Reactor to Rheology: Coupled models for polymers

Chinmay Das

School of Mathematics
University of Leeds
Leeds, UK

Correlation and Disorder in Classical and Quantum Systems
ICTS-TIFR, Bangalore

UNIVERSITY OF LEEDS

Daniel Read (U Leeds)

Tom McLeish (U Leeds/Durham)

Dietmar Auhl
Petra Bacova
Taihyun Chang
Jaap den Doelder
John Embery
Christine Fernyhough
David Hoyle
Lian Hutchings
Nat Inkson
Michael Kapnistos
Mark Kelmanson
Helen Lentzakis
Angel Moreno
Pradeep Shirodkar
Johannes Soulages
Iakovos Vittorias
Dimitris Vlassopoulos
and others...

polymer IRC μPP² EPSRC Engineering and Physical Sciences Research Council

University of Bradford, Nottingham, Durham, Sheffield, Reading, Crete
BASF, Dow, DSM, Basell,, ExxonMobil, SCG Chemicals
and others...

Rough outline

- Introduction to polymer molecules and their dynamics in the molten state
- Virtual molecules in imaginary flow
- Gelation in α-olefin/diene copolymers
- Outlook

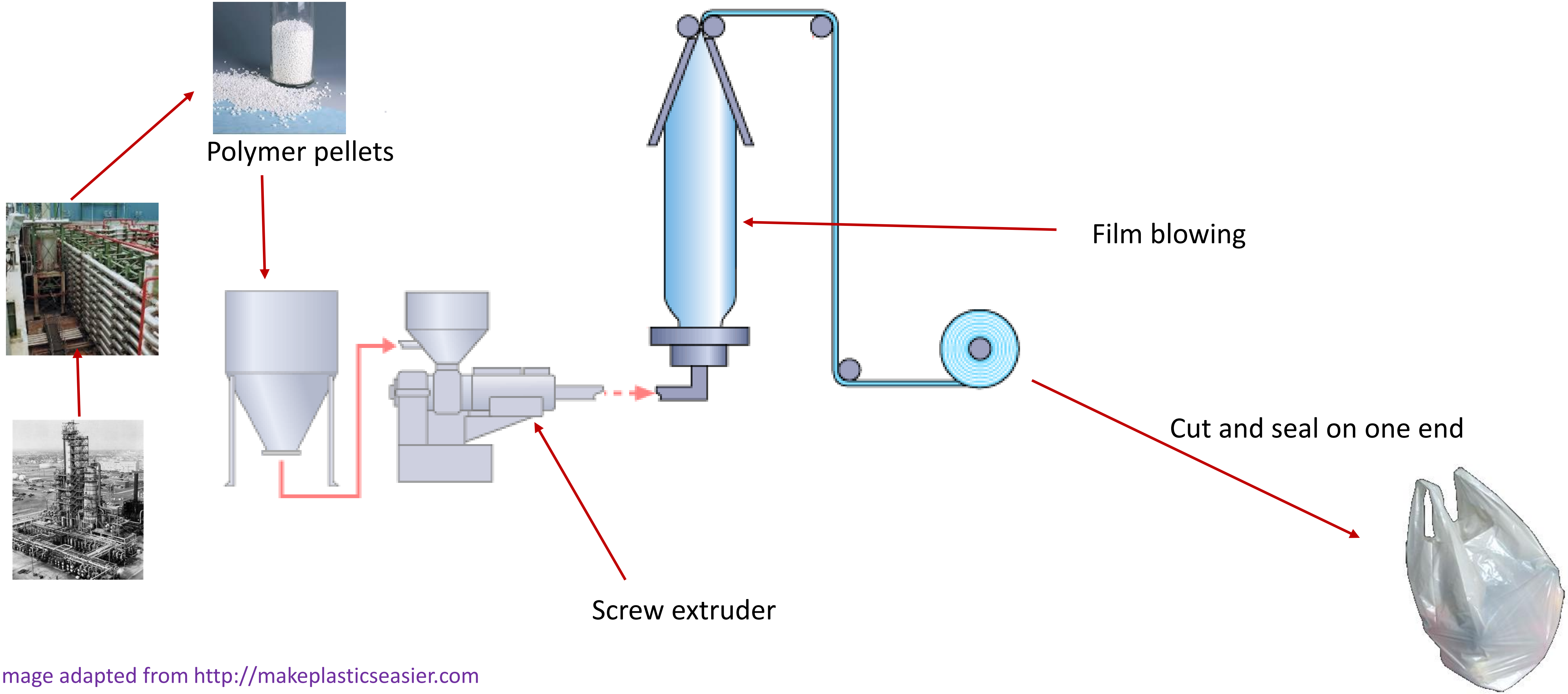
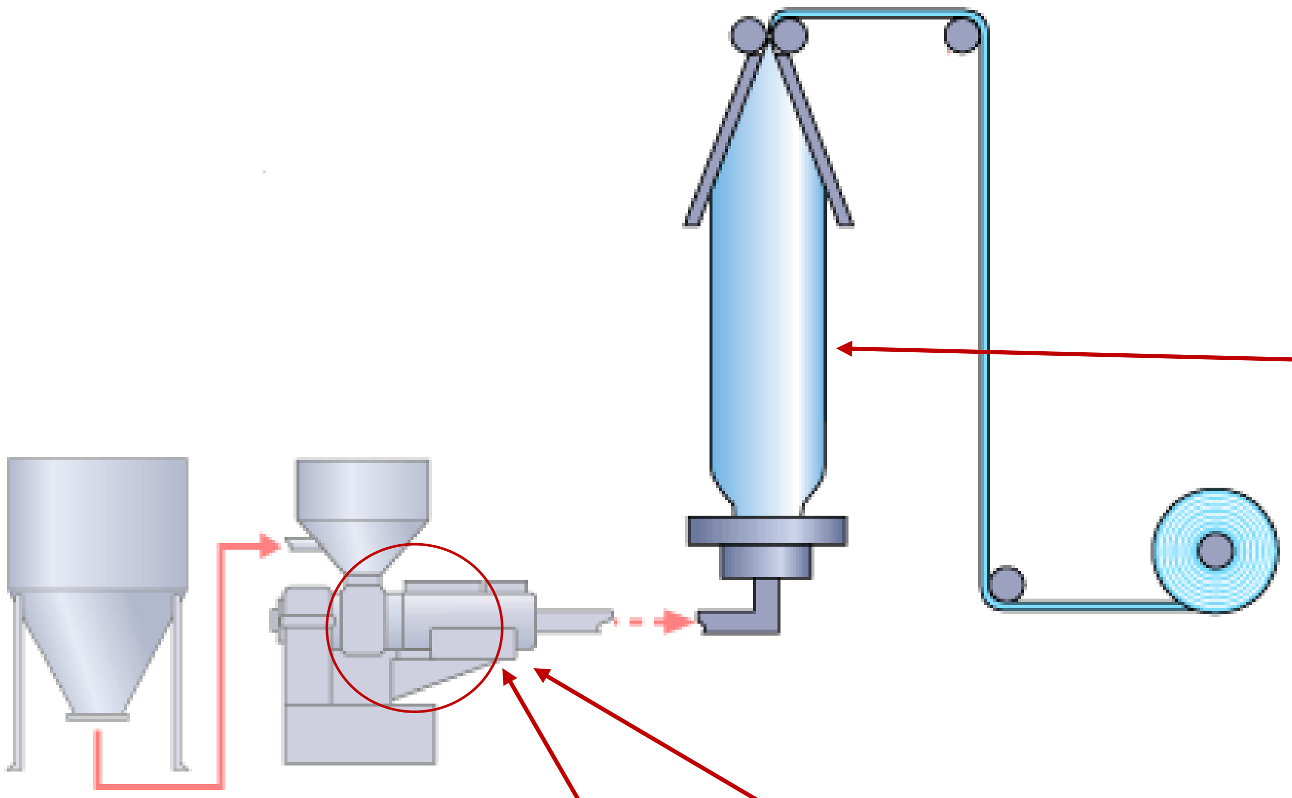
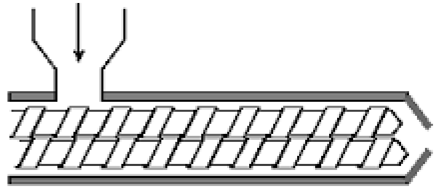


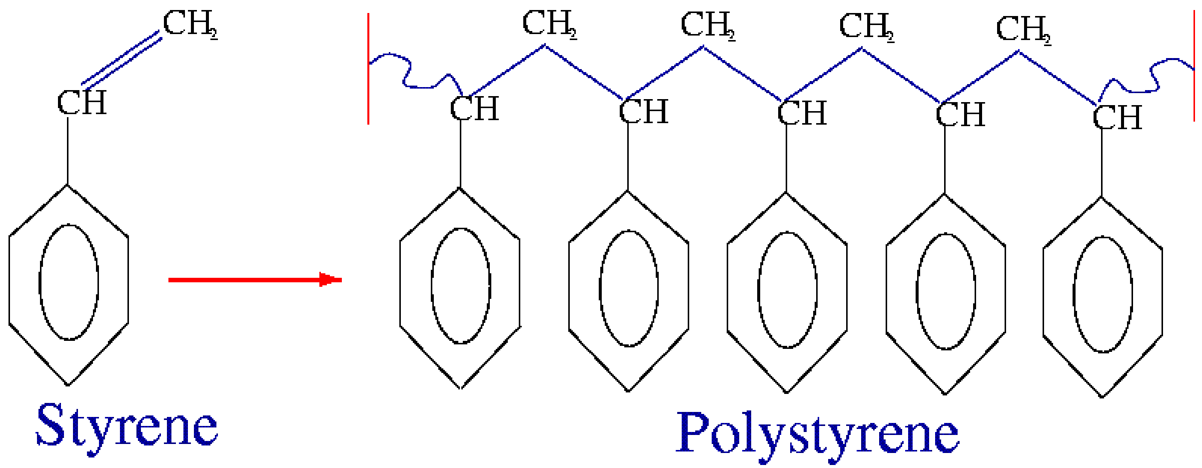
Image adapted from http://makeplasticseasier.com

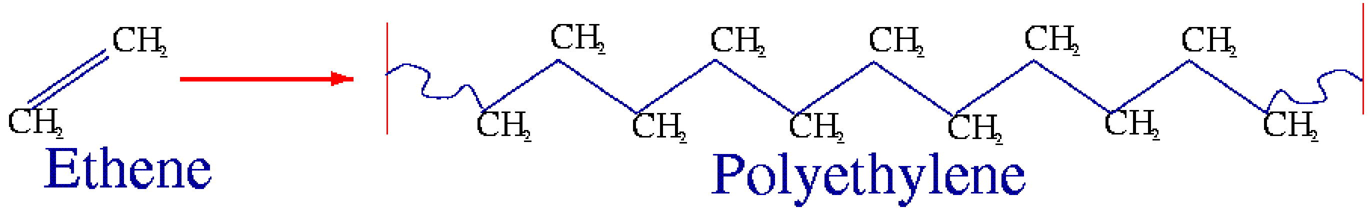


Film blowing
Planner extension
Need resistance to flow
(Else the film will fall apart before solidifying)



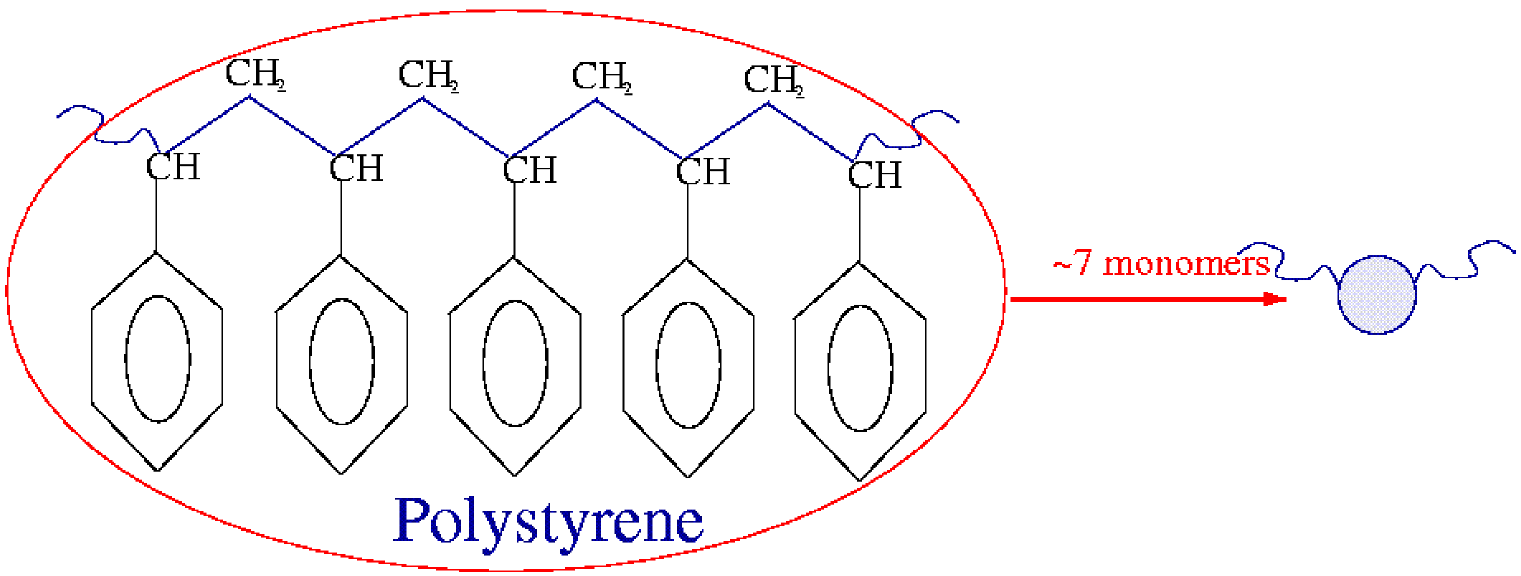
Screw extruder
Strong shear
Need low resistance to flow
(more plastic bags at the same time, less viscous heating)

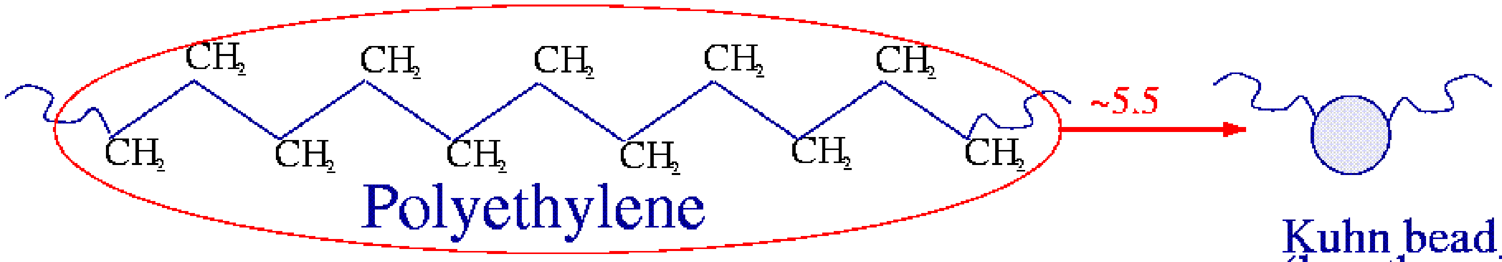




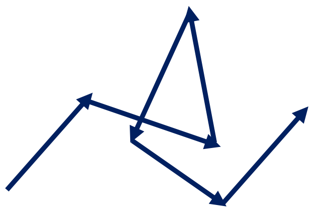
Polymers: Long repeating chains of monomer units

Can be branched





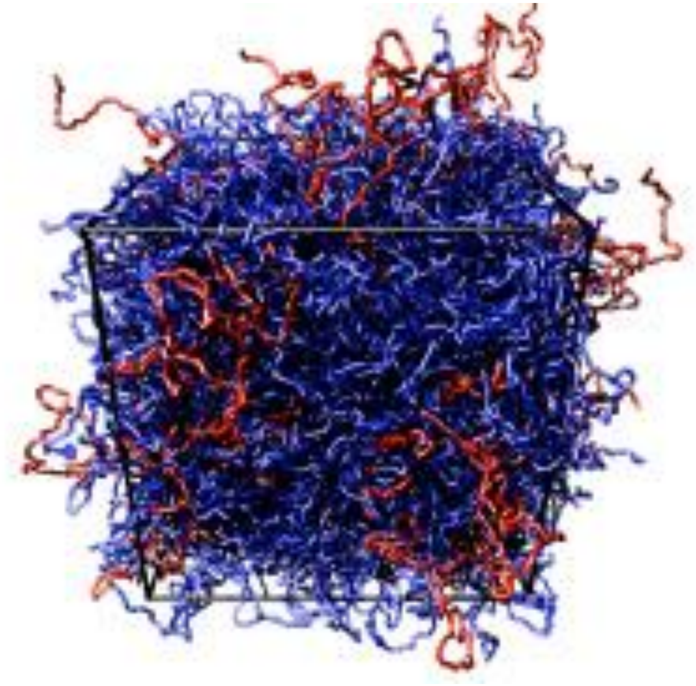
Kuhn bead
(length scale b)



Random walk conformation in melt
Entropy dominated

Energy scale k_BT

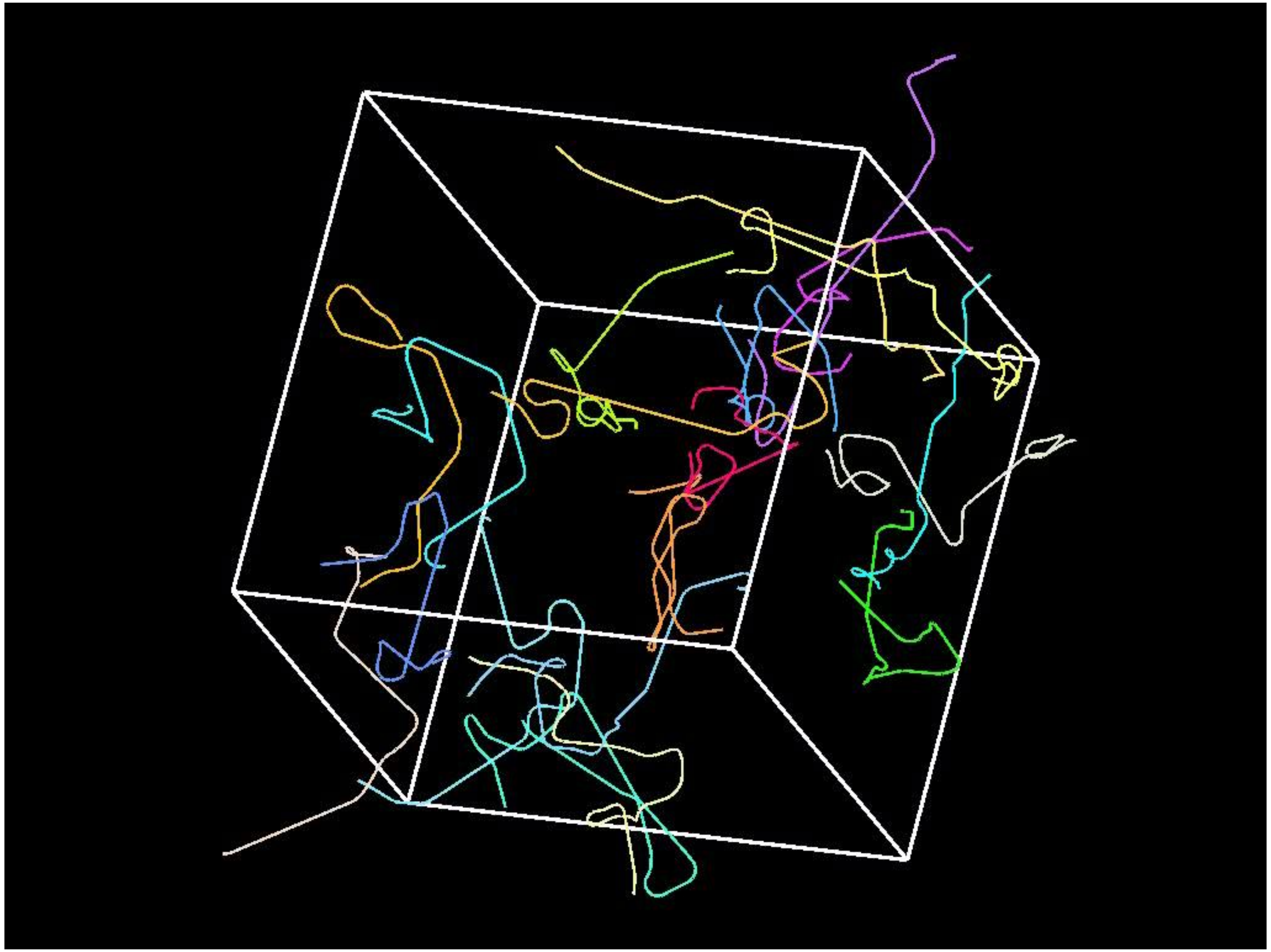
Tube theory



Long time and length scales:
Chemical details are hidden in a small number of parameters

Bead-spring model
(soft potential, but stiff enough to ensure
that chains don’t cross each other).

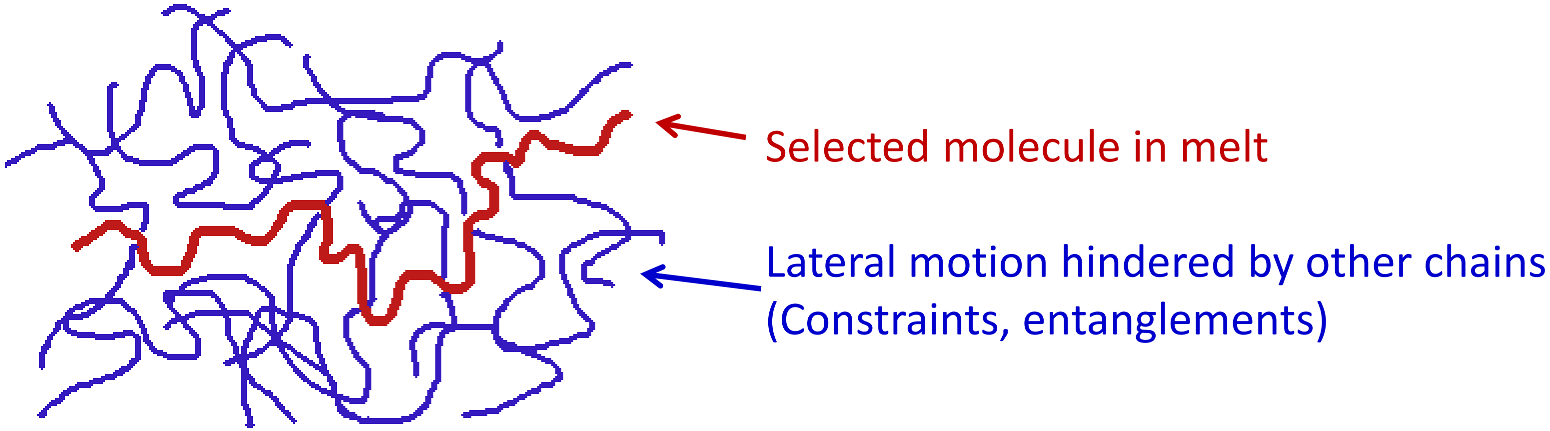
Image adapted from http://cheresearch.engin.umich.edu

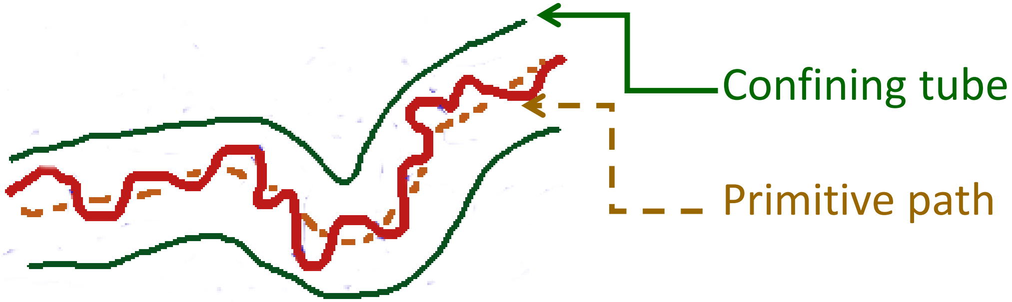


Unfold molecules from periodic box

Long linear molecules:
In certain timescale, the chains are approximately confined in a tube like region.

