DYNAMICS OF POLYMER SOLUTIONS
2008 APS symposium honoring P.-G. de Gennes

William W. Graessley, Princeton University

1) **Molecular Size, Radius of Gyration** R_g

2) **Osmotic Pressure** π**, Interaction Parameter** χ

3) **Plateau Modulus** G_N^o **(Entanglement Molecular Weight** M_e **)**

4) **Zero-Shear Viscosity** η_o **(Characteristic Molecular Weight** M_c**)**

5) **Monomeric Friction Coefficient** ζ_o

FLEXIBLE CHAIN LINEAR POLYMERS

chain length $\propto M$

coil size R_g

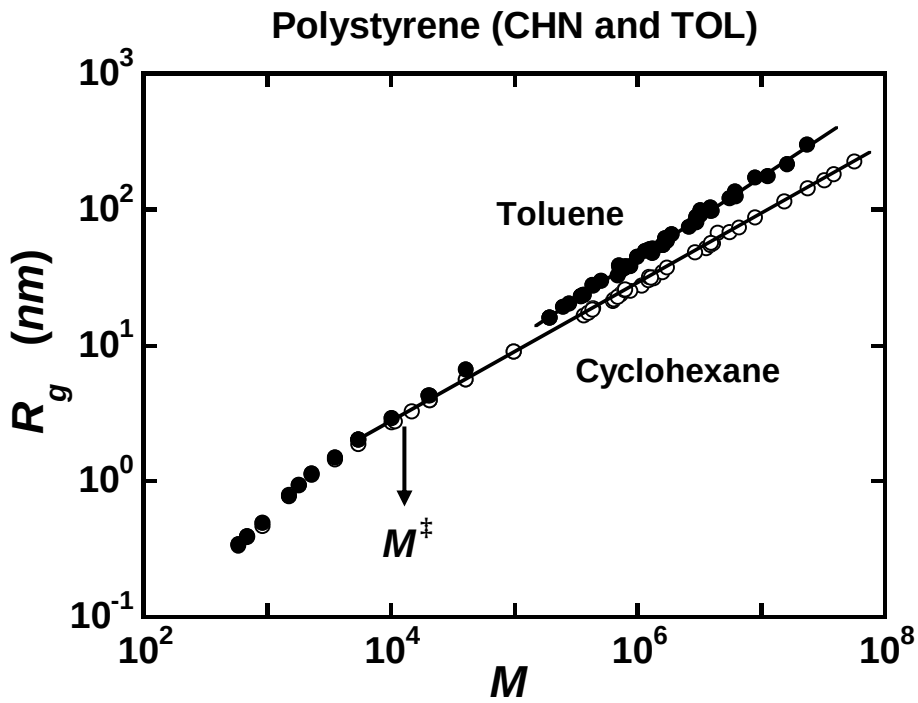
good solvent $R_g \propto M^{0.588}$

(self-avoidance, excluded volume interaction)

theta solvent $R_g \propto M^{0.5}$

(volume exclusion cancelled)

CHAIN DIMENSIONS, GOOD AND THETA SOLVENTS

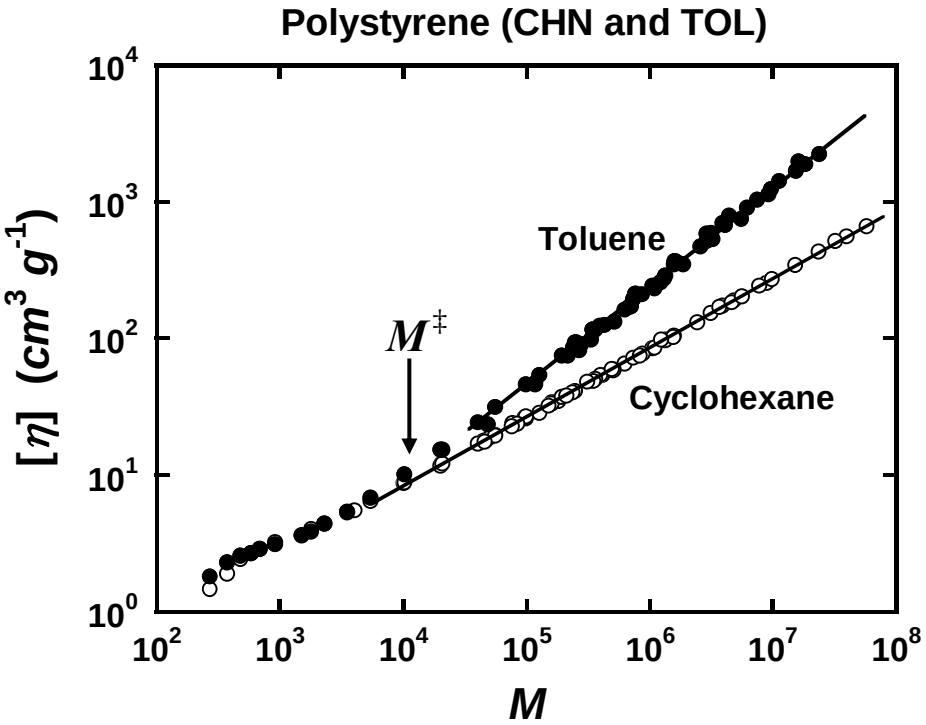


$$R_g = M^{\nu} \qquad M >> M^{\ddagger}$$

$$\nu = 0.5 \ \text{theta}; \ \nu = 0.59 \ \text{good}$$

for $M < M^{\ddagger}$, good and theta sizes are the same

INTRINSIC VISCOSITY, $[\eta] = \lim_{c \to 0} \frac{\eta(c) - \eta_s}{\eta_s c}$, A PERVADED VOLUME MEASURE



