Introduction to Extensional Rheology

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DoDyNet - Elementary Modules I

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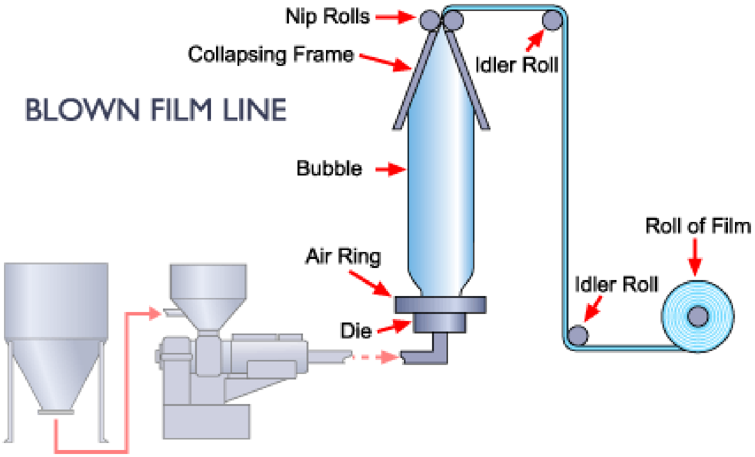
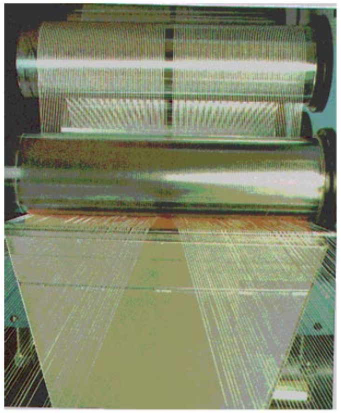
Where do we meet extensional flow?

Do you know this feeling?

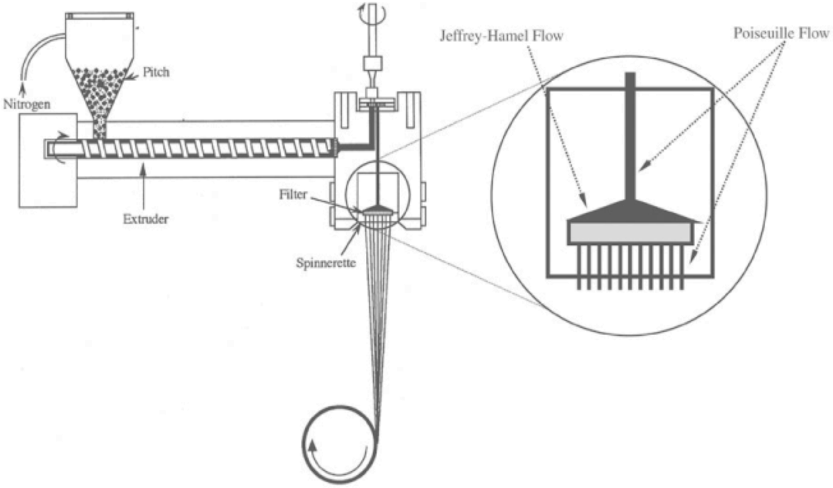
Where do we meet extensional flow?

Film blowing

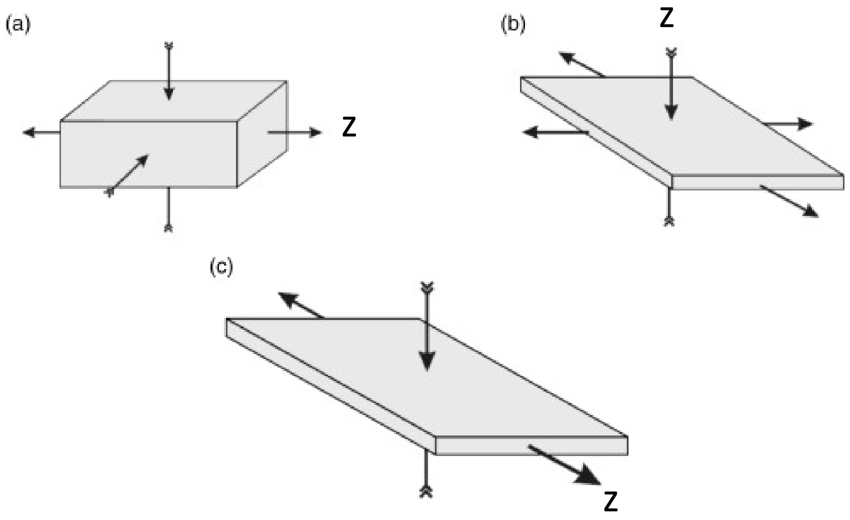




Fiber spinning



Typical extensional flows



Velocity fields: $(\nabla \cdot \mathbf{v}) = 0$

$$v_x = -\frac{1}{2}\dot{\epsilon}(1+b)\,x$$

$$v_y = -\frac{1}{2}\dot{\epsilon}(1-b)\,y$$

$$v_z = +\dot{\epsilon}z$$

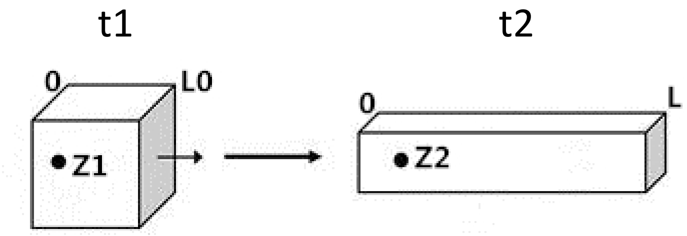
$\dot{\epsilon}$ Strain rate, 1/s

(a) Uniaxial extensional flow $b = 0, \dot{\epsilon} > 0$ Elongational flow

(b) Biaxial extensional flow $b = 0, \dot{\epsilon} < 0$

(c) Planar extensional flow $b = 1$

Uniaxial extensional flow



Velocity fields:

$$v_x = -\frac{1}{2}\dot{\epsilon}\,x$$

$$v_y = -\frac{1}{2}\dot{\epsilon}\,y$$

$$v_z = +\dot{\epsilon}\,z$$

Consider constant strain rate:

- $L(t)$ increases exponentially with time
- The distance between two particles along the stretching direction increases exponentially with time

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$$v_z = \frac{dz}{dt} \qquad \frac{dz}{dt} = \dot{\epsilon} z$$

$$\frac{1}{z} dz = \dot{\epsilon} dt$$

$$\int_{z1}^{z2} \frac{1}{z} dz = \int_{t1}^{t2} \dot{\epsilon} dt$$

$$ln\left(\frac{z2}{z1}\right) = \dot{\epsilon}(t2 - t1)$$

$$\boxed{\frac{z2}{z1} = e^{\dot{\epsilon}(t2-t1)}}$$

Partical A: z_1-->z_2

Partical B: z'_1-->z'_2

$$z'_2 - z_2 = (z'_1 - z_1)e^{\dot{\epsilon}(t_2-t_1)}$$

$$\frac{L}{L_0} = e^{\dot{\epsilon}t} \qquad \ln\left(\frac{L}{L_0}\right) = \dot{\epsilon}t \qquad \dot{\epsilon}t = \epsilon$$

Stretch ratio

Hencky strain

Hencky strain rate (Stretch rate, Elongation rate…)

What happens if we stretch it with constant velocity $\frac{dL}{dt}$

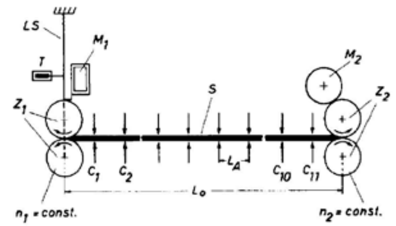
Not convenient to define the velocity field…(homework)

How to produce uniaxial extensional flow experimentally?

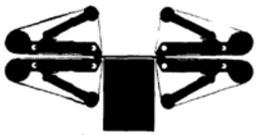
A VERY difficult task…

Historical - Extensional Rheometer Designs:

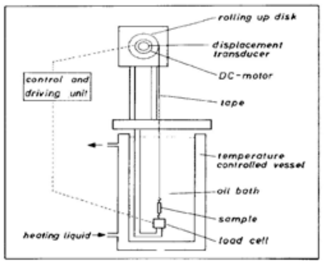
- The Rheometrics Melt Extensiometer (RME) (Improved from Meissner type rheometer)
- The Münstedt Tensile Rheometer (MTR)
- Sentmanat Extensional Rheometer (SER)
- Filament Stretching Rheometer (FSR)



Meissner (1969), (1971), rotary clamp

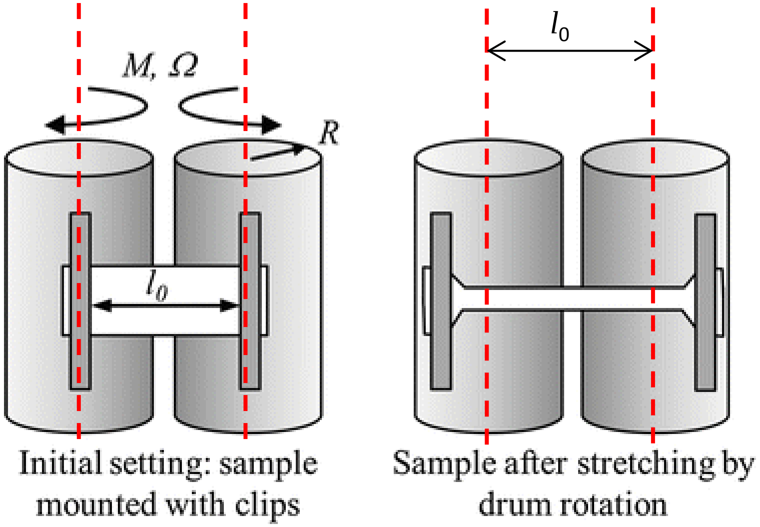


Meissner and Hostettler (1994), conveyor belt

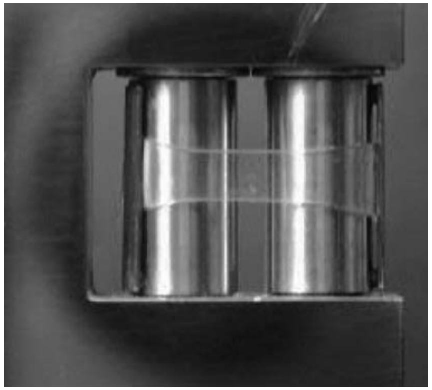


Münstedt and Laun (1979)

SER & FSR



l_0= gage length (initial sample length)
R= drum radius
M= torque
Ω= rotation speed



Sentmanat Extensional Rheometer (SER)
Sentmanat (2004)

$$\dot{\epsilon} = \frac{\Omega R}{l_0/2} = \frac{2\Omega R}{l_0}$$

$$v_z = +\dot{\epsilon} z$$

$$F = M/R$$

A is calculated, not measured

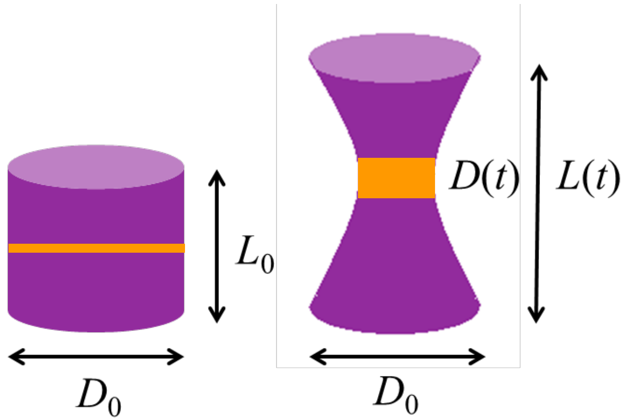
Extensional Viscosity Fixture (EVF)
TA Instruments

$$\sigma_E = F/A$$

(But can be measured, e.g. by camera)

SER & FSR

$$\varepsilon_z = \ln \frac{L(t)}{L_0}$$

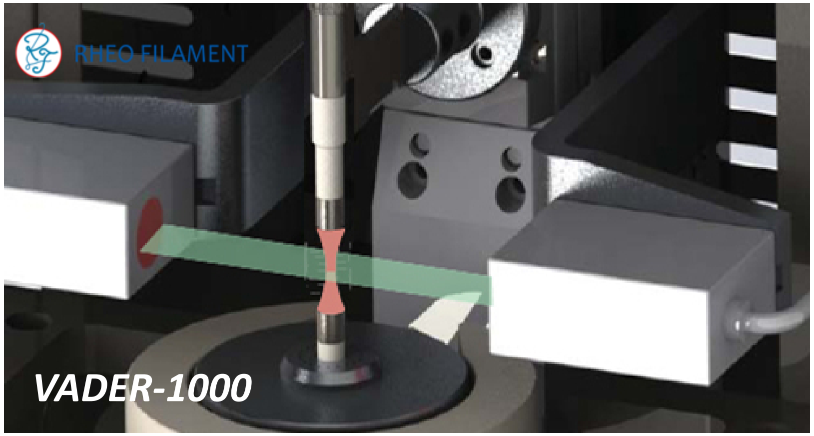


Filament Stretching Rheometer (FSR)

Hencky Strain $\epsilon(t) = -2\ln\frac{D(t)}{D_0}$

Stress $\sigma_E = \langle \sigma_{zz} - \sigma_{rr} \rangle = \frac{F(t) - m_f g/2}{\pi (D(t)/2)^2}$

$$\begin{aligned} \sigma_{zz} &= F_z/A = F/A - p_{atm} \\ \sigma_{xx} &= F_x/A = -p_{atm} \end{aligned}$$



DTU (2015)

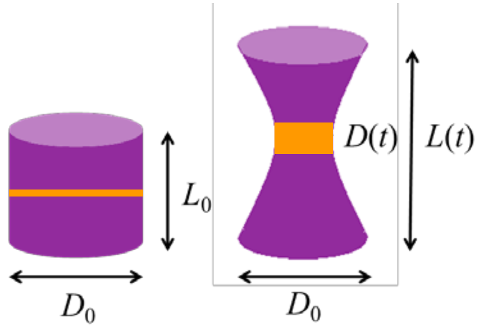
Something ignored:

Surface tension, inertia

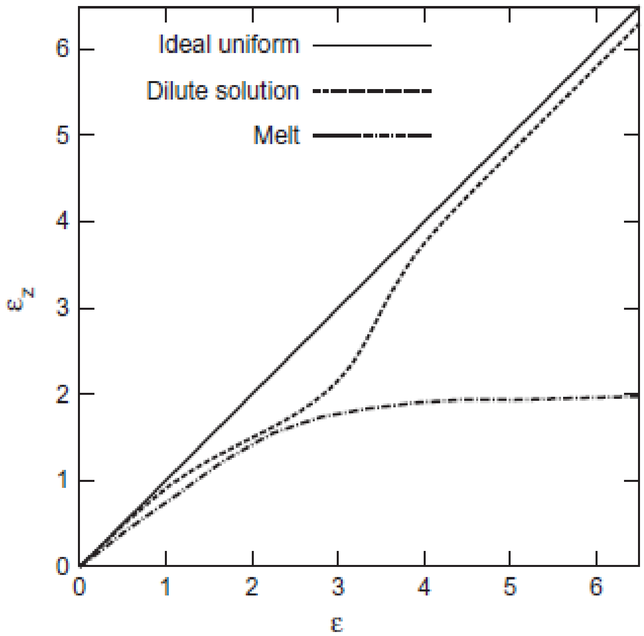
How to make stretch rate constant ???

