Analytical Rheology

Linear Viscoelasticity of Model and Commercial Long-Chain-Branched Polymer Melts

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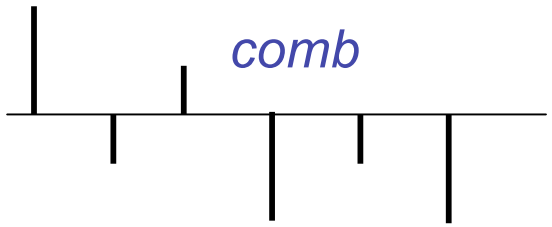
03/06

Motivation

linear



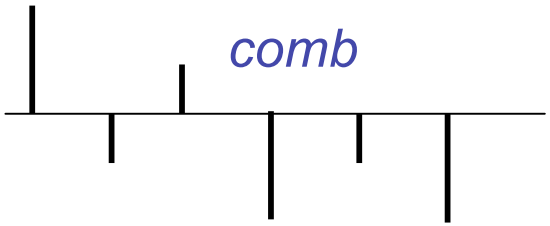
Long Chain Branching

LCB > 100 C-atoms

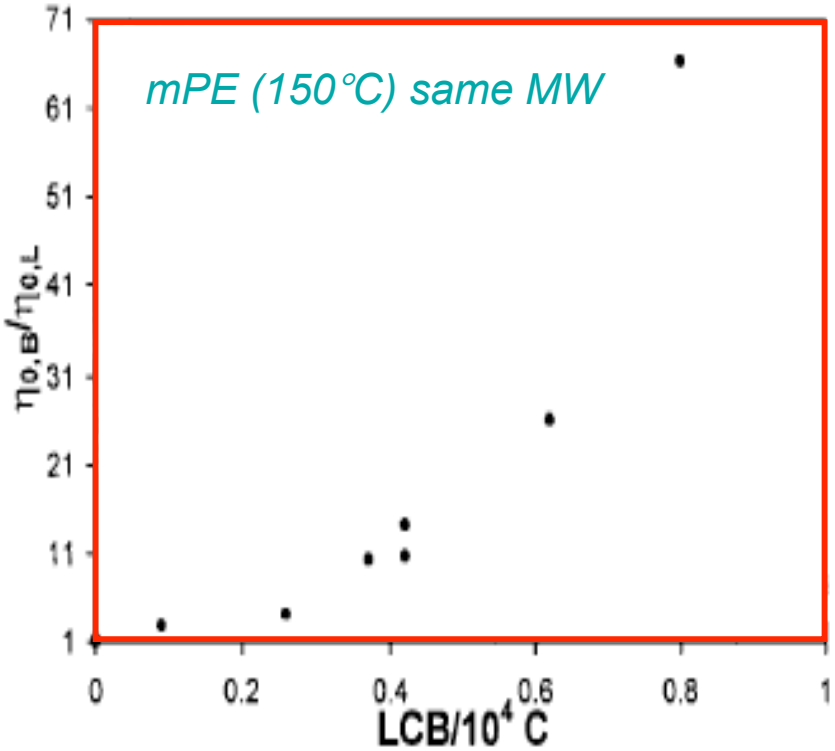
In LDPE ~ 10 LCB/1000 backbone carbon atoms

Polyethylene and polypropylene > 50% of the total synthetic polymer produced world-wide.

Motivation



Long Chain Branching



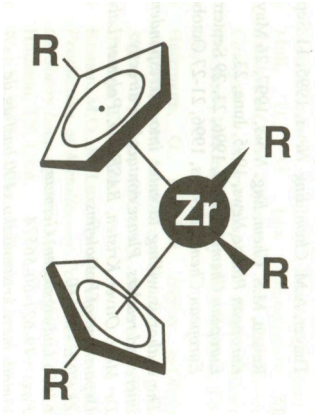
❖ Rheological properties → processing properties

❖ LDPE: strain hardening, shear thinning

Wood-Adams and Dealy, *Macromolecules* **2000**

Analytical Rheology of Long-Chain Branched Polyethylenes

- *spectroscopy, chromatography*
- *rheology is sensitive*
- *need accurate rheological models of branched structures*

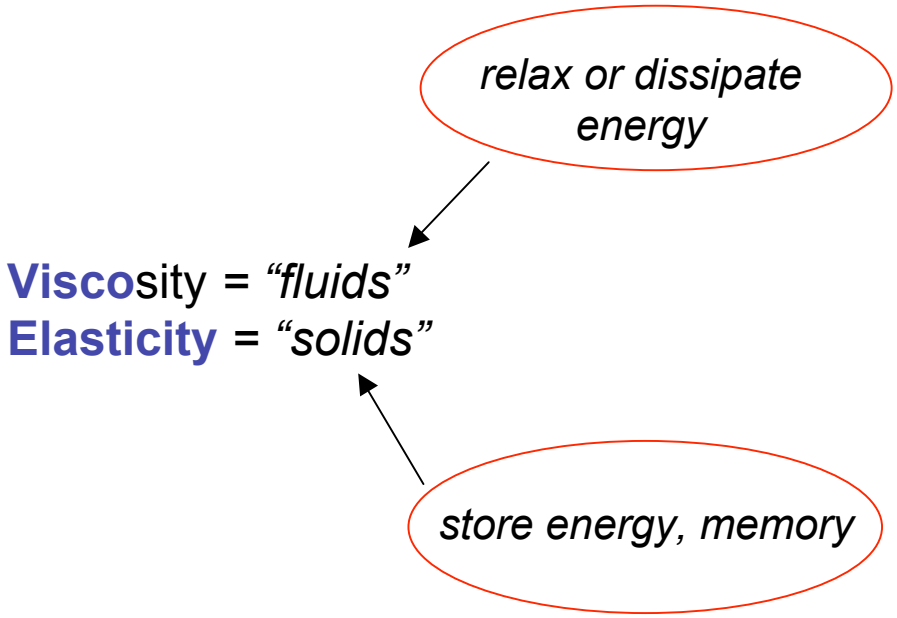


metallocene catalysts

Polymer solutions/melts are viscoelastic

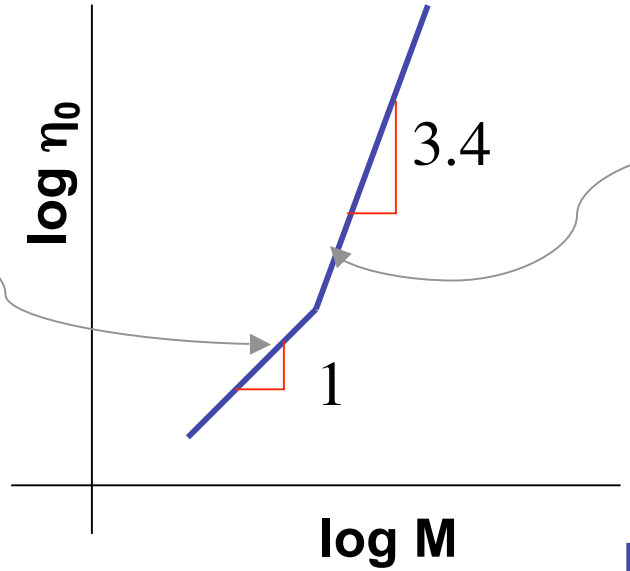
Elastic Recoil

http://burghdt3.chem-eng.northwestern.edu



Entangled Polymer Melts

UNENTANGLED

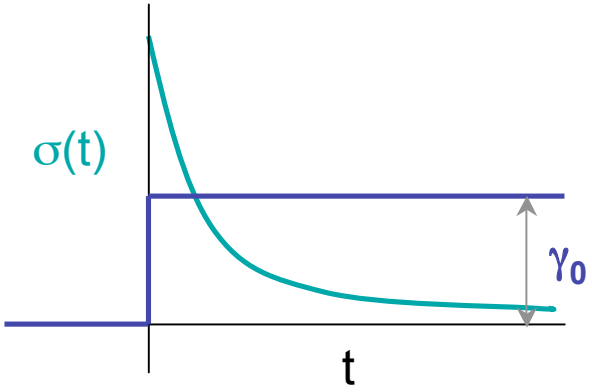


ENTANGLED

high interpenetration

http://zeus.plmsc.psu.edu/~manias

Linear Viscoelasticity



Relaxation Modulus

$$G(t) = \sigma(t)/\gamma_0$$

Dynamic Moduli

Storage Modulus

$$G'(\omega) = \omega \int_0^\infty G(t)\ \sin(\omega t)\ dt$$

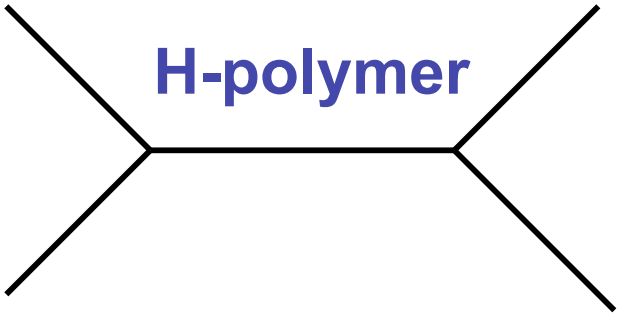
$$G''(\omega) = \omega \int_0^\infty G(t)\ \cos(\omega t)\ dt$$

