Electronic Supplementary Information

Sodium dodecyl sulfate modulates the structure and rheological properties of Pluronic F108 - poly(acrylic acid) coacervates

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The pH for the formation of the coacervates was selected based on turbidimetric titration of the solution of 105mM F108 respect to PEO unit, 20mM PAA respect to repeat unit and different concentration of SDS. The turbidity of the solution was measured as a function of pH using a 2 cm path length fibre-optic probe colorimeter (Brinkmann PC 950). The colorimeter was calibrated against Milli-Q water (100% transmittance). The pH of the solution was measured with a pH-meter (SevenCompact Duo S213-meter pH/Conductivity S213, METTLER TOLEDO) that was calibrated against buffers with pH of 4.01, 7.00 and 10.01. The pH of the PAA/F108 solution was decreased from pH = 3.50 to pH = 1.50 in increments of 0.05 using 1M HCl. Figure S1 illustrates the turbidimetric titration for a variety of SDS concentrations.
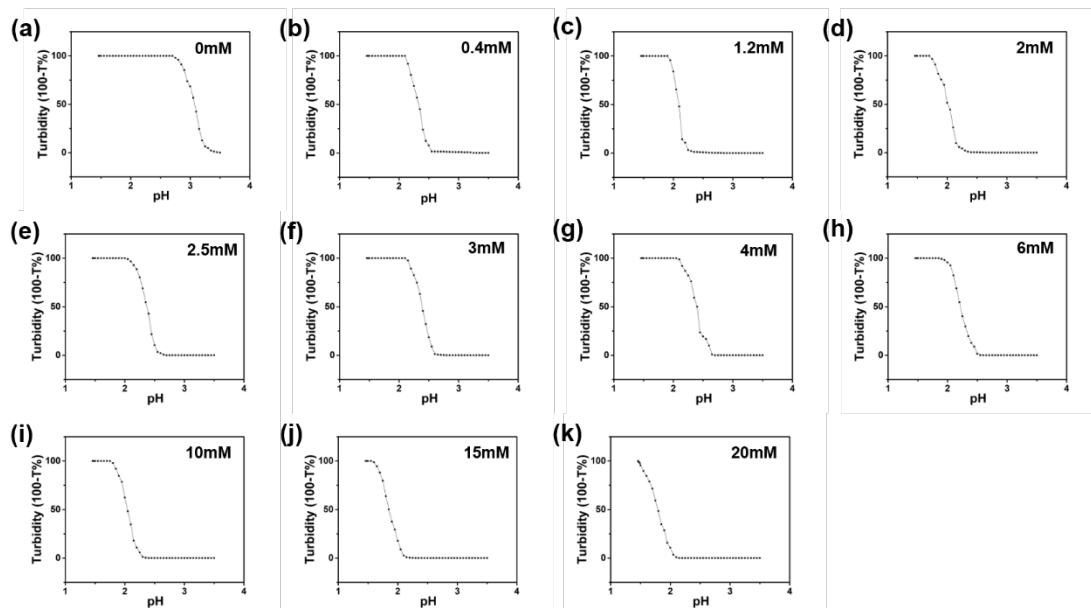

Figure S1. Turbidity measurements to determine the pH dependence for the formation of PAA/F108/SDS coacervates. The [SDS]$_{Sol}$ was varied from 0 – 20 mM with fixed concentration of PAA and F108.

