Lecture 3

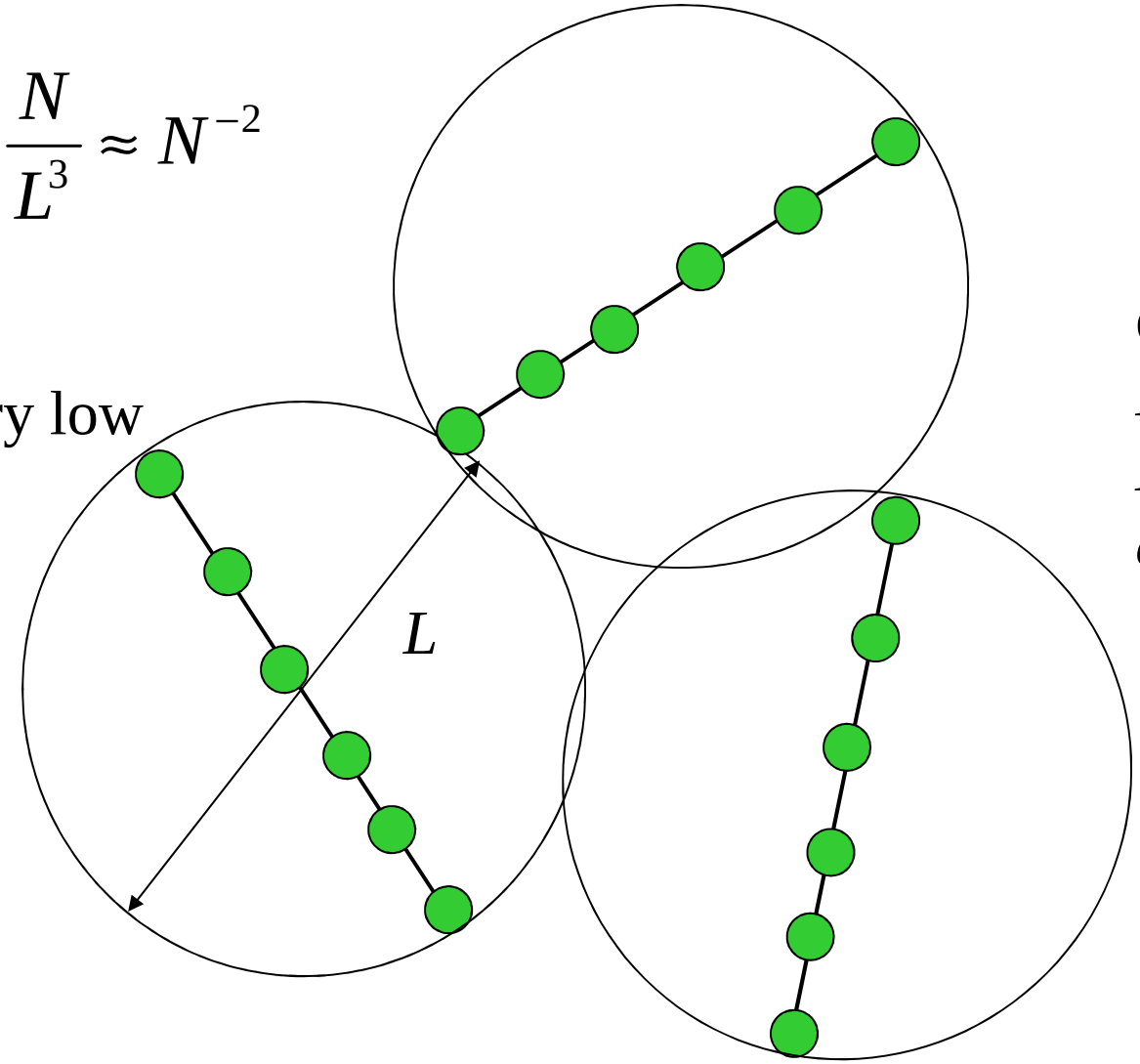
Semidilute Polyelectrolyte Solutions

Overlap Concentration c*

$$c^* \approx \frac{N}{L^3} \approx N^{-2}$$

$L \sim N$

c* is very low



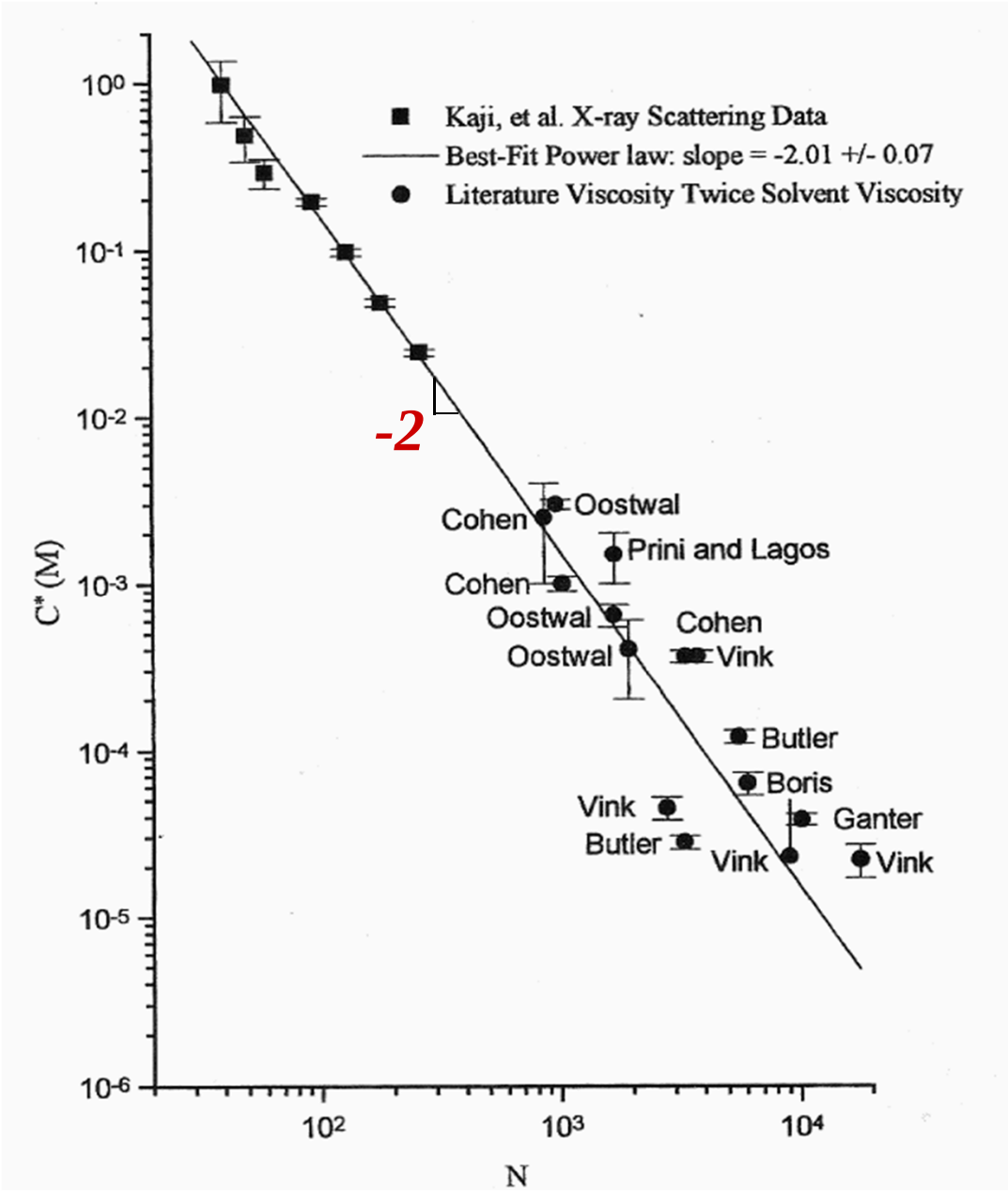
e.g. *200k PSS*
$N \approx 10^3$
$L \approx 100$ *nm*
$c^* \approx 10^{-3}$ *M*

For c < c* - dilute solution

For c > c* - semidilute solution

Overlap Concentration

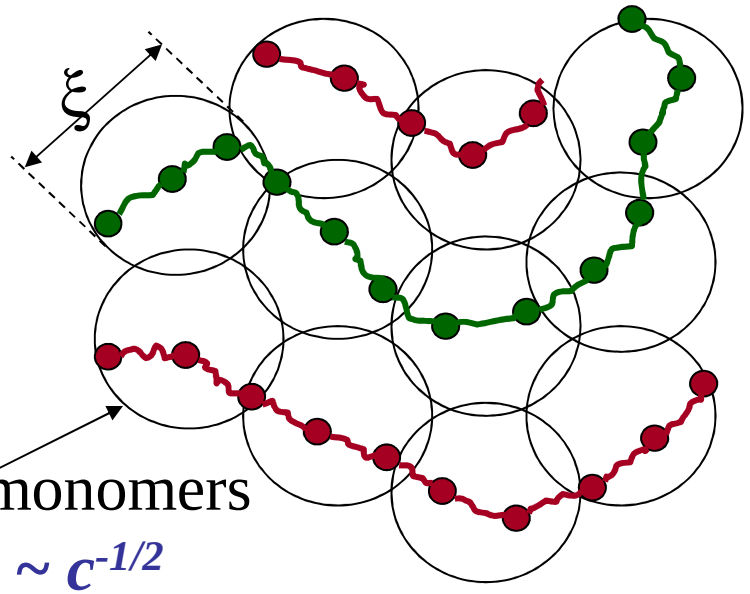
$c^* \sim 1/N^2$



D. Boris

Semidilute Solutions

de Gennes et al ‘76



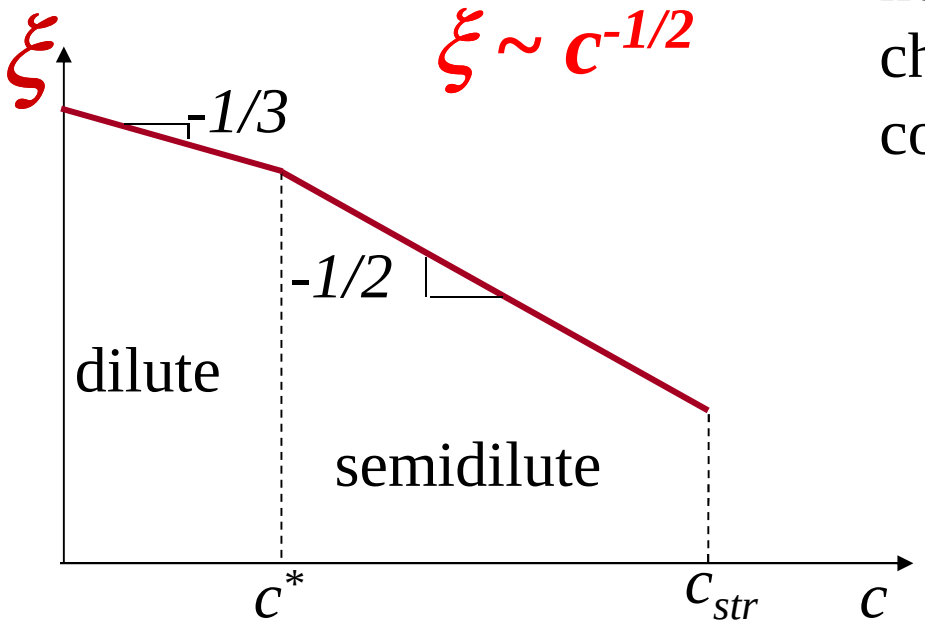
$g \sim c^{-1/2}$

Correlation length ξ – distance between neighboring chains

r < ξ – strong electrostatic repulsion
dilute-like behavior
chains are strongly stretched

r > ξ – interactions are screened by neighboring chains
chains are random walks of correlations “blobs” of size ξ

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



Chain size $R \approx \xi(N/g)^{1/2}$

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

Contour length is still L

$R^2 \approx L\xi$

Scattered Intensity

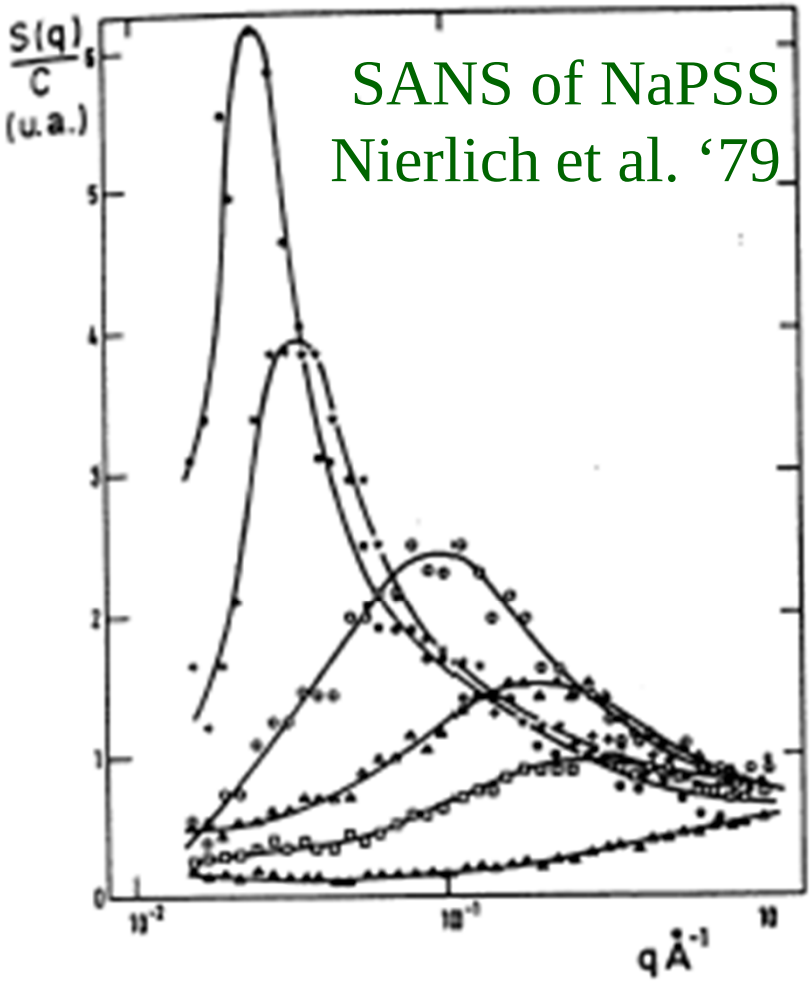


Fig. 3. — Scattered intensity per monomer of a solution of Na PSS_D (M_w = 72 000) in H_2O *versus* polymer concentration.

