Dobrynin Research Group

THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

How to measure the effects of solvents and charged groups on polymer excluded volume and Kuhn length

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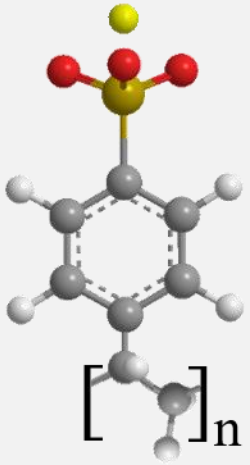
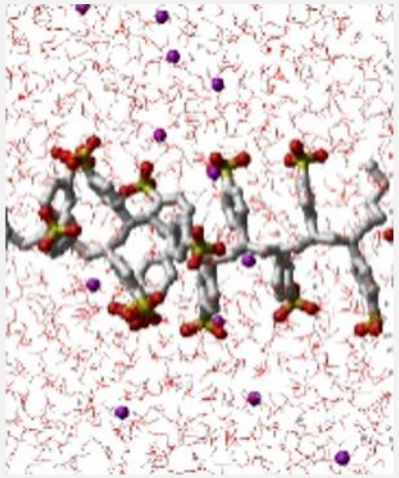
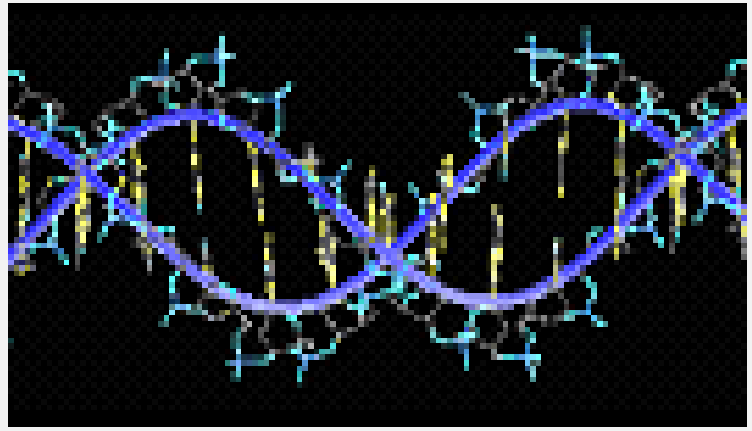
Polyelectrolytes

Sodium Poly(styrene sulfonate) (NaPSS)

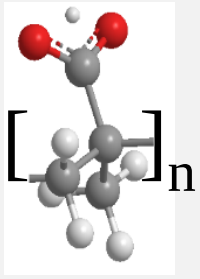




DNA

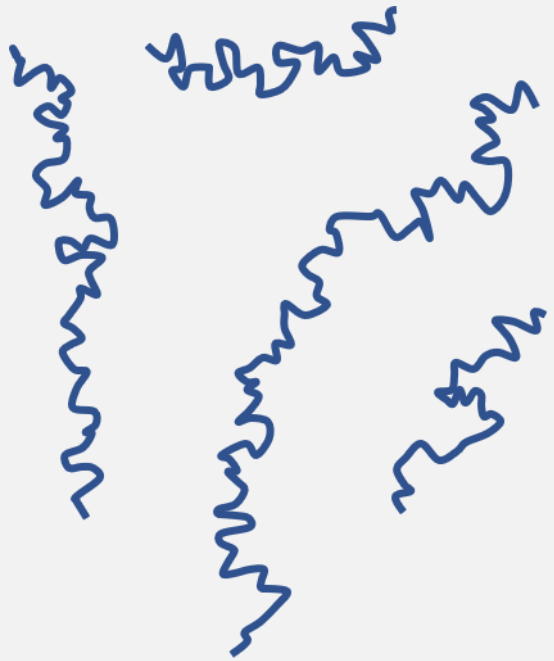


Poly(methacrylic acid)

