Electronic Supplementary Material (ESI) for Soft Matter.

Early stage kinetics of polyelectrolyte complex coacervation monitored through stopped-flow light scattering

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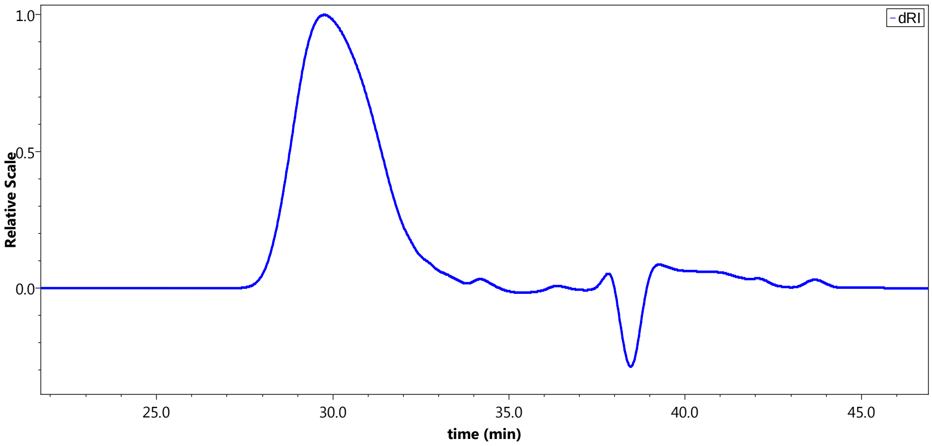
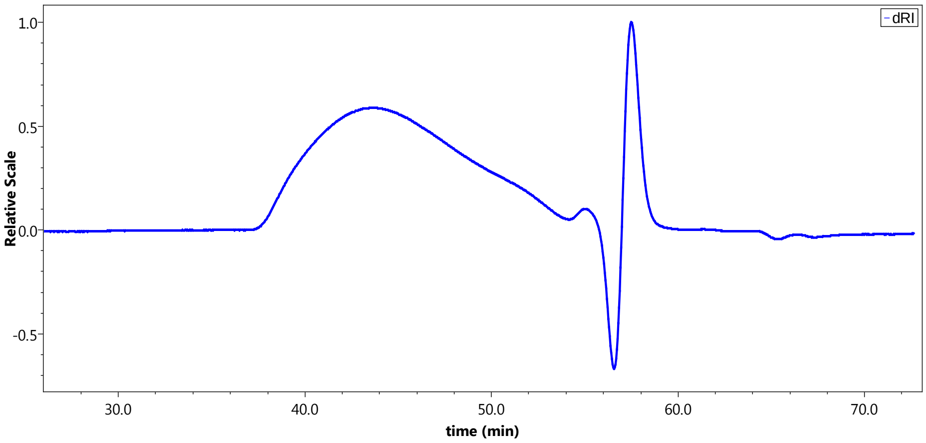
1. Experimental Section

1.1 SEC-MALS characterization of PAA and PDADMAC. Non-purified PAA and purified PDADMAC were characterized by size-exclusion chromatography with a multiangle light scattering detection (WYATT, Dawn Heleos) and a differential refractive index detector (WYATT, Optilab rEX) in order to determine the average molecular weights and dispersity of both polymers. PAA was analyzed in 0.01M Na_2HPO_4 / 0.2 M $NaNO_3$, pH 9 using two columns from Shodex (OHpak SB-804 HQ) and a guard column. PDADMAC was analyzed in 0.3 M CH_3COOH / 0.2 M CH_3COONa using three Tosoh TSK gel columns (G6000PWXL, G4000PWXL, G3000PWXL) and a guard column. The flow rate was set to 0.6 mL/min and the injected volume was 100 µL. The dn/dc values were determined for each polymer with a differential refractive index detector (WYATT, Optilab rEX) in same buffer conditions as for the chromatographic elution. Differential refractive index (dRI) chromatogram traces and average molecular weight results are given below.