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

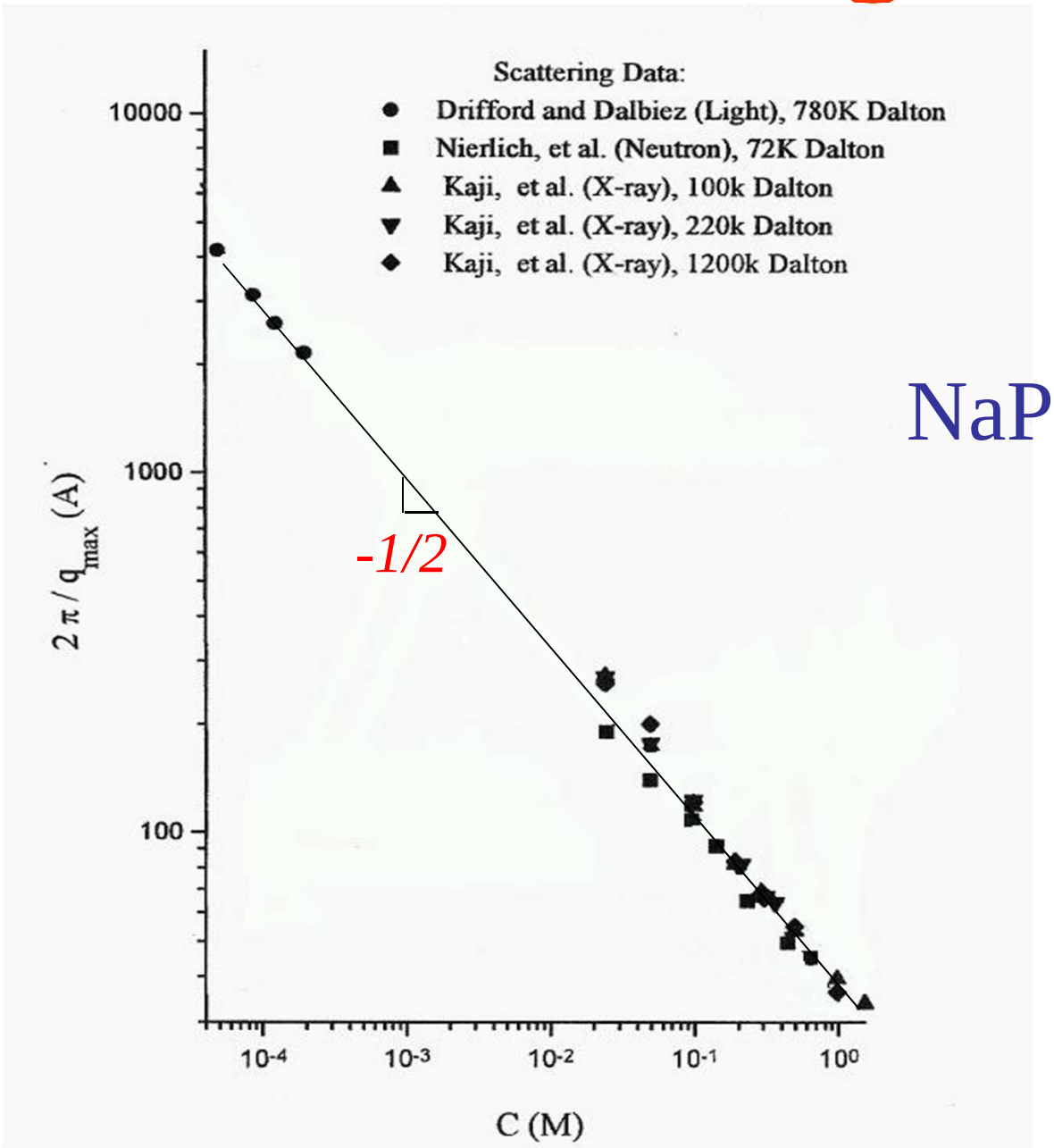
Correlation peak is one of the distinguishing properties of polyelectrolyte solutions.

Intensity growth with decreasing q for $q > 1/\xi$ is due to scattering from larger sections ($1/q$) of the chain.

Intensity decrease with decreasing q for $q < 1/\xi$ is due to electrostatically – induced suppression of density fluctuations.

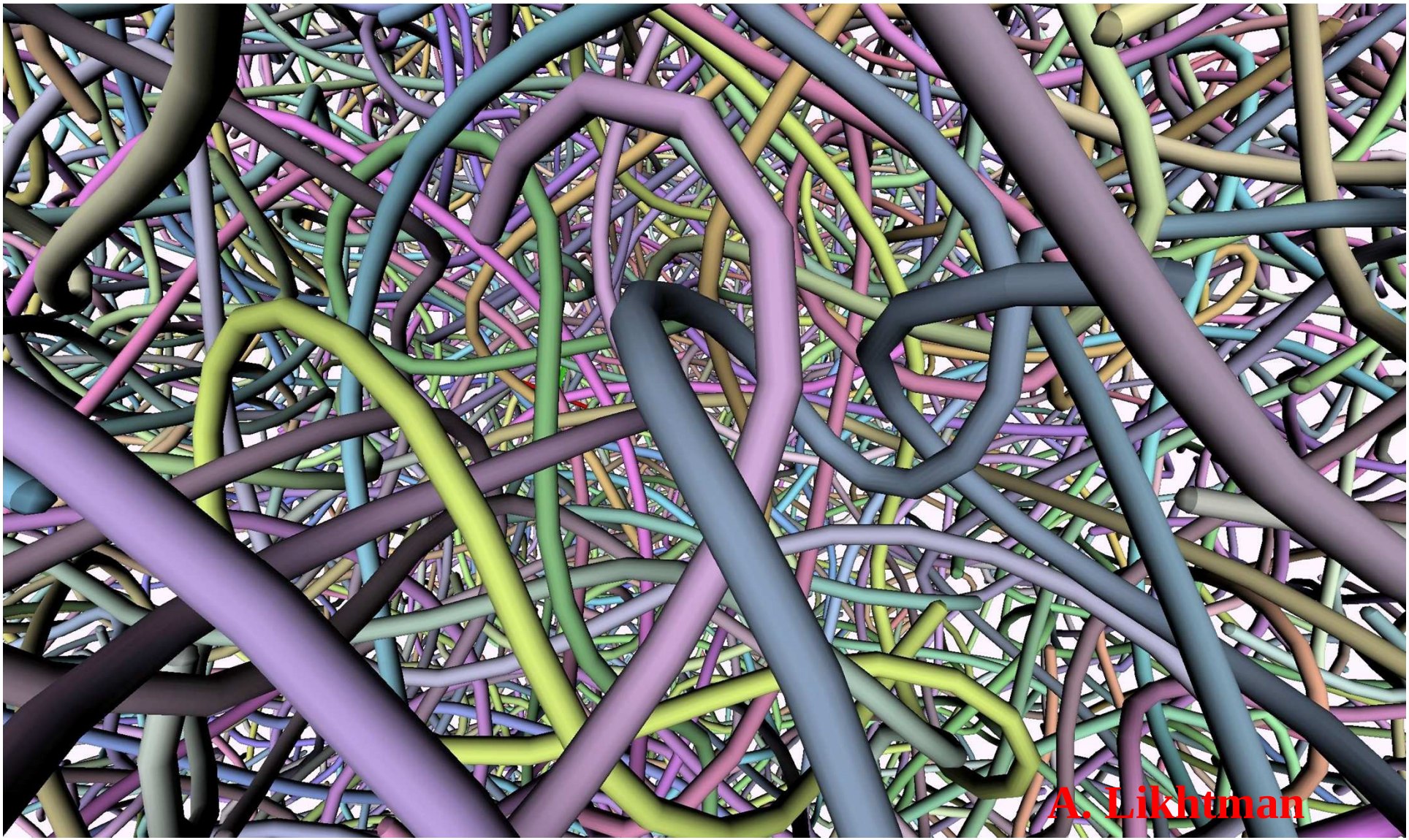
High osmotic compressibility ~ $1/S(0)$.

Correlation Length



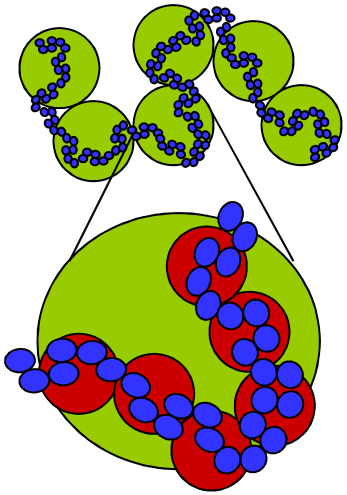
NaPSS

Dynamics of Polymer Solutions



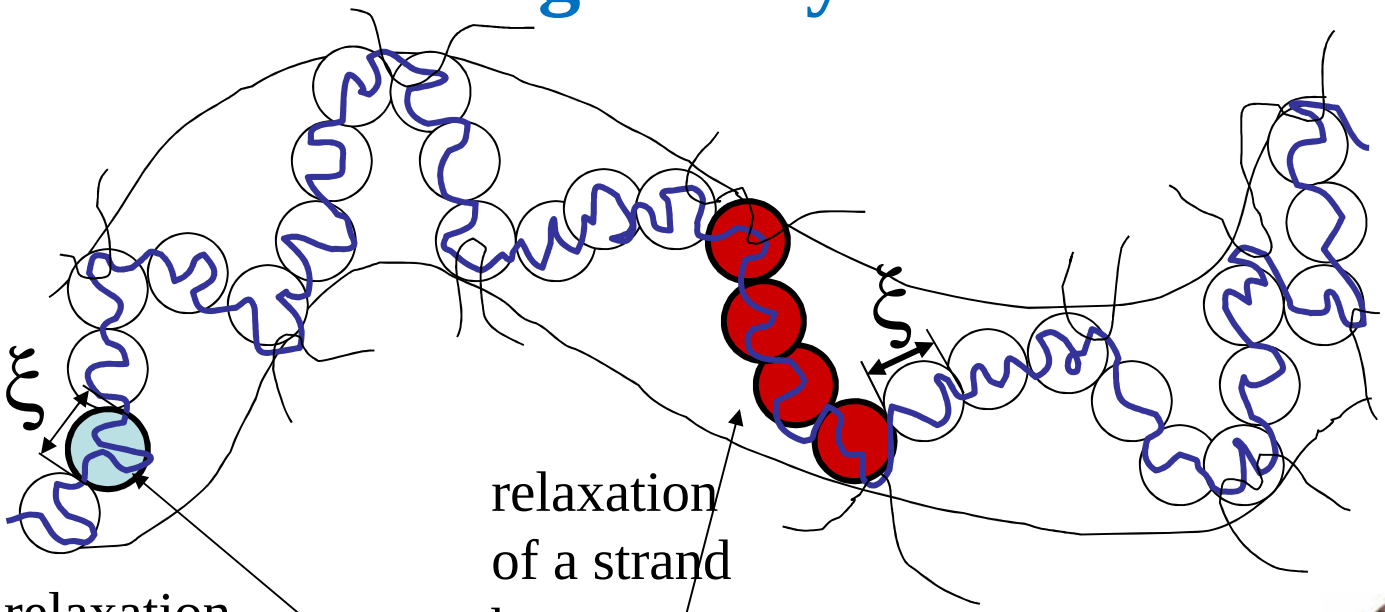
A. Likhtman

Self-Similar Dynamics



Chains are fractal – they look the same on different length scales and move in the same way on different time scales.

Relaxation Time of Entangled Solutions of Uncharged Polymers



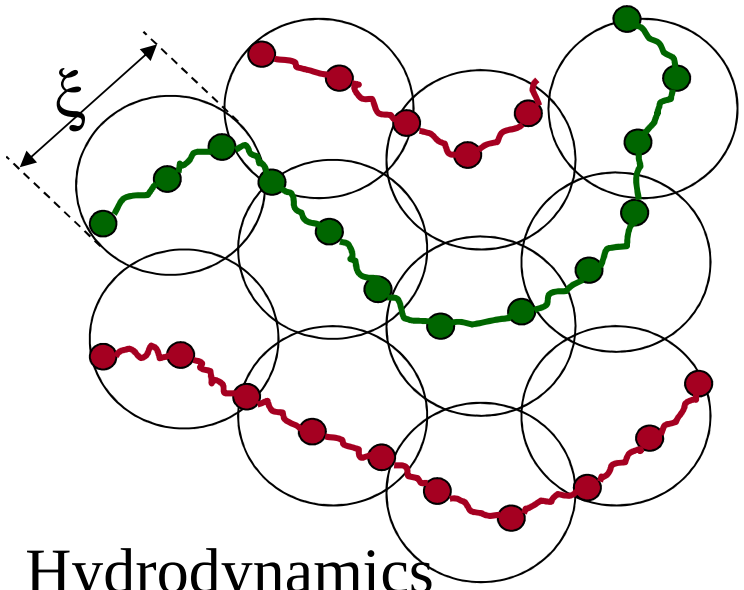
relaxation of correlation blob

relaxation of a strand between entanglements

$$\tau_{rep} = \tau_{\xi}(N_e/g)^2(N/N_e)^3$$

Dynamics of Polyelectrolytes

Semidilute Unentangled Solutions



Hydrodynamics
is screened for $r > \xi$

Chain sections of size ξ are hydrodynamically coupled to solvent inside correlation volume.