Loss Modulus

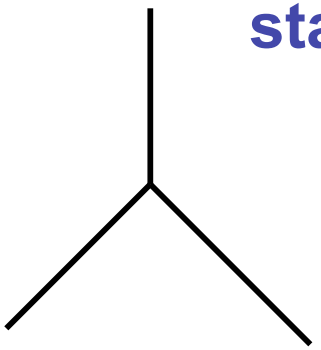
Branched Polymers

linear

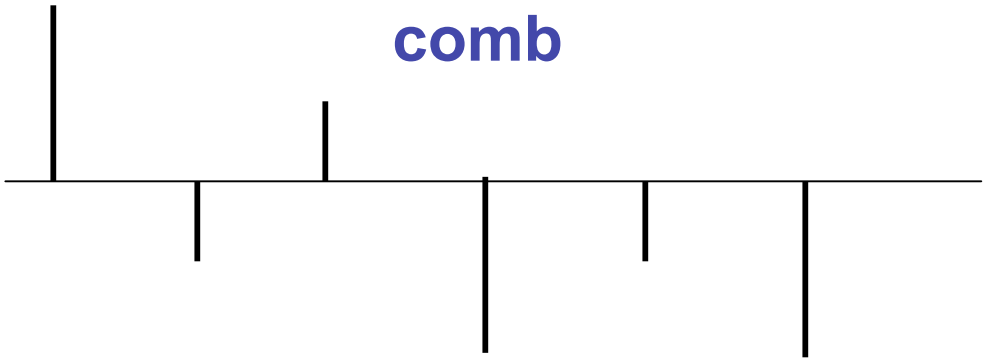
H-polymer



star

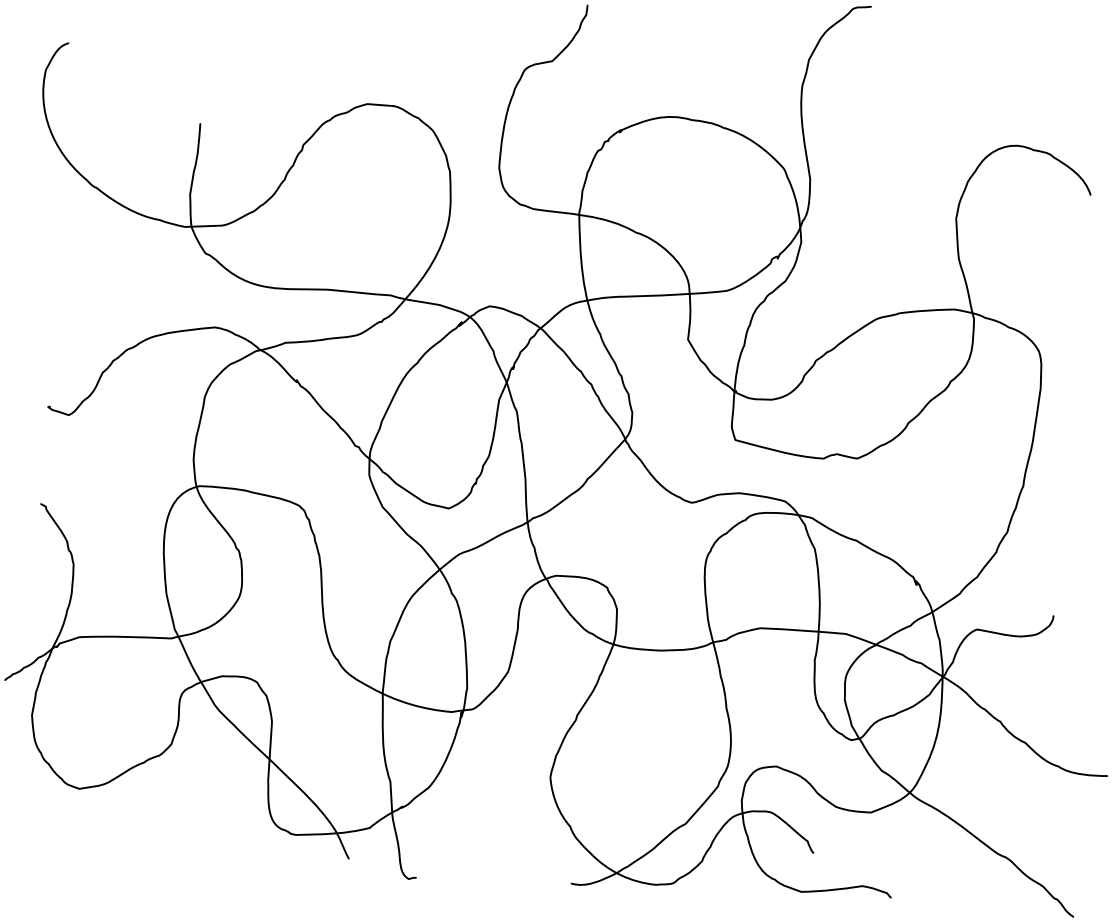


comb



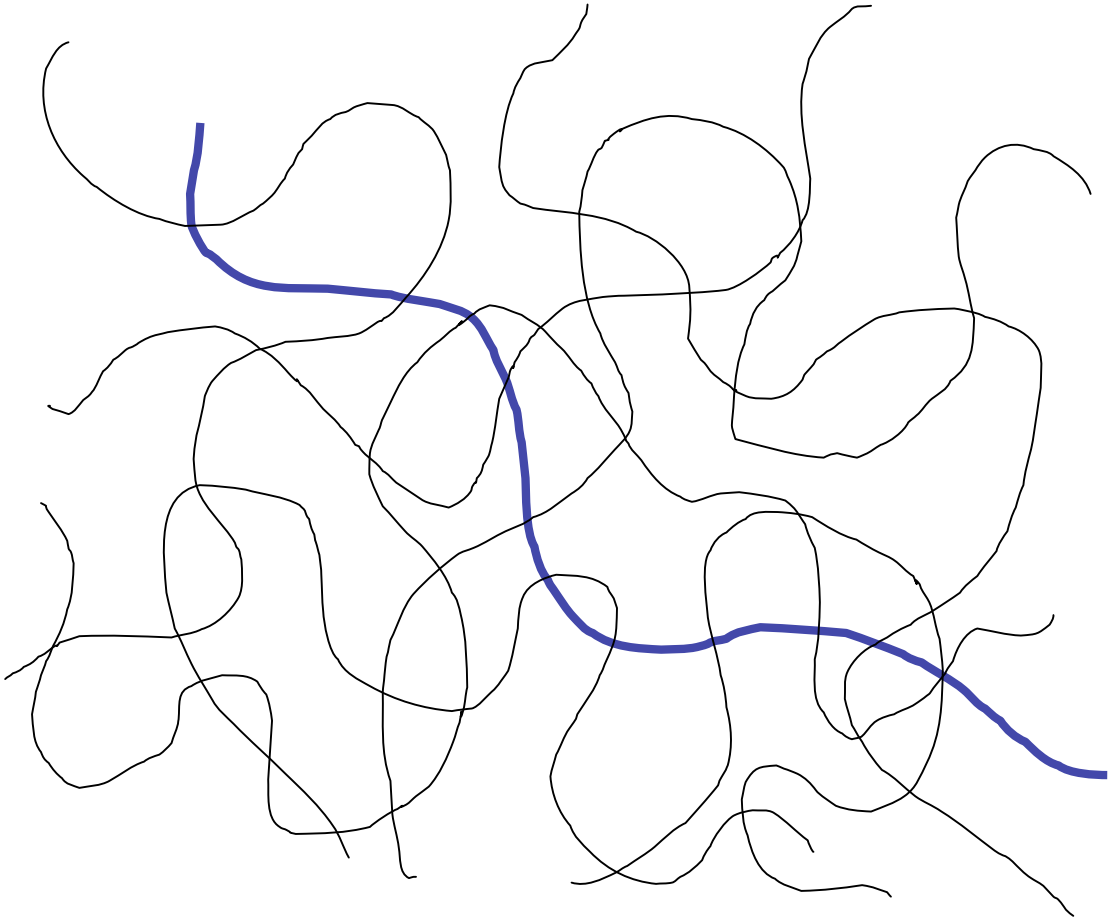
Long **C**hain **B**ranching

The Tube Model



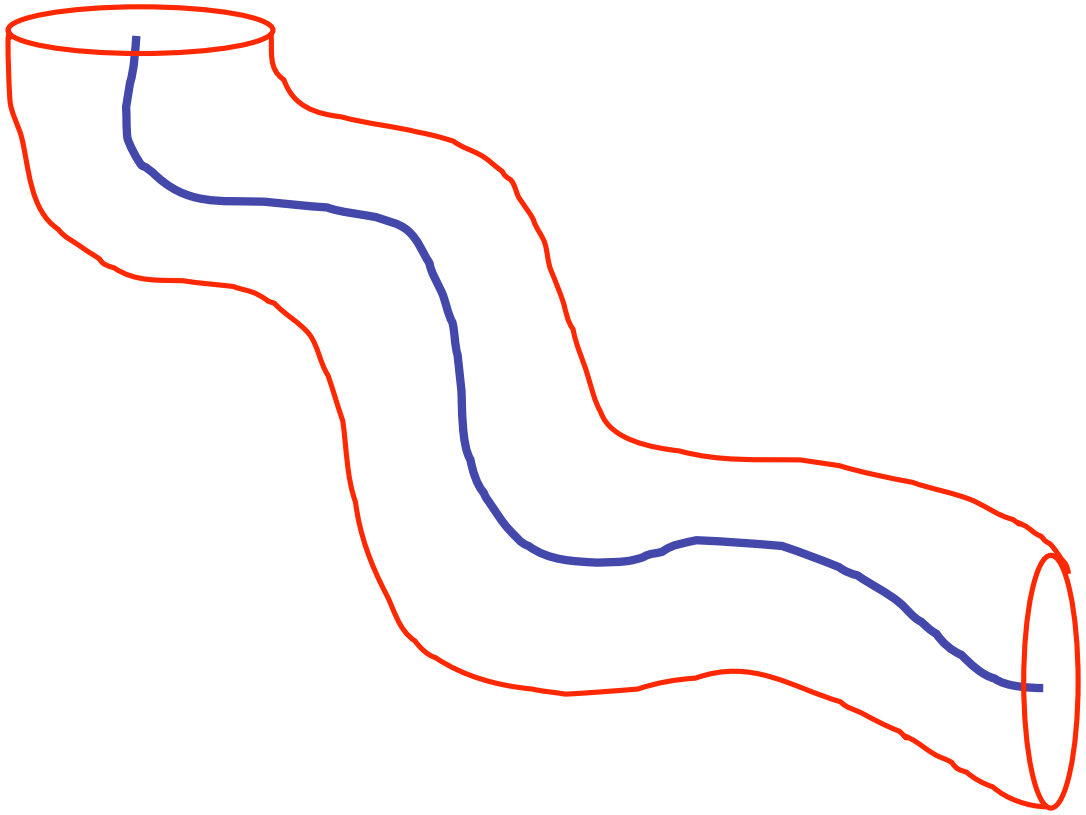
courtesy: Richard Graham

The Tube Model



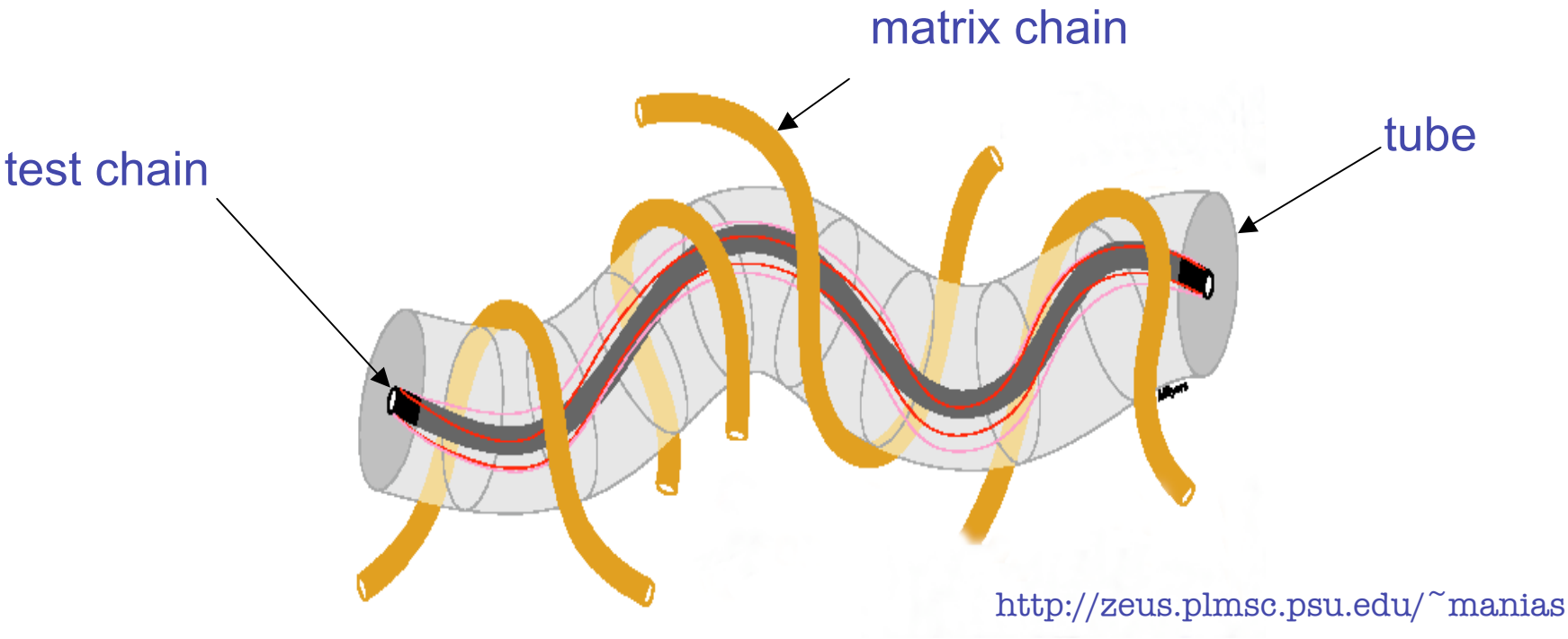
courtesy: Richard Graham

The Tube Model

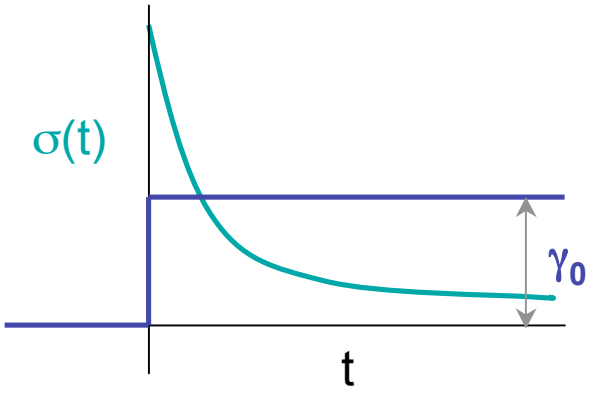


courtesy: Richard Graham

The Tube Model

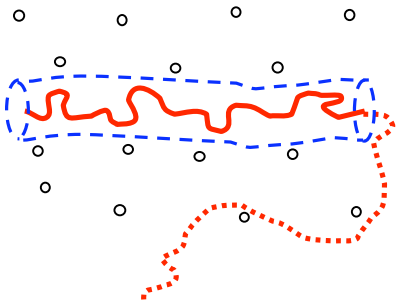


Stress Relaxation



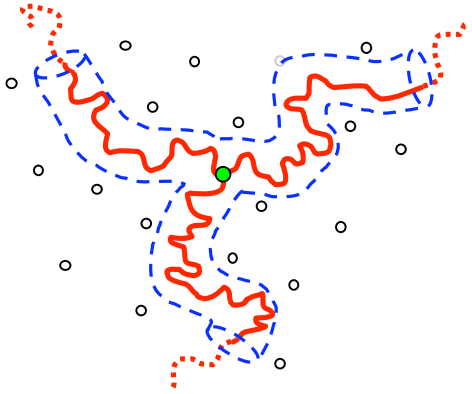
Relaxation Modulus

$G(t) = \sigma(t)/\gamma_0$



Reptation

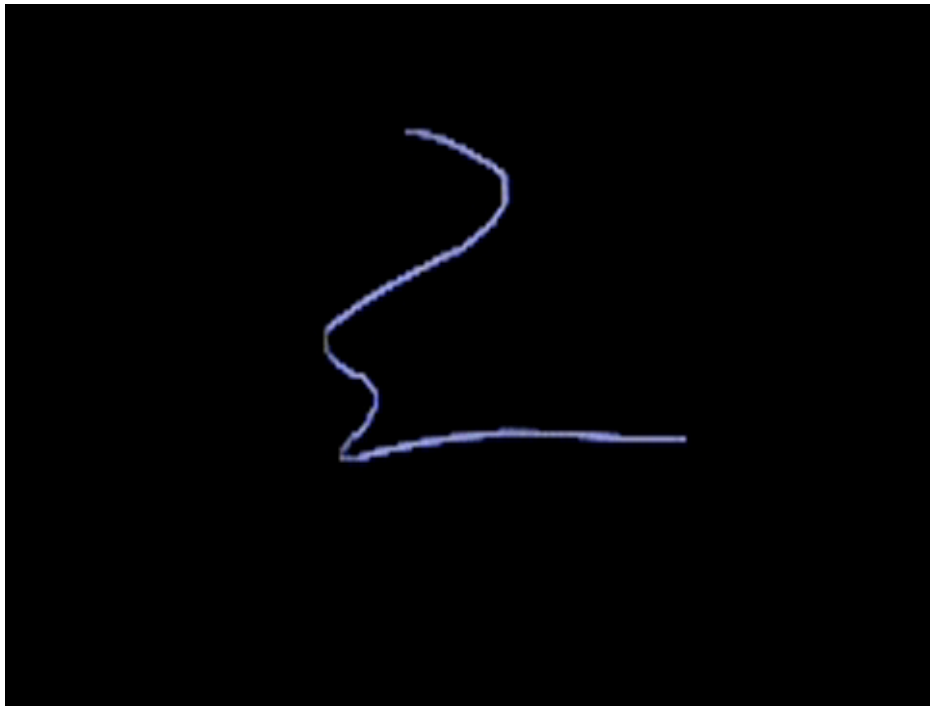
$\tau_{linear} \sim M^{3.4}$



Arm Retraction

$\tau_{arm} \sim \exp(M)$

Reptation

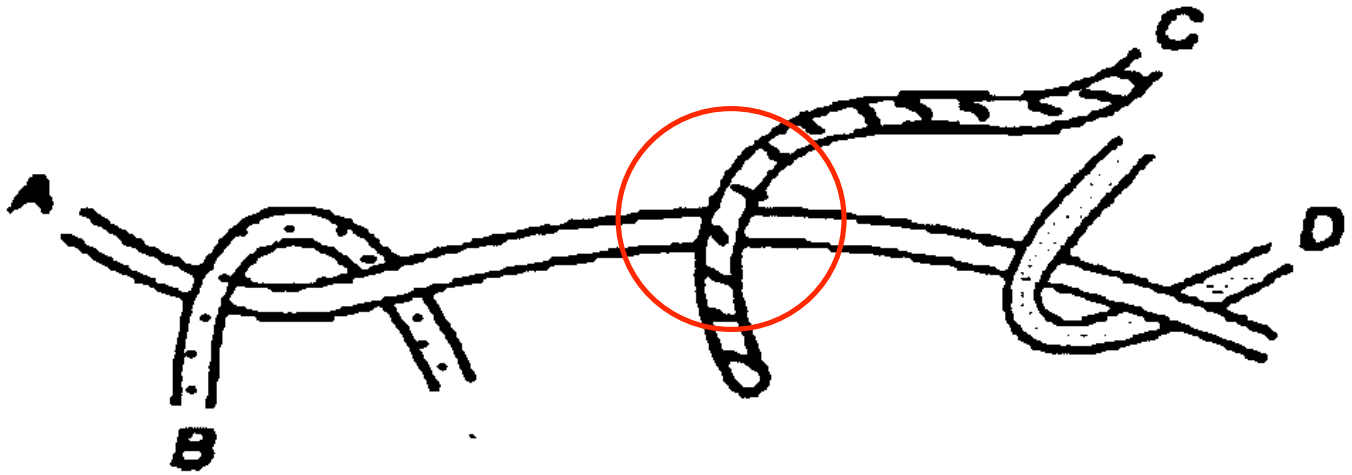


courtesy: IRC Leeds

Arm Retraction

courtesy: IRC Leeds

Third Mode: Constraint Release



A = test chain
B, C, D = matrix chains

Equations for Monodisperse Stars

Early-time fluctuations

$$\tau_{early}(\xi) = \frac{9}{16}\pi^3 \tau_e S_a{}^4 \xi^4$$

Retraction Potential

$$U(\xi) = \nu S_a \xi^2$$

Dynamic Dilution

$$U_{eff}(\xi) = 2\nu S_a \frac{1-(1-\xi)^{1+\alpha}[1+(1+\alpha)\xi]}{(1+\alpha)(2+\alpha)}$$

Late-time retraction

$$\tau_{late}(\xi) = \tau_e S_a^{3/2}\left(\frac{\pi^5}{6}\right)^{1/2} \frac{\exp[U_{eff}(\xi)]}{\left[\xi^2(1-\xi)^{2\alpha} + \left(\frac{1+\alpha}{3S_a}\right)^{2\alpha/(\alpha+1)} \Gamma\left(\frac{1}{\alpha+1}\right)^{-2}\right]^{1/2}}$$

$$\nu = 3/2 \qquad S_a = M_a / M_e$$

$$\alpha = \text{"}dilution\ exponent\text{"}$$

$$M_e = \frac{4}{5}\frac{\rho RT}{G_N^0} \qquad \tau_e = \frac{\zeta (M_e/M_0)^2 b^2}{3\pi^2 k_B T}$$

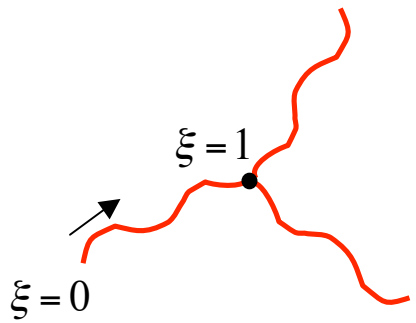
$$M_e(\phi) = M_e / \phi^\alpha$$

Crossover equation

$$\tau_a(\xi) = \frac{\tau_{early}(\xi)\exp[U_{eff}(\xi)]}{1+\tau_{early}(\xi)\exp[U_{eff}(\xi)]/\tau_{late}(\xi)}$$

Complex modulus

$$G^*(\omega)/G_N^0 = (1+\alpha)\int_0^1 d\xi (1-\xi)^\alpha \left[\frac{i\omega\tau(\xi)}{1+i\omega\tau(\xi)}\right]$$



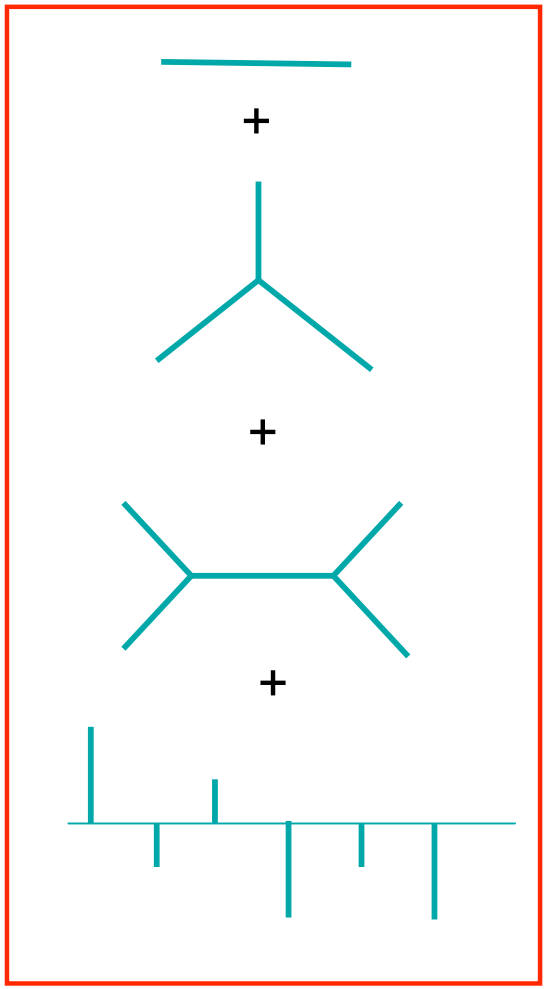
Ball and McLeish, *Macromolecules*, **1989**

