Contributions of Nobel Laureate P. G. de Gennes to **Polyelectrolyte Solutions**

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de Gennes: Polyelectrolytes

P. G. de Gennes, P. Pincus, R. M. Velasco, F. Brochard, **Remarks on polyelectrolyte conformation** *J. de Phys. (Paris)* **37**, 1461-73 (1976).
~300 citations!

P. Pfeuty, R. M. Velasco, P. G. de Gennes, **Conformation properties of one isolated polyelectrolyte chain in D dimensions**,
J. de Phys. (Paris) Lett. **38**, 5-7 (1977).

P. G. de Gennes, **Global molecular shapes in polyelectrolyte solutions**,
in Colston Papers No. 29: Ions in Macromolecular and Biological Systems (1978).

P. G. de Gennes, Scaling Concepts in Polymer Physics, 299-304 (1979).

J. Hayter, G. Janninck, F. Brochard-Wyart, P. G. de Gennes, **Correlations and dynamics of polyelectrolyte solutions**, *J. de Phys. (Paris) Lett*. **41**, 451-4 (1980).

Polyelectrolytes before 1976

- Rodlike in dilute solution from charge repulsion
- Oosawa/Manning counterion condensation
- Polarizability: polyelectrolytes raise dielectric constant
- Salt screens charge interactions and gradually makes polyelectrolyte solutions ‘normal’
- Fuoss empirical law for viscosity $\eta \sim \sqrt{c}$
- Katchalsky Cell Model for osmotic pressure

F. Oosawa, Polyelectrolytes, Marcel Dekker (1971).
A. Katchalsky, *Pure Appl. Chem.* **26**, 327 (1971).

Polyelectrolytes have a peak in their scattering function

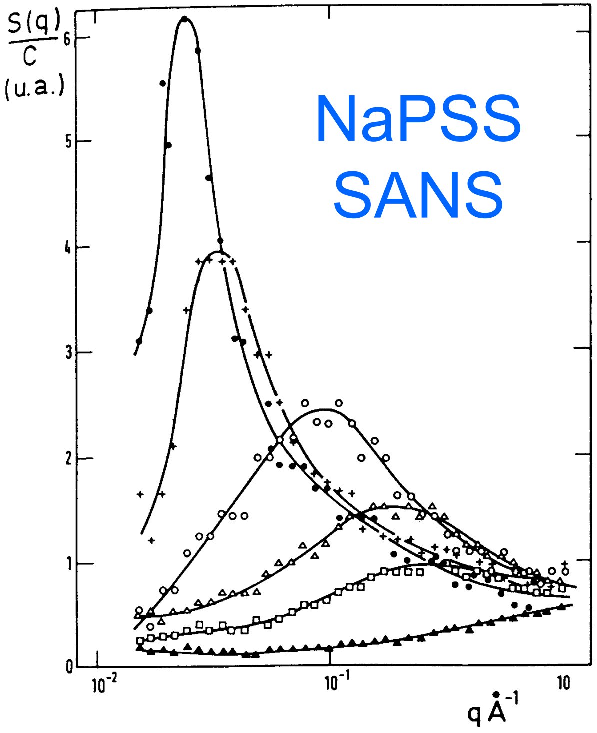
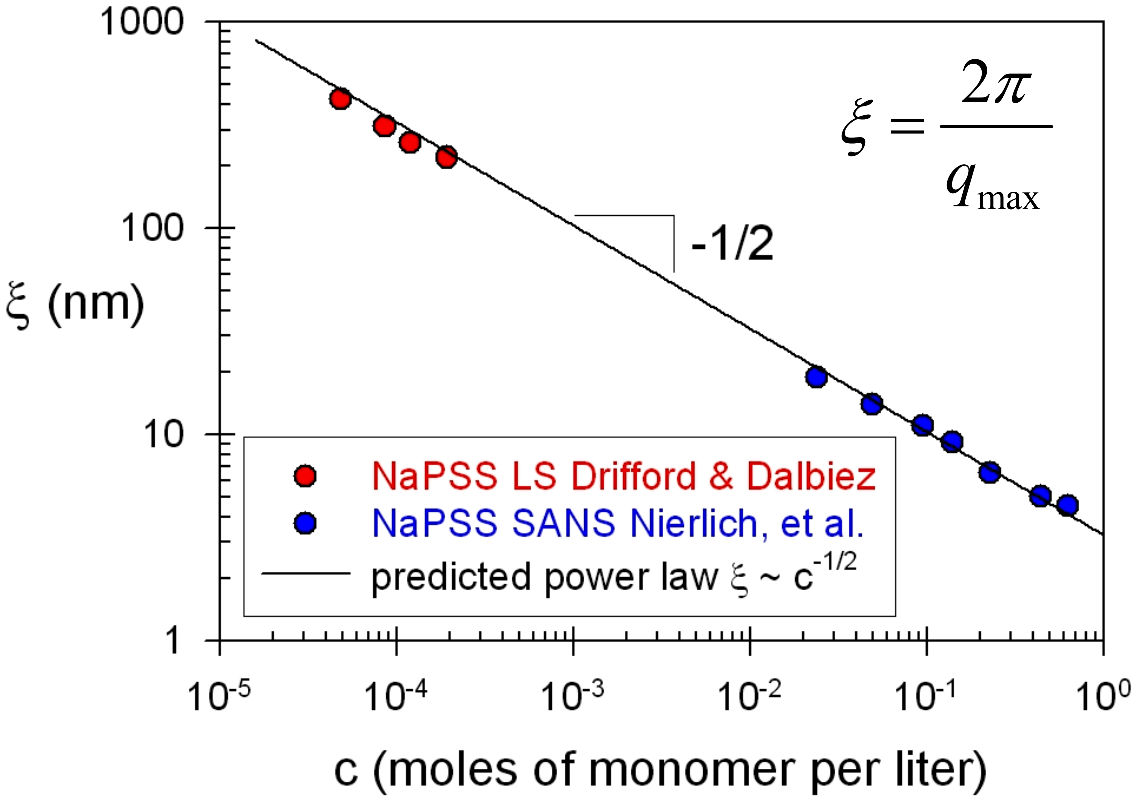


Fig. 3. — Scattered intensity per monomer of a solution of Na PSS_D ($M_w = 72\,000$) in H_2O *versus* polymer concentration.

● $c = 10^{-2}$ g.cm^{-3}; + 1.96 × 10^{-2} g.cm^{-3};
○ 4.76 × 10^{-2} g.cm^{-3}; △ 9.09 × 10^{-2} g.cm^{-3};
☐ 13.04 × 10^{-2} g.cm^{-3}; ▲ 23 × 10^{-2} g.cm^{-3}.

