

# Polyelectrolyte Solution Rheology

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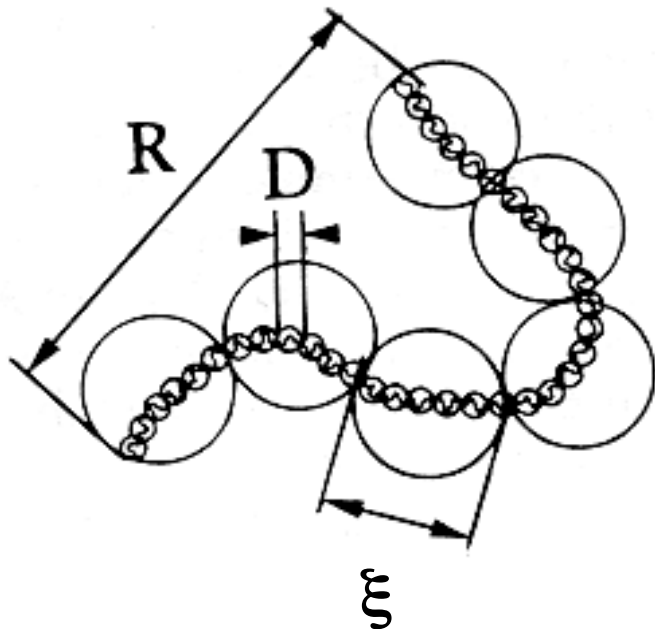
The Department of Materials Science and Engineering  
**MATSE**

Institute of Solid State Physics SOFT Workshop August 9, 2010

# 1976 de Gennes model for semidilute polyelectrolytes

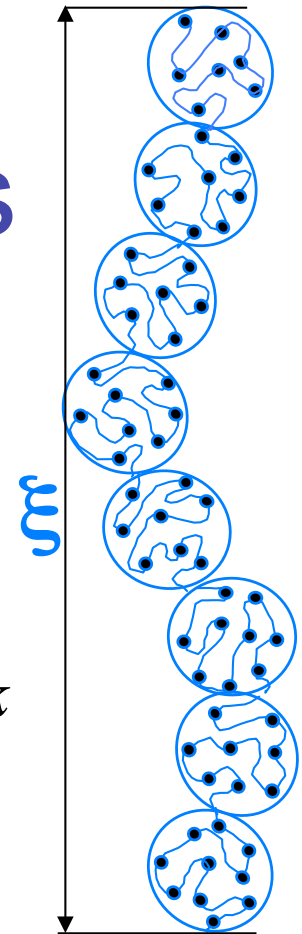
$r > \xi$ : **SCREENED  
ELECTROSTATICS**

*A random walk of  
correlation blobs*



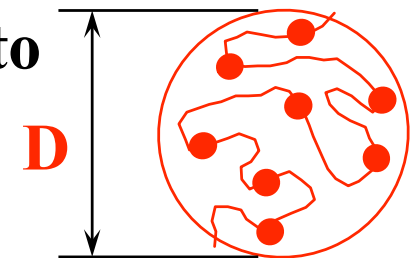
$D < r < \xi$ : **STRONG  
ELECTROSTATIC  
STRETCHING**

*A directed random walk  
of electrostatic blobs*

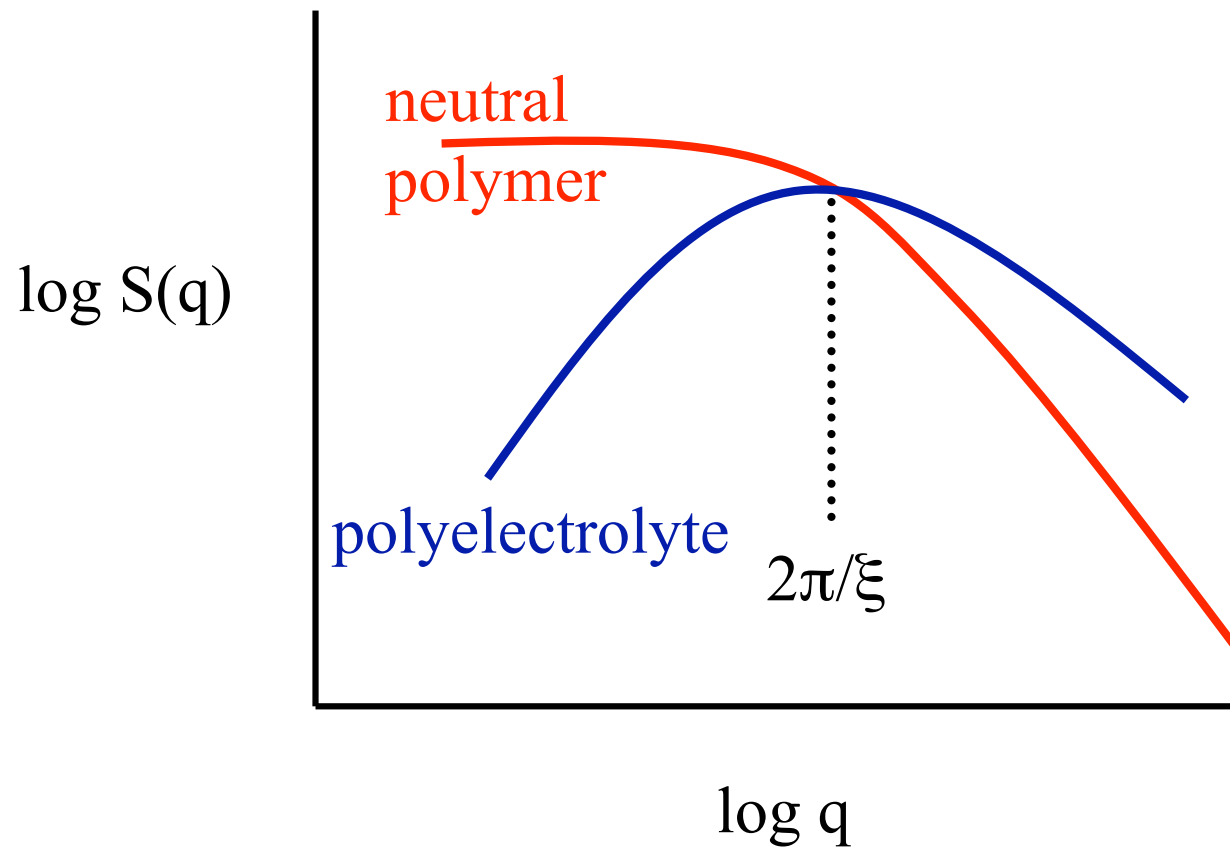


$r < D$ : **WEAK  
ELECTROSTATICS**

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



# Semidilute 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.

# Semidilute polyelectrolytes have a peak in their scattering function

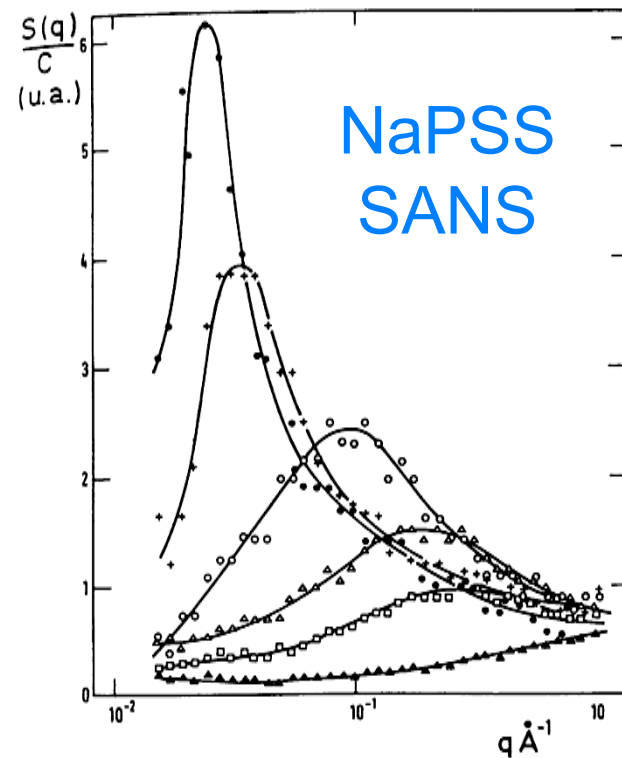
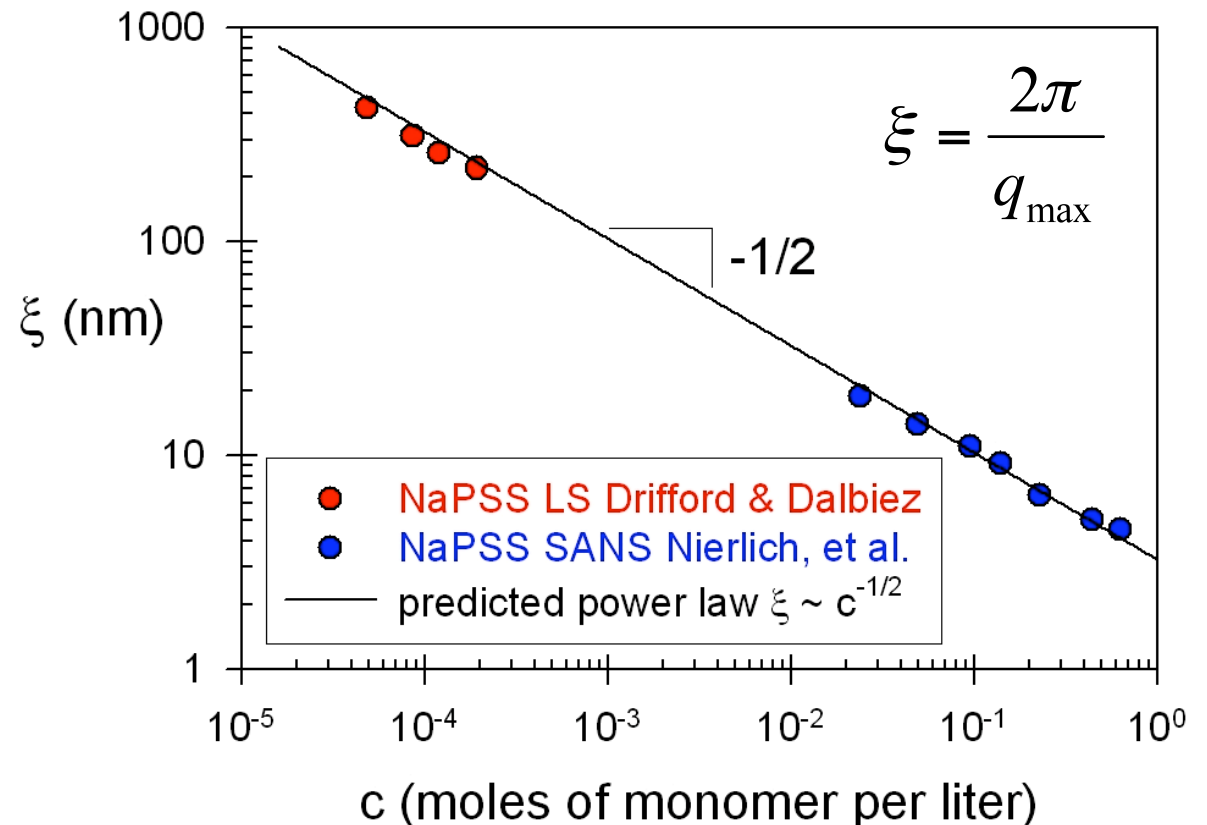