Animation from Carsten Svaneborg
https://www.pks.mpg.de





Length scale: **tube diameter, a**
(persistence length of primitive path,
contains chain of one entanglement)

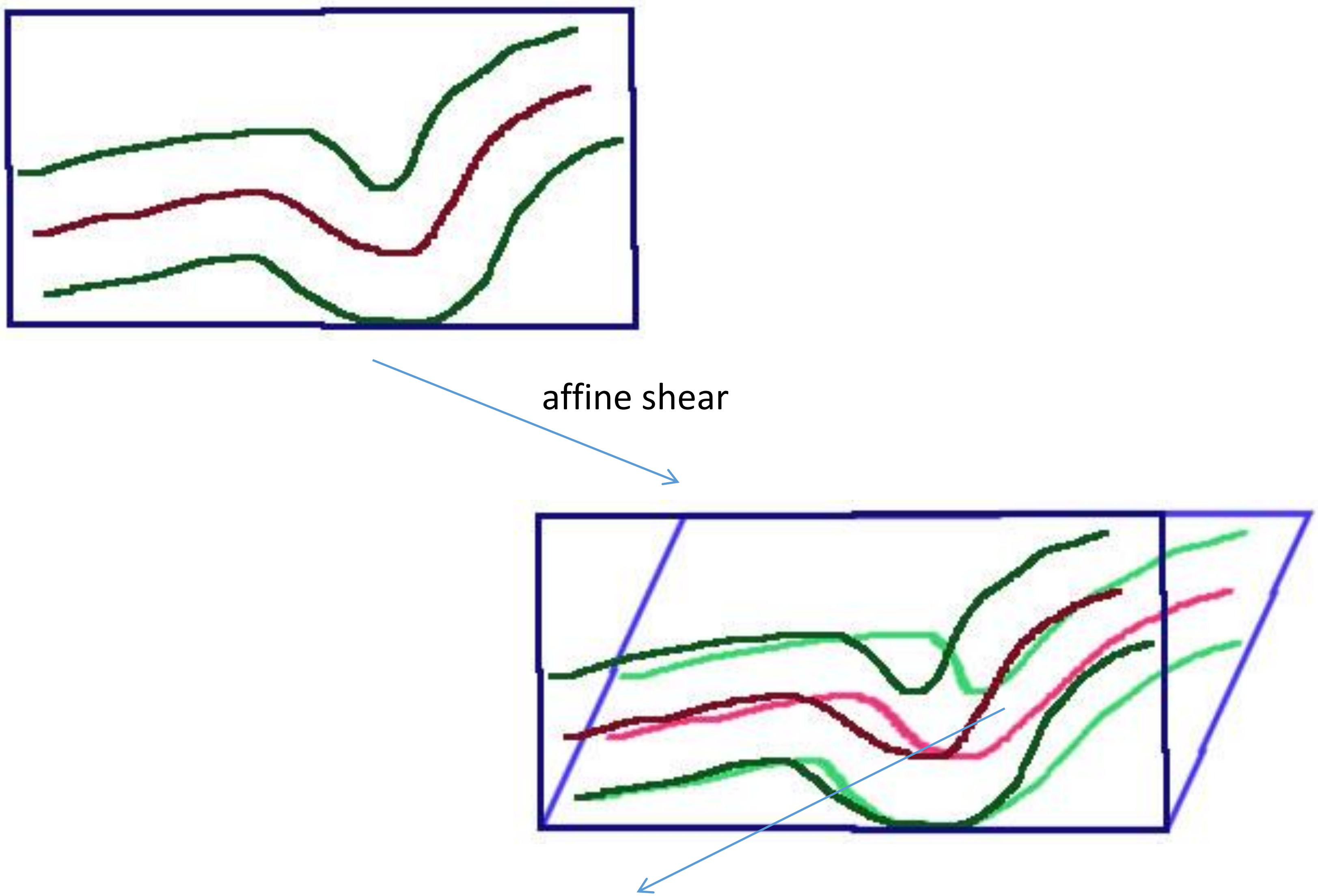
Entanglement molar mass, M_e

Polyethylene: ~7 Kuhn beads
Polystyrene: ~24 Kuhn beads

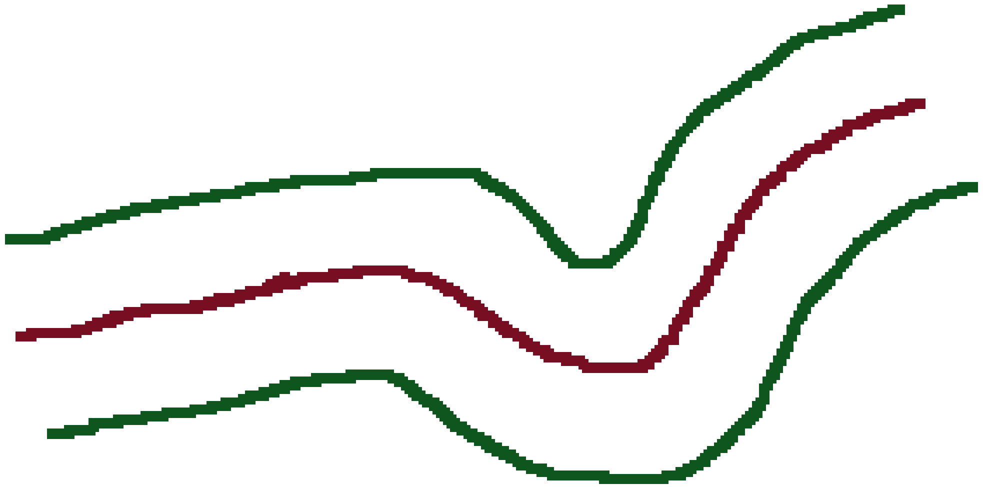
Time scale: **Entanglement time, τ_e**
(Rouse Relaxation time of one entanglement;
Time scale at which chains become aware of the tube)

de Gennes, Edwards

Stress decay



Deformation changes conformation
Chains can revert back to equilibrium conformation by going out of old tube



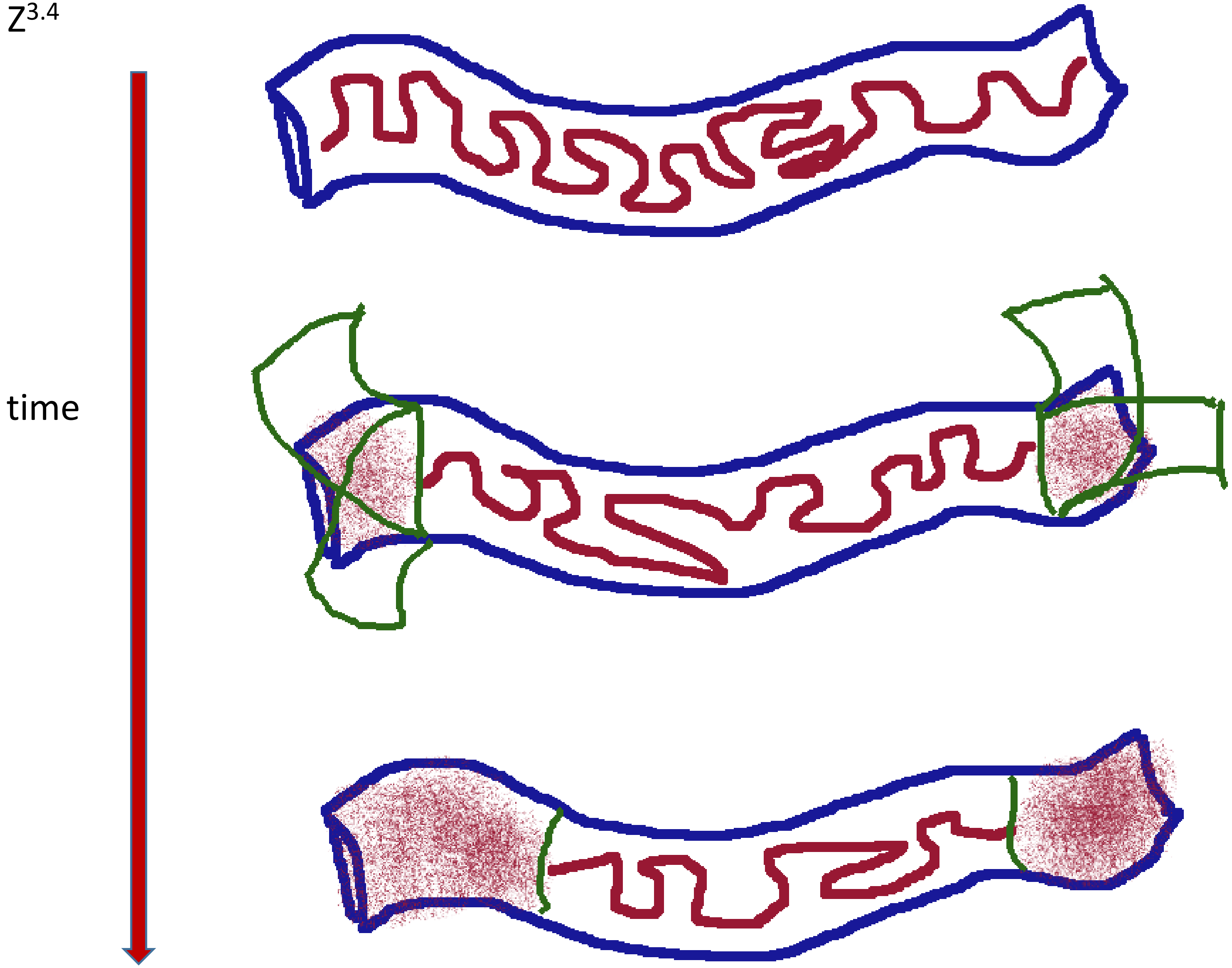
Reptation:

1-d diffusion of kinks.
Length to diffuse ≈ Z (Chain ends are under entropic tension)
Friction ≈ Z
$\tau_d \approx Z^3$

de Gennes, Edwards

Contour length fluctuation

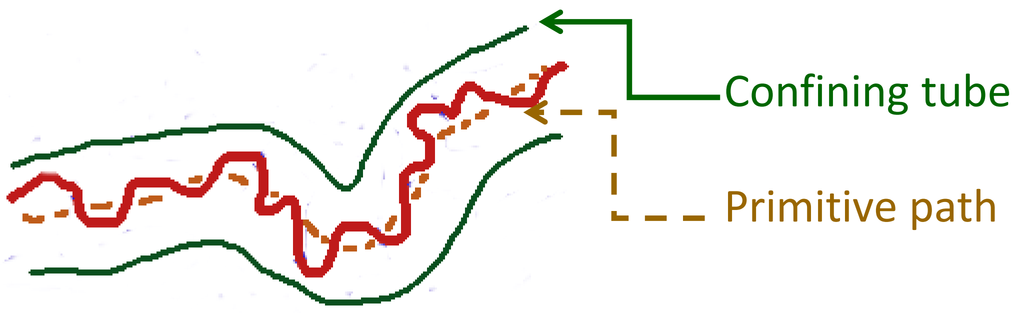
Experiments: $\tau_d \sim Z^{3.4}$

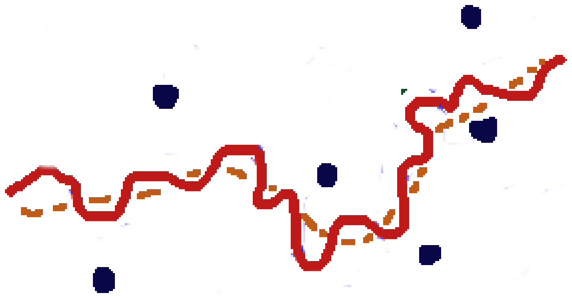


Random walk of end bead does not cost much.

Doi, Edwards

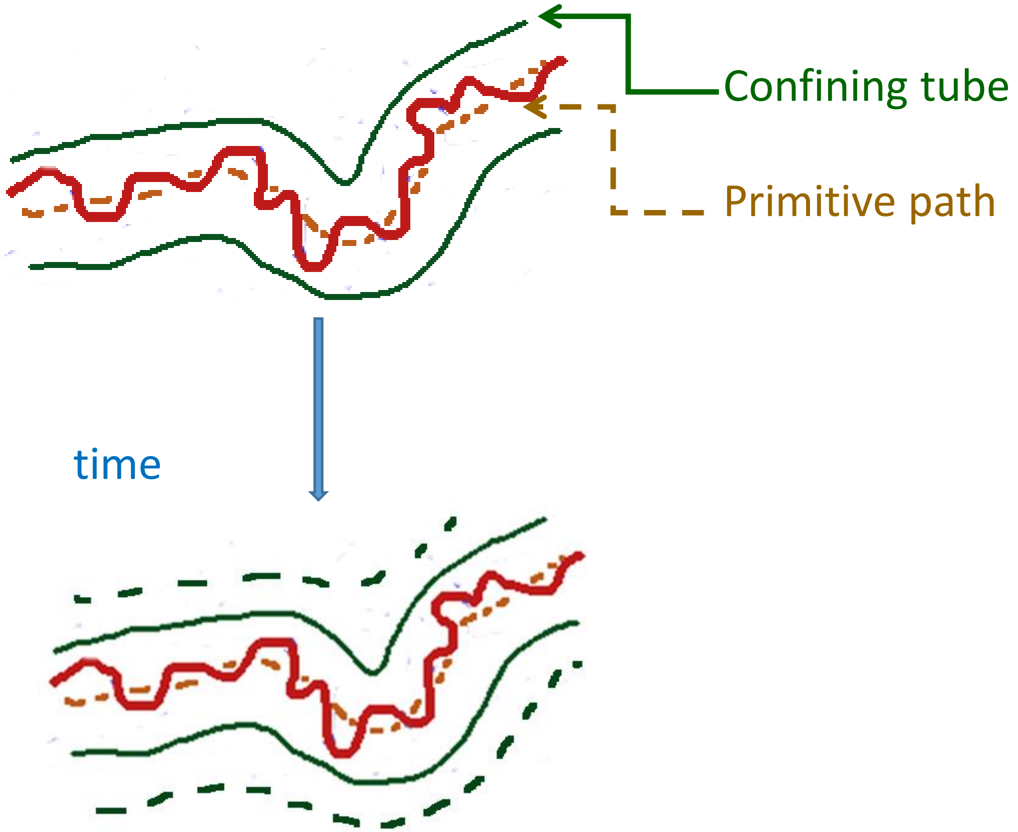
Constraint release

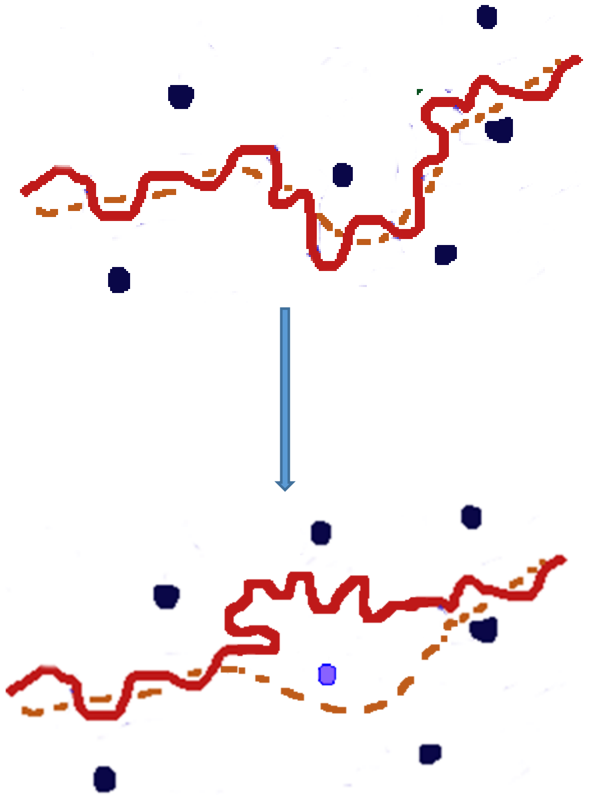




Discrete view

Constraint release





Tube dilation (Softening of confining potential with relaxation)

ϕ_{ST} : Density of entanglements

Experiments on branched polymer relaxation:
Effective number of entanglement on the chain: $Z \rightarrow Z\, \phi_{ST}^{\alpha}$

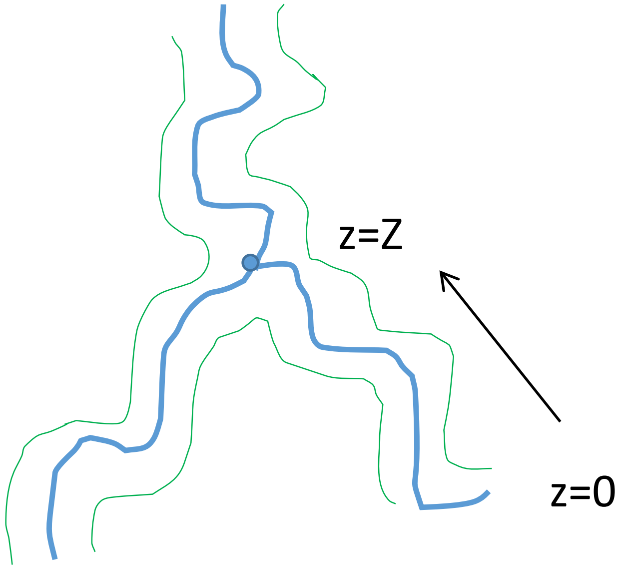
Stress decay
$G(t) \sim G0\, \phi(t)\, \phi_{ST}(t)$

$\phi(t) \rightarrow$ fraction of surviving old tube

Marucci

Deep retraction

Star polymer



Retraction potential: $$\beta\frac{dU}{dz} = \frac{3z}{Z}\phi^{\alpha}$$

Assume all friction located at chain end.

$$\tau_K(z) = \left(\frac{3\pi^5 Z^3}{2\phi_0^{\alpha}}\right)^{1/2} \tau_e \int_0^z dz' e^{\beta U(z')}$$

Softening due to constraint release goes in the exponential.
Dynamic tube dilation is extremely important for branched polymers.

Kuzzu, Doi; Pearson, Helfand; Ball, McLeish

Side branches

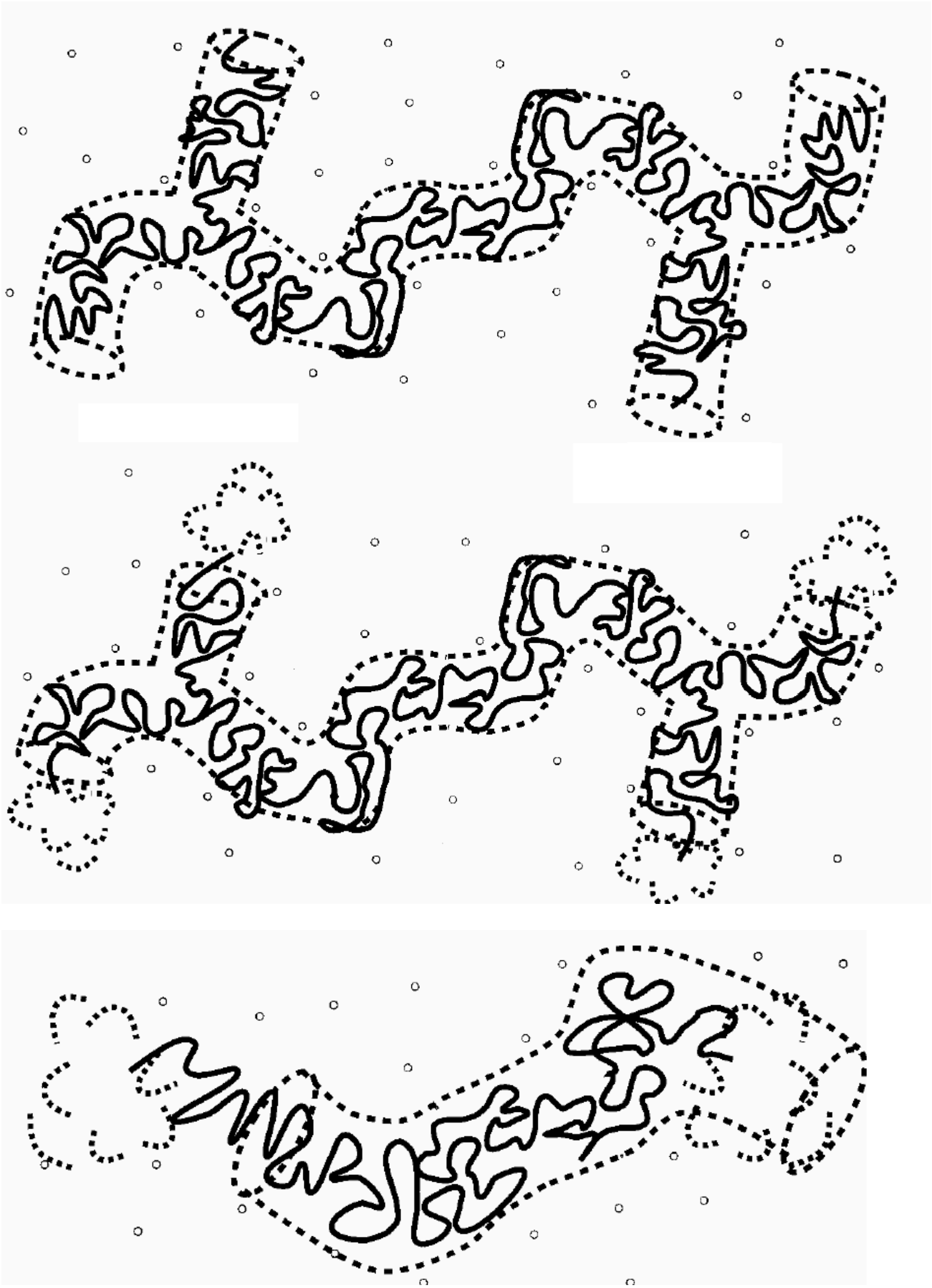
Short art retracts at time t_a

At this timescale, branchpoint can take random hop of order a

Associated friction : $\zeta_a \sim \frac{k_B T}{a^2} t_a$

“backbone” reptation slows down from this extra friction.

H-polymer



“backbone” can only escape once side-arms have had chance to relax.

Low density Polyethylene (LDPE)

Molecules made up of 100 to a million carbons per molecule (all of them in the same sample).
Number of branch points per molecule between zero (linear molecule) and a few hundreds.

Problems:
We do not know the actual molecules.
Even if someone told us the detailed composition and the tube picture is correct,
it will be humanly impossible to figure out the stress response.

(Number of different relaxation models connected by if-then-else statements.)

Even for a two or three component blend, it is difficult to write down a closed form for stress decay.
Each new branching topology needs lengthy calculations.

Ron Larson 2001
Combinatorial rheology of branched polymer melts

Take differential approach and let the computer do the hard work.

After a step strain,

1. Figure out what can relax in a small time interval.
2. Update tube diameter accounting for the relaxed portions.

} Loop till everything has relaxed.

Can have different molecules in the computation having different mass/branching
(Larson ignored multiple levels of branching)

Each affecting relaxation of all other molecules by affecting the dynamics of the tube diameter.

- Have some way to generate an ensemble of representative molecules on computer
- Incorporate branch-on-branch structures
- Figure out ways to predict stress in non-linear flows
  (Polymer processing almost always involve highly non-linear flow)

And rebrand it!

