ± 0.01
20	85	500	6.9	50	2200	45	309.7	0.42833	0.21 ± 0.01
25	90	500	6.6	50	2200	45	295.0	0.36419	0.17 ± 0.01
30	95	500	6.3	50	2200	45	281.8	0.47203	0.21 ± 0.01
35	90	500	6.6	50	2200	45	295.0	0.31929	0.15 ± 0.009
40	90	500	6.6	50	2200	45	295.0	0.47465	0.23 ± 0.01
50	95	500	6.3	20	2200	111	695.2	0.23392	0.26 ± 0.03

Table S4a: UV-Vis data for concentration of PSS in supernatant phase at varying temperatures for sample prepared at C_{pi} =0.6 mol/L and C_{KBr} =2.0 mol/L

T (°C)	Supernatant volume (µl)	Added 2.5 mol/L KBr volume (µl)	Dilution factor (β)	Absorption (A)	$C_{PSS,SUP}$ (mol/L)
10	40	2400	61	0.8697	0.085 ± 0.004
20	40	2400	61	0.4299	0.042 ± 0.002
30	40	2400	61	0.3027	0.030 ± 0.002
40	40	2400	61	0.2717	0.027 ± 0.001

Table S4b: UV-Vis data for concentration of PSS in coacervate phase at varying temperatures for sample prepared at C_{pi} =0.6 mol/L and C_{KBr} =2.0 mol/L

T (°C)	Supernatant volume (µl)	Added 2.5 mol/L KBr volume (µl)	Dilution factor (β)	Absorption (A)	$C_{PSS,SUP}$ (mol/L)
10	40	2400	61	0.3723	0.358 ± 0.020
20	40	2400	61	0.5048	0.485 ± 0.027
30	40	2400	61	0.5924	0.570 ± 0.031
40	40	2400	61	0.5735	0.551 ± 0.030