Table S1. Peak assignments of ^{1}H NMR spectra for determining the composition of the coacervates

Chemical shift	Functional group	Sign	Material
0.9 to 1.1 ppm	Methyl group on PPO	$A_{(0.9\text{-}1.1\ ppm)}$	F108
1.1 to 1.9 ppm	Methylene group	$A_{(1.15\text{-}1.9\ ppm)}$	PAA
2.0 to 2.4 ppm	Methine group	$A_{(1.95\text{-}2.4\ ppm)}$	
1.3 to 1.4 ppm	$(\text{-CH}_2\text{-})_9$	$A_{(1.3\text{-}1.4\ ppm)}$	SDS

The NMR spectrum shows that the SDS signal ($\delta H=1.3\text{-}1.4$ ppm) is overlapped by the methylene group of PAA ($\delta H=1.15\text{-}1.9$ ppm). To calculate the fraction of SDS, we first calculate the ratio of

the peak area between the methylene group and methyl group of PAA. $A_{(x\text{-}y\,ppm)}$ refers to the area of peak integrated from x to y ppm.

$$r = \frac{A_{(1.1-1.9\,ppm)}}{A_{(2.0-2.4\,ppm)}} \,(1)$$

Then the peak area of SDS is determined by using equation 3.

$$A_{(1.3-1.4\,ppm)} = A_{(1.1-1.9\,ppm)} - A_{(2.0-2.4\,ppm)} * r \,(2)$$

The relative mass of each component is calculated with the respect of repeat unit (PAA is respect to the acrylic acid, F108 is respect to the PEO part) using equation 4 ~ 6

$$m_{PAA} = \frac{A_{(2.0-2.4\,ppm)}}{1} M_{PAA} \,(3)$$

$$m_{F108} = \frac{A_{(0.9-1.1\,ppm)}}{3} * \frac{n_{PEO}}{n_{PPO}} * \frac{M_{PEO}}{M_{F108} - M_{PPO} * n_{PPO}} * M_{F108} \,(4)$$

$$m_{SDS} = \frac{A_{(1.3-1.4\,ppm)}}{18} * M_{SDS} \,(5)$$

$M_{component}$ refers to the molecule weight of component while $n_{component}$ refers to the number of polymerizations of the component. The relative mass of PAA, F108, SDS were then transformed into weight fraction.
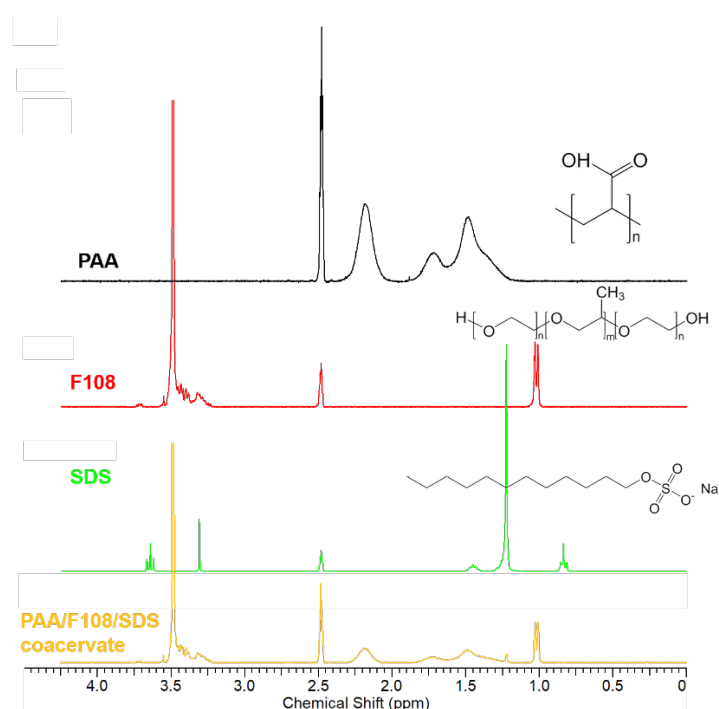