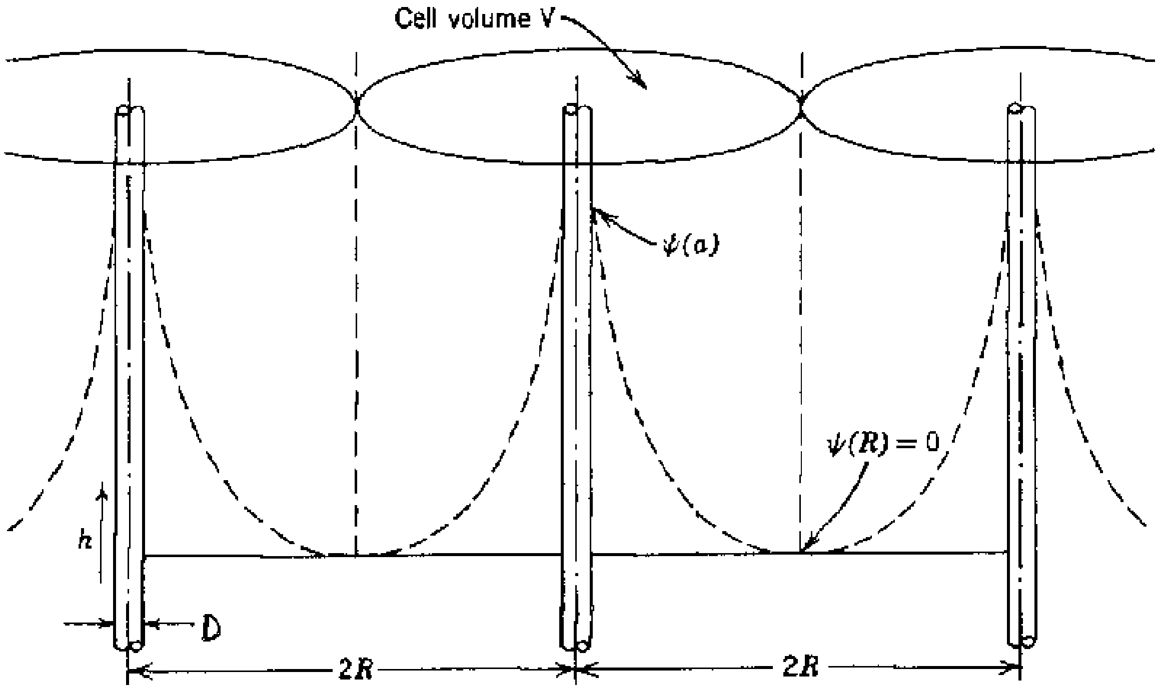


$$\xi = \frac{2\pi}{q_{\max}}$$

M. Nierlich, et al., *J. de Phys. (Paris)* **40**, 701 (1979).

pre-1976 explanations of the peak in the scattering function

- Bragg spacing of an ordered phase
- Nematic phase
- Katchalsky Cell Model



Katchalsky Cell Model explains the very high osmotic pressure

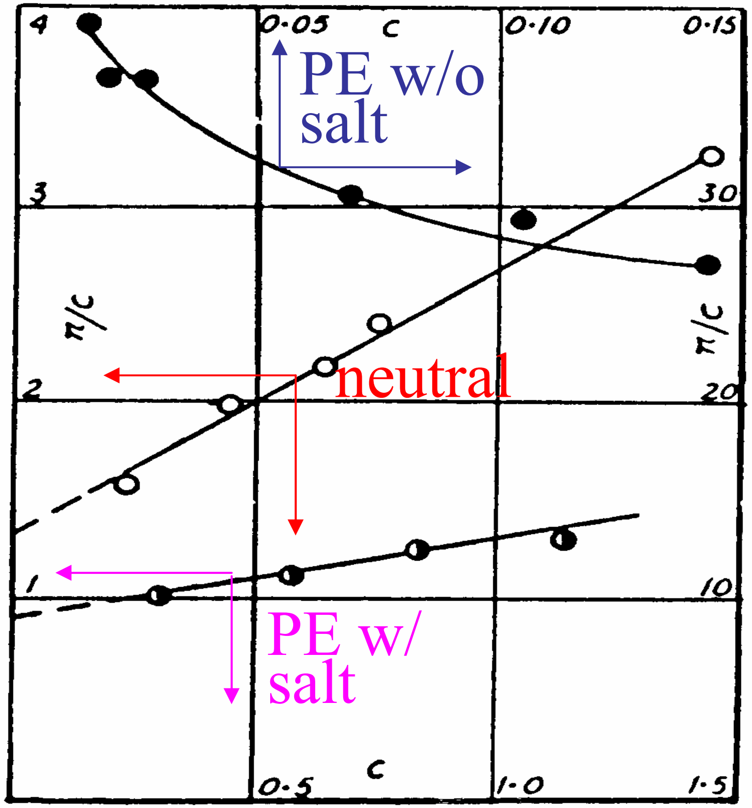


FIG. 3.—Reduced osmotic pressure. Open circles, polyvinylpyridine in alcohol, co-ordinates left and below; solid circles, polyvinylbutylpyridinium bromide in alcohol, co-ordinates right and above; half-black circles, polyvinylbutylpyridinium bromide in alcoholic lithium bromide solution (0·610 N).

Without salt, semidilute polyelectrolyte solutions have enormous osmotic pressure

kT per free counterion

$$\pi = fckT$$

Typically 100x larger than neutral polymers at the same concentration!

R. M. Fuoss, *Disc. Faraday Soc.* **11**, 125 (1951).

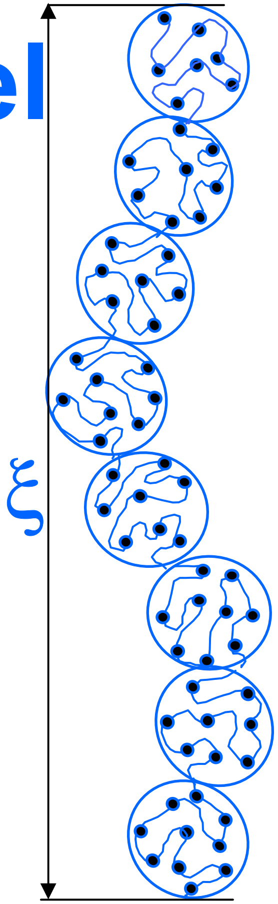
de Gennes' arguments against a semidilute ordered phase

- Polyelectrolyte solutions are not birefringent
- *S(q)* has only one broad peak (no sharp reflection)
- No observation of defects (i.e., no disclinations nor the turbidity they usually cause)
- Addition of salt smoothly transitions the chain to revert to the neutral polymer conformation (whereas an ordered phase might abruptly melt)

P. G. de Gennes, P. Pincus, R. M. Velasco, F. Brochard, **Remarks on polyelectrolyte conformation** *J. de Phys. (Paris)* **37**, 1461-73 (1976).