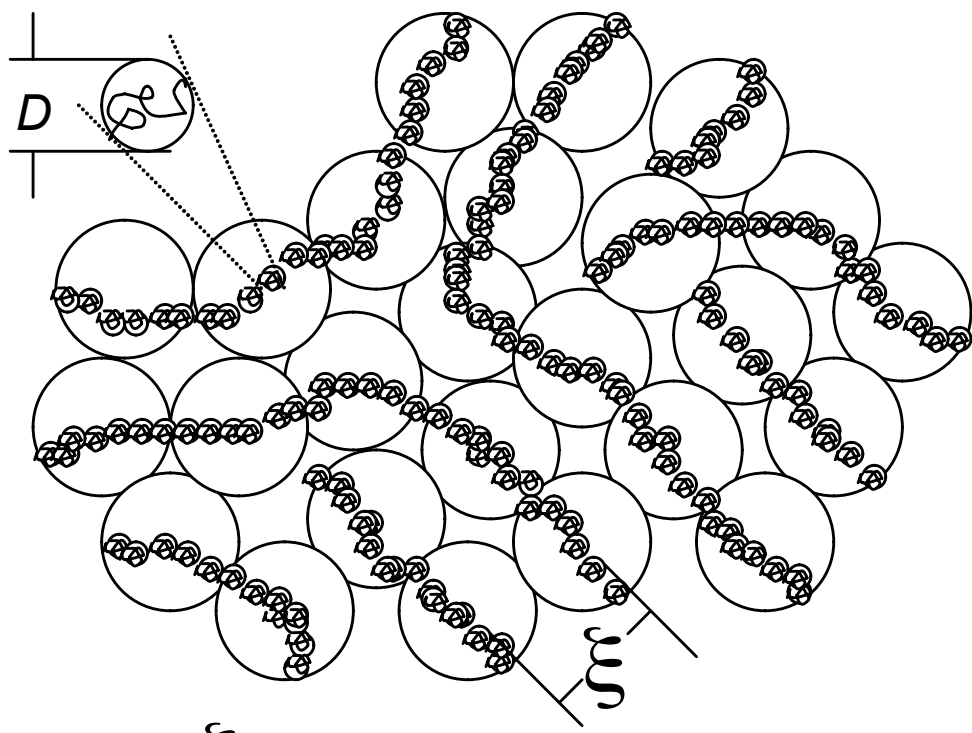
Fig. 3. — Scattered intensity per monomer of a solution of Na PSS<sub>D</sub> ( $M_w = 72\,000$ ) in H<sub>2</sub>O versus polymer concentration.

- $c = 10^{-2} \text{ g.cm}^{-3}$ ; +  $1.96 \times 10^{-2} \text{ g.cm}^{-3}$ ;
- $4.76 \times 10^{-2} \text{ g.cm}^{-3}$ ; △  $9.09 \times 10^{-2} \text{ g.cm}^{-3}$ ;
- $13.04 \times 10^{-2} \text{ g.cm}^{-3}$ ; ▲  $23 \times 10^{-2} \text{ g.cm}^{-3}$ .

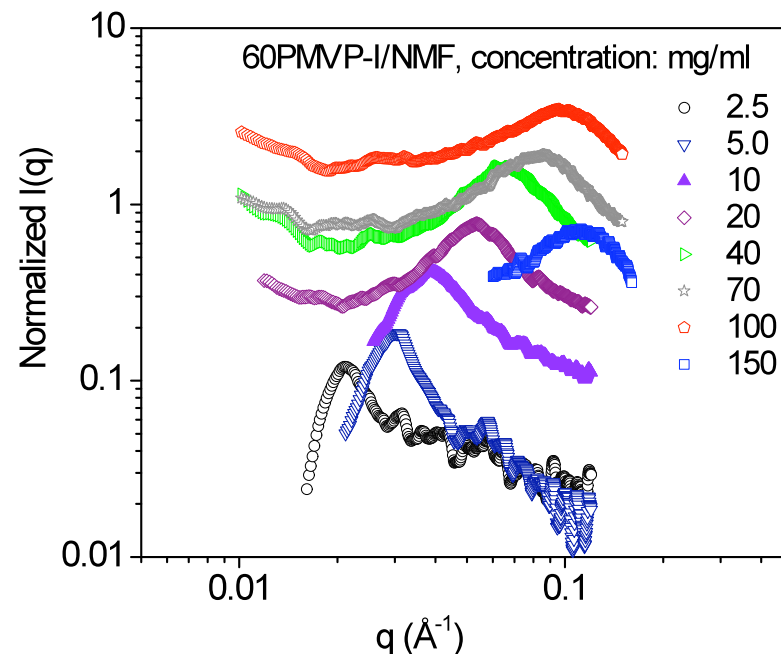


M. Nierlich, et al., *J. de Phys. (Paris)* **40**, 701 (1979).

# Small-angle X-ray scattering from semidilute polyelectrolyte solutions



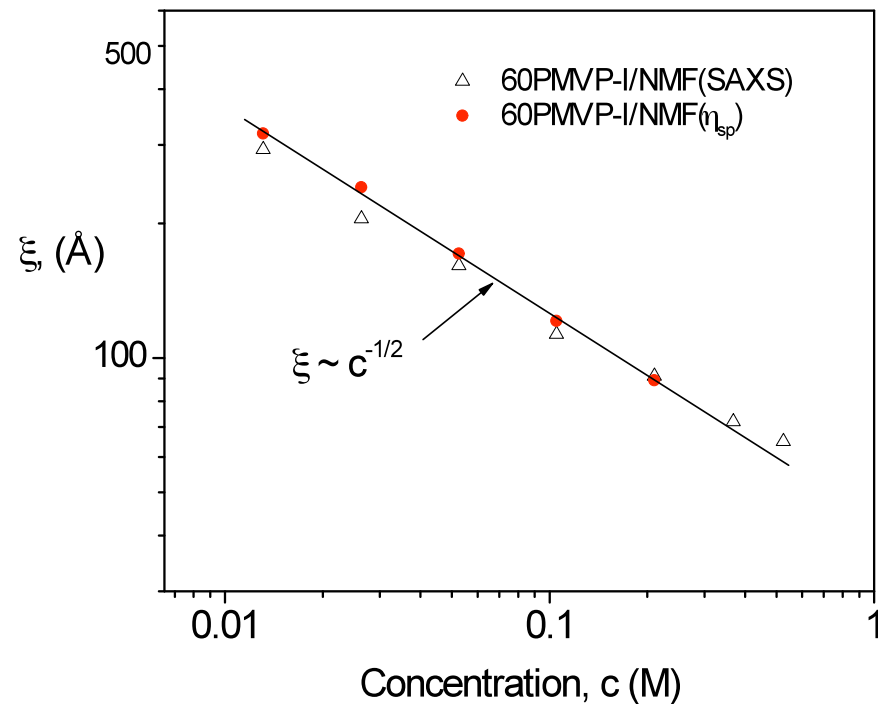
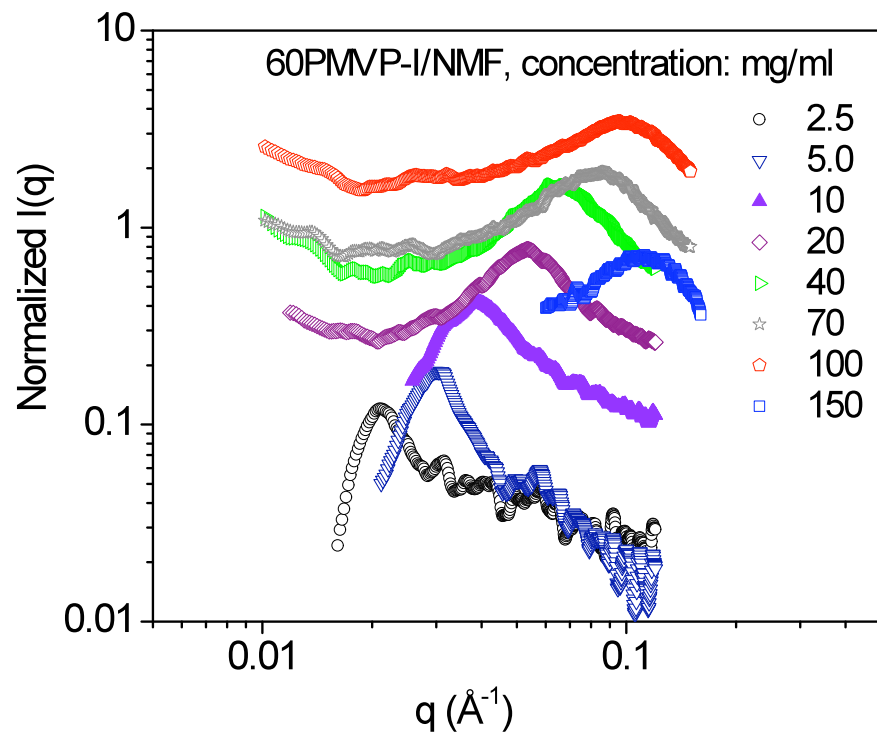
SAXS dominated by I<sup>-</sup> counterions  
Quaternized poly(2-vinyl pyridine)  
in N-methyl formamide



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

S. Dou and RHC, *Macromolecules*, **41**, 6505 (2008).

# Polyelectrolyte Solution Correlation Length from SAXS of QP2VP-/ in NMF



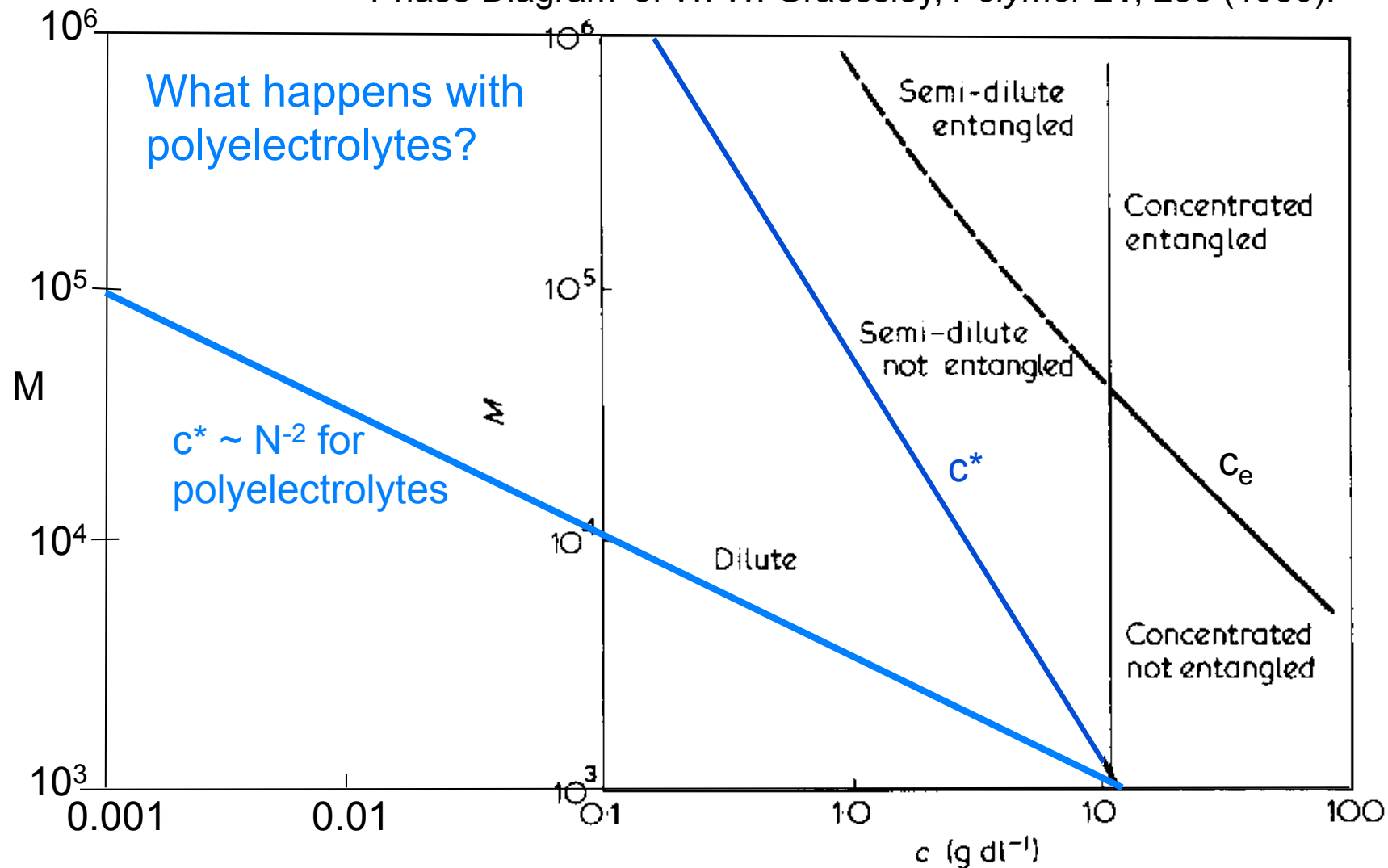
SAXS determination of correlation length  $q_{\max} \sim c^{1/2}$   
 $\xi = 2\pi / q_{\max}$