Milner and McLeish, *Macromolecules*, **1997**

Milner and McLeish, *Macromolecules*, **1998**

Theories for Branched Polymers

- Star polymer
  - *Milner and McLeish, Macromolecules (1997)*
- Linear polymer
  - *Milner and McLeish, Phys Rev Lett (1998)*
- Star/linear blend
  - *Milner et al., Macromolecules (1998)*
- H polymer
  - *McLeish et al., Macromolecules (1999)*
- Comb polymer
  - *Daniels et al., Macromolecules (2001)*
- Mixture of general branched polymers
  - *Larson, Macromolecules (2001): hierarchical model*

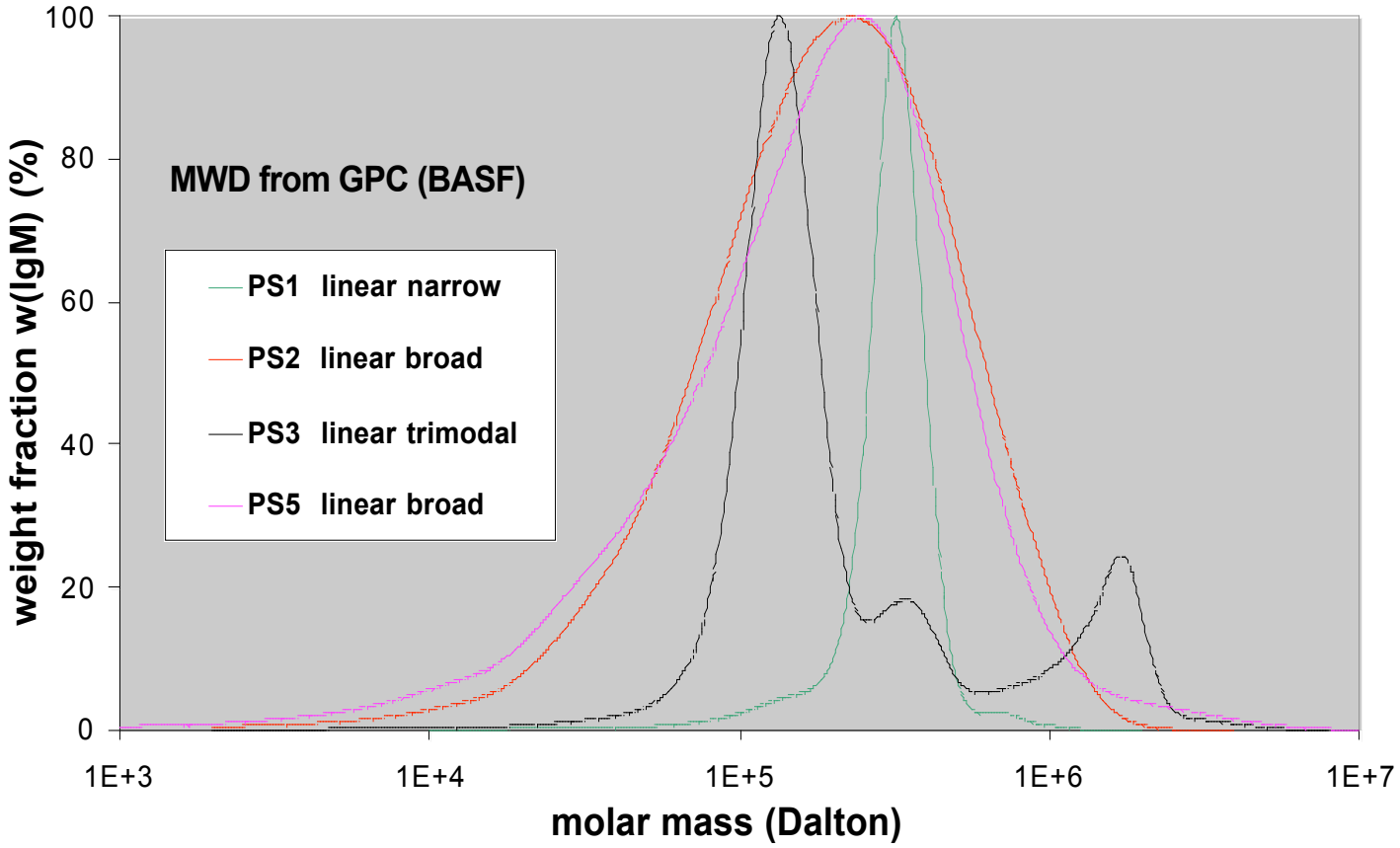


Park, Shanbhag, Larson, *Rheol. Acta.*, **2005**
Larson, *Macromolecules*, **2001**

Successes of the Tube Theory: Preview

Laun/Schmidt Benchmark Experiment

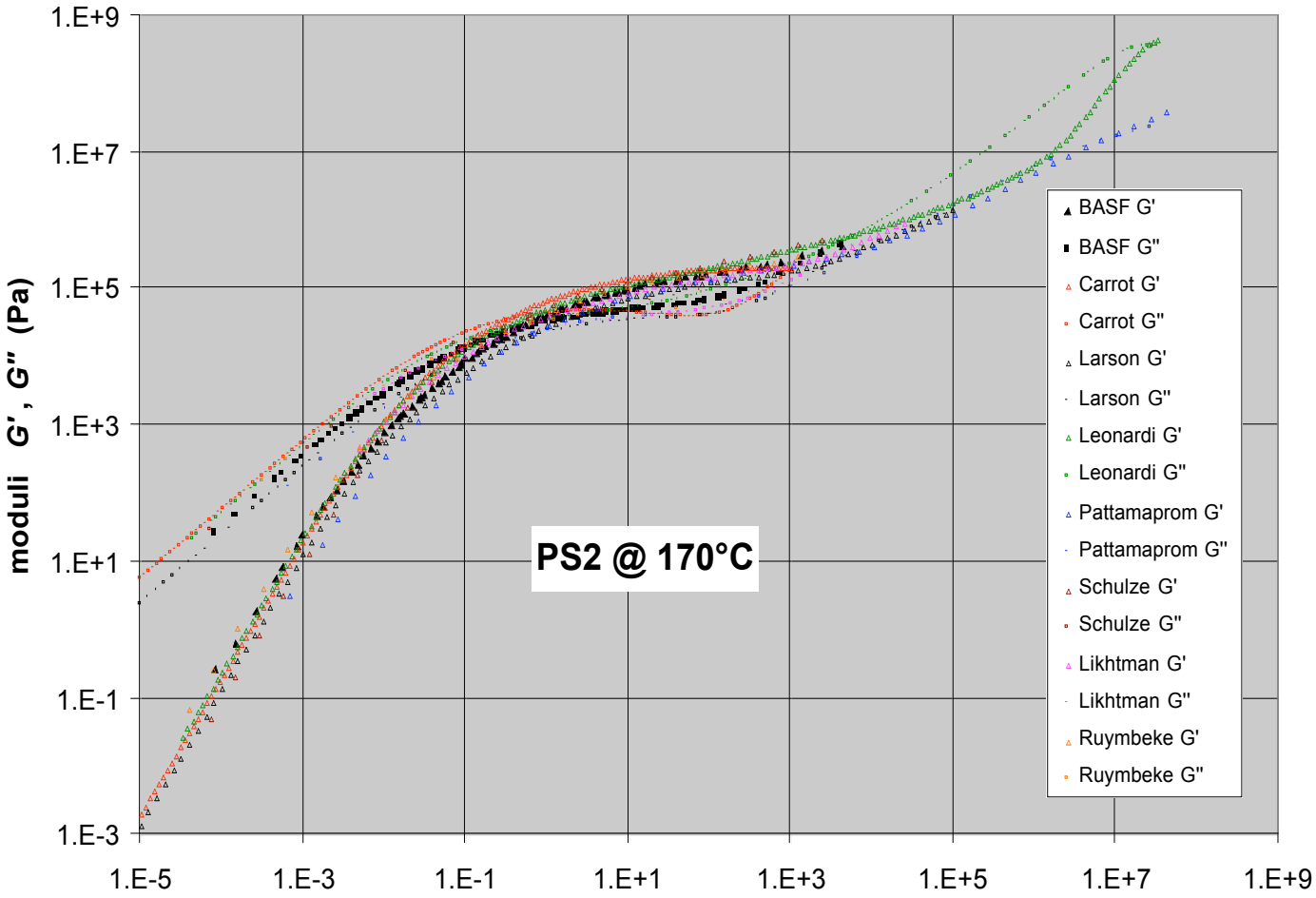
Analytical Rheology of Commercial Linear Polymers



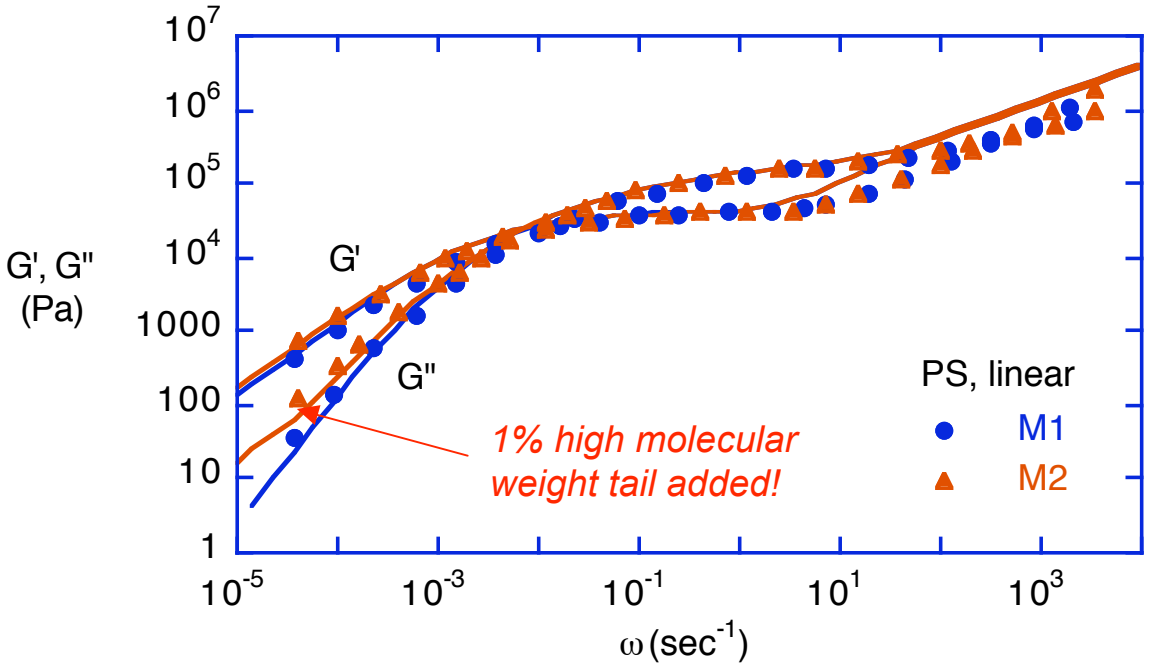
Polystyrene samples from Dr. Christian Schade, BASF

Successes of the Tube Theory: Preview

Overview on moduli predictions for PS2



Successes of the Tube Theory



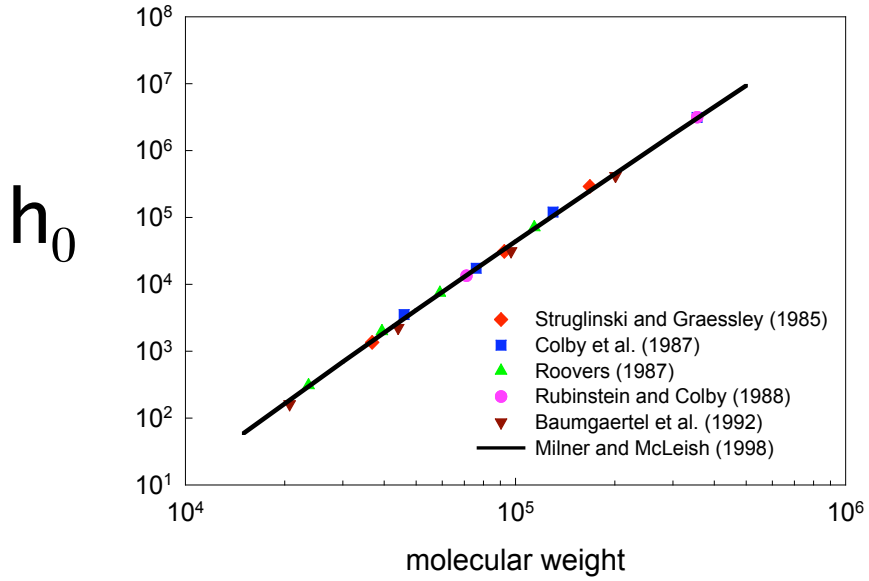
Polydisperse polystyrene, Graessley and coworkers

(lines theory of Pattamaprom, et al.)

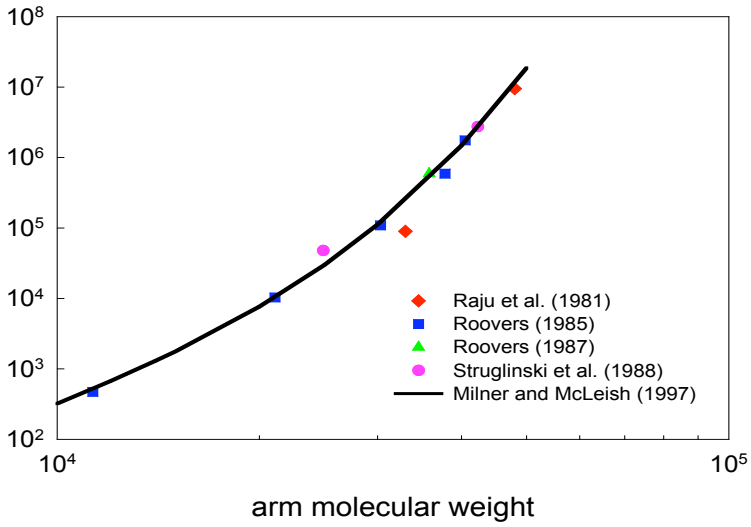
Determination of Model Parameters (1,4-PBd)

G_N=1.15E+6 (Pa), M_e=1650, τ_e=3.7E-7 (sec)

zero-shear viscosity of linear 1,4-polybutadiene at T=25 °C



zero-shear viscosity of star 1,4-polybutadiene at T=25 °C



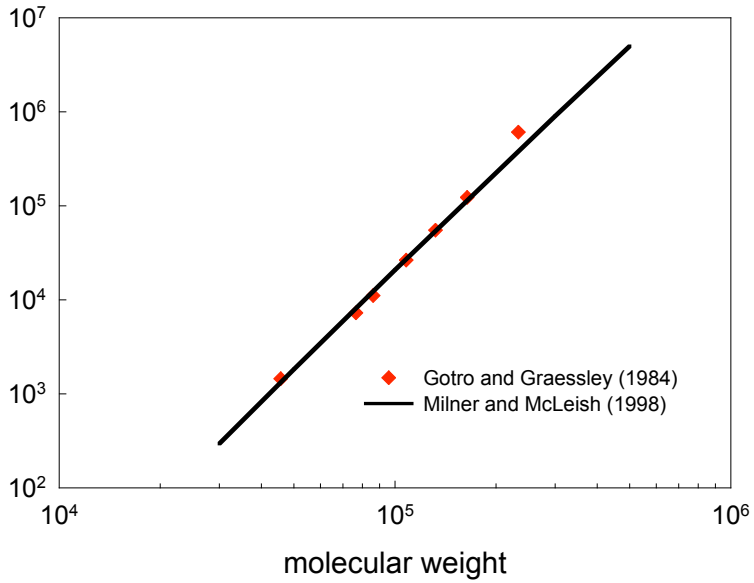
a = 4/3

Park, Shanbhag, Larson, *Rheol. Acta.*, **2005**

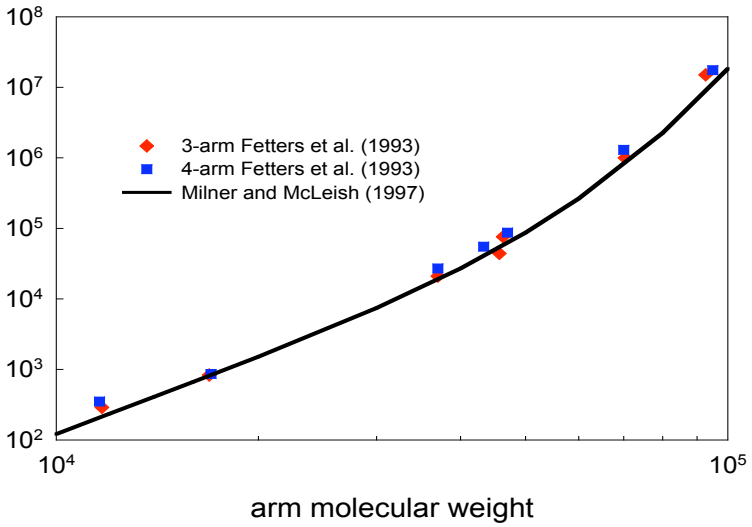
Determination of Model Parameters (PI)