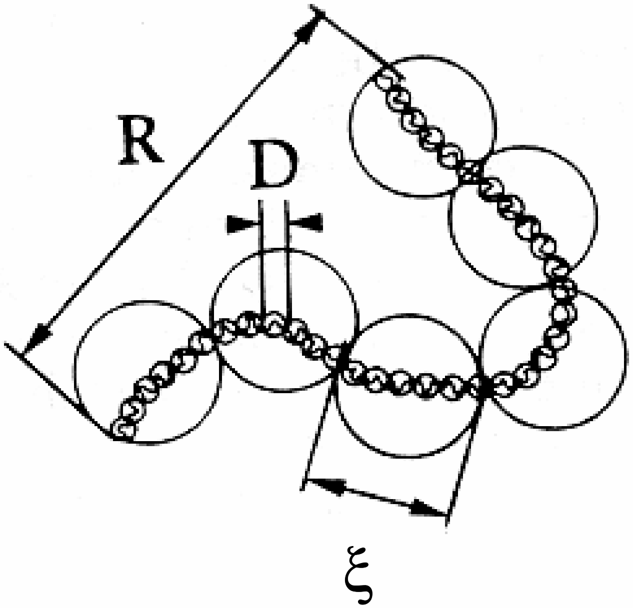
P. G. de Gennes, **Global molecular shapes in polyelectrolyte solutions**, in Colston Papers No. 29: Ions in Macromolecular and Biological Systems (1978).

1976 de Gennes isotropic model for semidilute polyelectrolytes



r > ξ: SCREENED ELECTROSTATICS

A *random walk* of correlation blobs

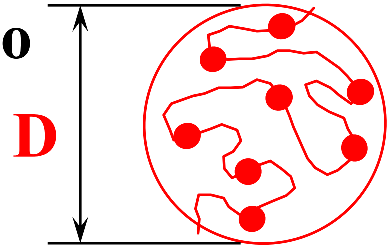


D < r < ξ: STRONG ELECTROSTATIC STRETCHING

A *directed random walk* of electrostatic blobs

r < D: WEAK ELECTROSTATICS

Conformation is similar to a neutral polymer, *swollen* in good solvent, *collapsed* in poor solvent



de Gennes semidilute correlation length

Correlation length starts at the chain size *L* at *c**

$$\xi \approx L\left(\frac{c}{c^*}\right)^{y}$$

Distance between chains – should not depend on *N*

Rodlike in dilute solution: $L \approx Nb$ $\quad c^* \approx \frac{N}{L^3} \approx \frac{1}{b^3 N^2}$

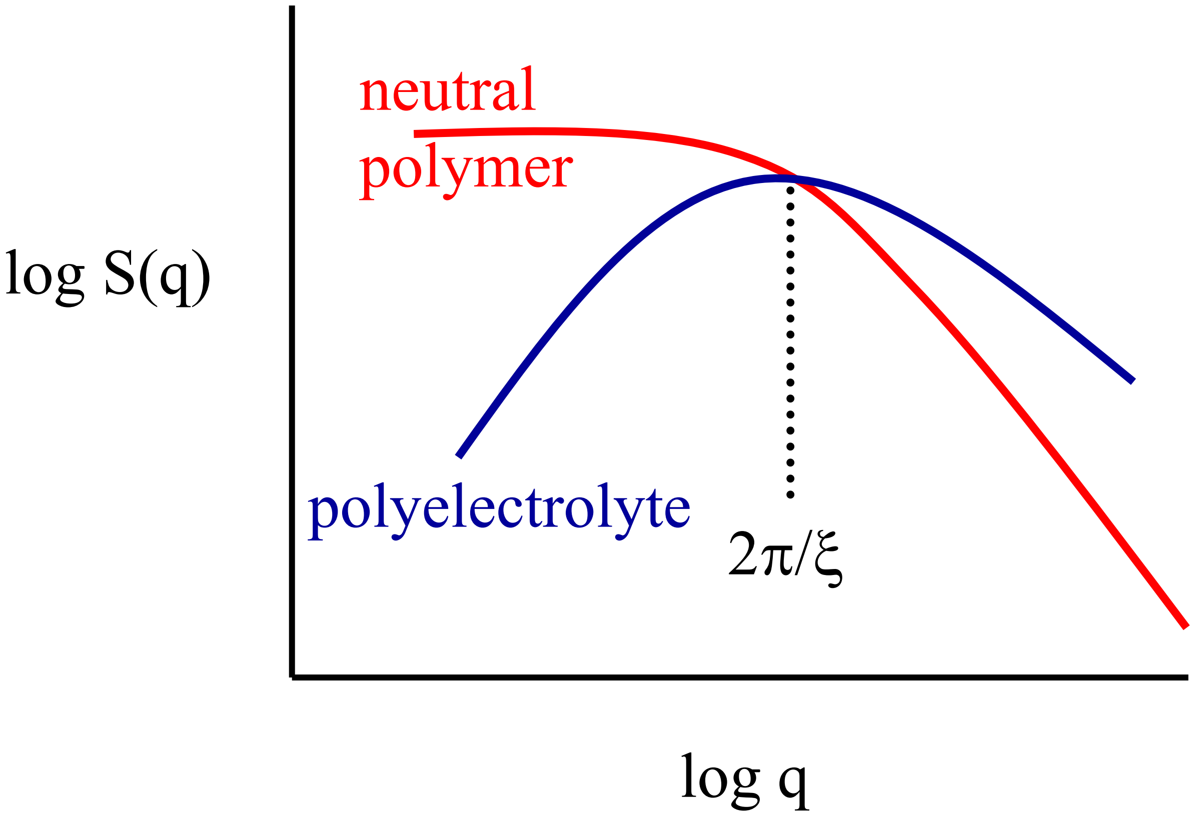
$$\boxed{\xi \approx L\left(\frac{c}{c^*}\right)^{-1/2}}$$

the experimental observation

"Remarkable coincidence" with concentration dependence of Debye length essentially enables one to use scaling for polyelectrolyte solutions.

P. G. de Gennes, **Global molecular shapes in polyelectrolyte solutions**, in Colston Papers No. 29: Ions in Macromolecular and Biological Systems (1978).