Figure S2. ^{1}H NMR spectra of individual PAA, F108, SDS and PAA/F108/SDS coacervate prepared with [PAA]$_{Sol}$ = 20mM. The coacervate was dried in vacuum oven at 50 °C for at least 24 h and then dissolved in deuterated DMSO (DMSO-d6) .
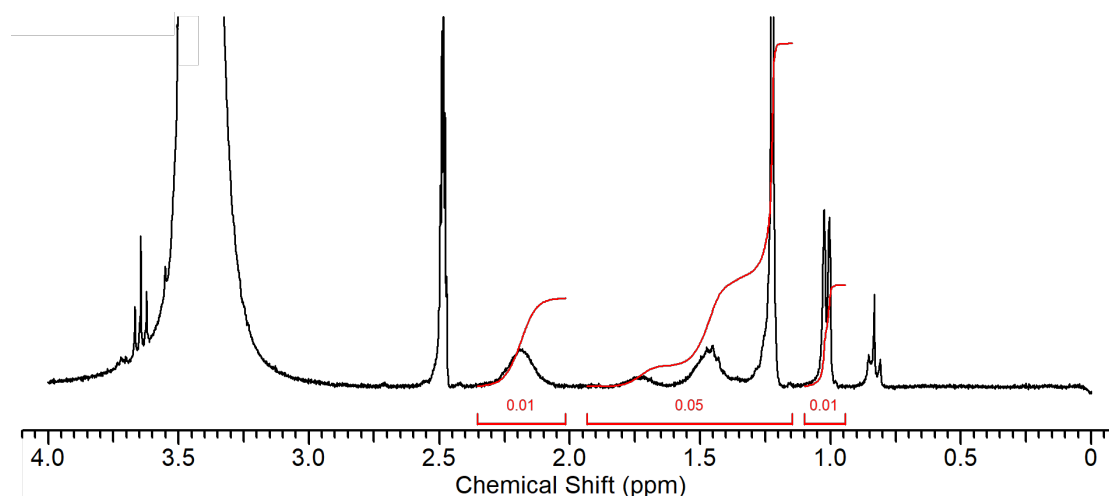
Figure S3. ^{1}H NMR spectra of a known mixture of PAA (35 wt%), F108 (50 wt%), and SDS (15 wt%). The composition calculated from the NMR spectra is PAA (33.2 wt%), F108 (51.1wt%), and SDS (15.7 wt%).
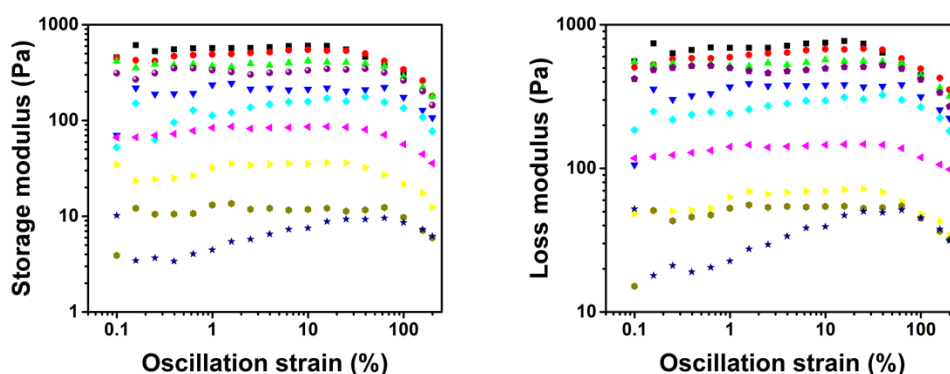

Figure S4. Strain sweep experiment from 0.1% to 200% at 1 rad/s for PAA/F108 coacervate with varying [SDS]$_{Sol}$ from 0 mM (top) to 9 mM (bottom).