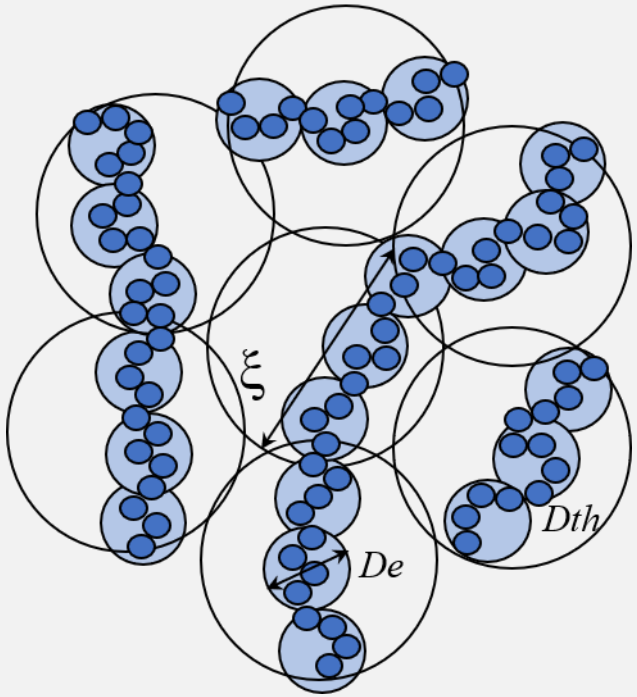


Church of the Holy Blob

Chains in Semidilute Solutions



Chains of Blobs



Chain Size:

$$R = \xi (N/g)^{0.5}$$

Correlation Length (Blob):

$$\xi = D_e\, g/g_e = l\, g/B_{pe}$$

Electrostatic Blob:

$$D_e = D_{th}(g_e/g_{th})^{0.588} = l\, g_e^{0.588}/B_g$$

Thermal Blob:

$$D_{th} = (lbg_{th})^{0.5} = l\, g_{th}^{0.5}/B_{th}$$

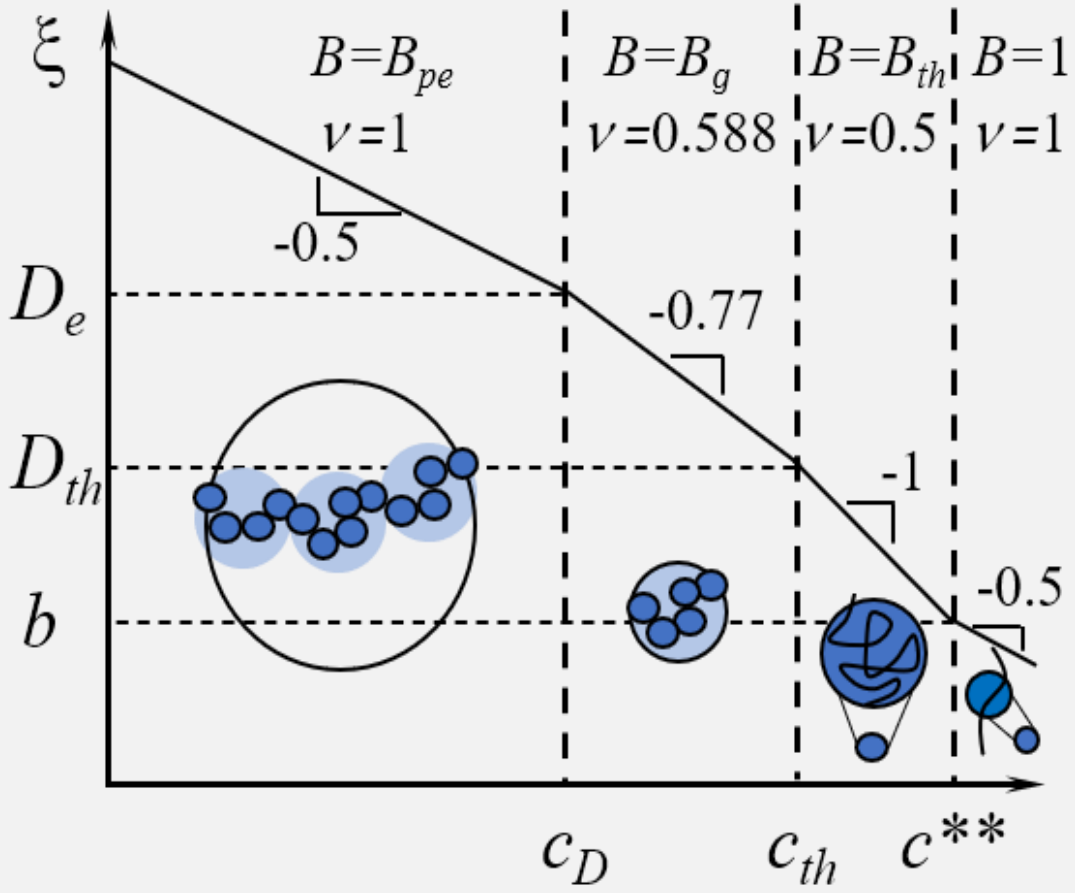
N – degree of polymerization
l – monomer projection length
b – Kuhn length