G_N=0.44E+6 (Pa), M_e=4054, τ_e=1.0E-5 (sec)

zero-shear viscosity of linear 1,4-polyisoprene at T=25 °C



zero-shear viscosity of star 1,4-polyisoprene at T=25 °C



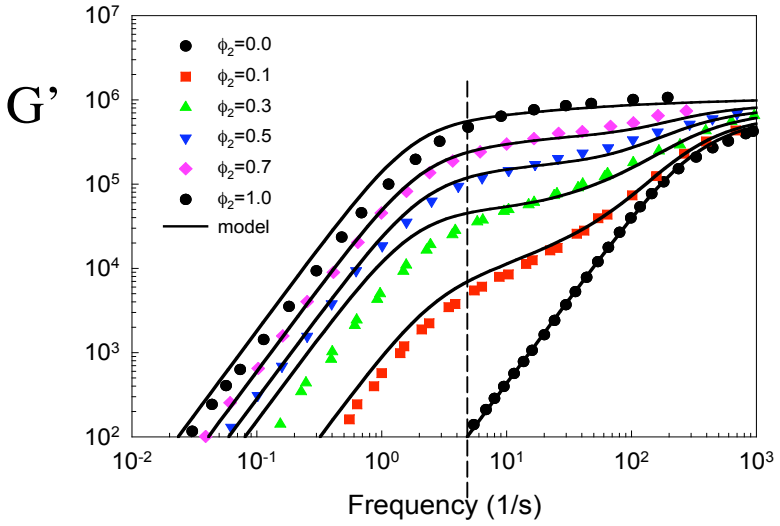
a = 4/3

Park, Shanbhag, Larson, *Rheol. Acta.*, **2005**

Hierarchical Model Prediction

Constraint release is by CR-Rouse motion

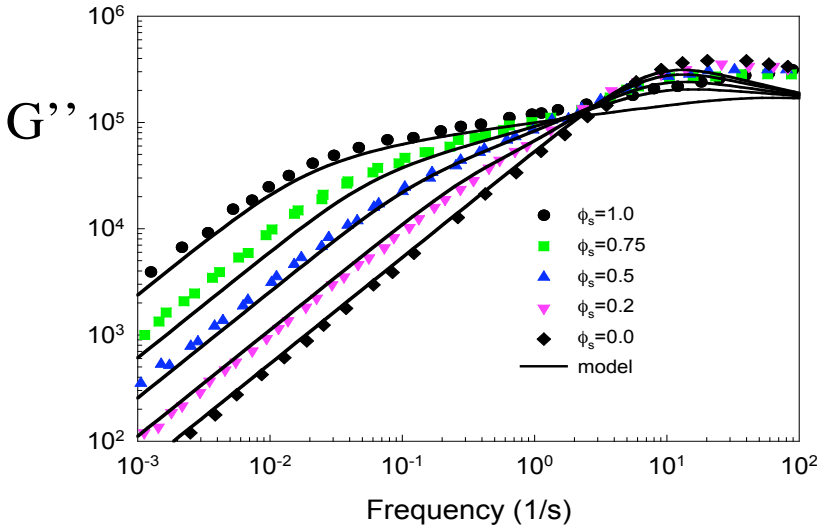
PBd linear (M_1=37K)/linear (M_2=168K) blend at T=25°C



$$Gr = M_2 M_e^2 / M_1^3 = 0.01 < Gr_c = 0.064$$

Struglinski et al., *Macromolecules,* **1985**

PBd 3-arm star (M=127K)/linear (M=100K) blend at T=25°C



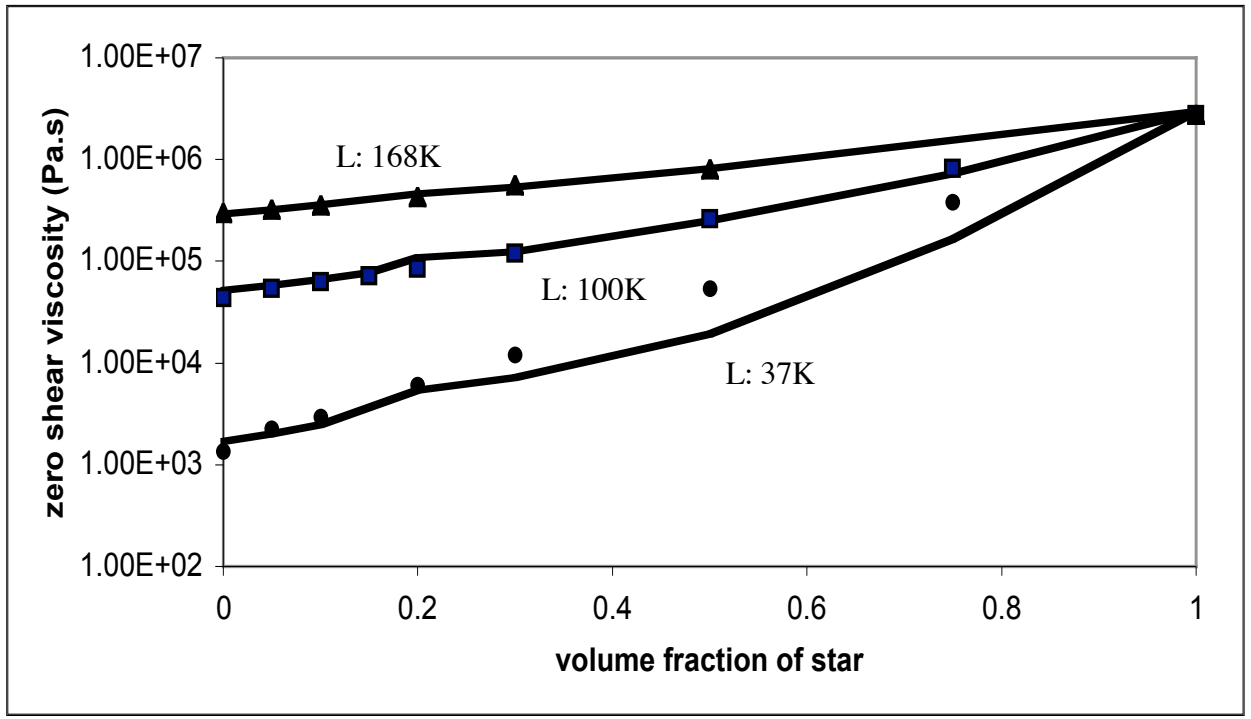
Struglinski et al., *Macromolecules,* **1988**

Park, Shanbhag, Larson, *Rheol. Acta.*, **2005**

Star/Linear Blends

PBd 3-arm star (127K) - linear blends at T=25 ^{0}C

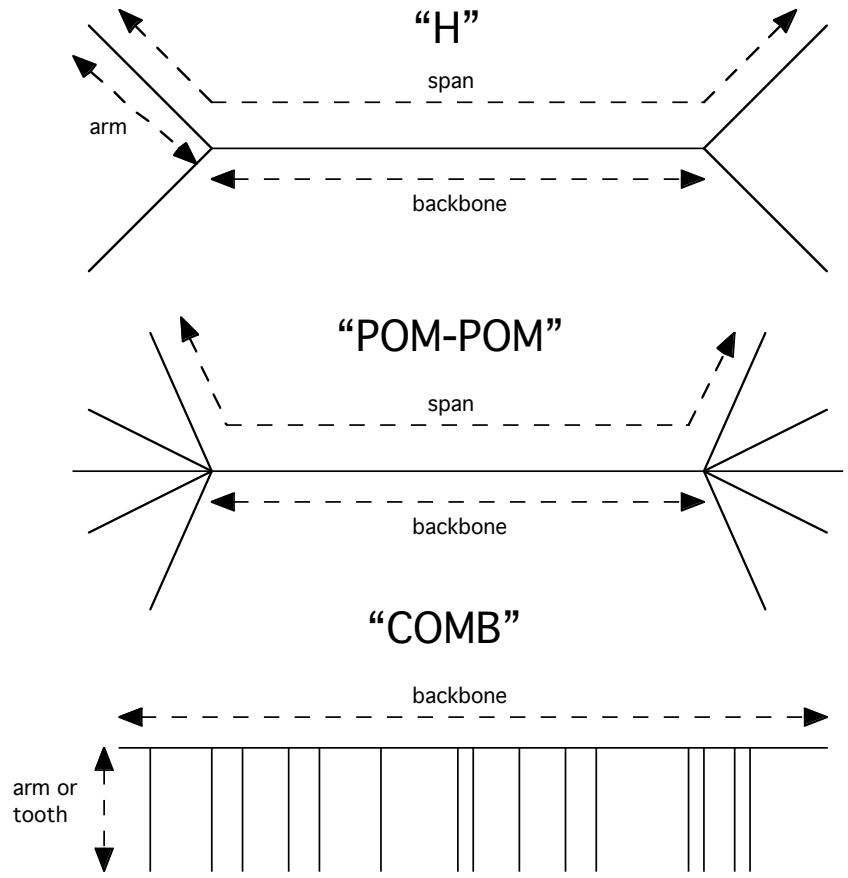
h_0



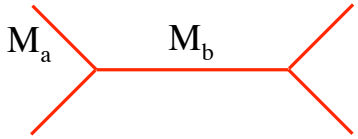
Struglinski et al., *Macromolecules,* **1988**

Multiple Side Branches

Relaxation of backbone requires motion of branch points

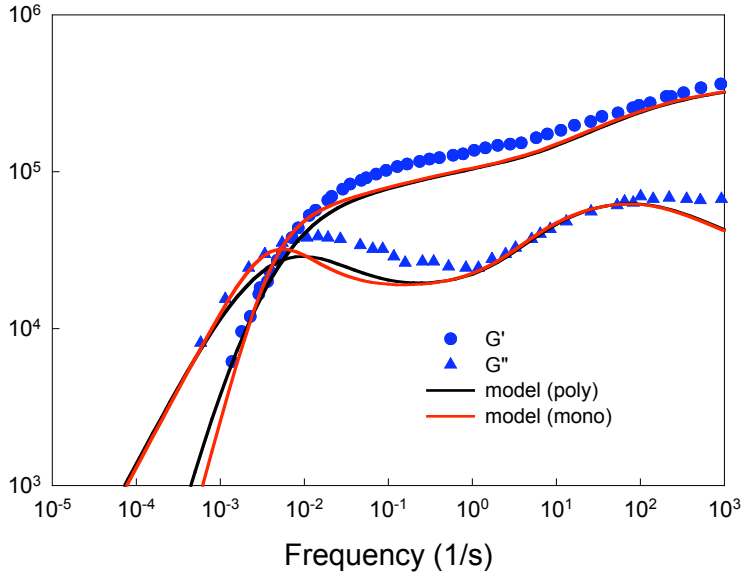


Hierarchical Model Prediction

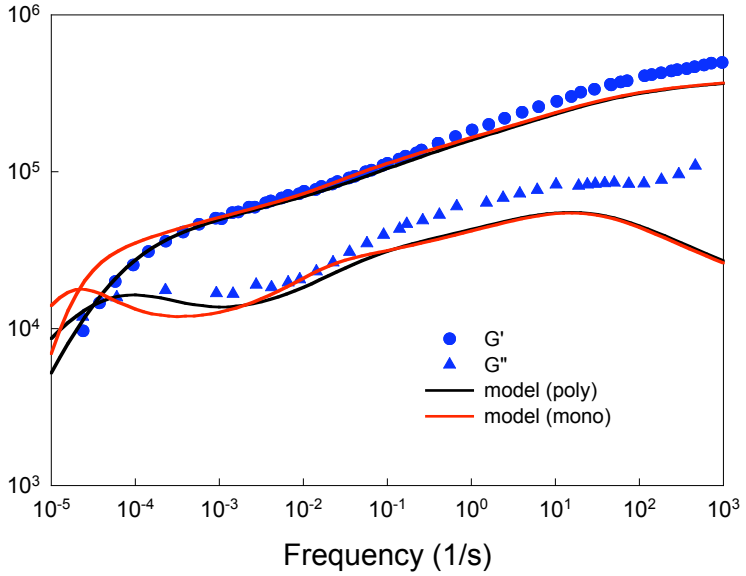


PI H polymer at T=25 °C

Ma=20000, Mb=110000
PI_a=1.01, PI_b=1.13



Ma=40000, Mb=164000
PI_a=1.05, PI_b=1.30



We take $D_{br} = p^2a^2/2qt_a$, with $p^2 = 1/12$

Park, Shanbhag, Larson, *Rheol. Acta.*, **2005**

McLeish et al., *Macromolecules,* **1999**

Commercial Single-Site Metallocenes

Reaction kinetics of LCB PE using single-site catalyst

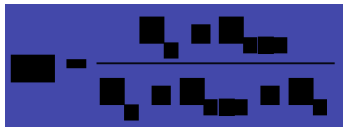
monomer addition

addition of unsaturated chain

generation of dead saturated chain

β-hydride elimination

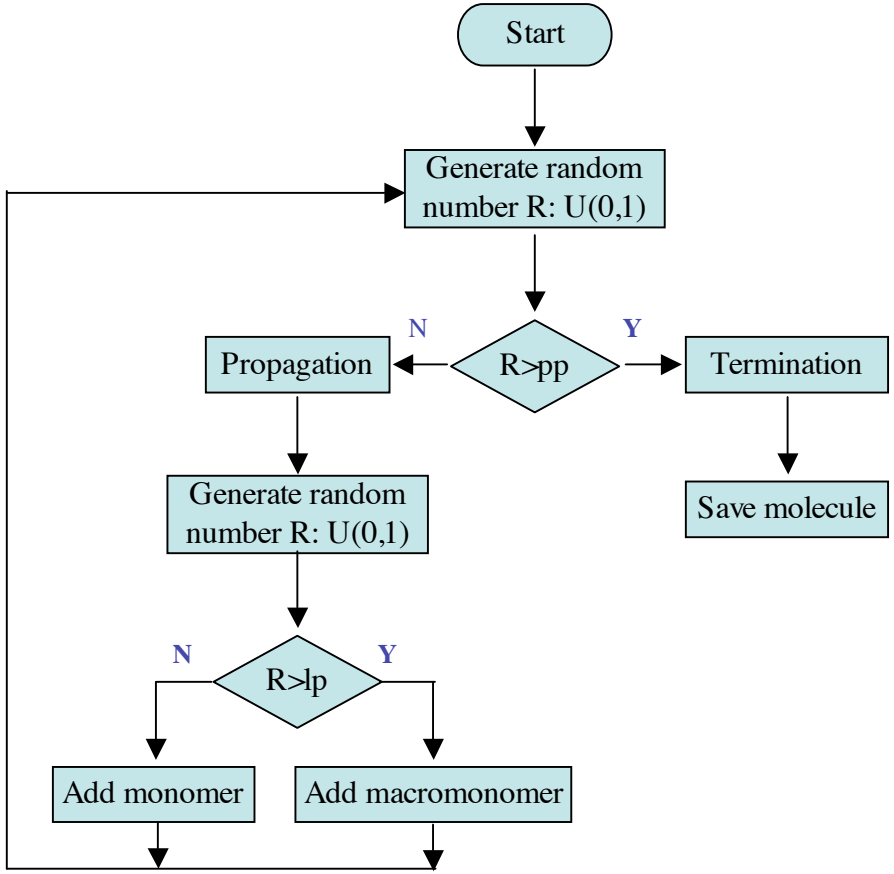
Monte Carlo probabilities



propagation probability

monomer selection probability

Algorithm for Monte Carlo simulation of LCB PE using single-site catalyst



Costeux et al., *Macromolecules,* **2002**

Lightly-branched metallocene-catalyzed HDPEs

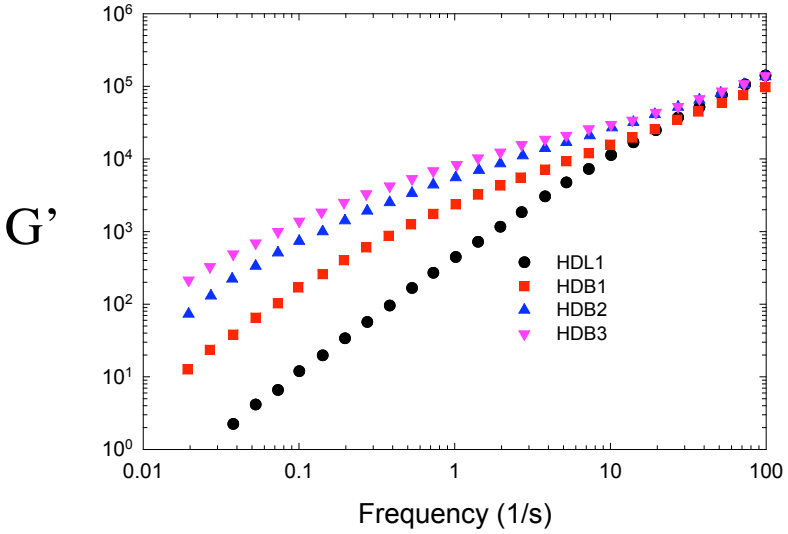
resin	Mw	Mn	λ (=LCB/1000C)	β	pp	lp
HDL1	93000	44700	0	0	0.999398	1
HDB1	77000	38900	0.026	0.067	0.999172	0.999948
HDB2	82000	42590	0.037	0.099	0.999179	0.999926
HDB3	86000	43200	0.042	0.116	0.999192	0.999916