Friction coefficient of correlation strand ξ

$\zeta_\xi \approx \eta_s \xi$ η_s – solvent viscosity

Friction coefficient of a chain

$\zeta \approx \zeta_\xi (L/\xi) \approx \eta_s L$

is independent of concentration.

Self-diffusion coefficient $D \approx kT/\zeta \approx kT/(\eta_s L)$

is independent of concentration.

Relaxation time $\tau \approx R^2/D \sim \xi \sim c^{-1/2}$ $R^2 \approx L\xi$

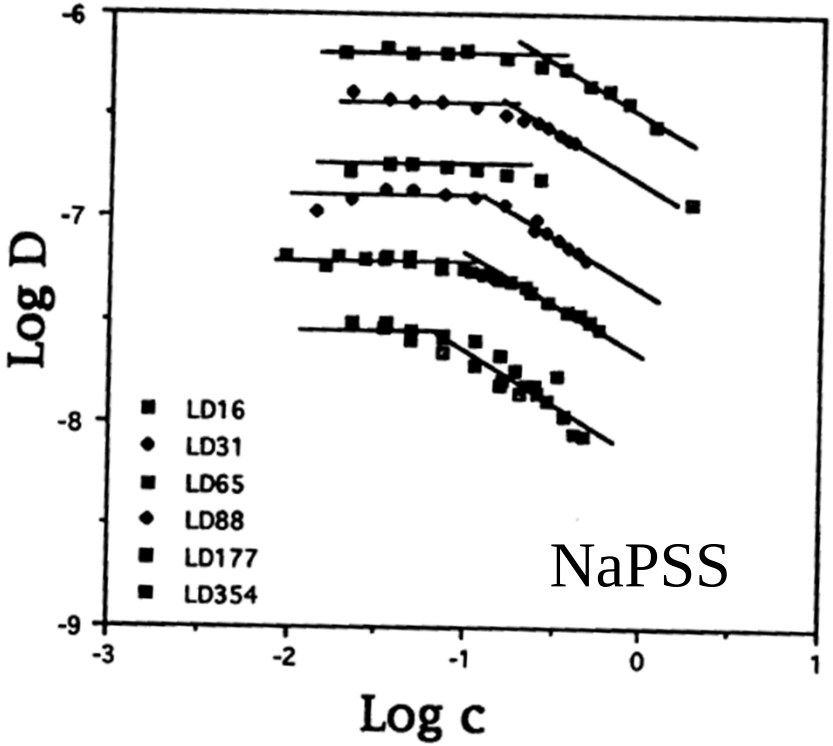
decreases with increasing concentration!!!

Concentration Dependence of Diffusion Coefficient

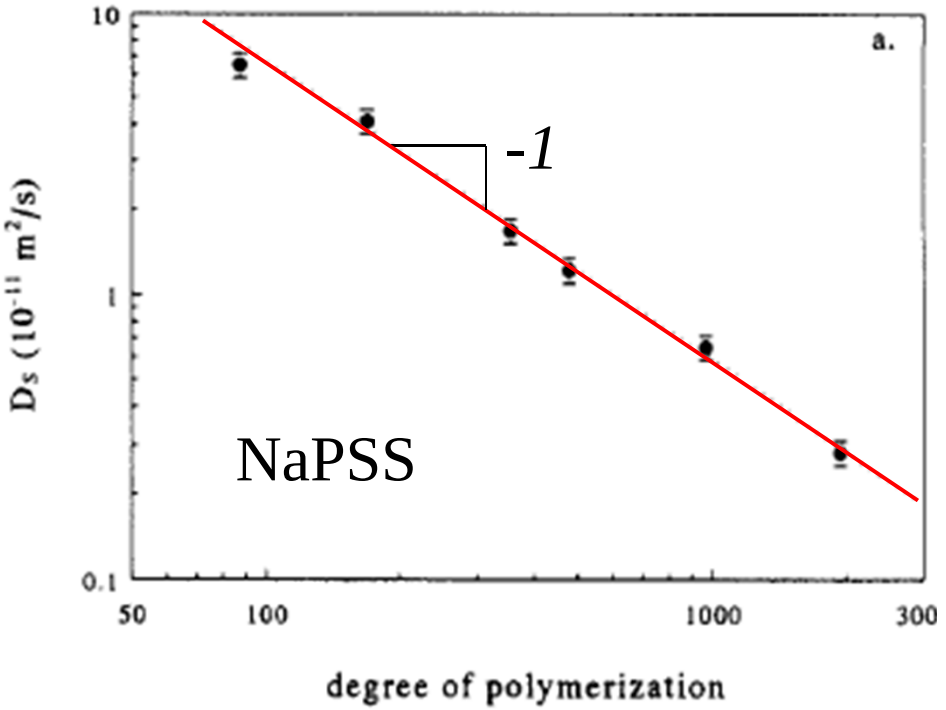
Self-diffusion coefficient is independent of concentration and reciprocally proportional to degree of polymerization.

$$D \sim c^0/N$$

Oostwal et al. ‘93



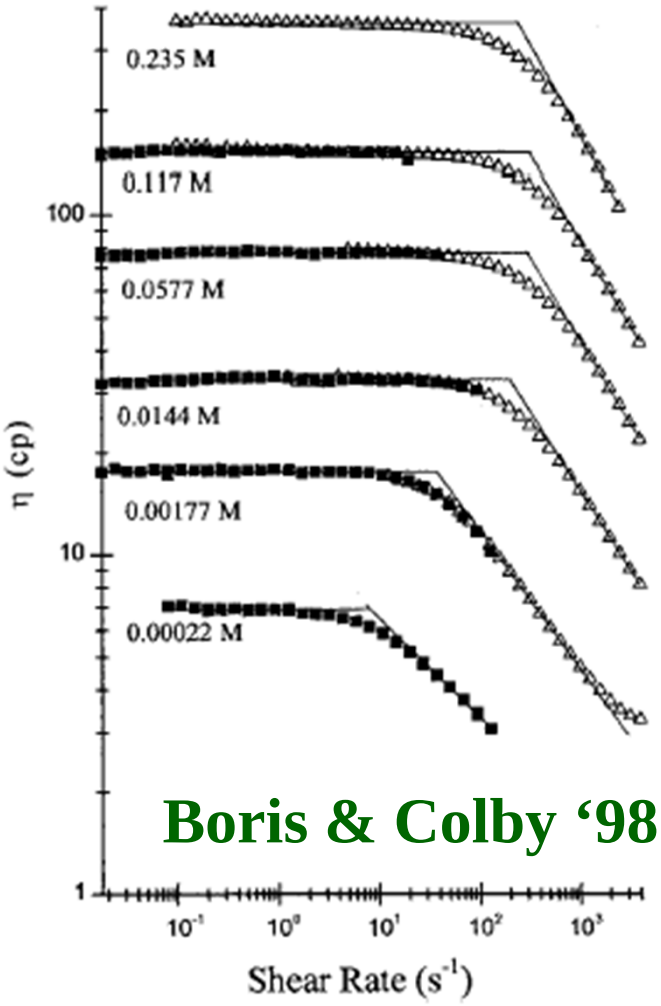
Pulsed field gradient NMR



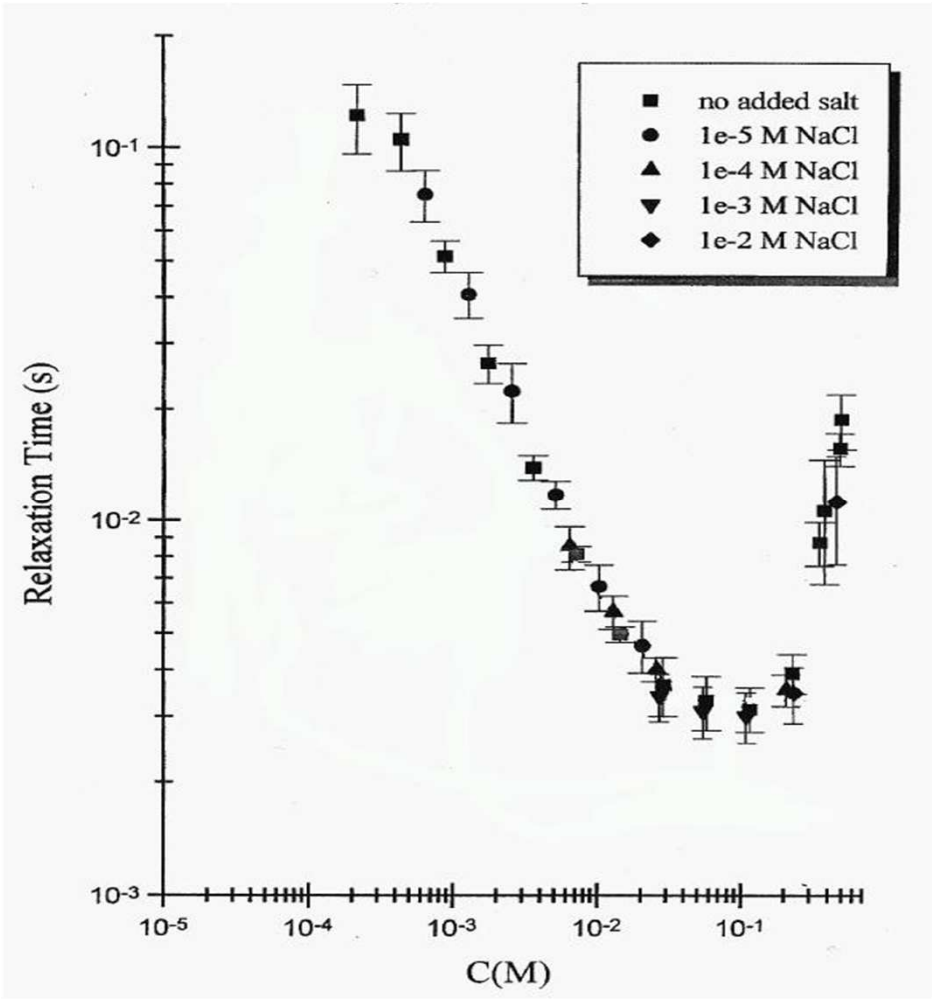
c = 2 × 10^{-2} M

Concentration Dependence of Relaxation Time

Relaxation time **decreases** with increasing concentration.



Boris & Colby '98



M_w=1200K PSS, *f=0.85*

Viscosity of Semidilute Unentangled Solutions

Modulus $G \approx kTc/N$

Relaxation time $\tau \sim c^{-1/2}N^2(uf^2)^{1/2}$

Viscosity $\eta \sim c^{1/2}N(uf^2)^{1/2}$

Fuoss Law

$\eta_{red} = (\eta/\eta_s - 1)/c \sim c^{-1/2}$

Reduced viscosity grows with decreasing concentration – another distinguishing property of polyelectrolyte solutions.