Open loop, close loop control…

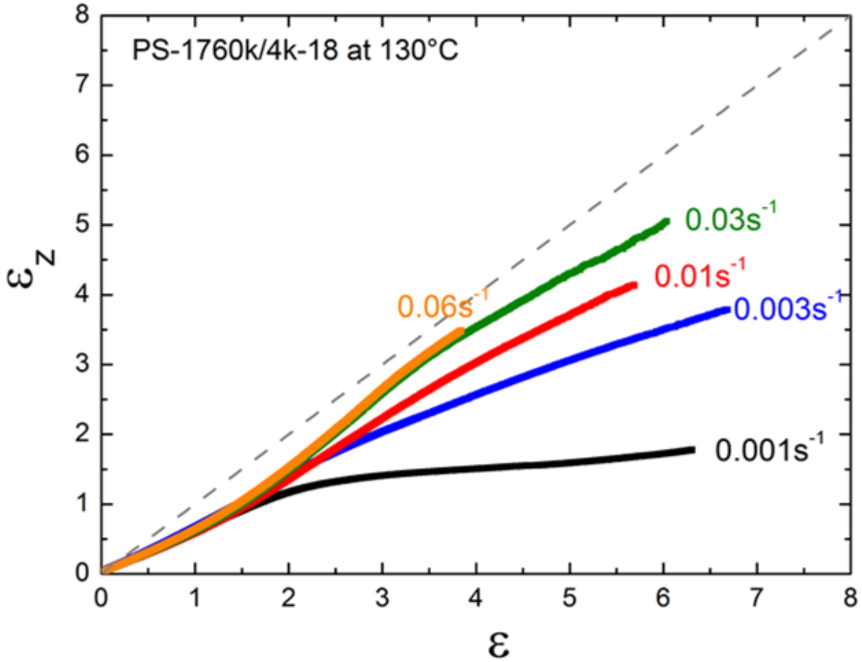
SER & FSR



L_0
D_0
$D(t)$
$L(t)$
D_0

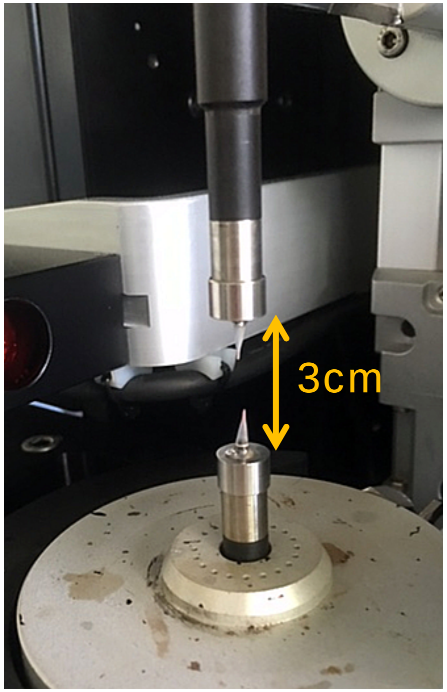


Ideal uniform
Dilute solution
Melt
ε_z
ε

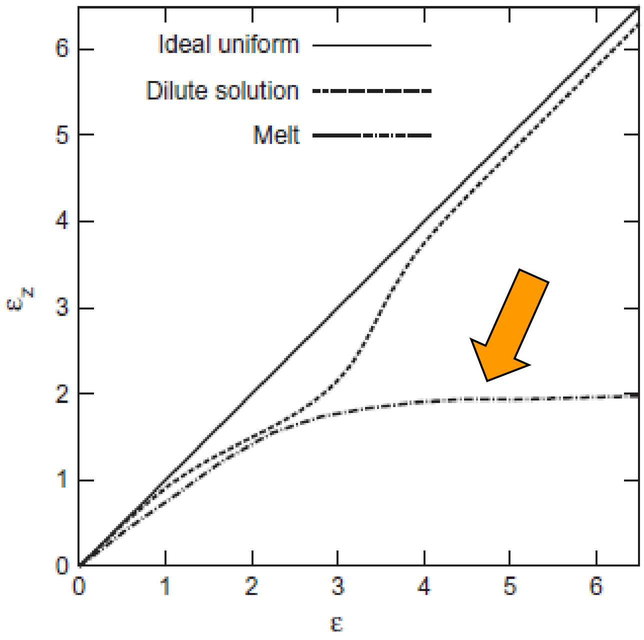


PS-1760k/4k-18 at 130°C
0.03s-1
0.01s-1
0.06s-1
0.003s-1
0.001s-1
ε_z
ε

SER & FSR

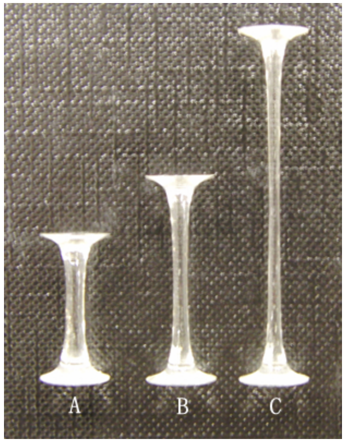


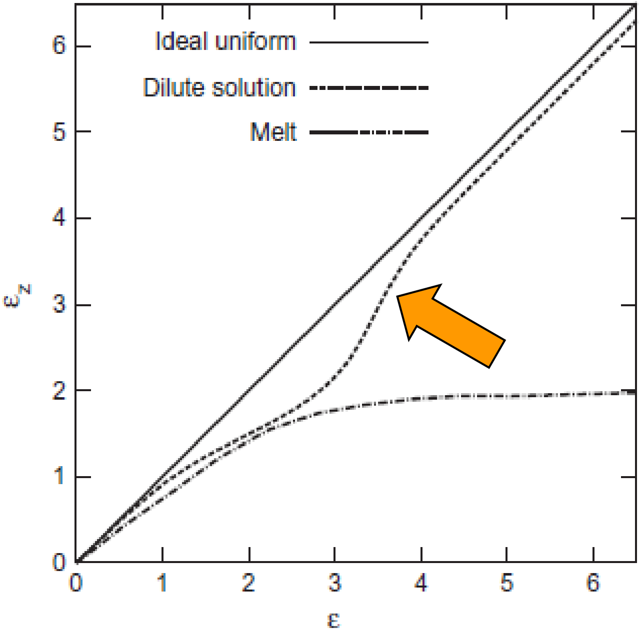
3cm



Ideal uniform
Dilute solution
Melt
ε_z
ε
0
1
2
3
4
5
6


>60cm


A
B
C


Ideal uniform
Dilute solution
Melt
ε_z
ε

LVE envelope & strain hardening

In general no connection between rheometric functions in shear and extension. **Except in small deformations.**

Recall the general linear viscoelastic (LVE) model:

$$\sigma_{ij}(t) = \int_{t'=-\infty}^{t} G(t-t')\dot{\gamma}_{ij}(t')dt'$$

$\dot{\boldsymbol{\gamma}} = (\boldsymbol{\nabla v}) + (\boldsymbol{\nabla v})^{\dagger}$

$G(t-t')$: Linear Viscoelastic Relaxation modulus

In uniaxial extension:

$$v_x = -\frac{1}{2}\dot{\epsilon}\,x$$
$$v_y = -\frac{1}{2}\dot{\epsilon}\,y$$
$$v_z = +\dot{\epsilon}\,z$$

$$\dot{\gamma} = \begin{pmatrix} -0.5\dot{\epsilon} & 0 & 0 \\ 0 & -0.5\dot{\epsilon} & 0 \\ 0 & 0 & \dot{\epsilon} \end{pmatrix} + \begin{pmatrix} -0.5\dot{\epsilon} & 0 & 0 \\ 0 & -0.5\dot{\epsilon} & 0 \\ 0 & 0 & \dot{\epsilon} \end{pmatrix}$$

$$= \begin{pmatrix} -\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 2\dot{\epsilon} \end{pmatrix}$$

In simple shear:

$$\dot{\gamma} = \begin{pmatrix} 0 & \dot{\gamma}_0 & 0 \\ \dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

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$\dot{\boldsymbol{\gamma}} = (\boldsymbol{\nabla v}) + (\boldsymbol{\nabla v})^{\dagger}$

$G(t-t')$: Linear Viscoelastic Relaxation modulus

In simple shear:

$$\sigma_{yx}(t>0) = \int_{t'=0}^{t} G(t-t')\dot{\gamma}_0 dt'$$

$$\dot{\gamma} = \begin{pmatrix} 0 & \dot{\gamma}_0 & 0 \\ \dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\eta^+(t>0) = \int_{t'=0}^{t} G(t-t')dt'$$

LVE envelope: $\eta^+ \text{ vs. } t$

↓

Transient shear viscosity, or Shear stress growth coefficient ('official name')

Multi-mode Maxwell model (with *n* modes)

$$G(t-t') = \sum_{k=1}^{n} \frac{\eta_k}{\lambda_k} e^{-(t-t')/\lambda_k}$$

$$\eta^+ = \sum_{k=1}^{n} \eta_k \left(1 - e^{-t/\lambda_k}\right)$$

LVE envelope & strain hardening

In general no connection between rheometric functions in shear and extension. **Except in small deformations.**

Recall the general linear viscoelastic (LVE) model:

$$\sigma_{ij}(t) = \int_{t'=-\infty}^{t} G(t-t')\dot{\gamma}_{ij}(t')dt'$$

$\dot{\boldsymbol{\gamma}} = (\boldsymbol{\nabla v}) + (\boldsymbol{\nabla v})^{\dagger}$

$G(t-t')$: Linear Viscoelastic Relaxation modulus

In uniaxial extension: $\sigma_{zz} - \sigma_{xx} = \int_{t'=0}^{t} G(t-t')(\dot{\gamma}_{zz} - \dot{\gamma}_{xx})dt' \;\; = 3\int_{t'=0}^{t} G(t-t')\dot{\epsilon}dt'$

$$\dot{\gamma} = \begin{pmatrix} -\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 2\dot{\epsilon} \end{pmatrix}$$

$$\eta_E{}^{+} = \frac{\sigma_{zz} - \sigma_{xx}}{\dot{\epsilon}} = 3\int_{t'=0}^{t} G(t-t')dt'$$

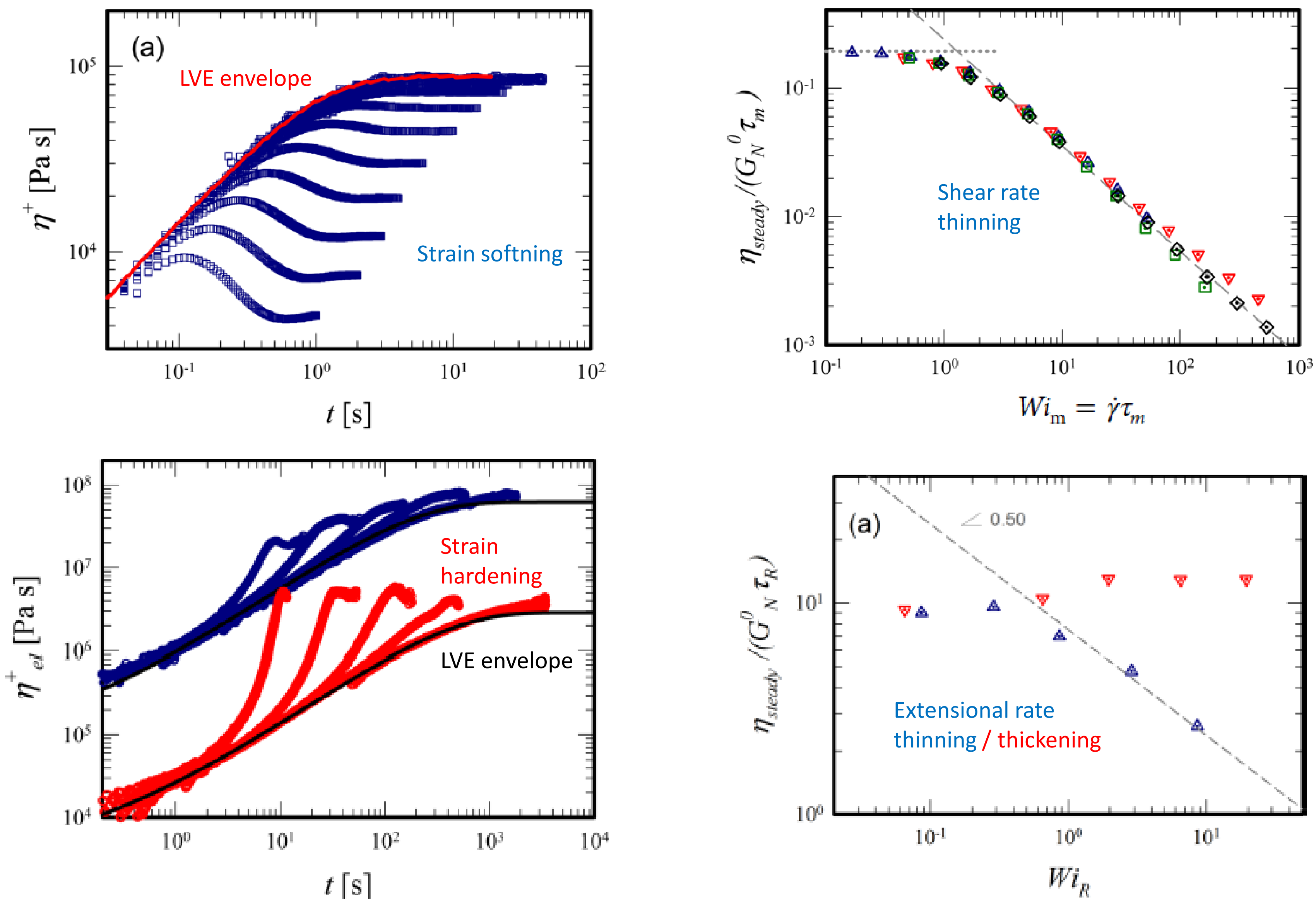
LVE envelope: $\eta_E{}^{+}$ vs. t

↓

Transient extensional viscosity, or Extensional stress growth coefficient ('official name')

$$\eta^{+}(t>0) = \int_{t'=0}^{t} G(t-t')dt'$$

LVE envelope & strain hardening



Figures from: Costanzo et al., Macromolecules 2016, 49, 3925–3935

LVE envelope & strain hardening

LDPE

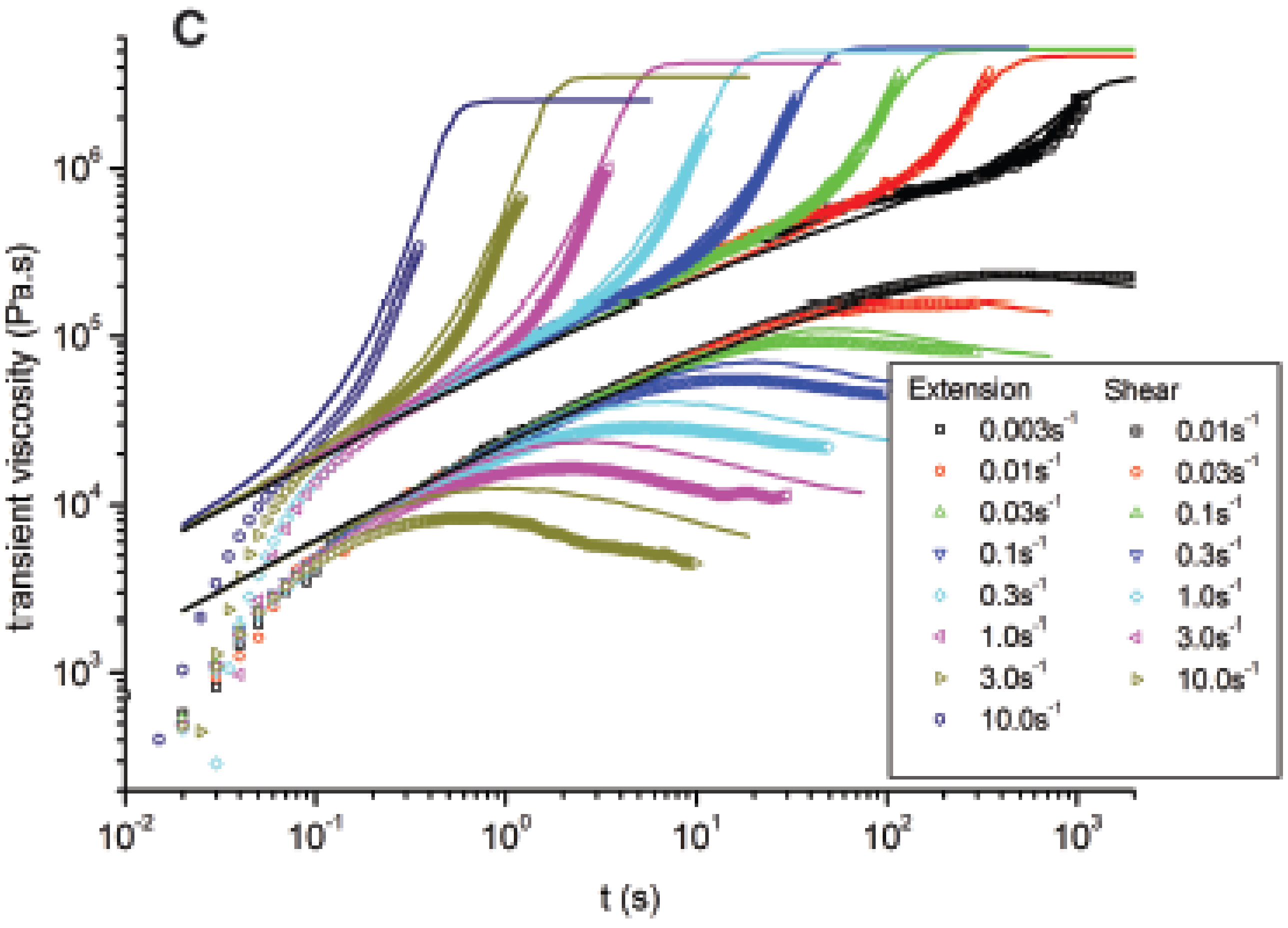


Figure from: Read et al., Science 2011, 333, 1871–1874

Extensional rheology

Linear molecules (melts & solutions)