Semidilute unentangled viscosity determination of correlation length  $\xi = \left( \frac{N}{c\eta_{sp}} \right)^{1/3}$

P. G. deGennes, P. Pincus, R. M. Velasco, F. Brochard, *J. Phys. (Paris)* **37**, 1461 (1976).  
 A. V. Dobrynin, RHC and M. Rubinstein, *Macromolecules* **28**, 1859 (1995).

# Semidilute Unentangled Solutions

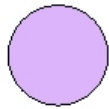
'Phase Diagram' of W. W. Graessley, *Polymer* **21**, 258 (1980).



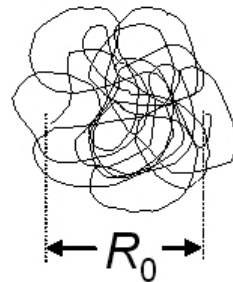
# Comparison of the 3 universality classes of polymer solutions: neutral- $\theta$ , neutral-good and polyelectrolyte with no salt

neutral polymers in

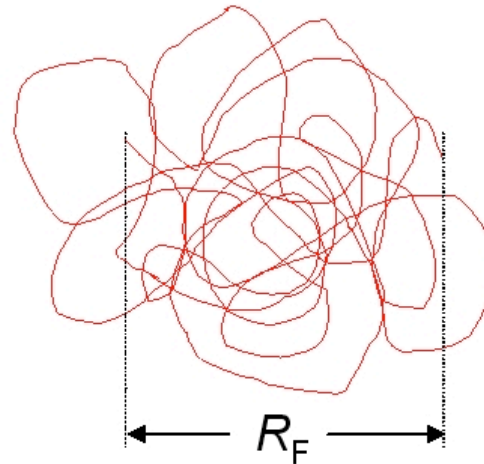
poor solvent



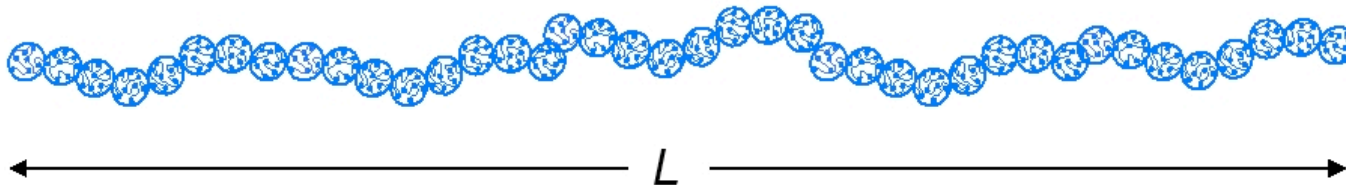
$\theta$ -solvent



good solvent



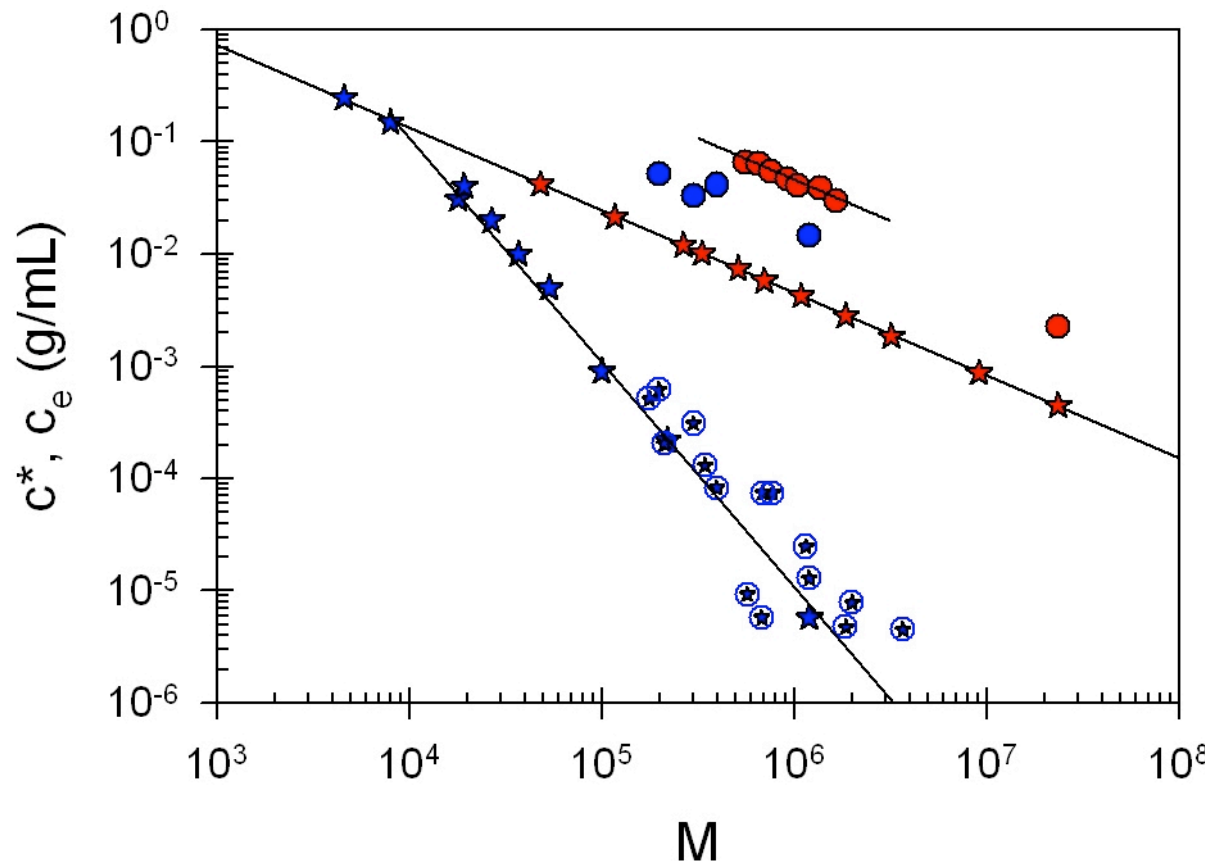
dilute polyelectrolyte with no salt



next few slides from RHC, *Rheol. Acta* **49**, 425 (2010) and references therein



# Comparison of the 3 universality classes of polymer solutions: neutral- $\theta$ , neutral-good and polyelectrolyte with no salt



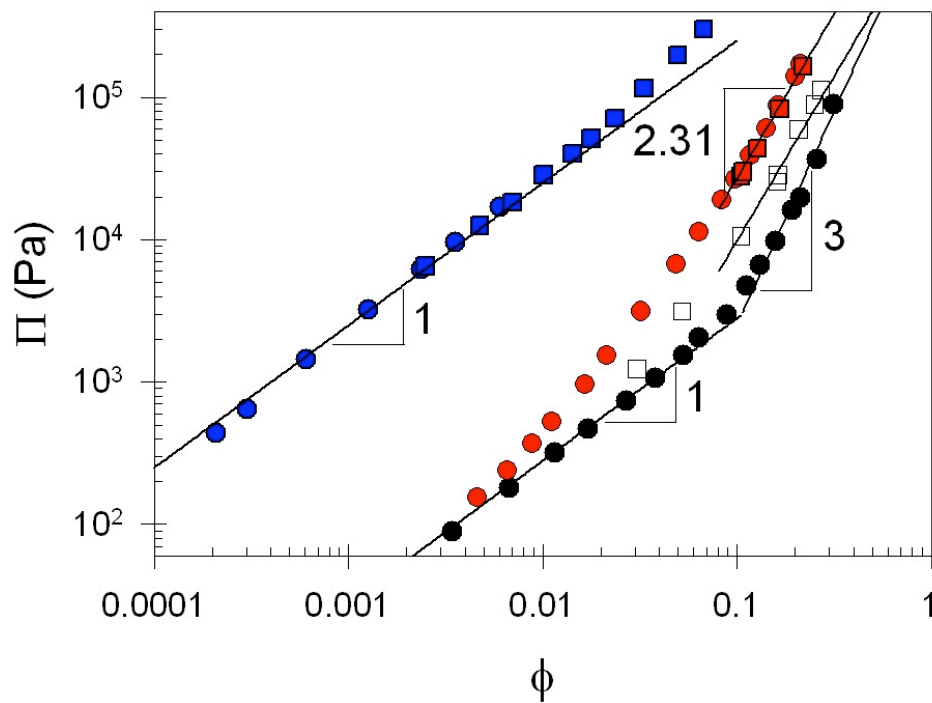
Red circles are entanglement concentration  $c_e$  and red stars are overlap concentration  $c^*$  of polystyrene in toluene (neutral good solvent)  $c_e \sim c^*$

Blue circles are entanglement concentration  $c_e$ , blue stars are overlap concentration  $c^*$  from SAXS and circled blue stars are  $c^*$  from viscosity of sodium poly(styrene sulfonate) in water (polyelectrolyte with no salt)

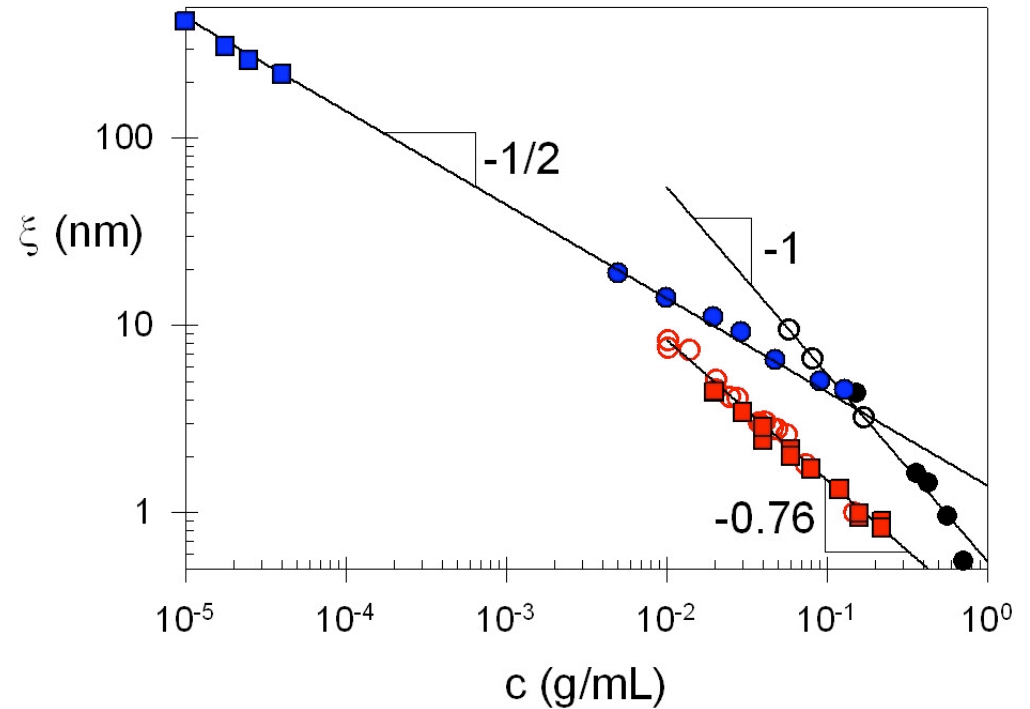
Lines have slopes of -2 and -0.74

Scaling expects  $c_e \sim c^*$   
not observed for polyelectrolytes

# Comparison of the 3 universality classes of polymer solutions: neutral- $\theta$ , neutral-good and polyelectrolyte with no salt