The strain sweeps performed in Figure S4 were used to determine the appropriate strain for frequency sweeps that use a different sample from the same coacervate. At low strain, the moduli are noisy due to being near the low torque limit of the rheometer. For the highest SDS concentration examined, the coacervate is extremely soft and the torque generated is near the low torque limit. This results in a non-linear response with strain.
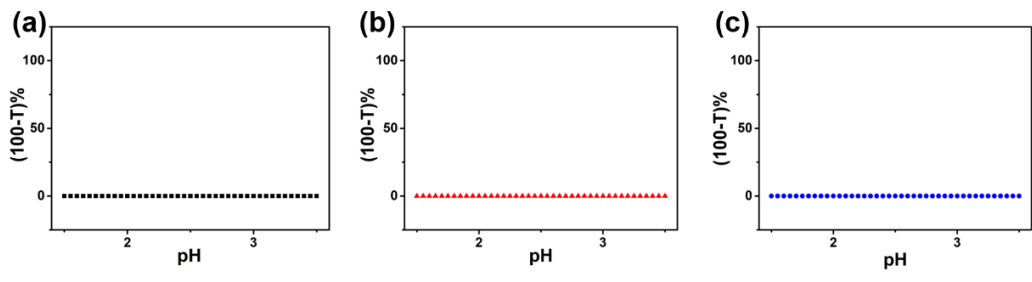
Figure S5. Turbidimetric titration of **(a)** pure PAA and **(b)** pure SDS **(c)** PAA/SDS mixed solution, demonstrating that these are stable (single phase) through the entire pH range examined.
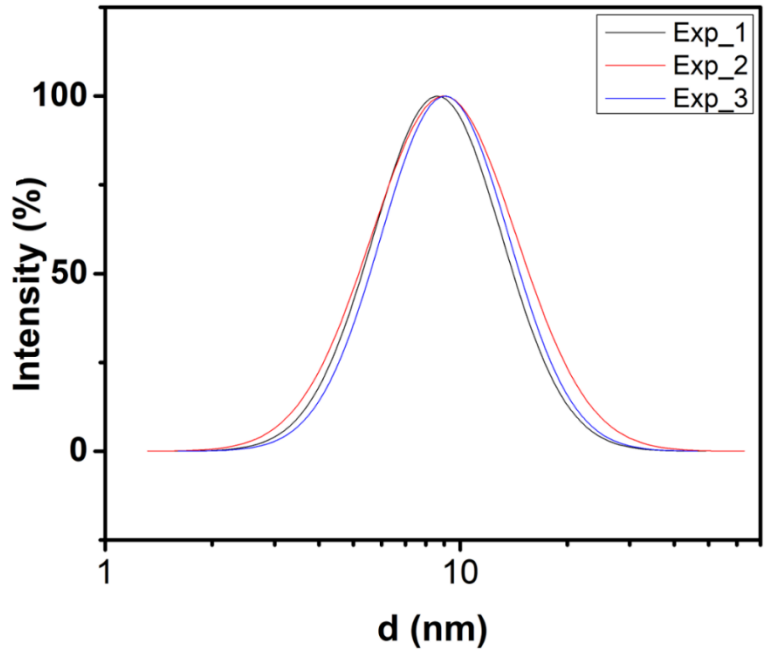