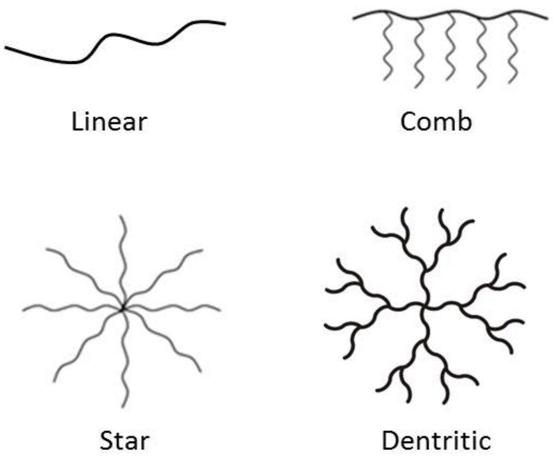
Branched molecules

Associating polymers with hydrogen bonding

Creep (constant stress) measurements

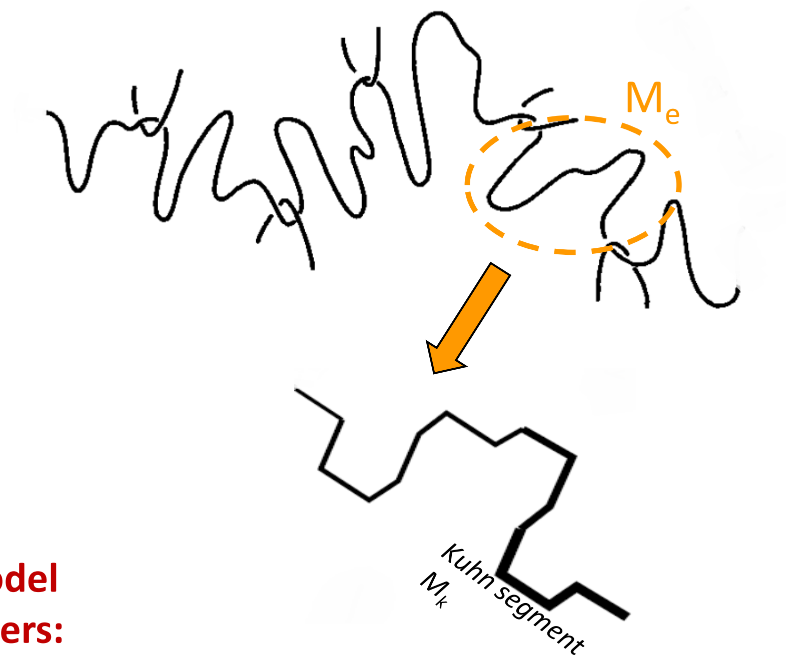
Combining with SANS

Influence on mechanical properties



Linear molecules (melts & solutions)

Simplest case: Monodisperse linear polymers



Tube model parameters:

Number of entanglements per chain: $Z = M/M_e$

Number of Kuhn steps per entanglement: $N_e = M_e/M_k$

Entanglement Relaxation time: τ_e

Linear molecules (melts & solutions)

Chain stretching

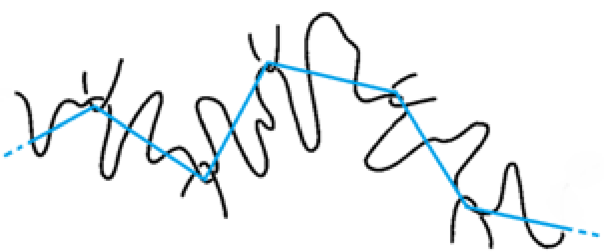
Maximum Stretch Ratio:

$$\lambda_{\max} = \frac{Nb}{Za} = \sqrt{\frac{N}{Z}} = \sqrt{N_e}$$

$$\dot{\varepsilon} > \tau_R^{-1}$$

$$\tau_R = Z^2 \tau_e$$

Rouse time



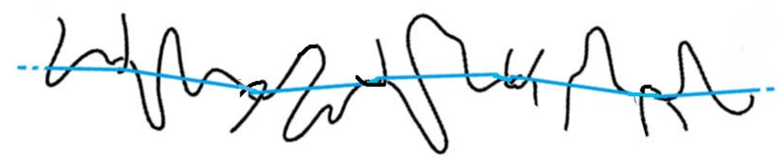
$$R^2 = Za^2 = Nb^2$$

$$\dot{\varepsilon} > \tau_d^{-1}$$

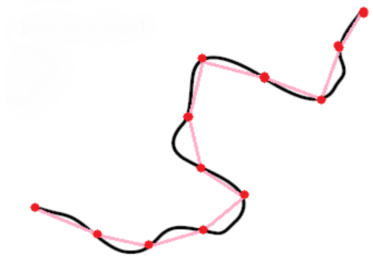
$$\tau_d = cZ^{3.4} \tau_e$$

Reptation time

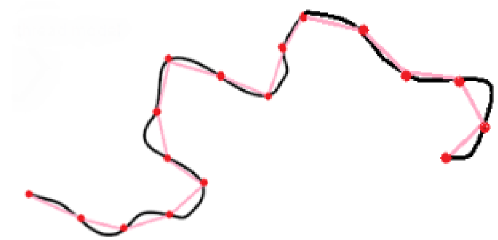
Chain orientation



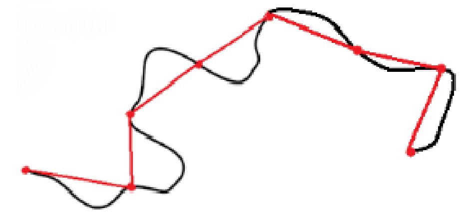
Linear molecules (melts & solutions)



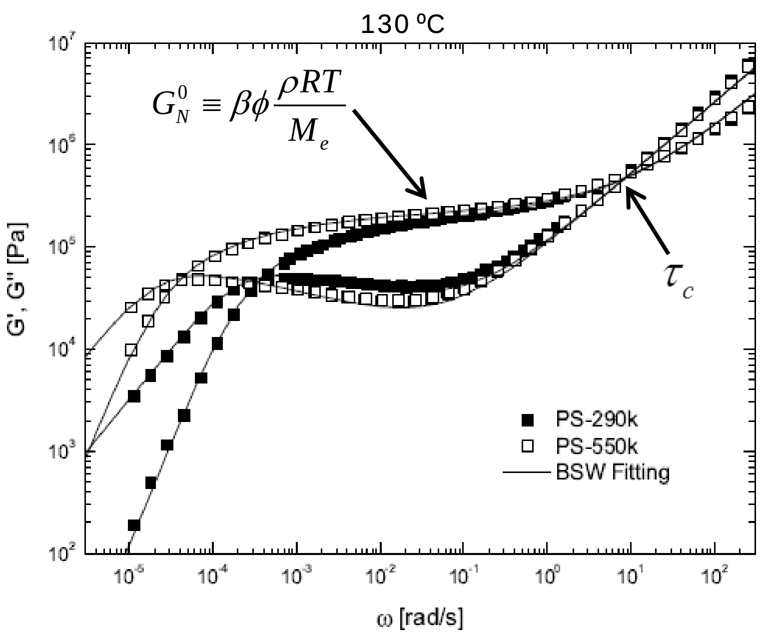
PS-290k (Z=22)

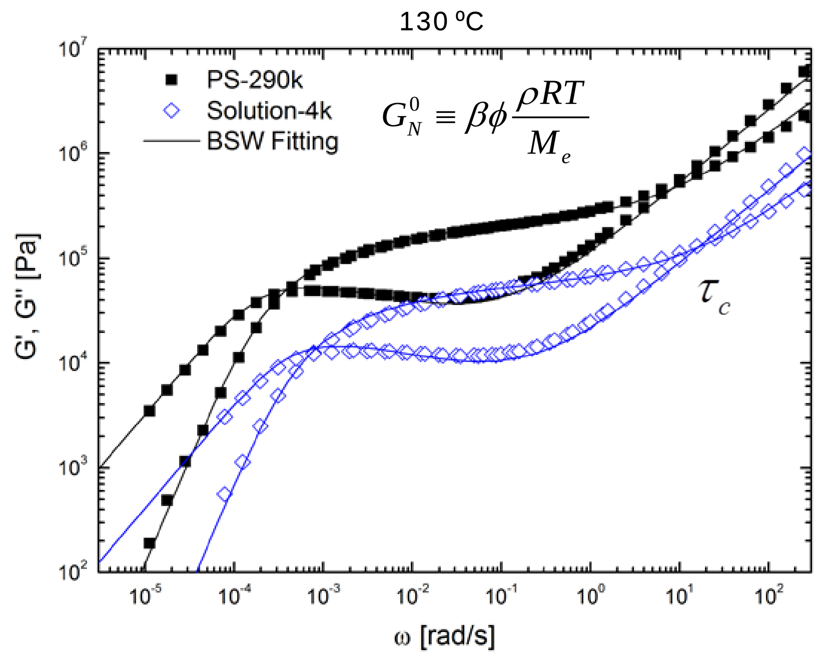


PS-550k (Z=41)



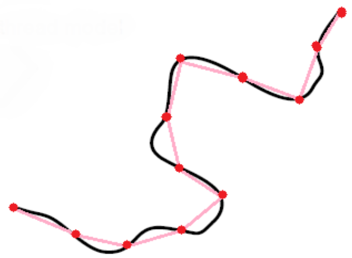
52% PS-550k (Z=22)



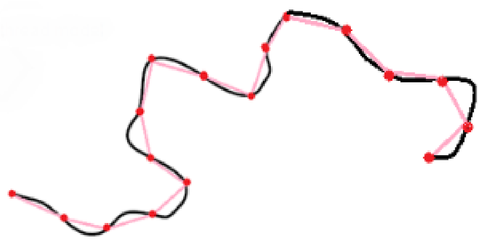


Huang et al., ACS Macro Letters 2, 741–744 (2013)

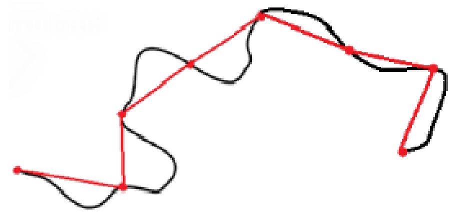
Linear molecules (melts & solutions)



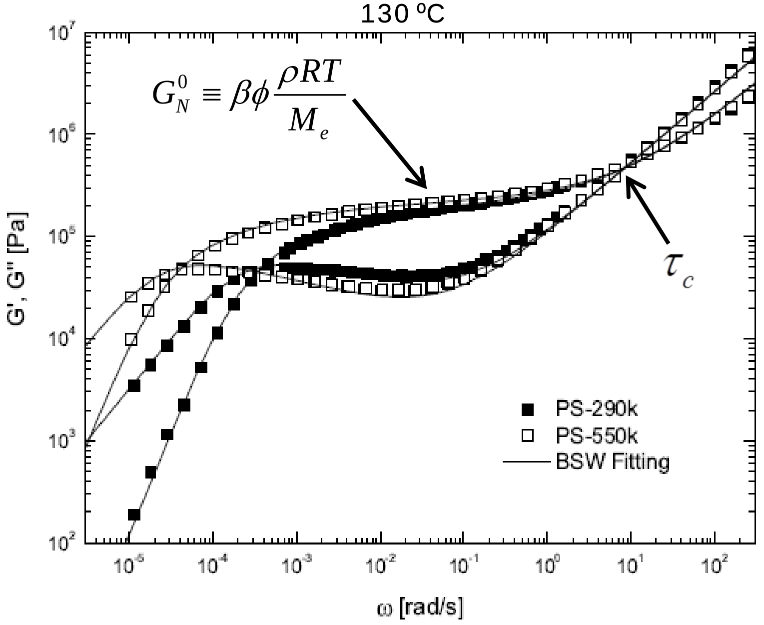
PS-290k (Z=22)

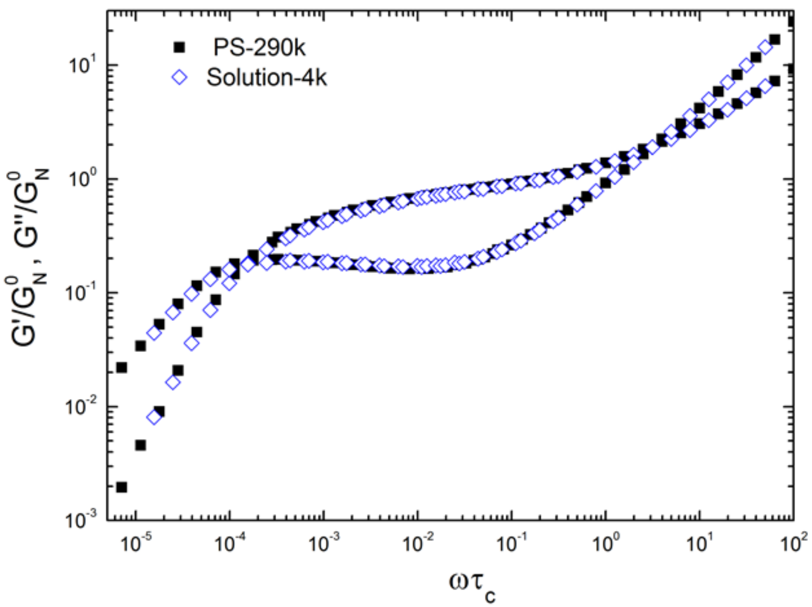


PS-550k (Z=41)



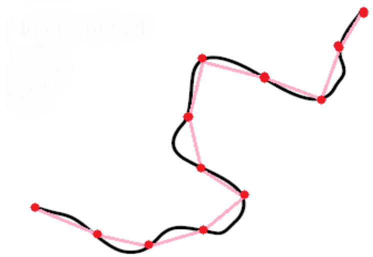
52% PS-550k (Z=22)



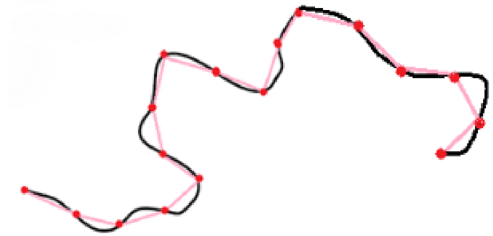


Huang et al., ACS Macro Letters 2, 741–744 (2013)

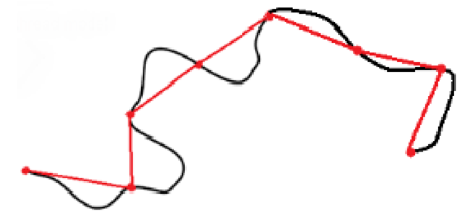
Linear molecules (melts & solutions)



PS-290k (Z=22)



PS-550k (Z=41)