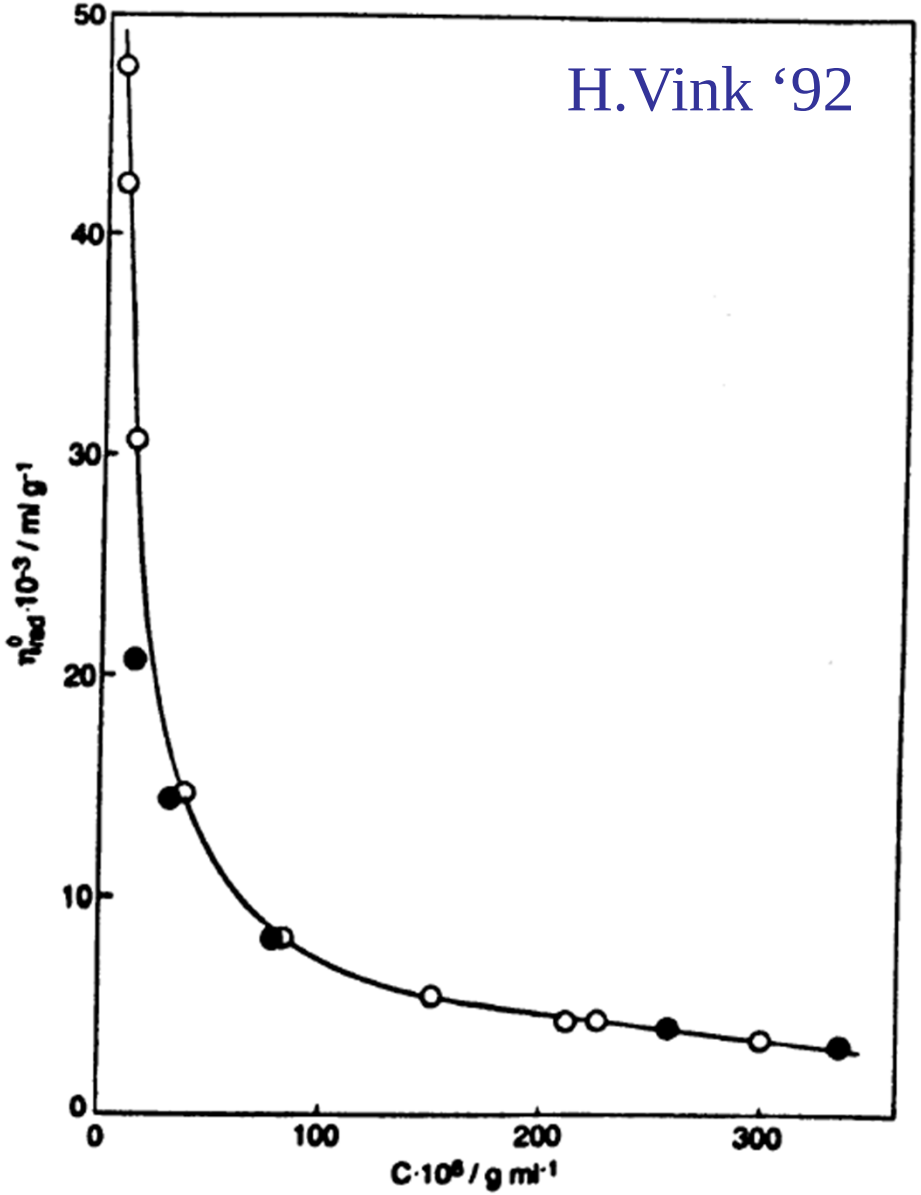
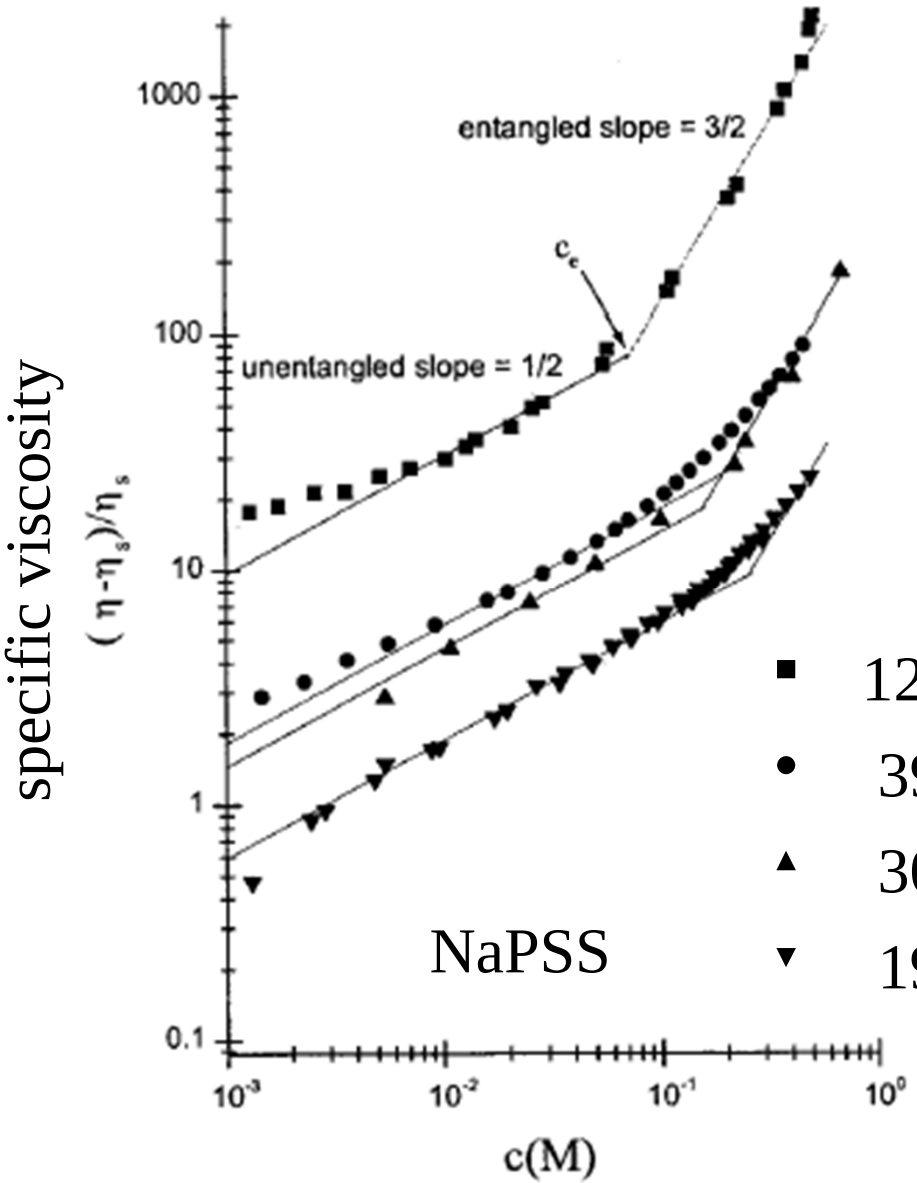


Figure 3 Concentration dependence of zero-shear reduced viscosity: ○, HPSS$_{ss}$; ●, NaPSS$_{ss}$

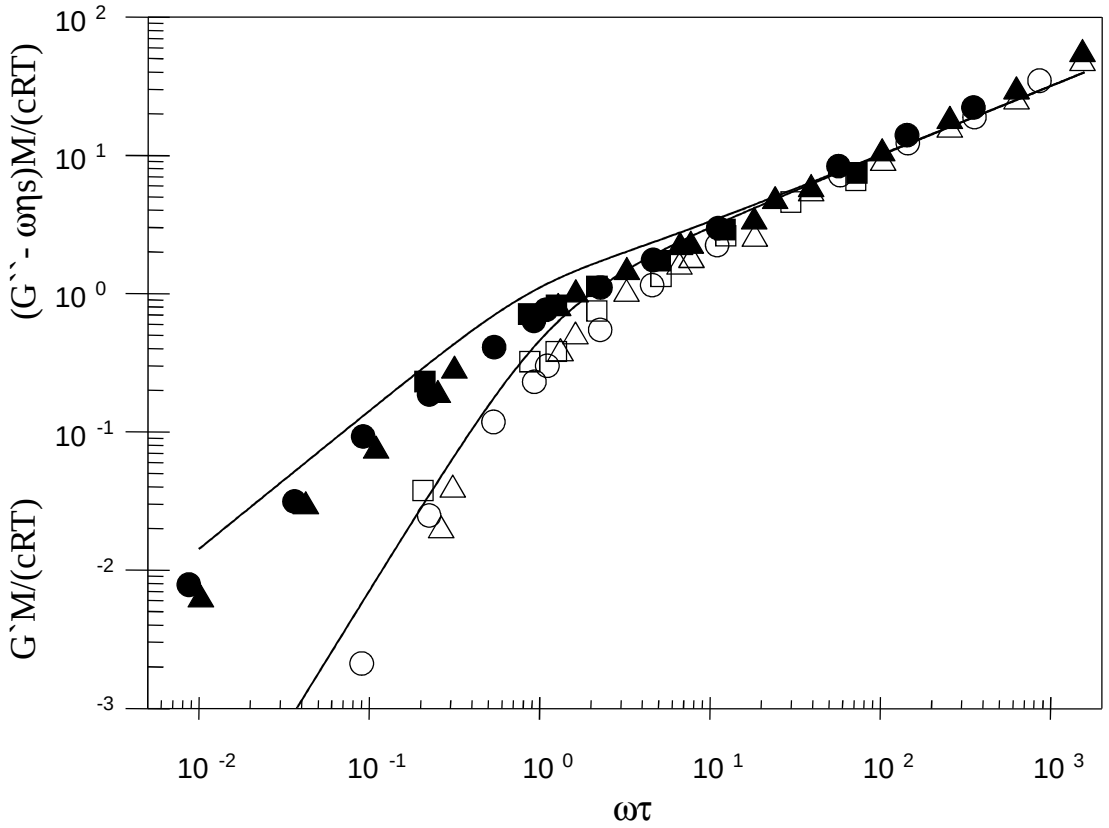
Concentration Dependence of Viscosity

Viscosity $\eta \sim c^{1/2}N(uf^2)^{1/2}$



- ■ 1200k (Boris & Colby)
- ● 398k (Oostwal)
- ▲ 300k (Prini & Lagos)
- ▼ 199k (Oostwal)

Unentangled Polyelectrolytes – Rouse Dynamics

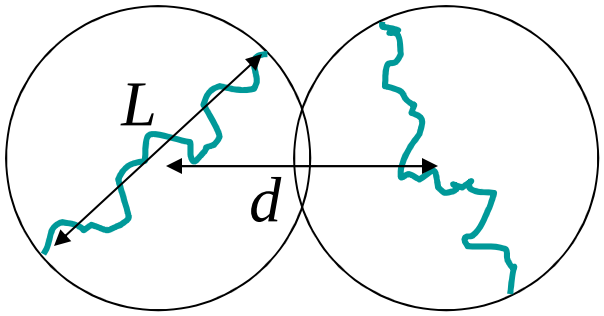


Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus G' and filled symbols are the loss modulus G''. Squares have $c = 0.5\ \mathrm{g\,L^{-1}}$, triangles have $c = 1.0\ \mathrm{g\,L^{-1}}$, and circles have $c = 2.0\ \mathrm{g\,L^{-1}}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* **94**, 4581 (1991).

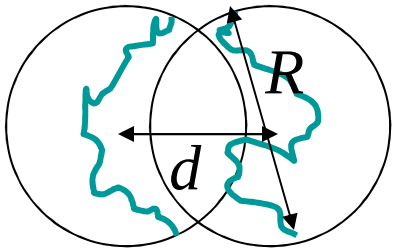
Dynamics of Unentangled Polymers

	General Equation	Neutral in Θ-solvent	Neutral in good solvent	Polyelectrolyte with no salt
Scaling Exponent	$\nu \equiv \partial(\log R_{dilute})/\partial(\log N)$	$\nu = 1/2$	$\nu = 0.588$	$\nu = 1$
Correlation Blob Size	$\xi \sim N^0 c^{-\nu/(3\nu-1)}$	$\xi \sim N^0 c^{-1}$	$\xi \sim N^0 c^{-0.76}$	$\xi \sim N^0 c^{-1/2}$
Polymer Size	$R \sim N^{1/2} c^{-(\nu-1/2)/(3\nu-1)}$	$R \sim N^{1/2} c^0$	$R \sim N^{1/2} c^{-0.12}$	$R \sim N^{1/2} c^{-1/4}$
Chain Relaxation Time	$\tau_{chain} \sim N^2 c^{(2-3\nu)/(3\nu-1)}$	$\tau_{chain} \sim N^2 c$	$\tau_{chain} \sim N^2 c^{0.31}$	$\tau_{chain} \sim N^2 c^{-1/2}$
Terminal Modulus	$G = N^{-1} c_n kT$	$G = N^{-1} c_n kT$	$G = N^{-1} c_n kT$	$G = N^{-1} c_n kT$
Polymer Contribution to Viscosity	$\eta - \eta_s \approx G\tau \sim N c^{1/(3\nu-1)}$	$\eta - \eta_s \sim N c^2$	$\eta - \eta_s \sim N c^{1.3}$	$\eta - \eta_s \sim N c^{1/2}$
Diffusion Coefficient	$D \approx R^2/\tau \sim N^{-1} c^{-(1-\nu)/(3\nu-1)}$	$D \sim N^{-1} c^{-1}$	$D \sim N^{-1} c^{-0.54}$	$D \sim N^{-1} c^0$

Entanglement Onset



$d \approx L$ at overlap $c \approx c^*$



In semidilute regime $c > c^*$

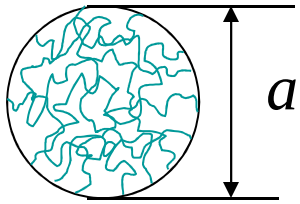
$d \sim c^{-1/3}$ $R \sim c^{-1/4}$

Number of overlapping chains

$n \approx cR^3/N \approx (c/c^*)^{1/4}$

$n_e = 5 - 10$ chains per entanglement volume

(Kavassalis & Noolandi '87)



Entanglement onset $c_e \approx c^* n_e^4$

3 – 4 decades of unentangled semidilute regime

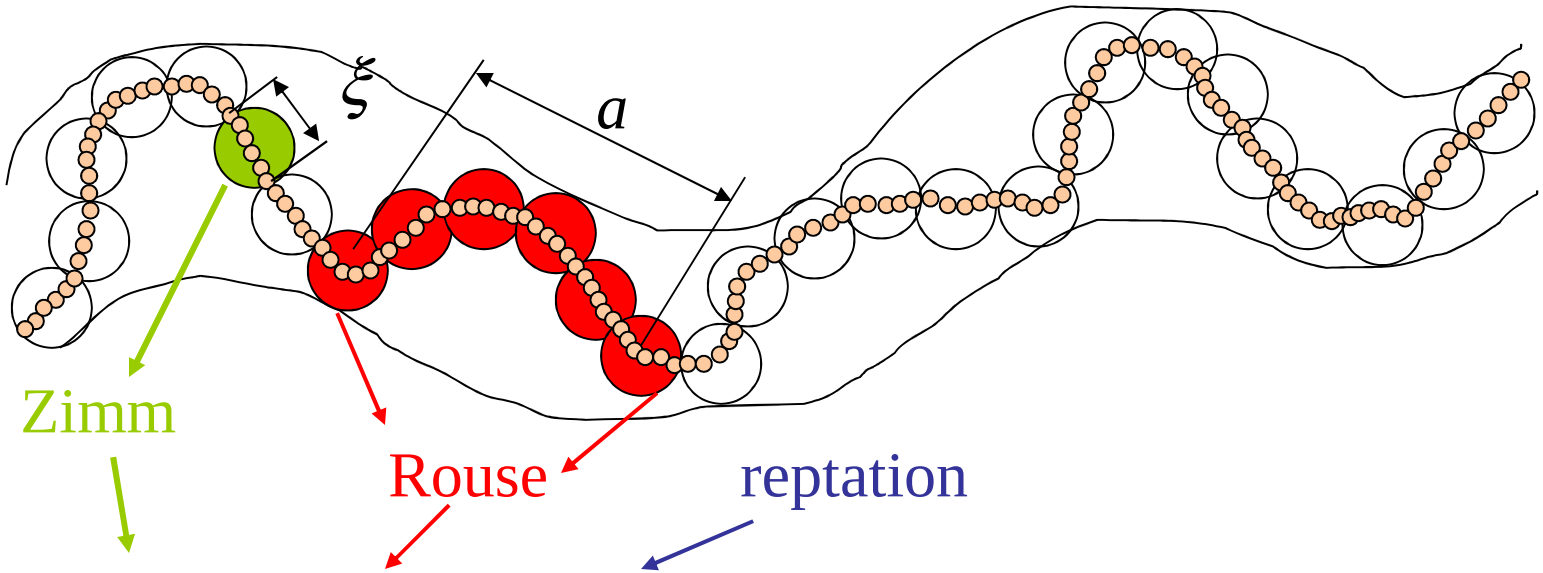
– unique feature of polyelectrolyte solutions