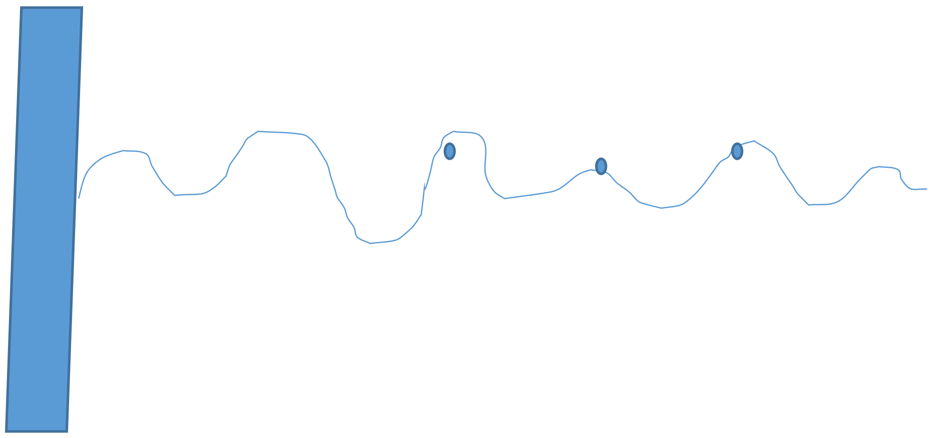
BoB

http://sourceforge.net/projects/bob-rheology

J Rheol., 50, 207 (2006); **58,** 737 (2014).
Science 333, 1871 (2011)

Multiple friction along the backbone

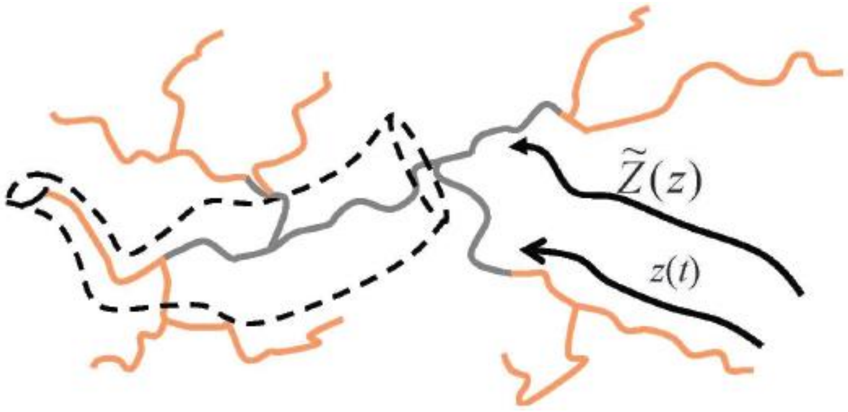
Find equivalent one dimensional problem by insisting that dissipation in retracting a certain length remain unchanged



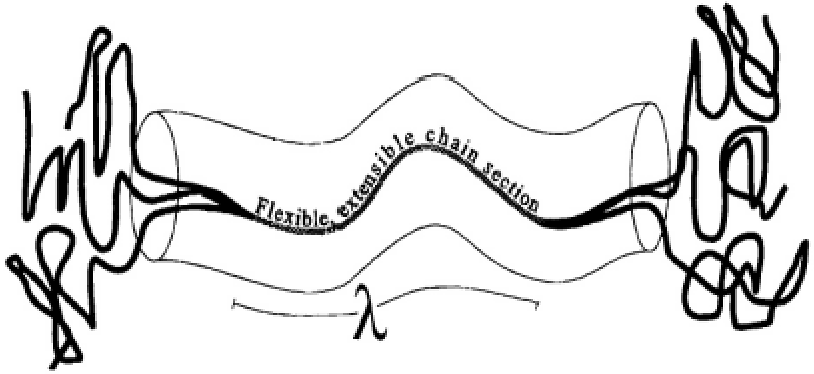
Distance to effective arm retraction pivot : $\tilde{Z}(t)$

Modify retraction potential as: $$\beta\frac{d\tilde{U}}{dz} = \frac{3z\phi^{\alpha}}{\tilde{Z}}$$

Added dynamics for the pivot point $\tilde{Z}(t)$



Nonlinear flow
Pom-pom model

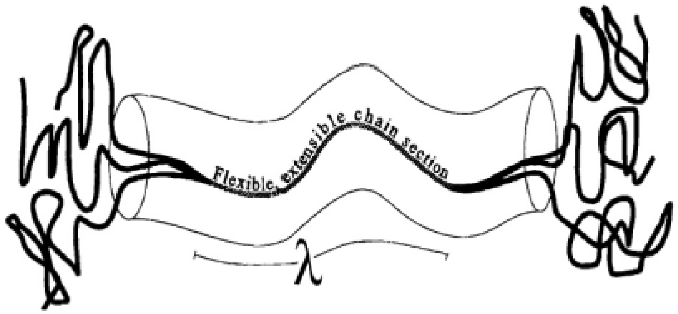


Flow aligns and stretches confining tube
Stretch can relax by withdrawing the branches
Maximum stretch grows with number of side-branches

Backbone:
Stretch relaxation time ➔ side arm retraction time
Orientation relaxation time ➔ reptation time

Larson, McLeish; Bishko et al

Pretend each bits of any molecule are something like a pompom molecule

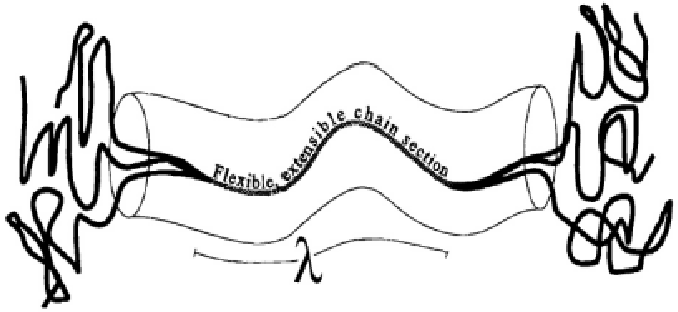


Pompom model:

- Orientation relaxation time
- Stretch relaxation time
- Number of side-arms

If you have a hammer everything looks like a nail

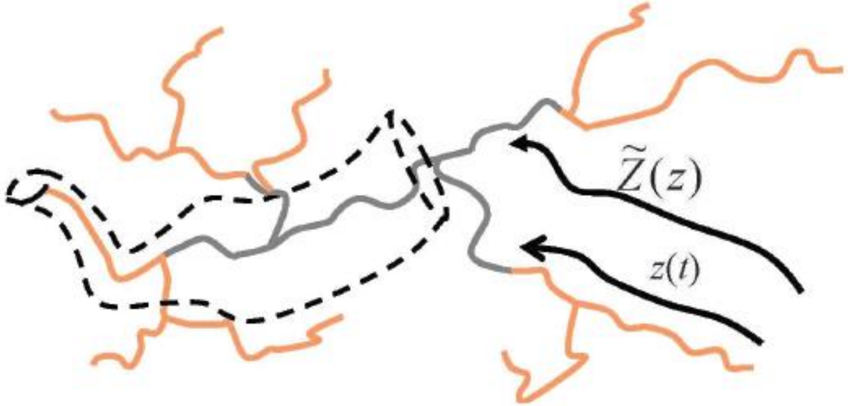
Pretend each bits of any molecule are something like a pompom molecule



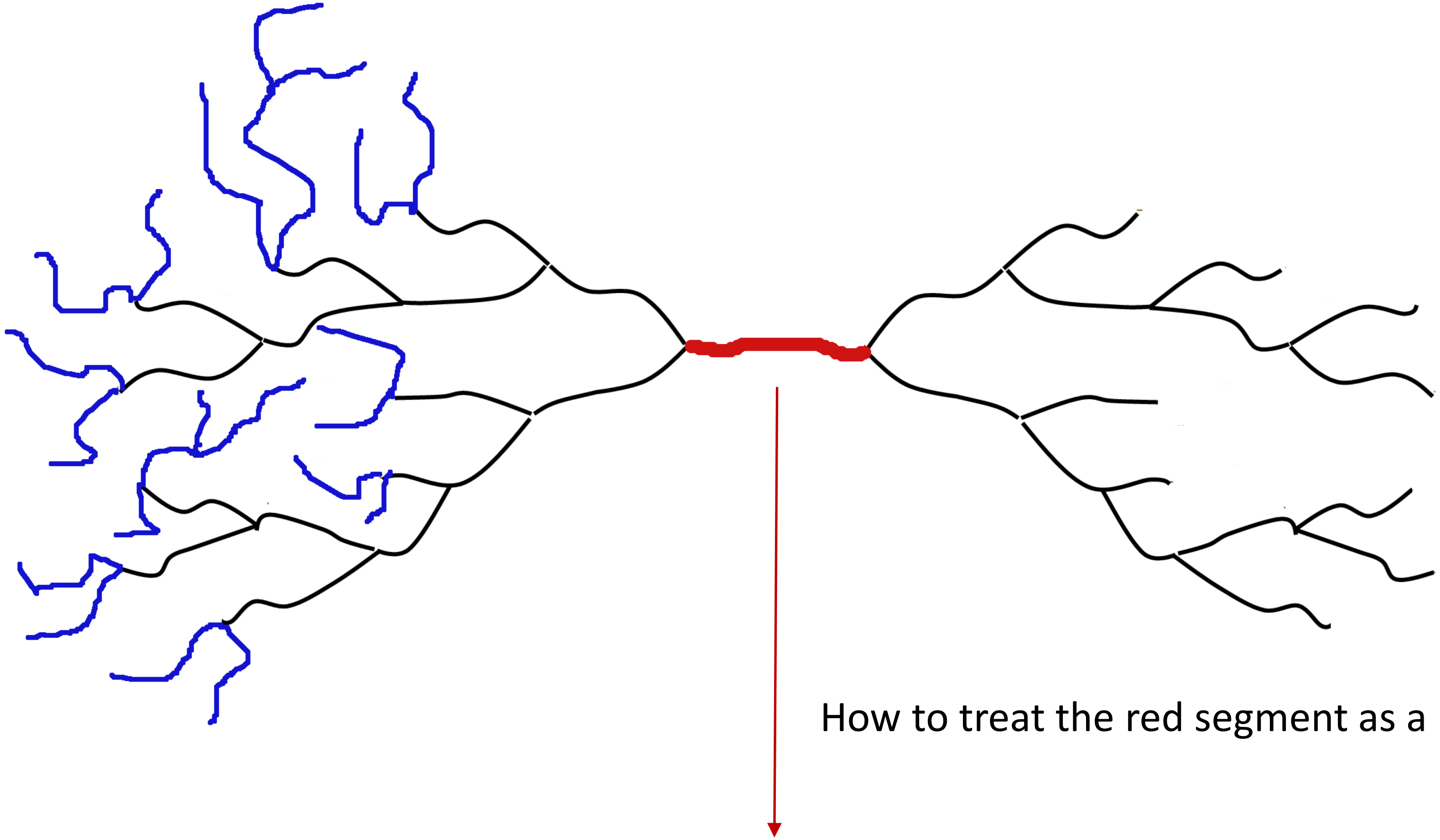
Pompom model:

- Orientation relaxation time ← Invert z(t)
- Stretch relaxation time ← Invert $\tilde{Z}(t)$
- Number of side-arms

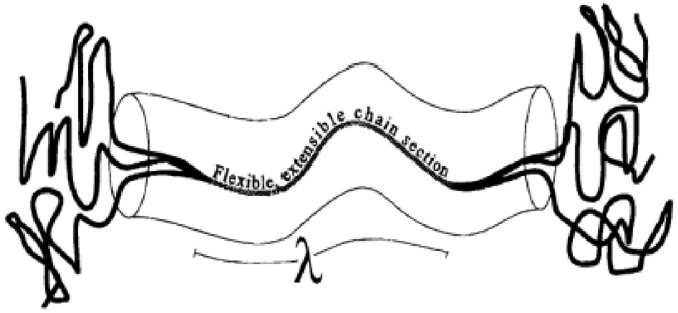
Calculated while finding linear relaxation

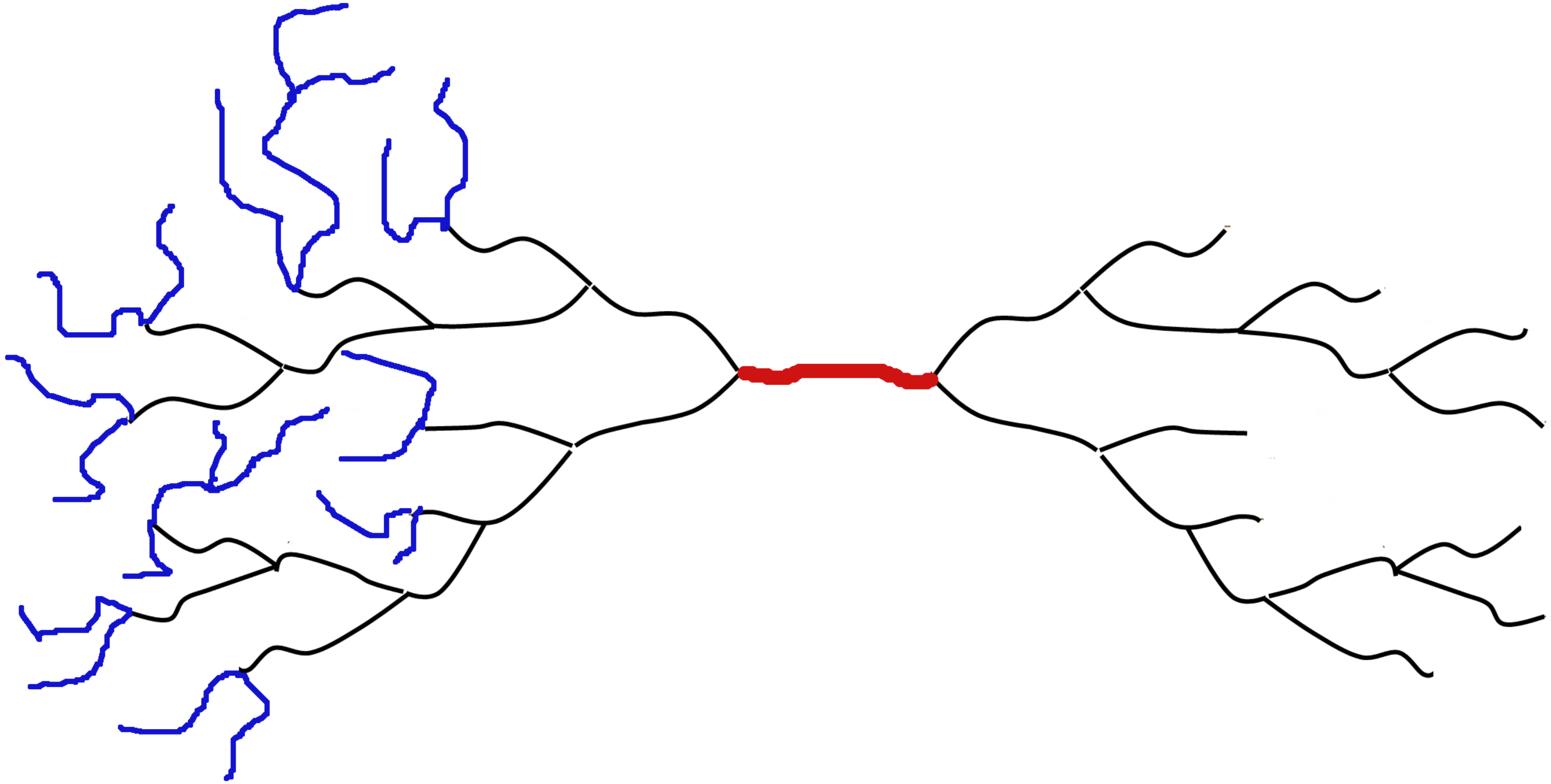


If you have a hammer everything looks like a nail



How to treat the red segment as a pompom molecule?

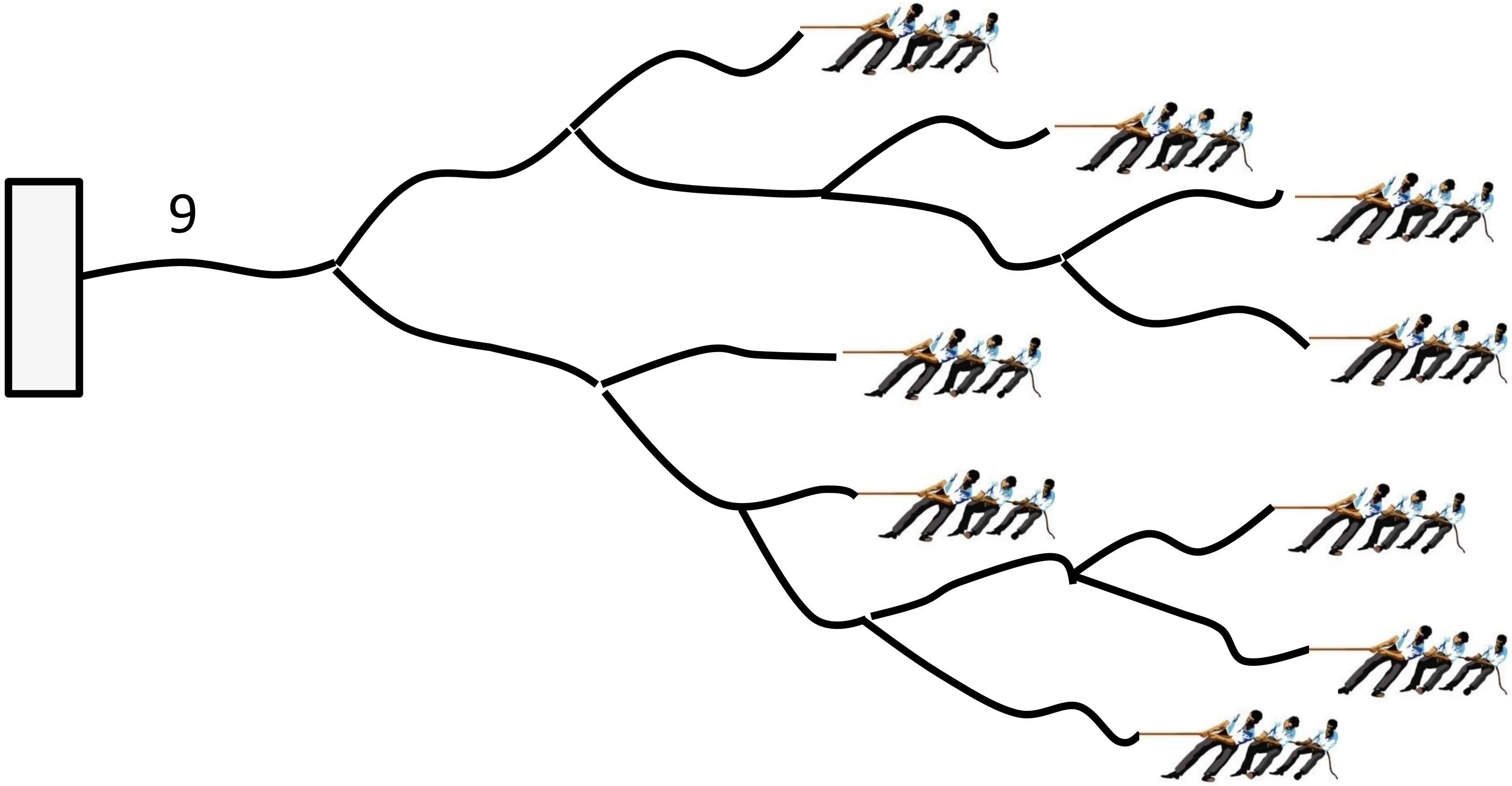




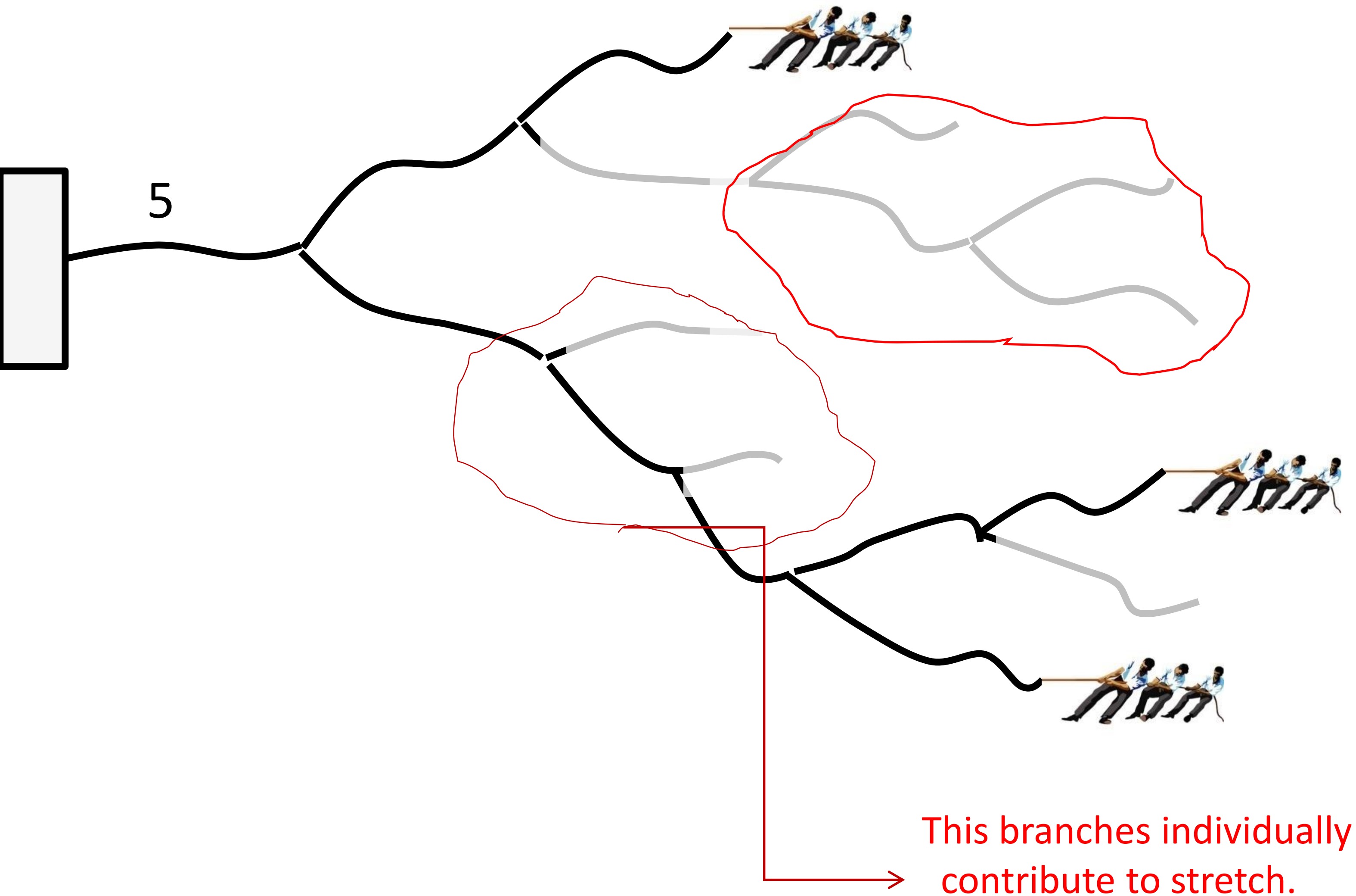
When stretched, first the right hand branch-point will withdraw in the red tube.
(On left, there are many more branches)

Concentrate on the right end of the red segment.

Maximum stretch

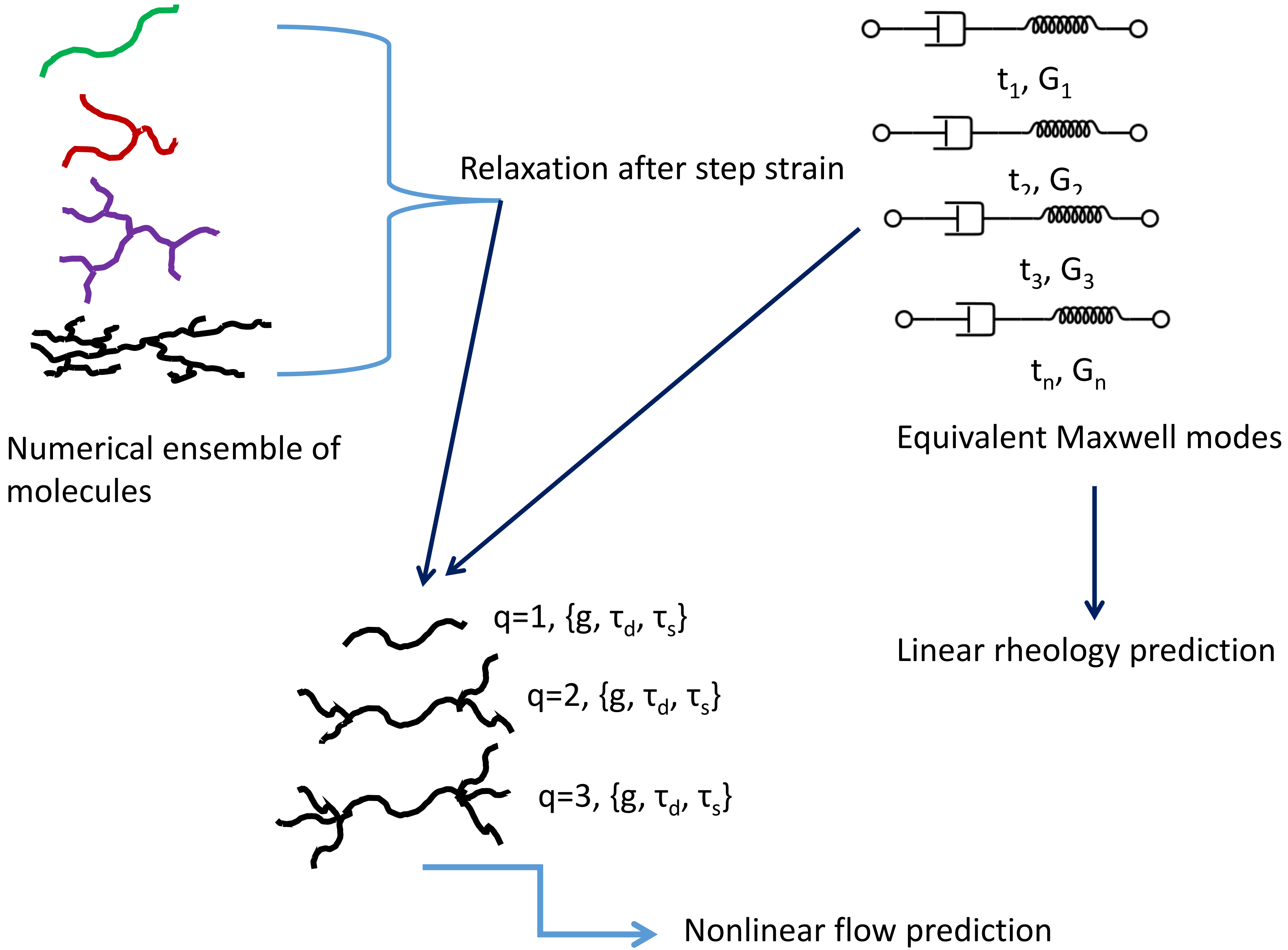


Each chain end provide 3 kT/a tension



This branches individually cannot contribute to stretch.
But together they just might.