λ: average branch point density per 1000C

$$\lambda = \frac{14\times10^3(2\beta)(\beta+1)}{M_w} = \frac{10^3}{2}pp(1-lp)$$

β: average number of branches per molecule

$$\beta \equiv \frac{M_n\lambda}{14\times10^3} = \frac{pp(1-lp)}{1-2\,pp+pp\times lp}$$



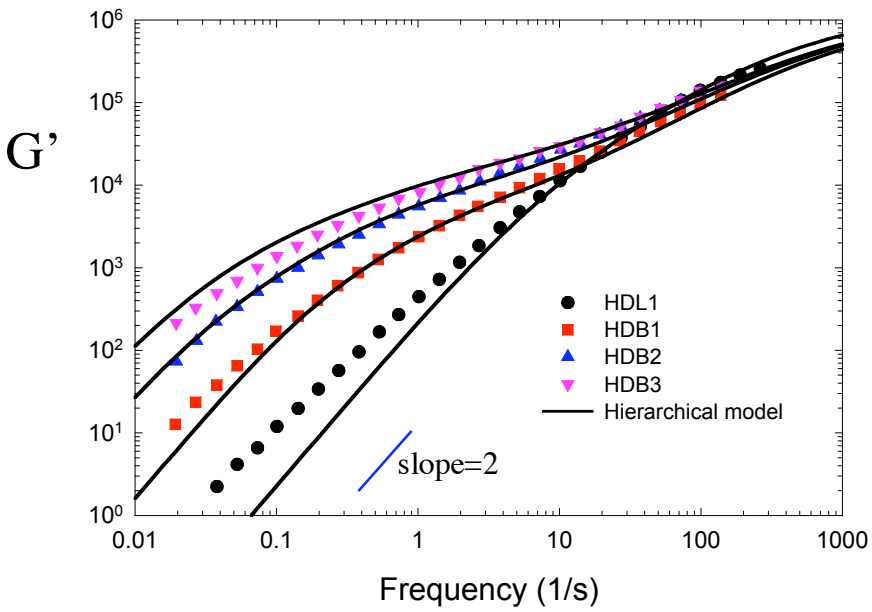
LCB mHDPE is a mixture of linear, star, H-polymers, combs, and hyper-branched structures

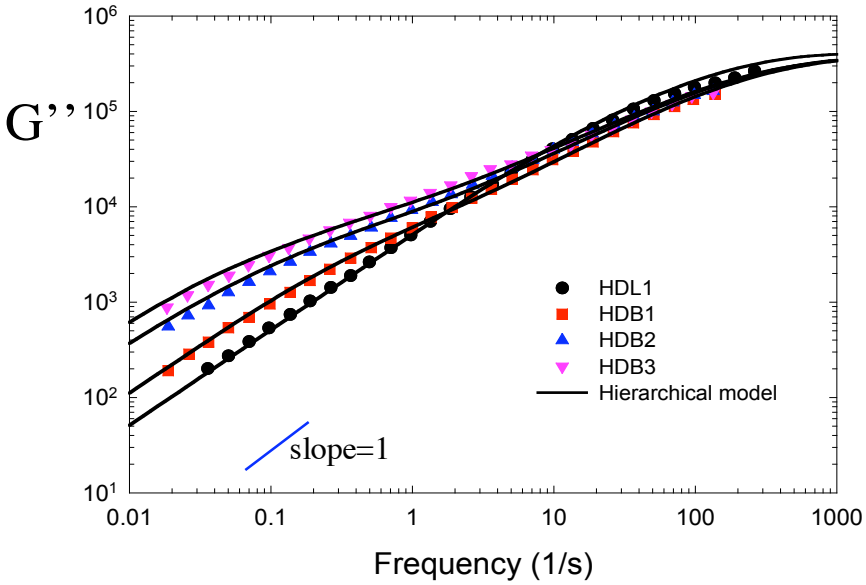
Data from Wood-Adams et al., *Macromolecules,* **2002**

Hierarchical Model Prediction

Metallocene-catalyzed polyethylene

G_N=2.0E+6 (Pa), M_e=1150, τ_e=4.0E-9 (s) at T=150 ^{0}C





10,000 chains in the ensemble

Wood-Adams et al., *Macromolecules,* **2002**

Park and Larson, *J. Rheol.*, **2005**

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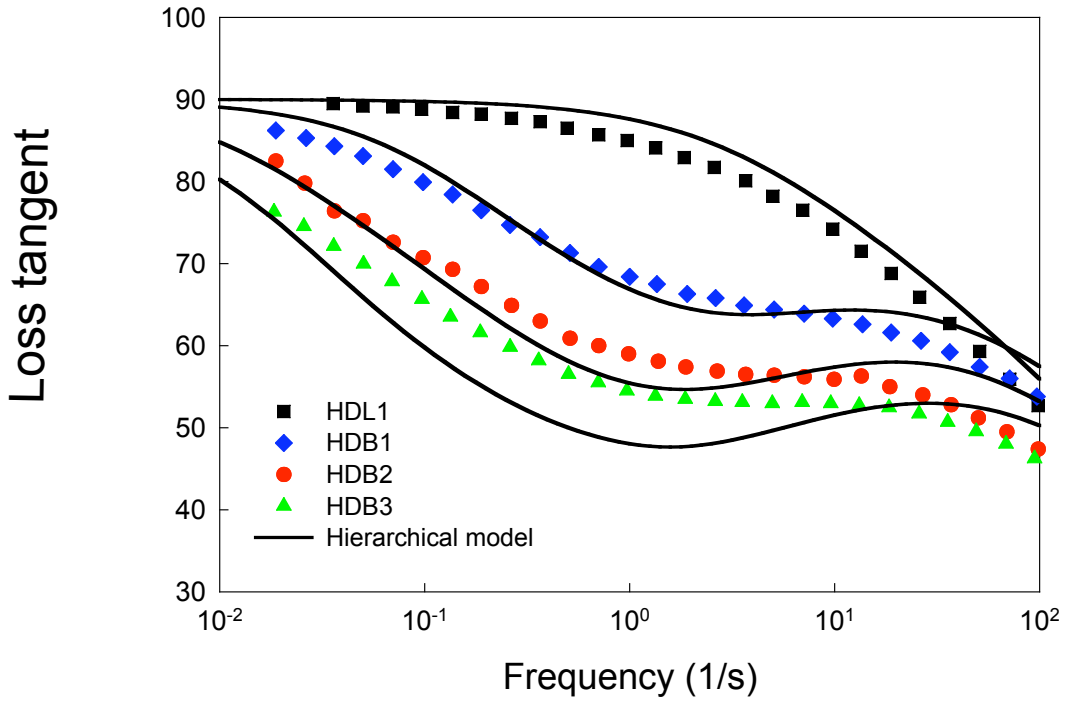
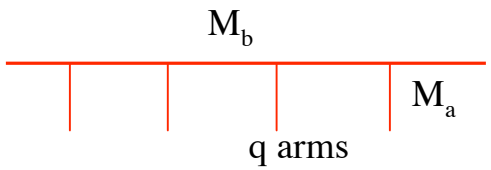


Wood-Adams et al., *Macromolecules,* **2002**

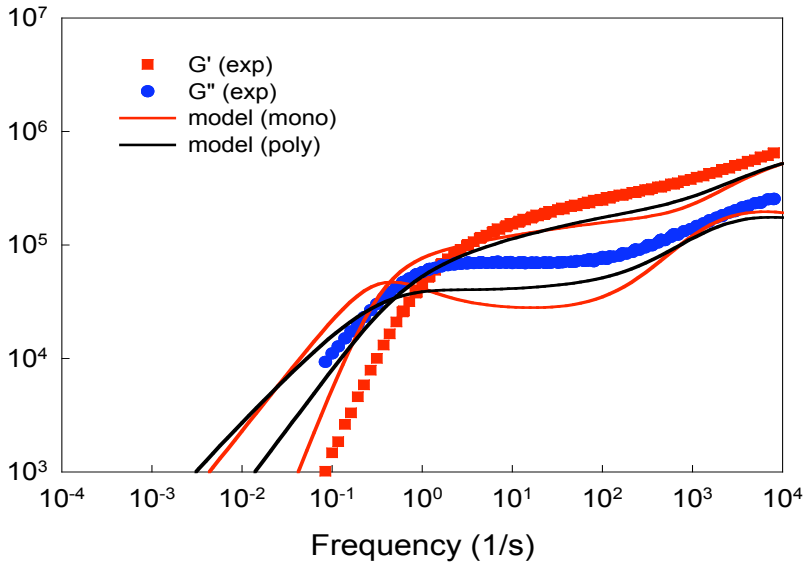
Park and Larson, *J. Rheol.*, **2005**

Hierarchical Model Prediction

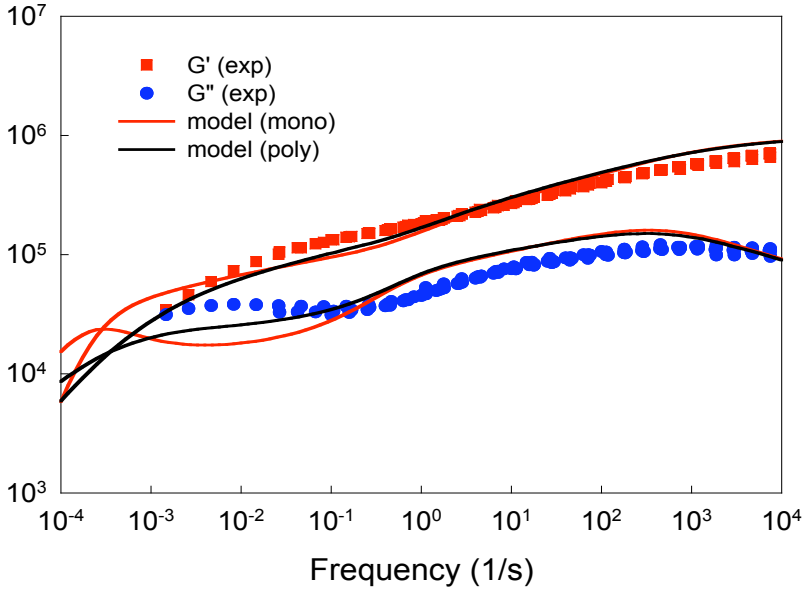


PBd comb polymer 25 °C

M_a=5.8K, M_b=62.7K, q=8,
PI_a=1.03, PI_b=1.03



M_a=17.7K, M_b=124.6K, q=5,
PI_a=1.01, PI_b=1.06



Daniels et al., *Macromolecules,* **2001**

Park, Shanbhag, Larson, *Rheol. Acta*, **2005**

For calculations with polydispersity, to obtain an ensemble of chains, polydisperse arms are randomly attached to polydisperse backbones via a Poisson process.

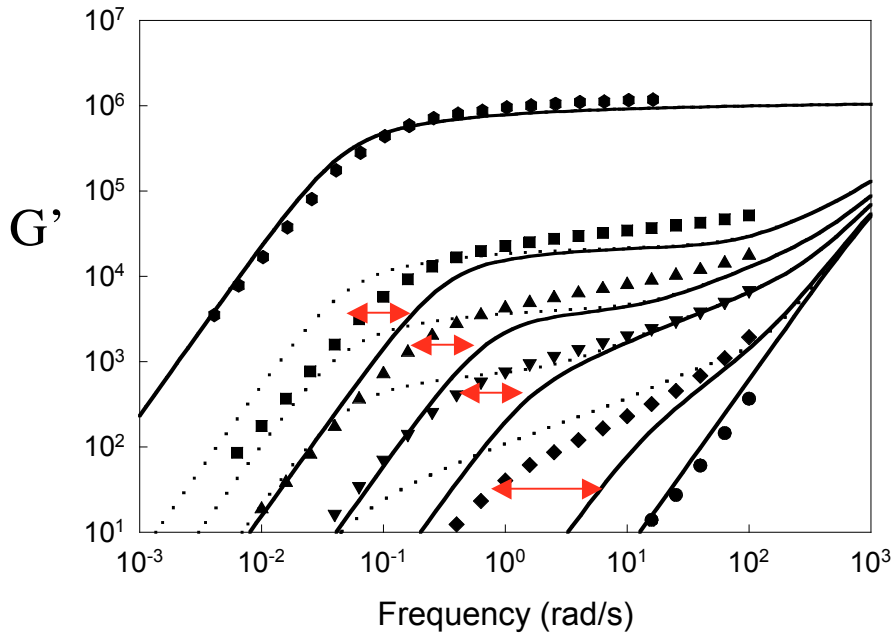
Test of Dynamic Dilution

Linear-Linear Binary Blend with Large Molecular Weight Ratio

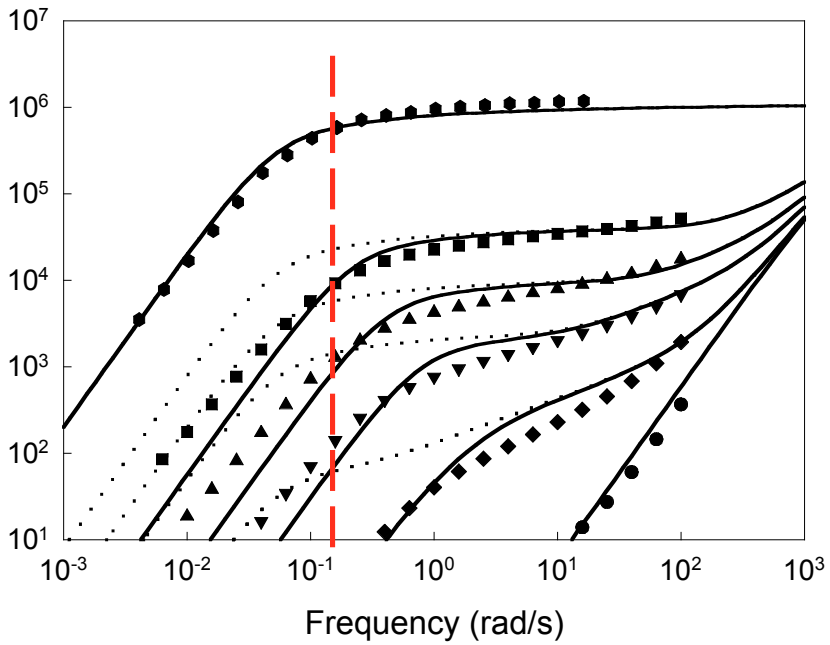
Blend of monodisperse 1,4 PBd: 20k/550k

$Gr = M_2 M_e^2 / M_1^3 = 0.16 > Gr_c = 0.064$

a = 4/3



a = 1



Solid lines: reptation in fat tube

Limitations of the Tube Theory

Issues for Tube Theory with LCB

- *Dynamic Tube Dilution*
- *Branch Point Motion*
- *Fluctuation Potential*
- *Nature of entanglement network, dilution exponent*