pervaded volume: $\upsilon_{per} \sim (4\pi/3) R_g^3$

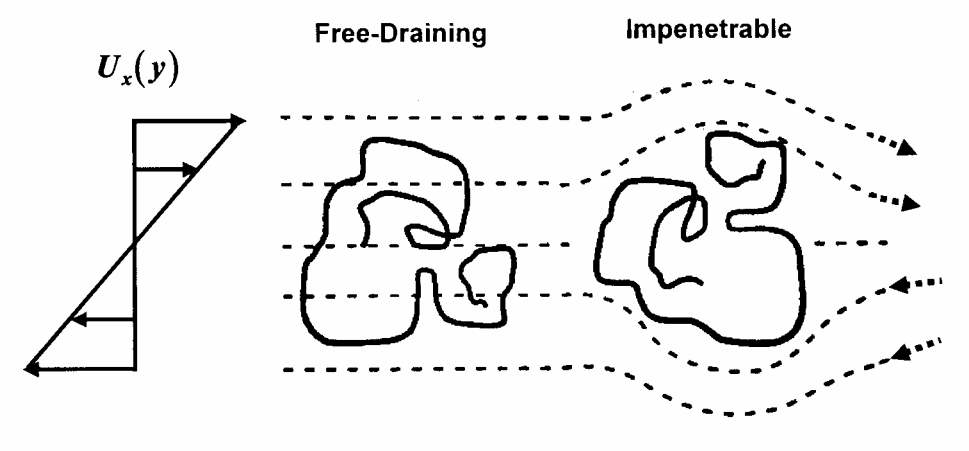
$$[\eta] \sim \frac{N_a \upsilon_{per}}{M} \propto \frac{R_g^3}{M}$$

self concentration:

$$c_{self} = \frac{M}{N_a \upsilon_{per}} = \rho \phi_{self} \sim \frac{1}{[\eta]}$$

theta solvent: $[\eta] \propto M^{0.50}$, **good solvent:** $[\eta] \propto M^{0.76}$

INFLUENCES ON FLEXIBLE COIL DYNAMICS IN SOLUTION



Dilute Range:

1) excluded volume

2) hydrodynamic interaction

---

overlap concentration c^* *or* ϕ^* **:**

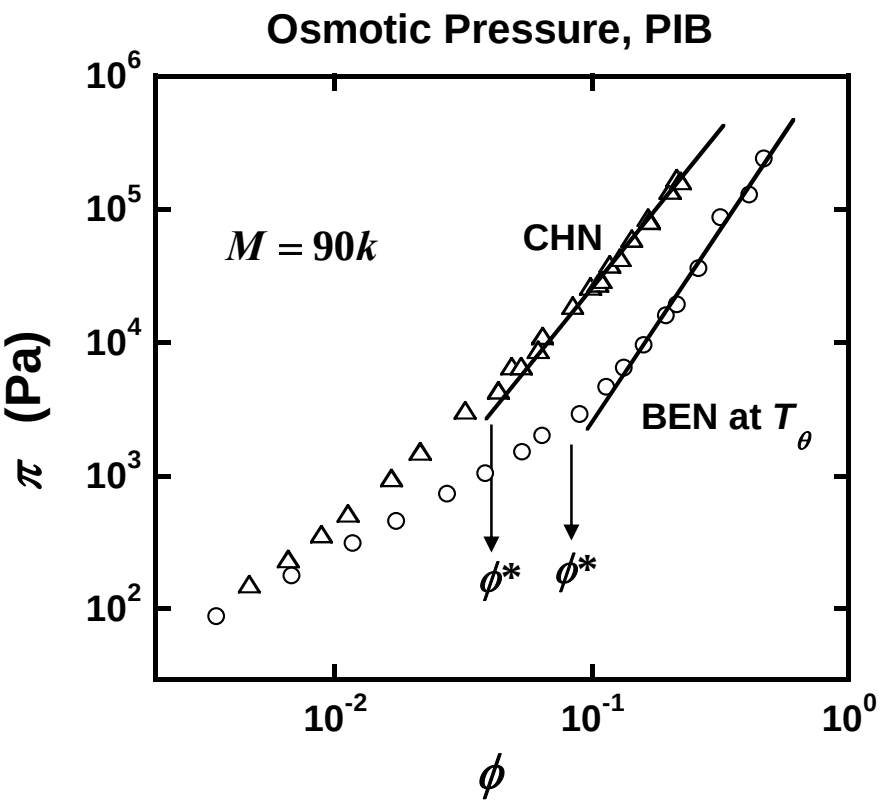
when c **(or** ϕ**) reaches** c_{self} **(or** ϕ_{self}**)**

Beyond Overlap:

3) hydrodynamic drag

4) mutual uncrossability

OSMOTIC PRESSURE: $\pi = \dfrac{\mu_s(c) - \mu_s(0)}{V_s}$



$$\pi = \frac{cRT}{M} \qquad c << c^*$$

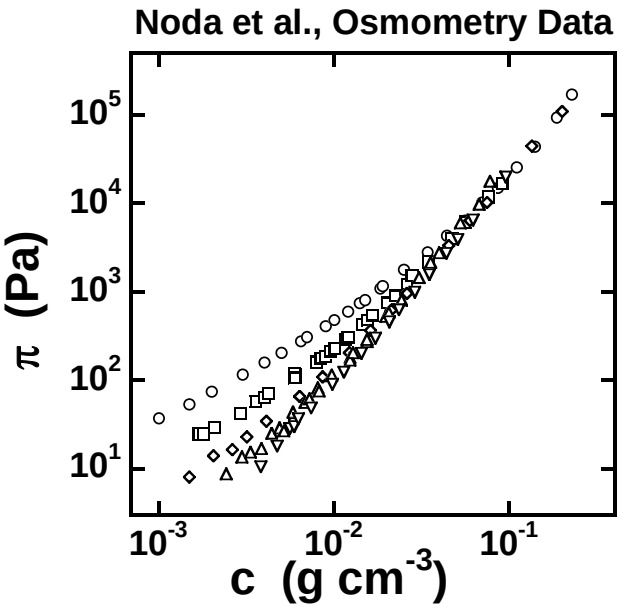
$$\pi = Bc^p \qquad c >> c^*$$

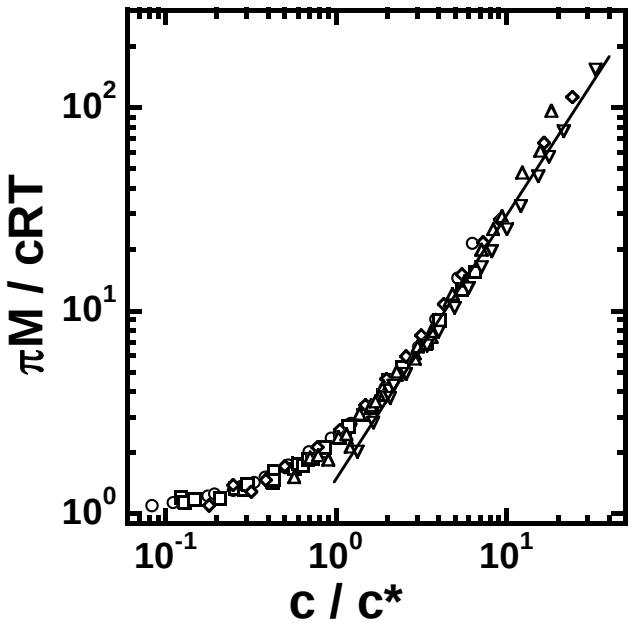
$$c^* \propto \frac{M}{R_g^3(0)} \; ; \; R_g(0) \propto M^\nu$$

at $c = c^*$ $\quad \dfrac{c^*}{M} = \left(c^*\right)^p \Rightarrow \dfrac{M}{MM^{3\nu}} = \left(\dfrac{M}{M^{3\nu}}\right)^p$

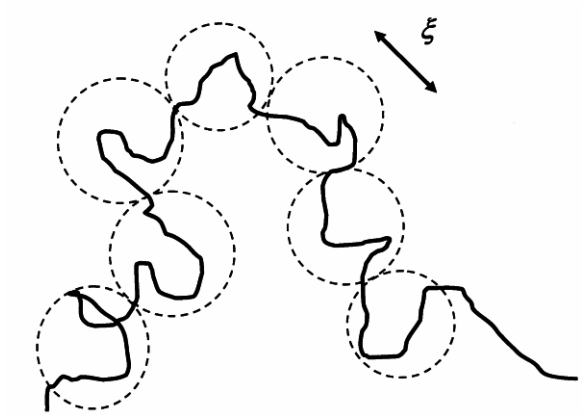
so $p = \dfrac{3\nu}{3\nu - 1}$ and thus

theta solvent $p = 3$; good solvent $p = 2.3$





$\phi > \phi^*$ **(semi-dilute)**



screening length, correlation volume

$$\frac{n(r)}{r^3} \propto \phi_{self}(r) \qquad \xi = r \text{ when } \phi_{self}(r) = \phi$$

Using $\xi = R_g(0)$ **at** $\phi = \phi^*$ **:**

$$\xi = R_g(0)\left(\phi/\phi^*\right)^{-\frac{\nu}{3\nu-1}} \quad ; \quad \pi \sim \frac{k_B T}{\xi^3}$$

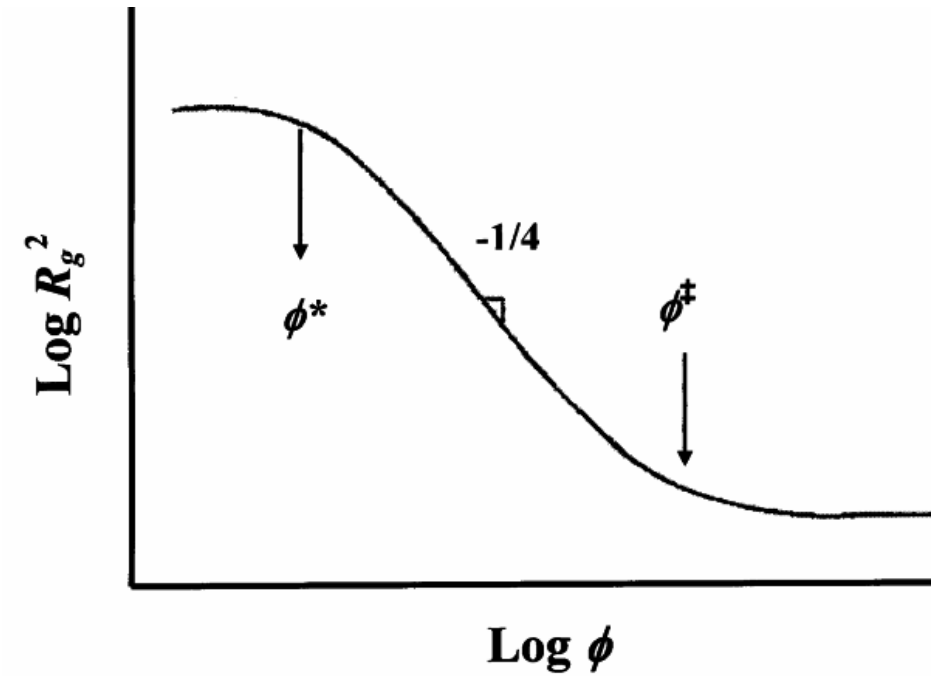
CHAIN DIMENSIONS VS CONCENTRATION

By screening analysis:

$$R_g^2(\phi) = R_g^2(0)\left(\phi/\phi^*\right)^{-\frac{2\nu-1}{3\nu-1}} = R_g^2(0)\left(\phi/\phi^*\right)^{-0.23}$$

Where does R_g reach $\left(R_g\right)_\theta$?

$$\phi^{\ddagger} = \phi^*\left(R_g(0)/\left(R_g\right)_\theta\right)^{2/0.23} \propto M^0$$



Polymer Species	$\phi^{\ddagger}$	$M^{\ddagger}$
PS	0.10	13,200
PαMS	0.10	17,000
PMMA	0.14	11,000
PDMS	0.11	13,000
PIB	0.070	19,000
PI	0.14	3,800
PBD	0.085	5,200
PE	0.050	6,500
iPP	0.11	6,600
PEO	0.070	6,700

WHY IS $M^{\ddagger}$ SO LARGE?

PS-TOL: $M^{\ddagger} \sim 10^4$ **, 200 Backbone Bonds, 20 Kuhn Steps**

Self-avoiding Walks ($\chi = 0$**) ,** $M^{\ddagger} \Rightarrow$ **~ 2 Kuhn Steps**

Flory coil swelling formula leads to $$\left(M^{\ddagger}\right)^{1/2}\left(1-2\chi\right) = \left(\frac{8\pi N_a V_s}{3\bar{\upsilon}^2}\right)\left(\frac{R_g^2}{M}\right)_{\theta}^{3/2},$$

then to $\chi = 0.34$ **, and finally to the inference,** $\phi^{\ddagger} \sim 0.32$ **for** $\chi = 0$**.**

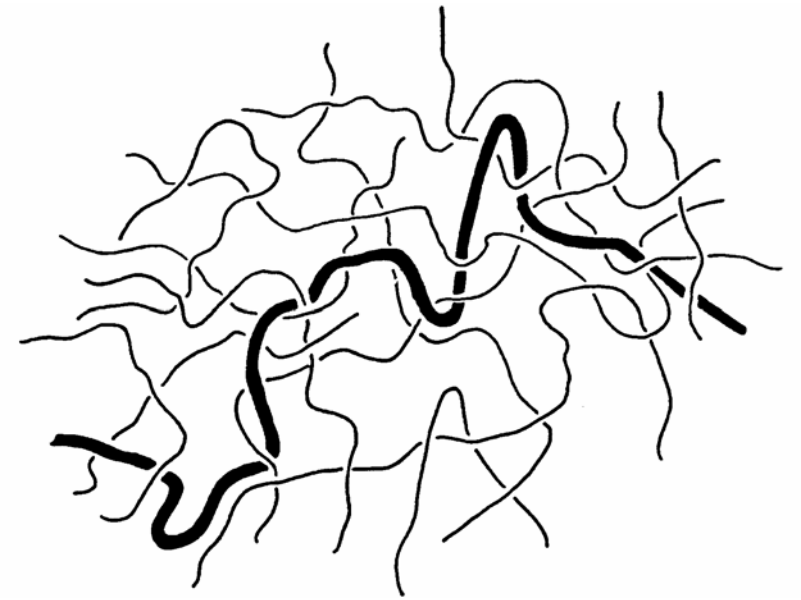
$\chi \gtrsim 0.3$ FOR MOST POLYMER SOLUTIONS. WHY?

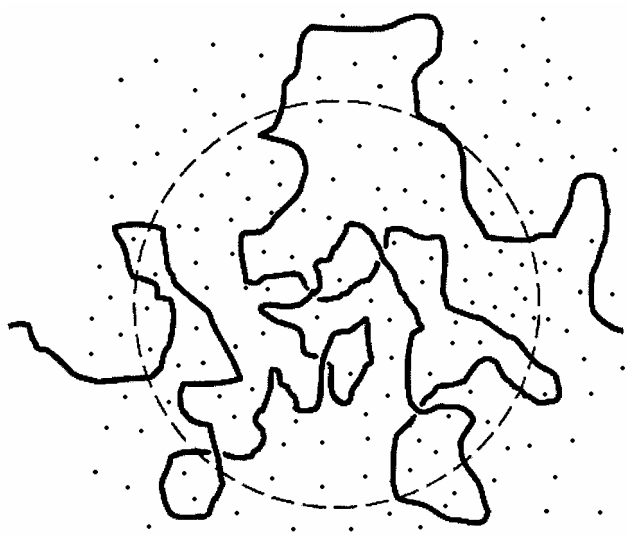
$$\frac{\chi RT}{V_S} \sim \left(\delta_S - \delta_P\right)^2 + \frac{\alpha_S T \delta_S^2}{2}\left(\frac{\alpha_S - \alpha_P}{\alpha_S}\right)^2 + \cdots$$