PAA



PDADMAC



Polymers	dn/dc (mL/g)	M_n (g/mol)	M_w (g/mol)	Polydispersity
PAA	0.1242	2560	3730	1.45
Purified PDADMAC	0.1887	44200	70100	1.59

1.2 Methods

Conductance SF technique. The conductivity stopped flow experiments were carried out on a SFM-4000 coupled to the MCS-200 Modular Conductivity System (Bio-Logic SAS, France) on BK-MCS software[1]. The MCS-200 is a rapid impedance spectrometer. It allows to measure steady-state spectra of the impedance of a solution and to follow rapid changes in the solution's impedance in the course of a reaction (time course measurements). The principle of the detection technique is to impose a high-frequency electrical voltage in the solution between two electrodes and to follow the time course of the resulting current. The SFM was equipped with a Berger Ball mixer. Samples have been shot through the FC-20 cuvette equipped with two gold electrodes. The constant of the cell has been measured to 8 cm^{-1}. The flow rate has been set at 16mL/s giving a dead time of 3.7 ms. Steady state impedance spectrum have been performed on the final mixture to define the frequency of excitation for kinetics establishment. The time resolution was 200 µs per data point. PAA/PDADMAC complexation at a mixing ratio z = 1.1 without added salt was studied by conductance SF technique. As comparison, the dilution of KCl solutions (8 mmol) with water at a mixing ratio of 1:1 was also recorded.

[1] mcs-200-conductivity-measurements

Light scattering measurement. Dynamic light scattering experiment was carried out on an ALV light-scattering apparatus with a 22mW He-Ne linear polarized laser operating at fixed wavelength of 632.8 nm. The scattered intensity of all the samples was recorded at a scattering angle of 90°. The temperature was kept at 20 °C. The static intensity was obtained by averaging the photon count rate over 60s. The intensity fluctuations were analyzed automatically and in a single run by means of an ALV-5000/EPP multi-τ digital correlator with 125 ns initial sampling time The distribution of relaxation times was obtained by applying the Contin method and the hydrodynamic radii derived through application of the Stokes Einstein equation.

Complexation kinetics by DLS. A Malvern Nanosizer operating at λ=633 nm with a detection angle of 90° was used to monitor the kinetics of complexation of the PAA/PDADMAC system at z = 1.1. The PAA solution was directly added into the PDADMAC solution in a low volume quartz cell (total volume of solution = 80 µL). Successive runs of 10s were performed to determine the variation of the scattered intensity (Derived Count Rate). A Contin analysis was applied to obtain the size distribution from which only the main peak was considered to plot the size variation versus time. Hydrodynamic diameter was determined through successive acquisitions of 10s.

Refractive index increments (dn/dc) of PECs . Refractive index increments of PECs were determined using a differential refractive index detector (WYATT, Optilab rEX) operating at λ=658 nm at 25°C. A defined volume of PEC suspension obtained at each molar fraction of PAA was injected at a flow rate of 0.6 mL/min using a 10^{-4}M NaOH solution as eluent. The dn/dc value was obtained from the integration of the corresponding peak area, considering the total polymer mass concentration.

Optical microscope observations. The morphology of the complexes was examined by optical microscopy (Nikon ECLIPSE E600 POL) with COHU high performance CDD camera.

Viscosity measurement of the coacervate phase. The complex solution made at stoichiometry was first centrifuged for 15 min at 10 000g. The supernatant phase was carefully removed by using a micropipet. The sediment phase remaining at the bottom was obtained as viscous liquid. The viscosity of the coacervate phase is measured in a parallel-plate geometry driven by a stress-controlled rheometer (AR2000, TA instruments). The upper aluminum plate has a diameter of 40 mm. The bottom plate consists in a Teflon coated Peltier unit to control the temperature of the sample. The gap between two plates is 500 µm and is filled with the viscous liquid. Viscosity measurement is performed at 20 °C.