In entangled regime $c > c_e$ $c \approx n_e N_e / a^3$

$a \approx n_e \xi$ – tube diameter

$N_e \approx n_e^2 g$ – number of monomers between entanglements

Semidilute Entangled Solutions



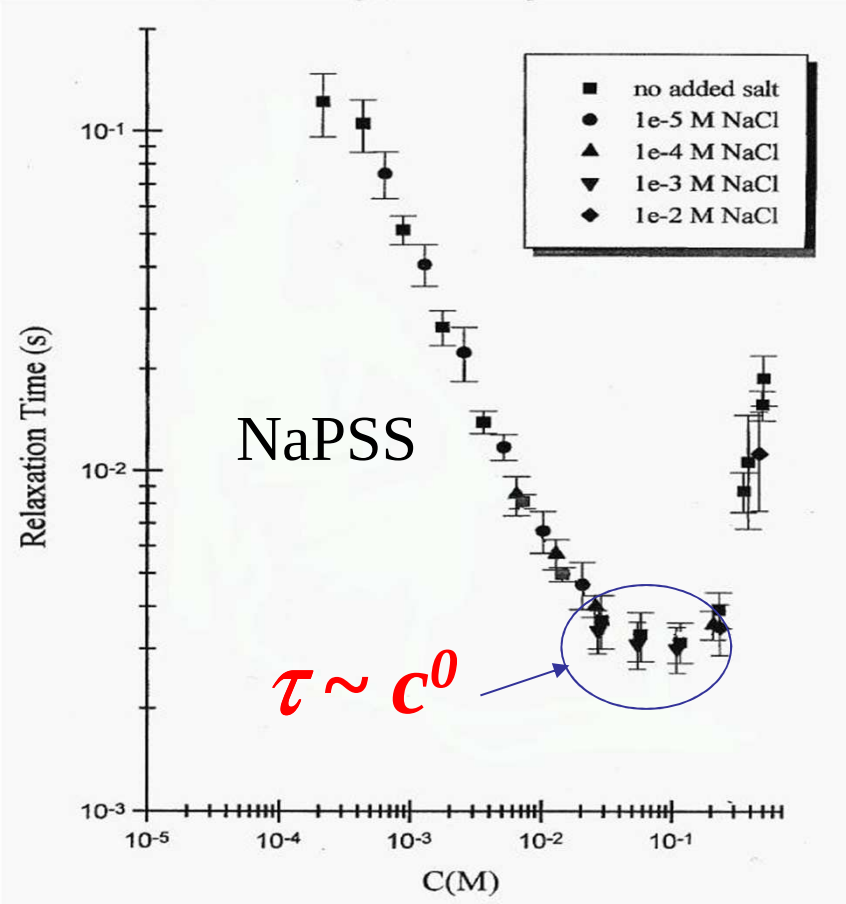
$$\tau \approx \tau_\xi (N_e/g)^2 (N/N_e)^3 \sim c^0 N^3$$

Relaxation time is c-independent!

Plateau modulus $G_e \approx kT\, c/N_e \sim c^{3/2}$

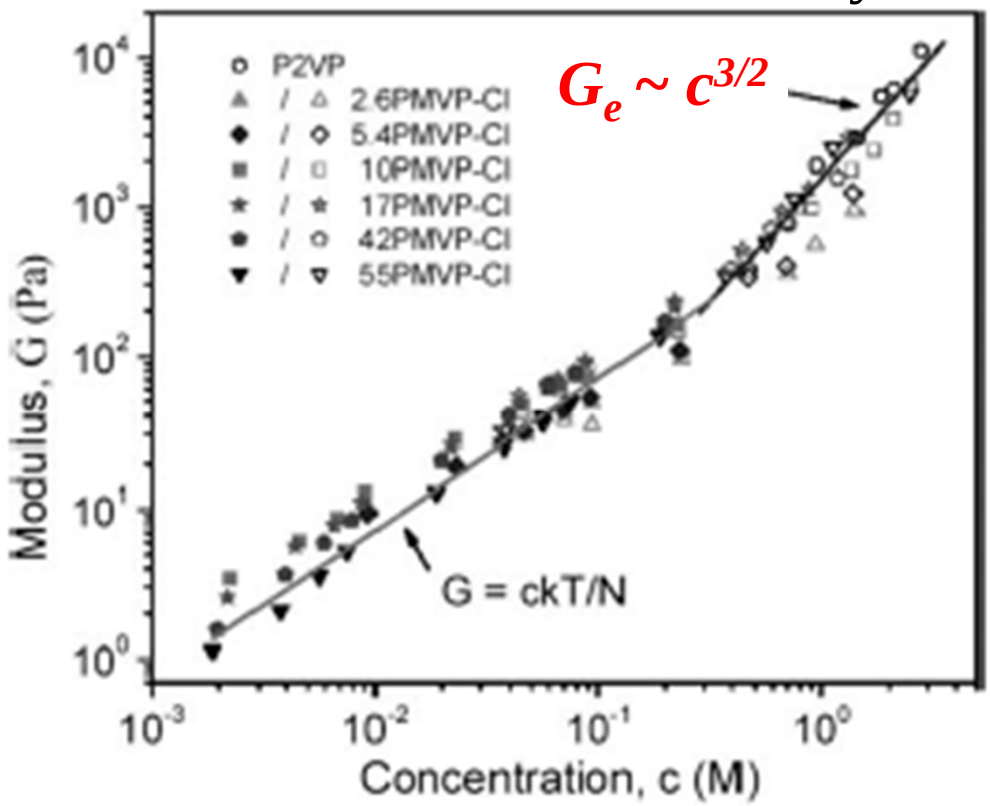
Viscosity $\eta \approx \tau G_e \sim c^{3/2} N^3$

Relaxation Time and Modulus of Entangled Polyelectrolyte Solutions



Boris & Colby '98

Dou & Colby



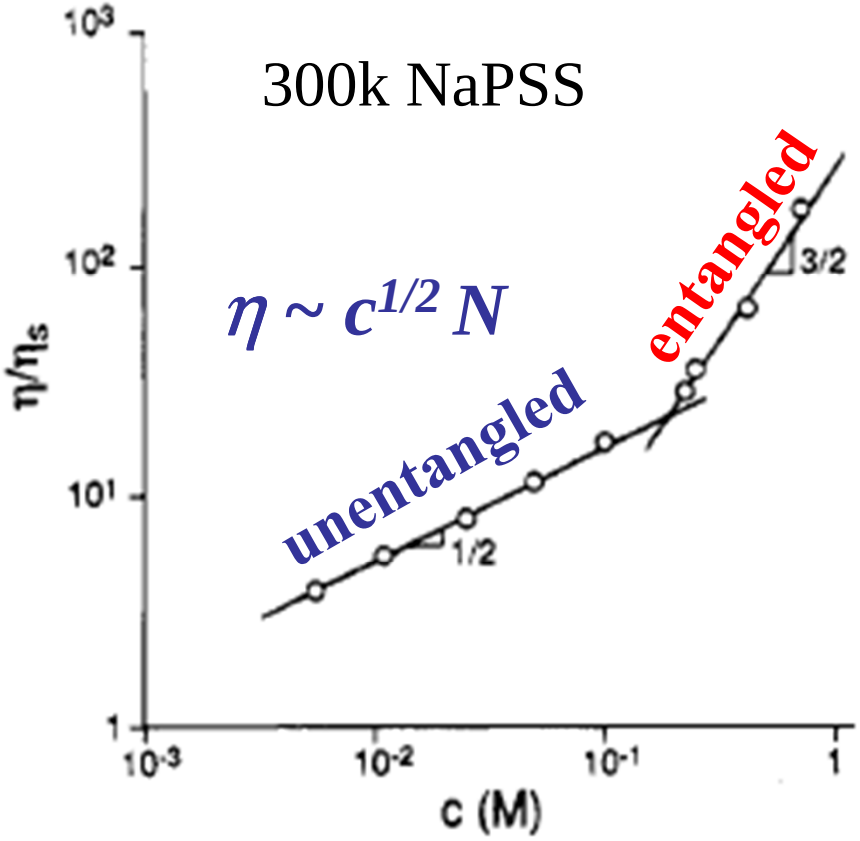
Random copolymer 2-vinyl pyridine and N-methyl-2vinyl pyridinium chloride in ethylene glycol