Osmotic Pressure  
 Polyelectrolyte  $kT$  per counterion  
 Neutral dilute  $kT$  per chain  
 Neutral semidilute  $kT$  per correlation volume



Correlation Length  
 PE no salt  $\xi \sim c^{-1/2}$   
 neutral-good  $\xi \sim c^{-0.76}$   
 neutral- $\theta$   $\xi \sim c^{-1}$

# Semidilute Unentangled Dynamics

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

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

## Polyelectrolytes

$$\xi \sim c^{-1/2}$$

$$R \sim N^{1/2}c^{-1/4}$$

$$\tau \sim N^2c^{-1/2}$$

$$G = ckT/N$$

$$\eta = G\tau \sim Nc^{1/2}$$

$$D = R^2/\tau \sim N^{-1}c^0$$

blob size  
polymer size  
relaxation time  
terminal modulus  
viscosity

diffusion coefficient

## Neutral Polymers

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$$D = R^2/\tau \sim N^{-1}c^0$$

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

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$$\tau \sim N^2c^{1/4}$$

$$G = ckT/N$$

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blob size  
 polymer size  
 relaxation time  
 terminal modulus  
 viscosity  
 diffusion coefficient

$$D = R^2/\tau \sim N^{-1}c^{-1/2}$$

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empirical Fuoss law first predicted by de Gennes

blob size

polymer size

relaxation time

terminal modulus

viscosity

## Neutral Polymers

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$$\tau \sim N^2c^{1/4}$$

$$G = ckT/N$$

$$\eta = G\tau \sim Nc^{5/4}$$

$D = R^2/\tau \sim N^{-1}c^0$  diffusion coefficient  $D = R^2/\tau \sim N^{-1}c^{-1/2}$

# Semidilute Unentangled Dynamics

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

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$$D = R^2/\tau \sim N^{-1}c^0$$

even stranger prediction,  
expects polyelectrolytes  
to be rheologically unique

blob size

polymer size

relaxation time

terminal modulus

viscosity

## Neutral Polymers

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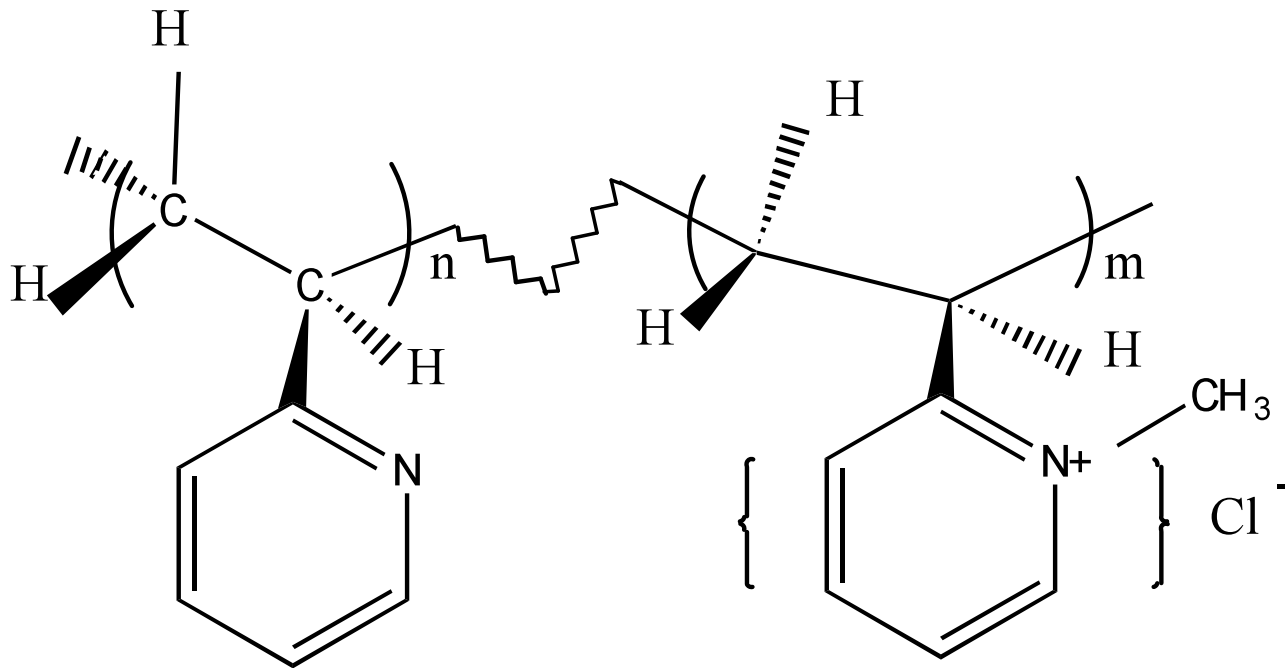
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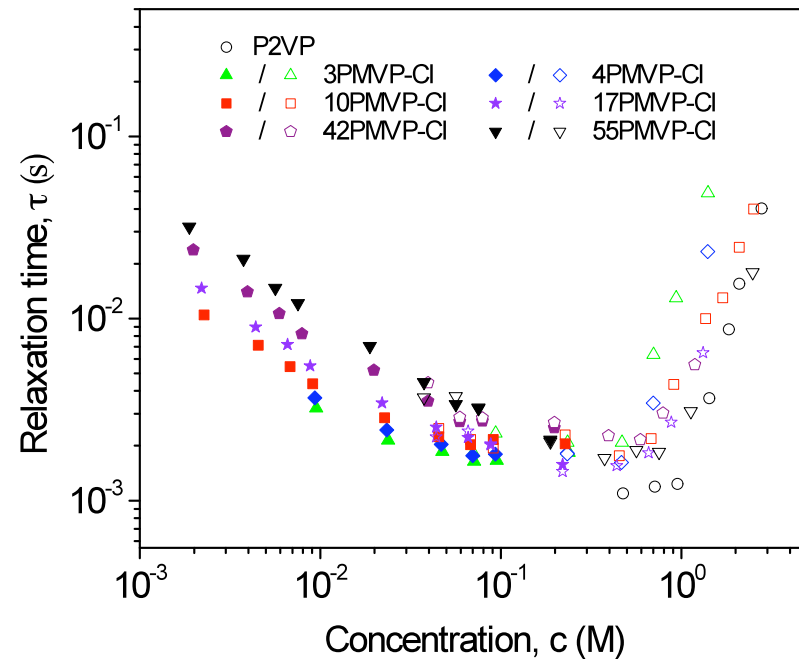
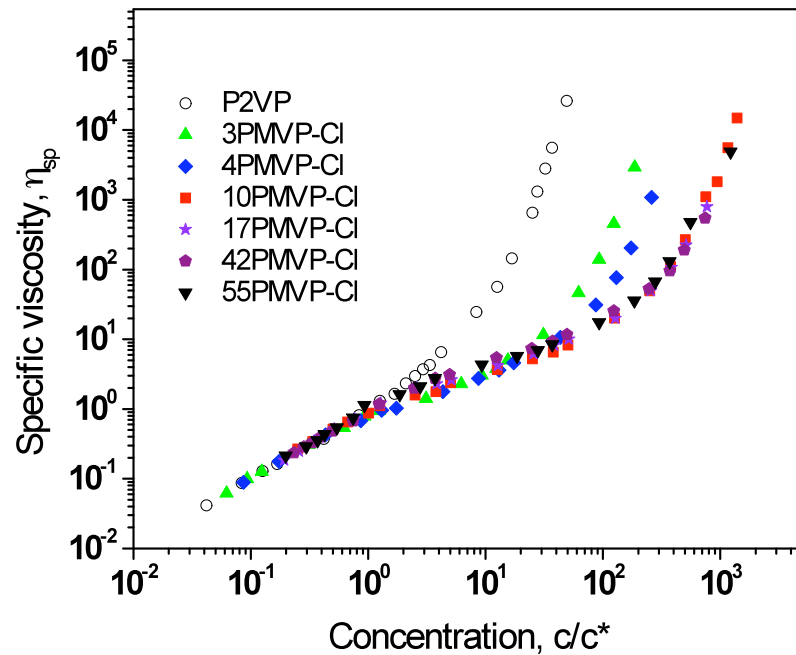
# Quaternized P2VP in ethylene glycol

- ethylene glycol does not react with air
- ethylene glycol has extremely low salt
- ethylene glycol is good solvent for neutral P2VP (the unquaternized parent polymer)



# Polyelectrolyte Solution Rheology

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



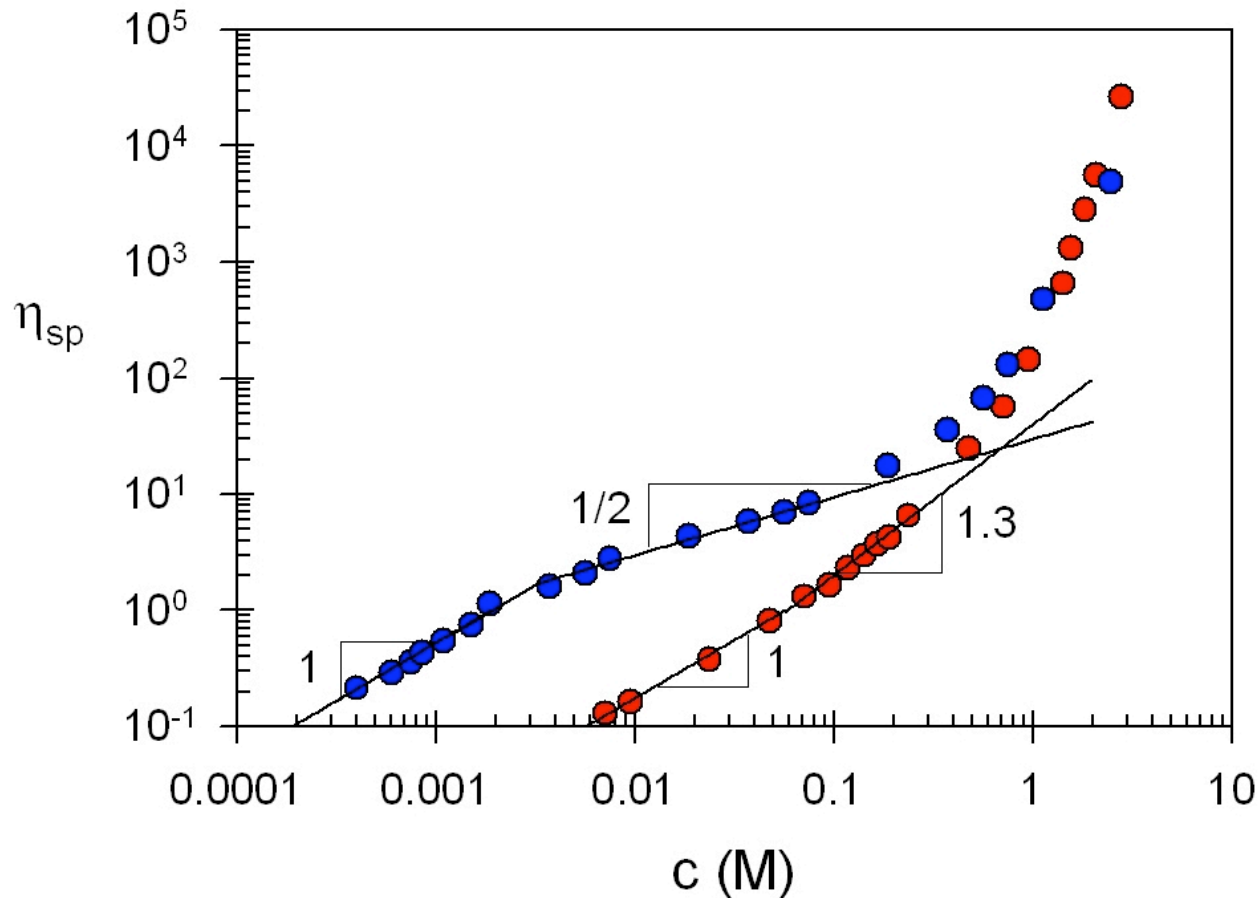
$c/c^*$  reduces all polyelectrolyte specific viscosity data on dilute and semidilute unentangled solutions to a common functional form with