Correlation Length

Space-filling blobs

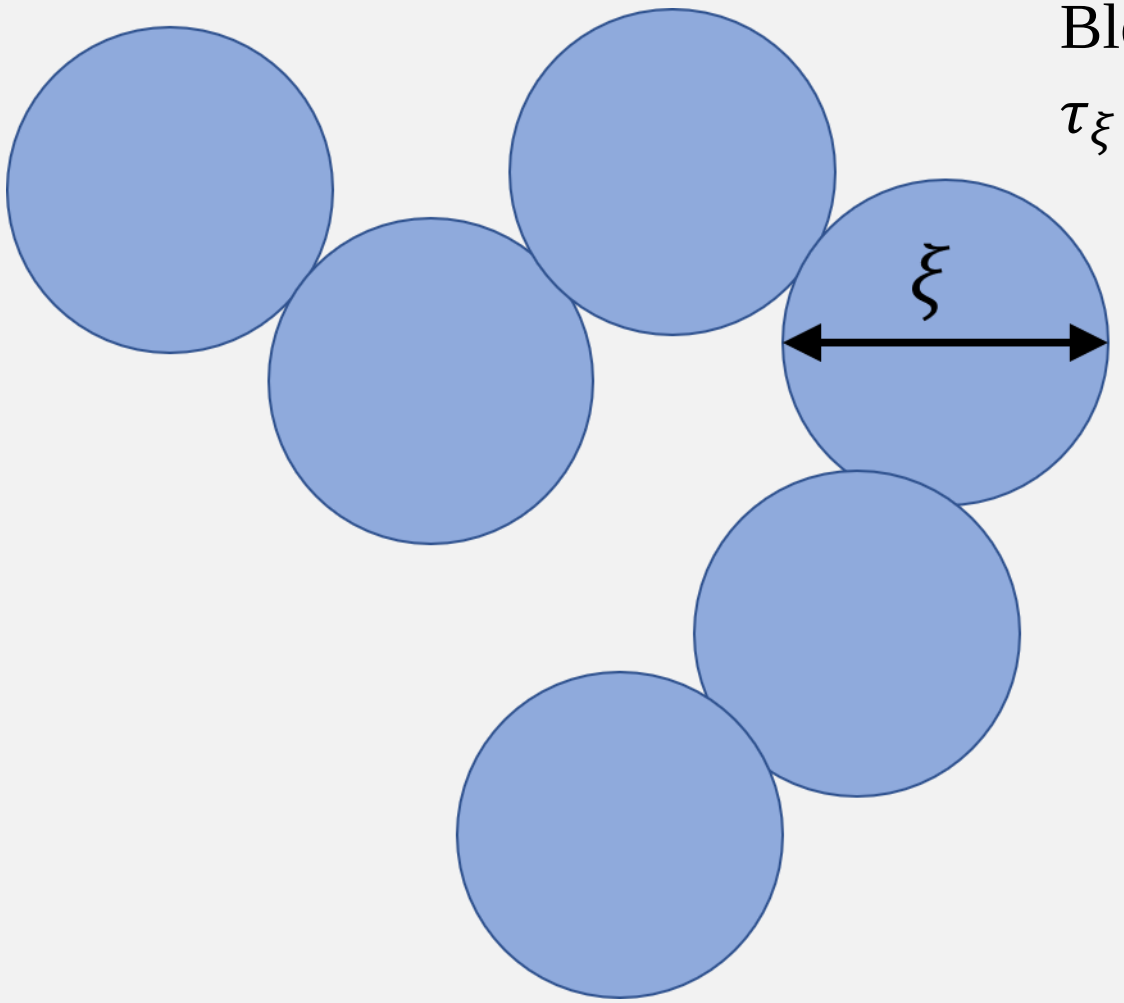
$$\xi = l g^{\nu}/B \qquad g = c\xi^3$$

$$\xi = l B^{1/(3\nu-1)} (c l^3)^{\nu/(1-3\nu)}$$



Macromolecules **2021**, 54, 1859

Unentangled (Rouse) Dynamics



Blob relaxation time

$$\tau_\xi = \frac{\eta_s}{k_B T}\xi^3$$

Longest chain relaxation time

$$\tau_R = \tau_\xi \frac{N^2}{g^2} = \frac{\eta_s}{k_B T}\frac{N^2}{gc}$$

