# Coarse-grained model for polyelectrolyte complexation

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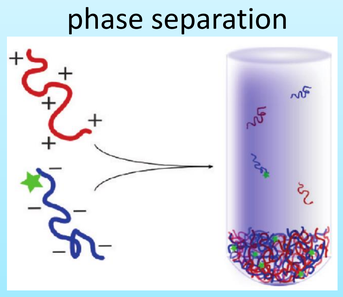
## Abstract

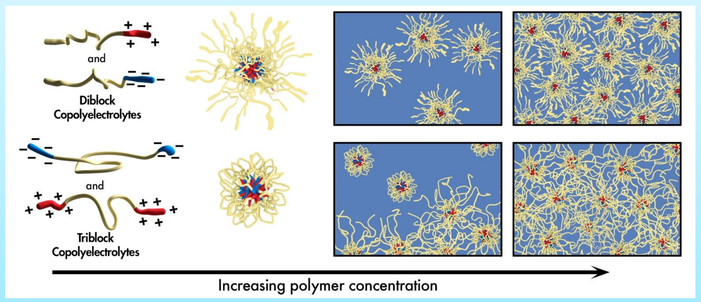
*Oppositely charged polyelectrolyte solutions can form two distinct liquid phases upon mixing: a polymer-rich complex coacervate phase and a polymer-deficient supernatant phase. The coacervation process and its resulting structural properties can be strongly influenced by variations in pH, added salt concentration, temperature, and ionic strength. Here, we propose a coarse-grained molecular dynamics model for polyelectrolyte complexation that utilizes GPU acceleration.The model successfully reproduced the coacervate phase formed by homopolymers, the mean size and distribution of diblock micelles, as well as the structural properties of triblock copolyelectrolyte gels. Our computational approach is unique in its ability to predict the dynamical modulus of polyelectrolyte complexes,and extensive comparison to collaborative and independent experimental findings validates its accuracy.*

## Polyelectrolyte complexes

Mixture of polyelectrolyte undergoes entropy driven phase separation



copolyelectrolyte solutions form micelle or networks

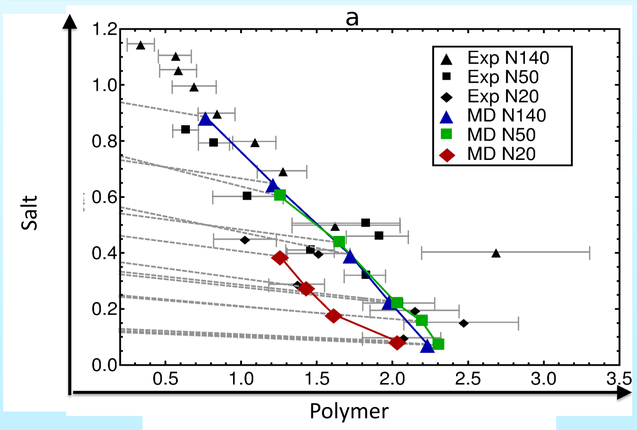



Spruijt et al., *Macromol.* 2010, **43**, 6476; S Srivastava, M Andreev, *Nature Comm.,* 2017, **8**, 14131.

## Coarse-grained model

- Coarse-grained MD
- Bead-spring chains
- LJ/WCA or TICG repulsion
- Electrostatics with constant $\epsilon_r$
- Ewald sum long range
- Strength from Bjerrum length $l_B$
- Langevin dynamics
- Constant volume
- Explicit counter-ions

## Homopolymers



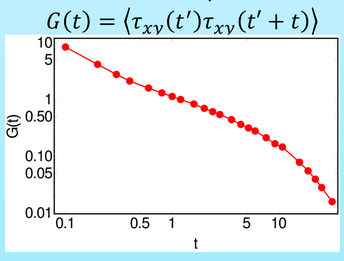

Phase diagram features:

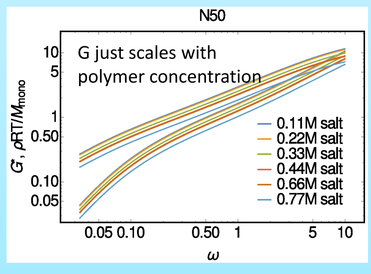
- Polymer concentration in coacervate as overall salt concentration
- Polymer concentration in supernatant is 0
- Molecular weight effects
- Salt concentration in coacervate is less than in supernatant

