Effect of Polyampholyte Net Charge on Complex Coacervation between Polyampholytes and Inorganic Polyoxometalate Giant Anions

Manuela Ferreira,[#] Benxin Jing,[#] Adrian Lorenzana, and Yingxi Zhu[*]

Department of Chemical Engineering and Materials Science,

Wayne State University, Detroit, MI 48202

[#] M. F. and B.J. equally contributed to this work

[*]Corresponding author (yzhu3@wayne.edu)

Supporting Information

Figure S1. a) pH-dependent UV-vis spectra of (i) 10 μM free fluorescein and (ii) 10 g/L *f-PA$_x$M$_y$* in buffer solutions of varied pH=2-10. The dash line indicates the location of primary UV-Vis absorbance peak, Abs$_{500}$, which shifts from 490 nm for the case of free fluorescein to 500 nm for *f-PA$_x$M$_y$* due to local environment change**. b)** pH-dependent UV-vis absorbance at absorption peak of 500 nm wavelength, Abs$_{500}$ (490 nm for free fluorescein) at C_{KCl} = 0.1M for free fluorescein (black squares), *f- PA$_{45}$M$_{55}$* (red circles), and *f-PA$_{55}$M$_{45}$* (blue triangles).

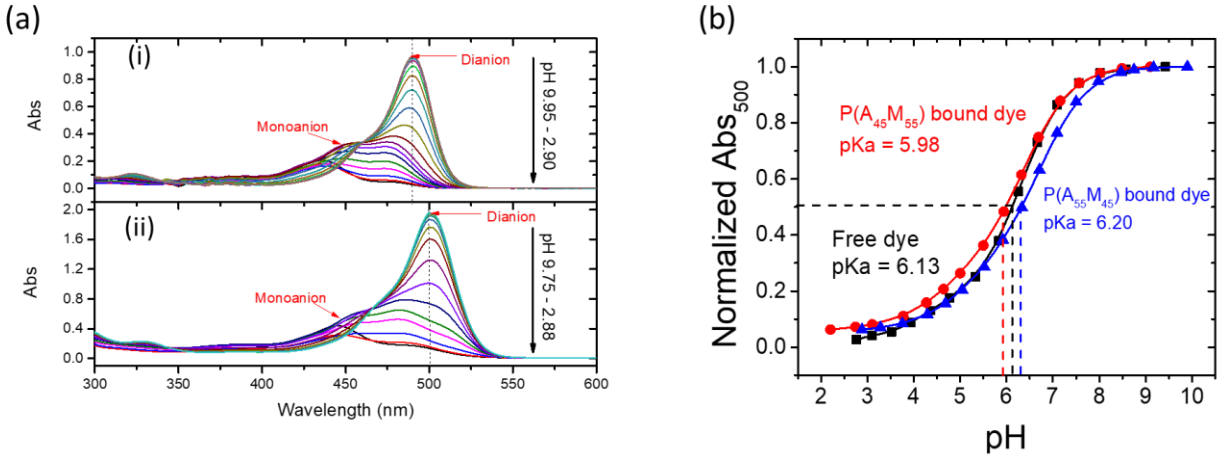

Figure S2. Fluorescence micrographs of the morphology of $PA_{50}M_{50} - \{W_{12}\}$ dense coacervates formed at $C_{A_xM_y}$ = 89.6 mM, $C_{e^-(W12)}/C_{A_xM_y}$ = 60%, and C_{LiCl} = 0.2 M, after repeat centrifugation to thoroughly remove the supernatant solution.

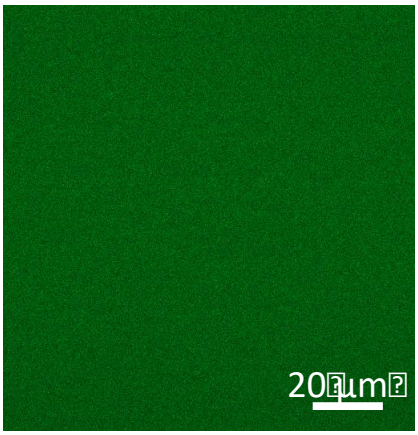

Figure S3. Linear frequency-dependent shear spectra of measured elastic moduli, G' (solid symbols) and viscous moduli, G'' (open symbols) of $PA_xM_y - \{W_{12}\}$ dense coacervates formed at constant $C_{A_xM_y}$ = 89.6 mM, $C_{e^-(W12)}/C_{A_xM_y}$ = 60%, and C_{LiCl} = 0.2 M at constant strain γ = 1% against ω at varied temperature, T = 2 °C (pink stars), 10 °C (green hexagons), 22 °C (magenta diamonds), 30 °C (blue triangles), 42 °C (red circles), and 58 °C (black squares) for (a) $PA_{45}M_{55}$, (b) $PA_{50}M_{50}$, and (c) $PA_{55}M_{45}$.

