Supplemental Material

Fluidity and water in nanoscale domains define coacervate hydrogels

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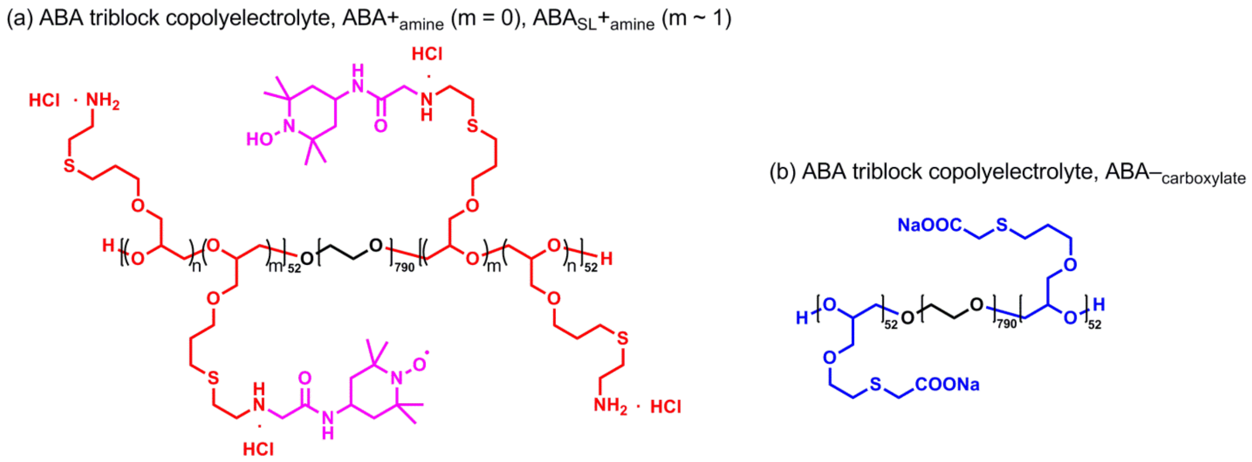
I. Viscous solution complexes

Oppositely charged triblock copolyelectrolytes whose pK_a values do not differ enough allow for partitioning of the A blocks are shown in Fig. S1. The difference in pK_a between the cationic A blocks of **ABA+$_{\text{amine}}$** and the anionic A blocks of **ABA-$_{\text{carboxylate}}$** is 5.8. This low ΔpK_a value is in contrast to the ΔpKa of 15.1 for **ABA+/ABA-** which yields domain partitioning and hydrogel formation.



(a) ABA triblock copolyelectrolyte, ABA+$_{\text{amine}}$ (m = 0), ABA$_{\text{SL}}$+$_{\text{amine}}$ (m ~ 1)

(b) ABA triblock copolyelectrolyte, ABA–$_{\text{carboxylate}}$

Fig. S1 Chemical structures of triblock copolyelectrolytes that form viscous solutions when mixed.