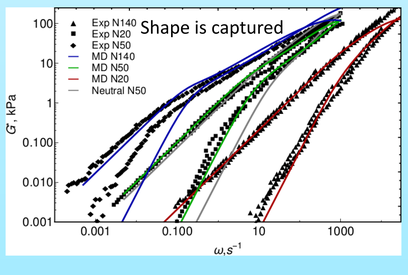
### Coacervate phase rheology

Stress autocorrelation/Green-Kubo

$$G(t) = \langle \tau_{xy}(t')\tau_{xy}(t'+t) \rangle$$

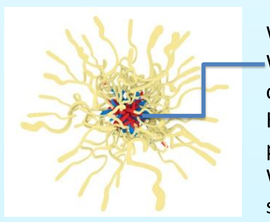


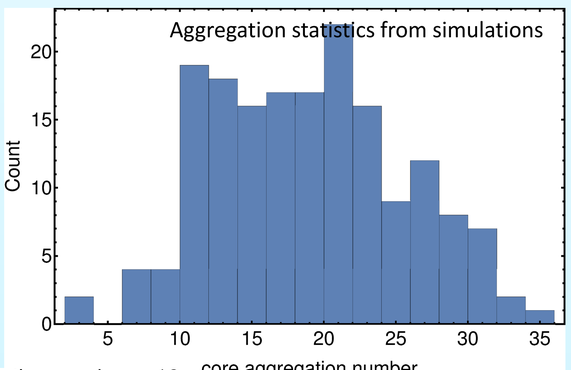



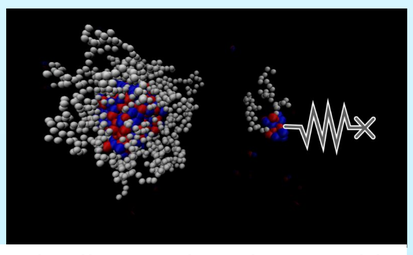

Spruijt et al., *Macromol.* 2010, **43**, 6476; Spruijt et al., *Macromol.* 2013, **46**, 1633.

## Copolymers

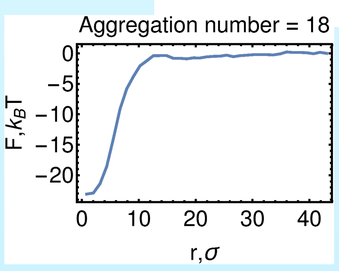


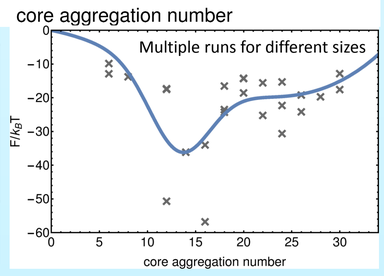
What is core size?
What is number of chains?
How it depend on parameters?
What is distribution of sizes?