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

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



# Comparison of the 3 universality classes of polymer solutions: neutral- $\theta$ , neutral-good and polyelectrolyte with no salt



poly(2-vinyl pyridine)  
in ethylene glycol  
(neutral-good solvent)

partially quaternized  
poly(2-vinyl pyridine)  
in ethylene glycol  
(polyelectrolyte with no salt)

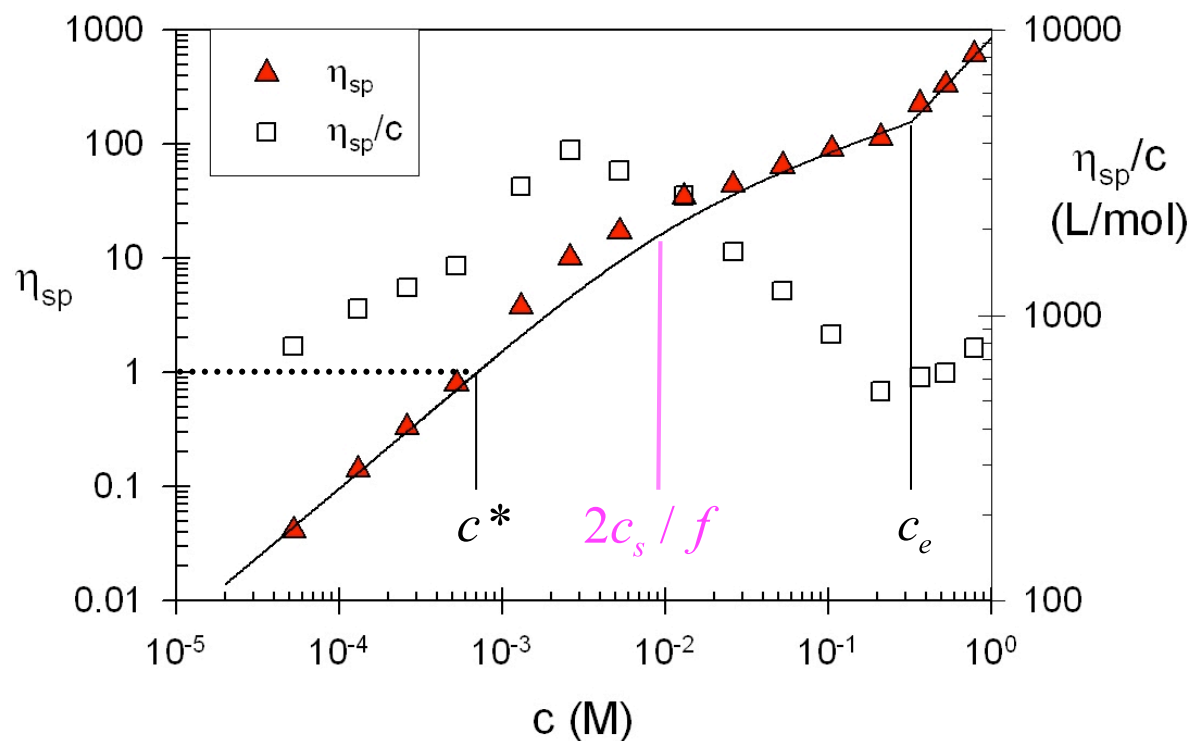
same chain length

ethylene glycol is unusual  
as it dissolves both neutral  
and polyelectrolyte and  
has no residual salt

# Conclusions: 60PMVP-I in EG

- EG has *very* little residual salt with  $\varepsilon = 37$
- EG is a good solvent for neutral P2VP
- Lack of salt contaminants allows full test and elegant demonstration of scaling for dilute and semidilute unentangled solutions
- Entangled solutions show the expected concentration dependences but  $c_e$  is not simply proportional to  $c^*$ , so scaling fails for  $c > c_e$

# Polyelectrolyte Solution Specific Viscosity of QP2VP-/ in NMF



$$\eta_{sp} \sim N\sqrt{c} \left[ 1 + \frac{2c_s}{fc} \right]^{-3/4} \quad \text{for } c^* < c < c_e$$

**Residual salt concentration:**

$$c_s = \left( \frac{f}{2} \right) \left( \frac{b}{B} \right)^2 N^{4/3} [\eta]^{-5/3}$$

Crossover at  $f c = 2 c_s$

**Low salt limit:**  $c > 2c_s / f$

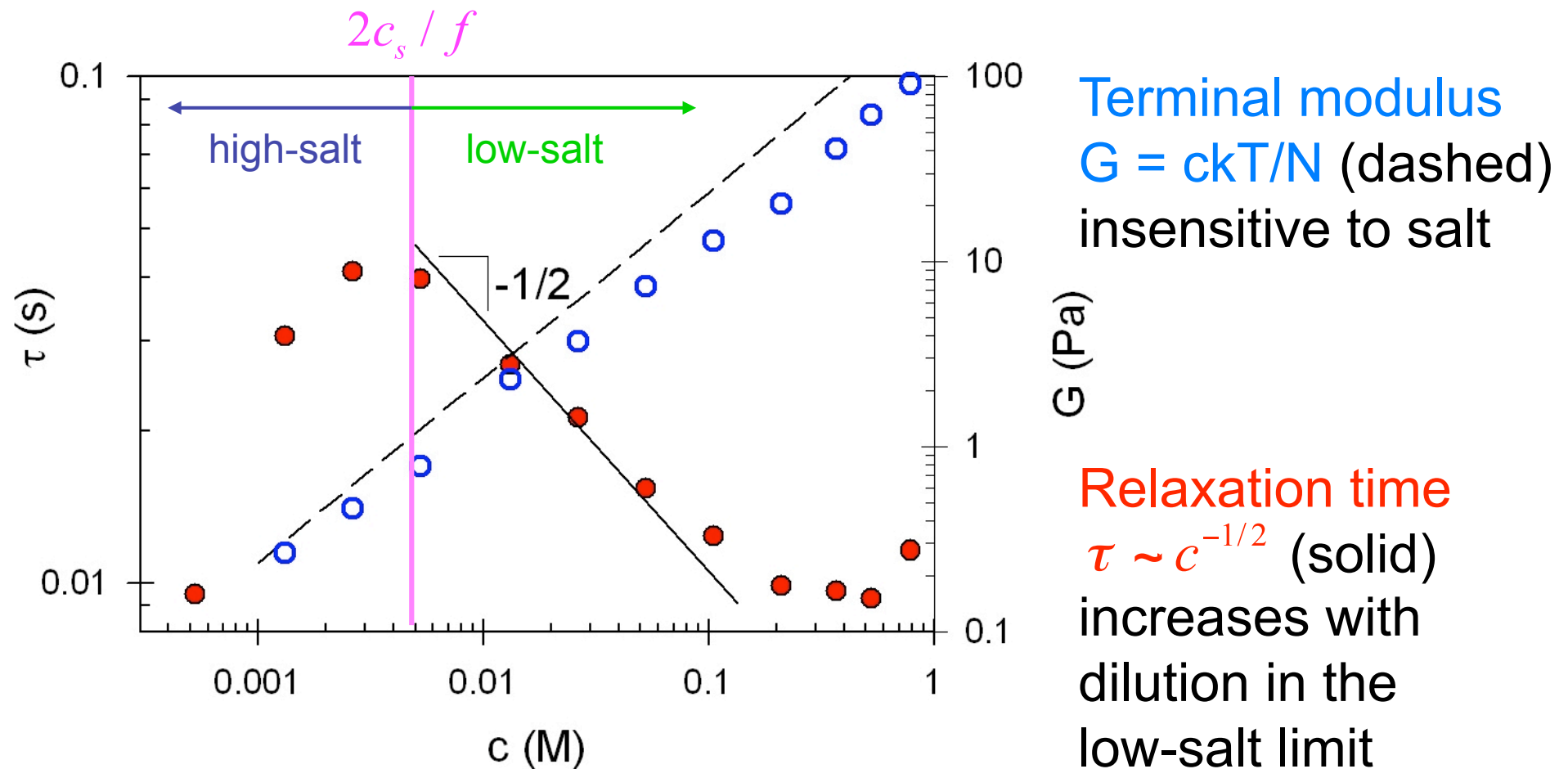
$$\eta_{sp} \sim c^{1/2}$$

**High salt limit:**  $c < 2c_s / f$

$$\eta_{sp} \sim c^{5/4}$$

(high-salt polyelectrolyte is the same as neutral good solvent)