Why would isotropic solutions of polyelectrolytes have a peak in their scattering function?

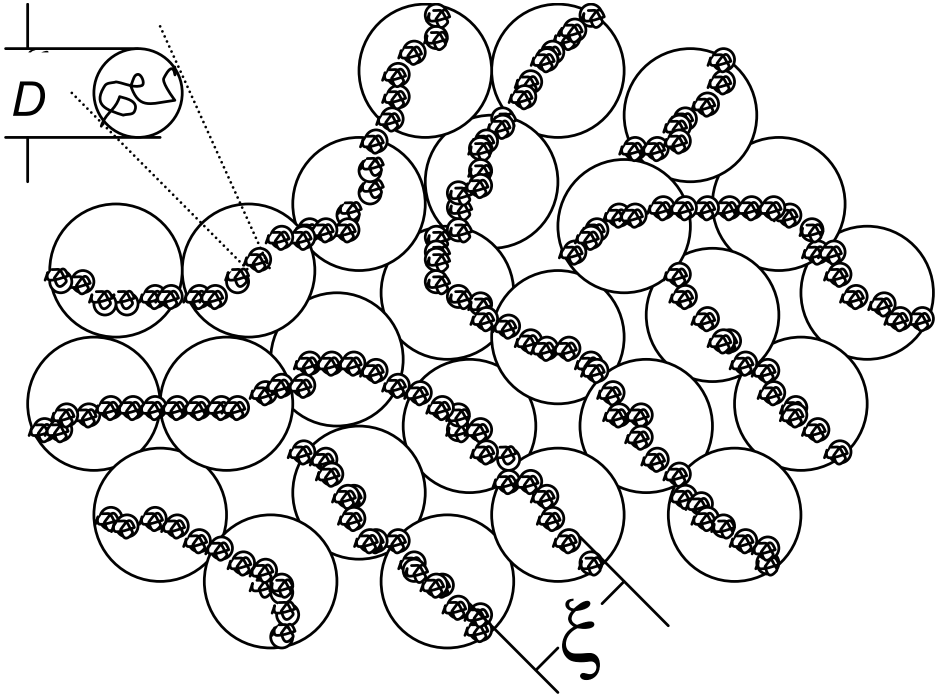


Neutral polymers overlap correlation volumes easily and have lots of scattering at low wavevector.

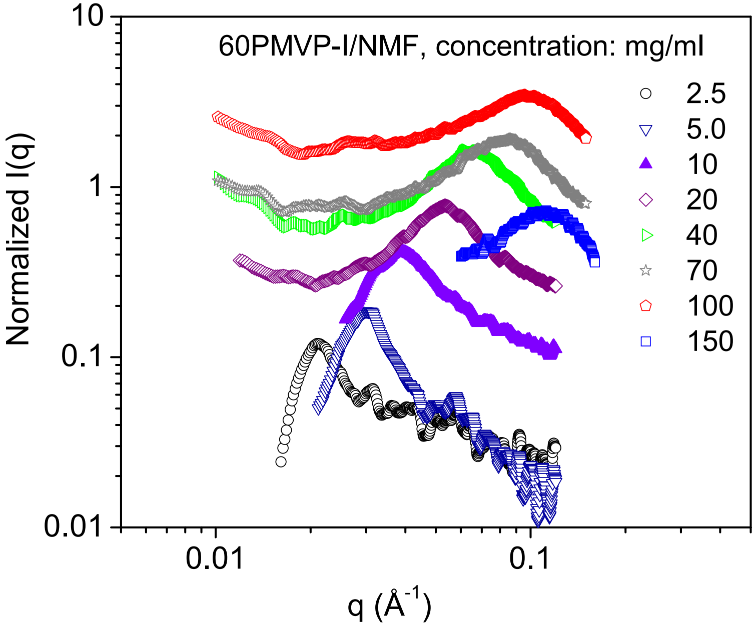
The osmotic pressure of their counterions prevents overlap of correlation volumes for polyelectrolytes.

Moreover, charge repulsion between neighboring chains favors a regular inter-chain spacing.

de Gennes isotropic semidilute solution



SAXS dominated by I^- counterions
Quaternized poly(2-vinyl pyridine)
in N-methyl formamide



Correlation volumes do not overlap and electrostatic interactions between the directed random walk chains forces them near the correlation volume centers

S. Dou and R. H. Colby, *Macromolecules*, submitted.

Dynamic Scaling in Semidilute Unentangled Solutions

Zimm time of a correlation volume $\frac{\eta_s}{kT}\xi^3$

Rouse time of a chain $\tau \cong \frac{\eta_s}{kT}\xi^3\left(\frac{N}{g}\right)^2 \cong \frac{\eta_s\xi^3 N}{kTg}\left(\frac{R}{\xi}\right)^2 \cong \frac{\eta_s N}{ckT}\left(\frac{R}{\xi}\right)^2$

Polyelectrolytes		**Neutral Polymers**
$\xi \sim c^{-1/2}$	blob size	$\xi \sim c^{-3/4}$
$R \sim N^{1/2}c^{-1/4}$	polymer size	$R \sim N^{1/2}c^{-1/8}$
$\tau \sim N^2c^{-1/2}$	relaxation time	$\tau \sim N^2c^{1/4}$
$G = ckT/N$	terminal modulus	$G = ckT/N$
$\eta = G\tau \sim Nc^{1/2}$	viscosity	$\eta = G\tau \sim Nc^{5/4}$
$D = R^2/\tau \sim N^{-1}c^0$	diffusion coefficient	$D = R^2/\tau \sim N^{-1}c^{-1/2}$

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with neutral polymers
$D \sim c^0$ ⇒ dilute solution

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empirical Fuoss law first predicted by de Gennes

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empirical Fuoss law first predicted by de Gennes

even stranger prediction!