Stopped-flow small angle neutron scattering experiment. The time resolved neutron experiment was carried out on the D22 instrument at the Institut Laue Langevin, Grenoble. For the kinetic measurements the instrument configuration (λ = 6 Å, D = 8m, Coll = 8m, detector offset = 400 mm) was used to cover a q-range from 2.5 10^{-3} to 0.045 $Å^{-1}$. The data were radially averaged, corrected from background and normalized in absolute scale using standard ILL software (Lamp and Grasp[2]). A second treatment was consisting in integrating after data correction and normalization the total number of counts in the detector window for each frame, to extract the evolution of I(0) as a function of time.

A Bio-Logic SFM-3 stopped-flow apparatus equipped with a Berger Ball mixer was used to mix rapidly the polyelectrolyte solutions. The mixing was done at a flow rate of 4 ml/s and a total volume of 804 µl was injected in a 1 mm thick thermostated neutron cell specially designed for the neutron experiment [3]. The dead time, mostly due to the cell filling was (0.250/flow rate) ms. The time per frame, with an initial time of 200 ms , was increased following a geometric series with an increment of 1.1 during 30 s. Each experiment was repeated 5 times to allow for accumulation and increase the statistics. This was followed by 5 s measurements until the end of the experiment.

[2] Lamp; Grasp

[3] I. Grillo, Current Opinion in Colloid & Interface Science 14 (2009) 402–408.

2. Viscosity of the coacervate phase

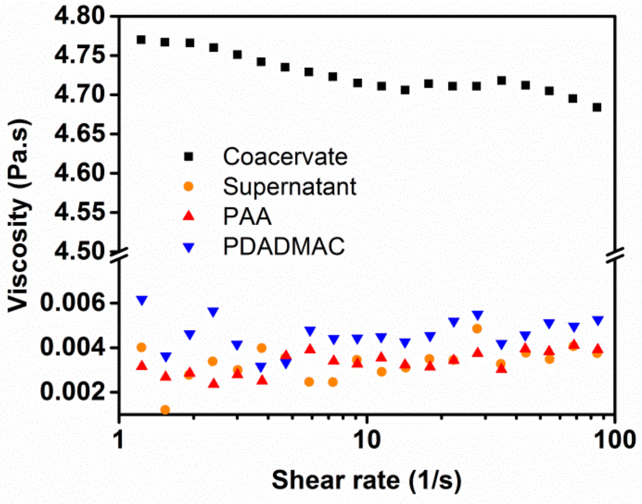


Figure S1. Viscosity of PAA/PDADMAC coacervate (black square) prepared at pH 10 at f_{PAA} = 0.5 and c_{total} = 6.48 g/L and its supernatant (orange circle). Data for the pure PAA (c = 2 g/L) and PDADMAC (c = 4.48 g/L) solutions at pH 10 are shown as comparison.

3. Raw kinetic data recorded by SF light scattering technique

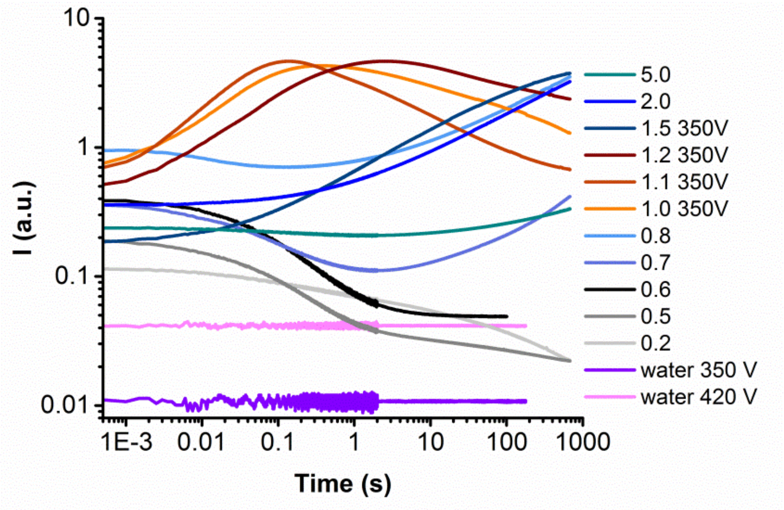


Figure S2. Raw data of PAA/PDADMAC complexes prepared at different mixing ratios *z* without added salt. All the curves are recorded at U = 420 V except the ones of mixing ratios from 1.0 to 1.5 at U = 350V.