# Polyelectrolyte Solution Modulus and Relaxation Time QP2VP-/NMF

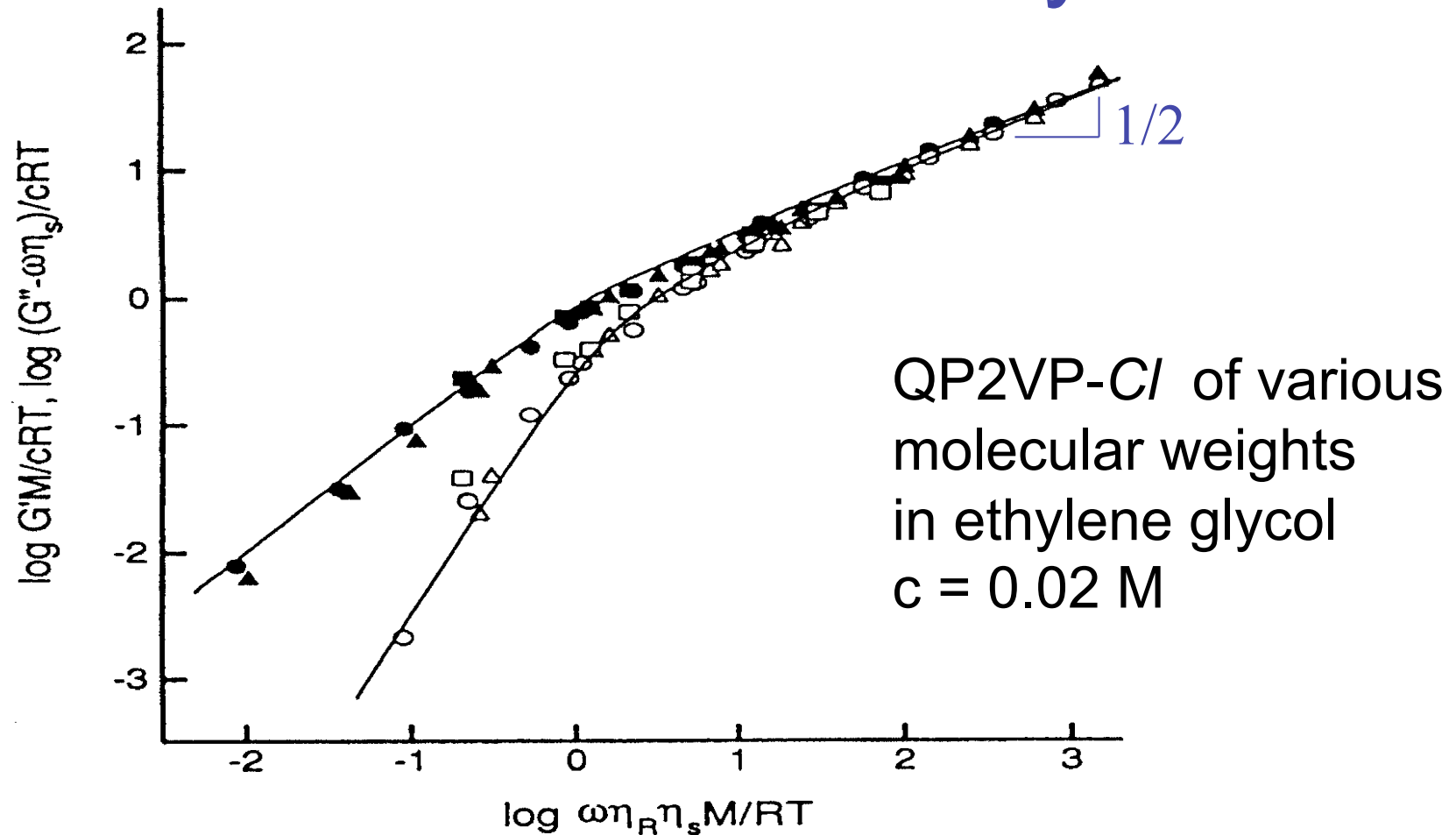


S. Dou and RHC, *Macromolecules* **41**, 6505 (2008).

# Conclusions: 60PMVP-I in NMF

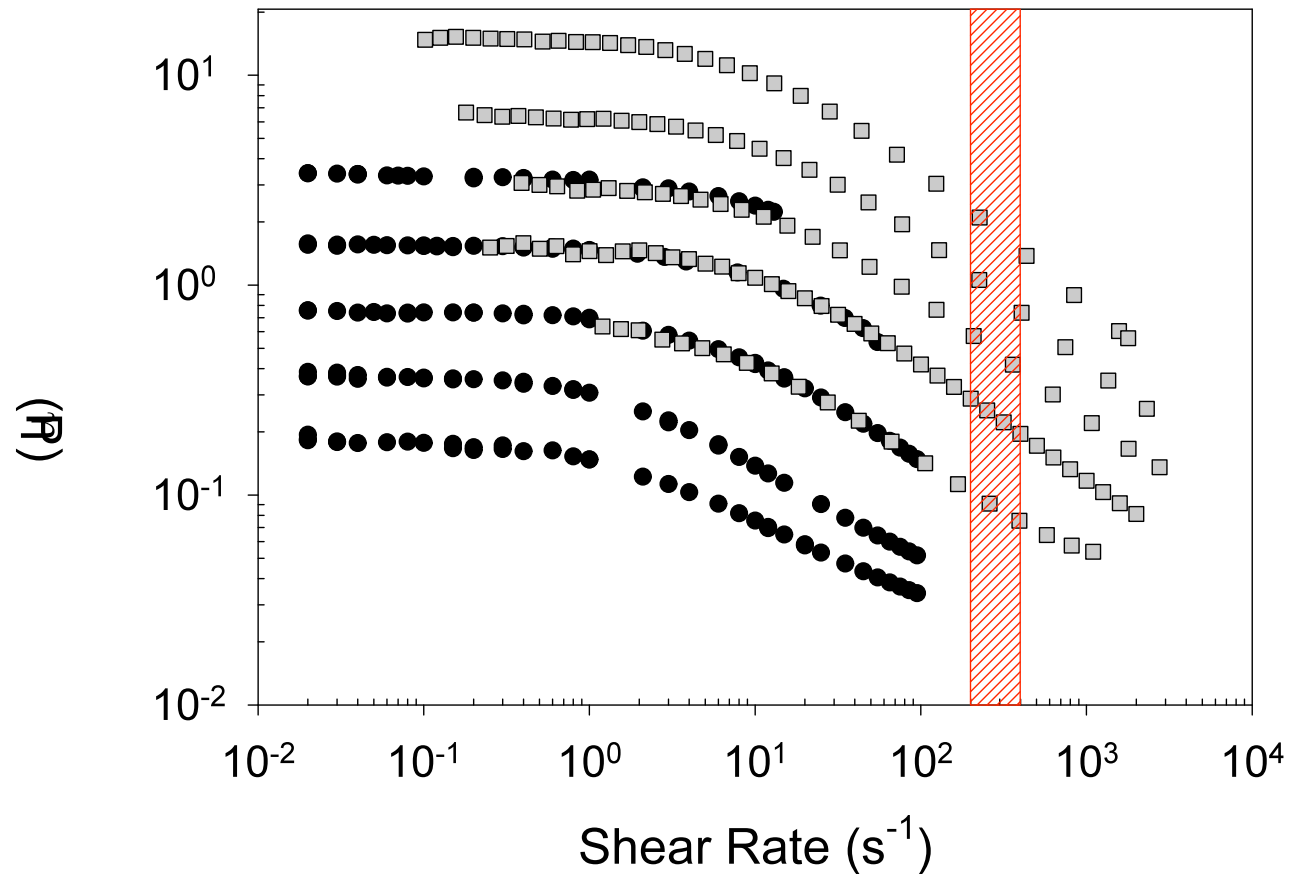
- NMF has high  $\epsilon = 182$  and large  $f = 0.27$
- NMF has  $c_s = 1.4$  mM residual salt
- NMF is a good solvent for neutral P2VP
- The Dobrynin 1995 scaling model describes viscosity  $\eta_{sp}(c)$
- The correlation length from SAXS and viscosity agree quantitatively and have the concentration dependence expected by the deGennes 1976 scaling model.

# The Rouse Model Describes Linear Viscoelasticity



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

# Shear Thinning Enhanced by Dilution



Gravity-  
driven  
capillary  
viscometer  
shear rate  
range

NaPAMS = sodium poly(2-acrylamido-2-methylpropane sulfonate)  
 $M = 1.7 \times 10^6$  with no added salt ( $2.2 \times 10^{-4} \text{ M} \leq c \leq 8.0 \times 10^{-2} \text{ M}$ )

W. E. Krause, J. S. Tan and RHC, *J. Polym. Sci.: Polym. Phys.* **37**, 3429 (1999).

# Unentangled – Rouse Model

- The Rouse Model describes linear viscoelasticity of unentangled polyelectrolyte solutions
- The Rouse Model qualitatively describes  $\eta(c)$ ,  $\tau(c)$ ,  $G(c)$ , and  $D(c)$  for unentangled semidilute solutions
- Shear thinning starts at lower rates as polyelectrolytes are diluted



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- Shear thinning starts at lower rates as polyelectrolytes are diluted

**This makes polyelectrolyte solutions rheologically unique!**

# Open Questions in Polyelectrolytes

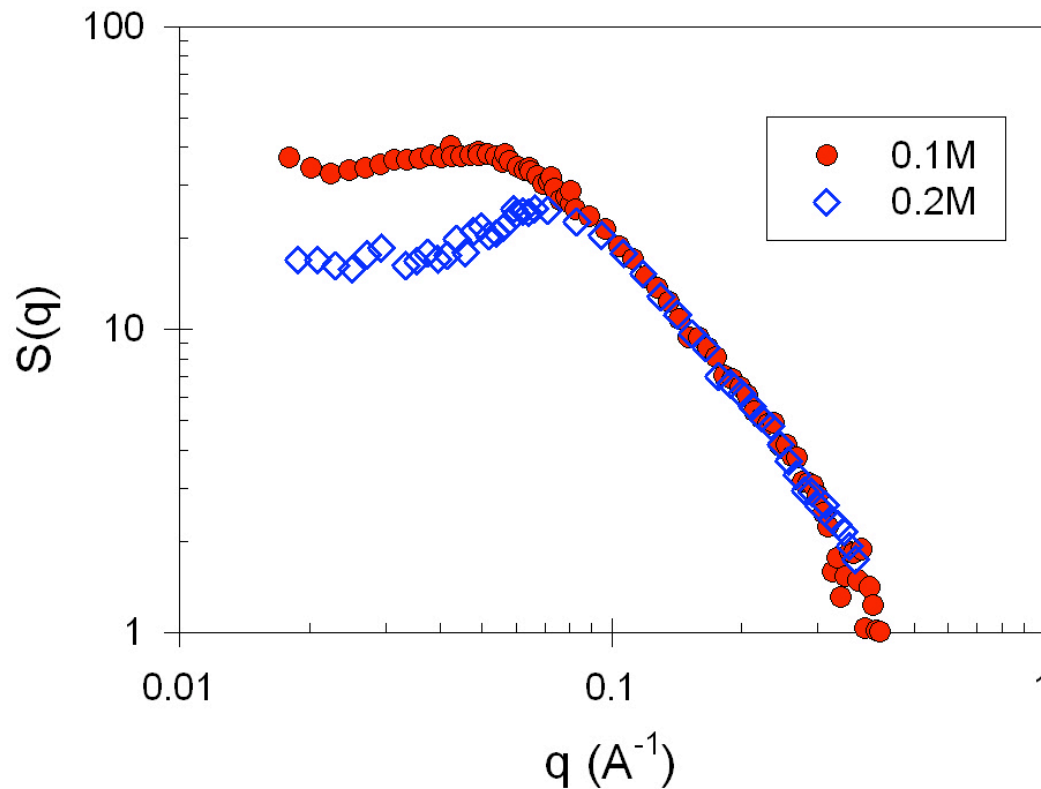
- $S(q)$  for  $q > 2\pi / \xi$  : What is the form factor for the directed random walk inside the correlation blob?
- $S(q)$  for  $q \ll 2\pi / \xi$  : What is the origin of the enormous scattering at very low wavevectors? Related to slow mode?
- How do polyelectrolytes (with conformation dominated 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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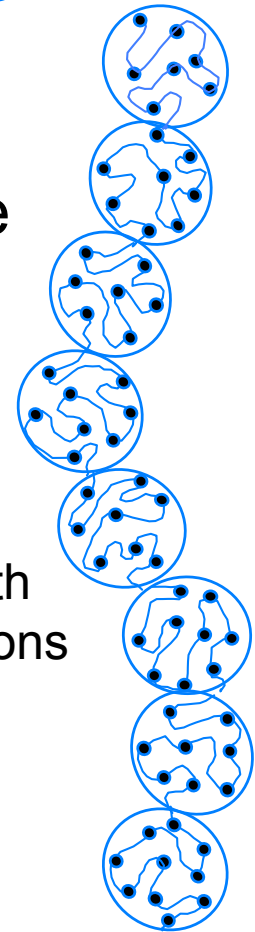


Experimental way to access the form factor of a dilute polyelectrolyte?