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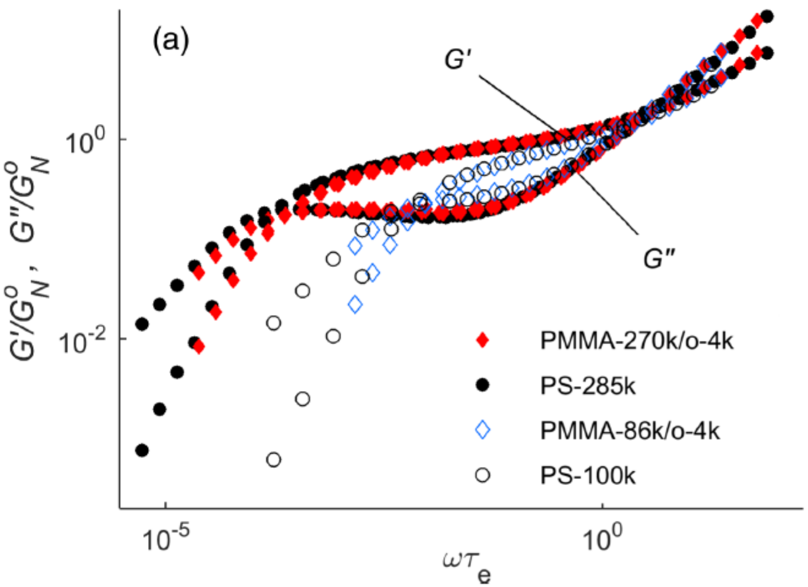
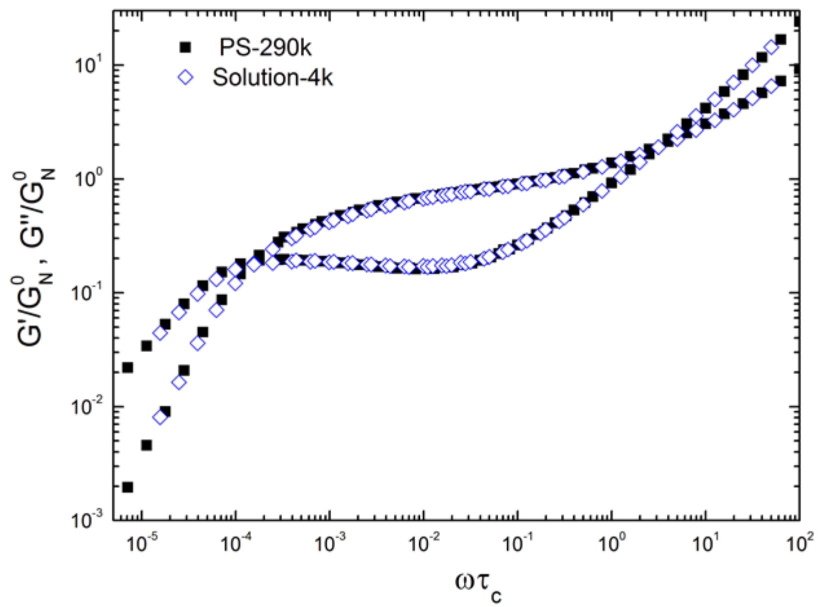
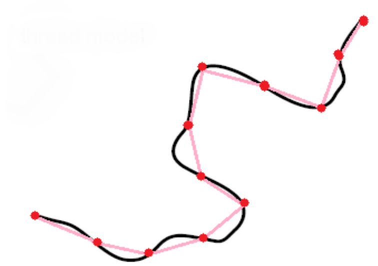


Wingstrand et al., PRL 115, 078302 (2015)



Huang et al., ACS Macro Letters 2, 741–744 (2013)

Linear molecules (melts & solutions)



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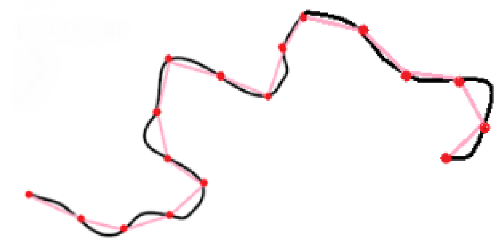
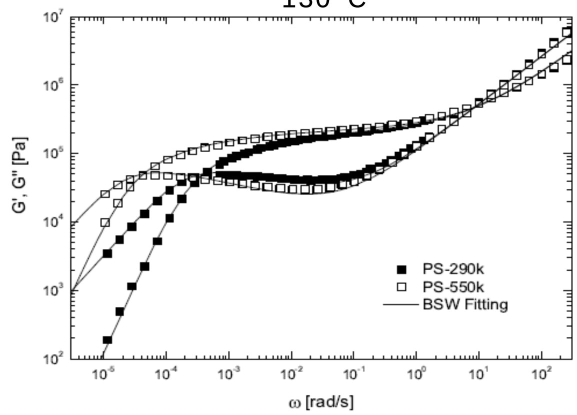
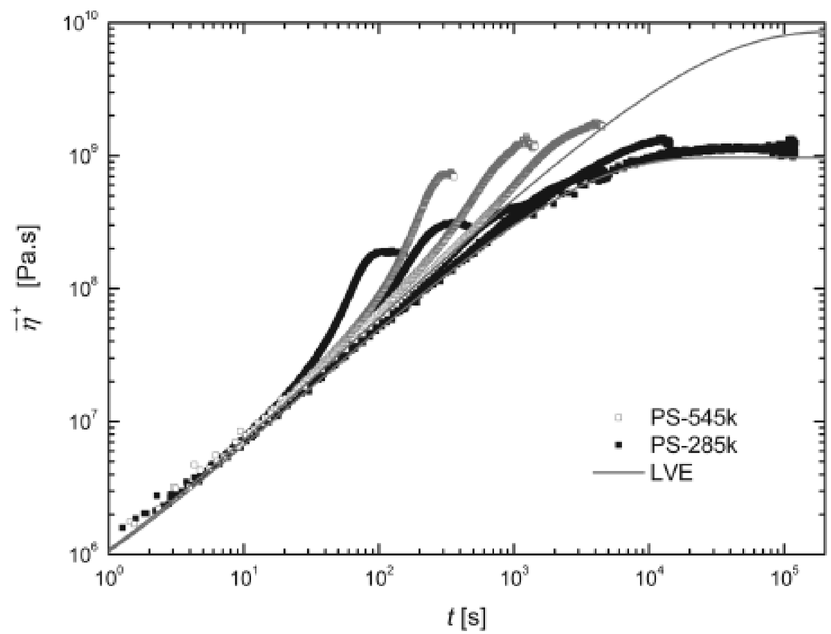
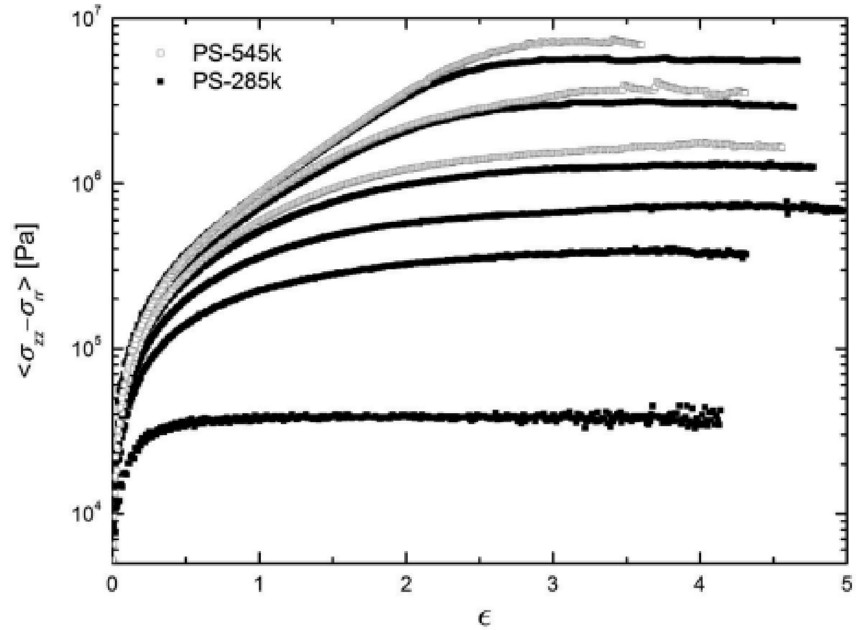


PS-550k (Z=41)

130 ºC

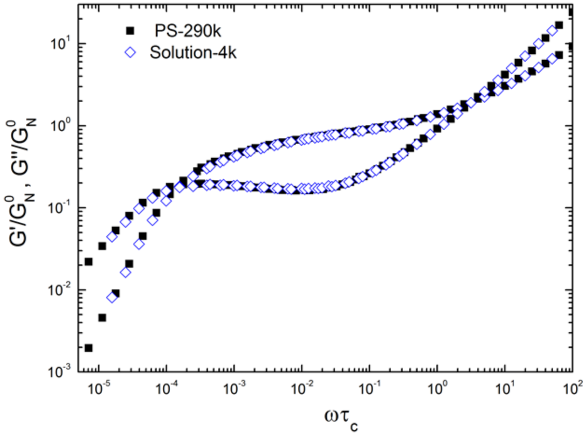


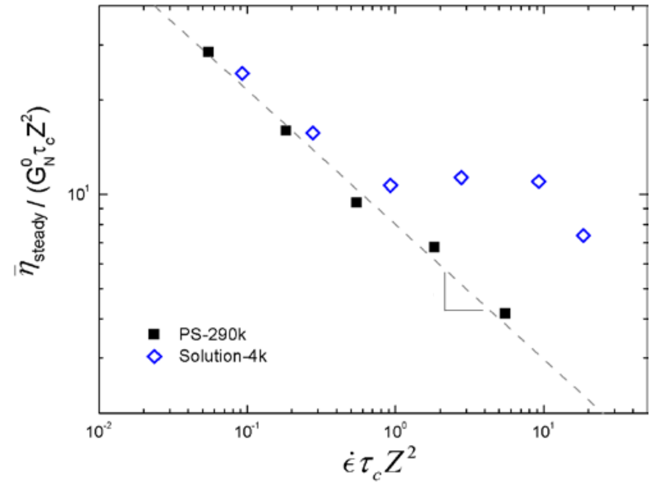


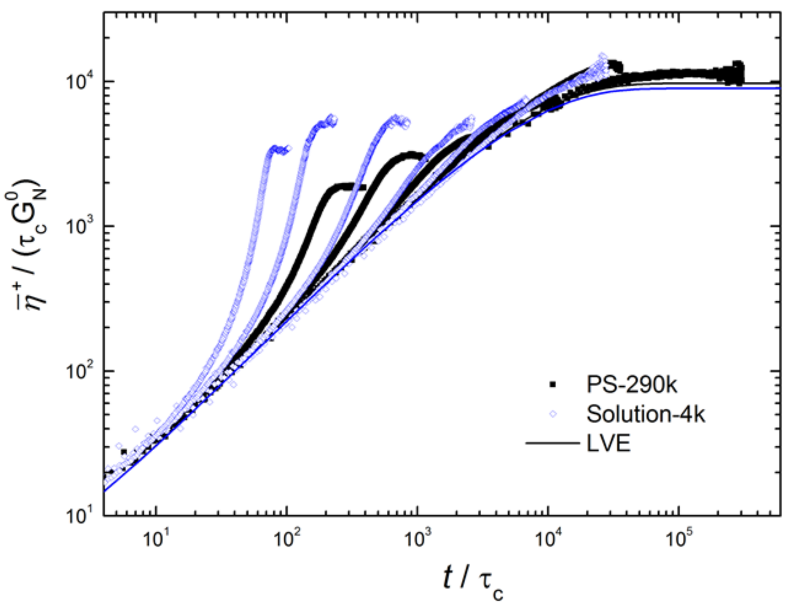


Huang et al., Macromolecules 2013, 46, 5026−5035

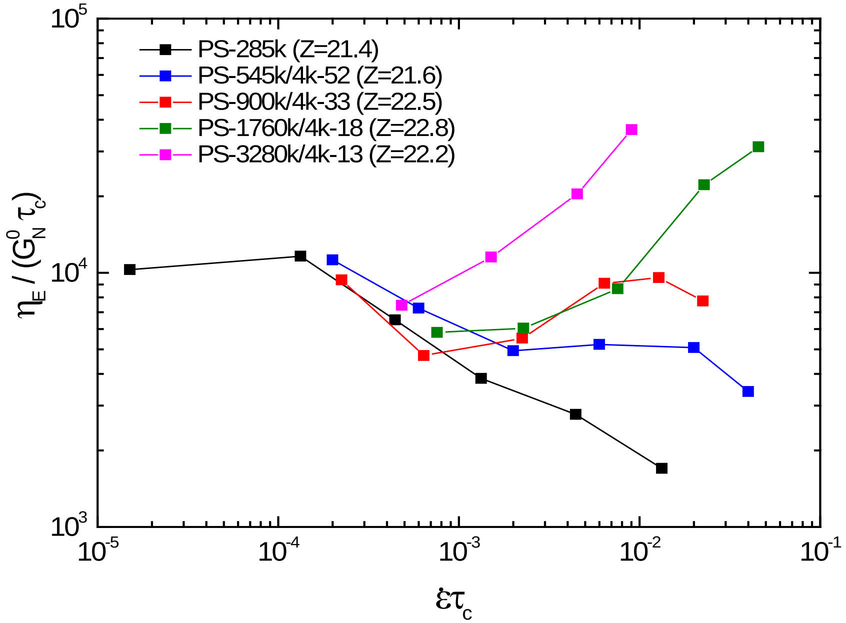
Linear molecules (melts & solutions)





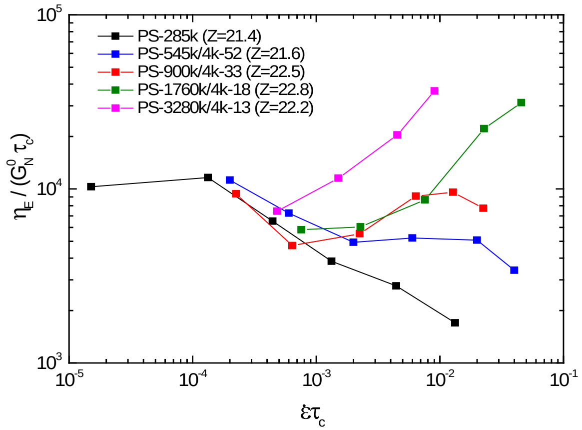


Huang et al., ACS Macro Letters 2, 741–744 (2013)



Huang et al., Macromolecules 48, 4158–4163 (2015)

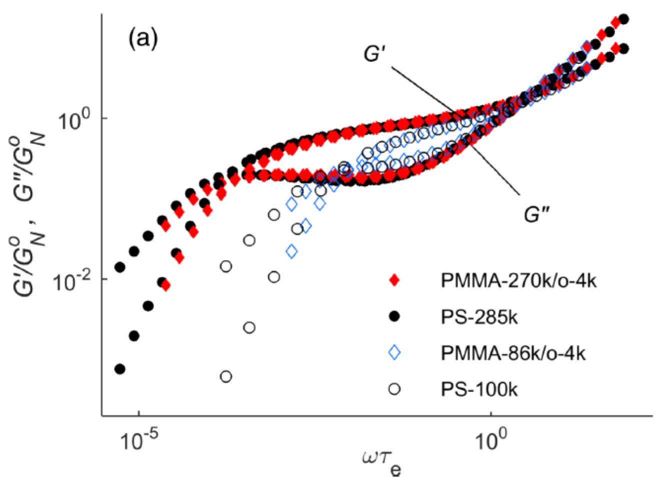
Linear molecules (melts & solutions)



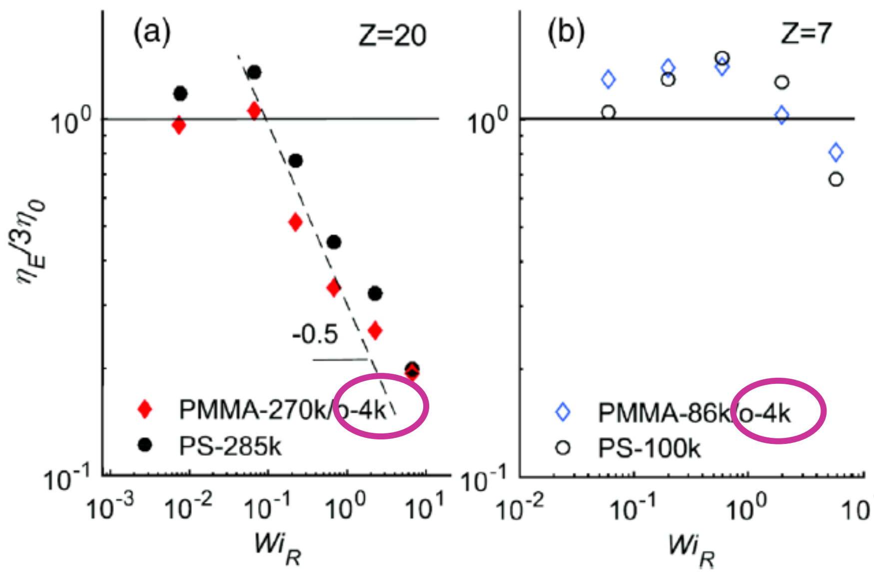
Maximum chain stretch ratio:

$$\lambda_{\max} = \sqrt{N_e}$$

Need to choose the oligomer as long as possible



Same Z, same N_e



Wingstrand et al., PRL 115, 078302 (2015)