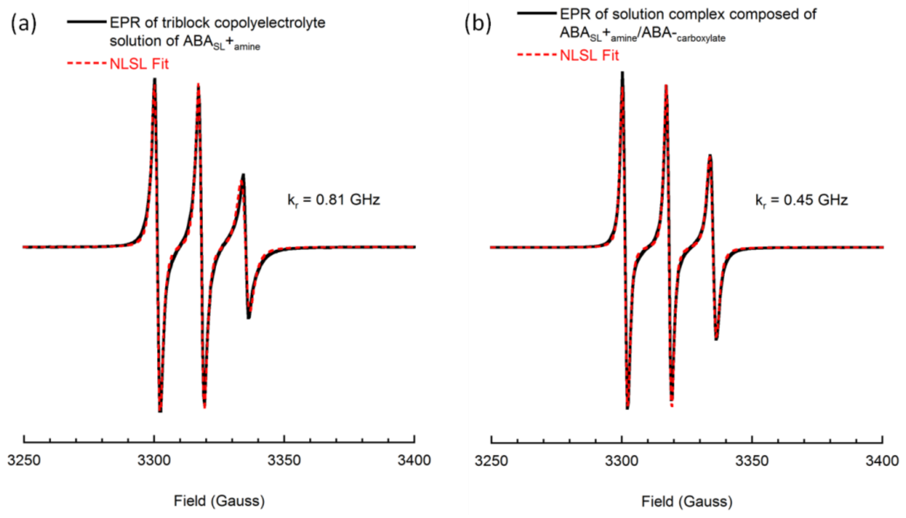


Fig. S2 EPR of (a) **ABA$_{SL}$+$_{amine}$** solution, and (b) **ABA$_{SL}$+$_{amine}$ / ABA-$_{carboxylate}$** solution complex.

Table S1 Rotational diffusion rates determined by EPR and water diffusion coefficients determined by ODNP of ABA triblock copolymers and their solution complexes. The spin labels are positioned in the A block of the cationic polyelectrolyte and show subtle differences in both rotational diffusion rate and water diffusion coefficient upon mixing.

	ABA$_{SL}$+$_{amine}$ (solution)	ABA$_{SL}$+$_{amine}$/ABA-$_{carboxylate}$ (solution complex)
Rotational diffusion rate k_r (GHz)	0.80	0.45
Water diffusion coefficient, D ($\times 10^{-9} m^2 s^{-1}$)	0.92	0.69

Table S2 Rotational diffusion rates determined by EPR and water diffusion coefficients determined by ODNP of ABA triblock copolymers and their solution complexes. Spin labeled PEO is added to the triblock copolymer solution complexes analogous to the hydrogel midblock probe in the main text. No change is detected in the EPR fit for rotational diffusion rate upon mixing, and a subtle change in water diffusion coefficient is observed.

	ABA+$_{amine}$/PEO$_{SL}$ (solution)	ABA$_{SL}$+$_{amine}$/ABA-$_{carboxylate}$/PEO$_{SL}$ (solution complex)
Rotational diffusion rate k_r (GHz)	0.80	0.80
Water diffusion coefficient D ($\times 10^{-9} m^2 s^{-1}$)	0.98	0.91

II. Homopolymer Complex Coacervates

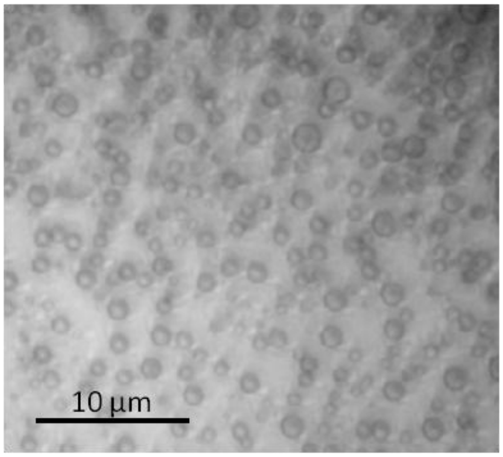


Fig. S3 Light microscope image of A block homopolymer complex coacervates (**A+**/**A-**)

III. Model for Fitting SANS Profile

Details of the fitting model have been available elsewhere.[1,2,3,4] A brief overview of the references will be discussed here. In the fitting, the hydrogels were assumed as spherical domains formed by complex coacervates that are connected by the PEO middle block in water matrix.

The scattering form factor for a micelle consisting of a spherical core and Gaussian corona chains attached to the core surface can be expressed with four contributions: the self-correlation of the core, the self-correlation of the corona chains, the cross term between the sphere and the

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[1] Pedersen, J. S.; Gerstenberg, M. C. *Macromolecules* **1996**, *29*, 1363–1365.

[2] Castelletto, V.; Hamley, I. W.; Pedersen, J. S. *J. Chem. Phys.* **2002**, *117*, 8124–8129.

