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

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1) Molecular Size, Radius of Gyration $R_g$

2) Osmotic Pressure $\pi$, Interaction Parameter $\chi$

3) Plateau Modulus $G_N^0$ (Entanglement Molecular Weight $M_e$)

4) Zero-Shear Viscosity $\eta_o$ (Characteristic Molecular Weight $M_c$)

5) Monomeric Friction Coefficient $\zeta_o$
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

\[ R_g = M^\nu \quad M \gg M^\dagger \]

\( \nu = 0.5 \) theta; \( \nu = 0.59 \) good

for \( M < M^\dagger \), 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: $\nu_{\text{per}} \sim \left(\frac{4\pi}{3}\right) R_g^3$

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

self concentration:

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

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

Polystyrene (CHN and TOL)

Pervaded volume: $\nu_{\text{per}} \sim \left(\frac{4\pi}{3}\right) R_g^3$

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INFLUENCES ON FLEXIBLE COIL DYNAMICS IN SOLUTION

Dilute Range:
1) excluded volume
2) hydrodynamic interaction

Beyond Overlap:
3) hydrodynamic drag
4) mutual uncrossability

overlap concentration \( c^* \) or \( \phi^* \):
when \( c \) (or \( \phi \)) reaches \( c_{self} \) (or \( \phi_{self} \))
OSMOTIC PRESSURE: \[ \pi = \frac{\mu_s(c) - \mu_s(0)}{V_s} \]

\[ \pi = \frac{cRT}{M} \quad c \ll c^* \]

\[ \pi = Bc^p \quad c \gg c^* \]

\[ c^* \propto \frac{M}{R_g(0)} ; \quad R_g(0) \propto M^\nu \]

at \( c = c^* \) \[ \frac{c^*}{M} = (c^*)^\nu \Rightarrow \frac{M}{MM^{3\nu}} = \left( \frac{M}{M^{3\nu}} \right)^p \]

so \( p = \frac{3\nu}{3\nu - 1} \) and thus

theta solvent \( p = 3 \); good solvent \( p = 2.3 \)
Noda et al., Osmometry Data

\[ \pi (\text{Pa}) \]
\[ c \ (\text{g cm}^{-3}) \]

\[ 10^{-3} \quad 10^{-2} \quad 10^{-1} \]

\[ 10^0 \quad 10^1 \quad 10^2 \]

\[ \pi \]
\[ M / cRT \]

\[ c / c^* \]

\[ \phi > \phi^* \] (semi-dilute)

screening length, correlation volume

\[ \frac{n(r)}{r^3} \propto \phi_{\text{self}}(r) \]

\[ \xi = r \quad \text{when} \quad \phi_{\text{self}}(r) = \phi \]

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

\[ \xi = R_g(0) \left( \frac{\phi}{\phi^*} \right)^{\frac{\nu}{3\nu-1}} ; \quad \pi \sim \frac{k_B T}{\xi^3} \]
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 \( \left( R_g \right)_\theta \)?

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

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<tr>
<th>Polymer Species</th>
<th>( \phi^\dagger )</th>
<th>( M^\dagger )</th>
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<tr>
<td>PEO</td>
<td>0.070</td>
<td>6,700</td>
</tr>
</tbody>
</table>
WHY IS $M^\dagger$ SO LARGE?

PS-TOL: $M^\dagger \sim 10^4$, 200 Backbone Bonds, 20 Kuhn Steps

Self-avoiding Walks ($\chi = 0$), $M^\dagger \Rightarrow \sim 2$ Kuhn Steps

Flory coil swelling formula leads to

$$\left( M^\dagger \right)^{1/2} (1 - 2\chi) = \left( \frac{8\pi N_a V_s}{3\nu^2} \right) \left( \frac{R_s^2}{M} \right)^{3/2},$$

then to $\chi = 0.34$, and finally to the inference, $\phi^\dagger \sim 0.32$ for $\chi = 0$.

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

$$\frac{\chi RT}{V_s} \sim (\delta_s - \delta_p)^2 + \frac{\alpha_s T \delta_s^2}{2} \left( \frac{\alpha_s - \alpha_p}{\alpha_s} \right)^2 + \ldots$$

CED mismatch    FV mismatch    ETC

On average, $\alpha_s / \alpha_p \sim 1.7$, leading to $\chi_{FV} \sim 0.3$
CONCENTRATED SOLUTIONS, $\phi^c < \phi < 1$

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:

\[ G_N^o = \text{plateau modulus} \]
\[ \eta_o = \int_0^\infty G(t) \, dt \quad \text{zero - shear viscosity} \]
\[ \tau_o = \frac{\int_0^\infty tG(t) \, dt}{\int_0^\infty G(t) \, dt} \quad \text{terminal relaxation time} \]
PLATEAU MODULUS VS CONCENTRATION

\[ G_N^0(\phi) = G_N^0 \phi^{2.3} \]

\[ M_e(\phi) = \frac{\rho \phi RT}{G_N^0(\phi)} = M_e \phi^{-1.3} \]

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

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

\[ G_N^0(\phi) = 1.15 \times 10^6 \phi^{2.29} \ (Pa) \]

\[ 5 < E(\phi, M) < 490 \]
OSMOTIC MODULUS vs ENTANGLEMENT MODULUS

Doi-Edwards theory:

\[ G_N^0(\phi) \propto \frac{\phi}{[\alpha(\phi)]^2} \]

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:

\[ G_N^0(\phi) \propto \phi^{7/3} \propto \phi^{2.33} \]

Milner 2005:

\[ G_N^0/\pi = 0.025 \left( \frac{R_s^i}{l_p} \right)^{2/3} \]
\[ \eta_o = (\text{monomeric friction}) \times (\text{structural factor}) \]

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

When corrected for end effects:

\[ \eta_o(\phi, M) \propto \phi M \quad \phi M < \phi M_c \]

\[ \eta_o(\phi, M) \propto (\phi M)^{3.4} \quad \phi M > \phi M_c \]

For PVAc:

\[ M_c = 9.5k \]

\[ M_c = 24.5k \]
\[ \phi M \ or \ \phi^{1.3} M \ for \ \eta_o? \]

Adjusted to constant monomeric friction coefficient:

\[ \eta = \eta_s \left( \frac{\phi M}{\phi^*} \right) \]

- \[ \phi^*_M = 2.0k \]
- \[ \phi^*_M = 6.3k \]
- \[ \phi^*_M = 110k \]

for PBD with:
- \[ M = 925k \]
- \[ \phi^* M = 7.6k \]
- \[ \phi^* M = 6.3k \]
- \[ \phi^* M = 2.0k \]

\[ \eta_o - \eta_s \] vs. \[ \phi M \]

\[ \eta_o - \eta_s \] vs. \[ \phi^{1.3} M \]
FREE VOLUME ADJUSTMENTS

\[ \eta_0 / M = \text{constant} \quad \zeta_0 \]

\[ \eta_0 (\text{Pa s}) / M (\text{Pa s}) \]

\[ \eta_0 (\text{Pa s}) \]

\[ M / M_e \]

\[ \phi \]