Linear molecules (melts & solutions)

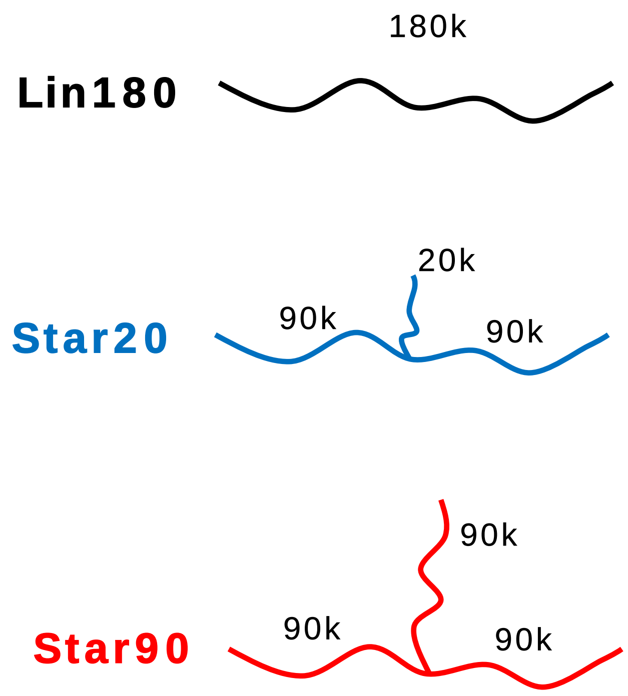
Simplest case: Not fully understood yet…

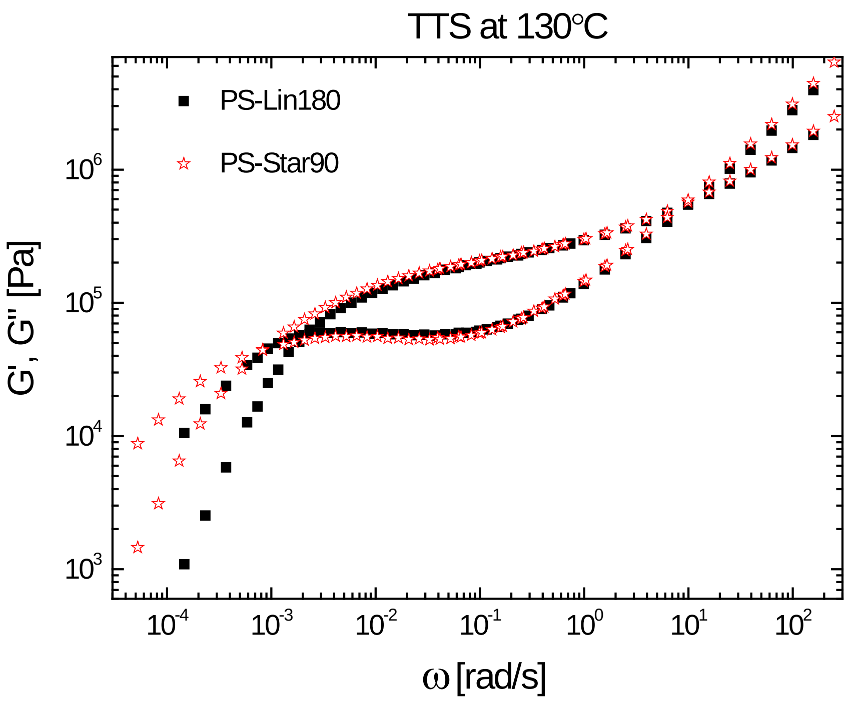
Entanglements = Mess…

Entanglements = Fun!

Branched molecules - Star

Simplest case: 3-arm star

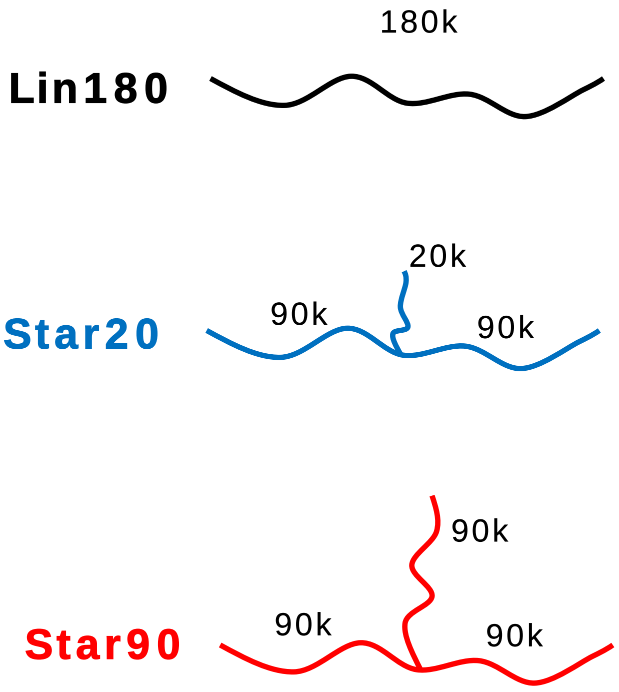


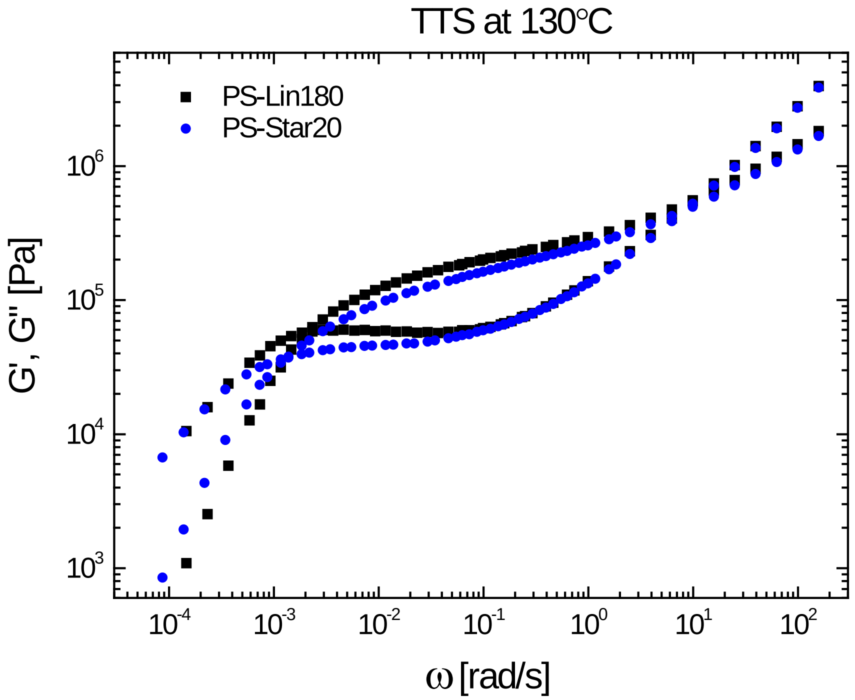


Huang et al., Macromolecules 49, 6694–6699 (2016)

Branched molecules - Star

Simplest case: 3-arm star





Huang et al., Macromolecules 49, 6694–6699 (2016)

Branched molecules - Star

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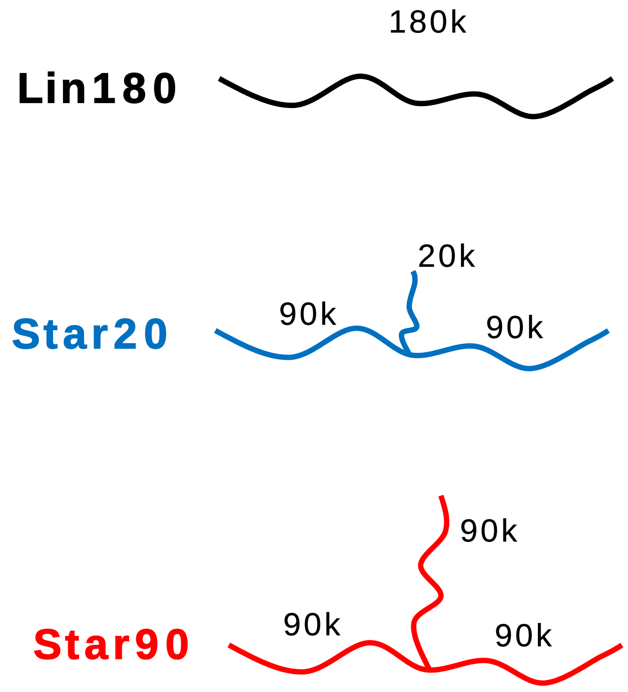
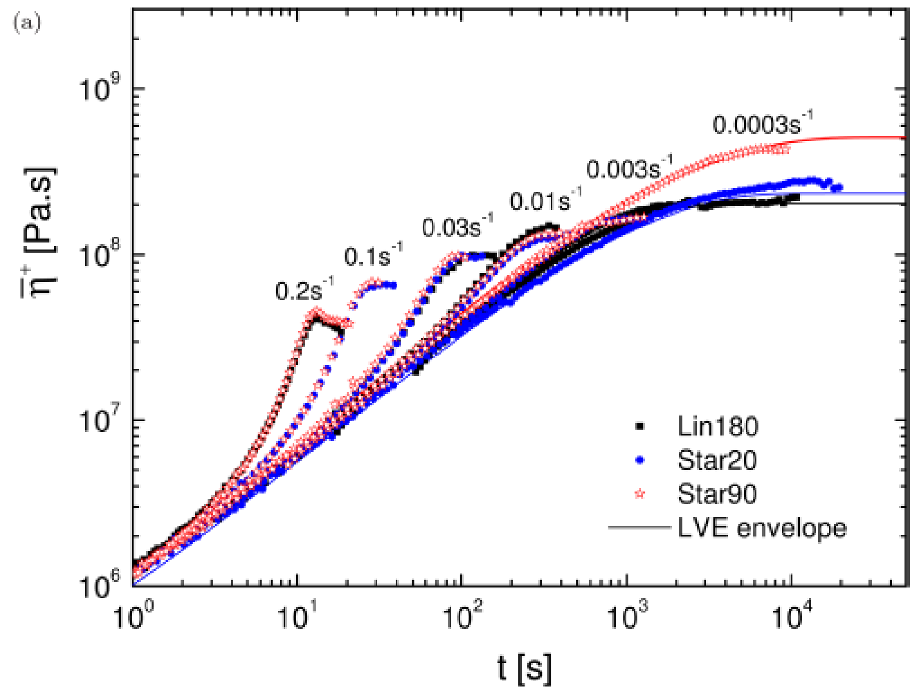
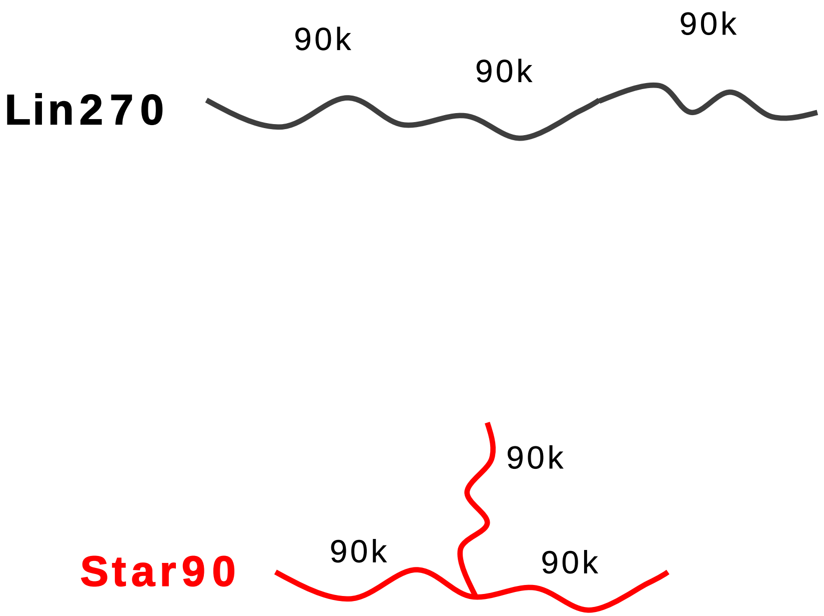


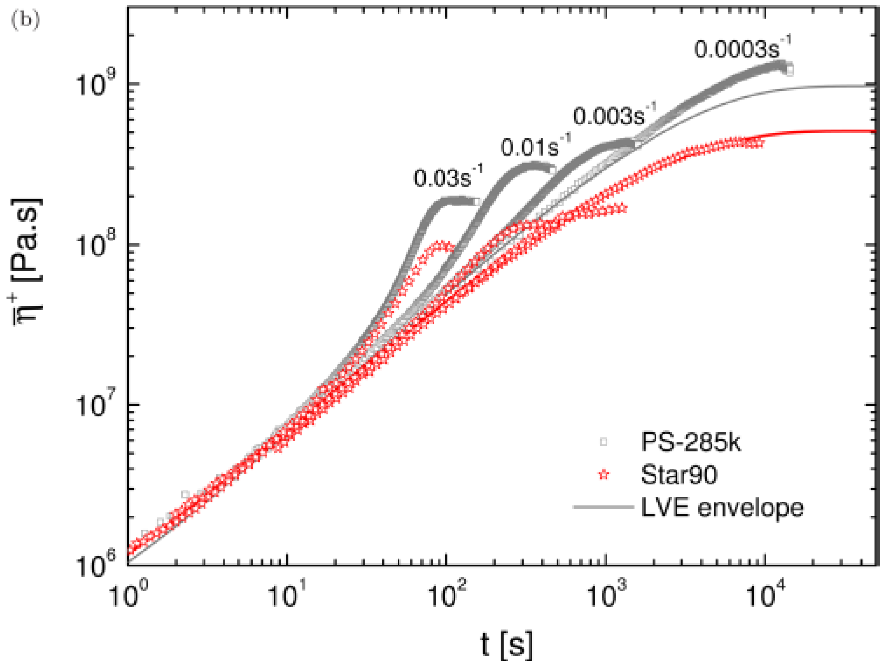


Huang et al., Macromolecules 49, 6694–6699 (2016)

Branched molecules - Star

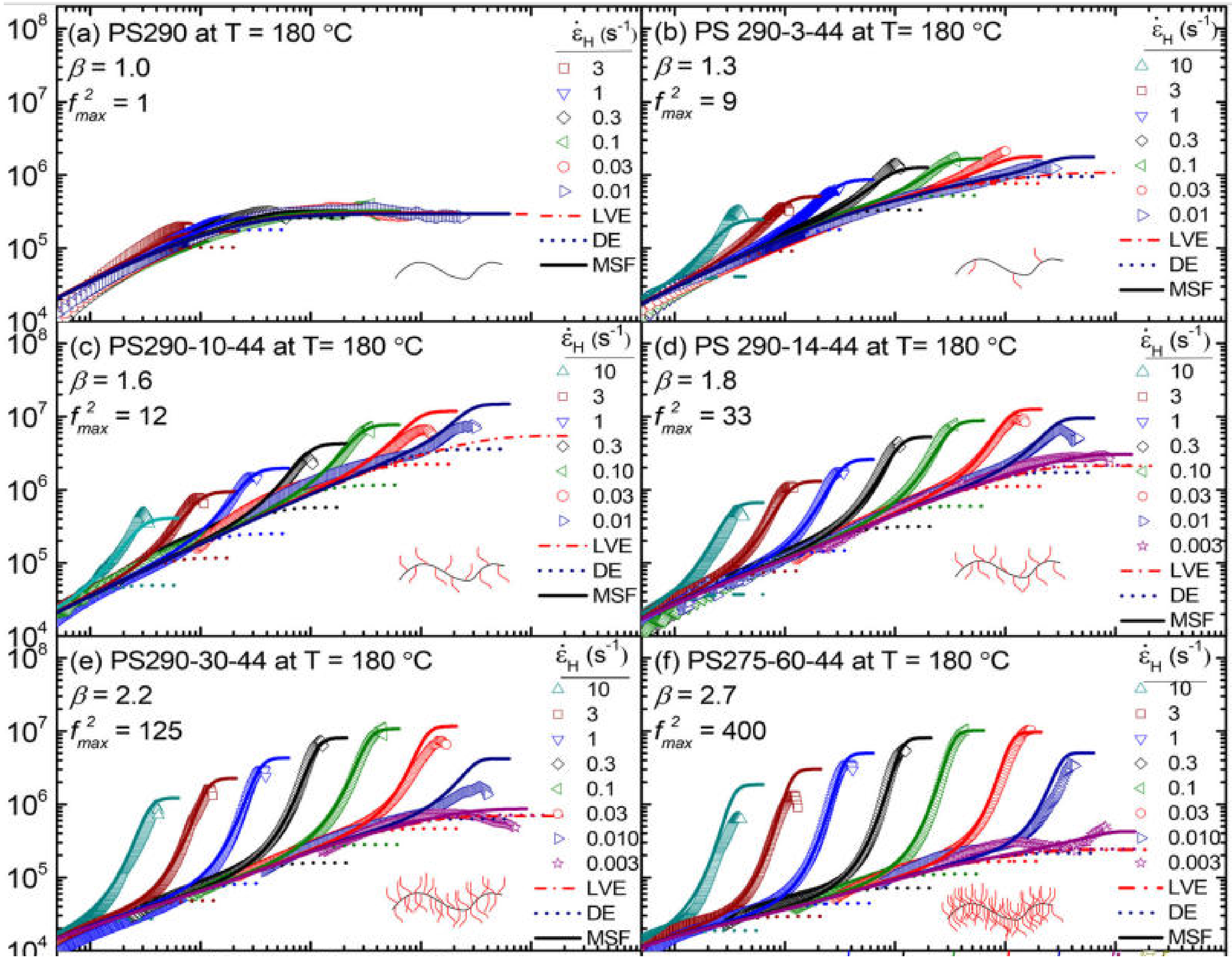
Simplest case: 3-arm star





Huang et al., Macromolecules 49, 6694–6699 (2016)