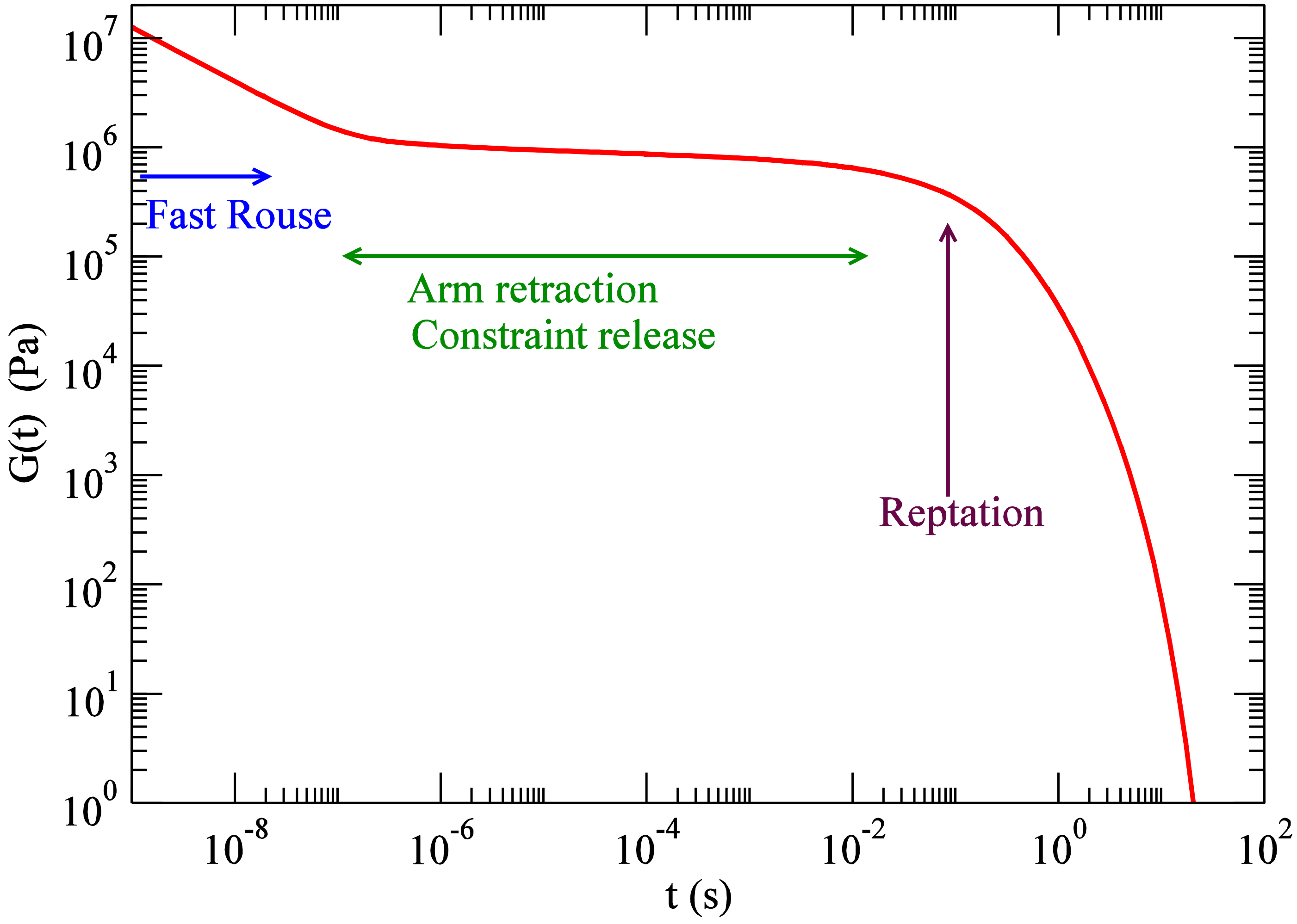
Fast relaxing side-arms may not hold tension
Fast is relative concept – relative to flow-rate.



Relaxation after step strain
t_1, G_1
t_2, G_2
t_3, G_3
t_n, G_n
Numerical ensemble of molecules
Equivalent Maxwell modes
Linear rheology prediction
q=1, {g, τ_d, τ_s}
q=2, {g, τ_d, τ_s}
q=3, {g, τ_d, τ_s}
Nonlinear flow prediction

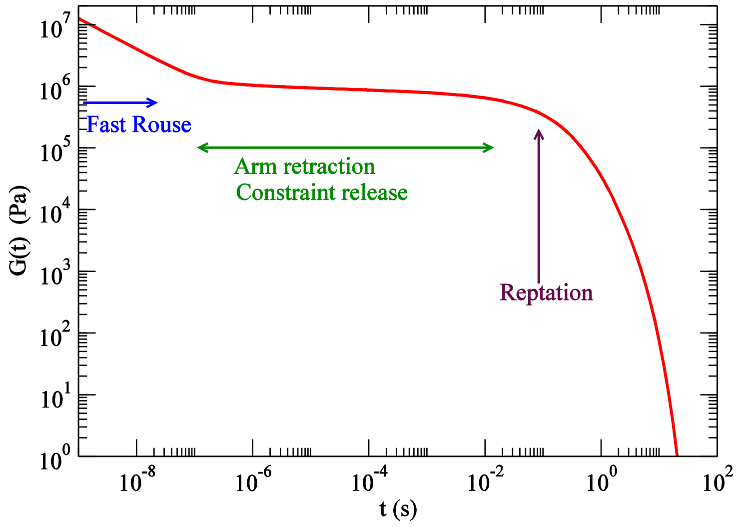
Experiments:

Linear Rheology

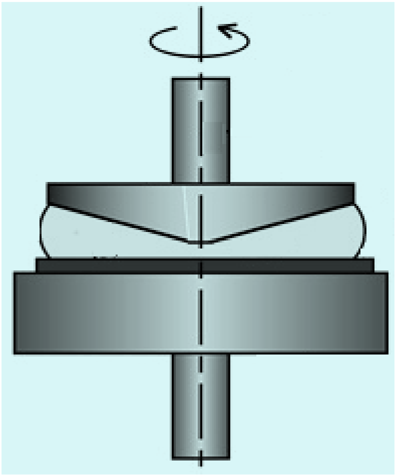


Experiments:

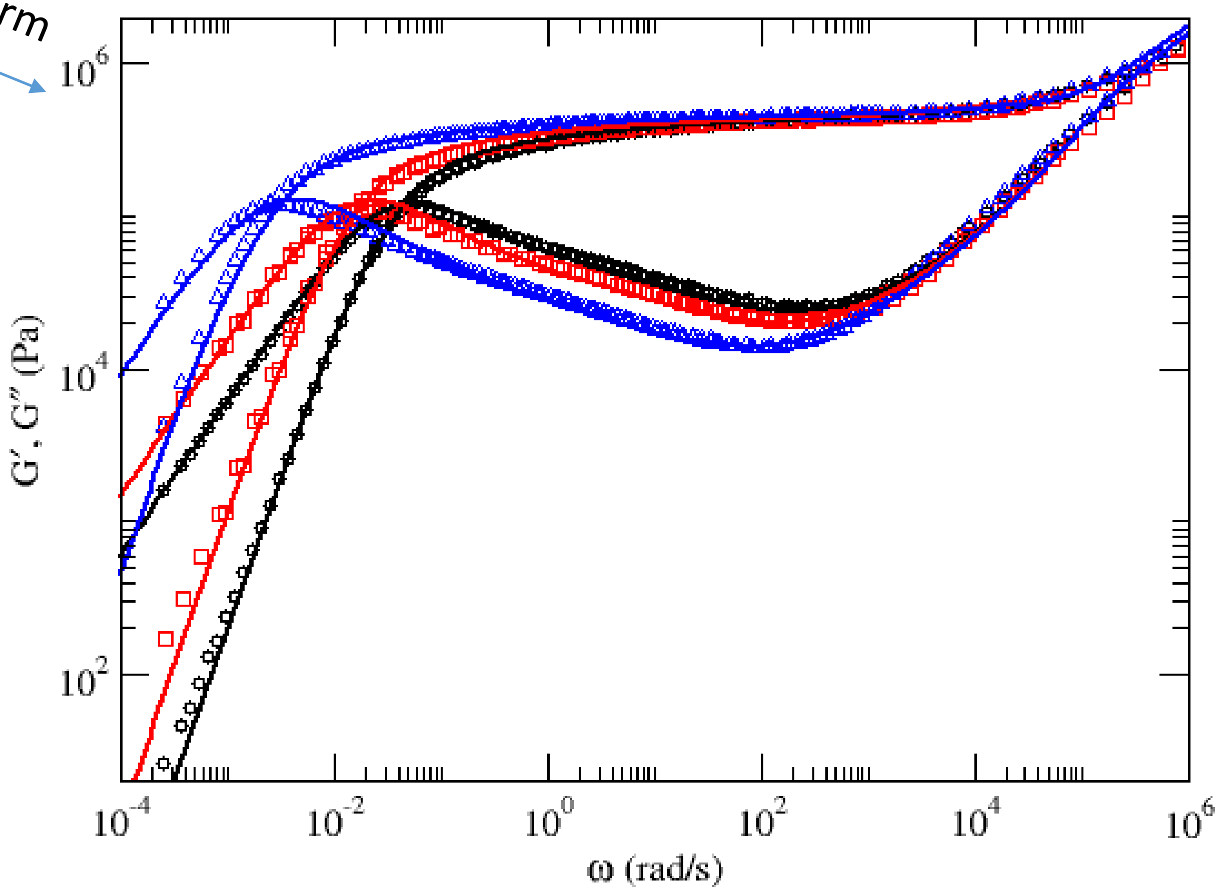
Linear Rheology



Fourier transform

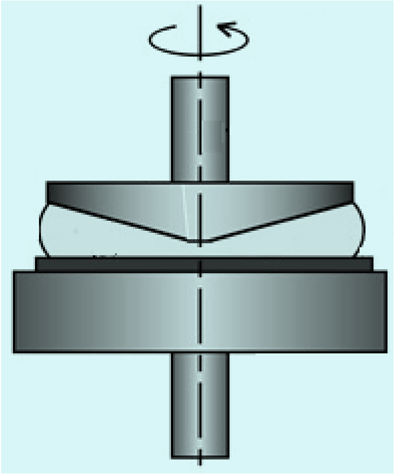


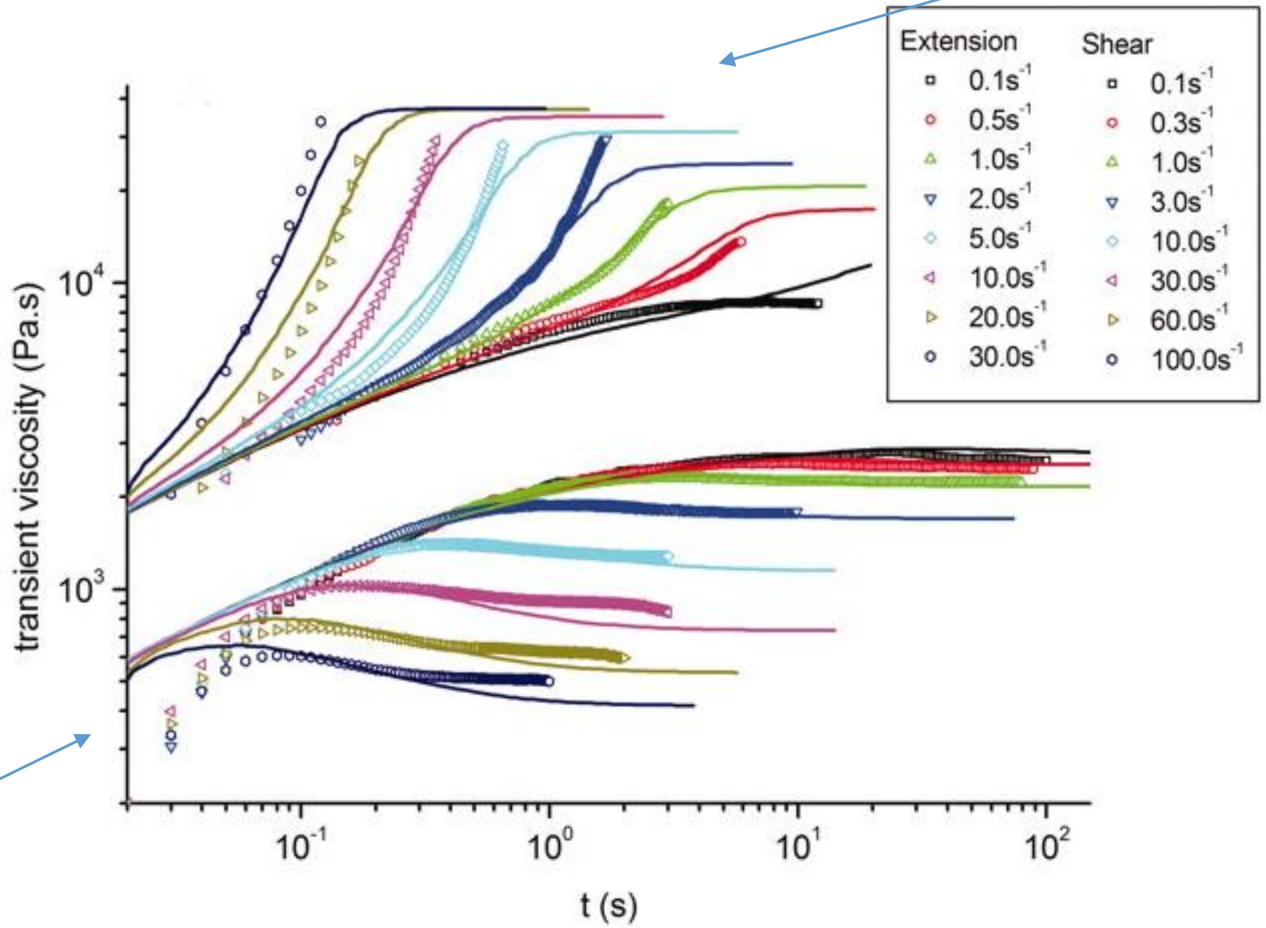
Cone and plate rheometer
Small amplitude oscillatory shear



Experimental data: Auhl et al 2008
Polyisoprene linear : 483K, 634K, 1131K g/mol

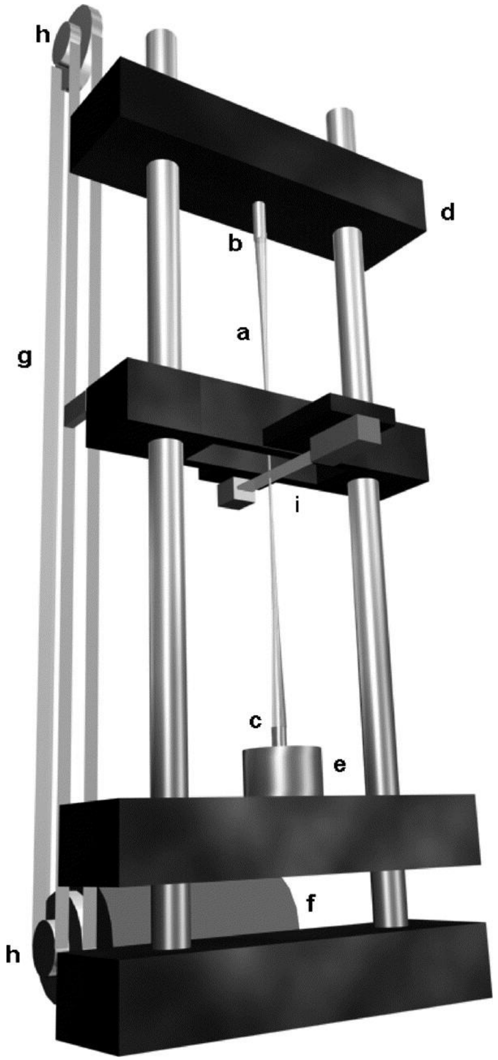
Continuous shear and extension





Start-up shear and uniaxial extension

LDPE; Read et al 2011



Filament stretching rheometer
Hassager and others

Model polymers

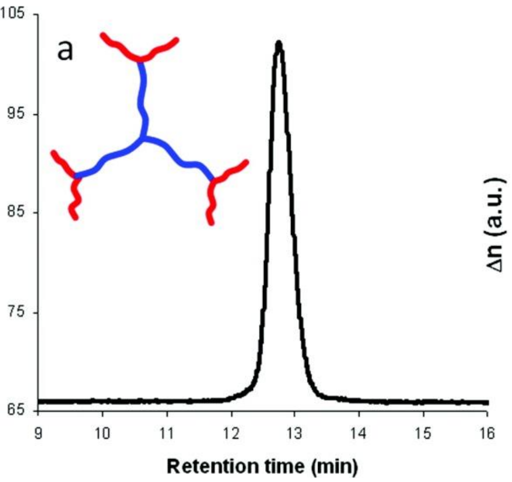
Cayley tree / Dendrimac

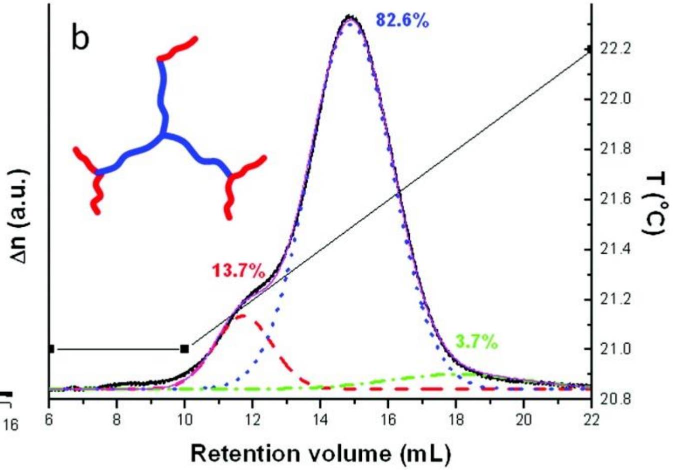
A few years PhD student time

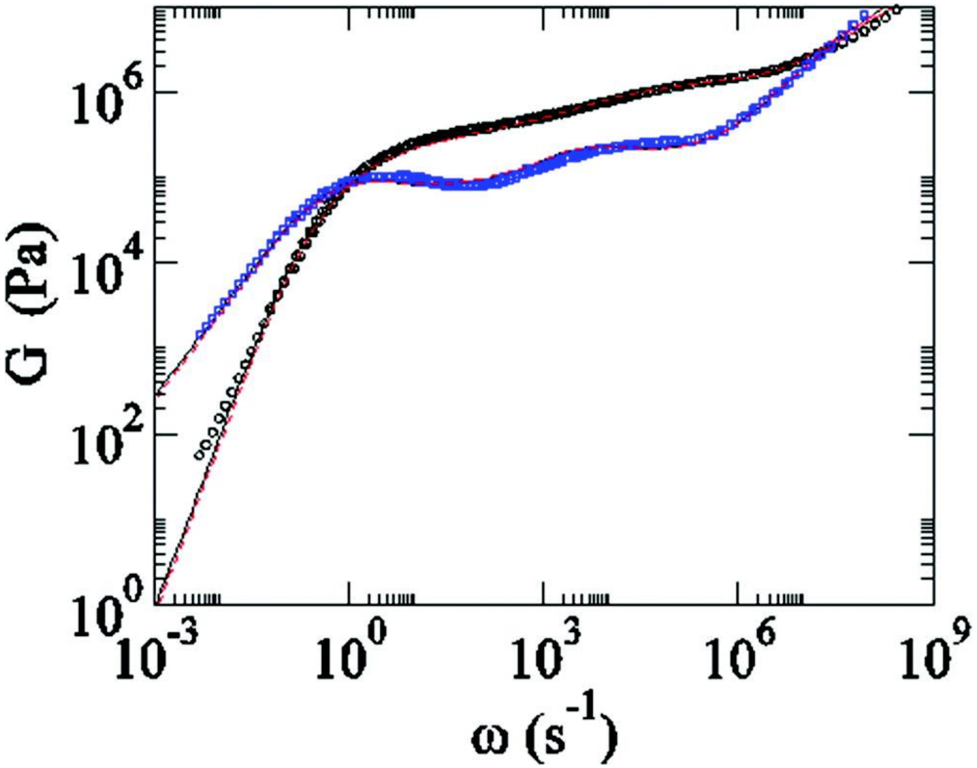
Available in gram quantities

Extremely pure

(i.e. hard to figure out the by-products)