Figure S6. DLS data for 0.5 wt% F108 aqueous solution at pH = 7. The experiment was performed in triplicate to illustrate robustness in the assembly of this batch of the surfactant at this concentration that is below the typically reported CMC for Pluronic F108.
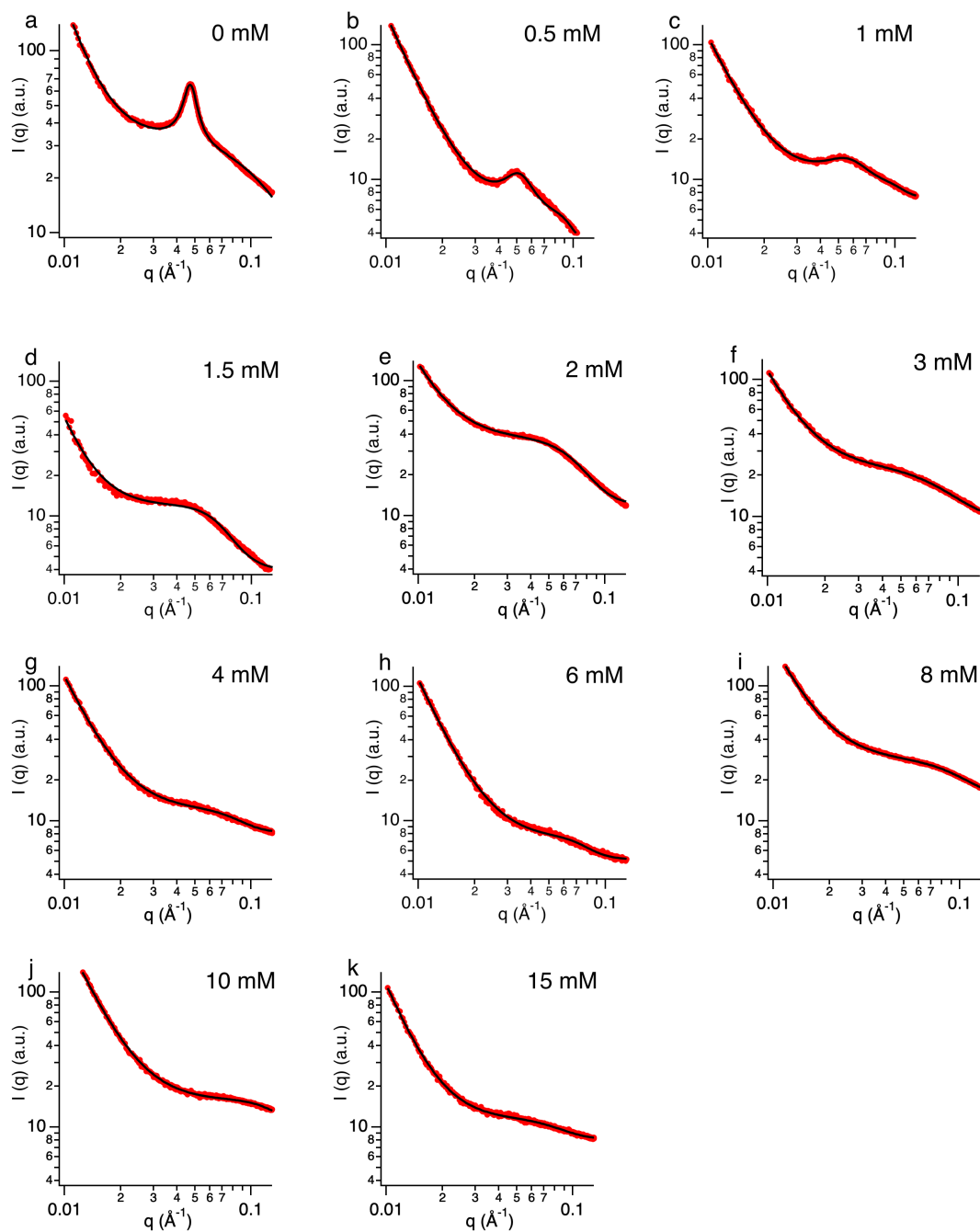
Figure S7. SAXS profiles for the PAA/F108 coacervates fabricated with [SDS]$_{Sol}$ of (a) 0 mM, (b) 0.5 mM, (c) 1 mM, (d) 1.5 mM, (e) 2 mM, (f) 3 mM, (g) 4 mM, (h) 6 mM, (i) 8 mM, (j) 10 mM, and (k) 15 mM. The solid black line is the fit to a correlation length model that includes a broad peak term for [SDS]$_{sol}$ <1.5 mM.

The correlation length models used for fitting the SAXS data are:

$$I(q) = \frac{A}{q^n} + \frac{C}{1+(q\xi_L)^m} + B \quad \text{for [SDS]sol} \geq 1.5$$

$$I(q) = \frac{A}{q^n} + \frac{C}{1+(q\xi_L)^m} + \frac{D}{(q-q_0)^2+\delta} + B \quad \text{for [SDS]sol} < 1.5$$

Table S2. Physical parameters obtained from the fits of the SAXS profiles for the different coacervates.