Branched molecules - Comb



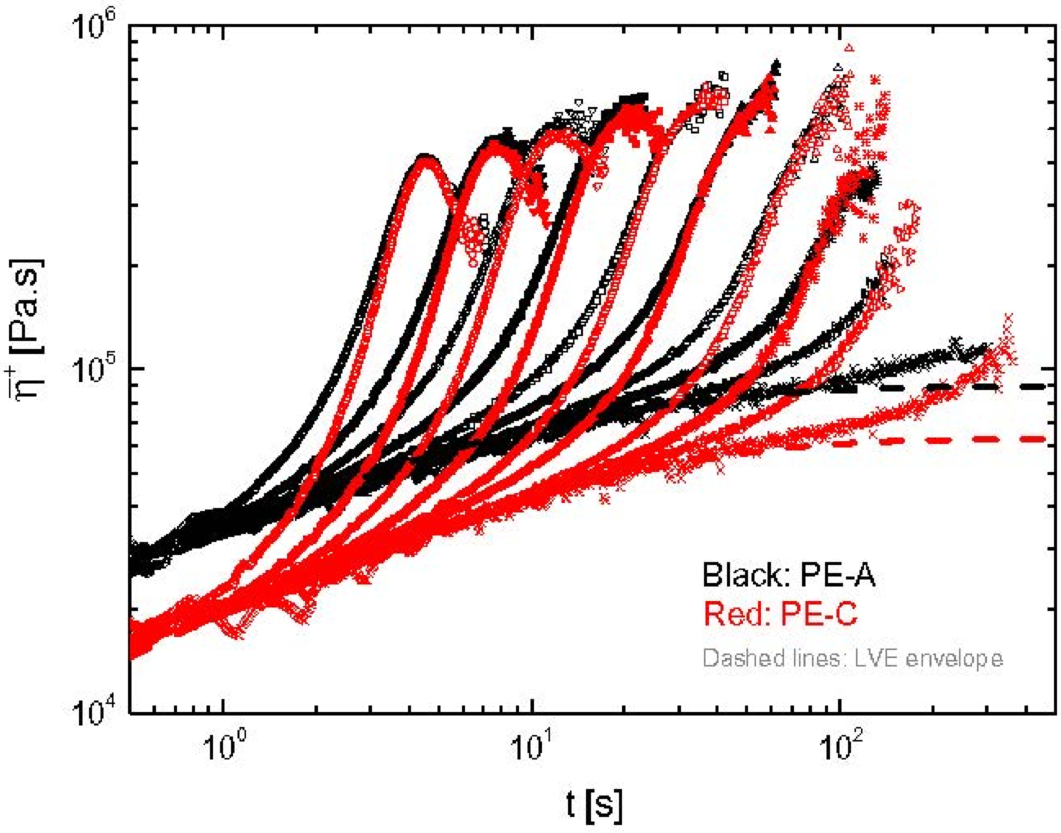
DE: $\boldsymbol{\sigma}(t) = \int_{-\infty}^{t} M(t-t')\boldsymbol{S}_{DE}(t,t')dt'$

MSF: $\boldsymbol{\sigma}(t) = \int_{-\infty}^{t} M(t-t')f^2(t,t')\boldsymbol{S}_{DE}(t,t')dt'$

Figures: *Abbasi et al., Macromolecules 2017, 50, 5964–5977*

Branched molecules - Commercial polymers

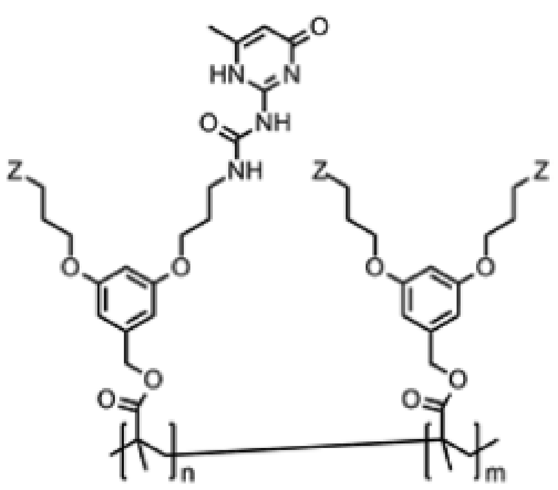
Most complicated case: randomly branched, polydisperse…

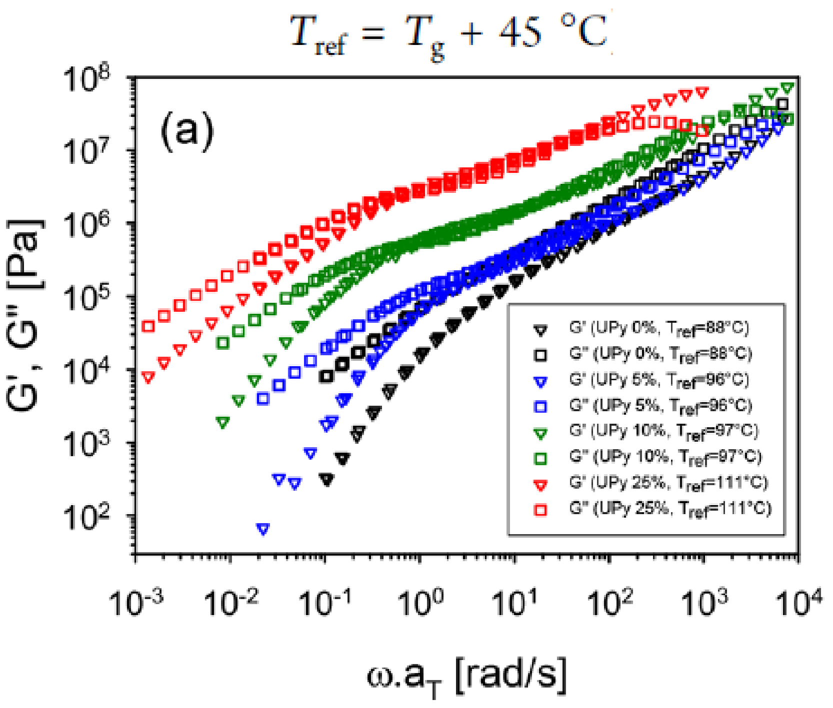


Huang et al., Rheol Acta (2016) 55:343–350

Associating polymers with hydrogen bonding

PMMA based dendronized polymers, with strongly hydrogen bonding 2-ureido-4[1H]-pyrimidinone (UPy) moieties



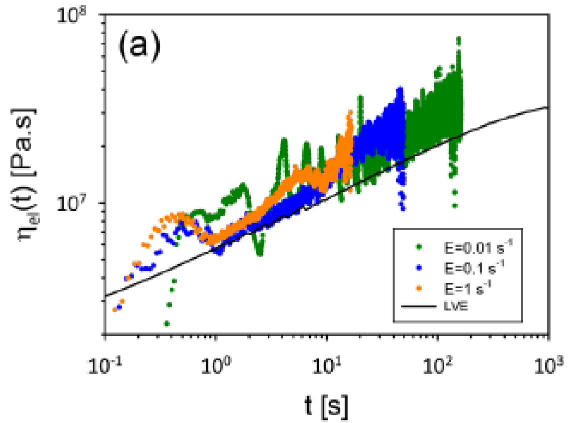


Scherz and Costanzo et al., Macromolecules 2017, 50, 5176–5187

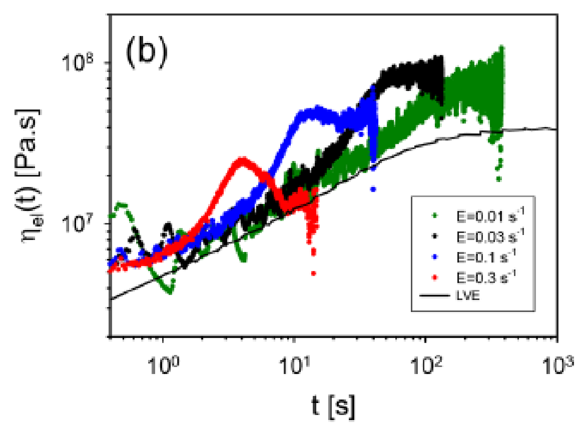
Associating polymers

Associating polymers with hydrogen bonding

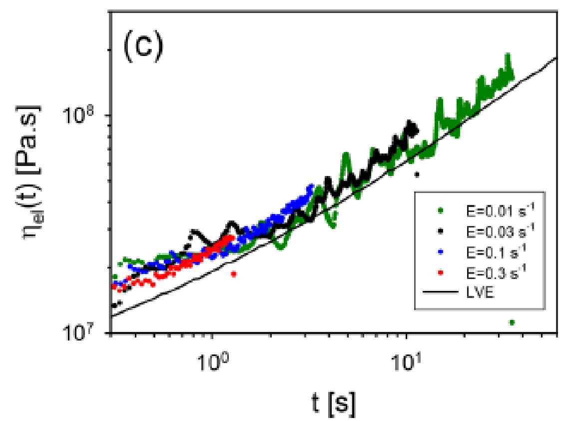
0%



5%



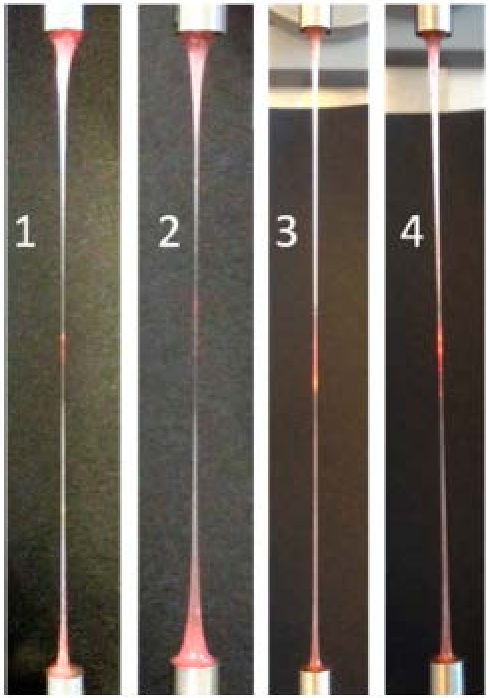
10%



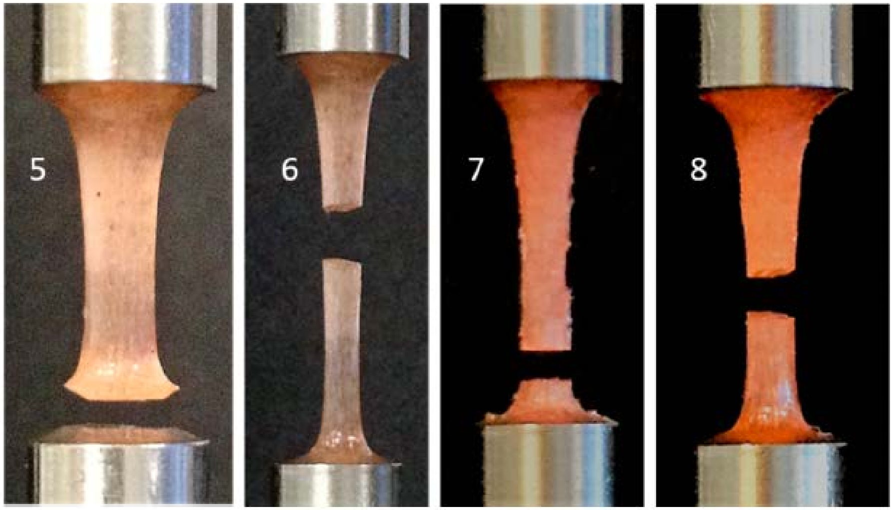
Scherz and Costanzo et al., Macromolecules 2017, 50, 5176–5187

Associating polymers

Associating polymers with hydrogen bonding



0%   5%

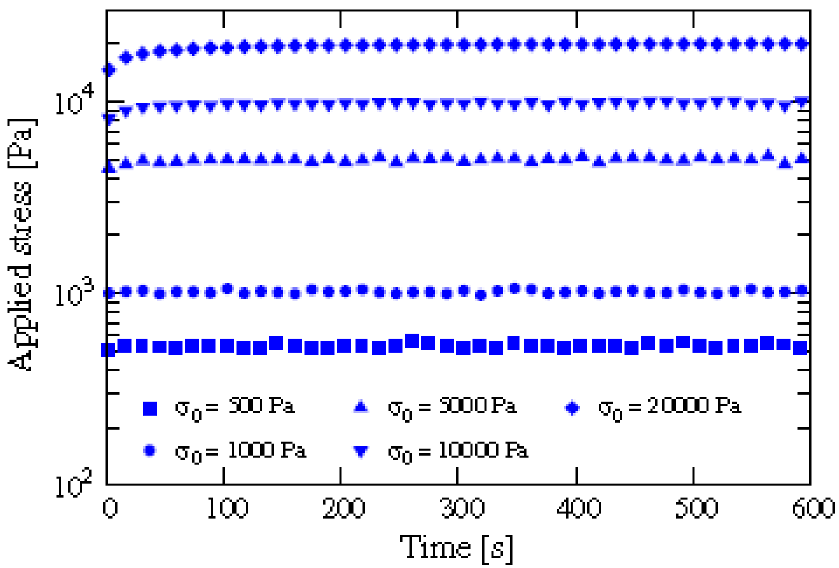


10%   25%

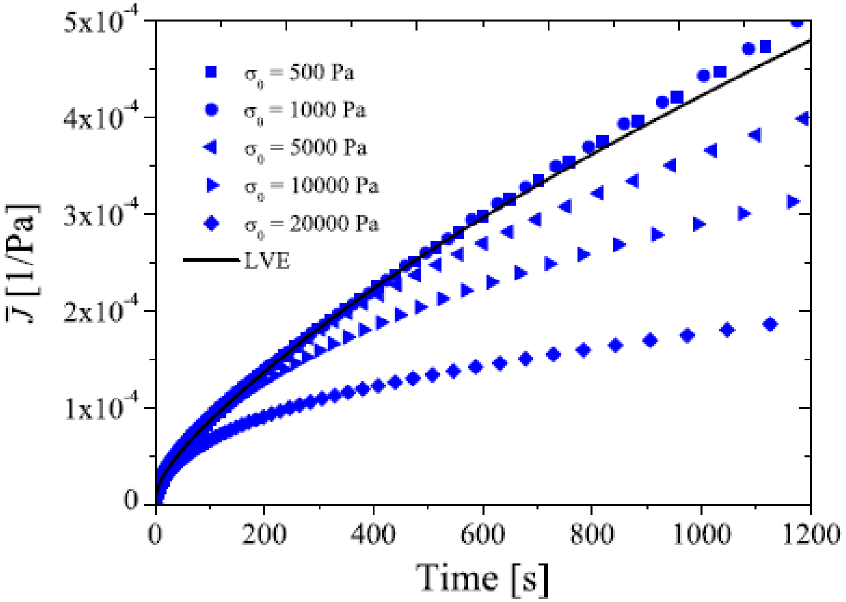
Scherz and Costanzo et al., Macromolecules 2017, 50, 5176–5187