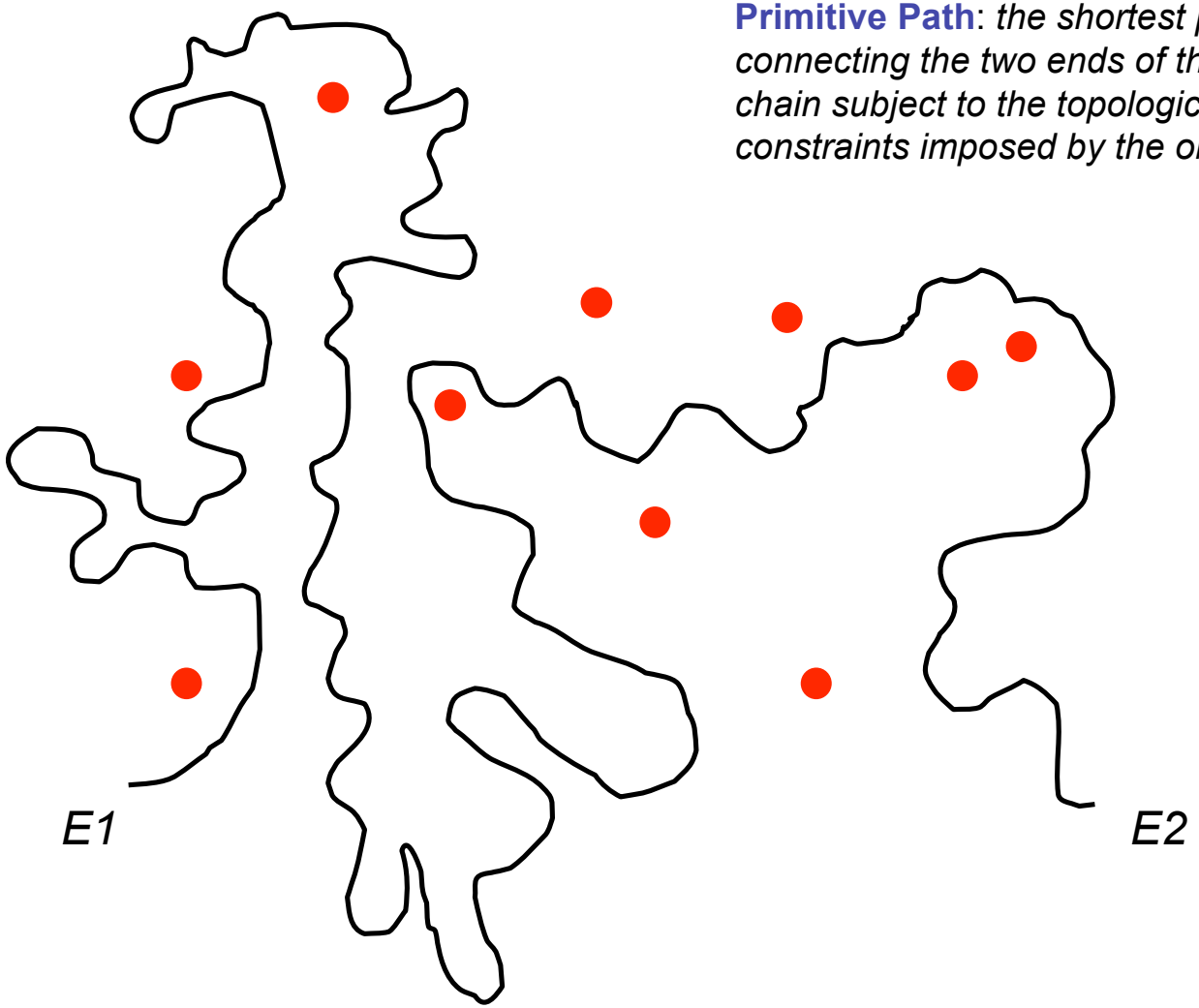
Need insights from more detailed models

- *Slip-Link Model*
  Entanglement
- *Bond-Fluctutation Model*
  "Monomer"

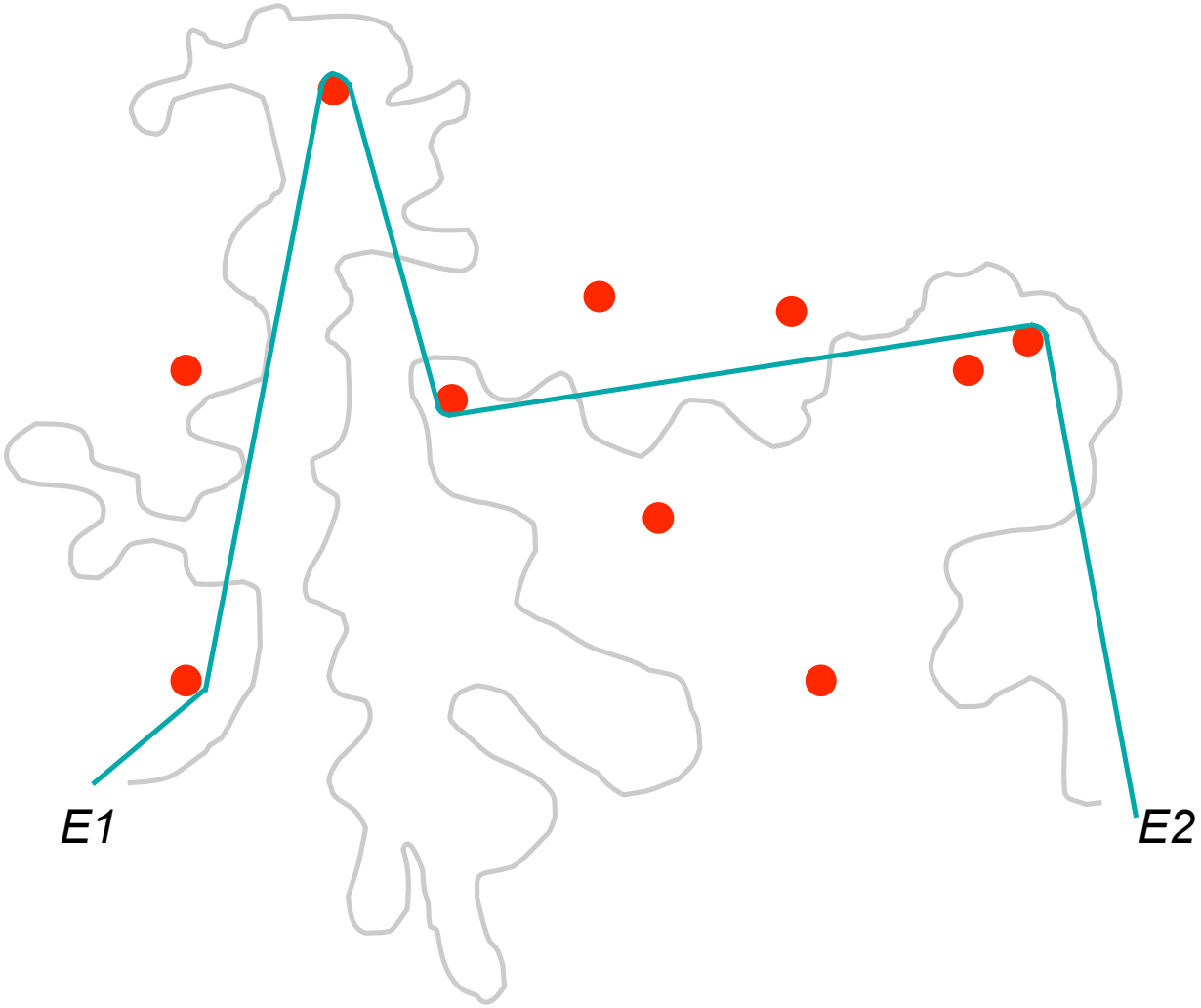
Shanbhag et al., *PRL*, **2001**
Shanbhag and Larson, *Macromolecules*, **2004**
Shanbhag and Larson, *PRL*, **2005**
Shanbhag and Larson, *Macromolecules*, **2006**

Primitive Path

Primitive Path: *the shortest path connecting the two ends of the polymer chain subject to the topological constraints imposed by the obstacles*

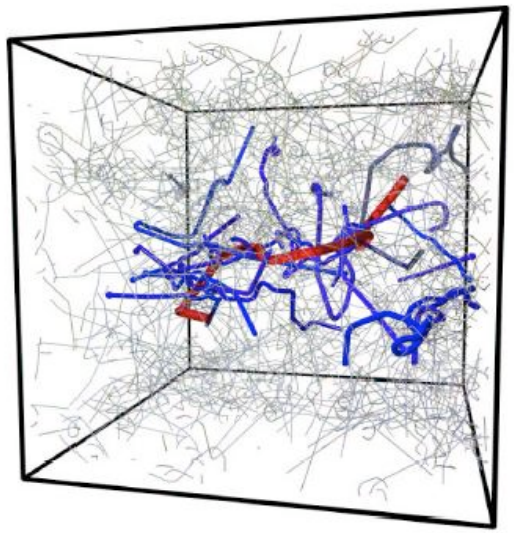


Primitive Path



Length of the primitive path is shorter from the length of the polymer chain

Primitive Path in a Melt

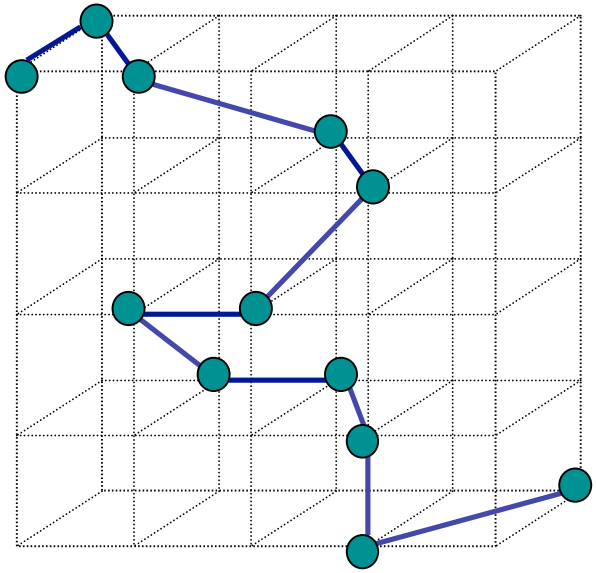


- Polymer chains themselves form obstacles for other chains
- Obstacles are not “fixed”
- Outstanding problem in polymer physics, until recently (?)

Everaers et al., *Science*, **2004**

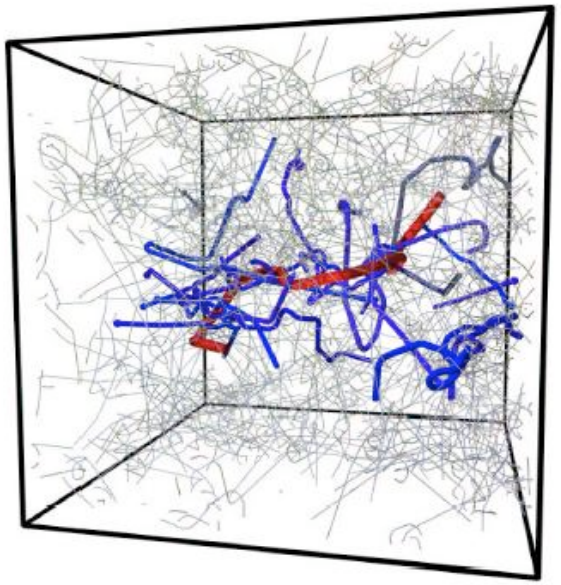
Primitive Path in a Melt

Bond Fluctuation Model



Efficient equilibration of chains

Primitive Path



Extract the primitive paths

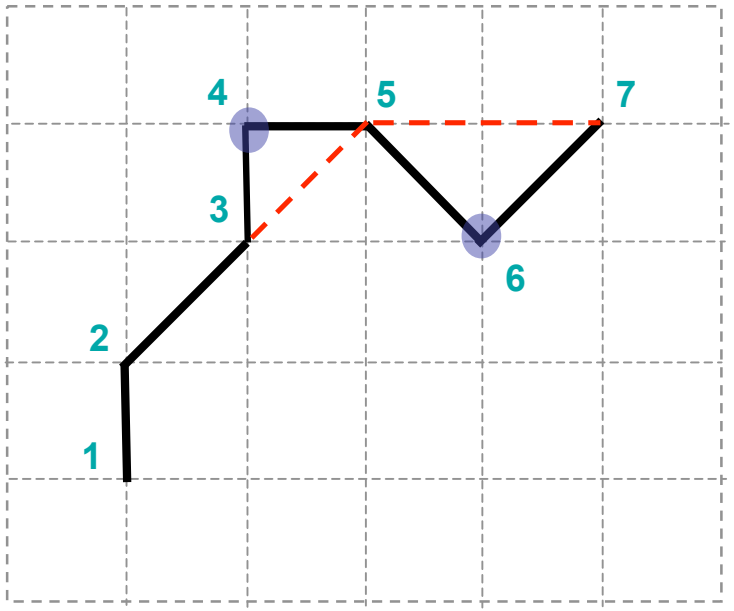
Shanbhag and Larson, *PRL*, **2005**

Shaffer, *J. Chem Phys.*, **1994**

Everaers et al., *Science*, **2004**

Locating Entanglement Points

How do I spatially locate entanglements on a primitive path?

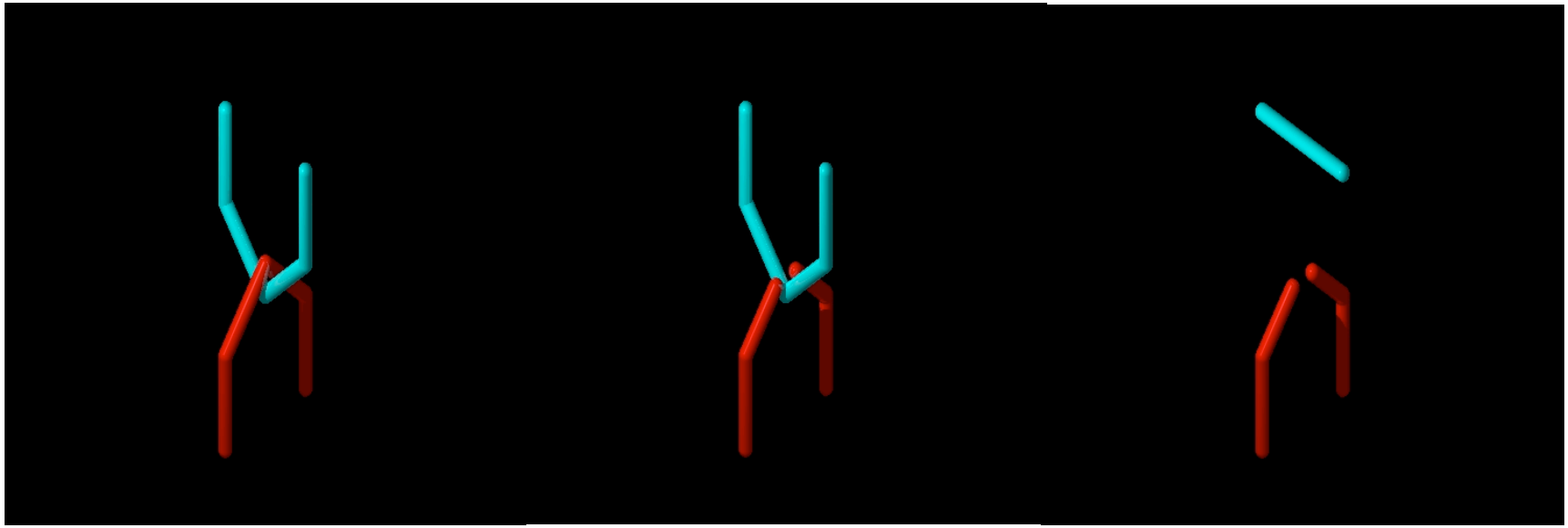


Z = 2 entanglements

Shanbhag and Larson, *Macromolecules*, **2006**

Nature of Coupling

"if an entanglement is released, how many additional entanglements are lost as a consequence?"



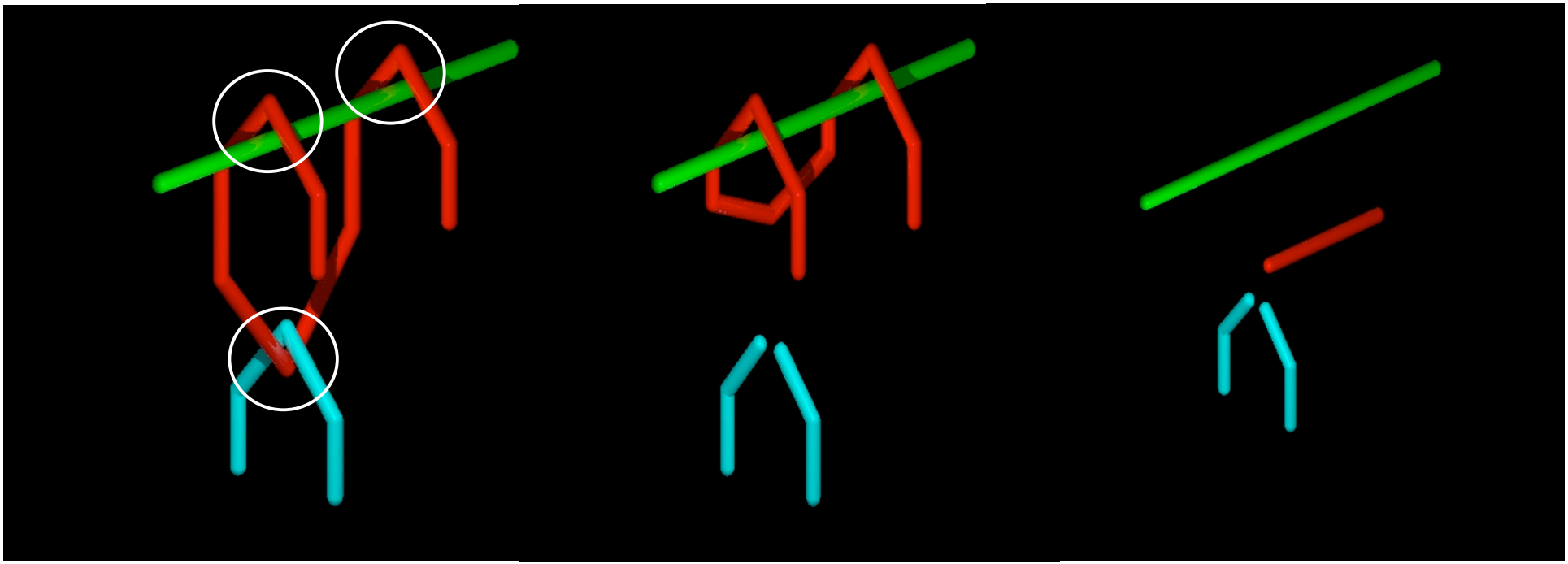
"binary coupling"*

related to dilution exponent $\alpha = \langle Z_{lost}/Z_{del} \rangle$

α*=1 for binary coupling*

*assumed in slip link models

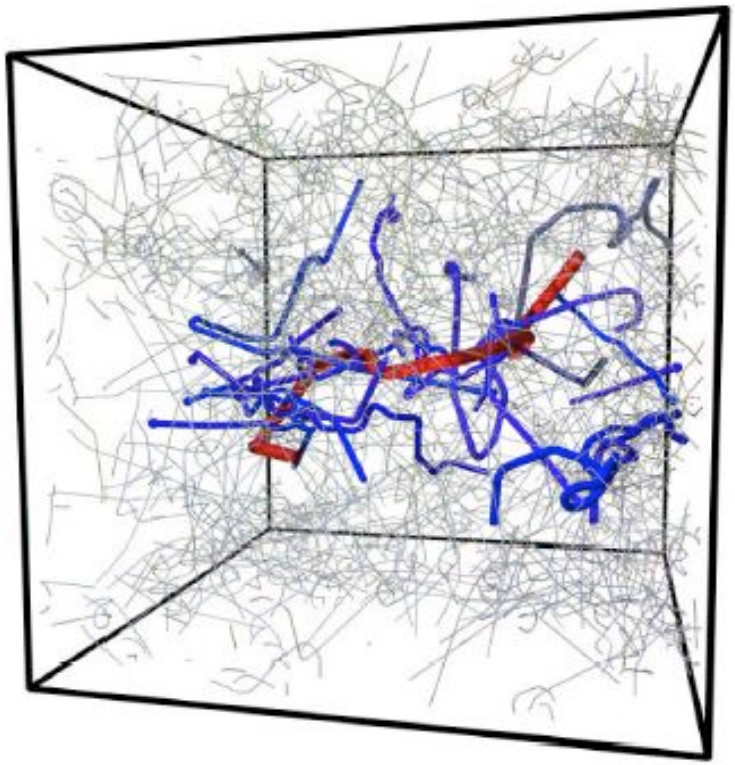
Nature of Coupling



completely unravels

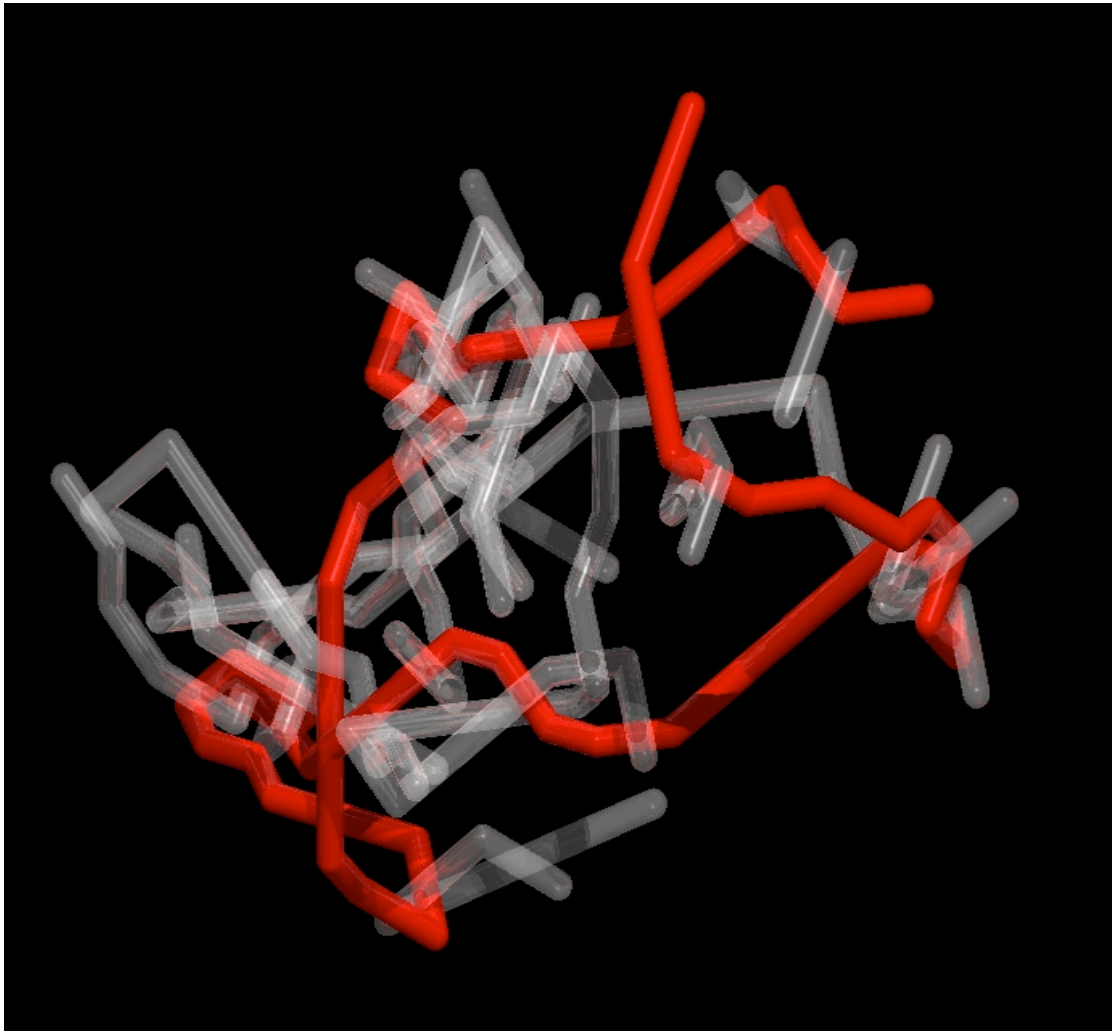
"1 entanglement releases 3 entanglements"