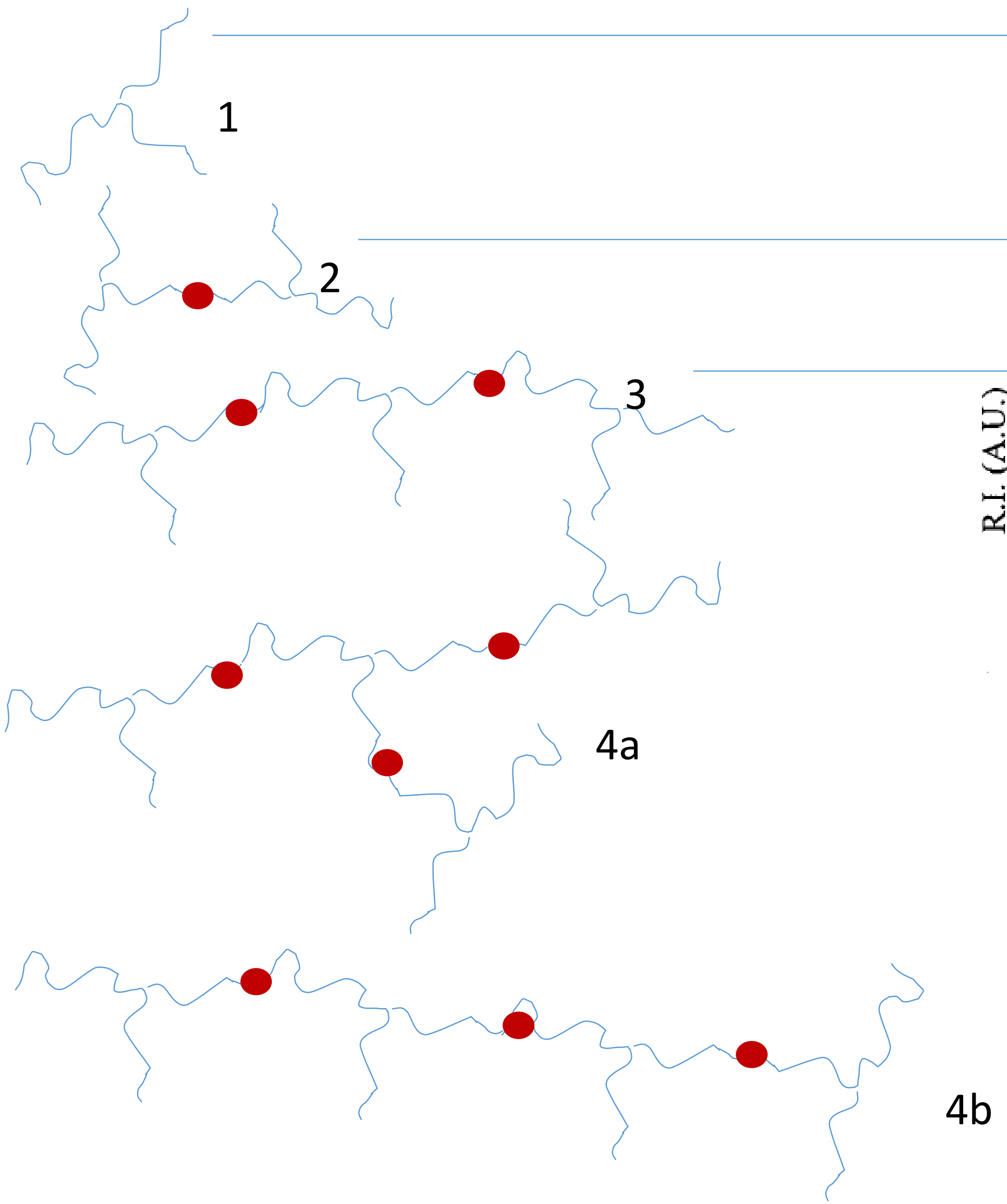


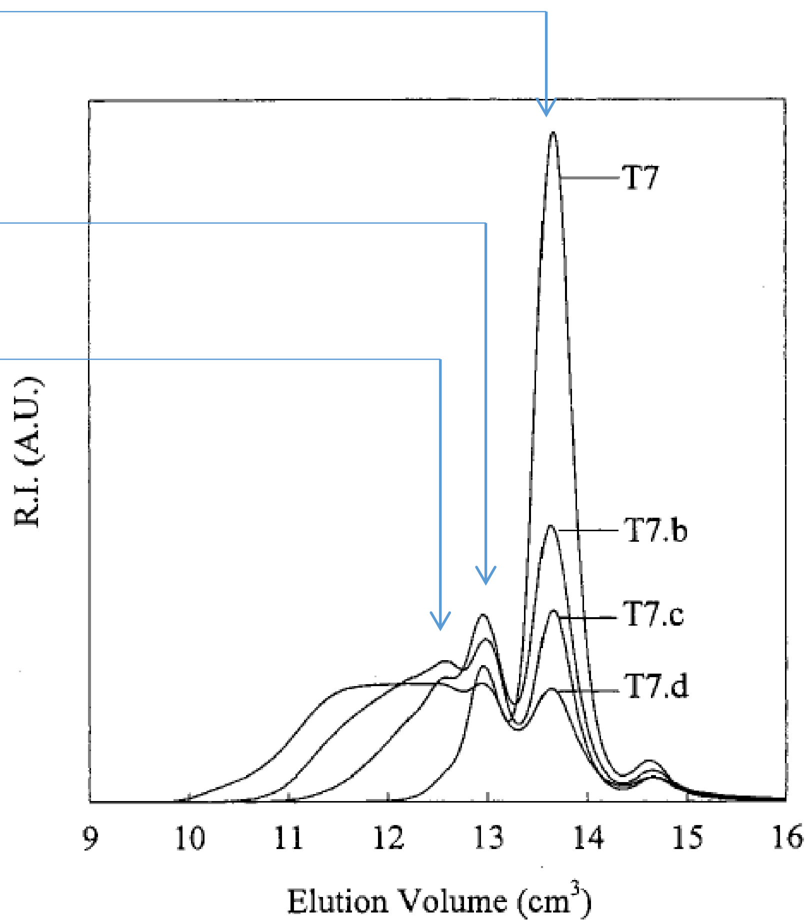




Hutching *et al*.; ACS Macro Lett.**1**, 404 (2012)

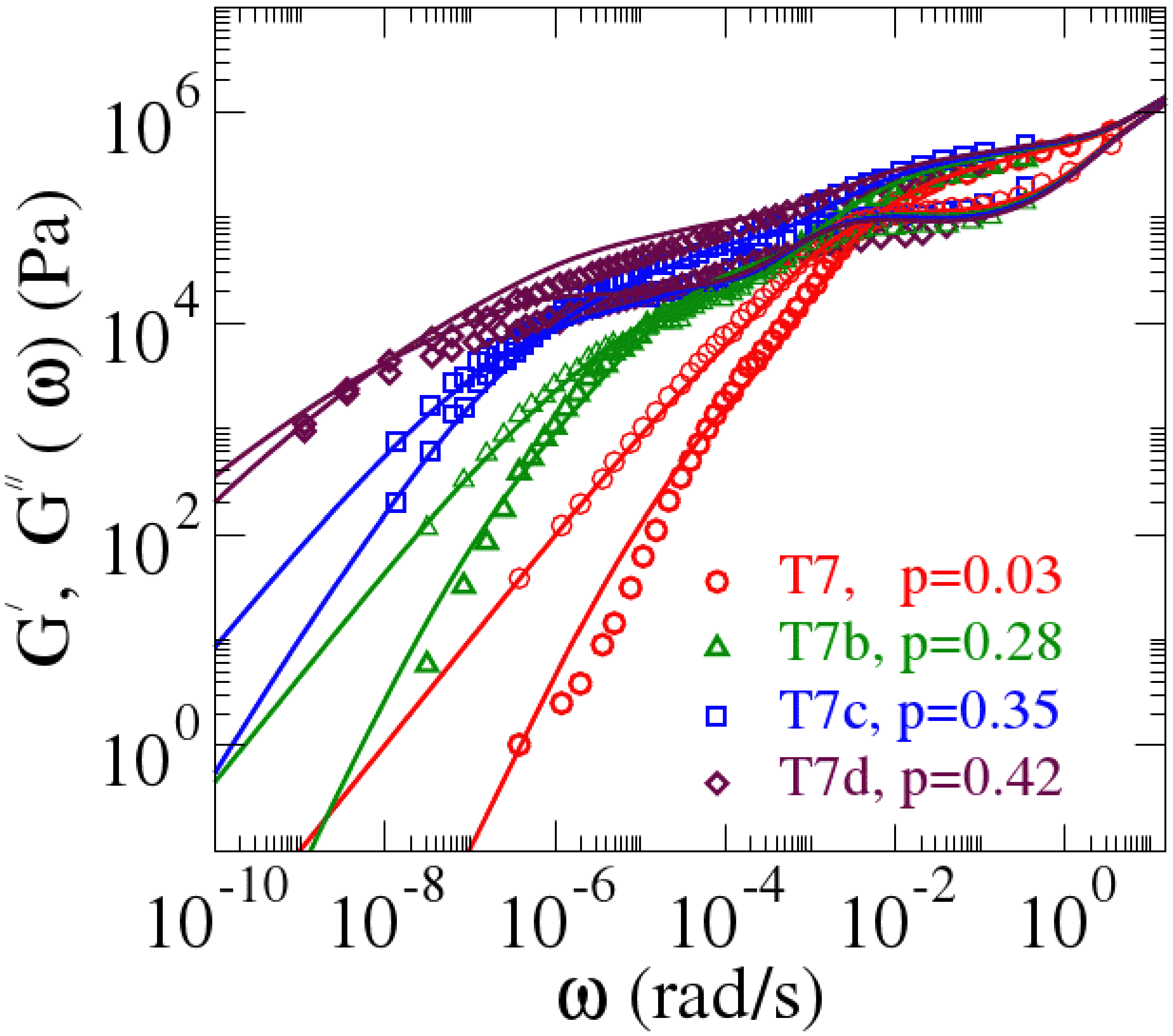
End-linked star polymers





PPS star with SH end-group
End-linked with di-isocyanate (HMDI)

Nicol, Nicolai, Durand; Macromolecules 34, 5205 (2001)



GPC estimates:

(0)

(0.24)

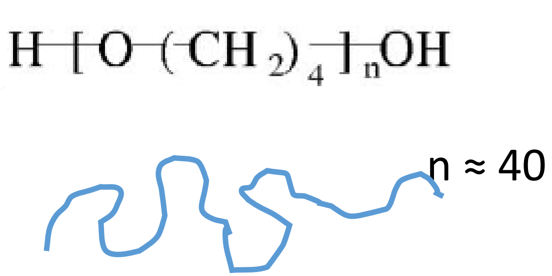
(0.35)

(0.41)

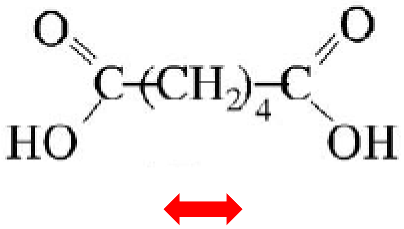
Trace oxygen can link some of the stars in parent resin.

den Doelder, Das, Read; Rheo Acta **50**, 469 (2011)

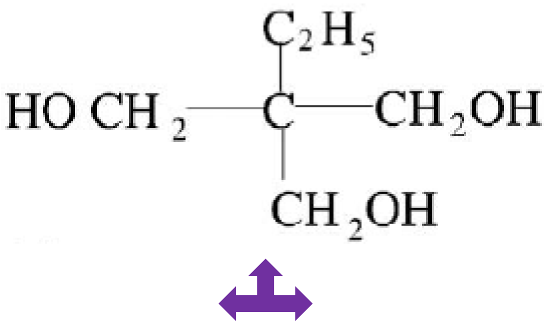
Randomly branched polymer from vulcanization class



PTMG

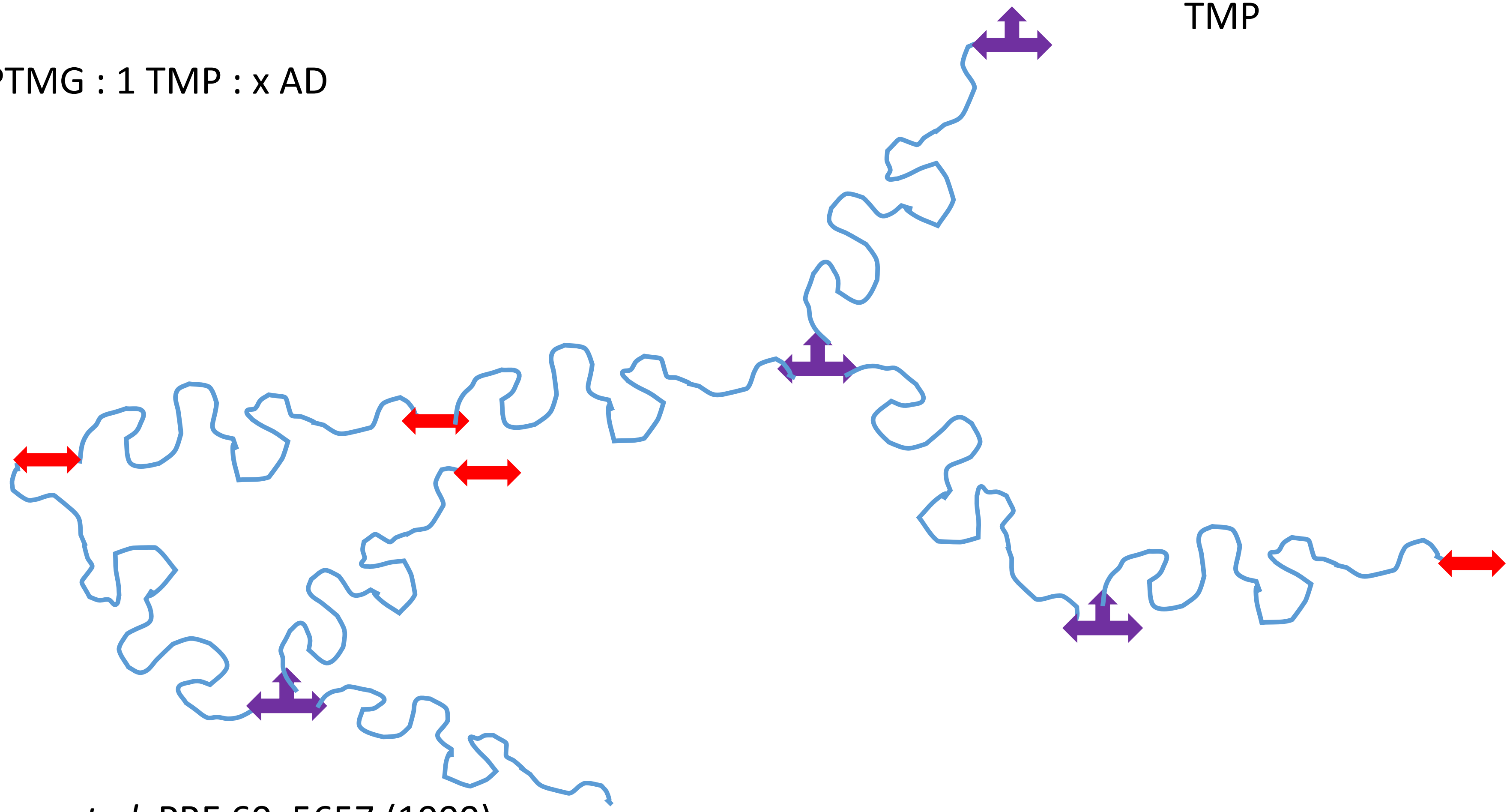


AD



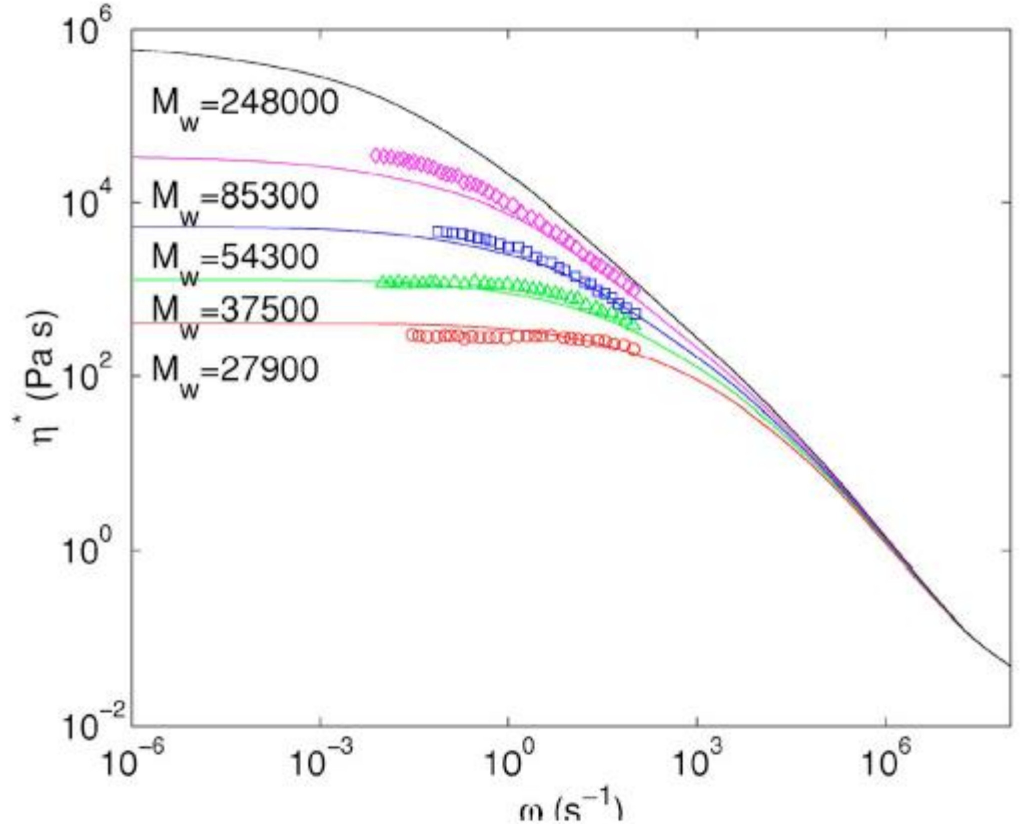
TMP

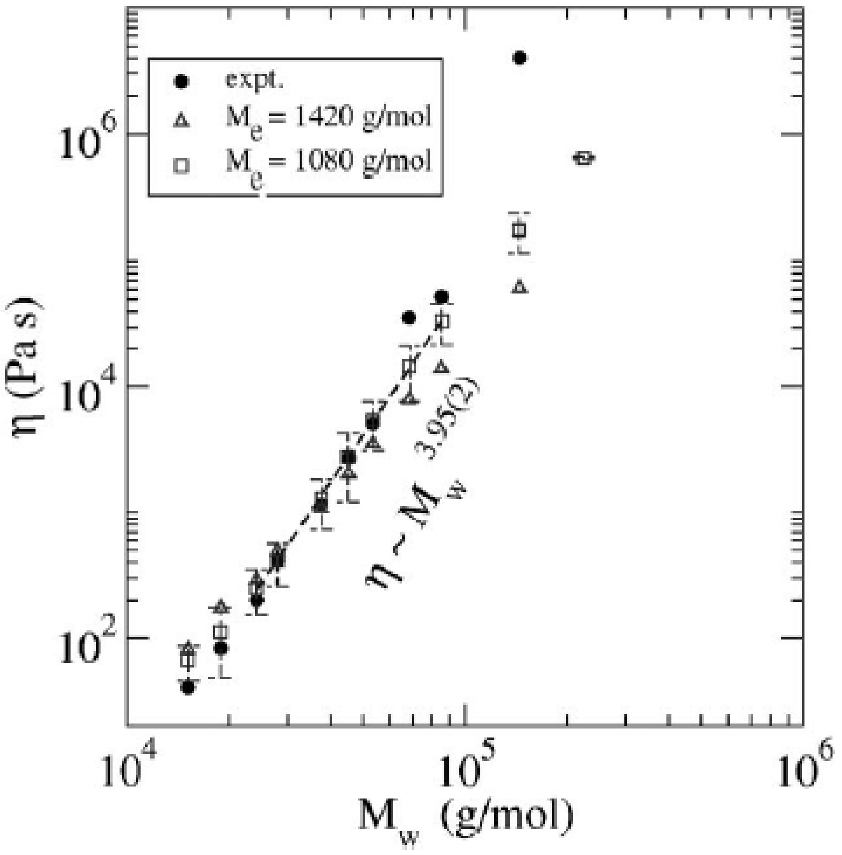
3 PTMG : 1 TMP : x AD



Lusignan *et al.* PRE 60, 5657 (1999)

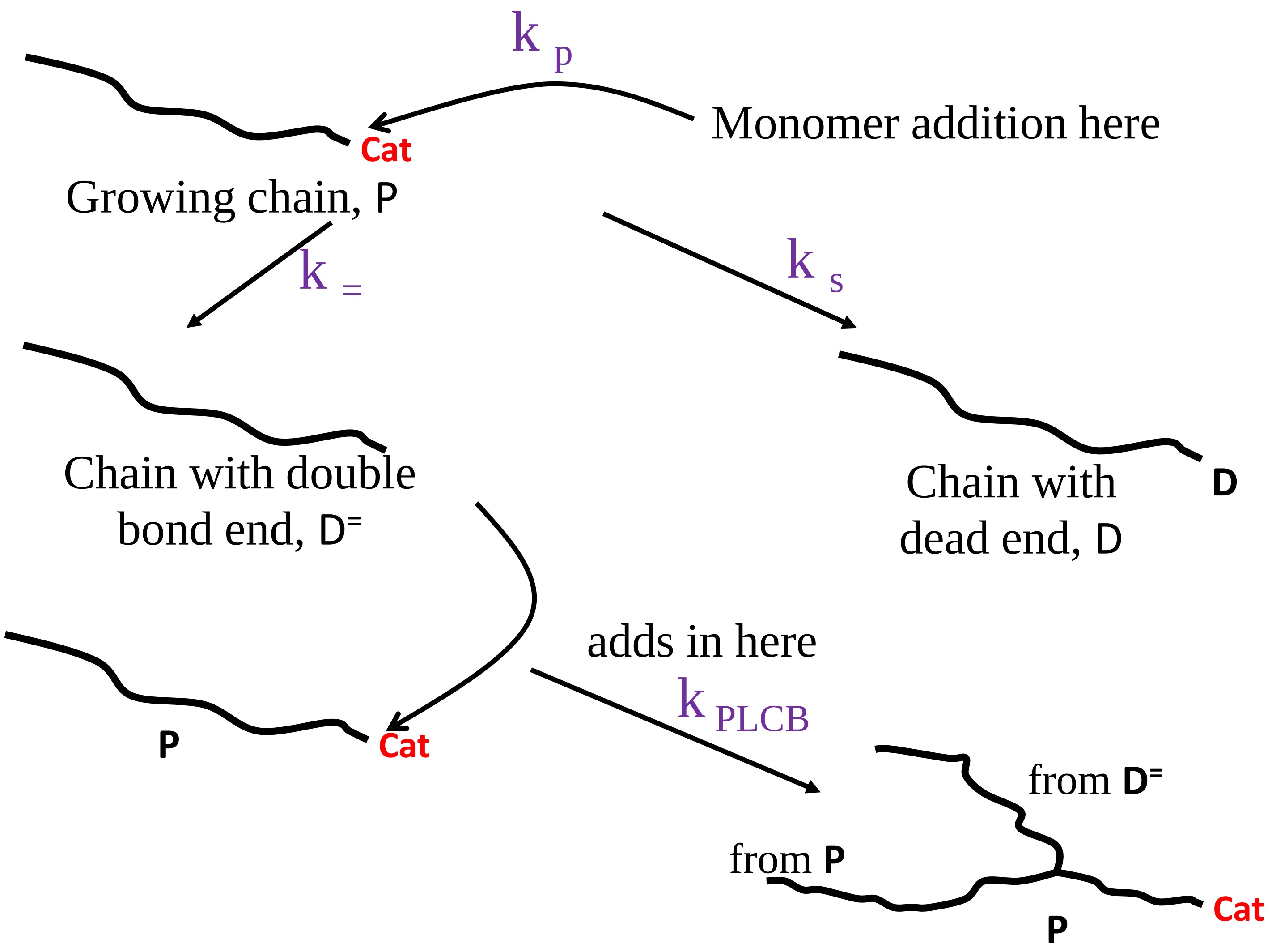
Fit structural data to find rate constants.