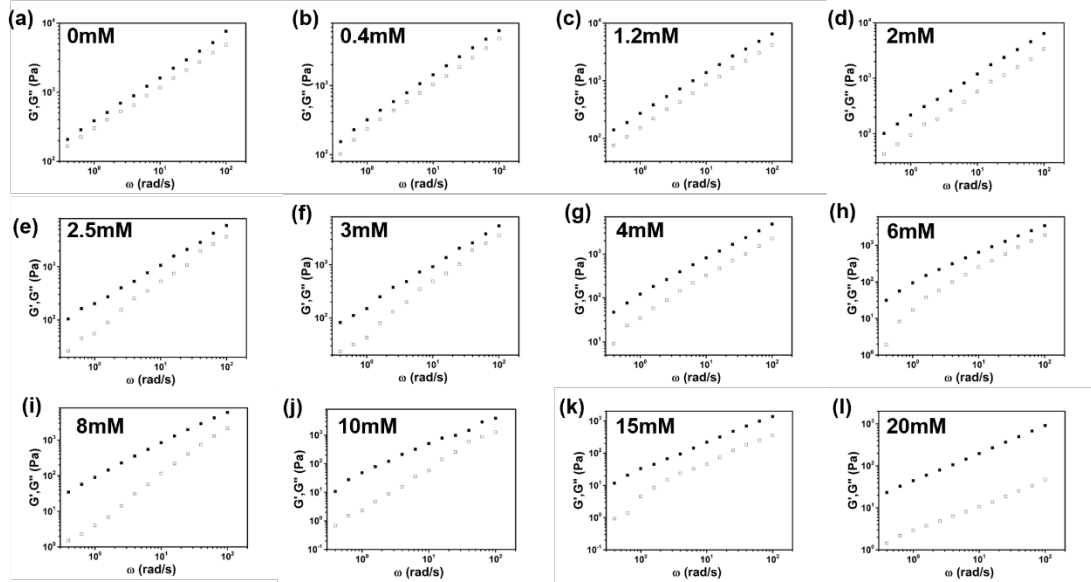| [SDS]$_{sol}$ (mM)	n	ξ_L (Å)	q_0 (Å^{-1})
0	2.82	10.72	0.04705
0.5	3.17	10.36	0.05093
1	2.98	9.18	0.05417
1.5	*3.22*	*6.19*	*0.04014*
1.5	3.66	14.05	---
2	3.25	14.48	---
3	2.94	12.19	---
4	3.03	11.99	---
6	3.14	12.76	---
8	2.88	9.87	---
10	3.02	9.38	---
15	3.32	8.10	---