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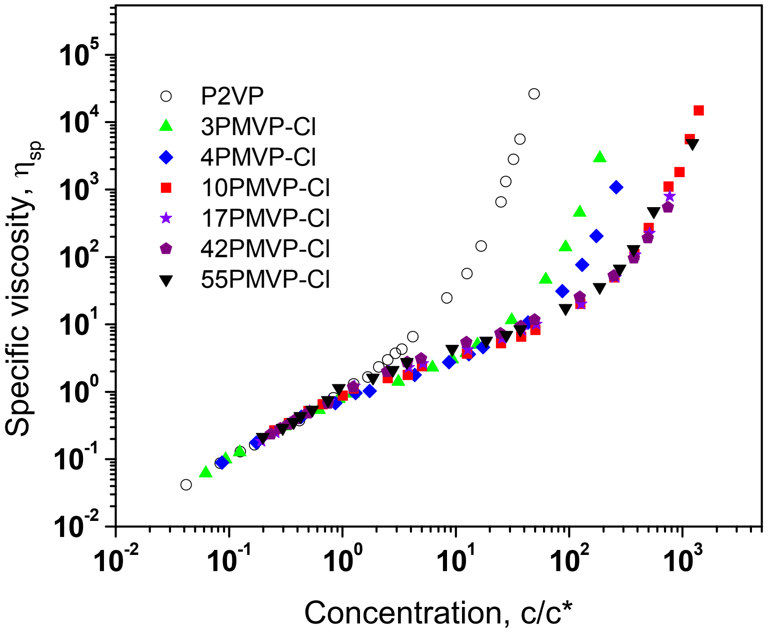
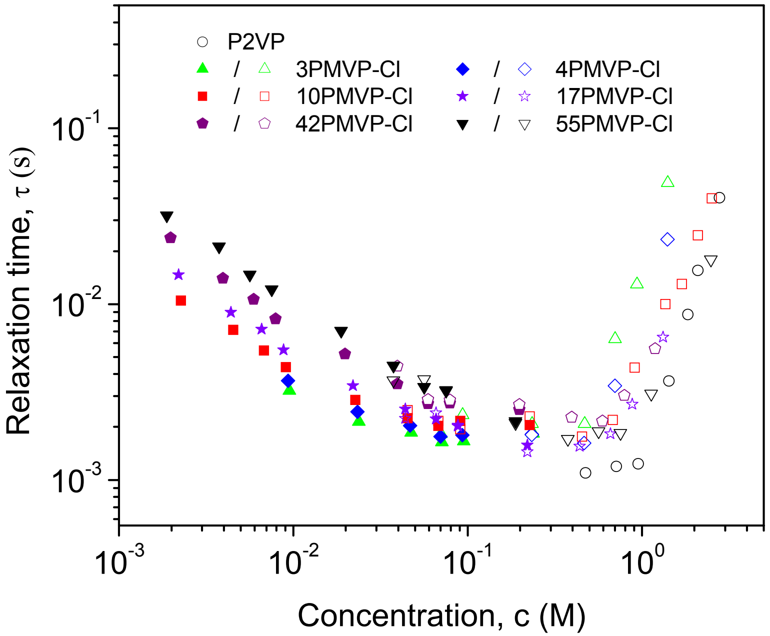
Polyelectrolyte Solution Rheology

Partially quaternized poly(2-vinyl pyridine) in ethylene glycol



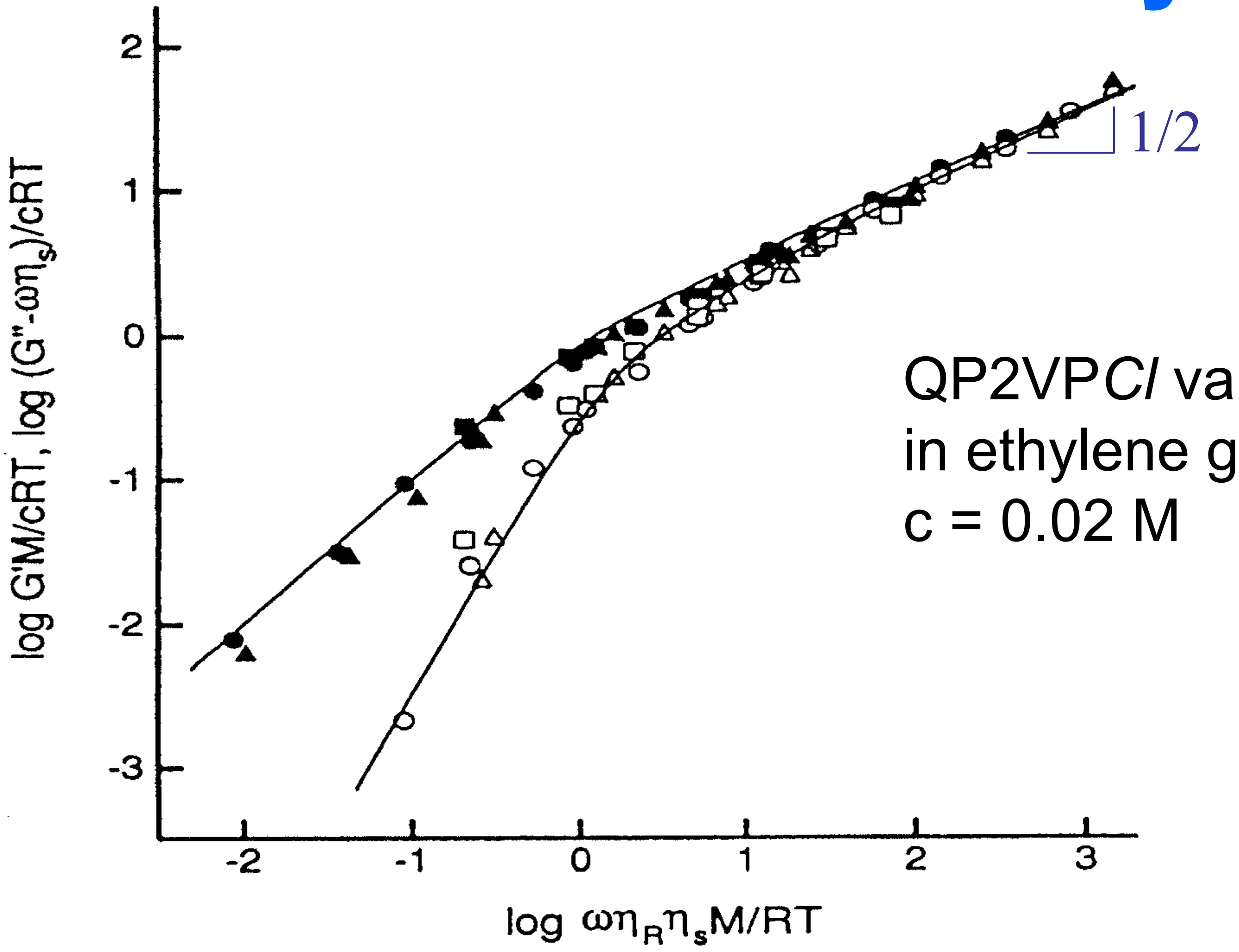


c/c* reduces all polyelectrolyte specific viscosity data on dilute and semidilute unentangled solutions to a common functional form with

$\eta_{sp} = \frac{c}{c^*}$ for $c < c^*$ and $\eta_{sp} = \sqrt{\frac{c}{c^*}}$ with $\tau \sim c^{-1/2}$ for $c > c^*$