Terminal shear modulus

$$G = k_B T c/N$$

Solution viscosity

$$\eta - \eta_s = G\tau_R = \eta_s\, N/g$$

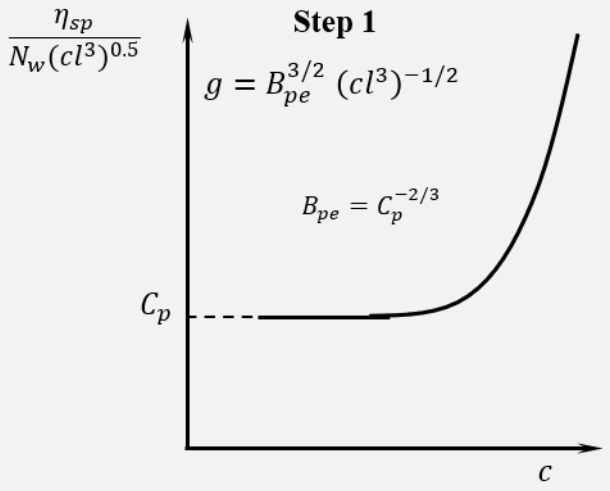
Specific viscosity

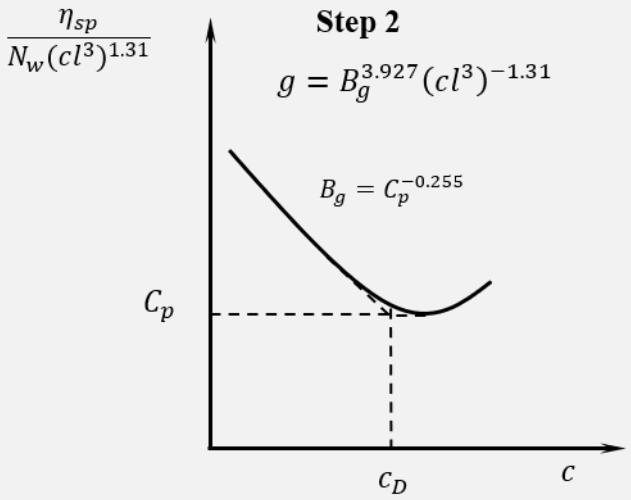
$$\eta_{sp,R} = \frac{N}{g}$$

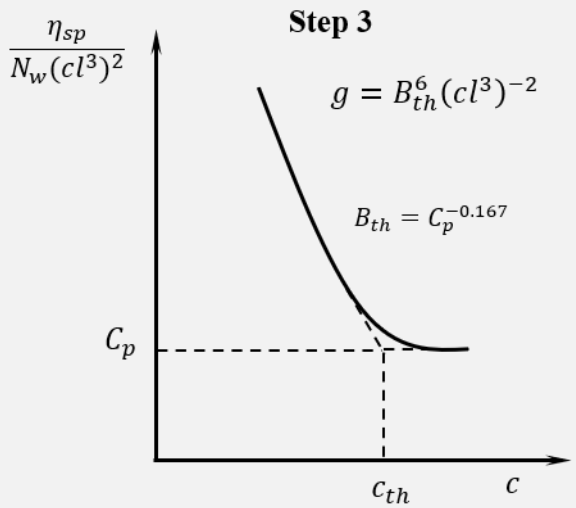
Viscosity Data Analysis

Polydispersity effect

$$\eta_{sp,R} = N_w/g \qquad g = B^{3/(1-3\nu)}(cl^3)^{1/(3\nu-1)} \qquad B = C_p^{\frac{1}{3}-\nu}$$







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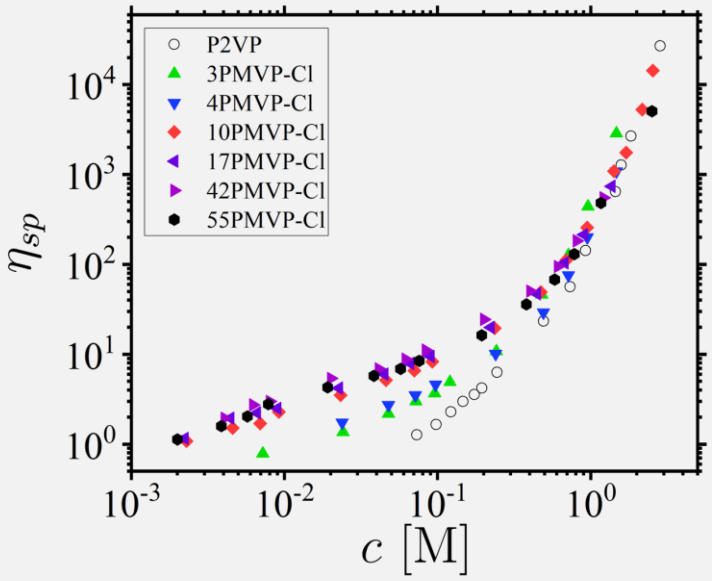
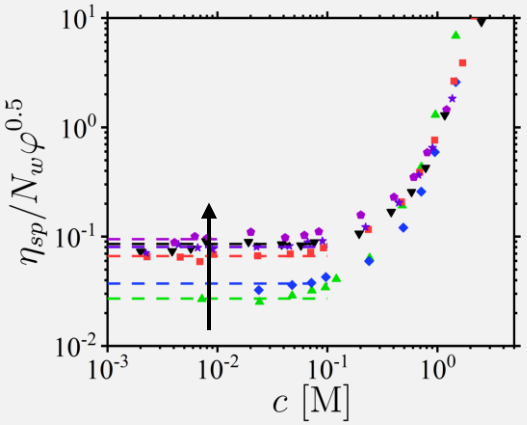
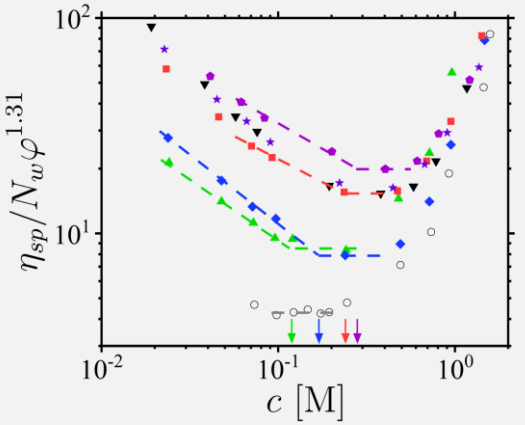
Salt-free Solutions of PMVP-Cl

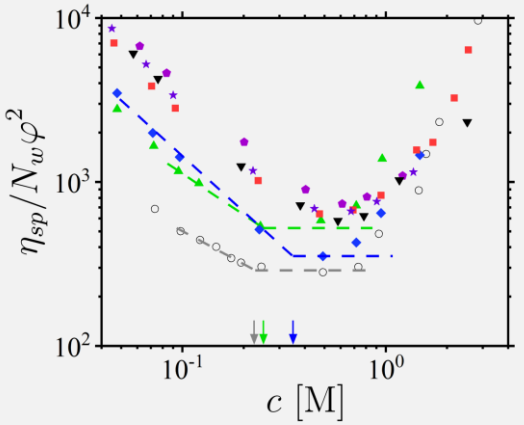
Ethylene glycol solutions of P2VP and N-methyl-2-vinyl pyridinium chloride random copolymers with $N_w = 3463$ and $l = 0.255\text{nm}$.





Increasing charge density decreases B_{pe}



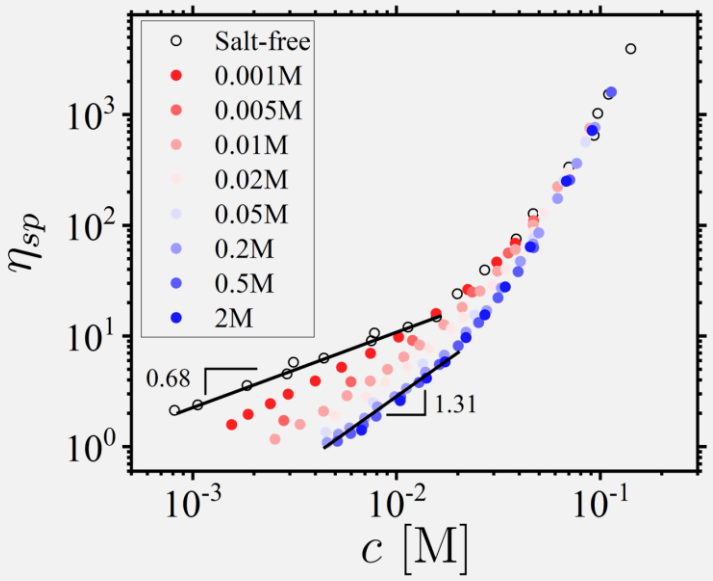


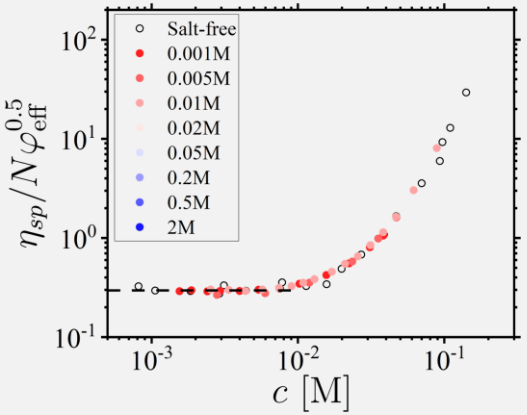
$$\varphi = cl^3$$

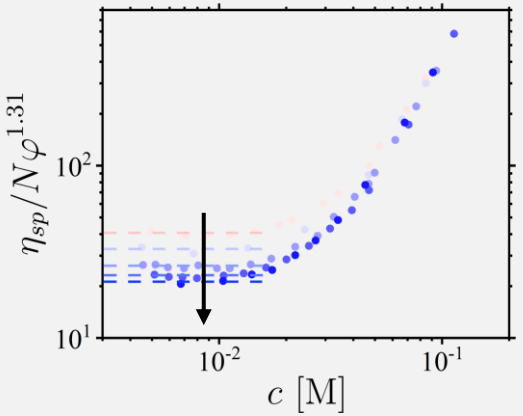
Viscosity data from: Dou & Colby *J. Polym. Sci. B* **2006**, 44, 2001

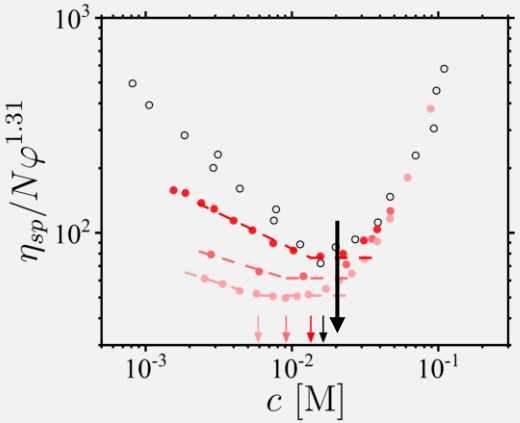
Salt Solutions of NaCMC

Aqueous solutions of sodium carboxymethylcellulose with $N_w = 1250$ and $l = 0.515$nm.









Low salt concentrations:
(*Macromolecules* **1995**, 28, 1859)

$$\xi = l\, B_{pe}^{0.5} (cl^3)^{-0.5} \left(1 + \frac{2c_s}{fc}\right)^{0.25}$$

$$\varphi_{\mathrm{eff}}^{0.5} = \varphi^{0.5} (1 + 2\, c_s / f\, c)^{-0.75}$$

Residual salt concentration: $c_s = 4 \times 10^{-4}$M

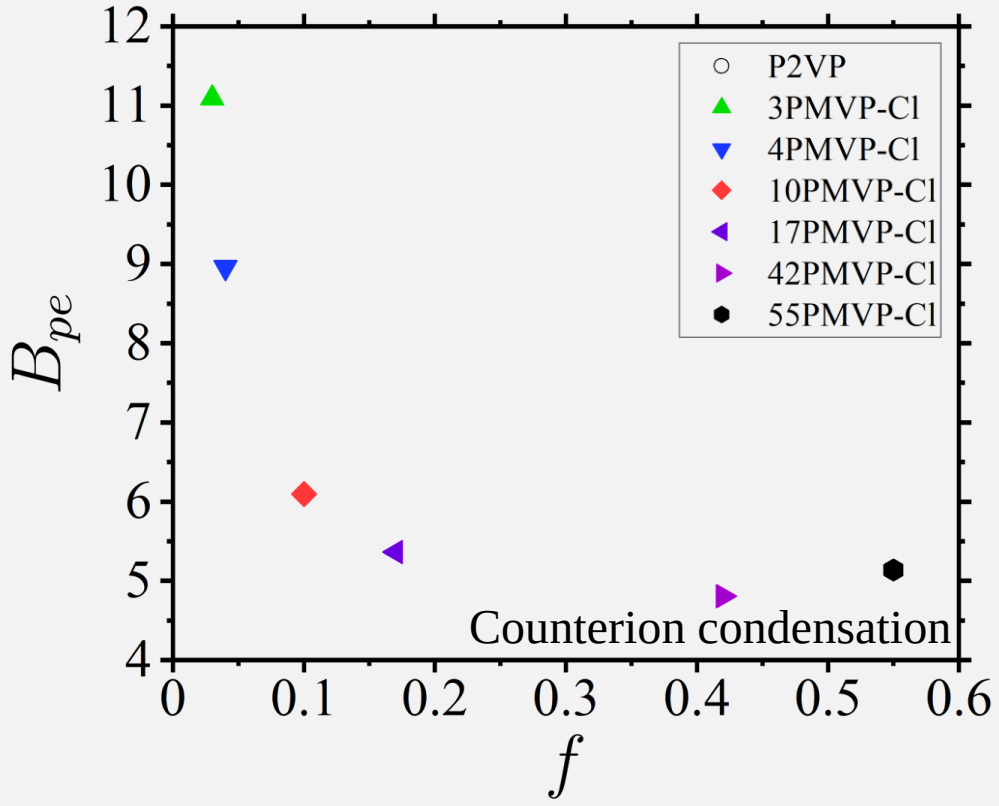
Increasing salt concentration increases B_g.

$$\varphi = cl^3$$

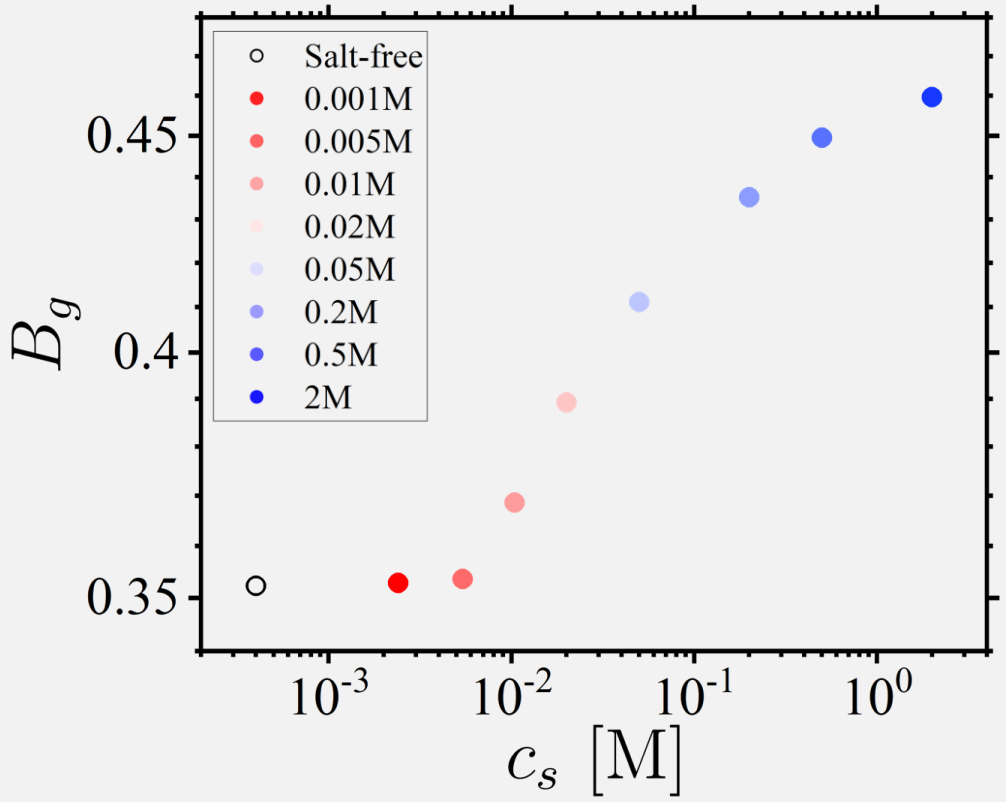
Viscosity data from: Lopez, C. G. *et al. Macromolecules* **2016**, 50, 332

Effect of Fraction of Charged Groups and Salt

J. Polym. Sci. B **2006**, 44, 2001

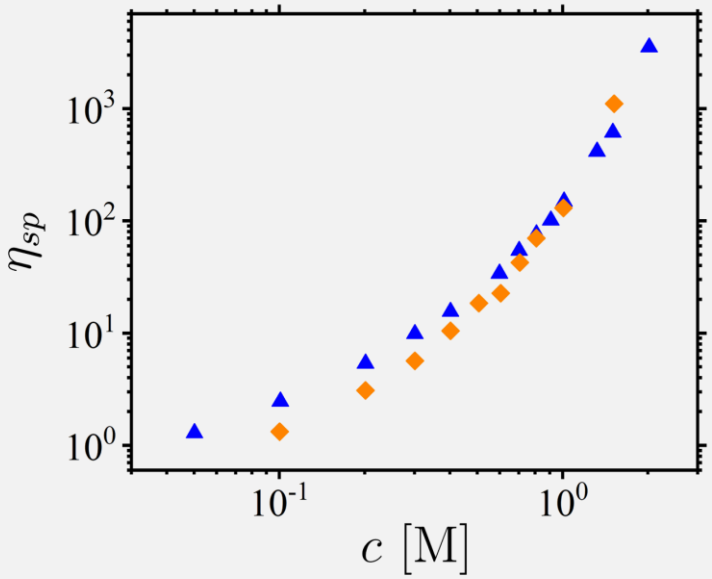


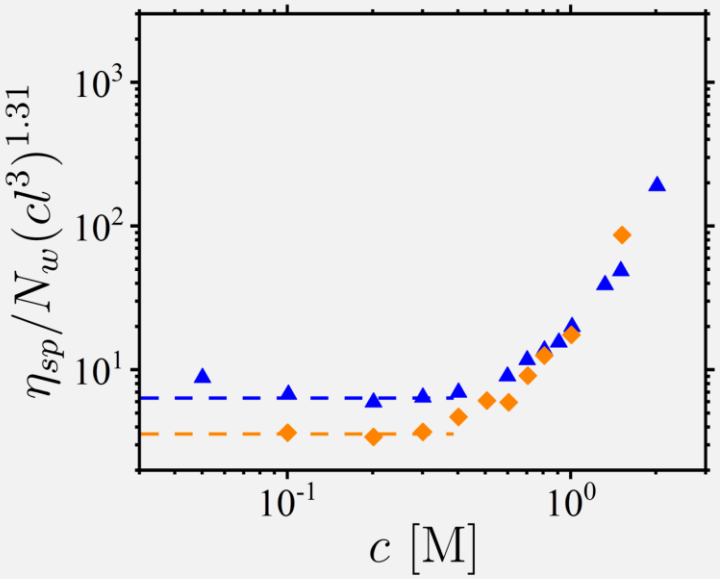
Macromolecules **2016**, 50, 332

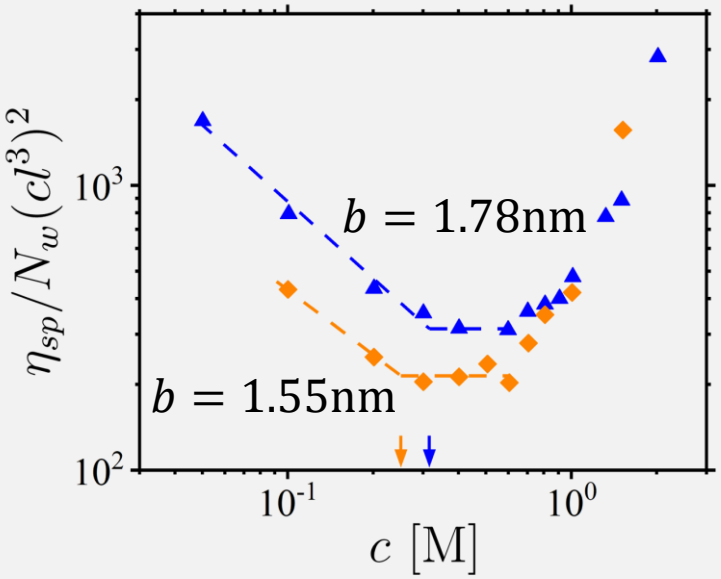


Solutions of PMMA in Ionic Liquids

Solutions of poly(methyl methacrylate) in ionic liquids [C_4(mim)][TFSI] (blue triangles) and [C_8(mim)$_2$][TFSI]$_2$ (orange rhombs), with N_w =889 and l = 0.255nm.







Different packing of solvent molecules around the backbone changes B_{th}, and by extension Kuhn length $b = lB_{th}^{-2}$.

Viscosity data from: He *et al.*, *Macromolecules* **2020**, 53, 7865

Conclusions

We have adapted the scaling theory of polymer solutions to quantify

- The effect of fraction of ionization on chain size
- The effect of added salt on solvent quality for polyelectrolytes
- The effect of solvent packing on Kuhn length

And you can too!

Acknowledgements

Collaborators

Andrey V. Dobrynin

Ryan Sayko

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