Figure S8. Frequency sweeps at 3% strain for PAA/F108 coacervate with varying [SDS]$_{Sol}$. (Storage modulus G', □, loss modulus G", ■)
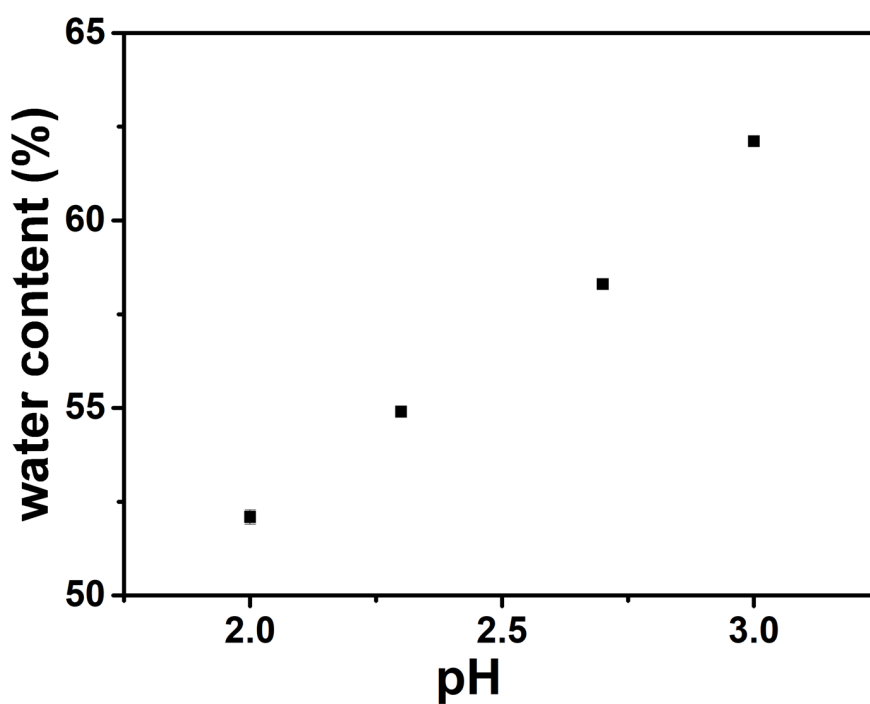
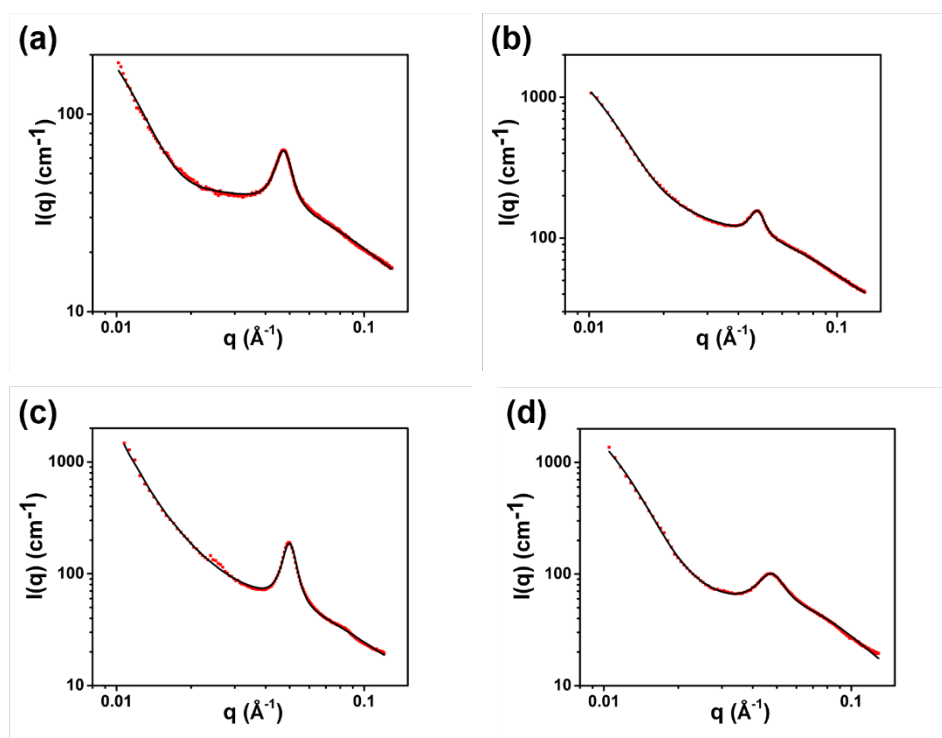**Figure S9.** Water content of PAA/F108 coacervates prepared at different pH.

Figure S10. SAXS profiles for the PAA/F108 coacervates fabricated with pH at (a) 2.0 (b) 2.3 (c) 2.7 (d) 3.0 with 0 mM [SDS]$_{Sol}$