S. Dou and R. H. Colby, *J. Polym. Sci., Polym. Phys*. **44**, 2001 (2006).

The Rouse Model Describes Linear Viscoelasticity



QP2VP*Cl* various M
in ethylene glycol
c = 0.02 M

D. F. Hodgson and E. J. Amis, *J. Chem. Phys*. **94**, 4581 (1991).

Open Questions in Polyelectrolytes

- $S(q)$ for $q > 2\pi/\xi$: What is the form factor for the directed random walk inside the correlation blob?
- $S(q)$ for $q << 2\pi/\xi$: What is the origin of the enormous scattering at very low wavevectors? Related to slow mode?
- How do polyelectrolytes (with conformation dominated by charge repulsion) crossover to ionomers (with conformation determined by dipolar attraction of ion pairs) at very high concentrations?
- Does the ordered phase predicted by de Gennes exist at ultra-low concentrations?
- What does entanglement mean in a polyelectrolyte solution?

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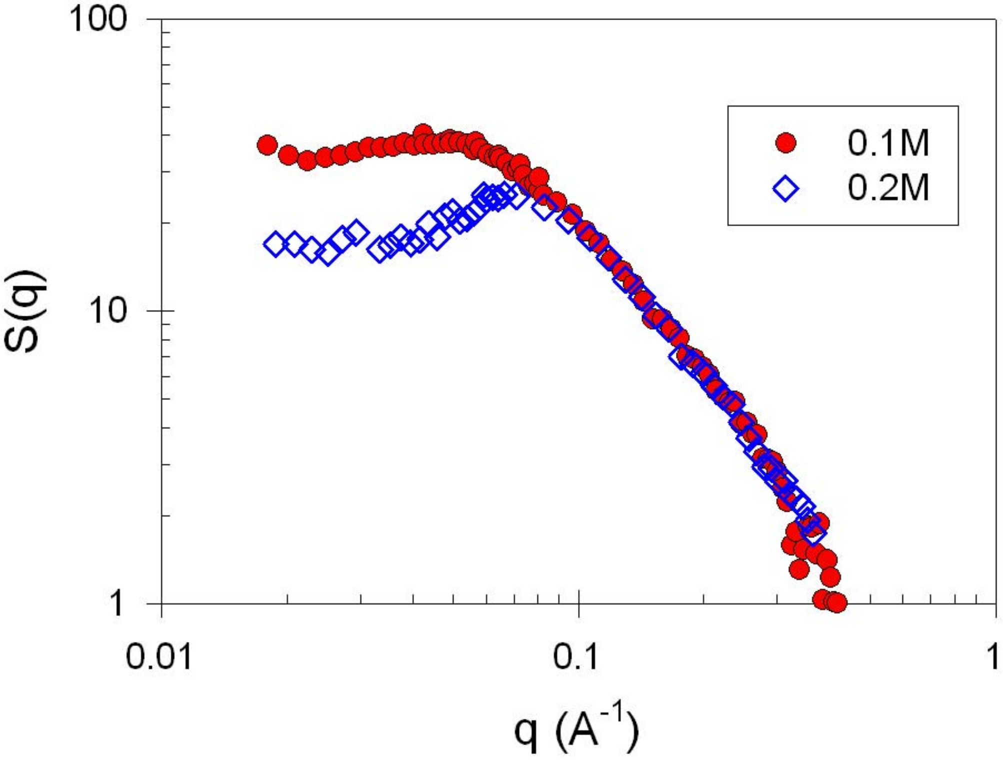
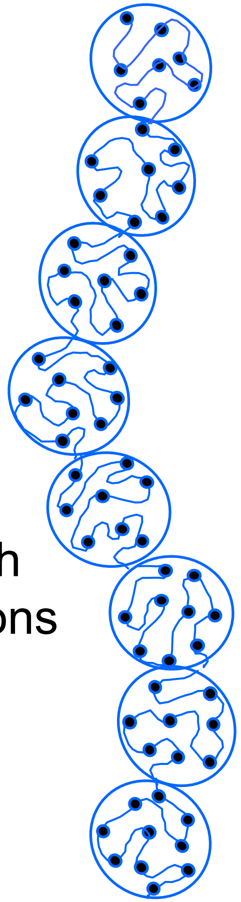


Experimental way to access the form factor of a dilute polyelectrolyte?

Sulfonated polystyrene with deuterated TMA$^+$ counterions that are contrast-matched

$S(q)$ inside the correlation blob shows universal form with $S(q) \sim q^{-1.6}$

Directed random walk? Bending on the scale of ξ?



J. R. C. van der Maarel, et al., *Macromolecules* **26**, 7295 (1993).

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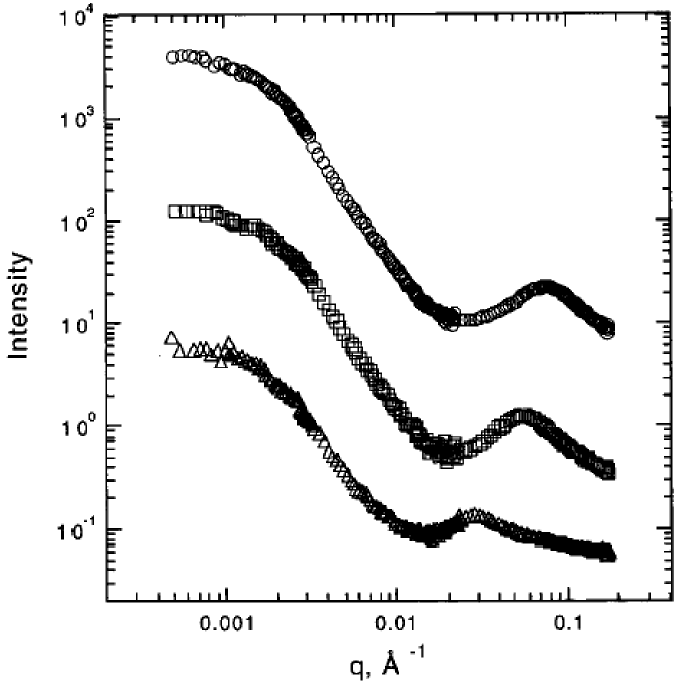

Figure 4. Log−log plot of SANS scattered intensity and SLS scattered intensity, $I(q)$, plotted versus the scattering vector q for PMVP in D_2O for three polymer concentrations: (△) 3.0 g/L, (□) 15 g/L, and (○) 30 g/L. Each set of SLS data has been shifted vertically to match the SANS data. For clarity of presentation the 15 and 30 g/L data have been shifted up by 1 and 2 decades, respectively.