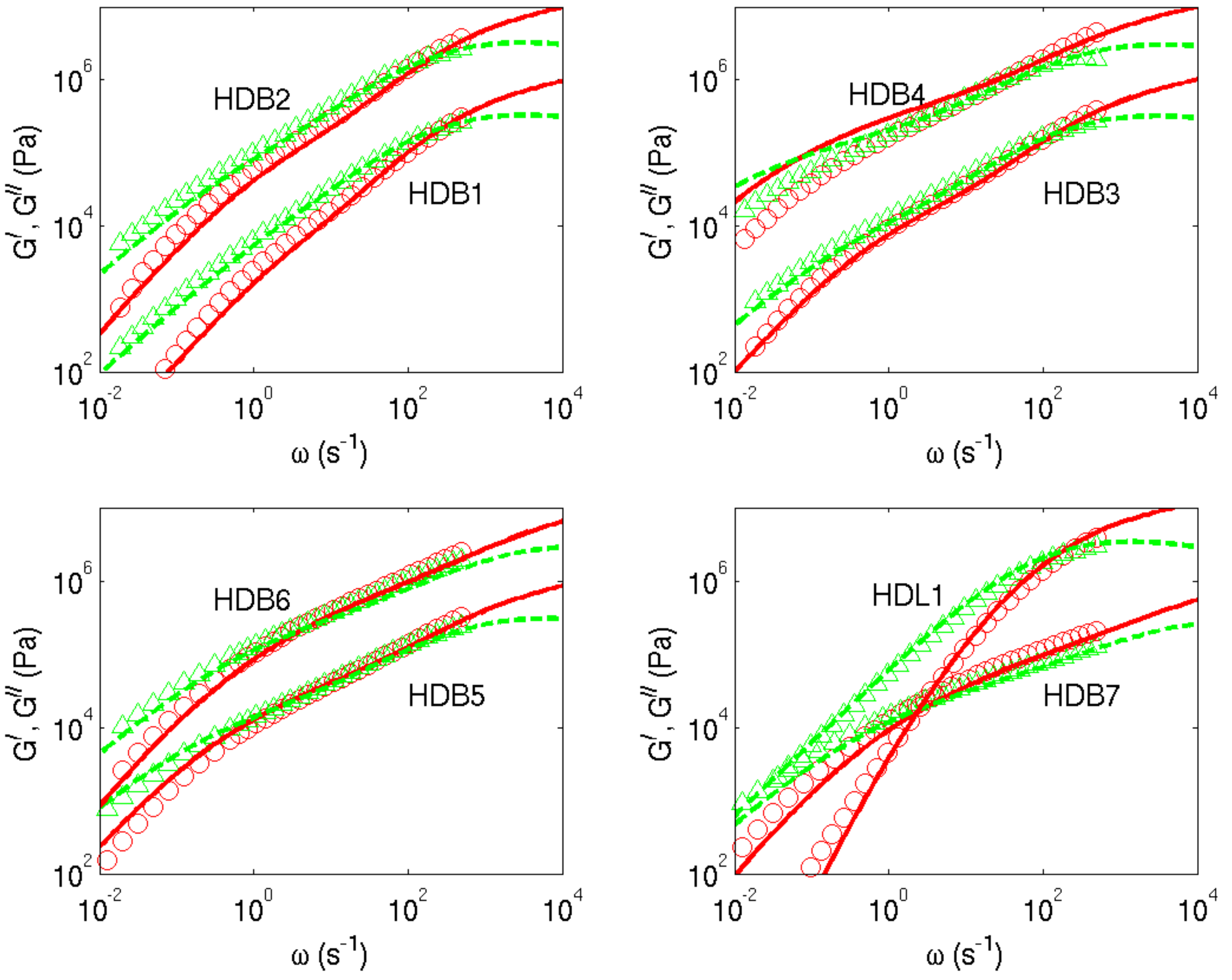


Das *et al.* PRE 74, 011404 (2006)

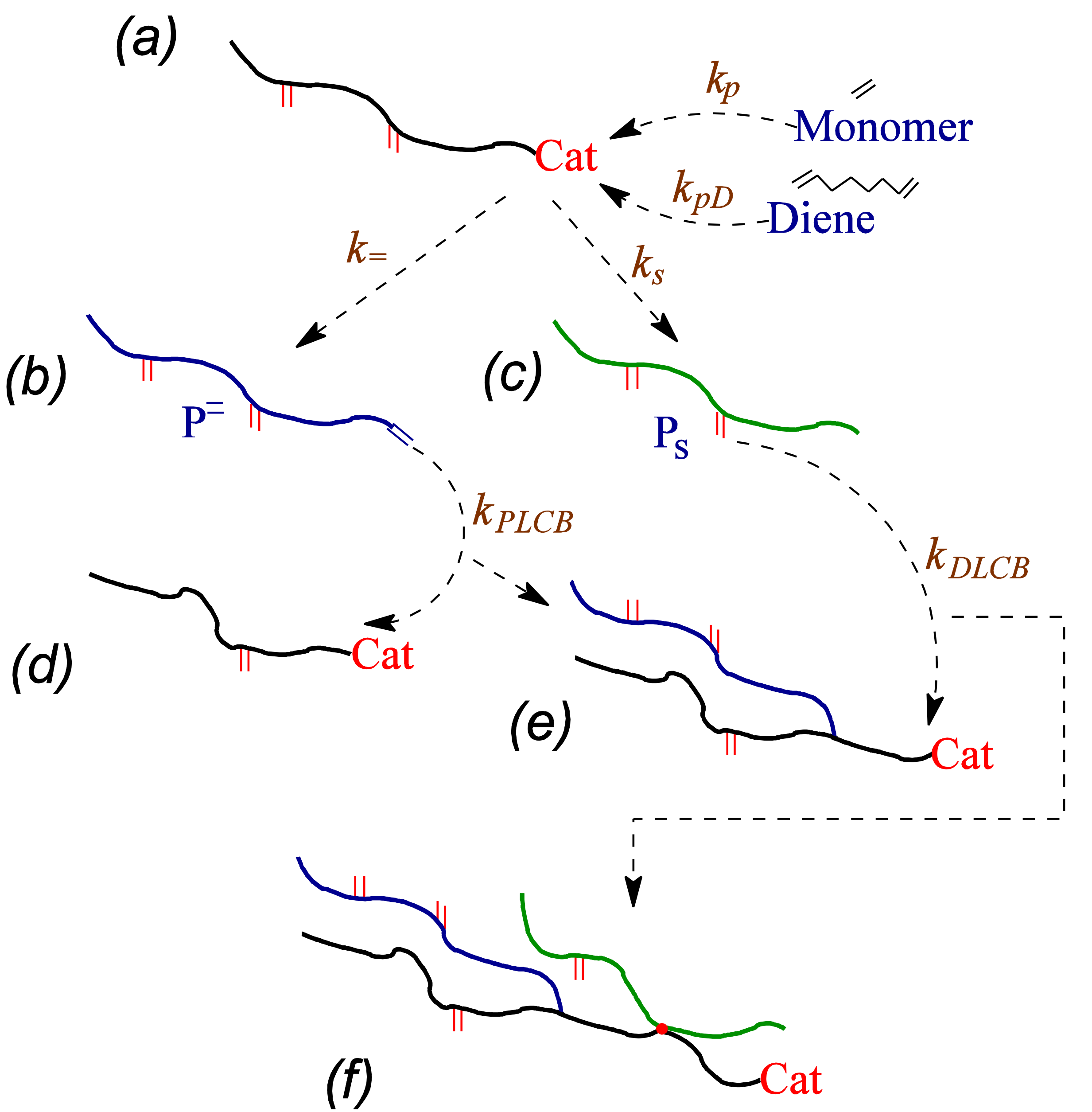
HDPE with metallocene catalyst



Convert rate constants to probabilities.
Use recursive Monte Carlo to generate representative molecules.

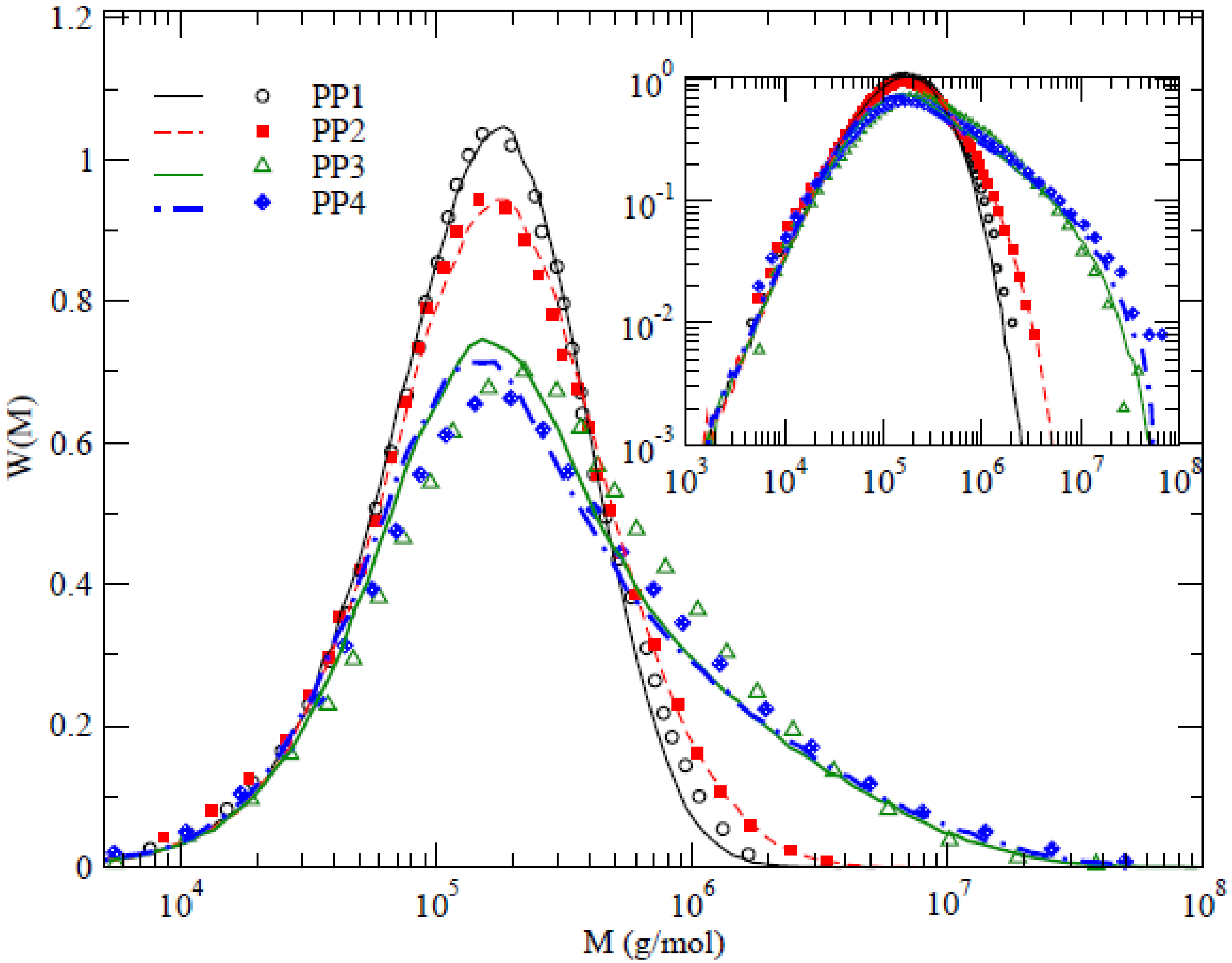


Dow HDPE series

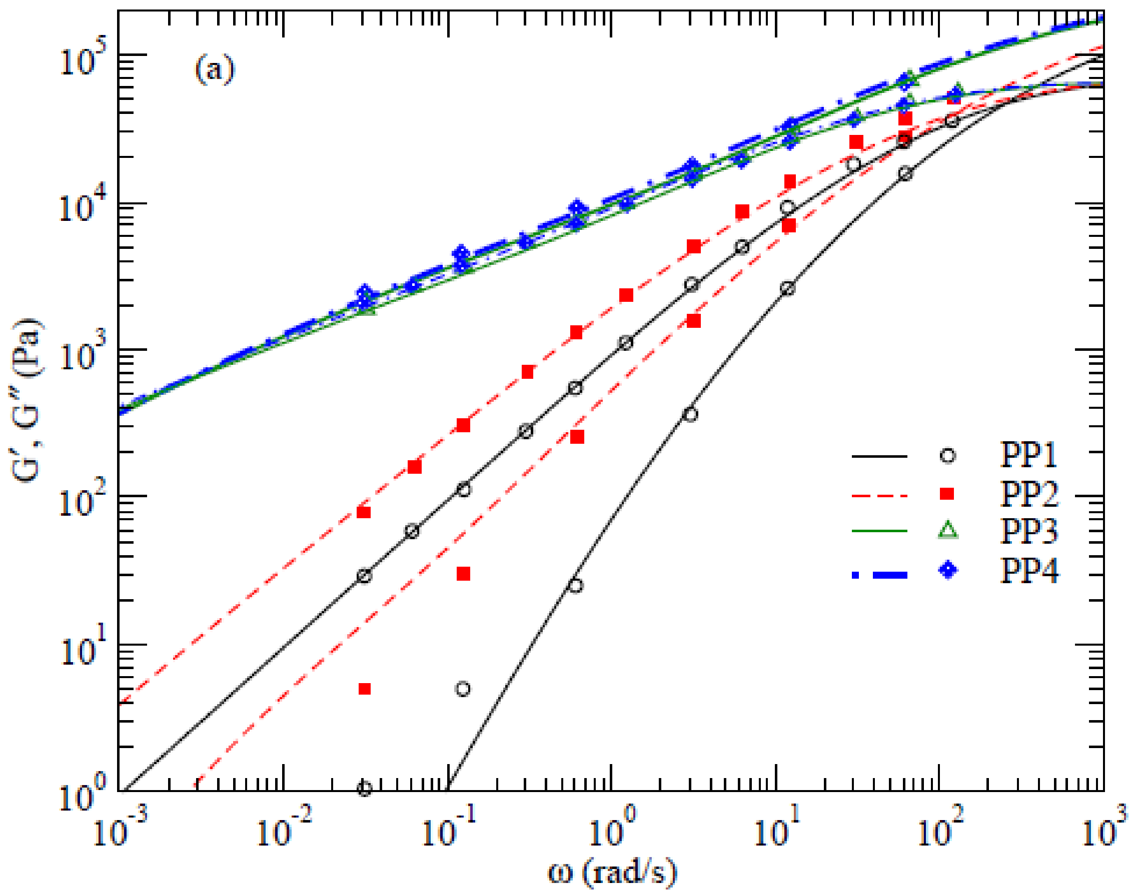


Chains with terminal double bonds are rare. Copolymerize with diene to have lots of pendant double bonds.

Propylene-diene

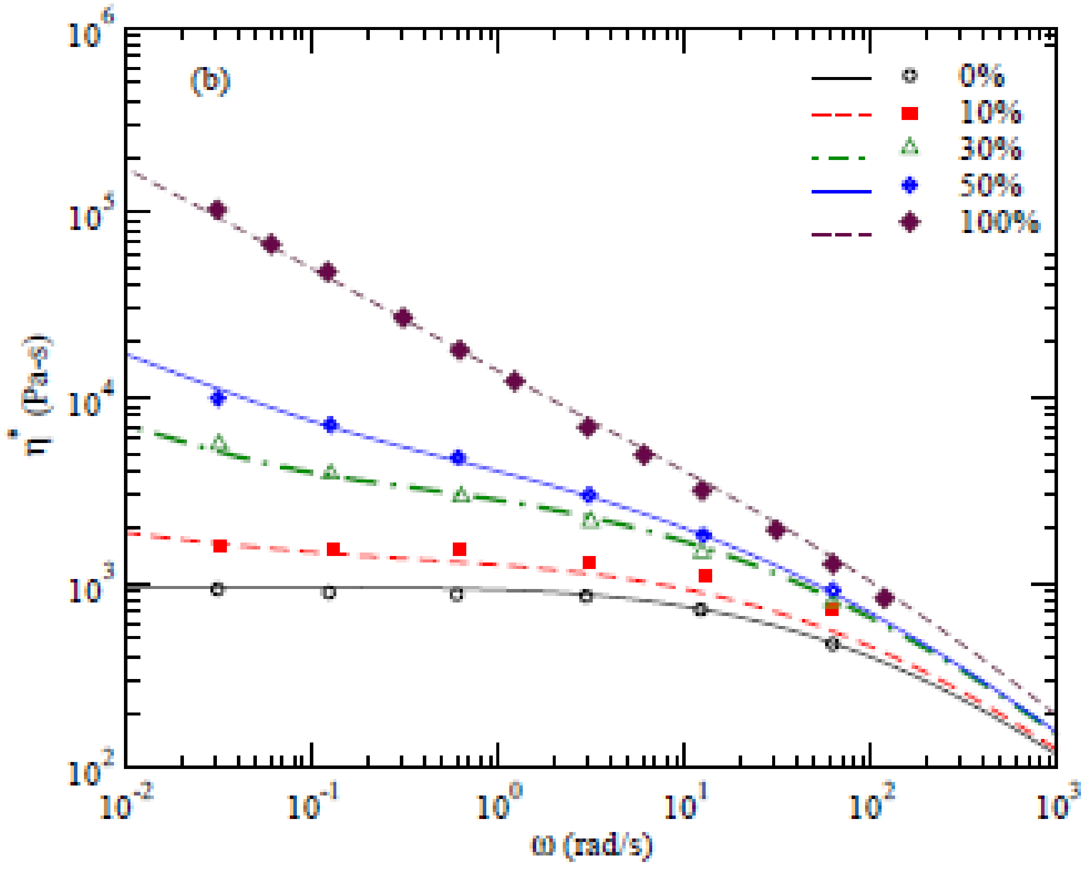


data from Ye et al., Ind. Eng. Chem. Res. 43, 2860 (2004)



Since we have the molecules, we can calculate SAOS response.

Blend our numerical resins numerically and compare with experimental blends...



Das, Read, Soulages, Shirodkar; Macromolecules, 47, 5860 (2014)

How to define gel-point?

Reduced distance to gel-point: $$\varepsilon = \frac{[D]_c - [D]}{[D]_c}$$

Molar mass develops a power-law tail: $$\phi_N(M) \sim M^{-\tau} f\left(\frac{M}{M_{char}}\right)$$

Largest molar mass where the power-law is valid diverges: $$M_{char} \sim \varepsilon^{-1/\sigma}$$

Low-order molar mass moments may remain finite depending on the exponent τ

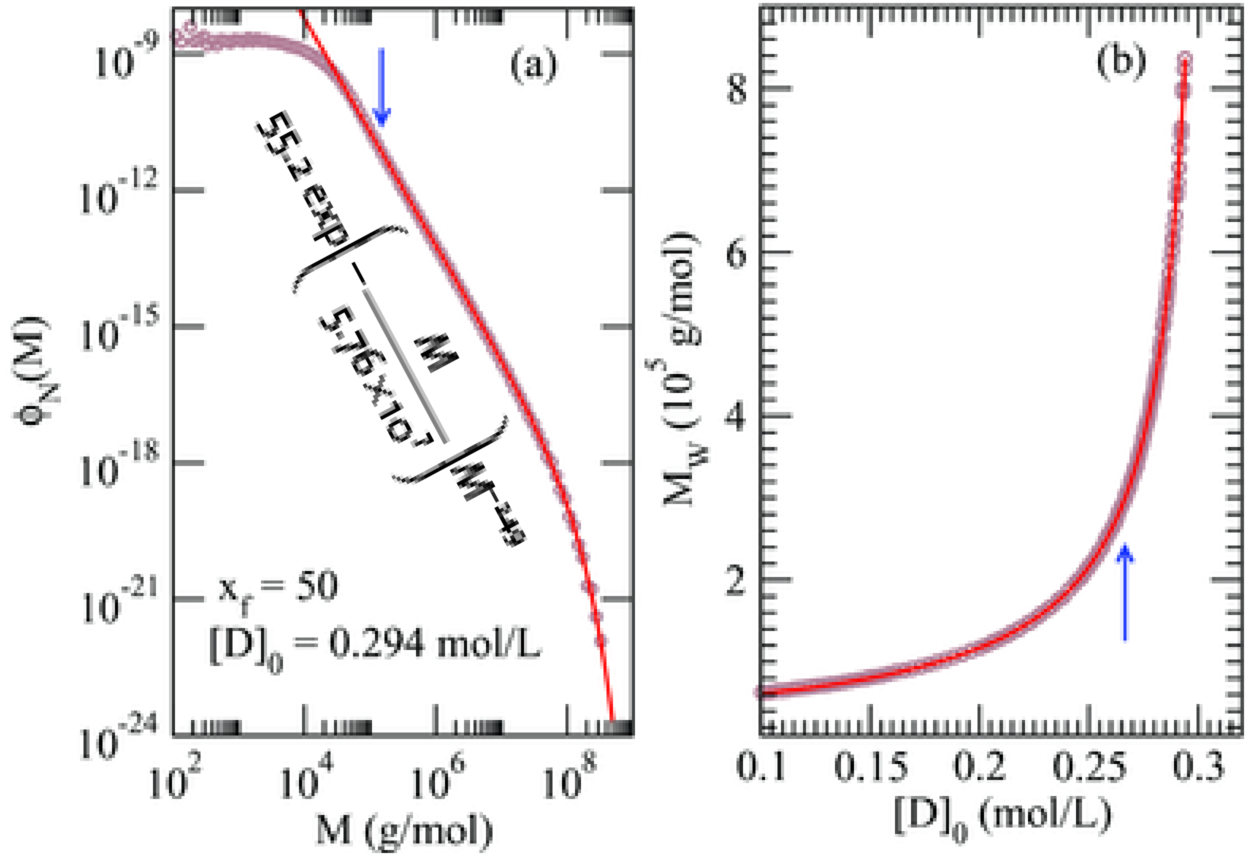
Polymer community often accepts that gelation means diverging M_W (2^{nd} moment)

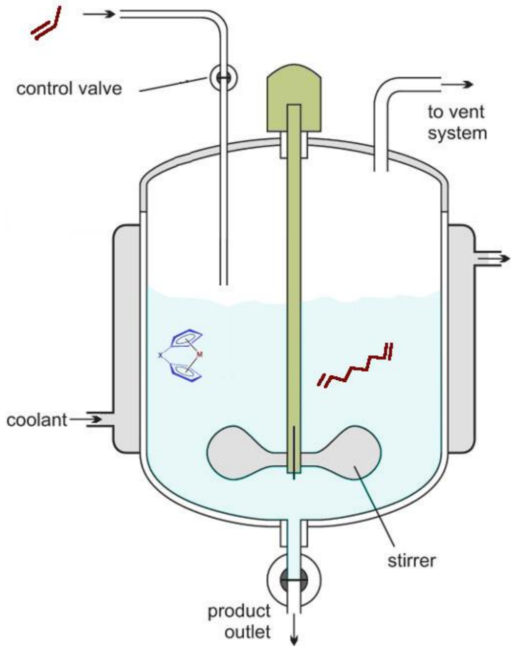
Semibatch reactor:

Mean-field gelation (percolation on Bethe lattice) remains valid

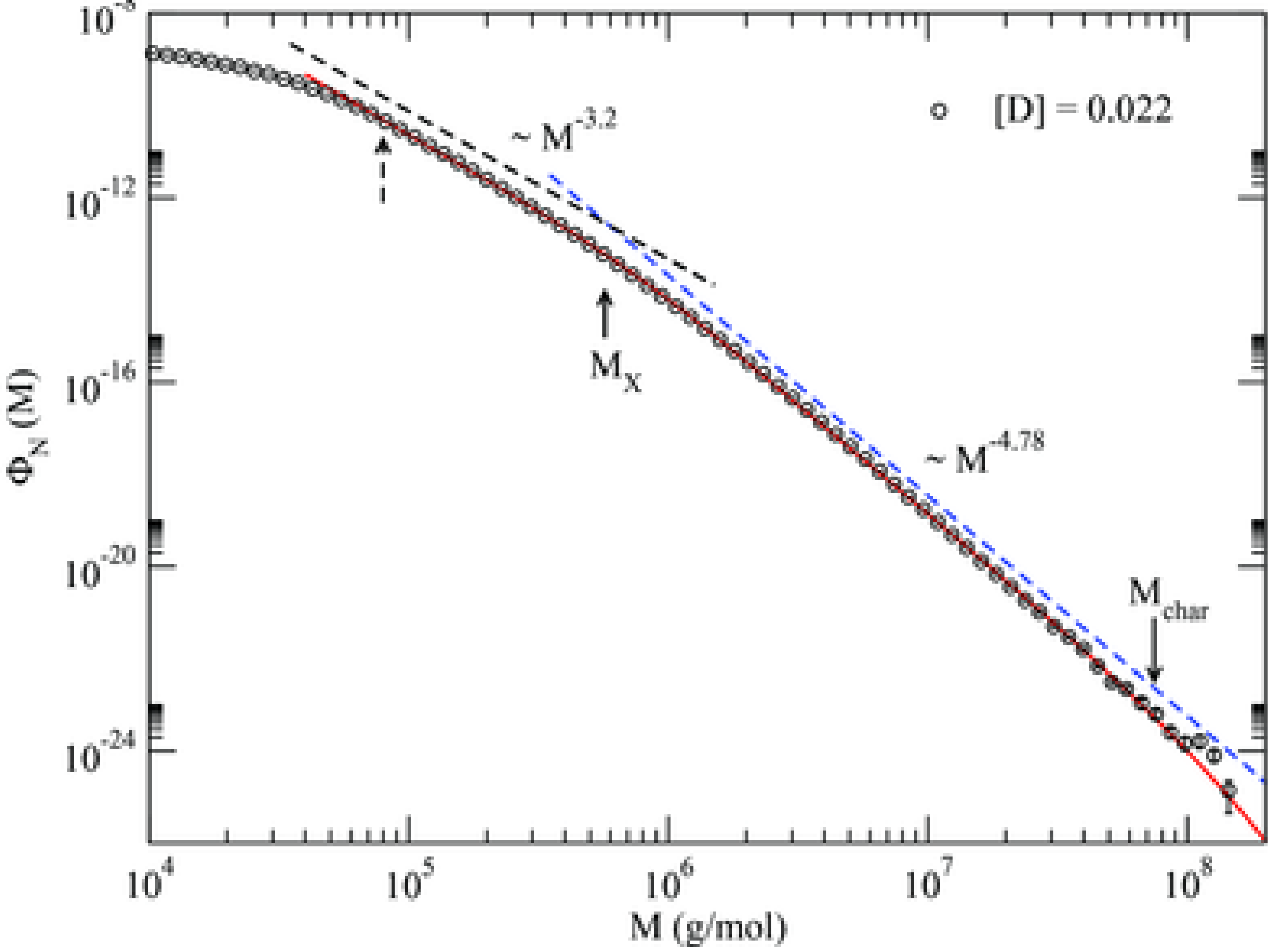
$\tau = 5/2$.