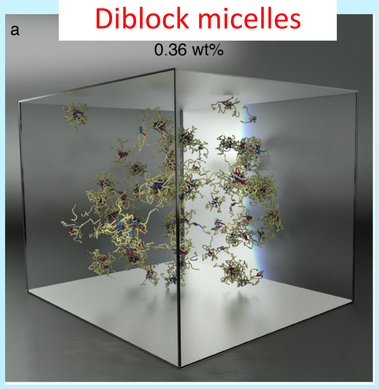



Umbrella sampling disassembly

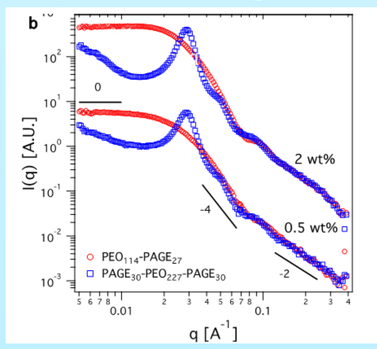


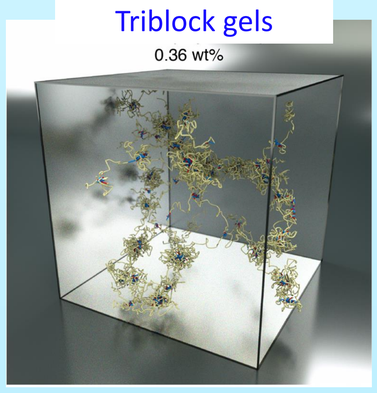

Diblock micelles

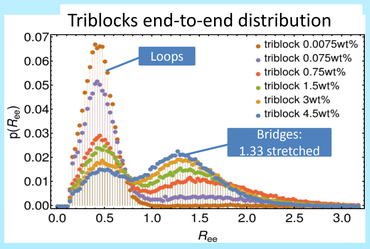


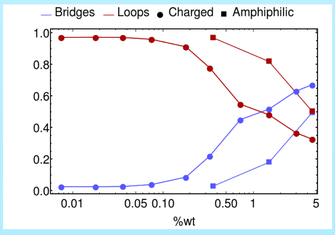

Experimental scattering data

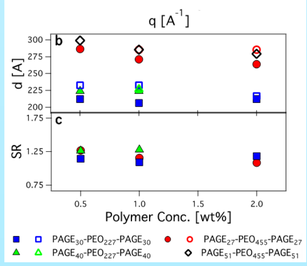



Triblock gels



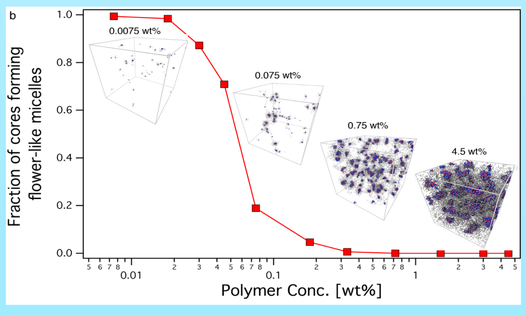




Triblock gels feature:

- Polymers are in loop or bridge conformation
- Fraction of bridges and loop depend on polymer concentration
- Bridge stretch weakly depend on concentration in agreement with experiment
- All the triblocks form a single percolating structure at low concentrations
- Gel phase forms at low polymer concentration
- Gel phase is more preferable state comparing to amphiphilic triblocks




S Srivastava, M Andreev, *Nature Comm.,* 2017, **8**, 14131.

## Ion mobility

Goal: to capture affect of added salt on dynamics

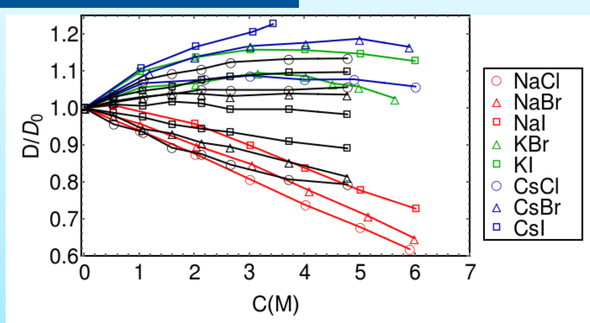
- introducing solvation effects into the model

$$\Delta H = -\frac{Z^2 e^2}{8\pi\epsilon_0 r_B}\left(1-\frac{1}{\epsilon_r}\right)$$

| | $r_B$ | $\epsilon_{water-ion}$ |
|---|---|---|
| $Na^+$ | 187 | 1.25 |
| $K^+$ | 233 | 1. |
| $Cs^+$ | 275 | 0.85 |
| $Cl^-$ | 186 | 1. |
| $Br^-$ | 200 | 0.93 |
| $I^-$ | 223 | 0.83 |

- LJ fluid
- Explicit solvent
- Constant pressure
- Modified cohesive potential for ion and water

$$\epsilon_{water-ion} = \epsilon\, r_0/r_B$$




Chremos, Douglas, *J Chem. Phys.* 2016**, 144**, 164904; Kim at al., *J Chem. Phys.* 2012, **116**, 12007.

## Conclusions

- model polyelectrolyte complexation with CG molecular dynamics
- homopolymer phase diagram is in qualitative agreement with experiment
- dynamic modulus for coacervate in agreement with experiment
- proposed way to capture salt concentration effect on dynamics
- calculated copolymer micelle cores size
- modelled gels formed by triblock copolyelectrolytes