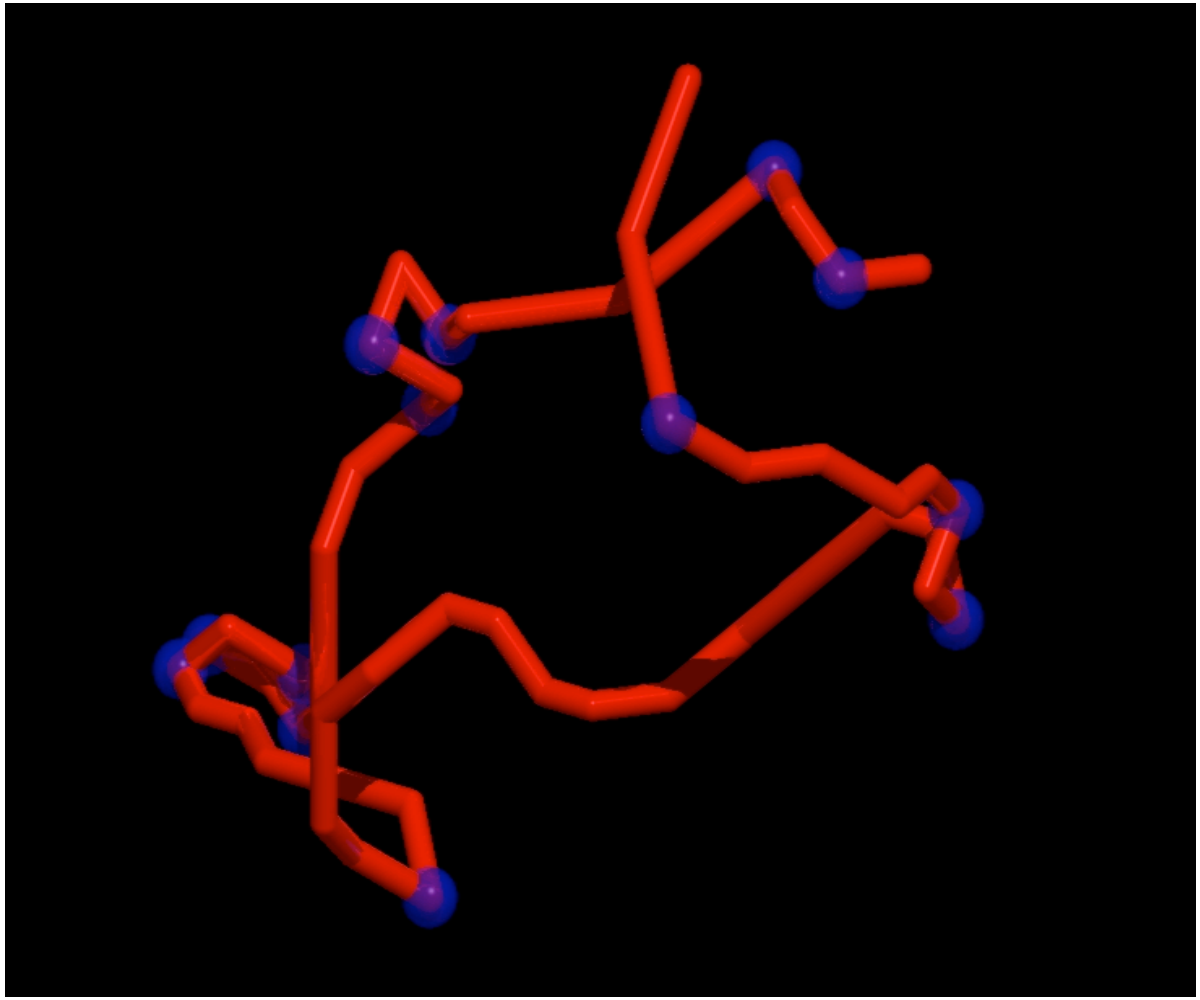
Nature of Coupling

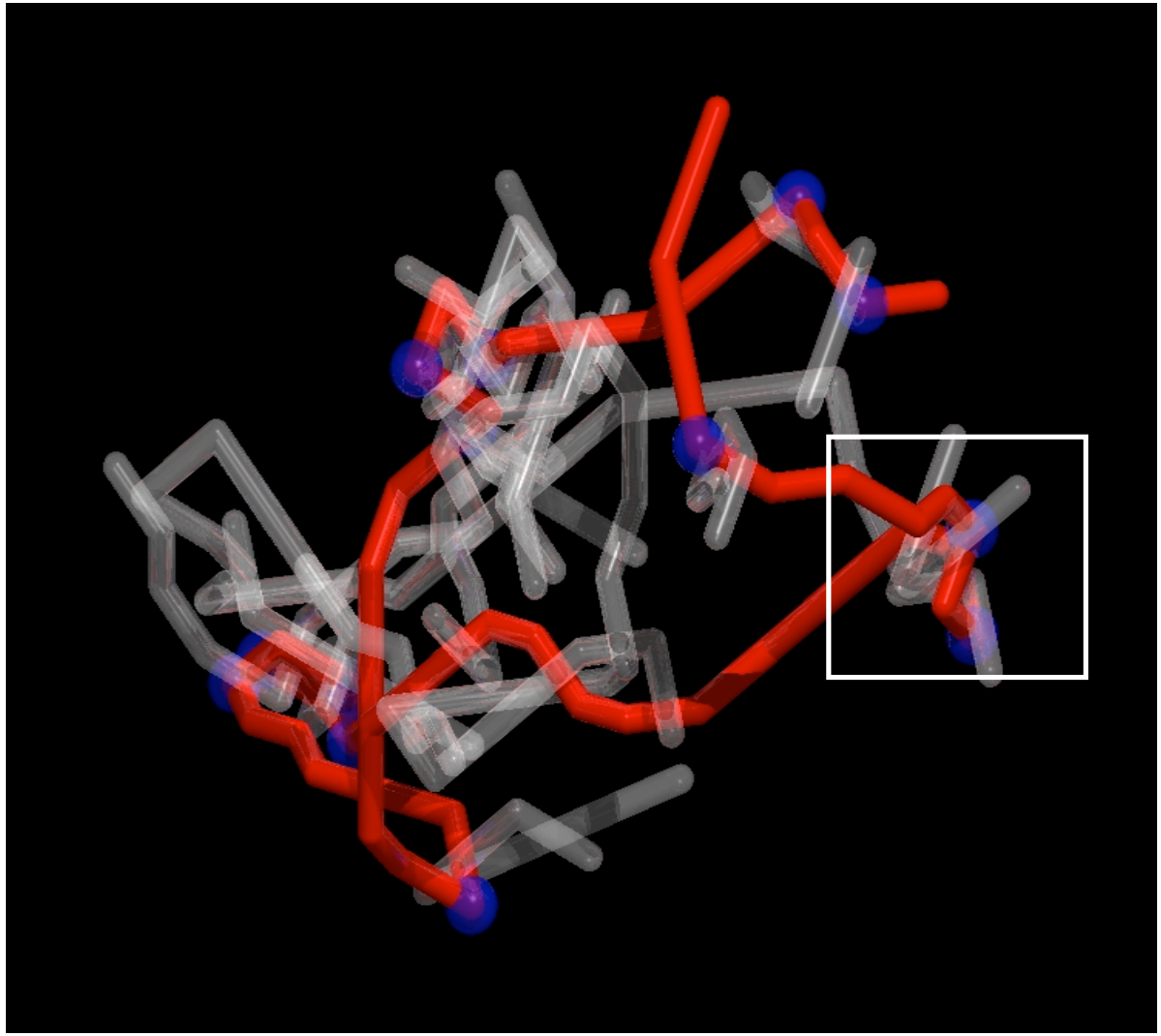


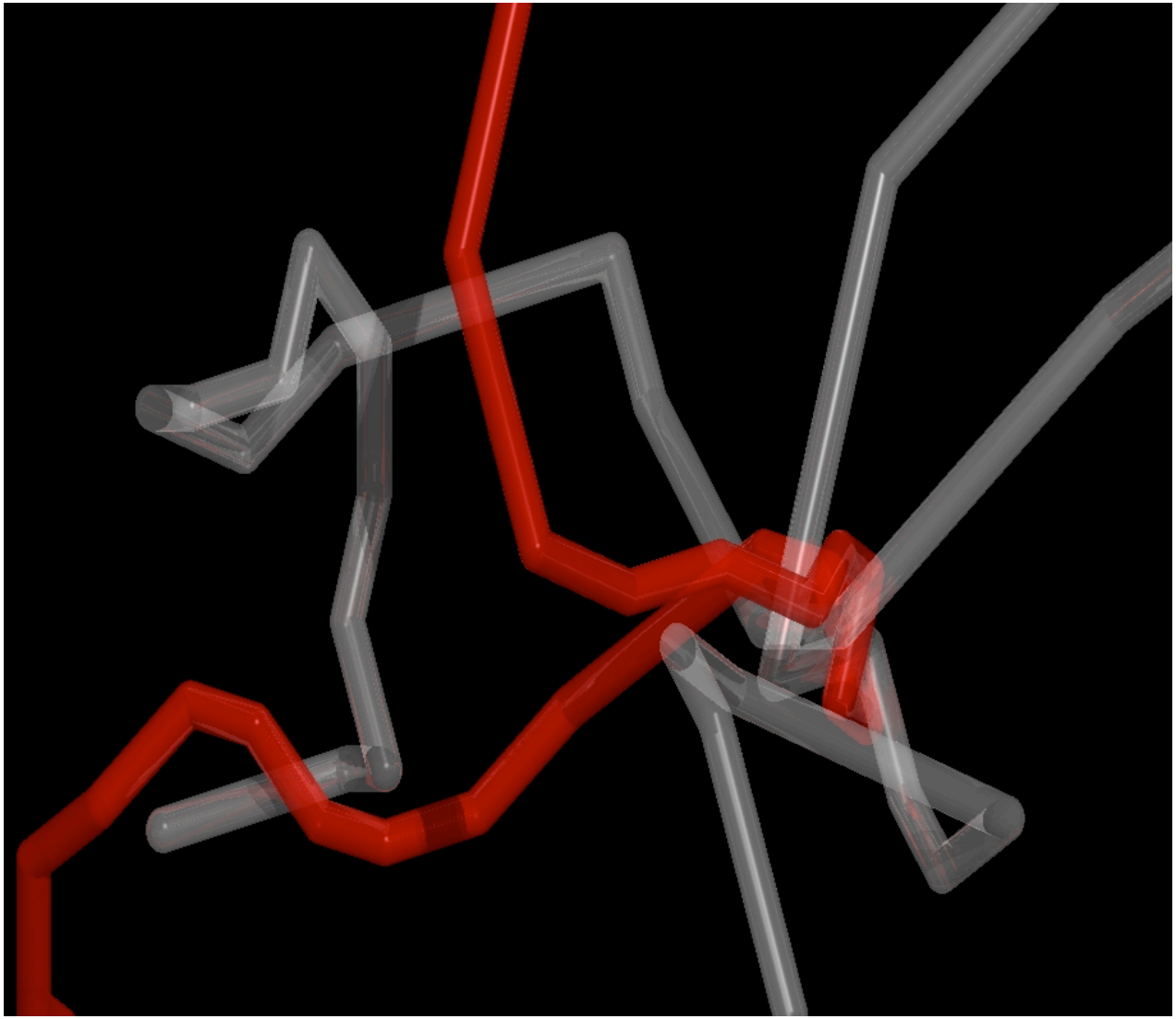
N=300, N_p~300
L_{box}=65, Φ=0.5

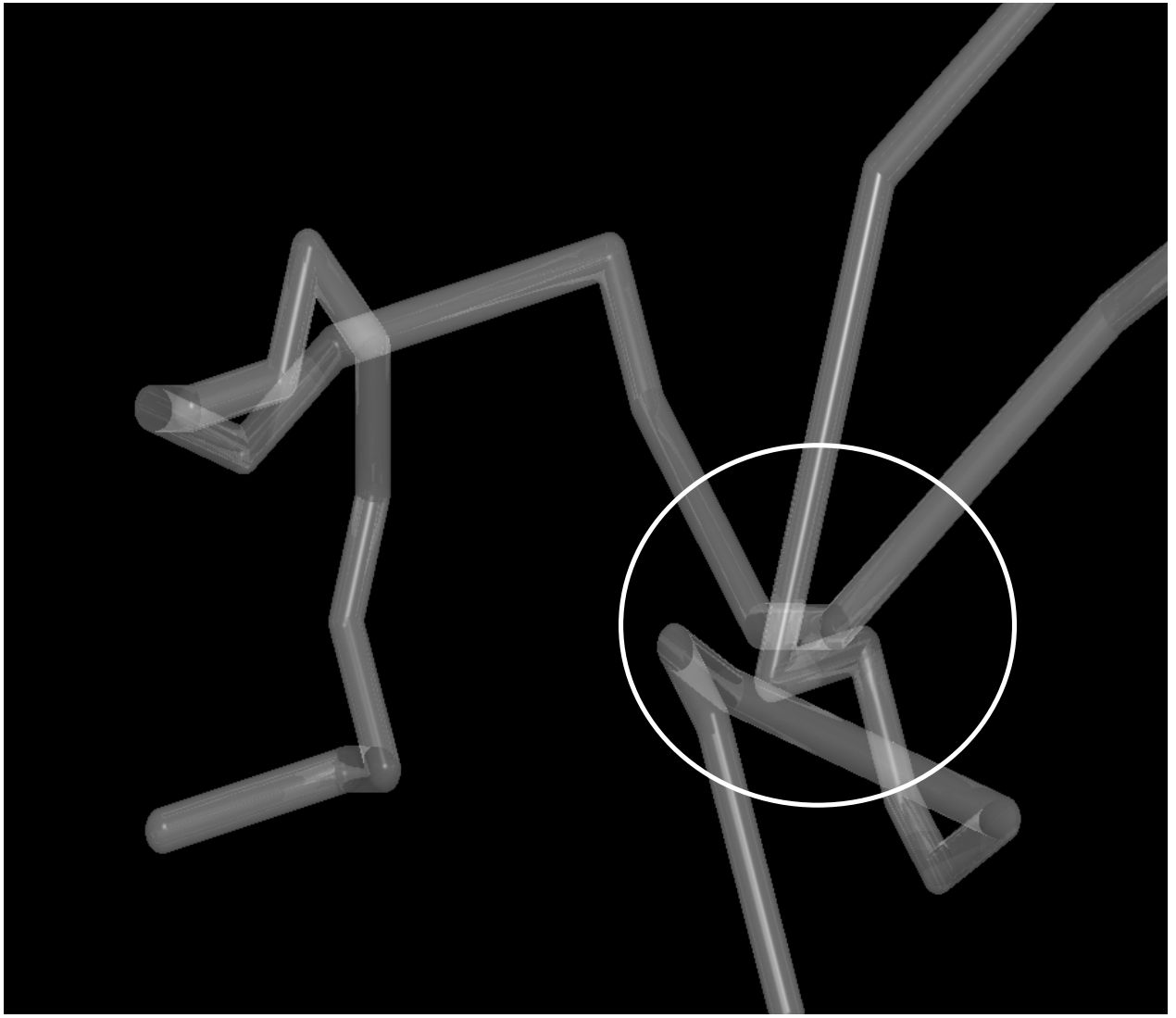
Everaers et al., *Science*, **2004**

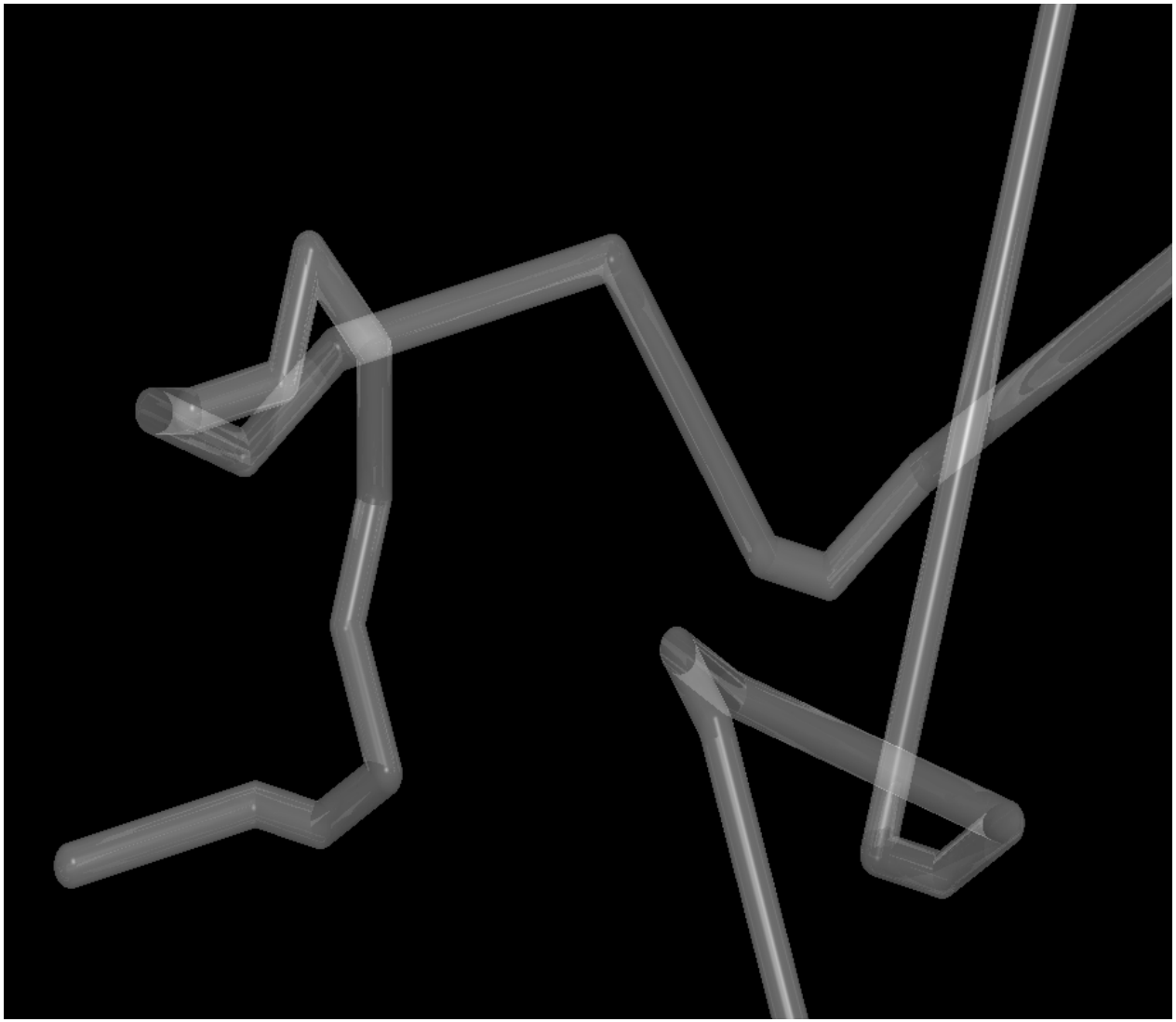








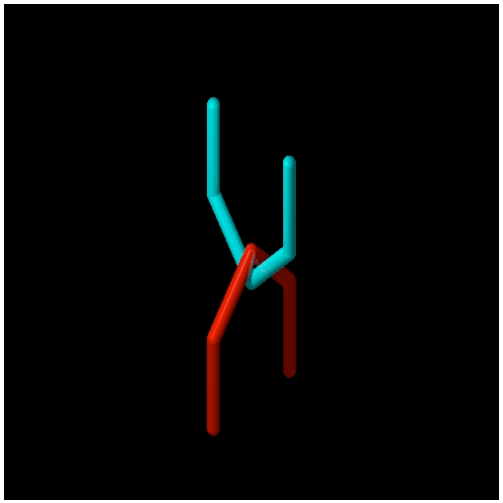




Nature of Coupling

Statistically run through all the chains

dilution exponent α = $\langle Z_{lost}/Z_{del} \rangle$=1.03



- supports the notion that entanglements are binary-contacts
- justifies the assumption made in slip link models
- implies that α = 4/3, which works best with the tube model, and the "true" value of α may be different

Shanbhag and Larson, *Macromolecules*, **2006**
Shanbhag et al., *PRL*, **2001**

Summary

- *Advances in catalyst technology (metallocene) allow us much greater control over branching details.*

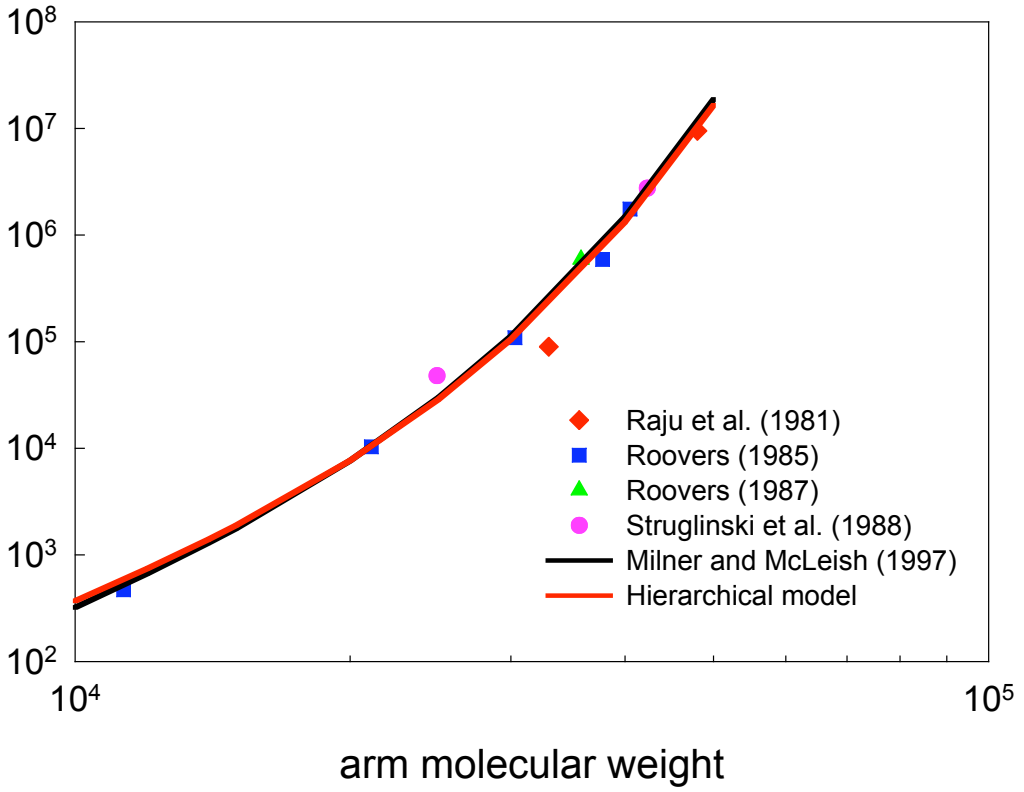
- *There is a need to understand the rheology of branched polymers because rheology is the most sensitive probe of molecular architecture.*

- *The analytical tube model needs significant revision to address branched polymers, and needs help from detailed simulations.*

Acknowledgements

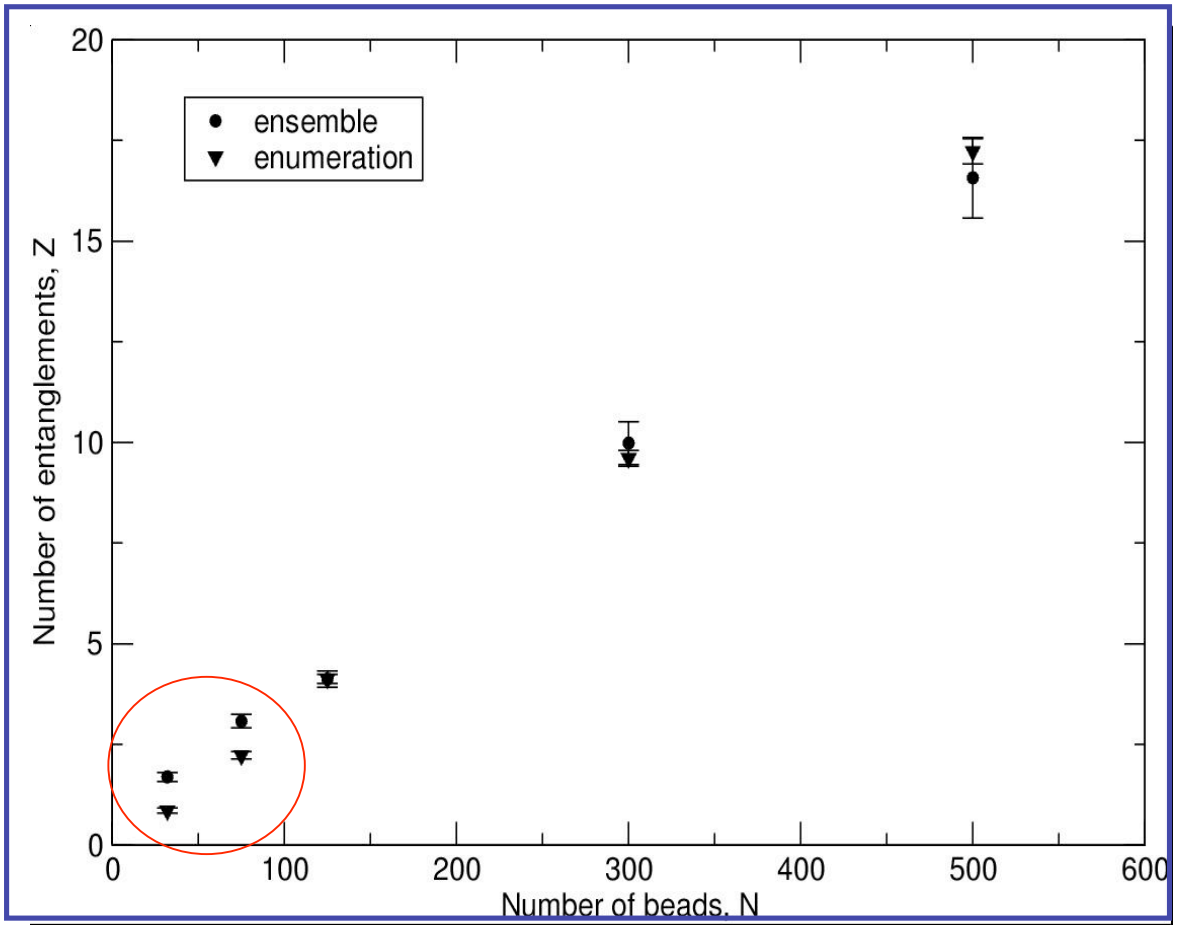
Comparison: Milner-McLeish model and the hierarchical model

zero-shear viscosity of star 1,4-polybutadiene at T=25 °C



Park, Shanbhag, Larson, *Rheol. Acta.*, **2005**

Comparison with Standard Method



Standard Method

$Z = \langle L_{pp}^2 \rangle / \langle R^2 \rangle$

(ensemble average)

N=# beads on chain
(1 bead ~ 5 C atoms)

Shanbhag and Larson, *Macromolecules*, **2006**