CED mismatch **FV mismatch** **ETC**

On average, $\alpha_S/\alpha_P \sim 1.7$ **, leading to** $\chi_{FV} \sim 0.3$

CONCENTRATED SOLUTIONS, $\phi^{\ddagger} < \phi < 1$





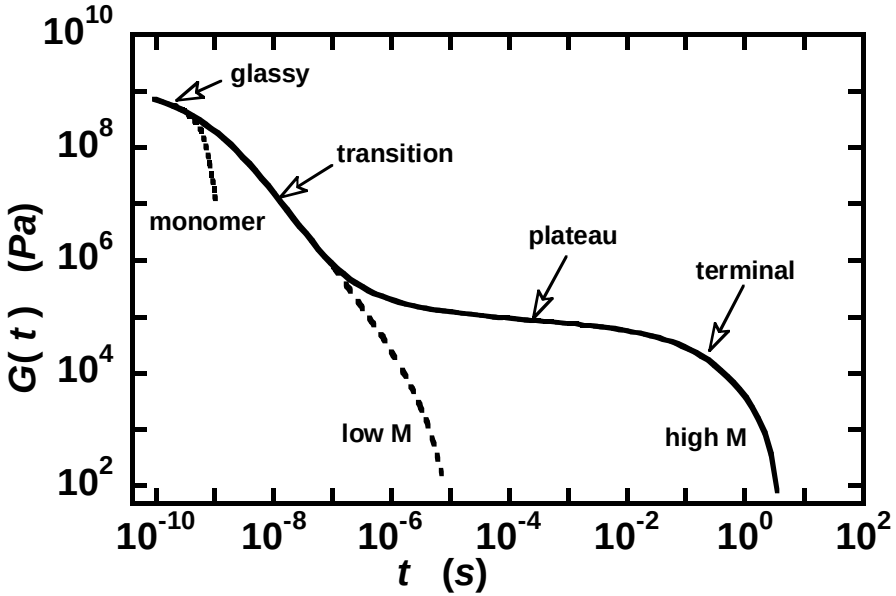
1) **Intramolecular interactions screened out**

2) **Free-draining flow patterns**

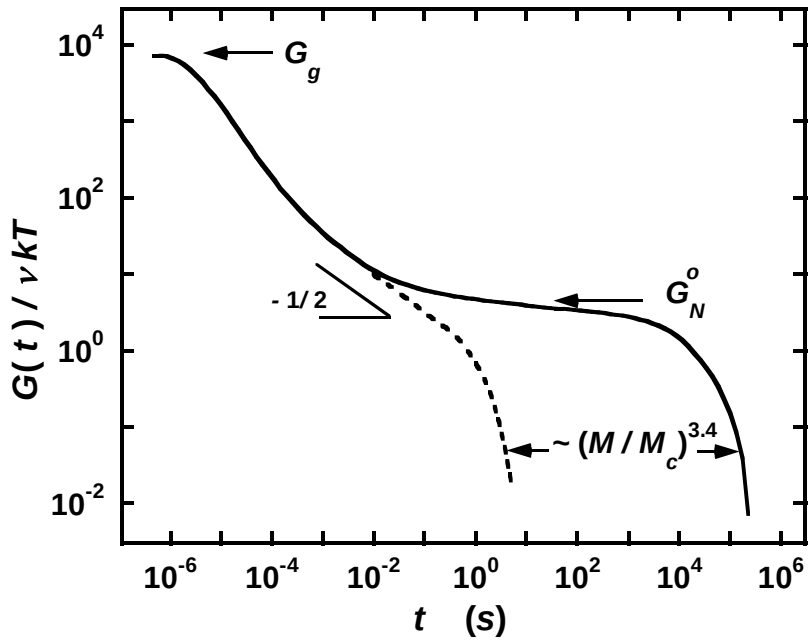
3) **Entanglement and local drag dominate the dynamics**

4) **Reptation is a primary mechanism for relaxation**

STRESS RELAXATION MODULUS



Simple Shear Deformation:



G_N^o = **plateau modulus**

$$\eta_o = \int_0^\infty G(t)\,dt$$ **zero - shear viscosity**

$$\tau_o = \frac{\int_0^\infty tG(t)\,dt}{\int_0^\infty G(t)\,dt}$$ **terminal relaxation time**