Sulfonated polystyrene with deuterated TMA<sup>+</sup> counterions that are contrast-matched

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

Directed random walk?  
Bending on the scale of  $\xi$ ?

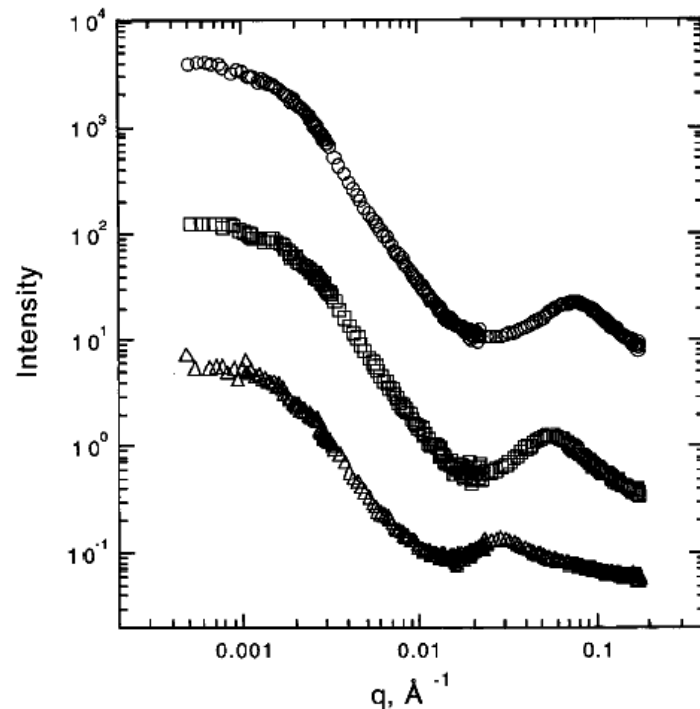


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**Figure 4.** Log–log plot of SANS scattered intensity and SLS scattered intensity,  $I(q)$ , plotted versus the scattering vector  $q$  for PMVP in  $D_2O$  for three polymer concentrations: ( $\Delta$ ) 3.0 g/L, ( $\square$ ) 15 g/L, and ( $\circ$ ) 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!

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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

**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



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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

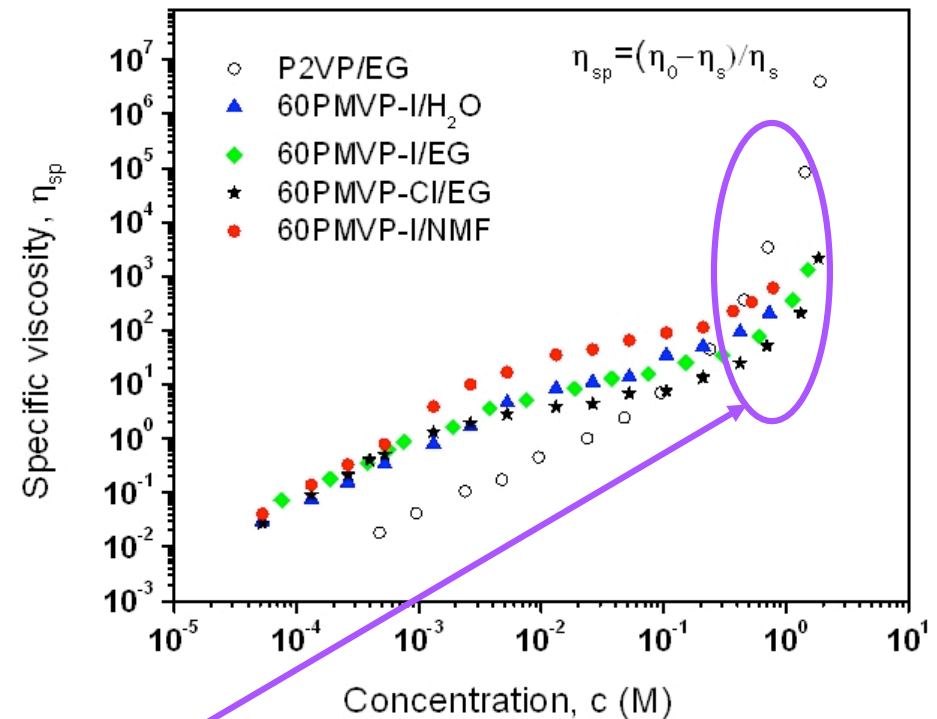
**Change dielectric constant, temperature or concentration**

# 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



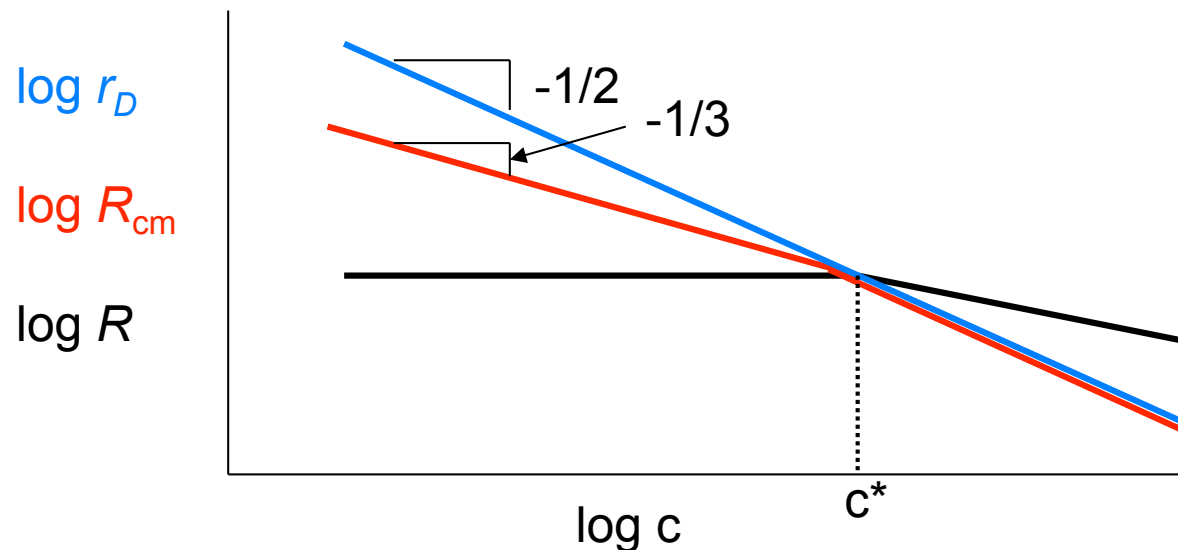
Polyelectrolytes have lower viscosity than the neutral polymer at high concentrations owing to dipolar attraction of condensed counterions. H. Schiessel & P. Pincus, *Macromolecules* **31**, 7953 (1998).

# 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  $q \ll 2\pi / \xi$  : 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?

# Open Questions in Polyelectrolytes

- Does the ordered phase predicted by de Gennes exist at ultra-low concentrations?



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).

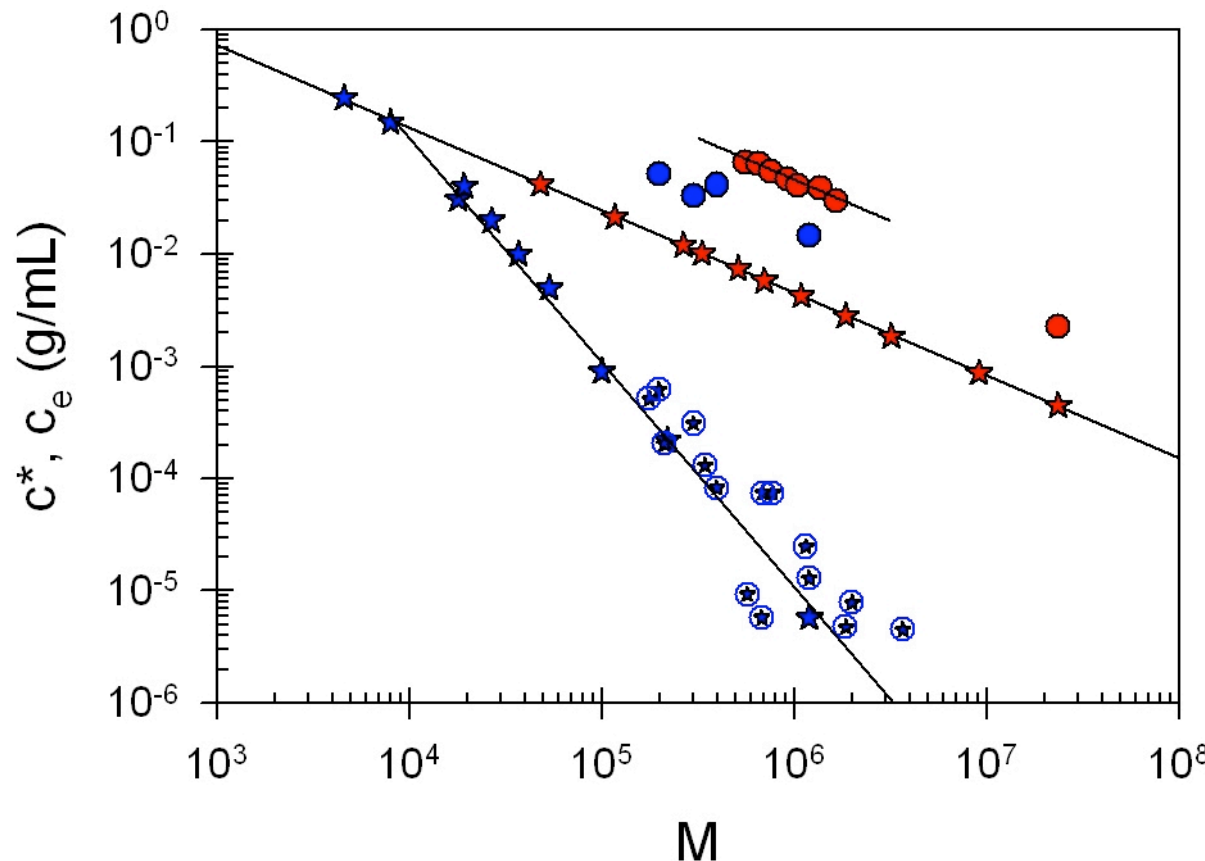
P. G. de Gennes, P. Pincus, R. M. Velasco, F. Brochard, **Remarks on polyelectrolyte conformation** *J. de Phys. (Paris)* **37**, 1461-73 (1976).