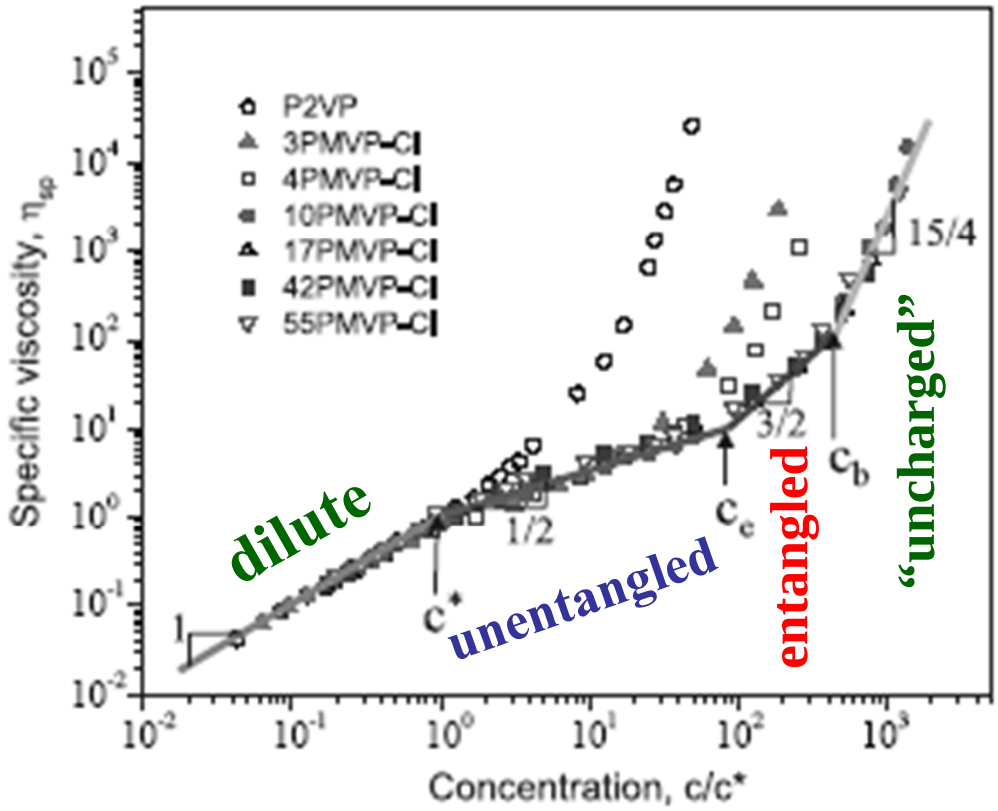
Viscosity of Entangled Solutions

$$\eta \sim c^{3/2} N^3$$

Dou & Colby

300k NaPSS





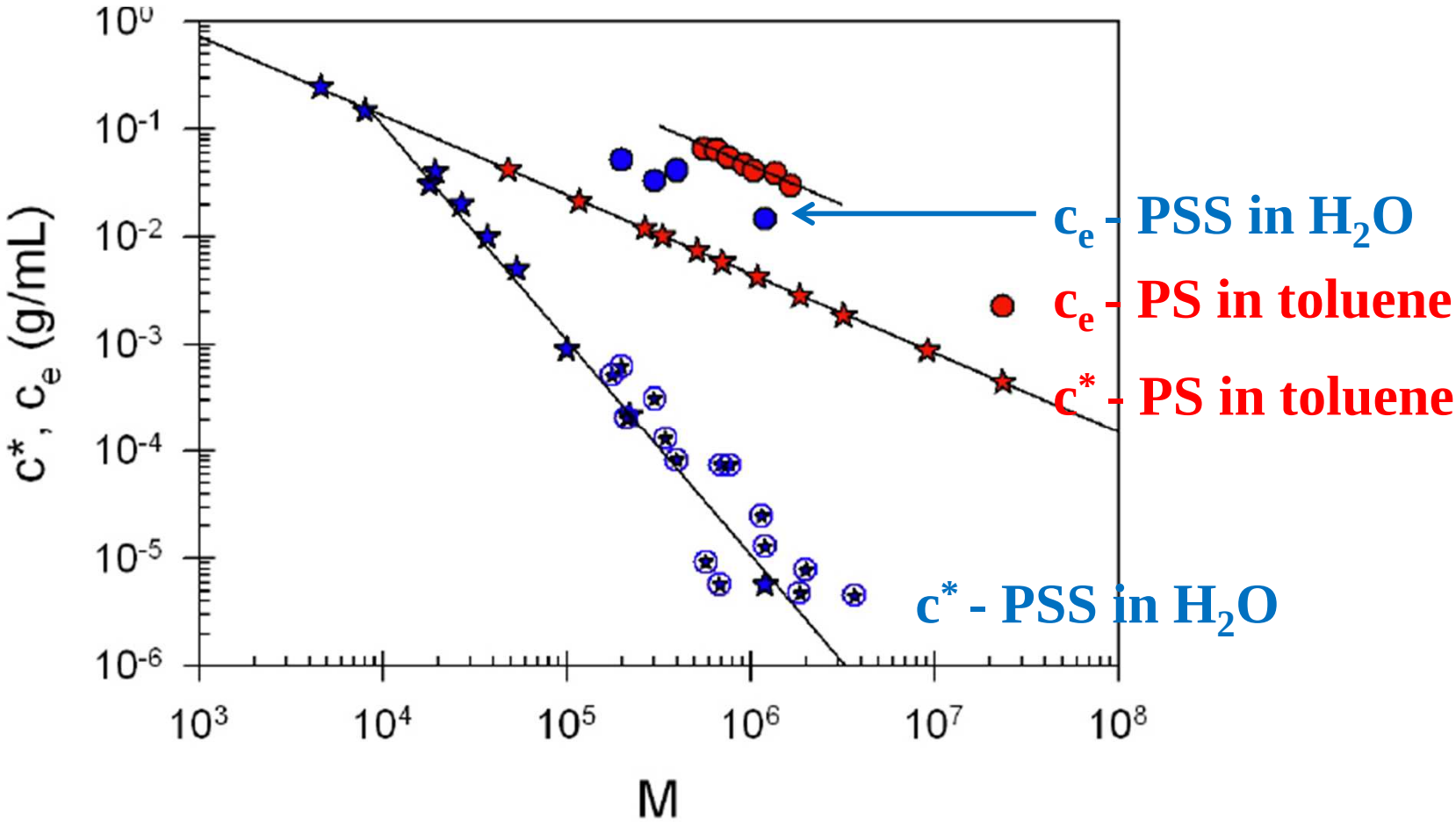
Prini & Lagos '64

Random copolymer 2-vinyl pyridine and N-methyl-2vinyl pyridinium chloride in ethylene glycol

Dynamics of Entangled Polymers

	General Equation	Neutral in Θ-solvent	Neutral in good solvent	Polyelectrolyte with no salt
Scaling Exponent	$\nu \equiv \partial(\log R_{dilute}) / \partial(\log N)$	$\nu = 1/2$	$\nu = 0.588$	$\nu = 1$
Correlation Blob Size	$\xi \sim N^0 c^{-\nu/(3\nu-1)}$	$\xi \sim N^0 c^{-1}$	$\xi \sim N^0 c^{-0.76}$	$\xi \sim N^0 c^{-1/2}$
Polymer Size	$R \sim N^{1/2} c^{-(\nu-1/2)/(3\nu-1)}$	$R \sim N^{1/2} c^0$	$R \sim N^{1/2} c^{-0.12}$	$R \sim N^{1/2} c^{-1/4}$
Tube Diameter	$a \sim \xi_*$	$a \sim N^0 c^{-2/3}$	$a \sim N^0 c^{-0.76}$	$a \sim N^0 c^{-1/2}$
Reptation Time	$\tau_{rep} \sim N^3 c^{3(1-\nu)/(3\nu-1)}{}_*$	$\tau_{rep} \sim N^3 c^{7/3}$	$\tau_{rep} \sim N^3 c^{1.6}$	$\tau_{rep} \sim N^3 c^0$
Terminal Modulus	$G_e = \dfrac{kT}{a^2 \xi}$	$G_e \sim N^0 c^{7/3}$	$G_e \sim N^0 c^{2.3}$	$G_e \sim N^0 c^{3/2}$
Polymer Contribution to Viscosity	$\eta - \eta_s \approx G\tau \sim N^3 c^{3/(3\nu-1)}{}_*$	$\eta - \eta_s \sim N^3 c^{14/3}$	$\eta - \eta_s \sim N^3 c^{3.9}$	$\eta - \eta_s \sim N^3 c^{3/2}$
Diffusion Coefficient	$D \approx R^2/\tau \sim N^{-2} c^{-(2-\nu)/(3\nu-1)}{}_*$	$D \sim N^{-2} c^{-7/3}$	$D \sim N^{-2} c^{-1.85}$	$D \sim N^{-2} c^{-1/2}$

Polyelectrolyte Entanglement Mystery



R. Colby

Things to Remember about Semidilute "Hydrophilic" Polyelectrolytes

Overlap concentration is very low ($c^* \sim 1/N^2$).

Characteristic scattering peak at $q \sim 1/\xi \sim c^{1/2}$.

Osmotic pressure is controlled by counterions.

Unentangled Solutions

Diffusion coefficient is concentration–independent.

Relaxation time decreases with concentration.

Viscosity $\eta \sim c^{1/2}$ – Fuoss Law.

Very wide unentangled semidilute regime (3 – 4 decades of c).

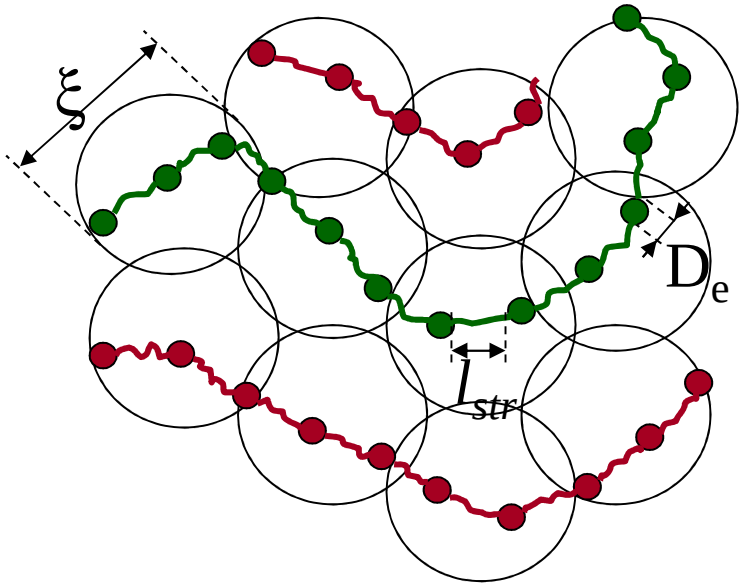
Entangled Solutions

Relaxation time is concentration–independent.

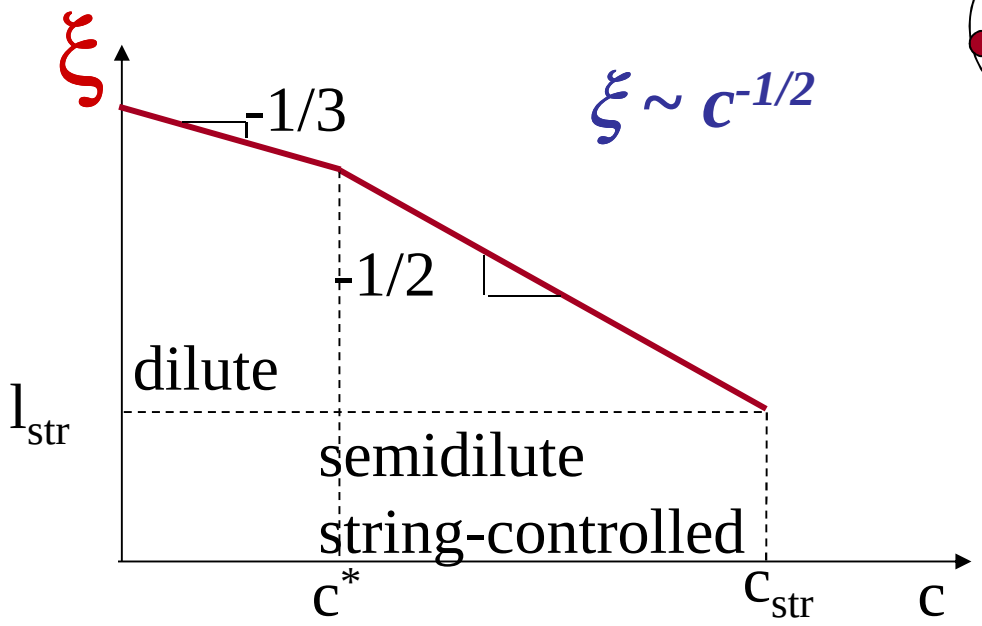
Hydrophobic Polyelectrolytes

If correlation length ξ is larger than distance between beads l_{str}
string-controlled regime is similar to semidilute “hydrophilic” regime.

$l_{str} < \xi < L$ $\qquad$ $c^* < c < c_{str}$

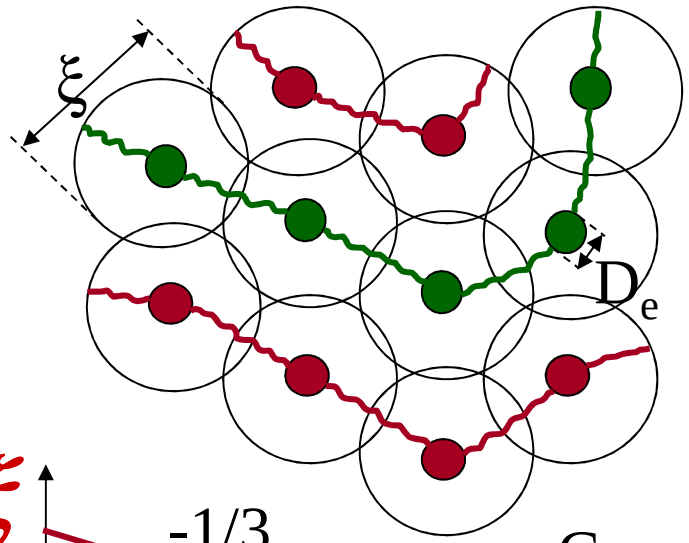


Correlation length

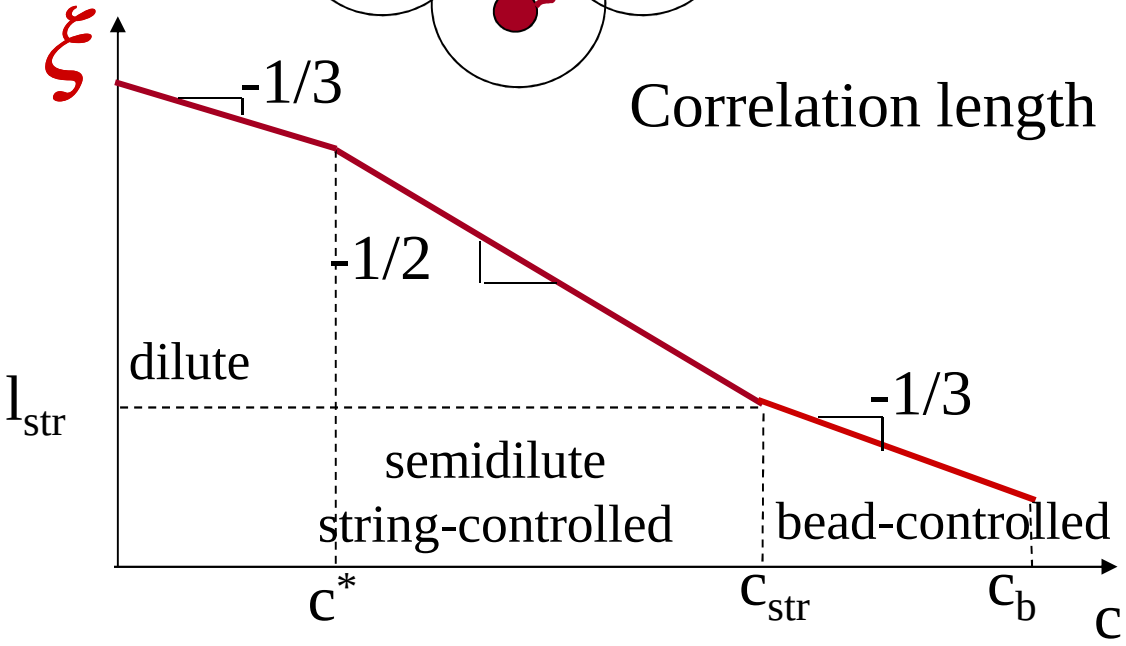


$\xi \sim c^{-1/2}$

Hydrophobic Polyelectrolytes
Bead-controlled regime



As soon as ξ decreases down to l_{str}, beads on neighboring chains screen electrostatic repulsion of beads on the same chain reducing the length of strings to the distance between beads ξ.