Huge forward scattering (at low q) suggests **structures on scales considerably larger than the chain size**!

Electrostatic attractions?

Possibly related to the slow mode in dynamic light scattering?

If they exist, these large structures seem to have no effect on macroscopic rheology or thermodynamics (osmotic pressure).

Inconsistent with the strong correlations on the scale of the correlation volumes!

B. D. Ermi and E. J. Amis, *Macromolecules* **31**, 7378 (1998).

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Phases of Ion-Containing Polymers

Polyelectrolyte: Many ions dissociate from the chain in a high-dielectric medium – dominated by <u>charge repulsion</u>

Ionomer: All counterions are paired with the ions attached to the chain in a low-dielectric medium and ion pairs cluster – dominated by <u>dipolar attraction</u>

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Phases of Ion-Containing Polymers

Polyelectrolyte: Many ions dissociate from the chain in a high-dielectric medium – dominated by charge repulsion

Chain of Dipoles Phase: Ions are mostly paired but do not aggregate to form ion domains

Ionomer: All counterions are paired with the ions attached to the chain in a low-dielectric medium and ion pairs cluster – dominated by dipolar attraction

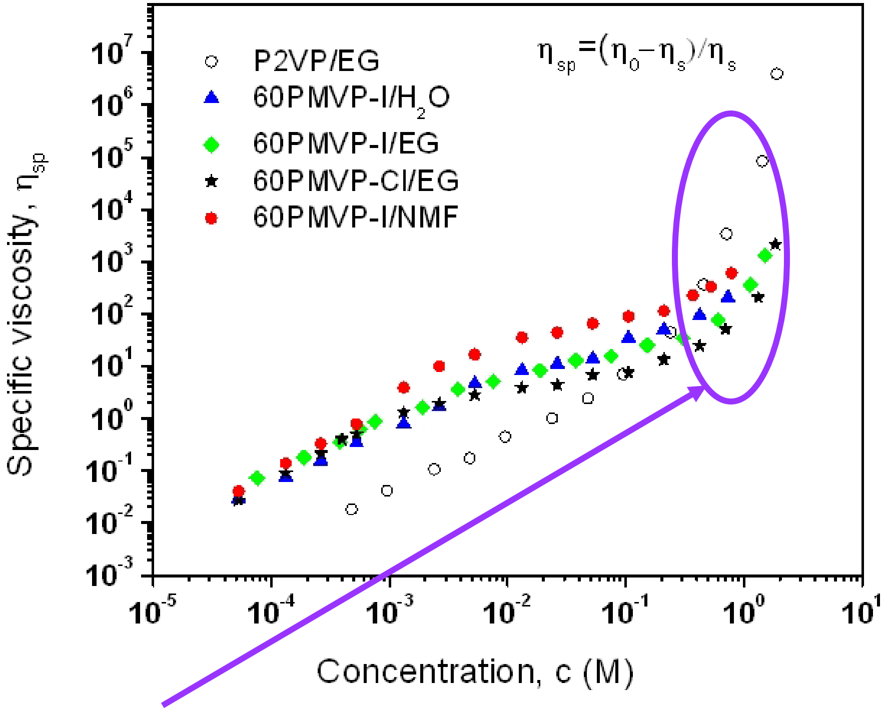
Change dielectric constant, temperature or concentration

Open Questions in Polyelectrolytes

- How do polyelectrolytes (with conformation dominated by charge repulsion) crossover to ionomers (with conformation determined by dipolar attraction of ion pairs) at very high concentrations?

The ‘**polyelectrolyte effect**’ always has the charges *increase* the viscosity relative to neutral polymer

Chain of Dipoles Phase: Ions are mostly paired but do not aggregate



Polyelectrolytes have lower viscosity than the neutral polymer at high concentrations owing to dipolar attraction of condensed counterions. H. Schiessel & P. Pincus, *Macromolecules* **31**, 7953 (1998).

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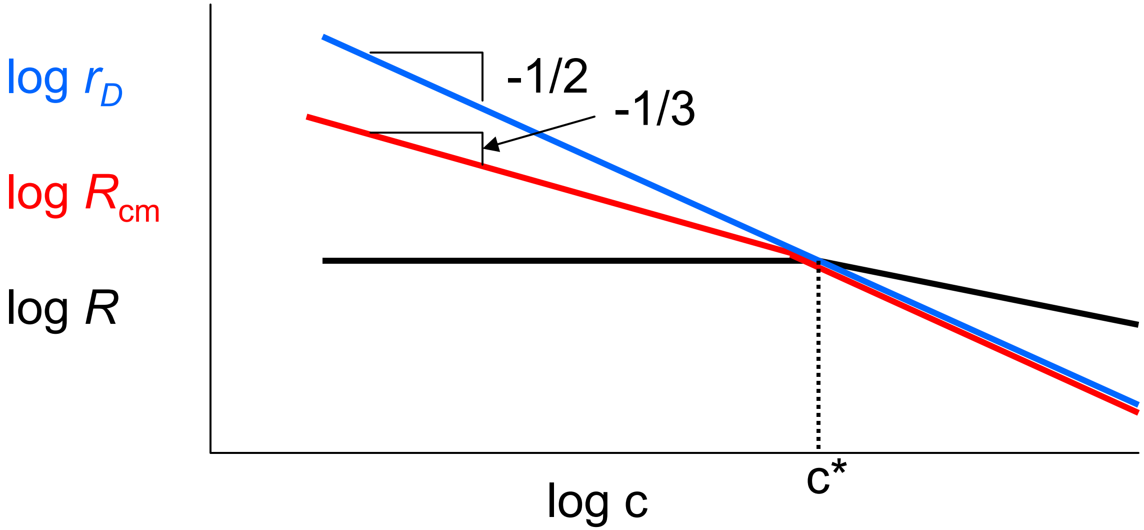

At sufficiently low c, the distance between chains $R_{cm} \sim c^{-1/3}$ is much smaller than the Debye screening length $r_D \sim c^{-1/2}$
The chains should strongly interact and order onto a lattice (dilute crystal).

P. G. de Gennes, P. Pincus, R. M. Velasco, F. Brochard, **Remarks on polyelectrolyte conformation** *J. de Phys. (Paris)* **37**, 1461-73 (1976).