[3] Castelletto, V.; Hamley, I. W.; Pedersen, J. S. *Langmuir* **2004**, *20*, 2992–2994.

[4] Pedersen, J. S.; Svaneborg, C.; Almdal, K.; Hamley, I. W.; Young, R. N. *Macromolecules* **2003**, *36*, 416–433.

corona chains, and the cross term between different corona chains.

$$\begin{aligned} P_{mic}(q) = {} & N_{agg}^2 \beta_{core}^2 A_{core}^2(q) + N_{agg} \beta_{corona}^2 P_{chain}(q) \\ & + 2N_{agg}^2 \beta_{core} \beta_{corona} A_{core}(q) A_{corona}(q) \\ & + N_{agg}(N_{agg} - 1) \beta_{corona}^2 A_{corona}^2 \end{aligned} \tag{A1}$$

Here q is the scattering vector, N_{agg} is the aggregation number, and β_{core} and β_{corona} are total excess scattering lengths of core and corona blocks, respectively. They are defined as $\beta_{\mathrm{core}} = v_{\mathrm{core}}\ (\rho^*_{\mathrm{core}} - \rho^*_{\mathrm{solvent}})$ and $\beta_{\mathrm{corona}} = v_{\mathrm{corona}}\ (\rho^*_{\mathrm{corona}} - \rho^*_{\mathrm{solvent}})$, where v_{core} and v_{corona} are the volume of the core and corona chains, respectively.

The self-correlation of the spherical core with radius R_c is given by

$$A_{core}^2(q) = \Phi^2(qR_c)\exp(-q^2\sigma_{\mathrm{int}}^2) \tag{A2}$$

where $\Phi(x) = 3[\sin(x) - x\cos(x)]/x^3$ is the hard-sphere form factor. The exponential term represents a decaying density at the core-corona surface, and σ_{int} takes into account the width of the interface.

The self-correlation of the corona chains is approximated by a Debye function:

$$P_{chain}(q) = \frac{2[\exp(-x) - 1 + x]}{x^2} \quad ; \quad x = q^2 R_g{}^2. \tag{A3}$$

The cross terms between core and corona and between corona chains include the form factor of the corona chains which is given as the normalized Fourier transform of the radial density distribution function of the corona chains, ρ_{corona}(r), as follows:

$$A_{corona}(q) = \frac{4\pi \int \rho_{corona}(r) \frac{\sin(qr)}{qr} r^2 dr}{4\pi \int \rho_{corona}(r) r^2 dr} \exp(-q^2 \sigma_{\mathrm{int}}^2 / 2) \qquad \text{(A4)}$$

In this study, a linear combination of two cubic *b* spline functions was chosen as ρ_{corona}(r).[4,5]

The total coherent scattering intensity takes into account both the form factor and a hard-sphere structure factor, $S(q)$:

$$I(q) = P_{mic}(q) + A_{mic}(q)^2 [S(q) - 1] \qquad \text{(A5)}$$

where $A_{\mathrm{mic}}(q)$ is the form factor amplitude of the radial scattering length distribution and expressed as

$$A_{\mathrm{mic}}(q) = N_{\mathrm{agg}} \left(\beta_{\mathrm{core}} A_{\mathrm{core}}(q) + \beta_{\mathrm{corona}} A_{\mathrm{corona}}(q)\right) \qquad \text{(A6)}$$

Equation (A5) can be modified by taking into account for polydispersity in micelle size.

$$I(q) = \int D(R_{\mathrm{c}}) \left(P_{\mathrm{mic}}(q) + A_{\mathrm{mic}}(q)^2 [S(q) - 1]\right) dR_{\mathrm{c}} \qquad \text{(A7)}$$

where $D(R_{\mathrm{c}})$ is Gaussian distribution function for core radii.

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[5] Bang, J.; Viswanathan, K.; Lodge, T. P.; Park, M. J.; Char, K. *J. Chem. Phys.* **2004**, *121*, 11489–11500.