Creep measurements

Applied



Measured

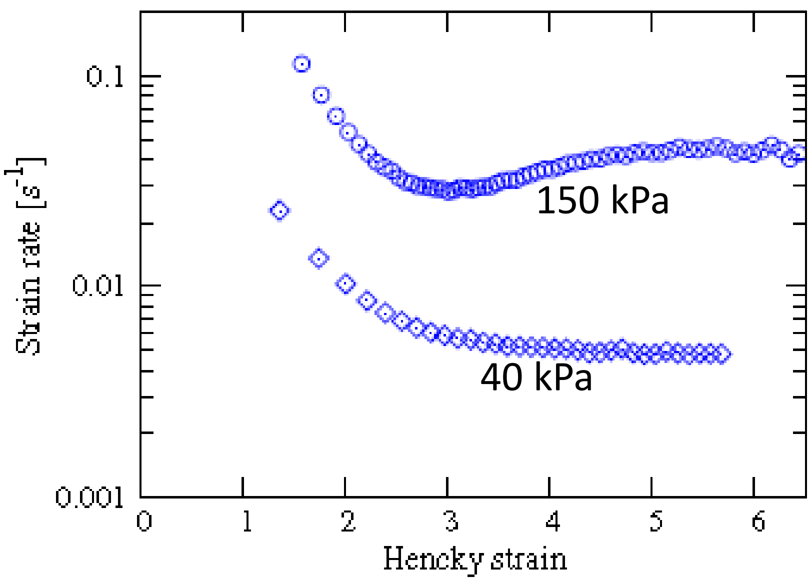


Extensional compliance

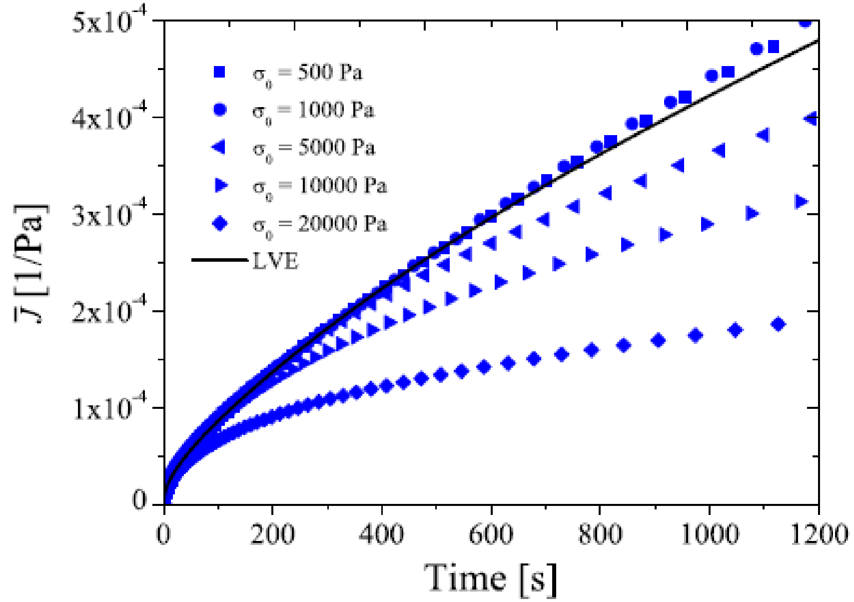
$$\bar{J}(t) = \epsilon(t)/\sigma_0$$

Figures: Alvarez *et al., PRL 110, 168301 (2013)*

Creep measurements



Measured



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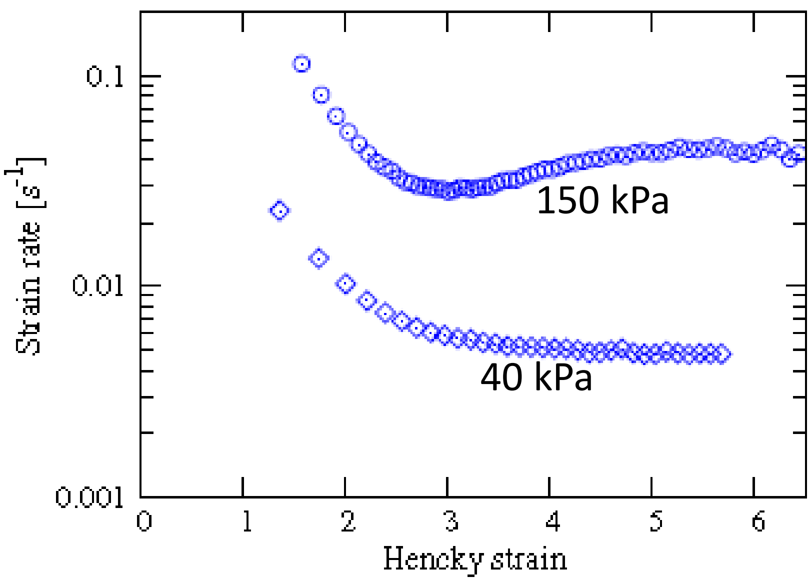
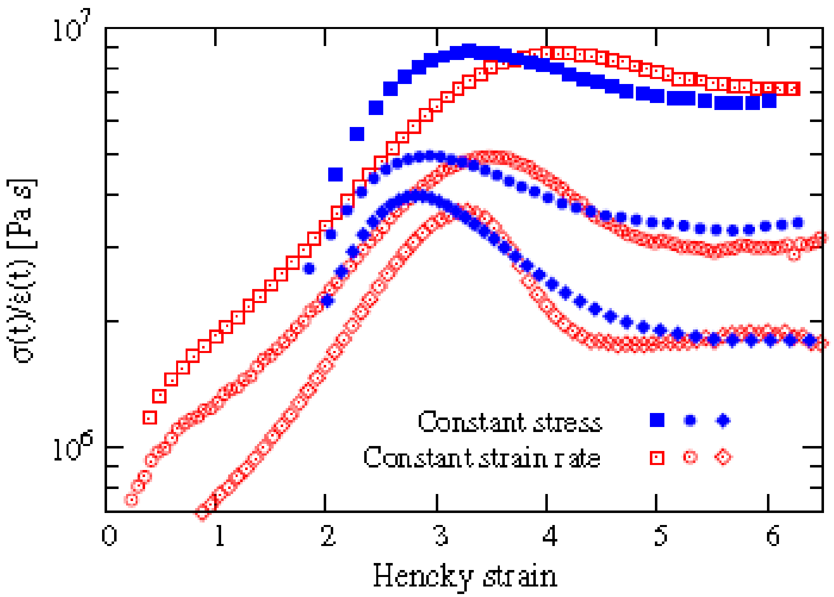
Figures: Alvarez *et al., PRL 110, 168301 (2013)*

Creep measurements

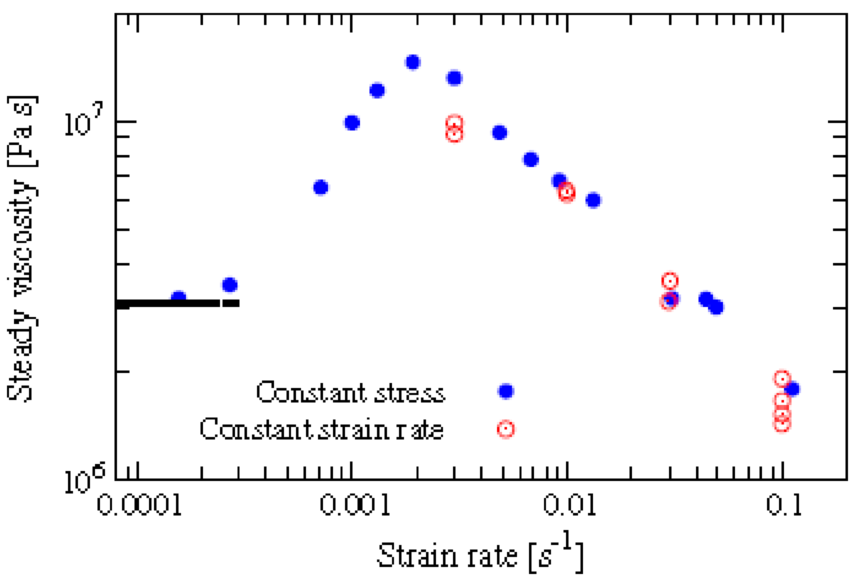


LDPE

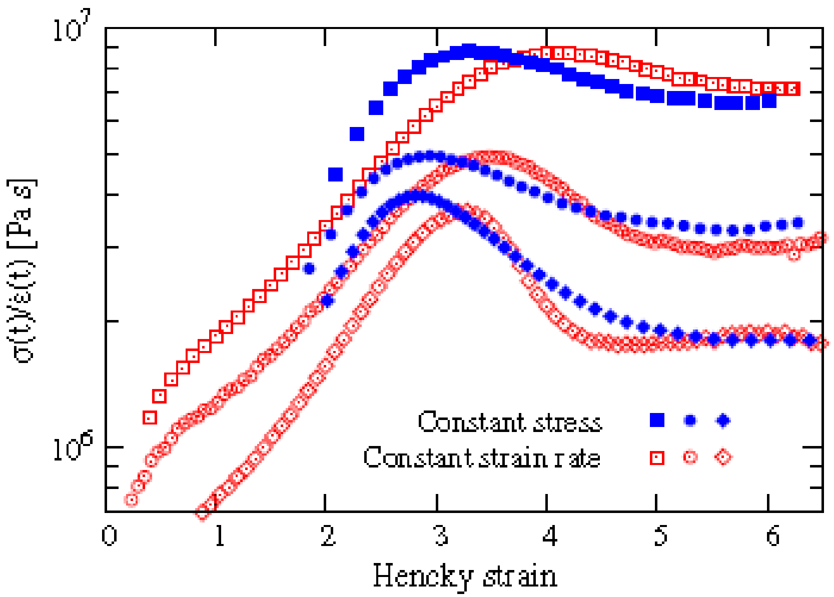


Figures: Alvarez *et al., PRL 110, 168301 (2013)*

Creep measurements

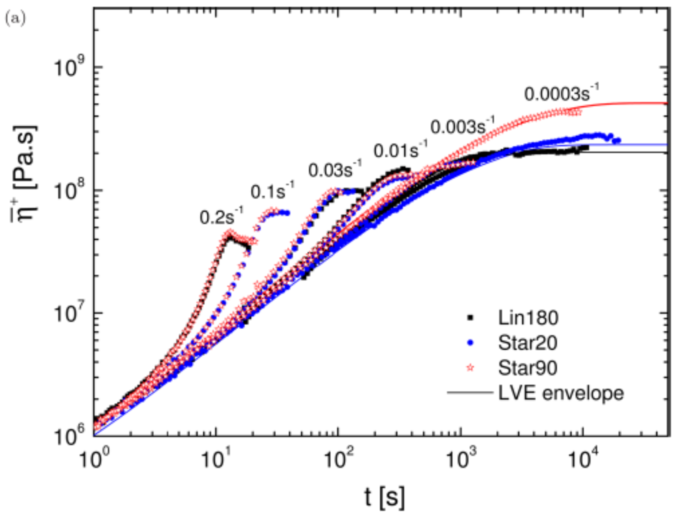


LDPE

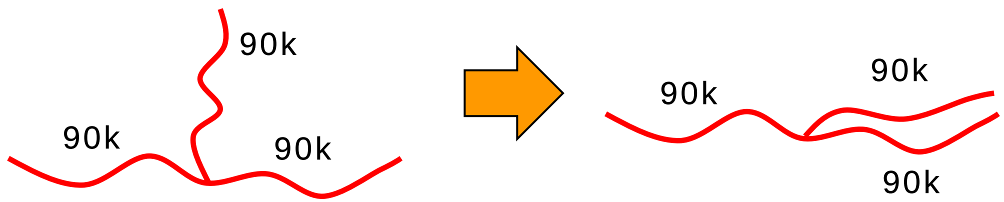


Figures: Alvarez *et al., PRL 110, 168301 (2013)*

Combining with SANS



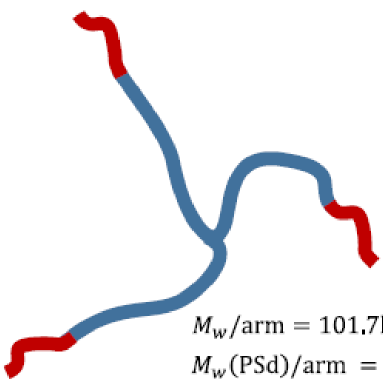
Hypothesis:

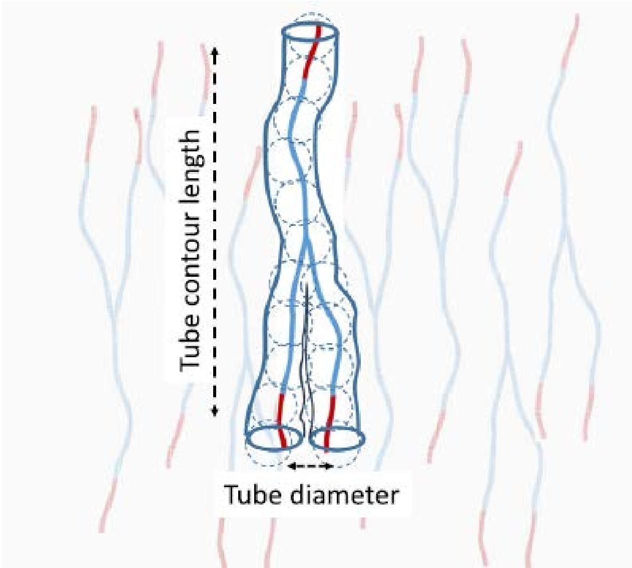


Extensional rheology cannot give direct information of molecular conformations

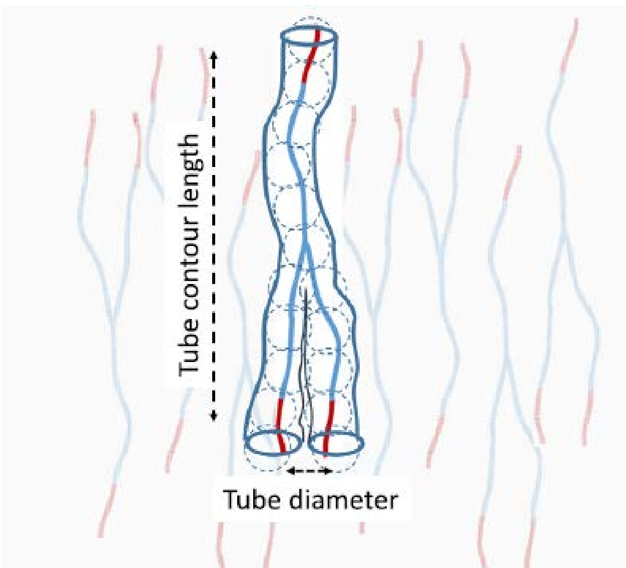
3-Arm Polystyrene Star-Polymer

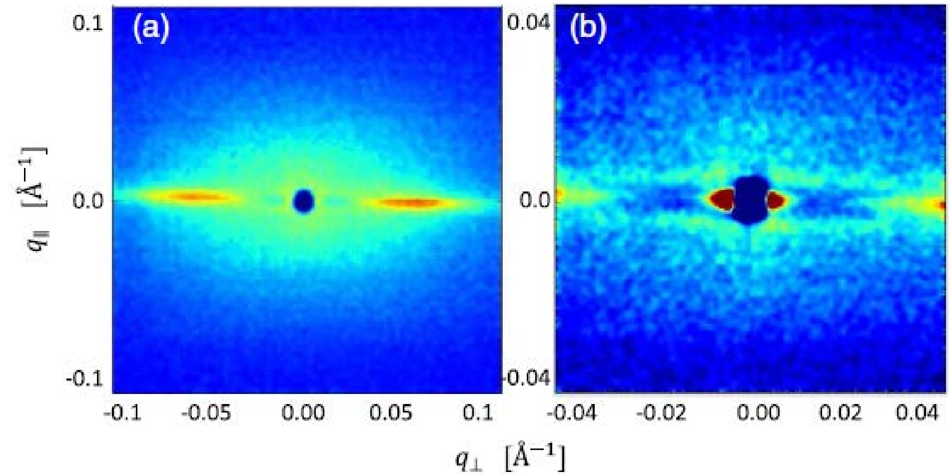
Each arm has end-block of deuterated monomers