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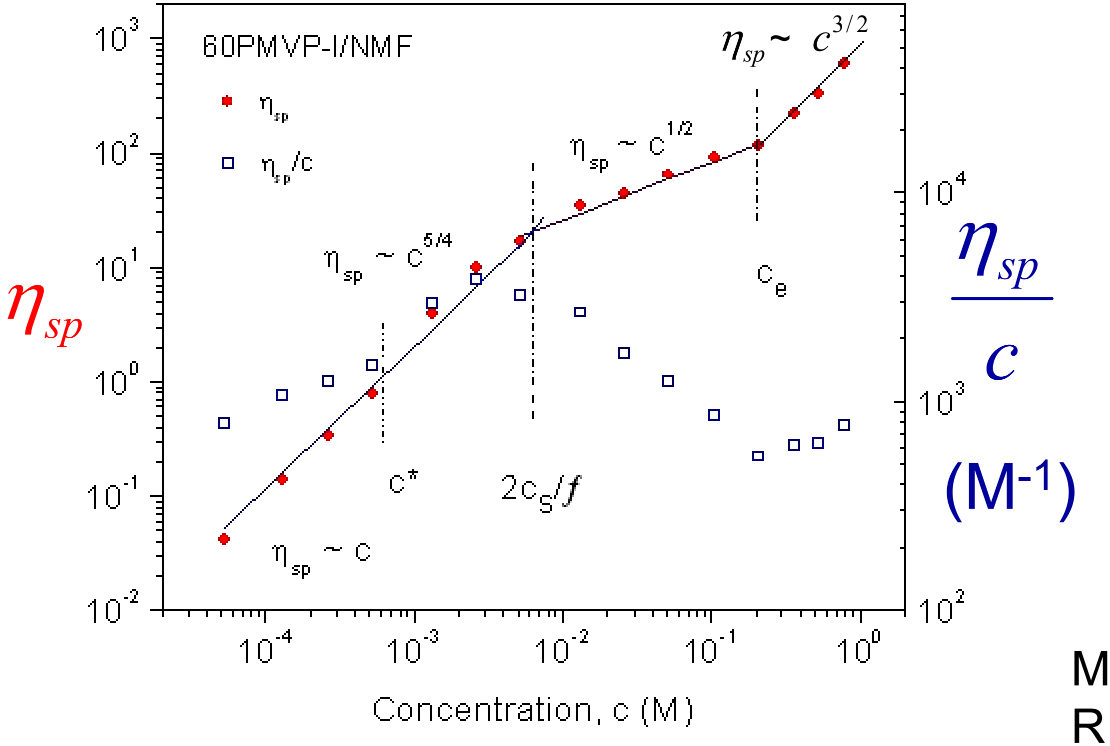


S. Dou and R. H. Colby, *Macromolecules*, submitted: quaternized poly(2-vinyl pyridine) in N-methyl formamide

The scaling model predicts:

$$\eta_{sp} \sim c \quad \text{for } c < c^*$$

$$\eta_{sp} \sim c^{5/4} \text{ for } c^* < c < 2c_s / f$$

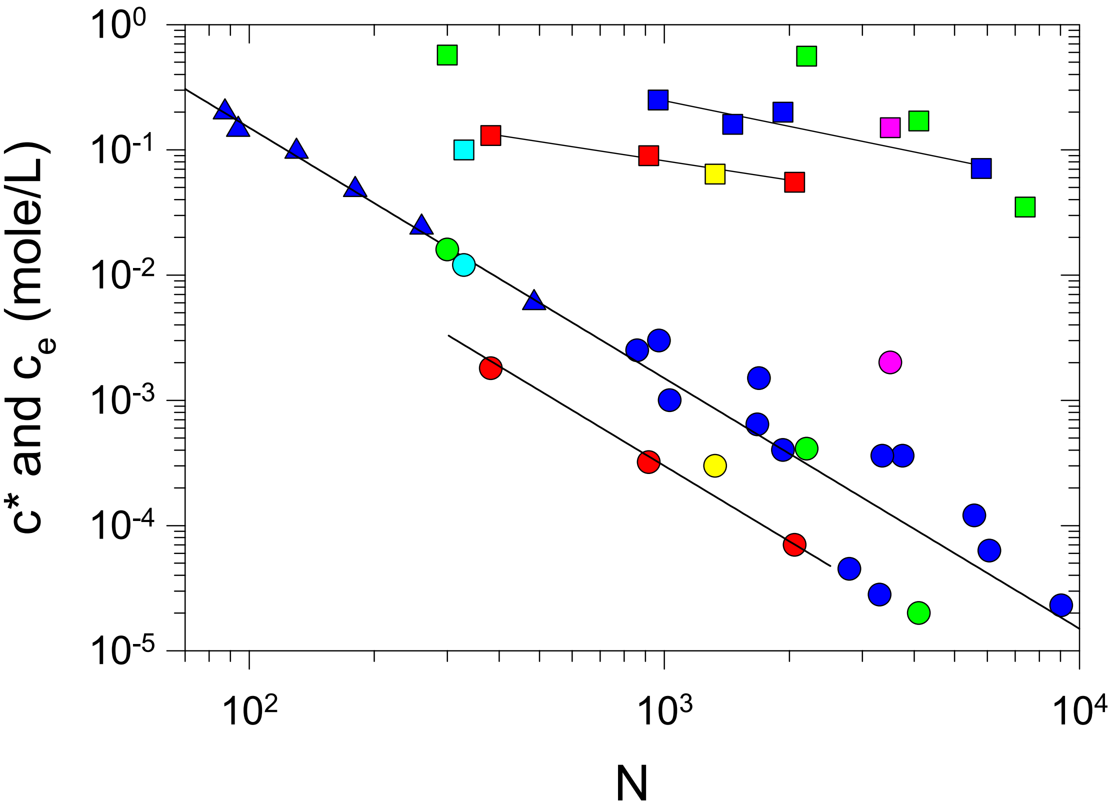
$$\eta_{sp} \sim c^{1/2} \text{ for } 2c_s / f < c < c_e$$

$$\eta_{sp} \sim c^{3/2} \text{ for } c > c_e$$

M. Rubinstein, A. V. Dobrynin and R. H. Colby, *Phys. Rev. Lett.* **73**, 2776 (1994).

Open Questions in Polyelectrolytes

- What does entanglement mean in a polyelectrolyte solution?



*Na*PSS
*Na*PAMS
*Na*IBMA
*Na*DIBMA
*Cl*P2VP in EG

Theory expects
$c_e \approx 10^3 c^* \sim N^{-2}$

Entanglement concentration is nearly independent of chain length!

Polyelectrolyte Solutions

- de Gennes described them as the “least understood form of condensed matter”
- de Gennes’ isotropic semidilute solution model has stood the test of time
- However, ion-containing polymers have many mysteries remaining to be solved.