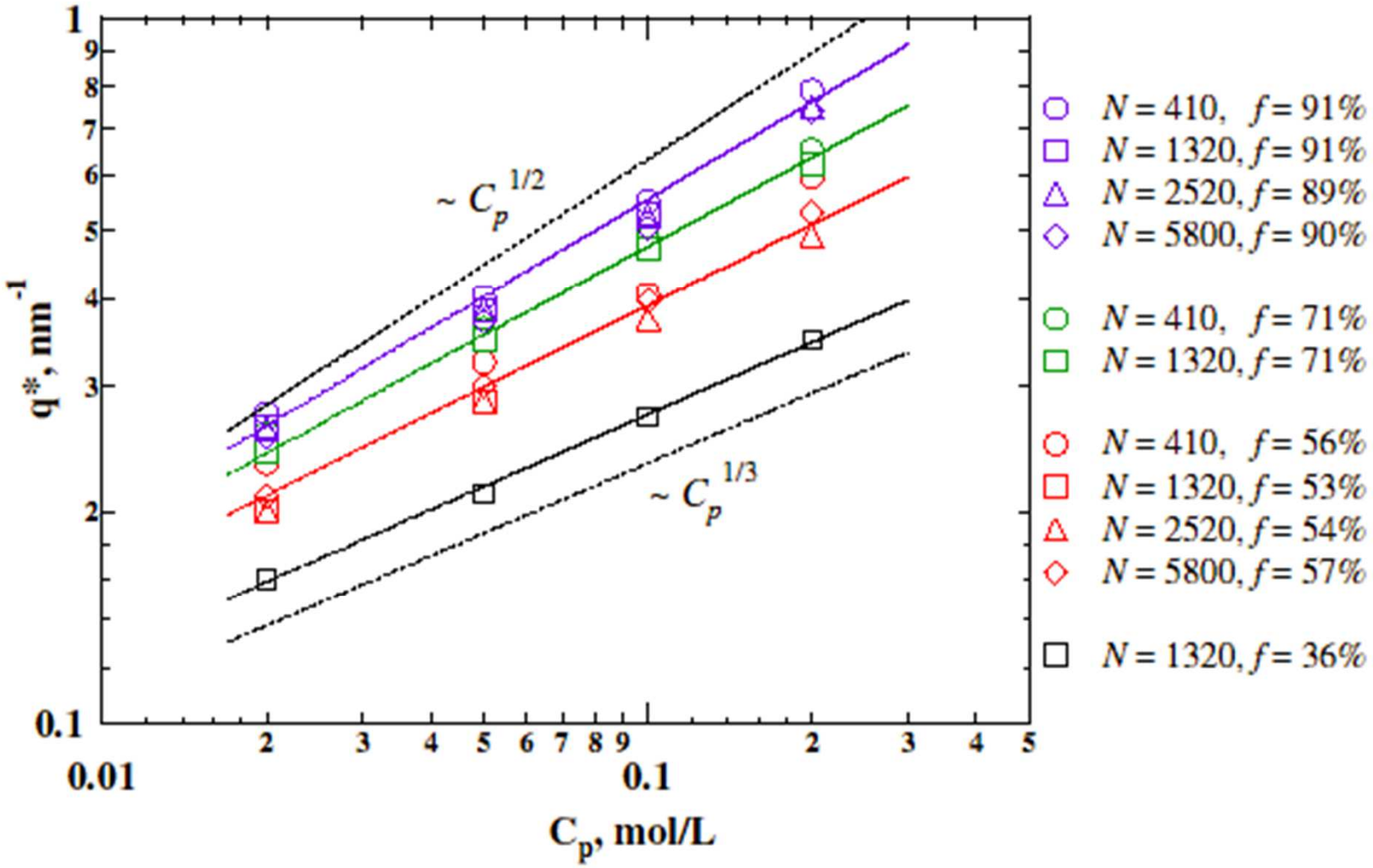


Correlation length $\xi \sim c^{-1/3}$

$c_{str} < c < c_b$

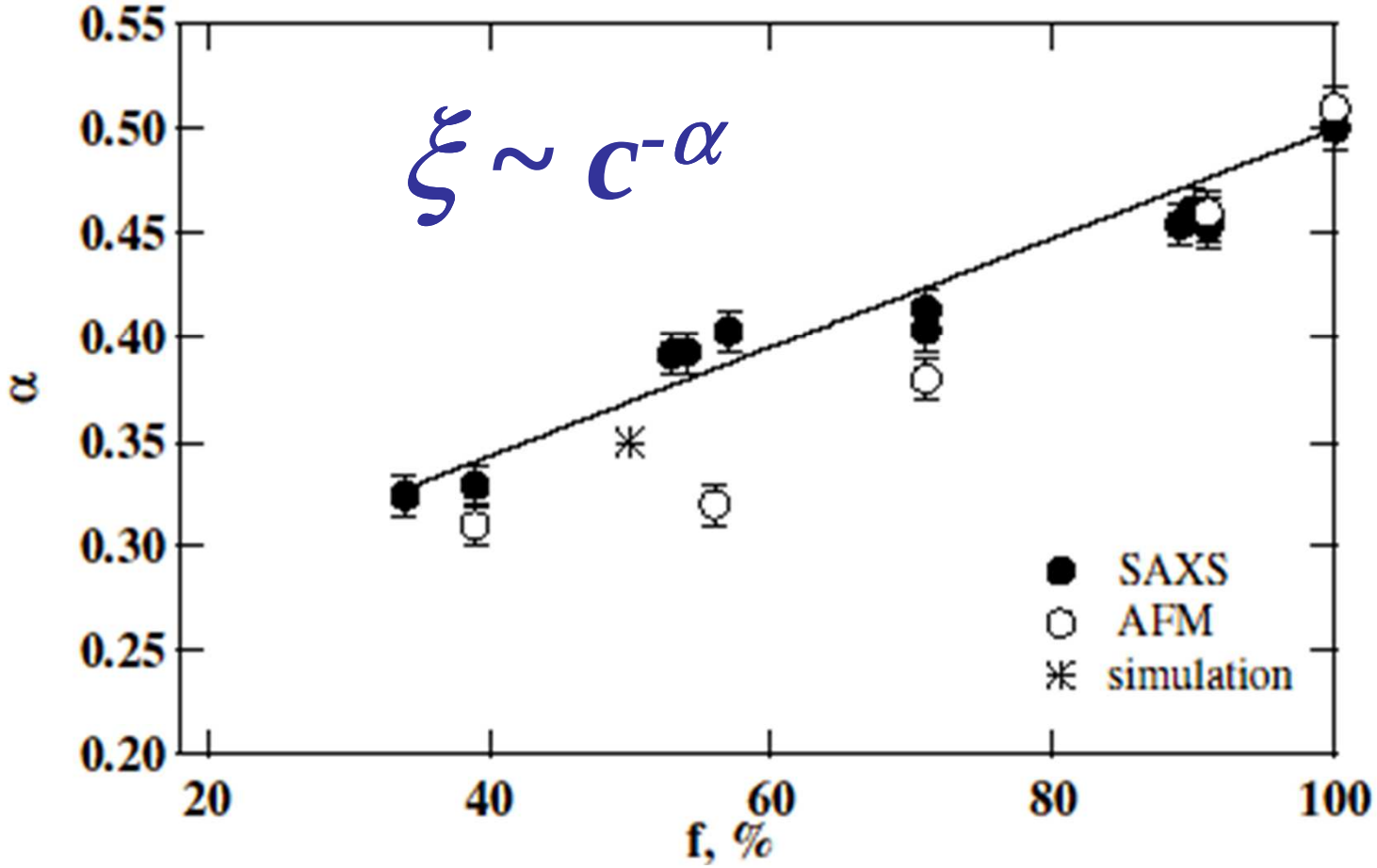
$l_{str} \cong \xi > D_e$

Correlation Length $\xi = 2\pi/q^*$



SAXS of PSS by Baigl, Ober, Qu, Fery, & Williams
Europhysics Letters 2003

Correlation Length Exponent



PSS data by Baigl, Ober, Qu, Fery, & Williams
Europhysics Letters 2003

Single Chain Form Factor

Spiteri & Boue '97

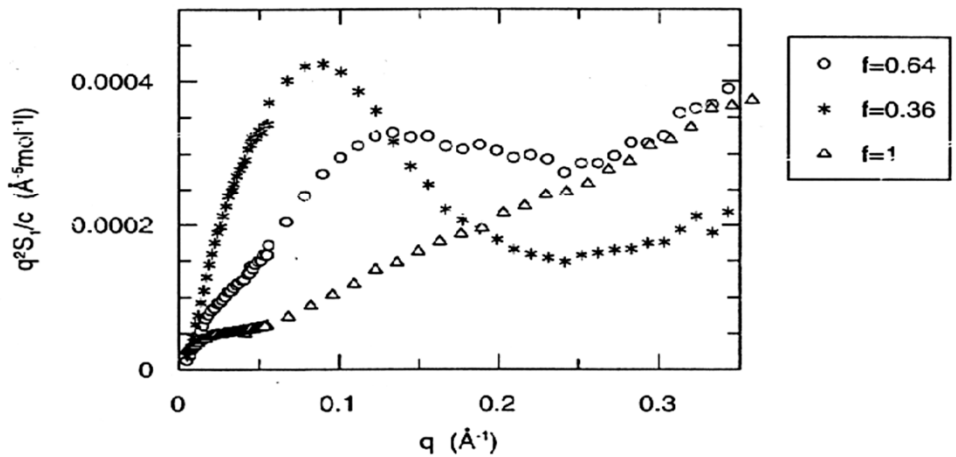


Fig. IV-4: Facteur de forme des polyions de taux de charge variable à la concentration c=0.34M. Représentation de Kratky.

NaPSS, $M_W(PS_H)=68\,000$, $M_W(PS_D)=73\,000$

Bead size vs fraction of charged monomers

Theory: $D_b \sim f^{-2/3}$ Experiment: $D_b \sim f^{-0.7}$

Effect of Added Salt

Spitery & Boue '97

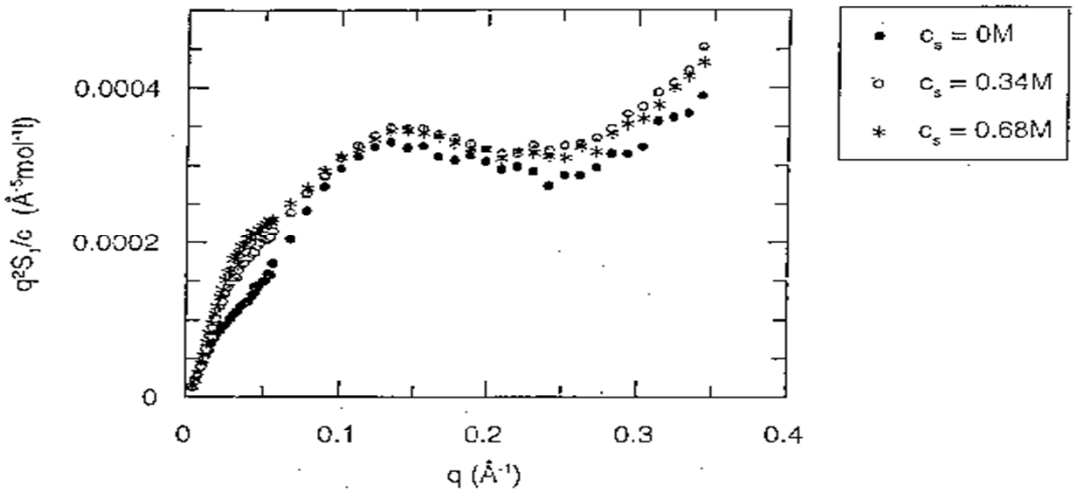


Fig. IV-8: Effet du sel ajouté sur l'échantillon f=0.64.