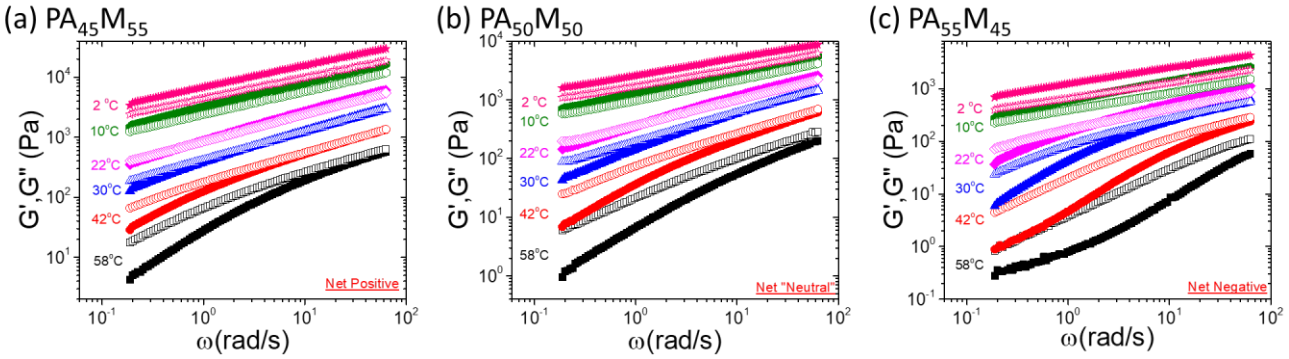

Figure S4. Temperature-dependent shift factor, a_T, from the time-temperature superimposition of the linear shear spectra of PA_xM_y –{W_{12}} dense coacervates with $PA_{45}M_{55}$ (black squares), $PA_{50}M_{50}$ (red circles), and $PA_{55}M_{45}$ (blue triangles) as shown in Figure S3a-c, respectively, where T_r = 22℃ is the room temperature, thus selected as the reference temperature in this work.

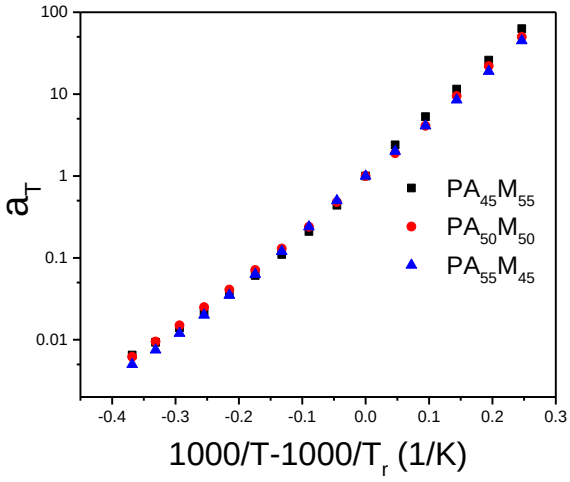

Figure S5. Time-temperature superposition master curves of shear moduli G' (solid symbol), G" (open symbol) of (a) $PA_{45}M_{55}$-{W_{12}} and (b) $PA_{50}M_{50}$-{W_{12}} gel against shifted angular frequency, ωa_T for the complexes formed at constant $C_{A_xM_y}$ = 89.6 mM, $C_{e^-(W12)}/C_{A_xM_y}$= 1200%, and C_{LiCl}= 0.2 M at constant strain γ = 1%. Linear shear spectra were obtained at varied T = 2-58℃ and T_r = 22℃ is selected for time-temperature superposition analysis.

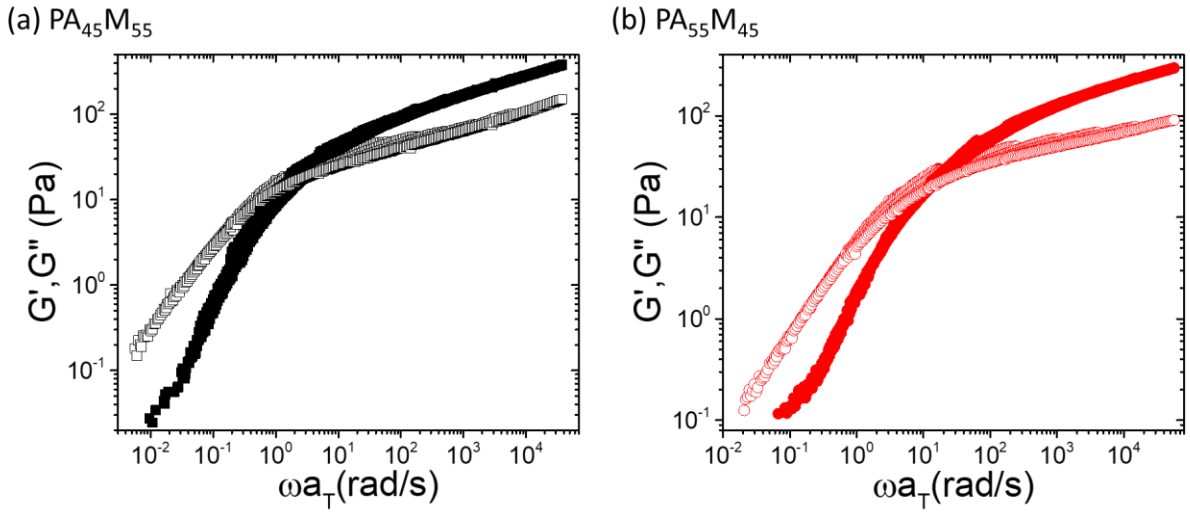

Figure S6. Linear frequency-dependent shear spectra of measured elastic moduli, G' (solid symbols) and viscous moduli, G'' (open symbols) of $PA_xM_y - \{W_{12}\}$ dense coacervates formed at constant $C_{A_xM_y}$ = 89.6 mM and C_{LiCl}= 0.2 M at constant temperature of 22 °C and strain γ = 1% against ω for (a) $PA_{45}M_{55}$, (b) $PA_{50}M_{50}$, and (c) $PA_{55}M_{45}$ at varied $C_{e^-(W12)}/C_{A_xM_y}$.