M_W diverges (but M_N remains finite) at the gel-point





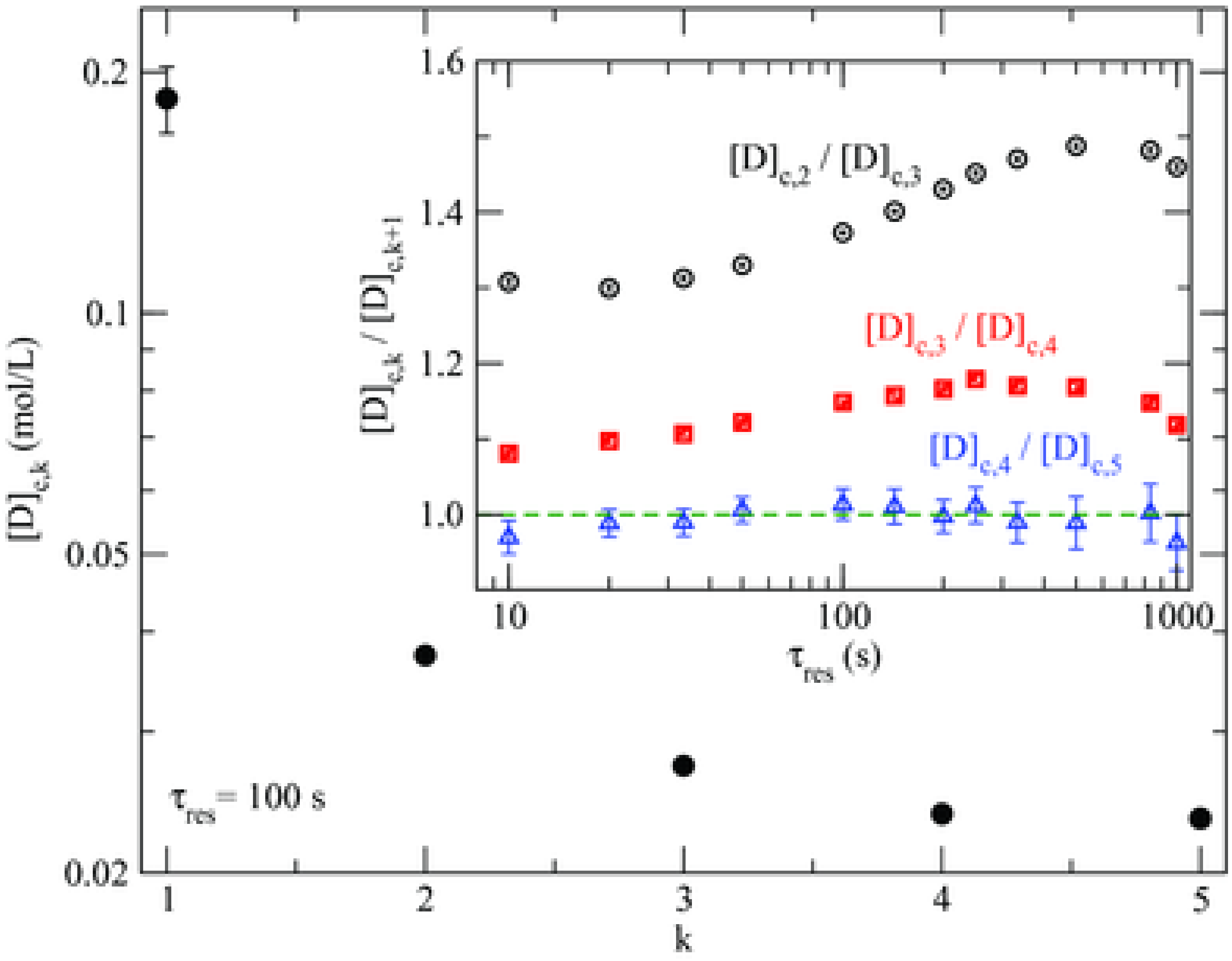
Continuous Stirred Tank Reactor



τ = 4.5

Valid only very close to gelation

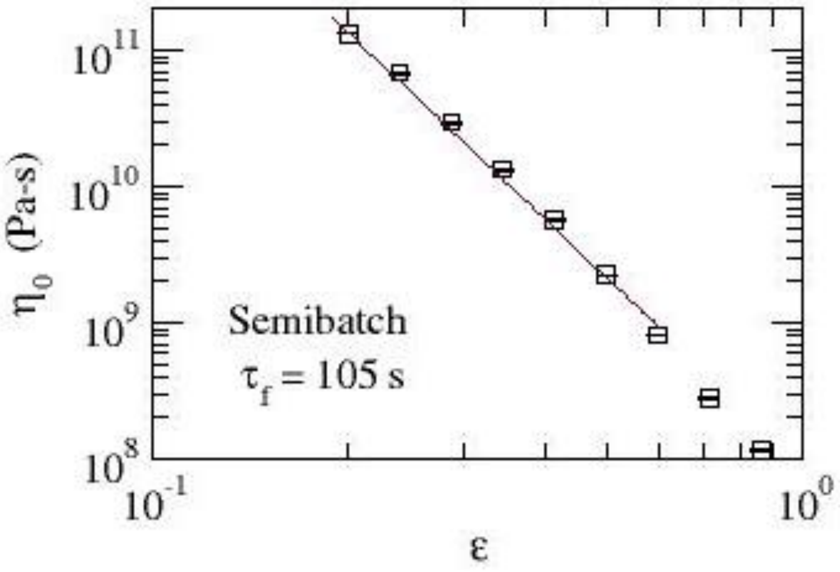
First moment to diverge is the 4th moment

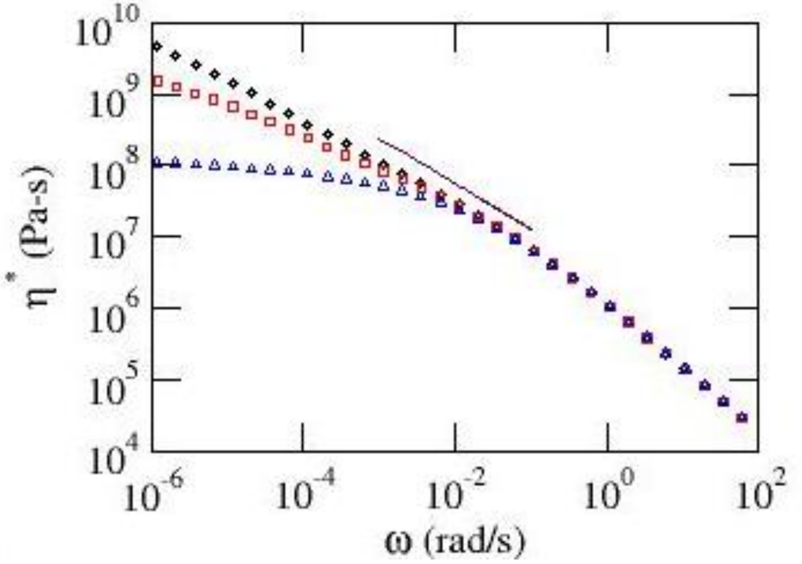


Apparent gel-point from extrapolating from k^{th} moment

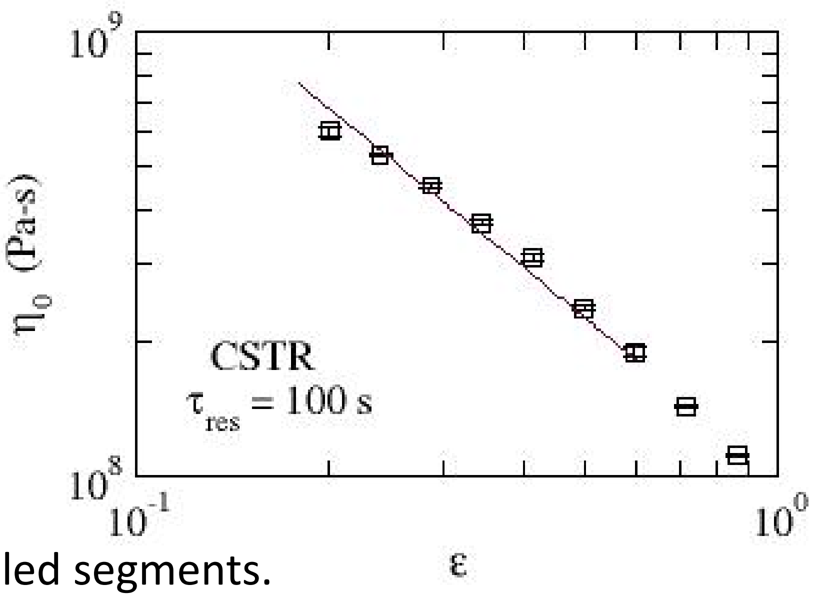
$$G(t) \sim t^{-u}$$

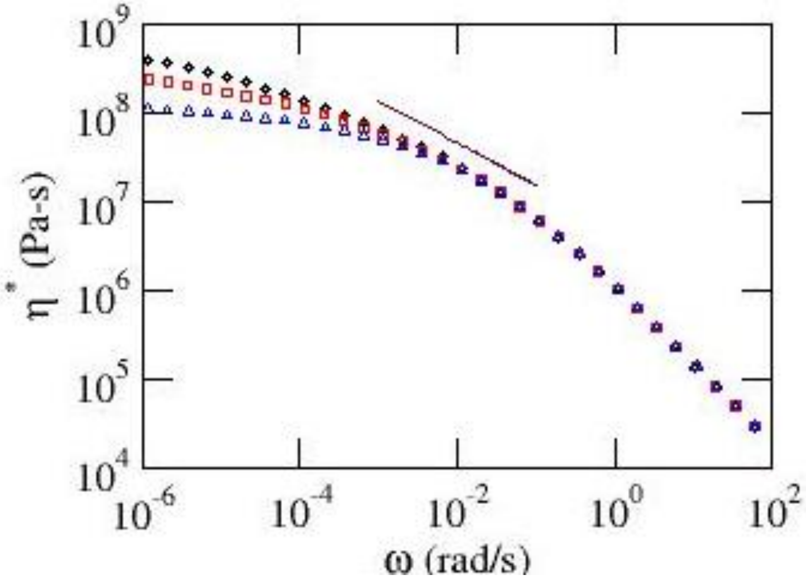
$$\eta_0 \sim \varepsilon^{-s}$$



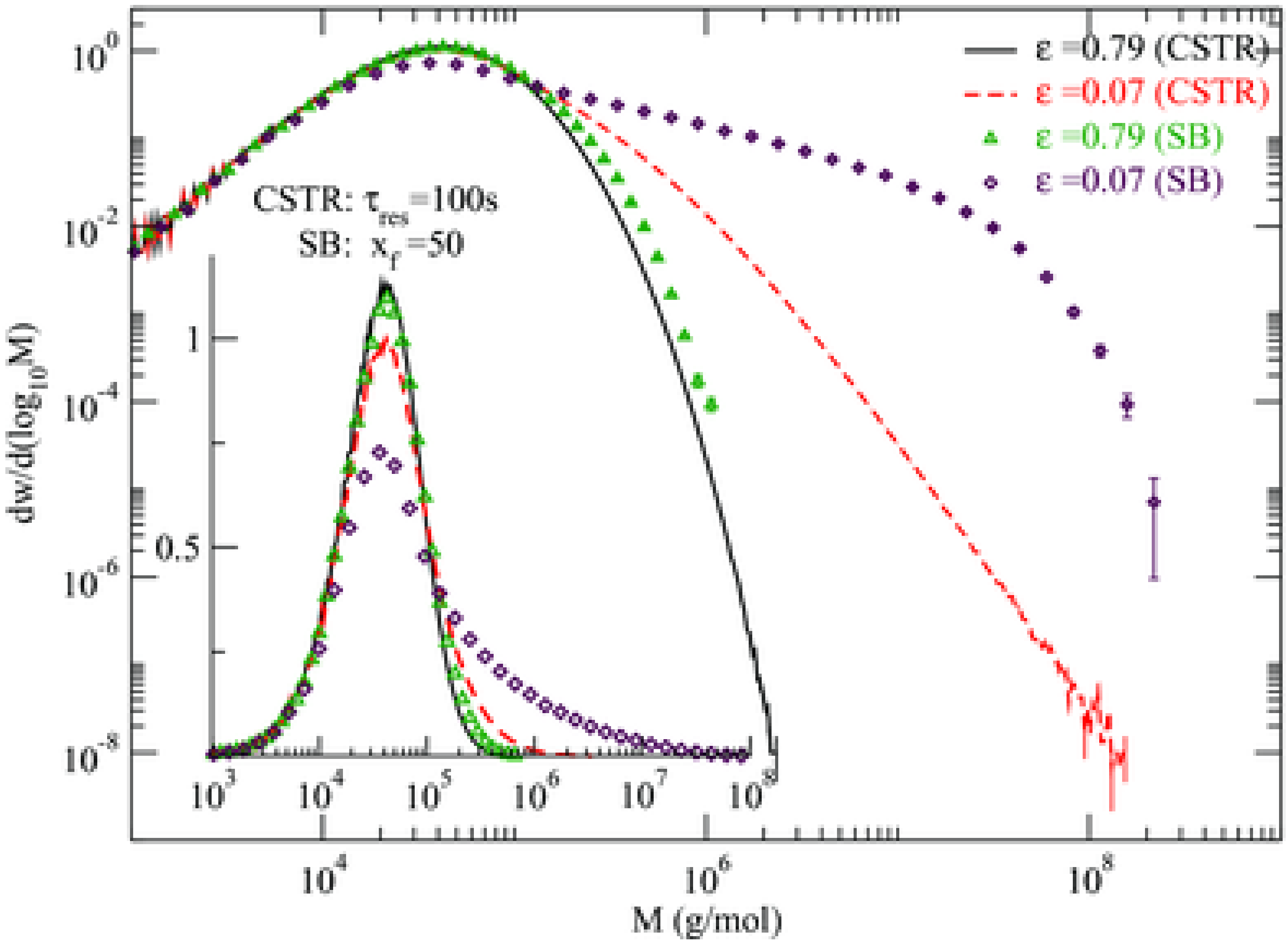


Semibatch: s = 4.5
(typical of gelation with entangled segments)





CSTR: s=1.2
(rather like gelation with unentangled segments.
Long time dynamics is constraint release Rouse having same form as short segments)

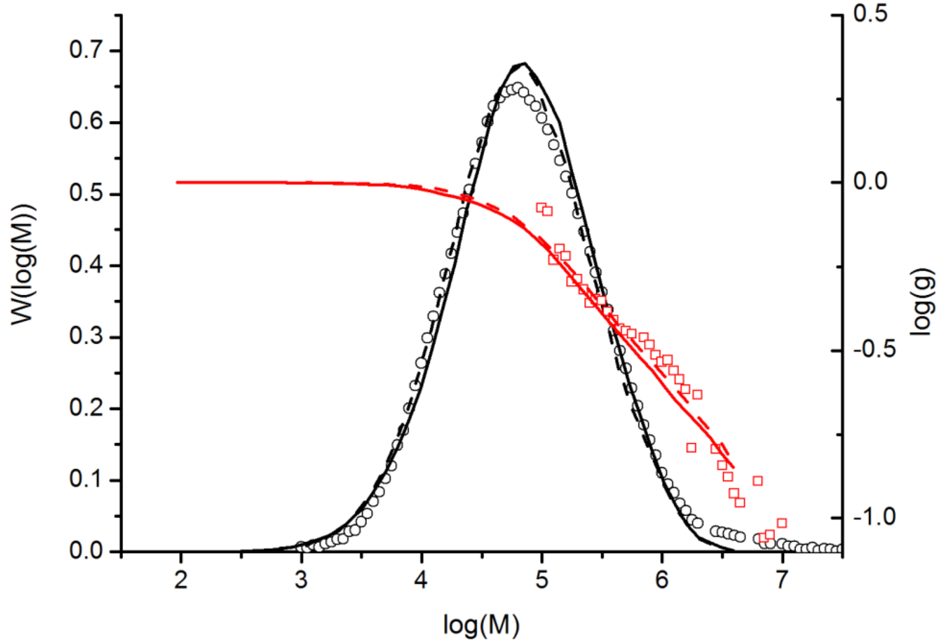


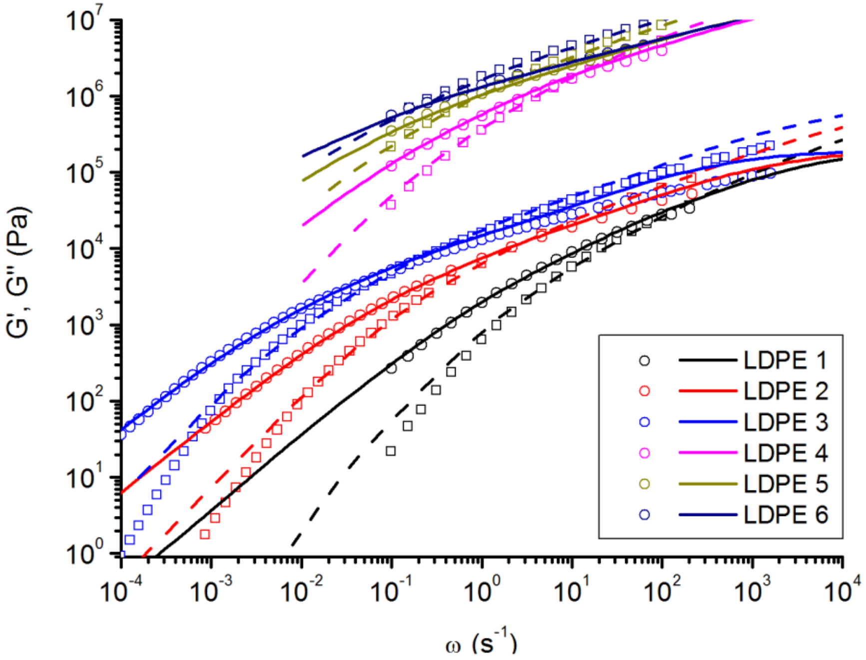
Experimentally should be hard to detect gelation in CSTR
Exponential distribution of residence time.
More time a rare molecule remains in the reactor, more branched it becomes.

LDPE: the stuff plastic bags are made of

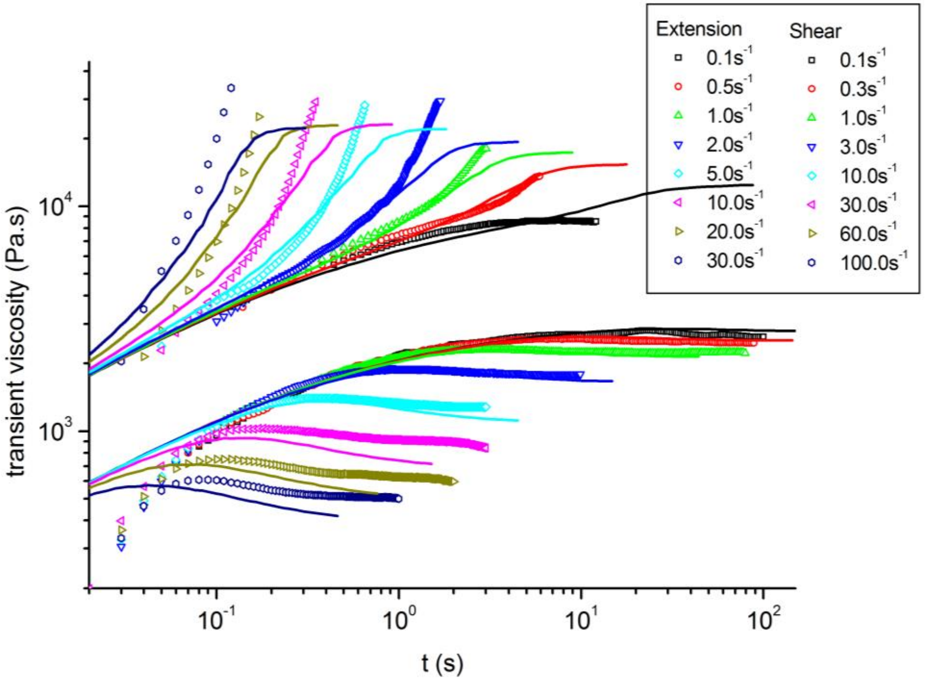
Free radical polymerization at high pressure

Initiator ➔ free radical
Propagation :: add monomers
Termination by combination or disproportionation
Chain transfer leading to side branches or scission

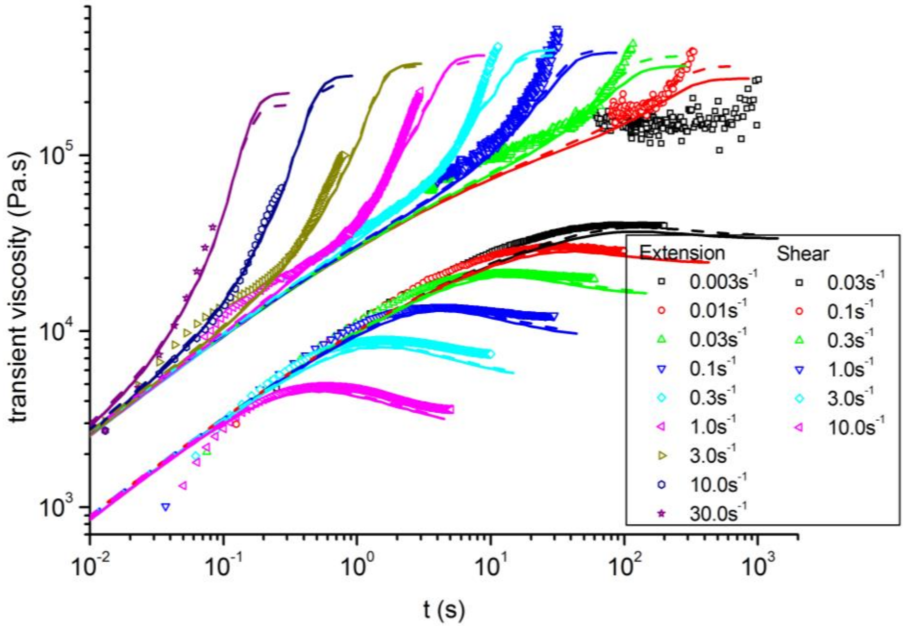




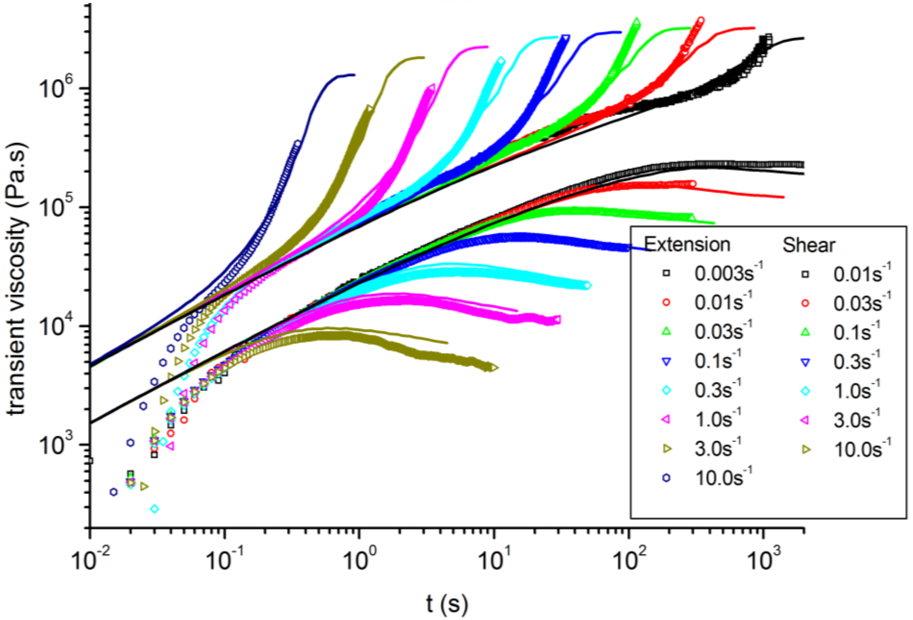
Rate constants by fitting molar mass distribution and the g-factor



transient viscosity (Pa.s)
t (s)
Extension
Shear
0.1s-1
0.5s-1
1.0s-1
2.0s-1
5.0s-1
10.0s-1
20.0s-1
30.0s-1
0.1s-1
0.3s-1
1.0s-1
3.0s-1
10.0s-1
30.0s-1
60.0s-1
100.0s-1