4. Kinetic curves recorded by conductance SF technique

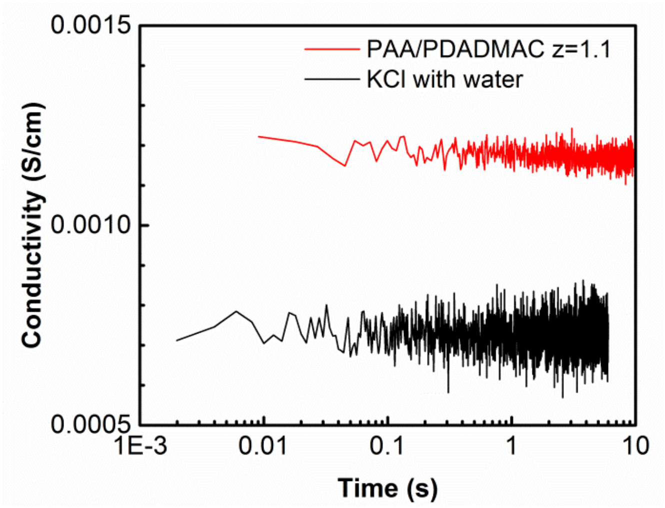


Figure S3. Kinetic curve of PAA/PDADMAC complex at pH 10 at mixing ratio z = 1.1 without added salt recorded by conductance SF technique. Mixing of KCl solution (8 mmol) with water at mixing ratio of 1:1 was also recorded as comparison. This result shows that the small ions releasing due to the complexation of two polyelectrolytes occurs during the dead time. There is no obvious ion release in the reorganization process of PECs, so the conductivity doesn't change with time. The sampling time in the first 2 seconds is 0.2ms, while 0.1s after 2 seconds.

5. Data fitting of the decay and growth kinetic curves

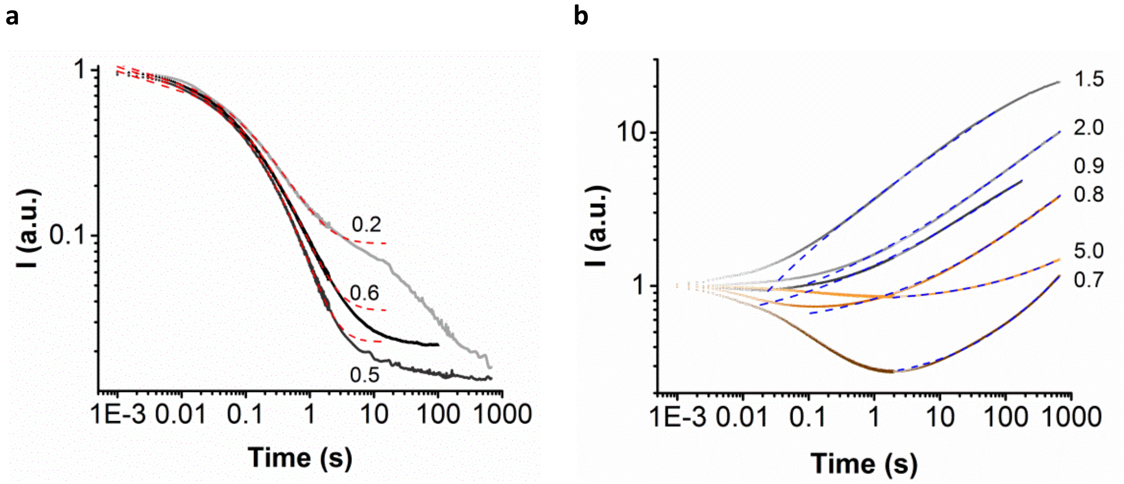


Figure S4. (a) Stretched exponential fitting ($I = I_\infty + A\,exp\left(-(t/\tau)^\beta\right)$) of the first decay process for PECs of *z* = 0.2 ~ 0.6. (b) Power law fitting ($I \sim \left(\frac{t}{\tau_g}\right)^d$) of the second growth stage for PECs of *f* = 0.7 ~ 2.0. The fitted results are indicated by the dash lines.

Table S1. Fitting parameters of the kinetic process of PAA/PDADMAC complexes at pH 10 without added salt

Z	Decay [a]			Growth [b]	
	β	τ/s	<τ>/s	τ_g/s	d
0.2	0.40	0.060	0.32		
0.5	0.45	0.076	0.32		
0.6	0.42	0.068	0.34		
0.7	0.47	0.048	0.19	4.53	0.542
0.8	0.77	0.012	0.019	0.78	0.380
0.9				0.42	0.315
1.1				0.0063	0.285
1.5				0.051	0.284
2.0				0.28	0.339
5.0	0.51	0.11	0.37	2.60	0.412

[a] Fitted with stretched exponential function $\boldsymbol{I = I_\infty + A\,exp\left(-(t/\tau)^{\beta}\right)}$. The parameters I∞ and A are the asymptotic and initial intensity respectively. τ is the relaxation time constant. β (0 < β < 1) is the stretching parameter. The mean relaxation time <τ> can be obtained by $\boldsymbol{<\tau> = \frac{\tau}{\beta}\Gamma\left(\frac{1}{\beta}\right)}$, where $\boldsymbol{\Gamma(x)}$ is the gamma function. [b] Fitted with power law $\boldsymbol{I \sim \left(\frac{t}{\tau_g}\right)^{d}}$.

6. Kinetic curves recorded in transmission mode

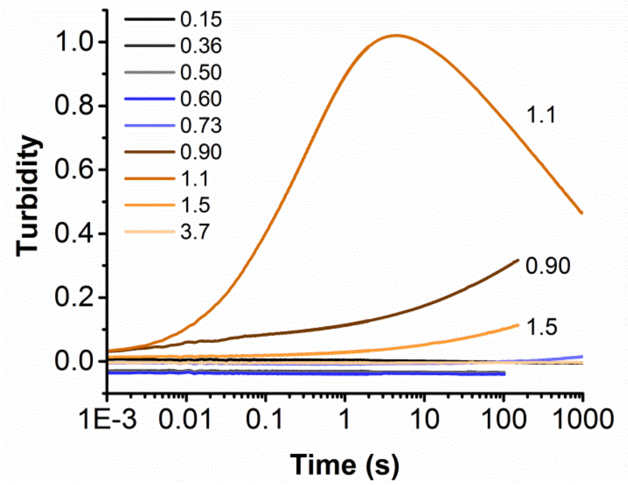


Figure S5. Kinetic curves of PAA/PDADMAC recorded in transmission mode at different mixing ratios at pH 10 without added salt.

7. Refractive index increment (dn/dc) of PECs

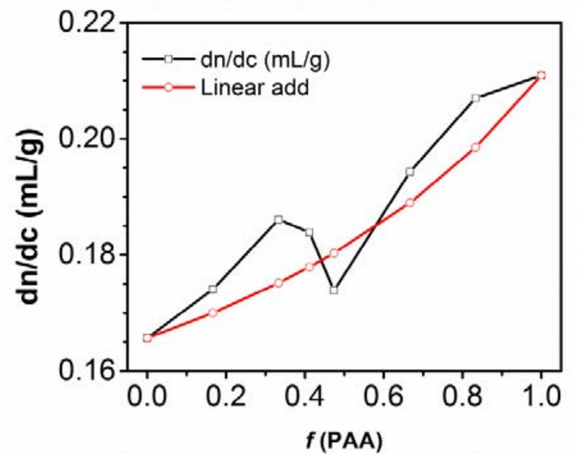


Figure S6. dn/dc of PAA/PDADMAC complexes at different mixing ratios at pH 10. The mixing ratio is expressed by the molar fraction of PAA, *f*=z/(1+z). Data shown in black squares are measured directly with a differential refractometer. Red circles represent the theoretical fraction-weighted linear sum of the PAA and PDADMAC dn/dc values at a given mixing ratio *f*.

8. Kinetic study by DLS (Malvern) of PAA/PDADMAC complexes prepared by one-shot mixing

To follow the intensity and the size evolution of the complexes, PAA/PDADMAC complexes were prepared by one-shot mixing at charge ratio z = 1.1 at pH 10 without added salt. After mixing for 10s, the sample was used for DLS measurement at 90° every 10s for 887 running times. During each measurement, the intensities were obtained from the average of count rate, while the hydrodynamic radius of the particles derived through application of the Stokes Einstein equation.

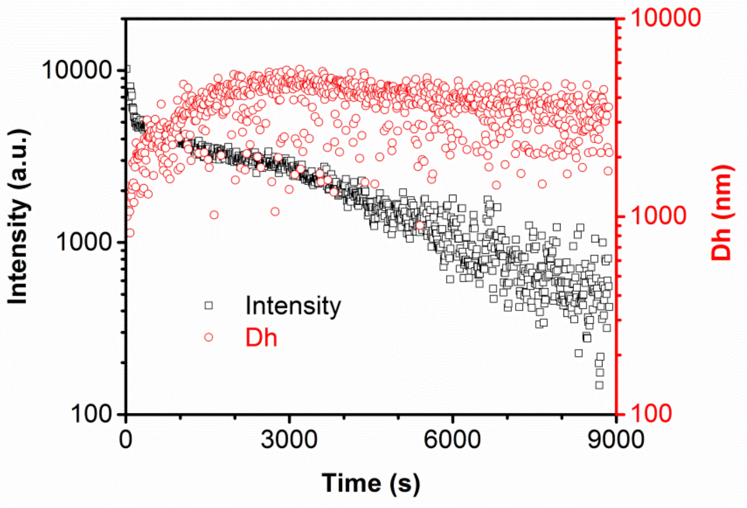


Figure S7. Evolution of light scattering intensity (at 90°) and hydrodynamic diameters of

PAA/PDADMAC complex at z = 1.1. The sample was measured immediately after preparation (about 10s) every 10s. The intensity decay agrees well with the decay part of the bell-shaped curves observed by SF light scattering technique (Figure 2). At the same time, the sizes of the particles keep increasing to a few microns, suggesting that neutralized PECs are condensed into coacervate droplets which contributes little to the scattering intensity.

9. Optical microscope images of PECs prepared by SF mixing

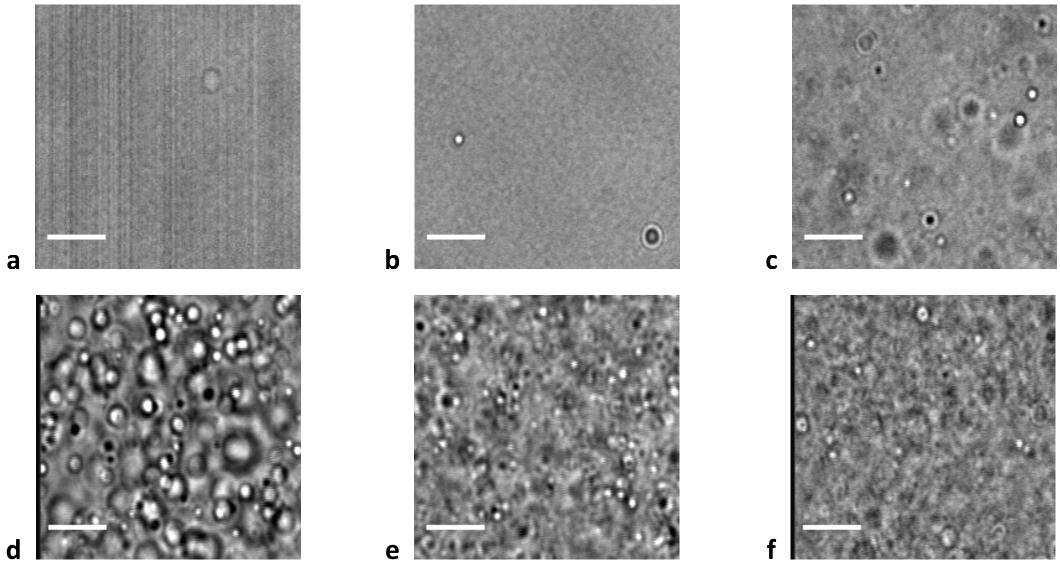


Figure S8. Optical images of PAA/PDADMAC complexes prepared at pH 10 with 0.01M NaCl at different mixing ratios. (a) *z* = 0.2; (b) *z* = 0.5; (c) *z* = 0.8 ; (d) *z* = 1.0; (e) *z* = 2.0; (f) *z* = 5.0. The scale length is 50 µm.

10. Data fitting of typical bell shape curves upon coacervation

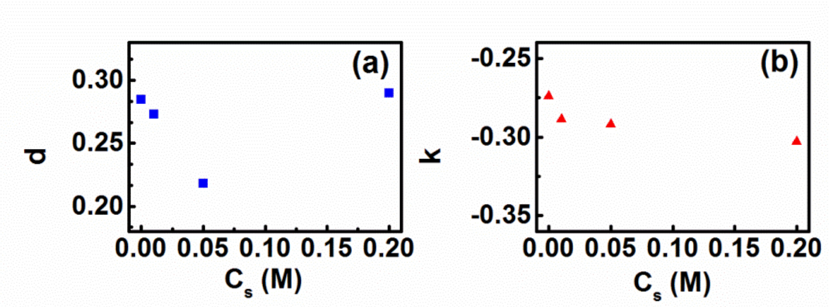


Figure S9. Power law fitting to the growth (a) and decay (b) parts of the coacervation stage (z = 1.0, stoichiometry) at different salt concentrations. For the growth part (a), d is the scaling factor from $I\sim\left(\frac{t}{\tau_g}\right)^d$. For the decay part (b), k is the scaling factor from $I\sim\left(\frac{t}{\tau_d}\right)^k$.

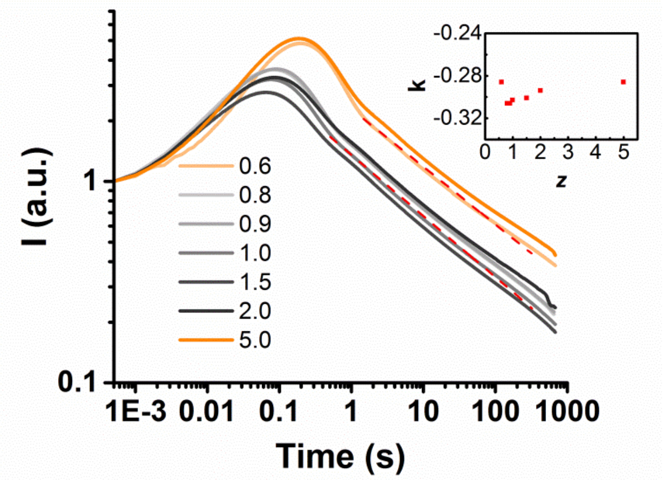


Figure S10. Kinetic curves of coacervate phases of PAA/PDADMAC at mixing ratios from 0.6 to 5.0 under 0.2M NaCl. The red dashed lines power law fits from $I \sim \left(\frac{t}{\tau_d}\right)^k$ suggest that coacervation shares a universal mechanism under different conditions. The inset shows the scaling factor *k* from a power law fit of the decay part of the coacervation process.