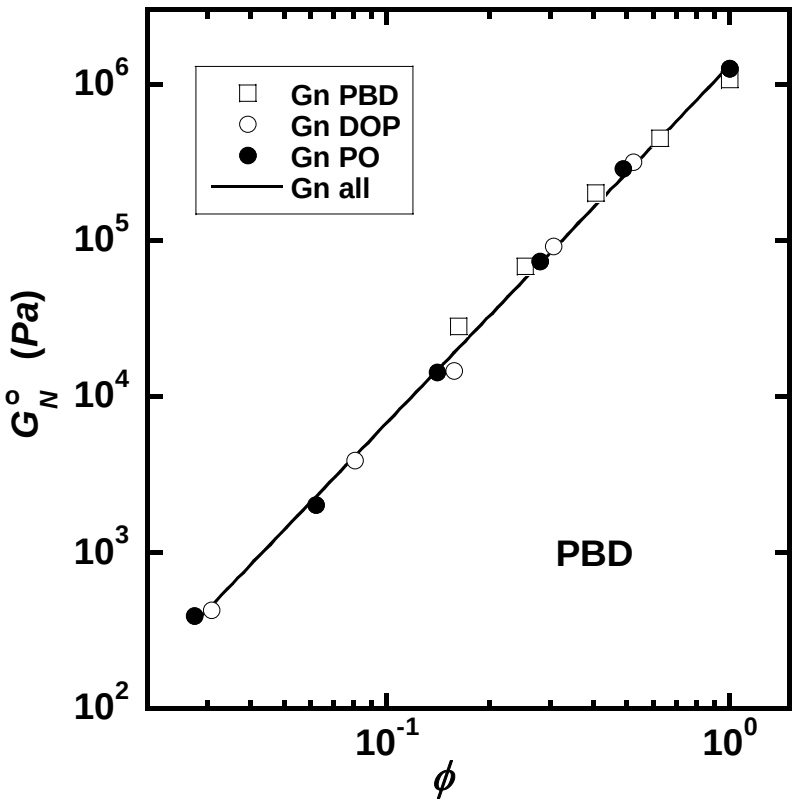
PLATEAU MODULUS VS CONCENTRATION

$$G_N^o(\phi) = G_N^o \phi^{2.3}$$

$$M_e = \frac{\rho RT}{G_N^o}$$

$$M_e(\phi) = \frac{\rho \phi RT}{G_N^o(\phi)} = M_e \phi^{-1.3}$$

$$E(\phi, M) = \frac{M}{M_e(\phi)} \quad \text{entanglements/chain}$$

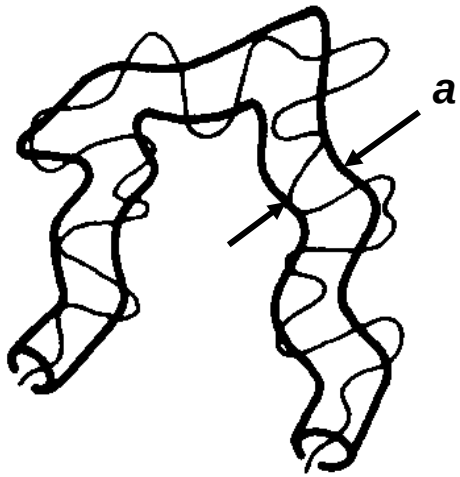


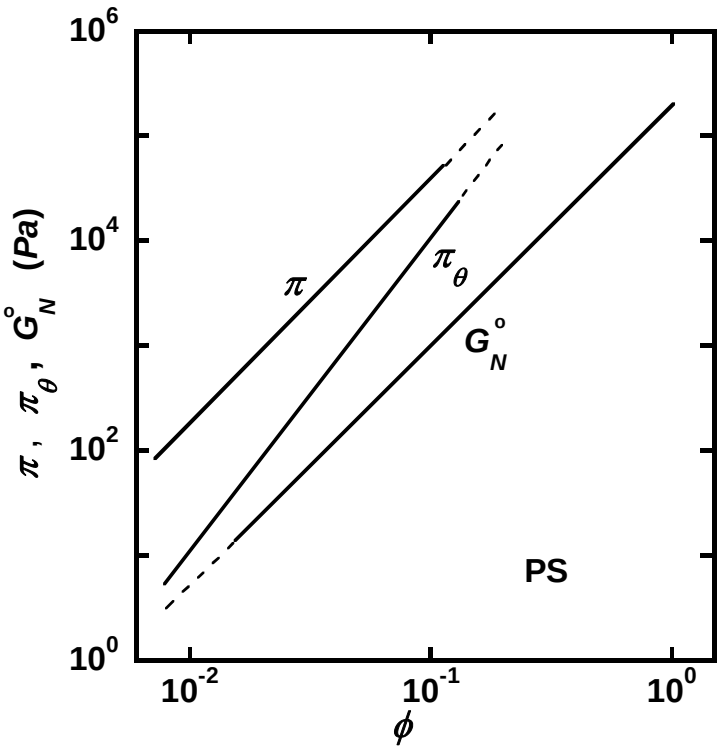
Polybutadiene, 925k, in a good solvent (PO), a near theta solvent (DOP) and a 1.8k PBD oligomer.

$$G_N^o(\phi) = 1.15 \times 10^6 \phi^{2.29} \ (Pa)$$

$$5 < E(\phi, M) < 490$$

OSMOTIC MODULUS vs ENTANGLEMENT MODULUS





Doi-Edwards theory:

$$G_N^{\circ}(\phi) \propto \frac{\phi}{\left[a(\phi)\right]^2}$$

binary contact density:

$$\nu(\phi) \propto \phi^2$$

distance between contacts:

$$d \propto \nu^{-1/3} \propto a \propto \phi^{-0.67}$$

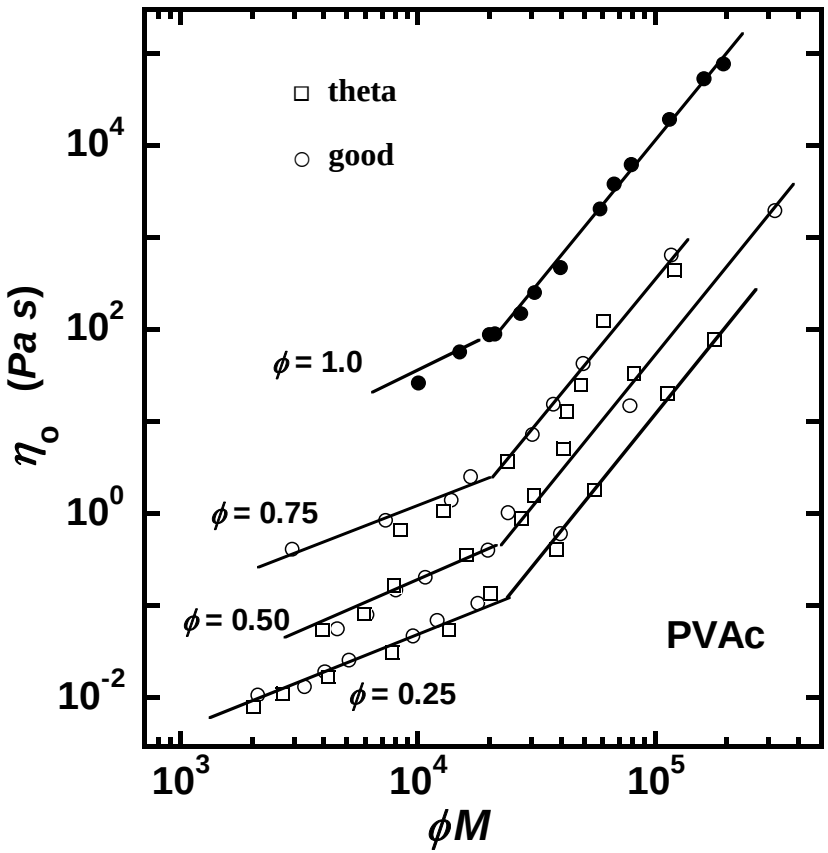
$$(a(\phi) = a(1)\phi^{-0.61} \quad \text{NSE})$$

so, for theta or good solvents:

$$G_N^{\circ}(\phi) \propto \phi^{7/3} \propto \phi^{2.33}$$

Milner 2005: $G_N^{\circ}/\pi = 0.025\left(R_g^{\ddagger}/l_p\right)^{2/3}$

VISCOSITY vs CONCENTRATION



η_o = (monomeric friction)x(structural factor)

$$\eta_o = \zeta_o(T,\phi,\cdots)\,F(\phi,M)$$

When corrected for end effects:

$$\eta_o(\phi,M) \propto \phi M \qquad \phi M < \phi M_c$$

$$\eta_o(\phi,M) \propto (\phi M)^{3.4} \qquad \phi M > \phi M_c$$

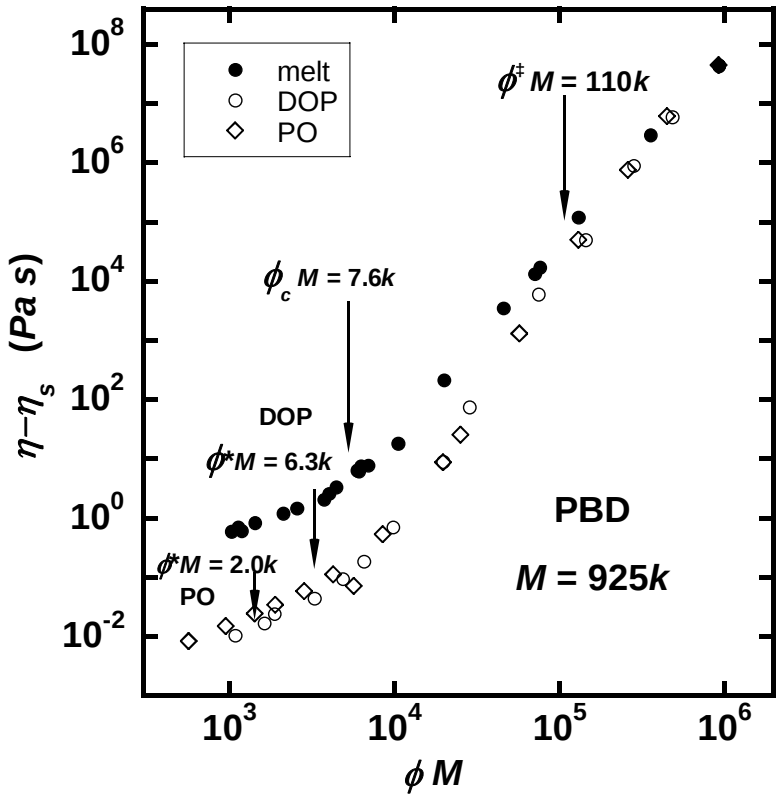
For PVAc:

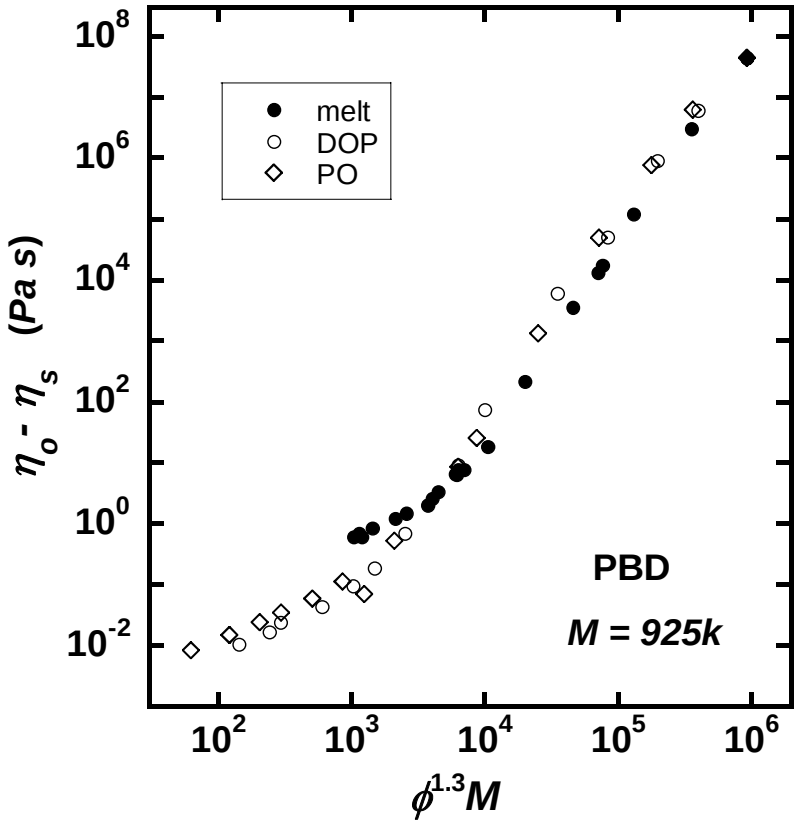
$$M_e = 9.5k$$

$$M_c = 24.5k$$

ϕM *or* $\phi^{1.3} M$ **for** η_o **?**

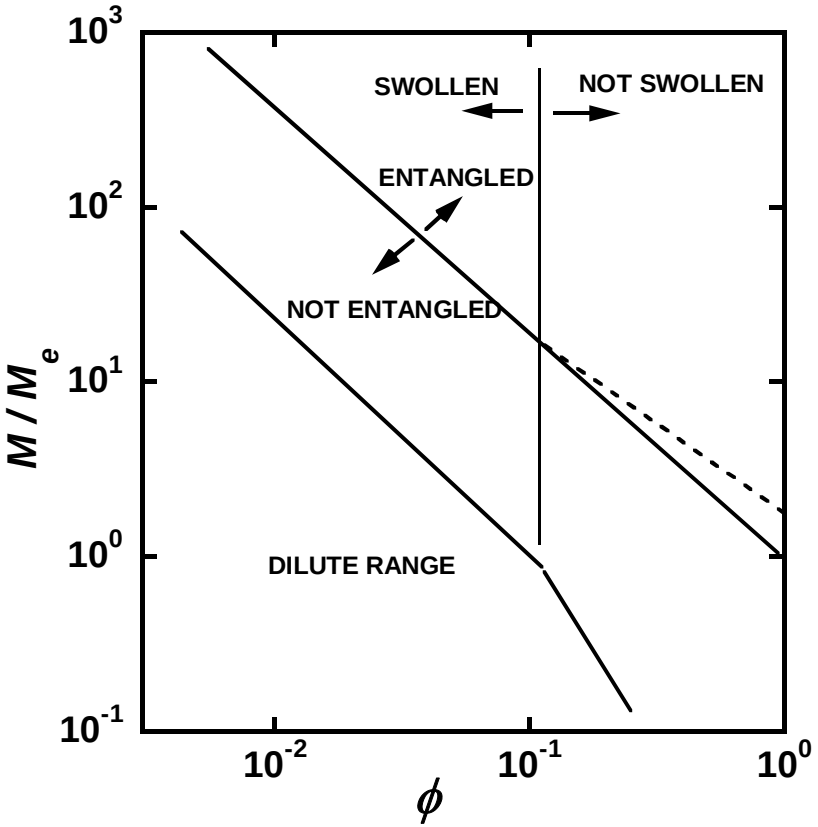
Adjusted to constant monomeric friction coefficient:



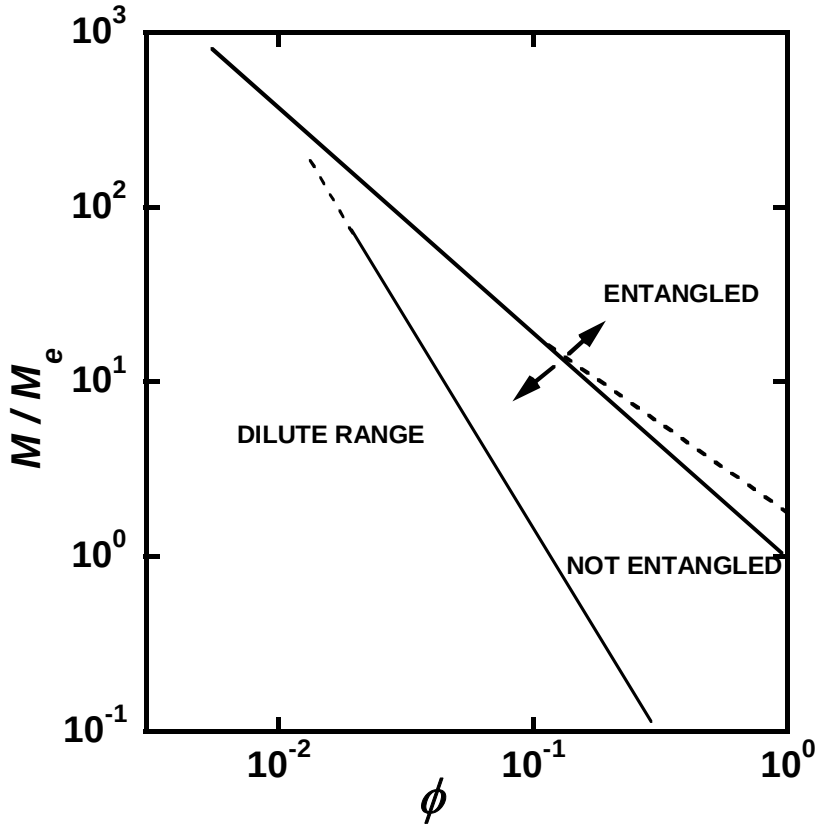


CONCENTRATION – MOLECULAR WEIGHT DIAGRAMS

good solvent ($\chi \sim 0.4$)



theta solvent ($\chi = 0.5$)



FREE VOLUME ADJUSTMENTS