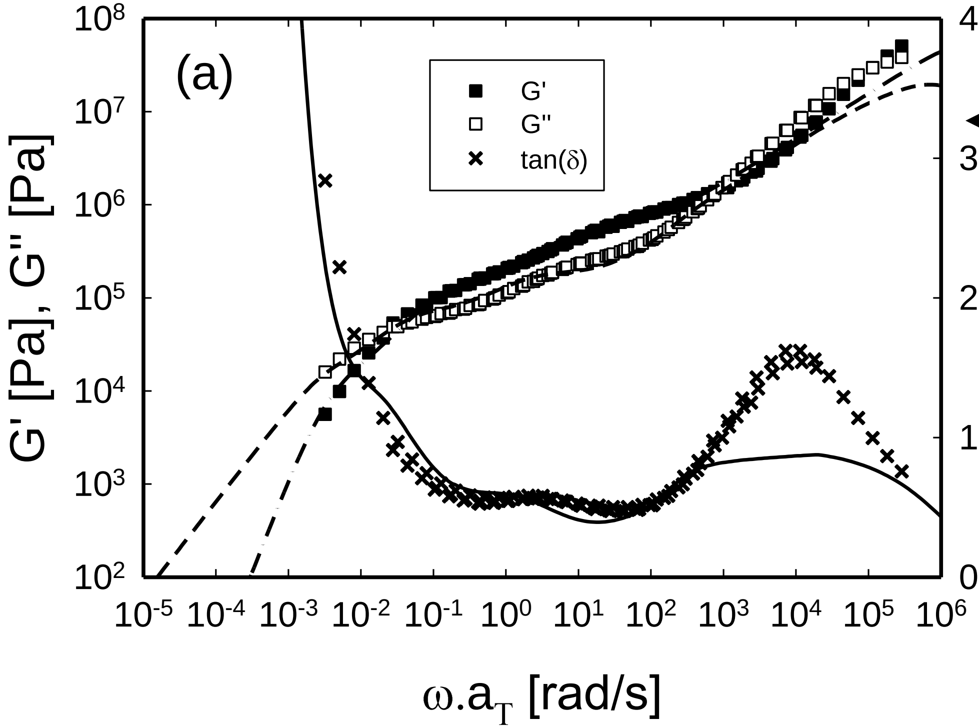
transient viscosity (Pa.s)
t (s)
Extension
Shear
0.003s-1
0.01s-1
0.03s-1
0.1s-1
0.3s-1
1.0s-1
3.0s-1
10.0s-1
30.0s-1
0.03s-1
0.1s-1
0.3s-1
1.0s-1
3.0s-1
10.0s-1

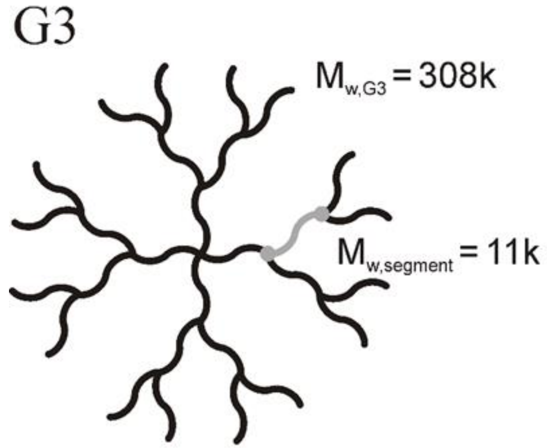


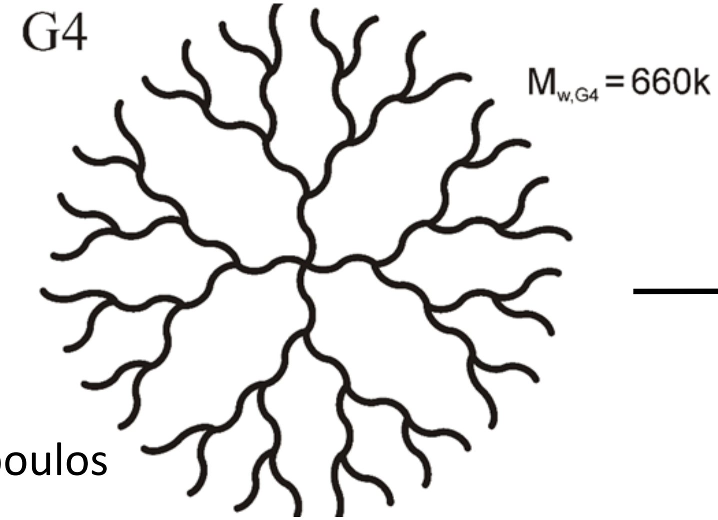
transient viscosity (Pa.s)
t (s)
Extension
Shear
0.003s-1
0.01s-1
0.03s-1
0.1s-1
0.3s-1
1.0s-1
3.0s-1
10.0s-1
0.01s-1
0.03s-1
0.1s-1
0.3s-1
1.0s-1
3.0s-1
10.0s-1

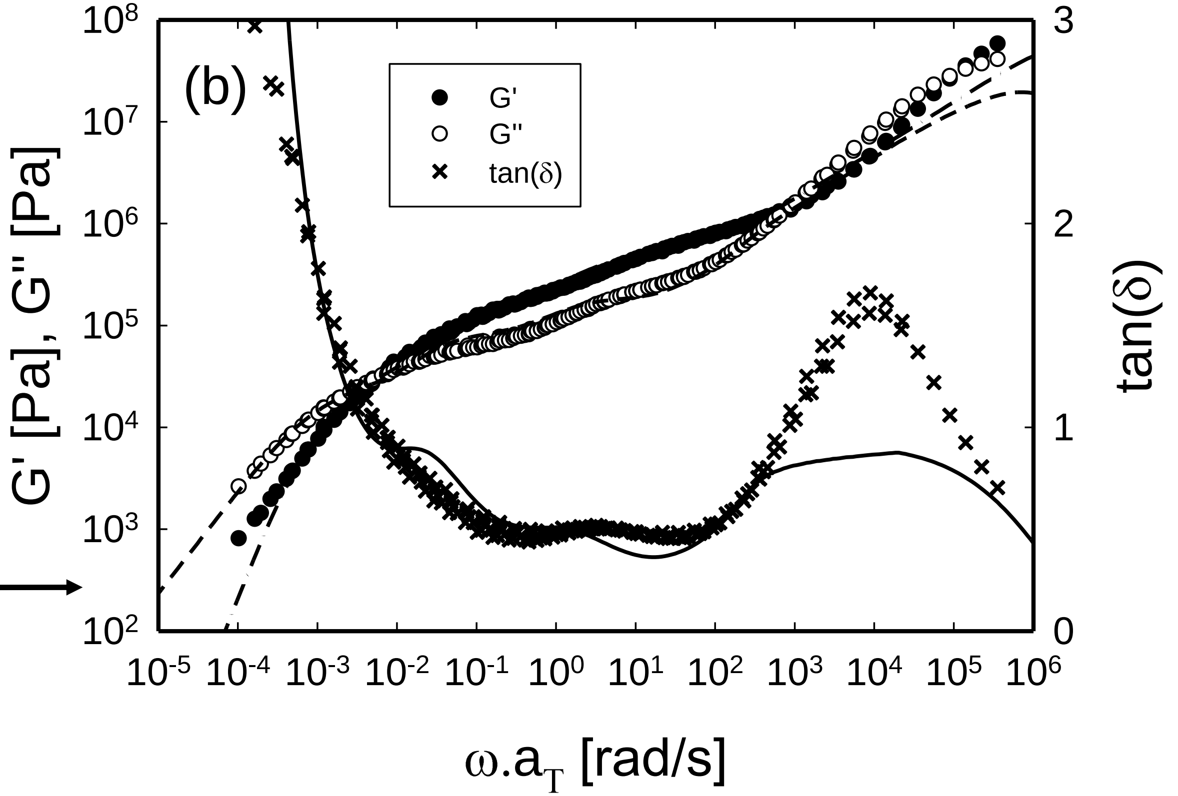
What next?

PMMA Cayley tree

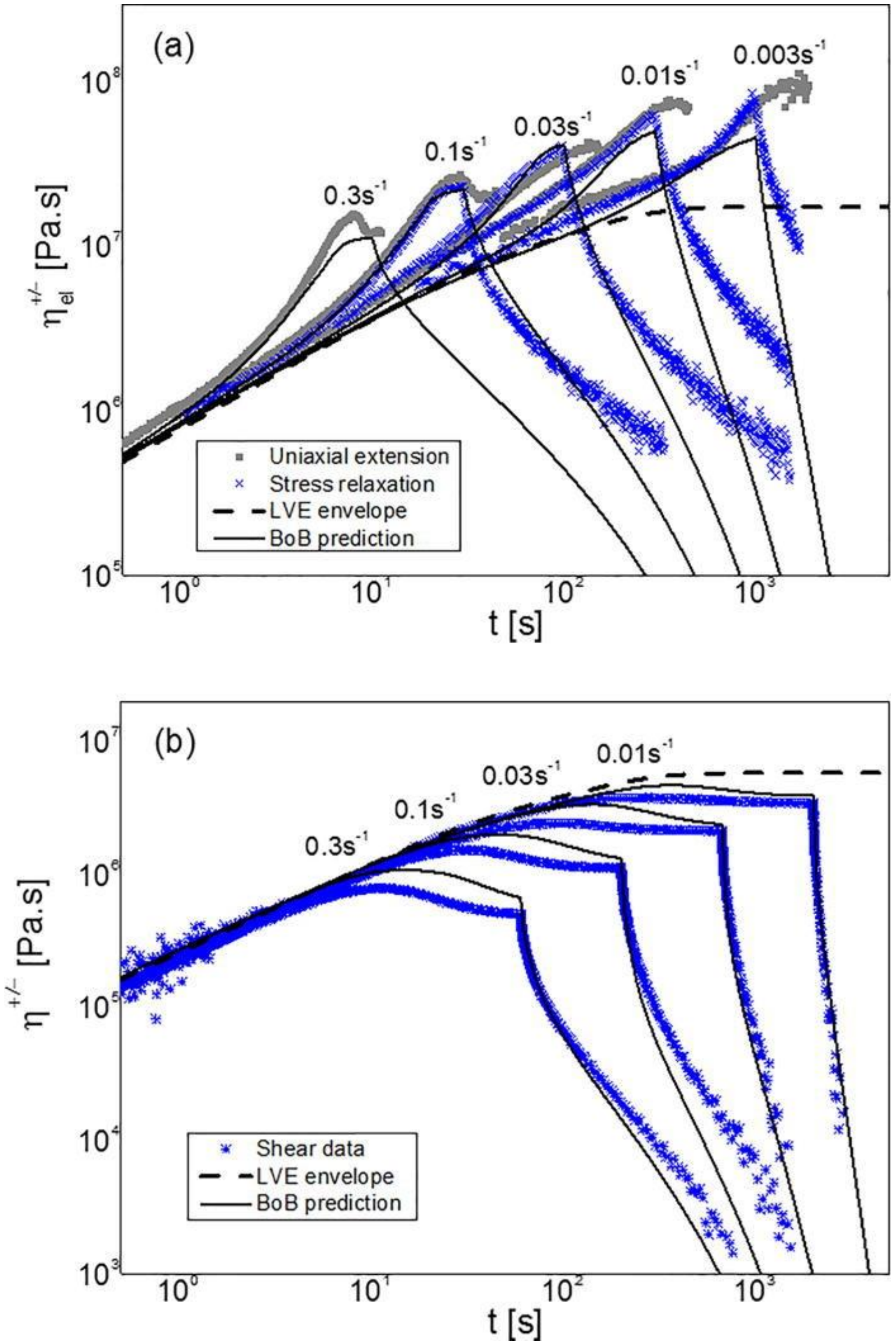


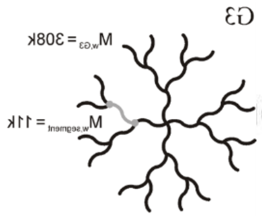


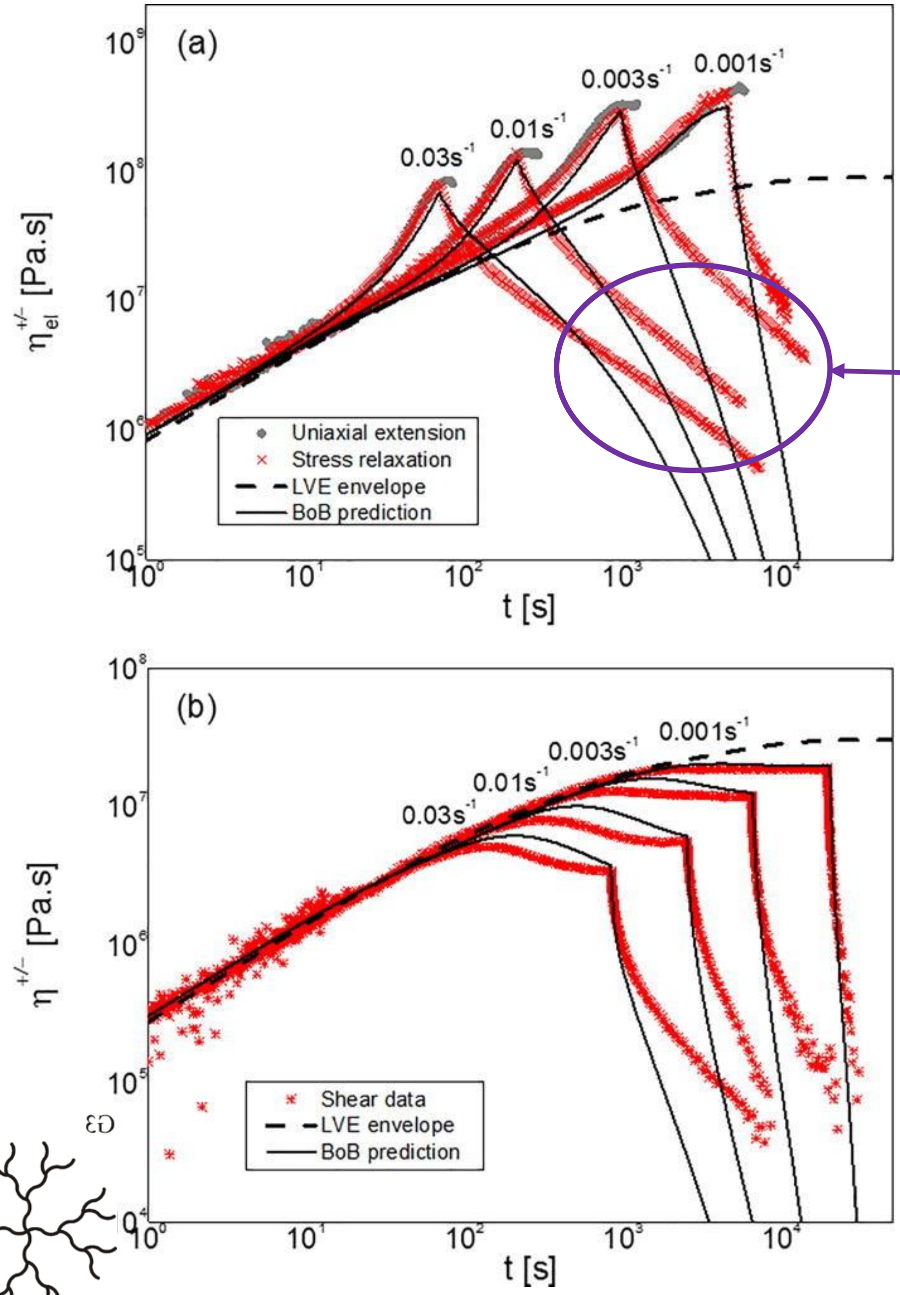




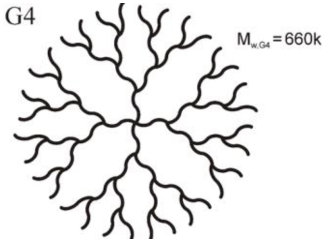
Huang, Costanzo, Das, Vlassopoulos
J. Rheol. 2016

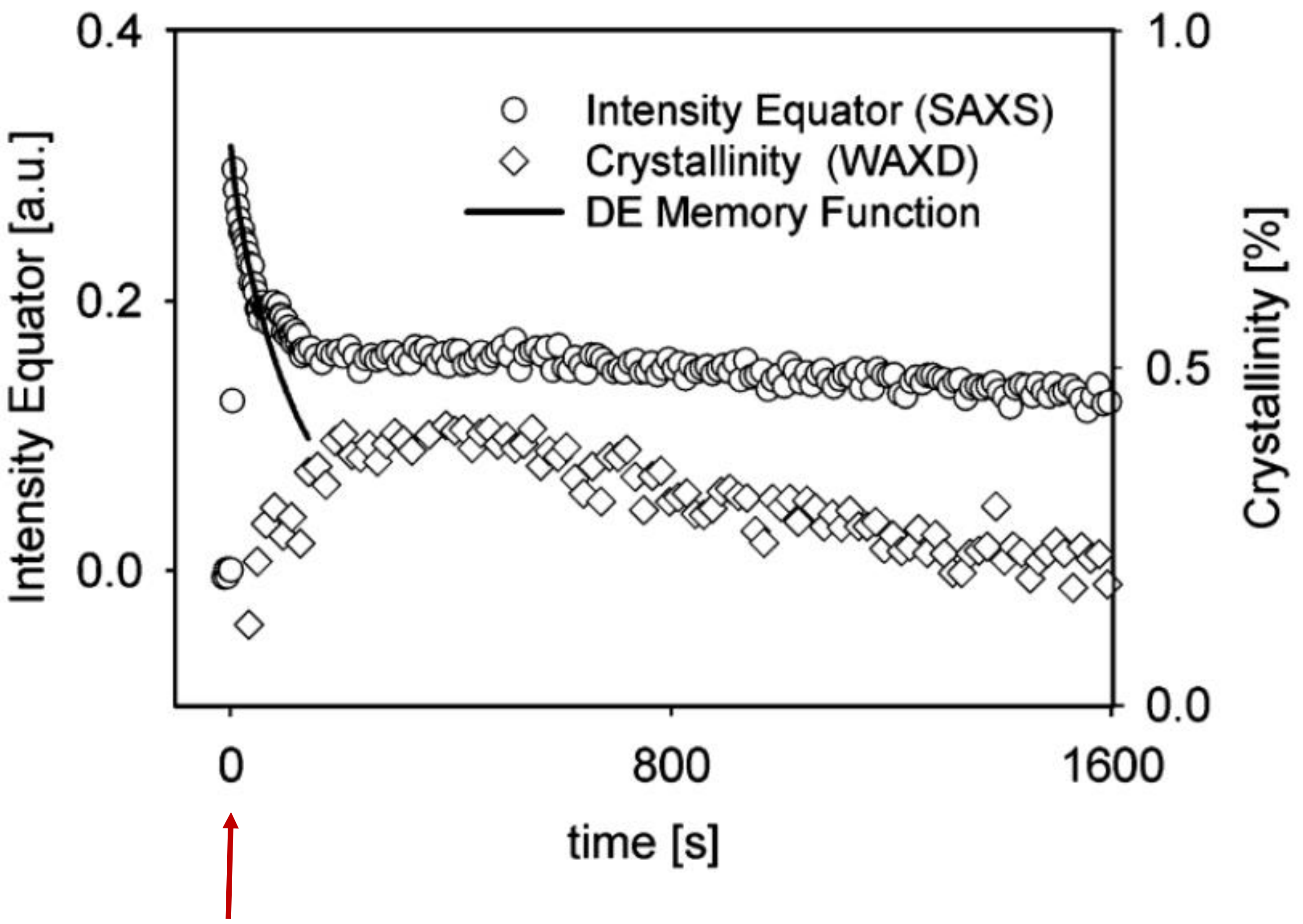






Residual stress with much longer than predicted relaxation time





Step shear above crystallization temp.
Bimodal linear PE.
Shear rate such that high molar mass fraction is stretched.

Balzano et al., PRL 2008

Flow induced crystallization in polymers: from molecules to processing

Richard Graham (Nottingharm) → Molecular dynamics under shear; Kinetic Monte Carlo

Daniel Read, Oliver Harlen, Chinmay Das (Leeds) → Constitutive model for polydisperse melt; Finite volume simulations

Tim Gough (Bradford) → Crystallization experiments; Micro-injection

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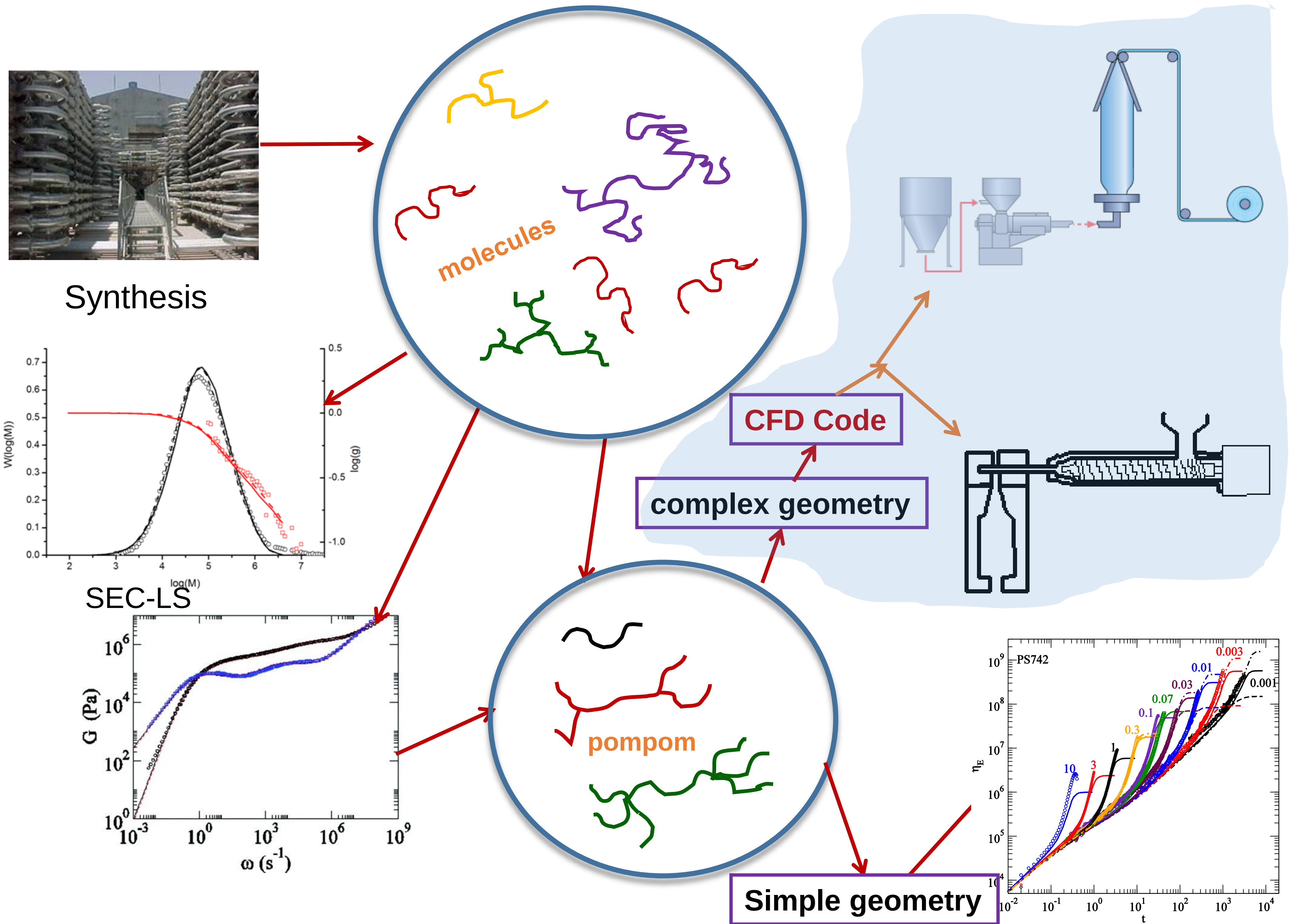
Outlook



Synthesis
molecules
SEC-LS
W(log(M))
log(M)
log(g)
G (Pa)
ω (s^{-1})
pompom
CFD Code
complex geometry
Simple geometry
PS742
η_E
t