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

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# Comparison of the 3 universality classes of polymer solutions: neutral- $\theta$ , neutral-good and polyelectrolyte with no salt



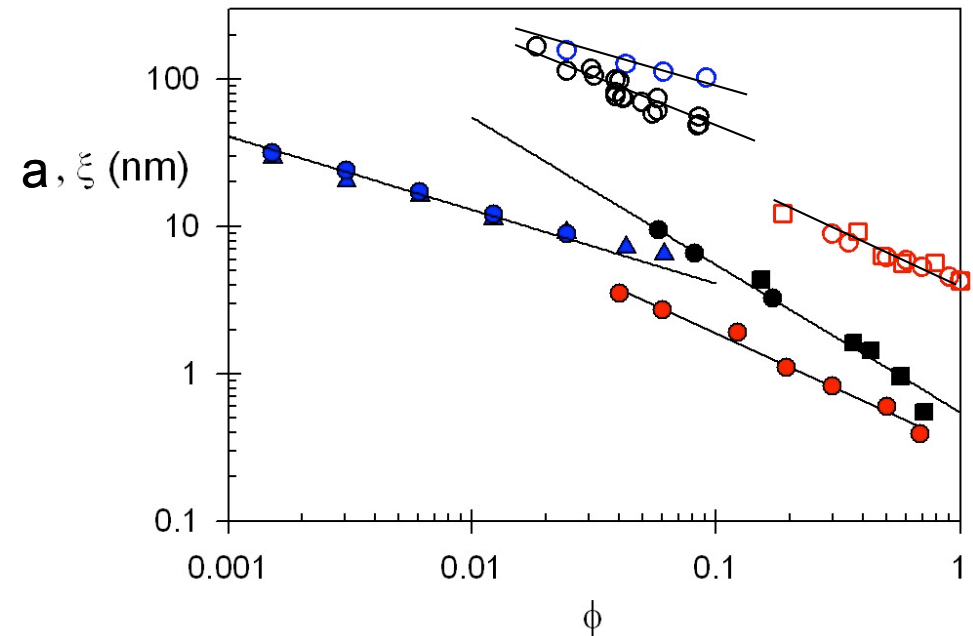
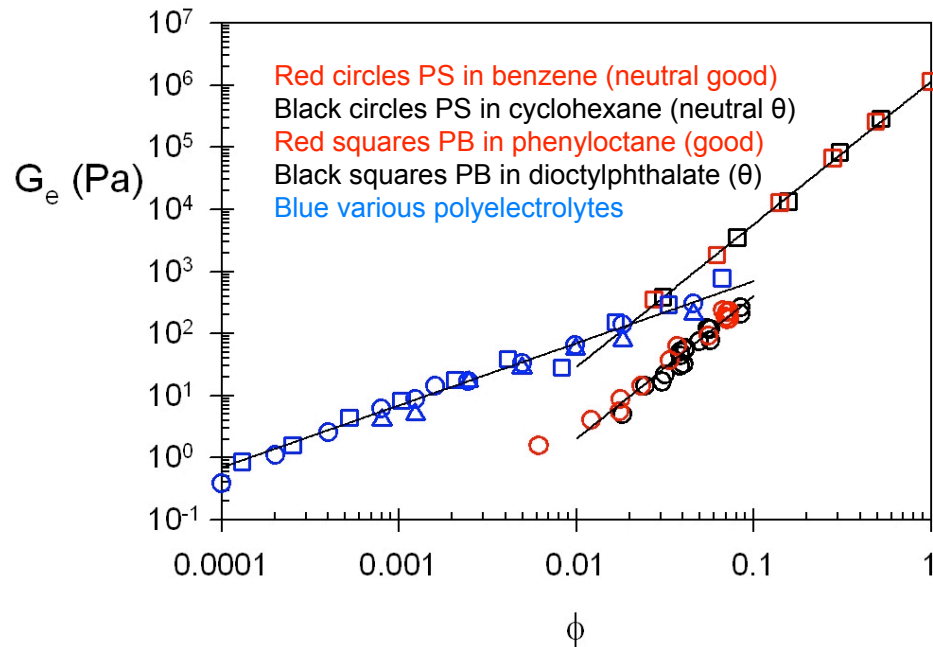
Red circles are entanglement concentration  $c_e$  and red stars are overlap concentration  $c^*$  of polystyrene in toluene (neutral good solvent)  $c_e \sim c^*$

Blue circles are entanglement concentration  $c_e$ , blue stars are overlap concentration  $c^*$  from SAXS and circled blue stars are  $c^*$  from viscosity of sodium poly(styrene sulfonate) in water (polyelectrolyte with no salt)

Lines have slopes of -2 and -0.74

Scaling expects  $c_e \sim c^*$   
not observed for polyelectrolytes

# Comparison of the 3 universality classes of polymer solutions: neutral- $\theta$ , neutral-good and polyelectrolyte with no salt



Terminal Modulus (lines are predicted slopes)

Polyelectrolyte with no salt  $kT$  per chain

Neutral good solvent  $G \sim c^{2.31}$

Neutral  $\theta$ -solvent  $G \sim c^{7/3}$

$$G = \frac{kT}{a^2\xi}$$

Tube Diameter (open)

Correlation Length (filled)

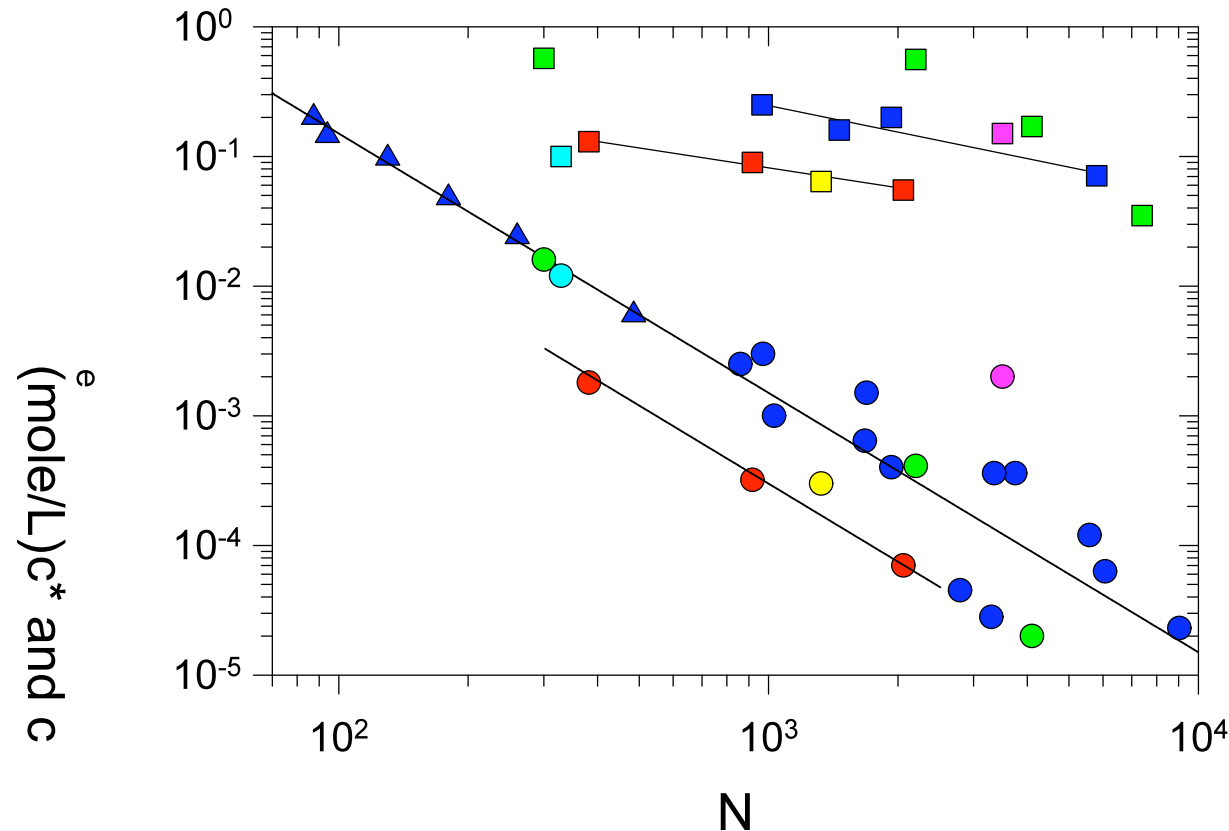
$a \sim c^{-1/2}$      $\xi \sim c^{-1/2}$

$a \sim c^{-0.76}$      $\xi \sim c^{-0.76}$

$a \sim c^{-2/3}$      $\xi \sim c^{-1}$

# Open Questions in Polyelectrolytes

- What does entanglement mean in a polyelectrolyte solution?



NaPSS  
NaPAMS  
NaIBMA  
NaDIBMA  
C/P2VP in EG

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

**Entanglement concentration is nearly independent of chain length!**

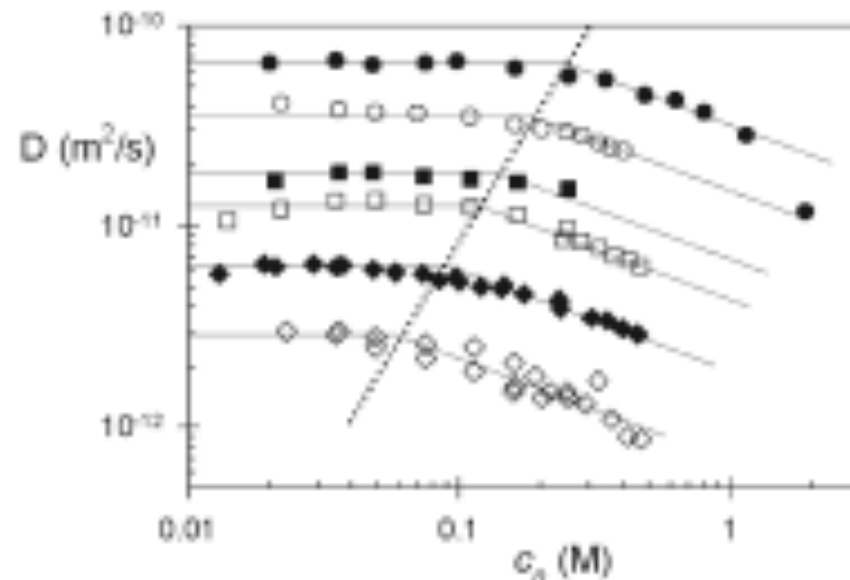
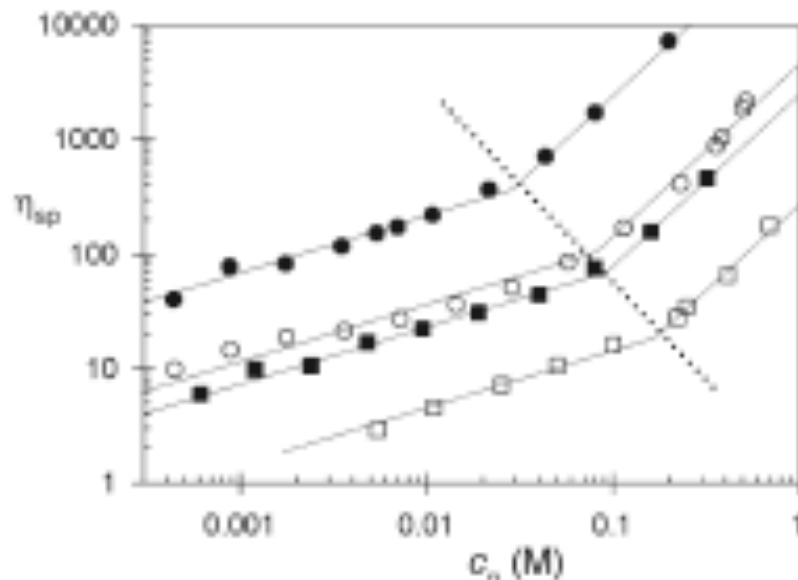


# Open Questions in Polyelectrolytes

- What does entanglement mean in a polyelectrolyte solution?

**NaPSS in water with no salt Specific Viscosity and Diffusion Coefficient**

Entanglement concentration is clearly evident in both data sets, with slopes of solid lines above and below  $c_e$  those predicted by the scaling theory. However, scaling expects  $\eta_{sp}(c_e) \approx n^2$  with  $n$  the (constant?) number of strands sharing an entanglement volume and expects  $D(c_e) \sim c_e^{1/2} / n^2$



The dashed lines both suggest  $n \sim c_e^{-0.9} \sim N^{-0.4}$

D.C. Boris and RHC, *Macromolecules* **31**, 5746 (1998). M.G.Oostwal, M.H. Blee, J. De Bleijser and J.C.Leyte, *Macromolecules* **26**, 7300 (1993).

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