For charge fraction f=0.64
at polymer concentration c = 0.34 M

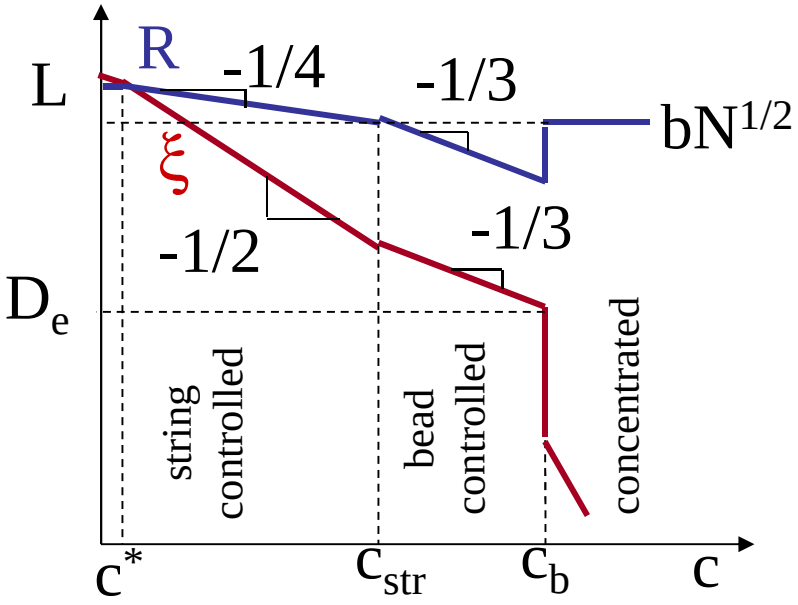
$$R_g(c_s = 0M) = 97 \pm 5A$$

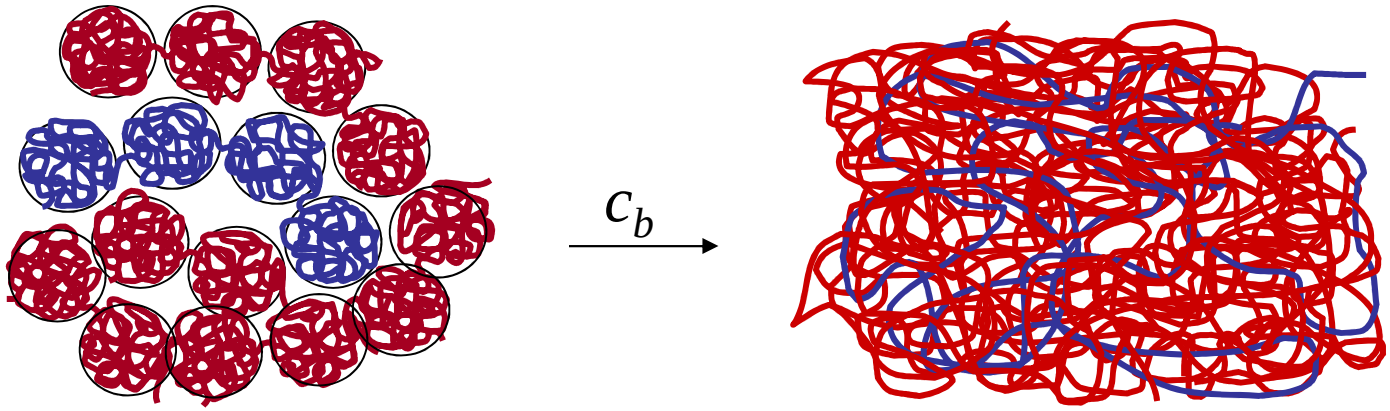
$$R_g(c_s = 0.34M) = 73 \pm 8A$$

$$R_g(c_s = 0.68M) = 66 \pm 5A$$

Transition at Bead Overlap

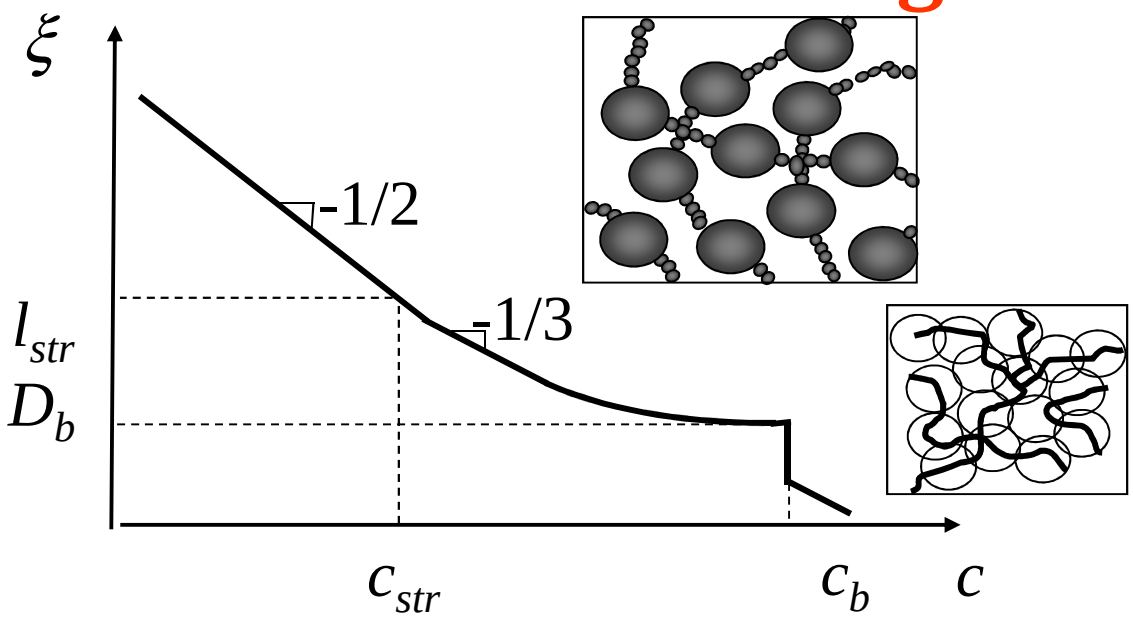
Necklace size in bead-controlled regime ($c_{str}<c<c_b$) is much smaller than the ideal chain size.

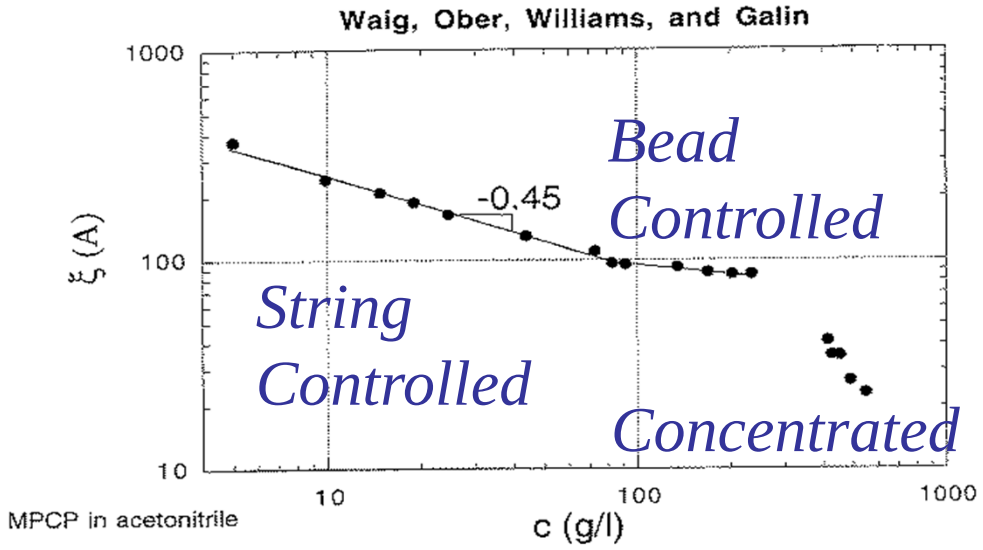


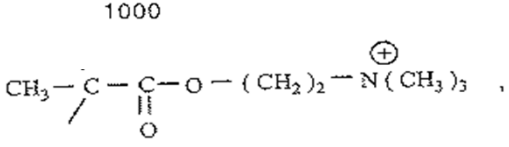


Above the bead overlap concentration c_b chains are ideal.

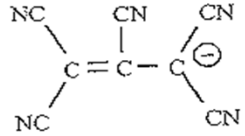
Correlation Length







Polyelectrolyte MPCP



Below crossover

Above crossover

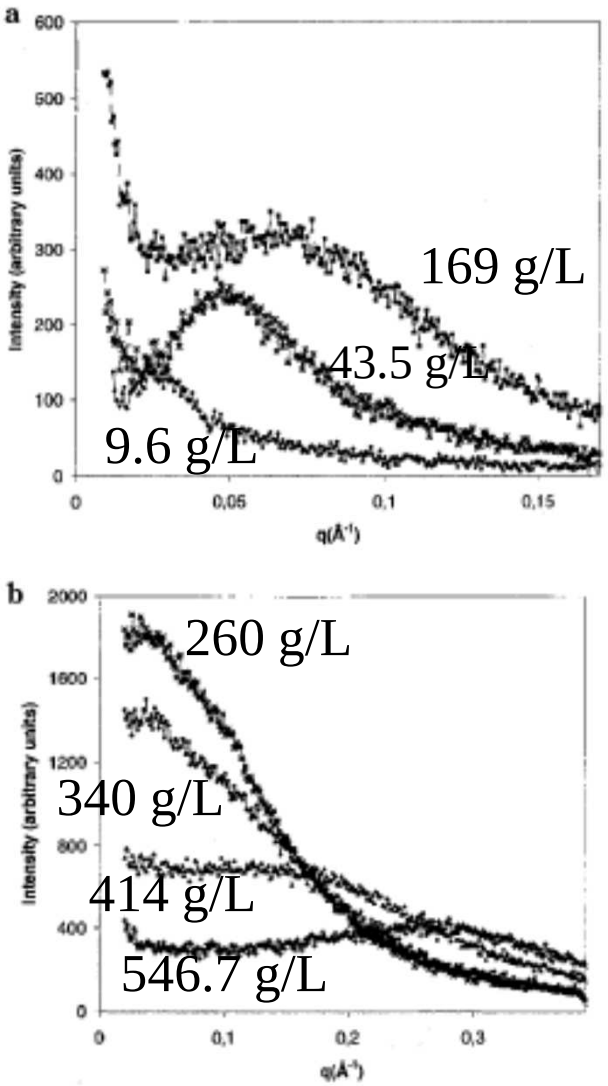
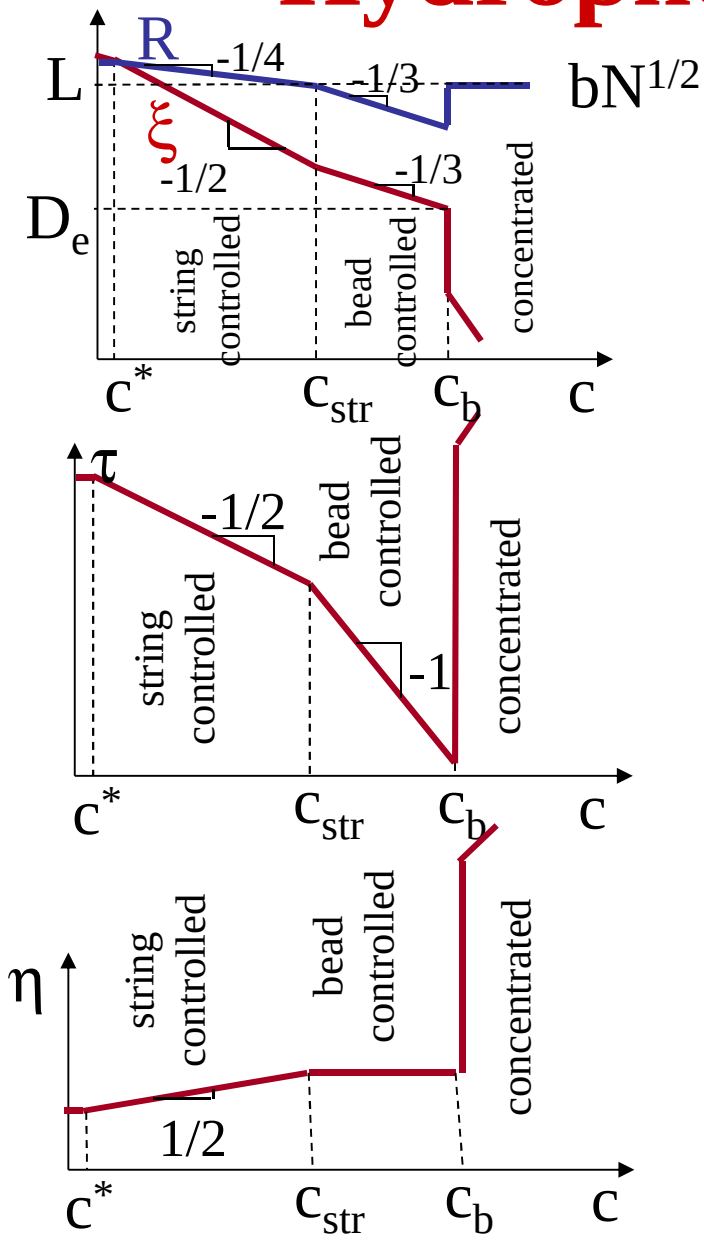


Figure 2. Small-angle X-ray scattering curves from MPCP in AC at a series of different concentrations (9.9−169 g/L). The scattered intensity in relative units is shown as a function of the momentum transfer (q). (a) Lower concentrations: ●, 9.6 g/L; ×, 43.5 g/L; □, 169 g/L. (b) Higher concentrations: ×, 260 g/L; ●, 340 g/L; ▲, 414 g/L; +, 546.7 g/L. Note the sharp decrease in intensity between 404 and 422 g/L followed by the reappearance of a peak.

Waigh, Ober, Williams & Galin Macromolecules 2001

“Gelling” Transition of Hydrophobic Polyelectrolytes



Conformational transition from a pearl necklace below the bead overlap concentration c_b to an ideal chain above the overlap with a sharp size increase leads to a dramatic increase of relaxation time and solution viscosity.

Size increase at bead overlap transition can be accompanied by chain entanglements.

$$\eta_{above} / \eta_{below} = (Z\, N/N_e)^2$$

$$Z = M_{bead}/M_{string}$$

Things to Remember about Semidilute "Hydrophilic" Polyelectrolytes

Overlap concentration is very low ($c^* \sim 1/N^2$).

Characteristic scattering peak at $q \sim 1/\xi \sim c^{1/2}$.

Osmotic pressure is controlled by counterions.

Summary of Hydrophobic Polyelectrolytes

Hydrophobic polyelectrolytes at low concentrations are similar to hydrophilic ones.

Properties of hydrophobic polyelectrolytes at concentrations higher than string overlap are even more unusual.

In the bead-controlled regime correlation length $\xi \sim R \sim c^{-1/3}$ and relaxation time $\tau \sim c^{-1}$.

"Gelling transition" at bead overlap with a sharp increase of chain size, relaxation time, and solution viscosity.

Open Questions

1. Effect of local fields on dissociation of “weak” charged groups (local shift of pKa)
2. Dielectric constant and ion binding in regions with high local *c*
3. Effect of screening by chains on Debye length
4. Entanglement onset in PSS solutions has weak *c*-dependence
   - Effect of electrostatic repulsion on tube diameter
5. Ionic strength dependence of electrostatic persistence length

Dozen of Length Scales

1. Bjerrum length $l_B = e^2/(\varepsilon kT) \approx 7$ Å in water at room T.
2. Debye screening length $r_D = (8\pi l_B c_s)^{-1/2} \approx 1nm$ in $0.1M$ 1-1 salt.
3. Gouy-Chapman length $\lambda = 1/(2\pi l_B \sigma) \approx 2.3nm$ for $\sigma = 0.1\ nm^{-2}$
4. Monomer size $b \approx 2.5$ Å for chemical and $b \approx 1\ nm$ for Kuhn.
5. Contour length between charges $b/f \approx 1nm$ for $f = 0.25$, $b \approx 2.5$Å
6. Persistence length $l_p \sim 1nm$ for flexible chains
7. Contour length $Nb \approx 250\ nm$ for $N = 10^3$ and $b \approx 2.5$Å
8. Electrostatic blob $D_e \approx b(uf^2)^{-1/3} \approx 9$Å for $u=2$, $f=0.1$, $b \approx 2.5$Å
9. Dilute no-salt chain size $L \approx D_e\ N/g \approx 70nm$
10. Correlation length in semidilute solutions ξ
11. Chain size R
12. Tube diameter a