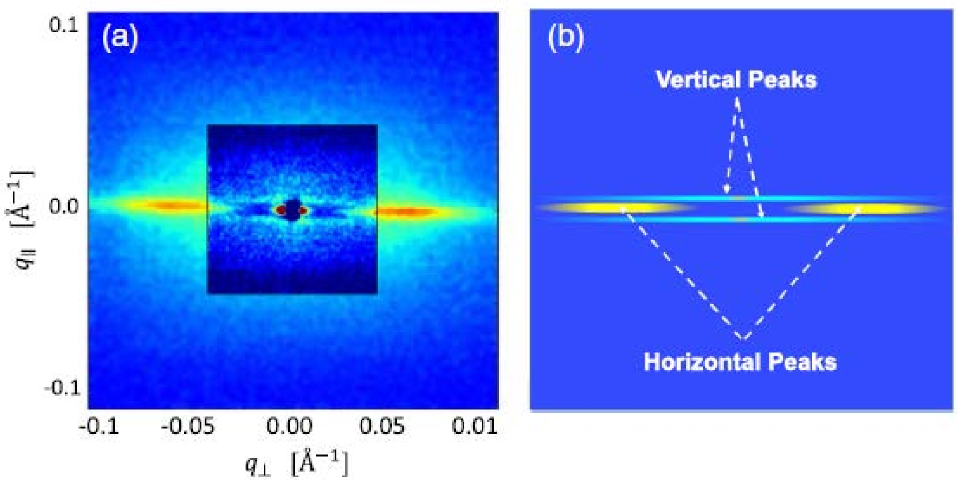




Combining with SANS





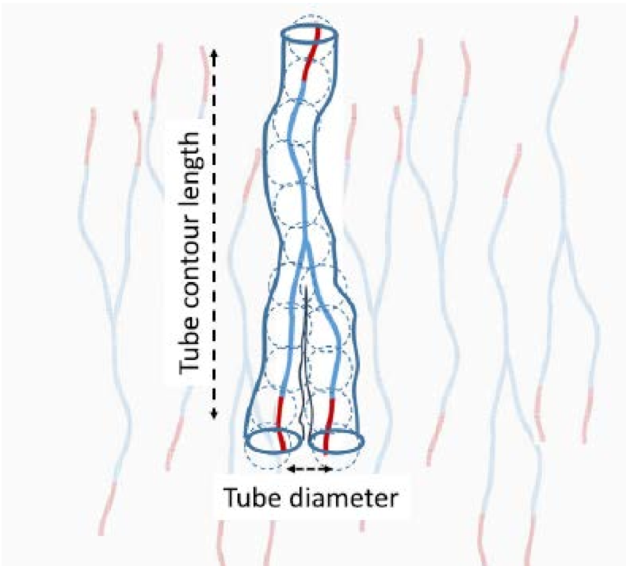


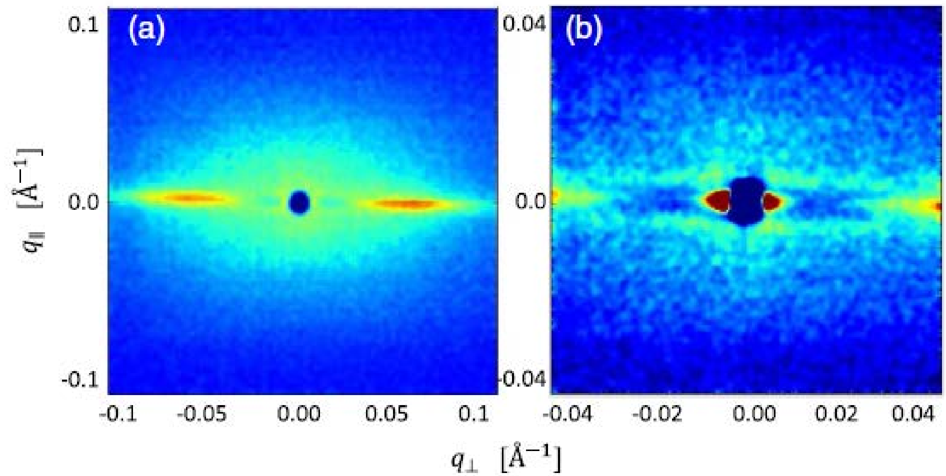
The distance resulting from the horizontal peaks is roughly 100 Å

Tube diameter for PS melt: 85 Å

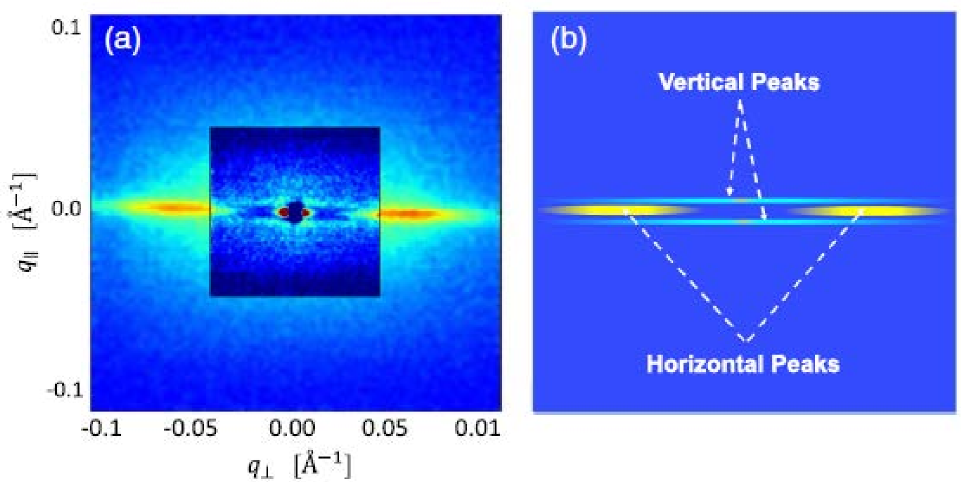
Mortensen et al., PRL 120, 207801 (2018)

Combining with SANS





Still need to compare with the corresponding linear chain…



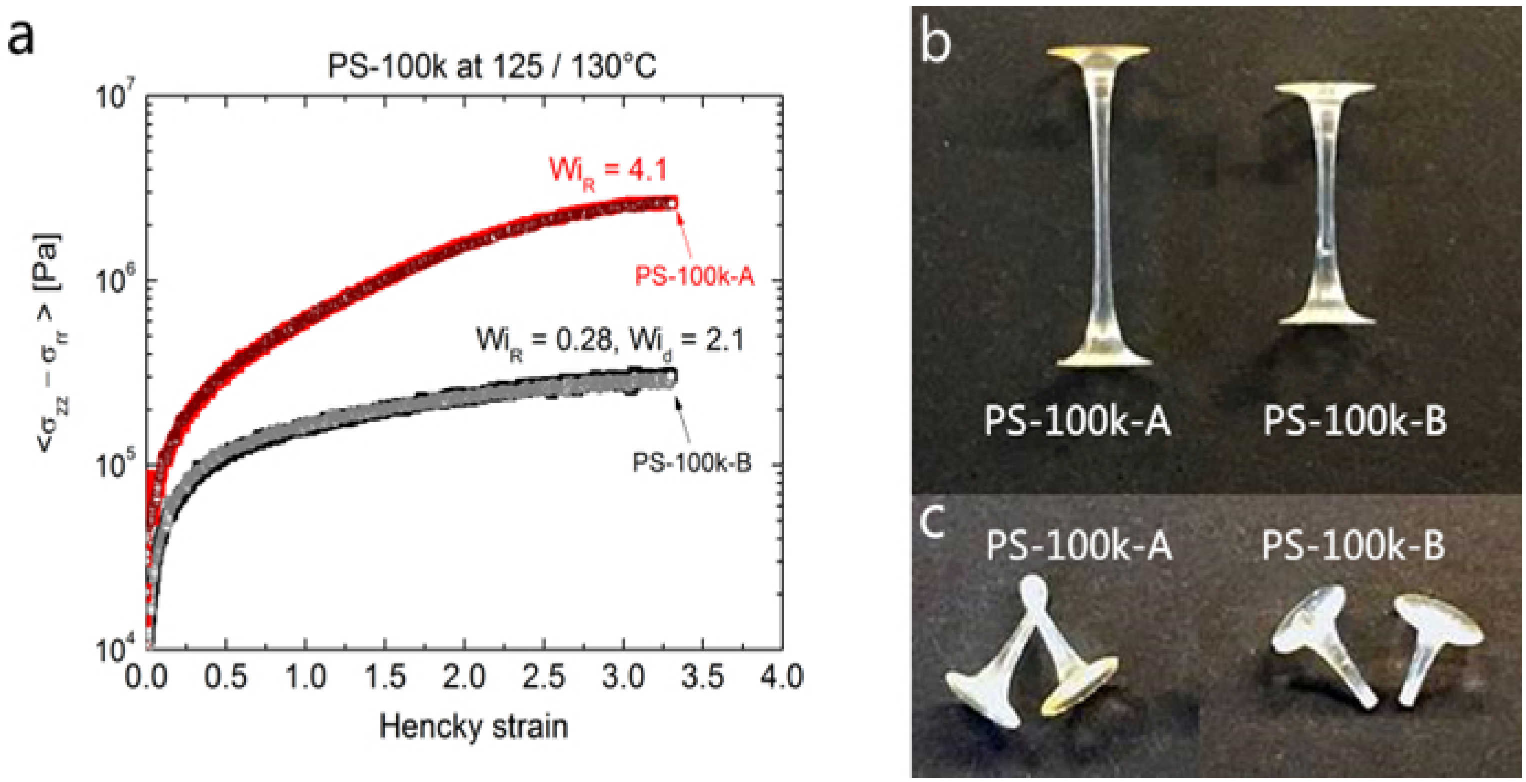
Mortensen et al., PRL 120, 207801 (2018)

Influence on mechanical properties

Is polystyrene always brittle at room temperature?

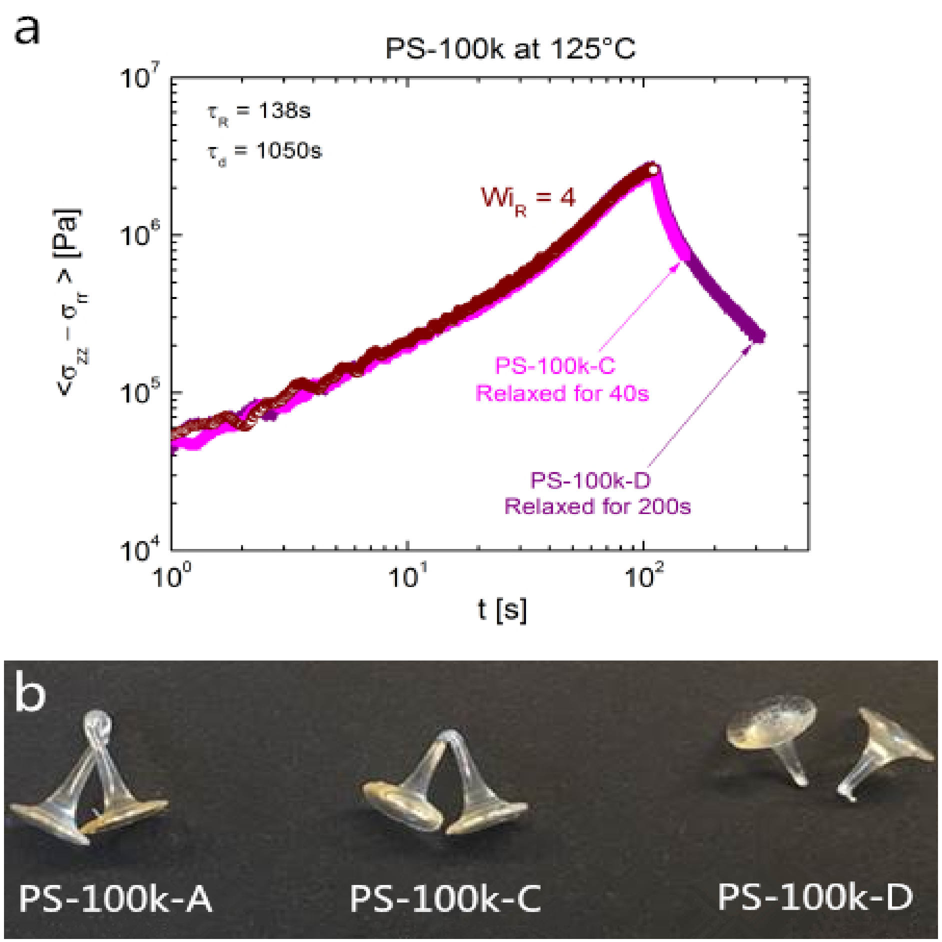
How to make flexible PS by just changing processing conditions?

Influence on mechanical properties



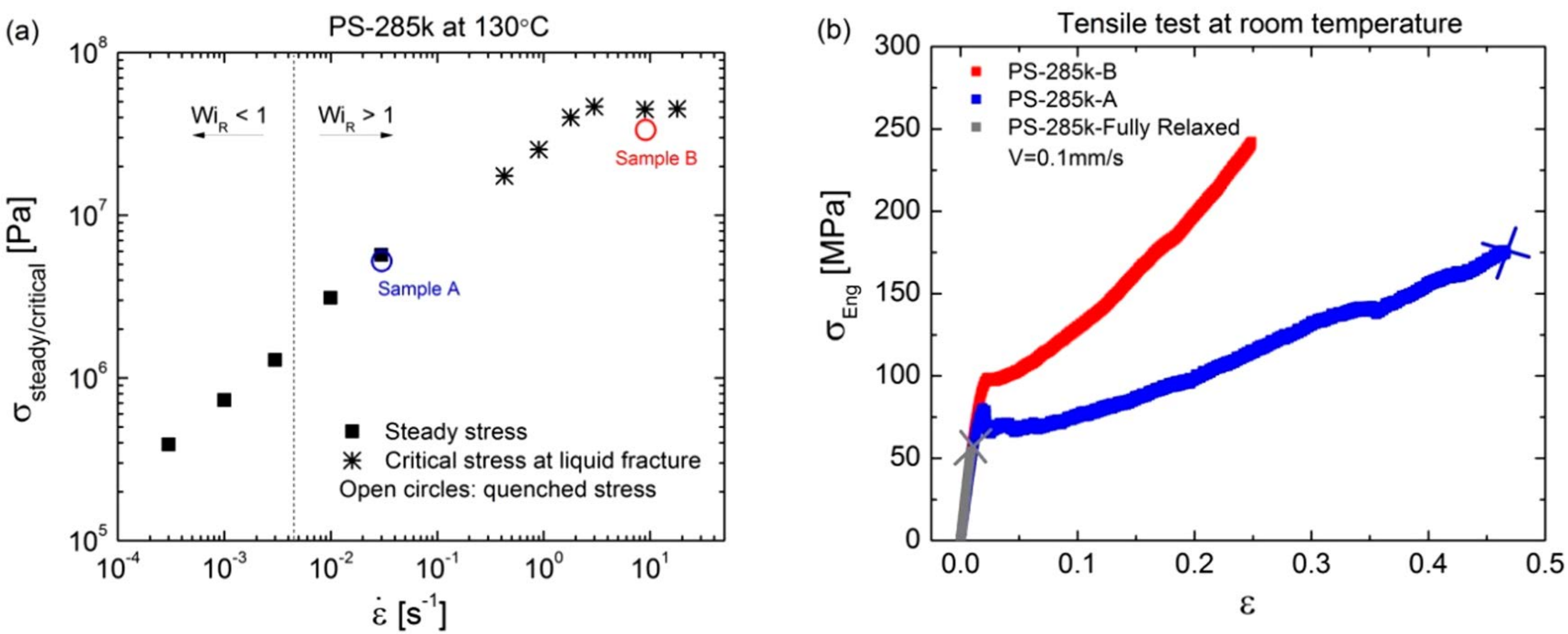
Huang et al., ACS Macro Letters 7, 1126–1130 (2018)

Influence on mechanical properties



Huang et al., ACS Macro Letters 7, 1126–1130 (2018)

Influence on mechanical properties



Huang et al., ACS Macro Letters 7, 1126–1130 (2018)

Thank you

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering