Practical nonlinear shear rheometry of polymers

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Useful reading

1. Macosko, Rheology: Principles, measurements and applications (1994)
2. Doi, Edwards, The theory of polymer dynamics, Oxford (1986)
3. Ferry, Viscoelastic Properties of Polymers (1980)
4. Larson, Structure and rheology of complex fluids (1999)
5. Rubinstein, Colby, Polymer Physics (2003)
6. Graessley, Polymer liquids and networks: Structure and rheology (2008)
7. Dealy, Read and Larson, Structure and rheology of molten polymers, 2nd ed. (2018)
8. Wang, Nonlinear polymer rheology, Wiley, 2018
9. Dealy, Wissbrun, Melt rheology and its role in plastics processing

Syllabus

Linear versus nonlinear behavior of polymers.

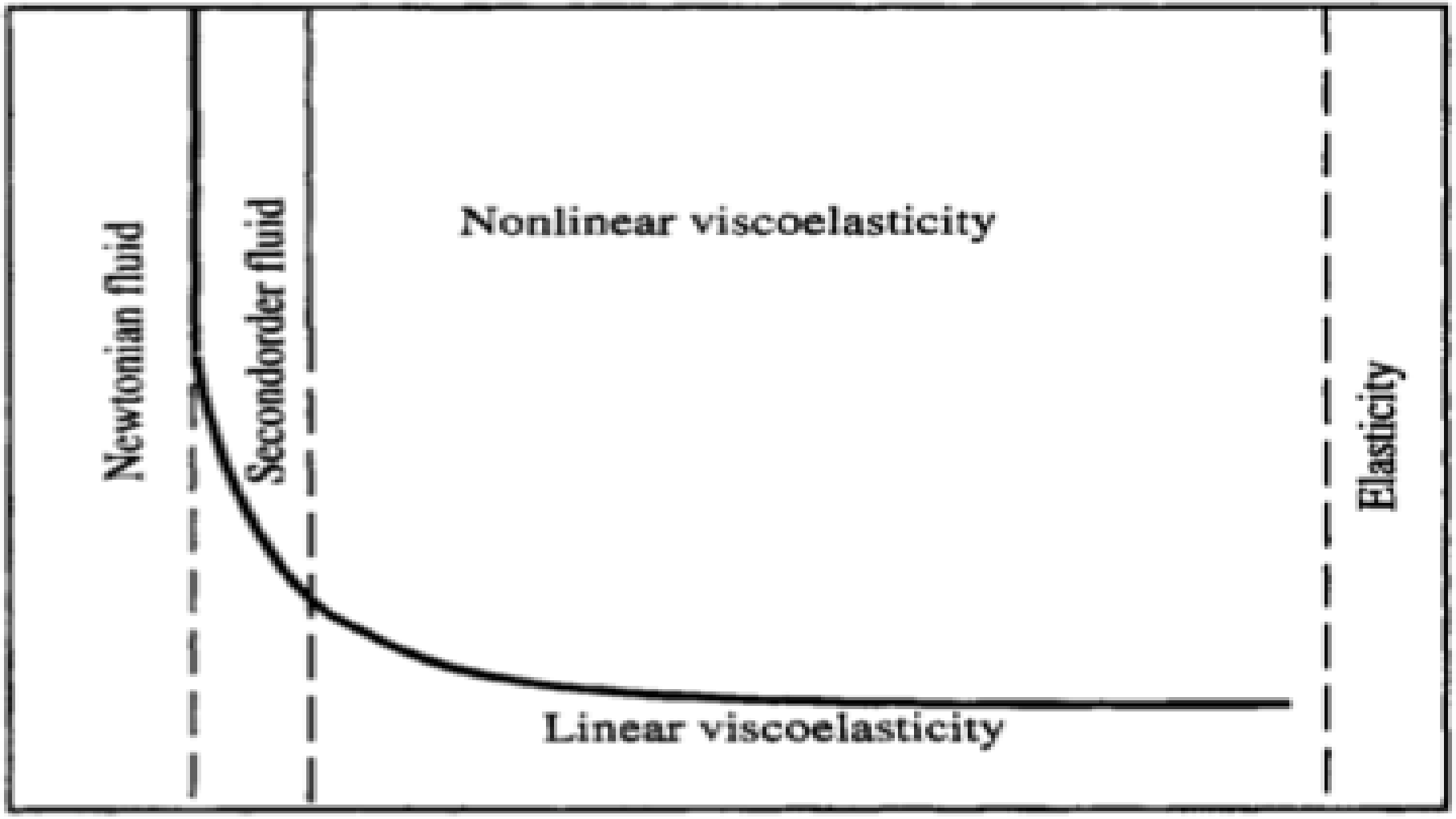
Shear thinning

How to obtain data in simple shear flow

Polymers in simple steady shear flow.

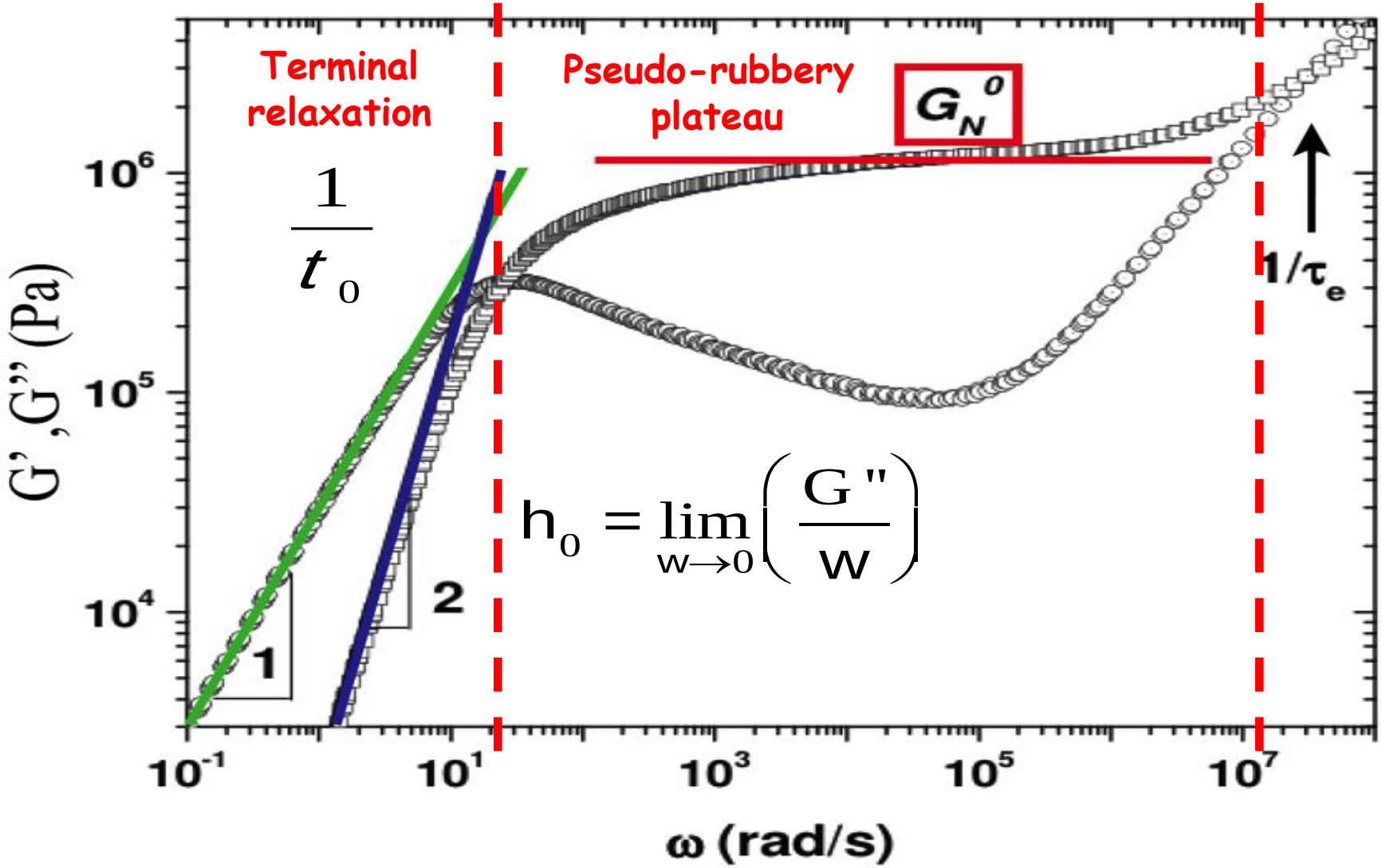
Other types of shear deformation.

Linear vs Nonlinear behavior



Pipkin (1972)

Linear regime for polymers



Oscillations at certain strain γ and frequency (and T).

What strain do we choose???

→Dynamic Strain Sweep

Monodisperse polybutadiene melt
M_w=99060 g/mol at 40°C

Van Ruymbeke *et al.*, Rheol.Reviews (2008)

Linear vs Nonlinear behavior

Linear measurements: Apply deformation (or stress) to probe structure, not to influence/change structure.

→ Structure independent of applied deformation

Nonlinear deformation (or stress) affects structure.

→ Type of deformation.

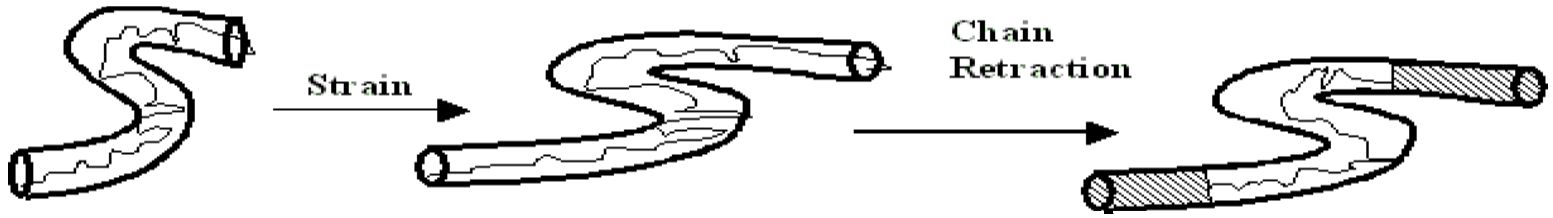
→ Deformation history.

<u>Strain or stress control (here strain)</u>

Polymers under nonlinear deformation

- Linear behavior = reptation, CLF, constraint release
- Orientation of the tube segments (rate > terminal relaxation)
- Stretch of the chain (rate > Rouse time)

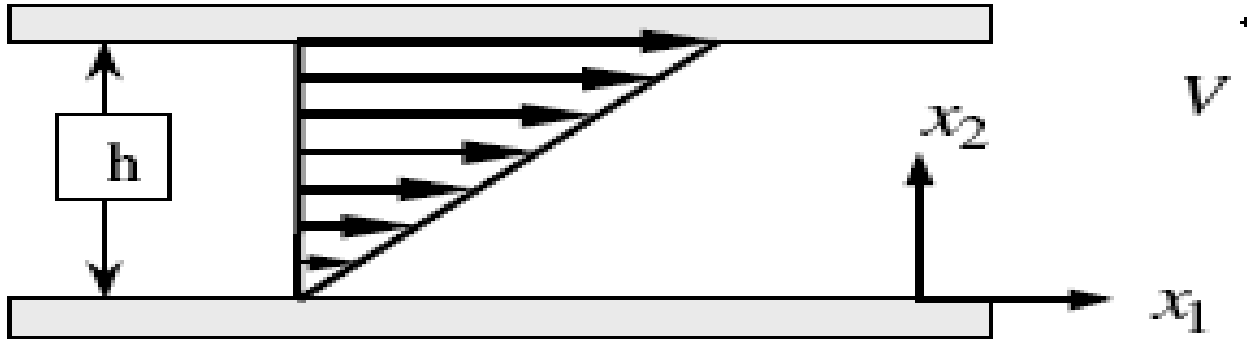
$$Wi = \dot{\gamma}\tau$$



- Effects of flow-field: Convective constraint release (CCR)

Marrucci
Ianniruberto

How to obtain data on polymers in simple shear flow?



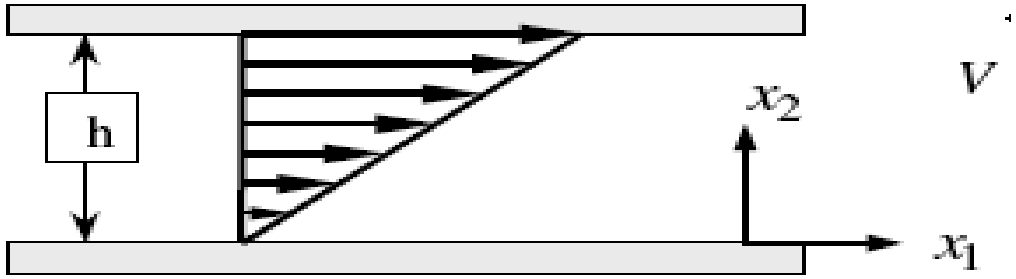
$V_1(x_1) = f(x_2)$

$$\frac{D\sigma_p}{Dt} = f\left(\sigma_p, \nabla \mathbf{v}\right)$$

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

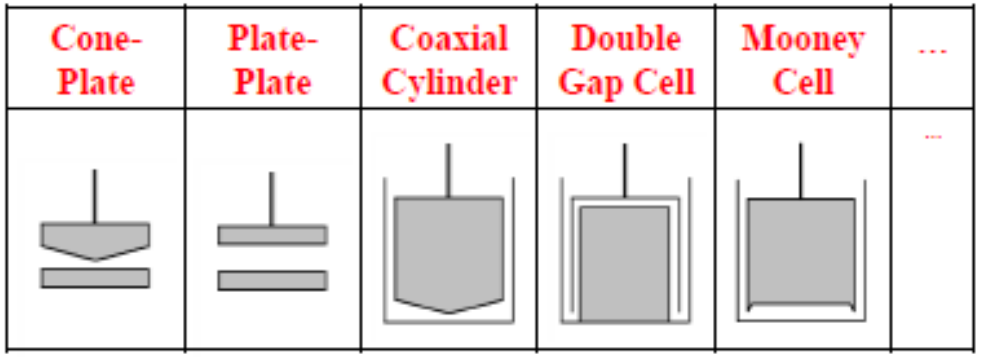
Simple shear flow

Sliding plate rheometer

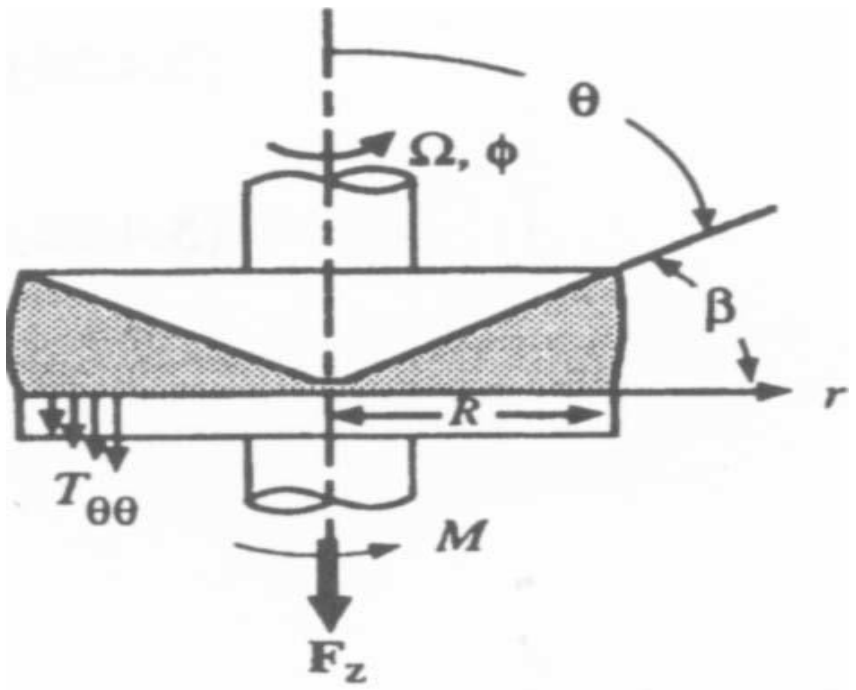


Ideal flow field but not commercially available (only home-made setups). Not on rotational rheometer.

Instabilities are a problem.



Cone and plate



$$u_\phi(r,\theta) = rf(\theta)$$

$$\gamma = \frac{\Omega}{\beta} \qquad \dot{\gamma} = \frac{\phi}{\beta}$$

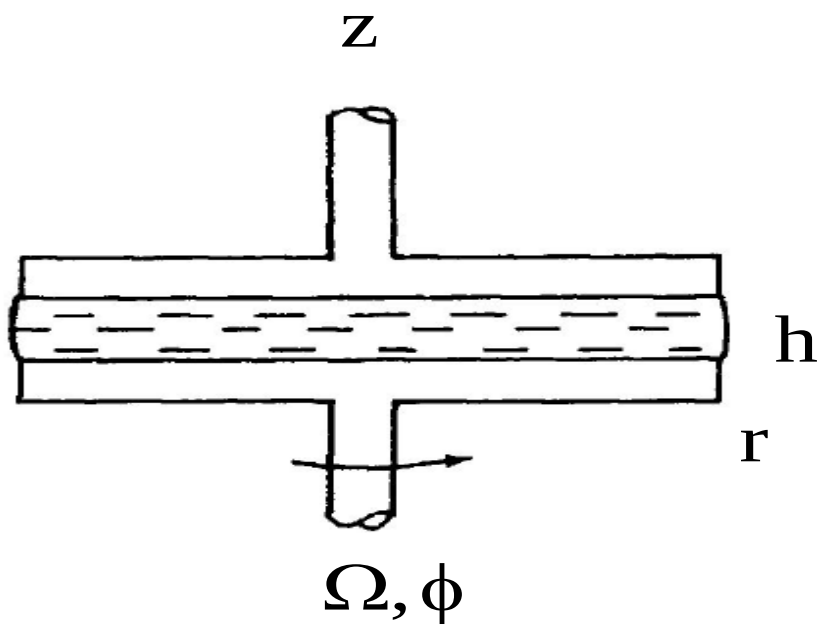
$$\sigma_{\phi\theta} = \frac{3M}{2\pi R^3}$$

$$\beta < 0.1 rad$$

- Readily commercially available for rotational rheometers
- In principle ideal simple shear flow
- Prone to instabilities (i.e. slip, edge fracture)
- Ok for not too elastic samples at low rates

Macosko, 1994

Parallel plates



$$u_\phi(r,z) = rf(z)$$

$$\gamma = \frac{\phi r}{h} \qquad \dot{\gamma} = \frac{r\Omega}{h}$$

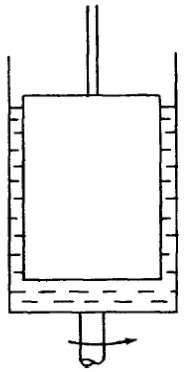
$$\sigma_{\phi z} = \frac{M}{2\pi R^3}\left(3 + \frac{d\ln M}{d\ln \dot{\gamma}_R}\right)$$

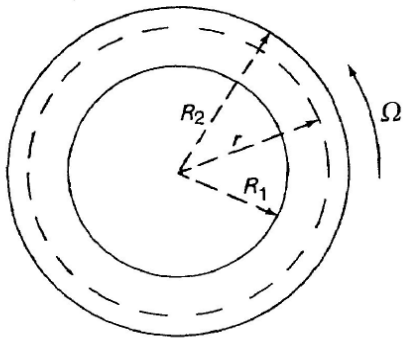
Good for LVE

Careful with NLVE: shear rate is not constant

Macosko, 1994

Concentric cylinders (Couette)





$$\frac{v_\theta}{r} = \Omega \frac{\left(\frac{1}{r^2} - \frac{1}{R_1^2}\right)}{\left(\frac{1}{R_2^2} - \frac{1}{R_1^2}\right)}$$

$$\dot{\gamma} = \left| r \frac{\partial (v_\theta / r)}{\partial r} \right| = \frac{2\Omega}{r^2 \left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right)}$$

$$\kappa = \frac{R_1}{R_2} \geq 0.99$$

$$R_1 \cong R_2 \cong \bar{R}$$

$$\dot{\gamma} \cong \frac{\Omega \bar{R}}{(R_2 - R_1)}$$

$$\gamma = \frac{\theta \bar{R}}{R_2 - R_1}$$

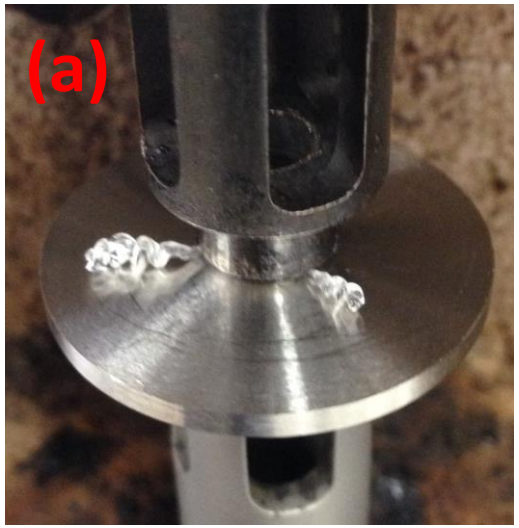
Best for low-viscosity fluids

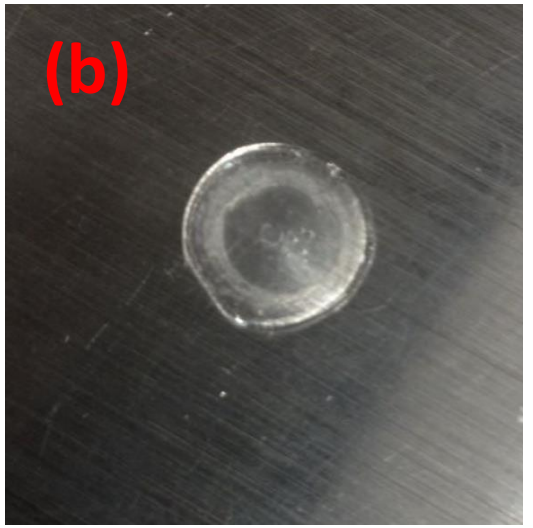
Macosko, 1994

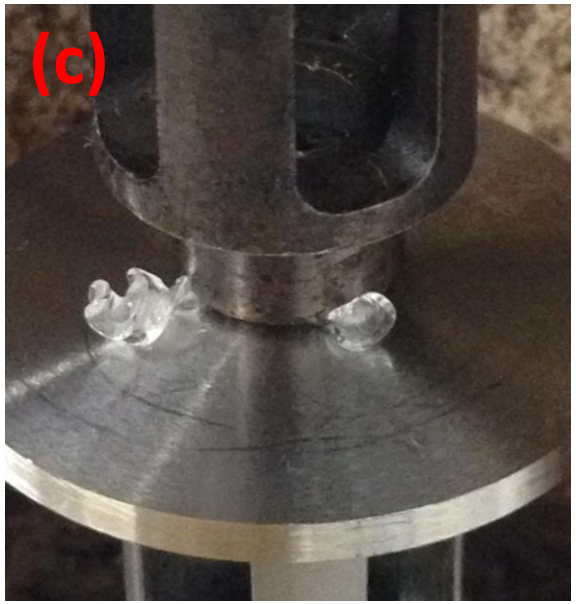
Shear measurements: fracture & slip

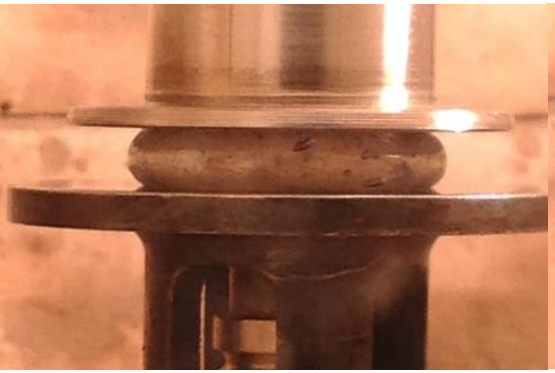
Shear measurements: fracture & slip

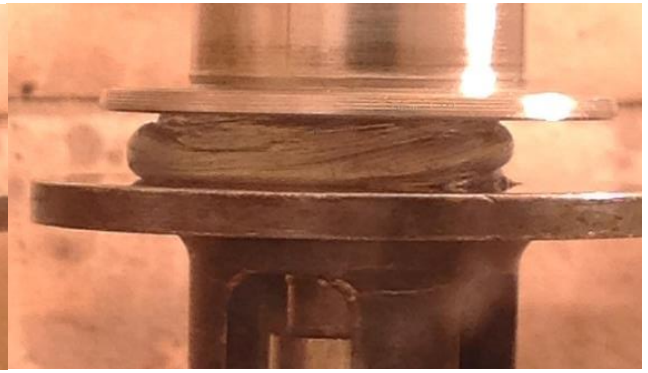
Shear measurements: fracture & slip



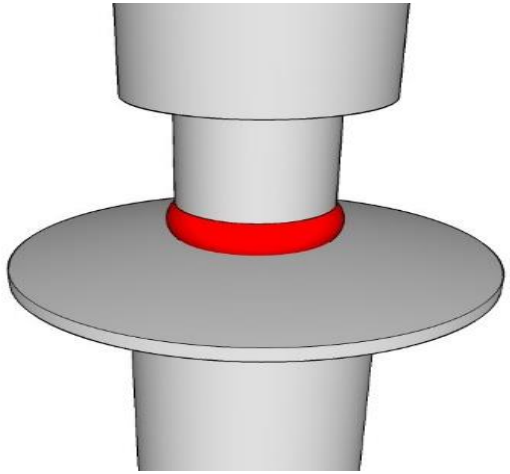


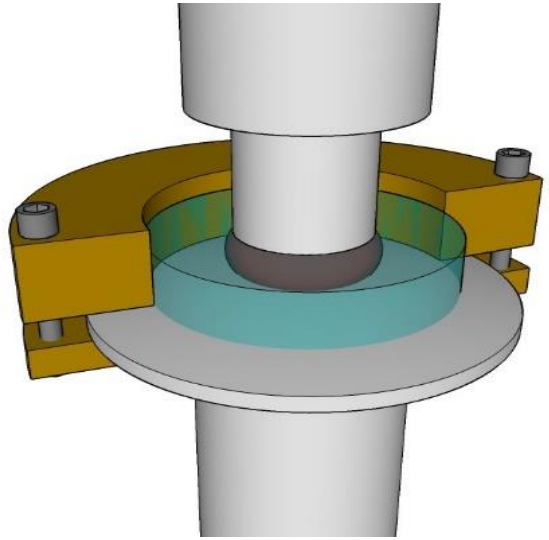






Reduce / eliminate fracture ?



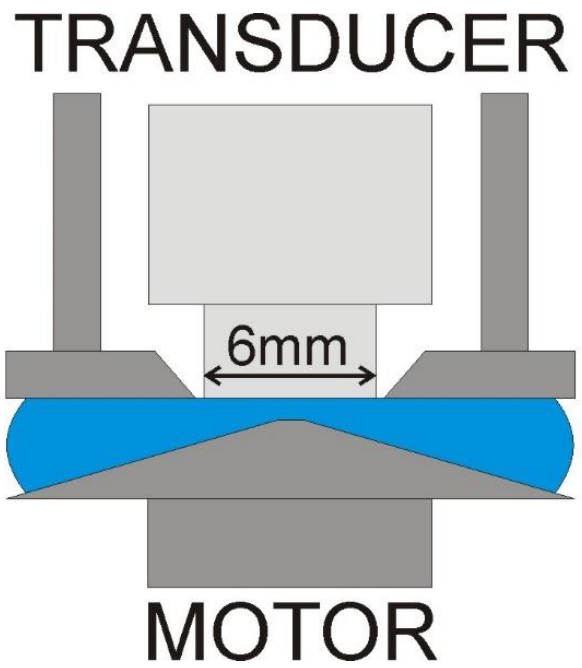


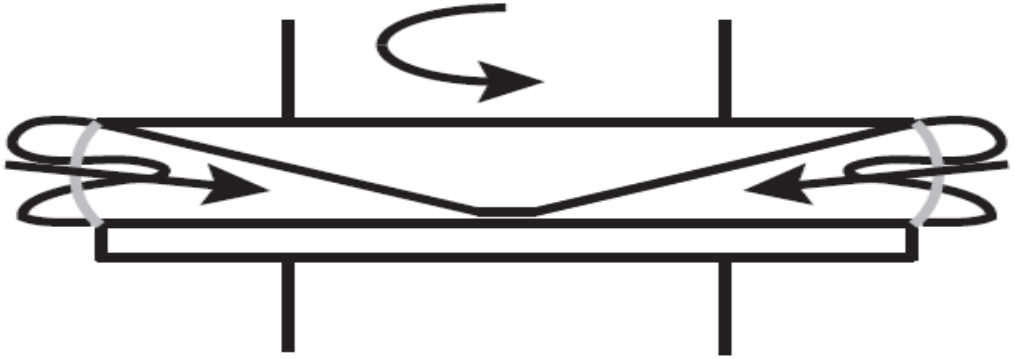
Hemingway, Fielding et al. PRL 2017

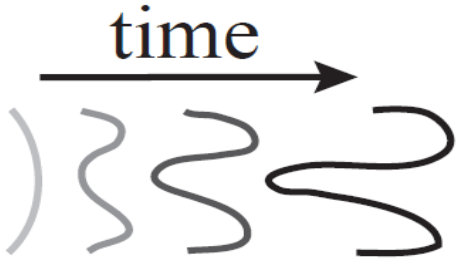
Measurements with Cone-partitioned plate (CPP) geometry

Pollet + Cross, J. Sci. Instrum. 1950
Meissner et al., J. Rheol. (1989)
Ravindranath + Wang, J. Rheol. (2008)
Schweizer et al., JOR 2013
Skorski and Olmsted, J. Rheol. 2011

Tanner + Kenntok, JOR 1983
Schweizer et al., J. Rheol. (2003-6)
Snijkers, DV, JOR 2011
Costanzo et al. Macromolecules 2016

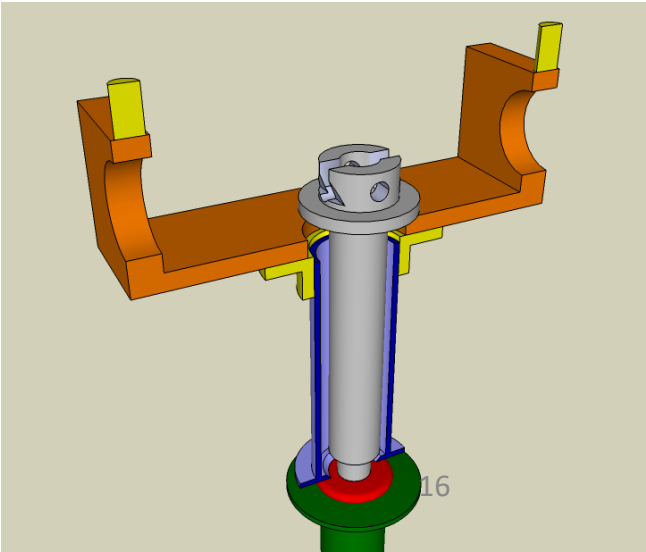




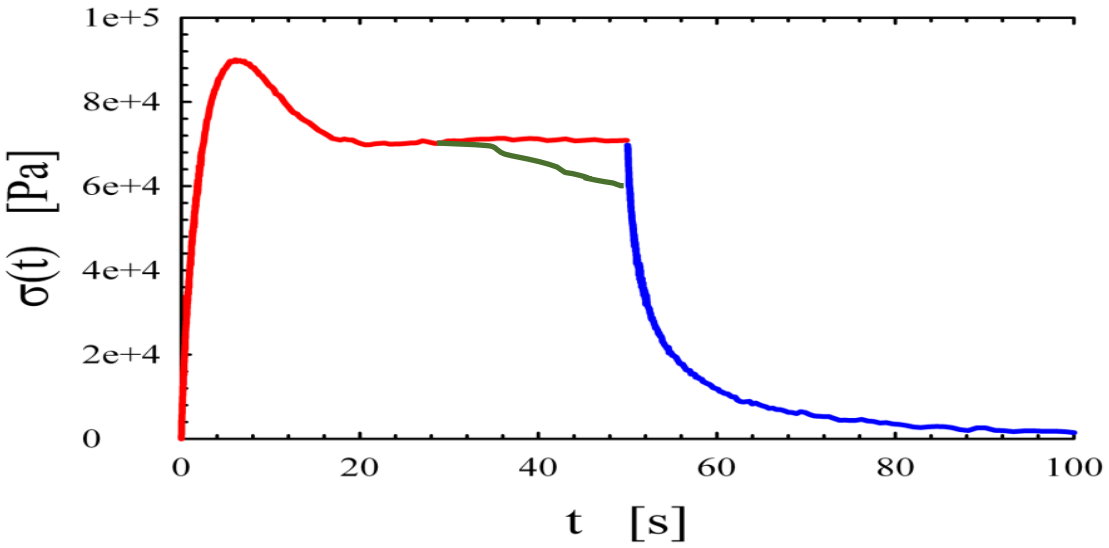


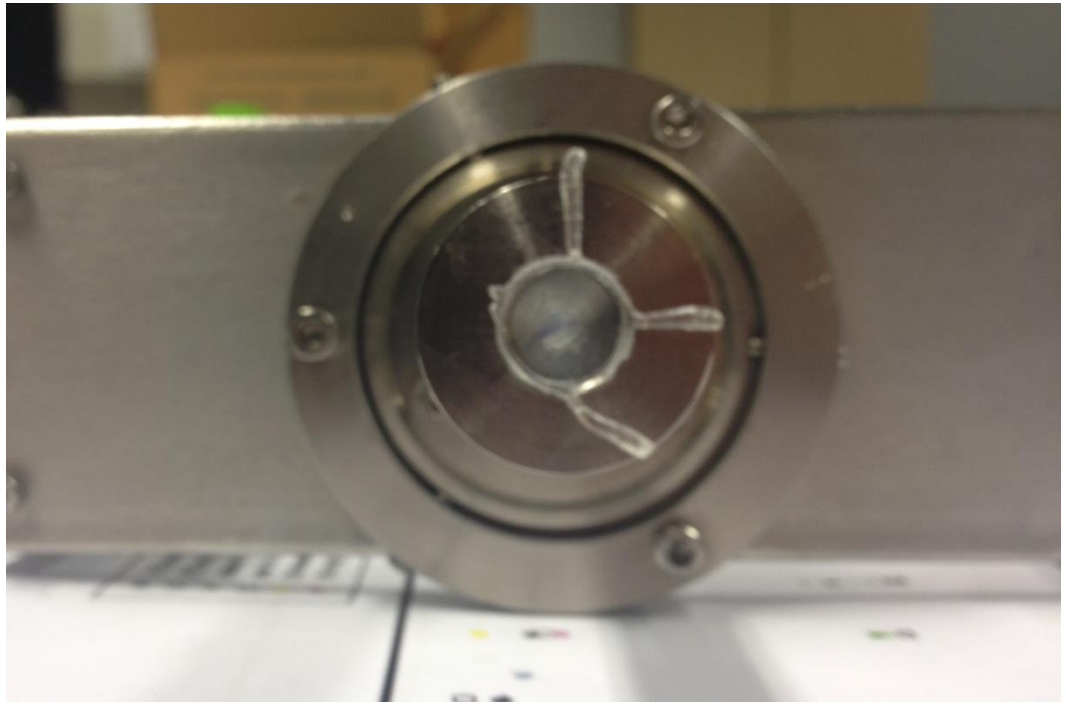
$$N_{2c} \sim \frac{\Gamma}{h}$$

Fracture does not influence measurement



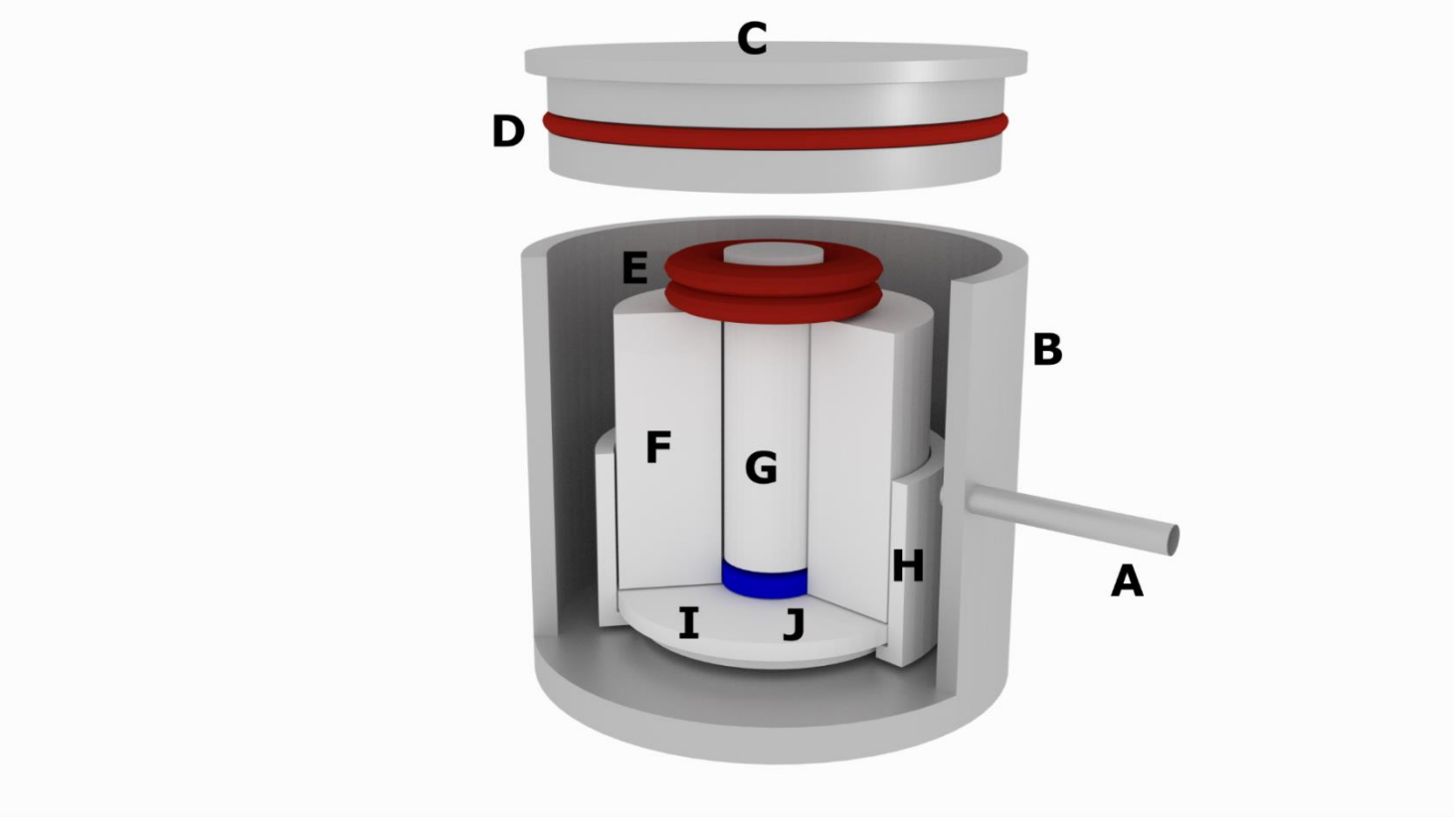
CPP and edge fracture

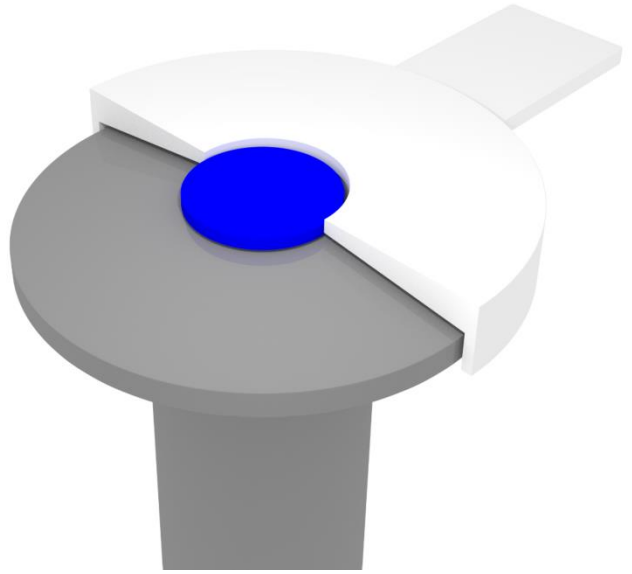




Costanzo et al., Macromolecules 2016

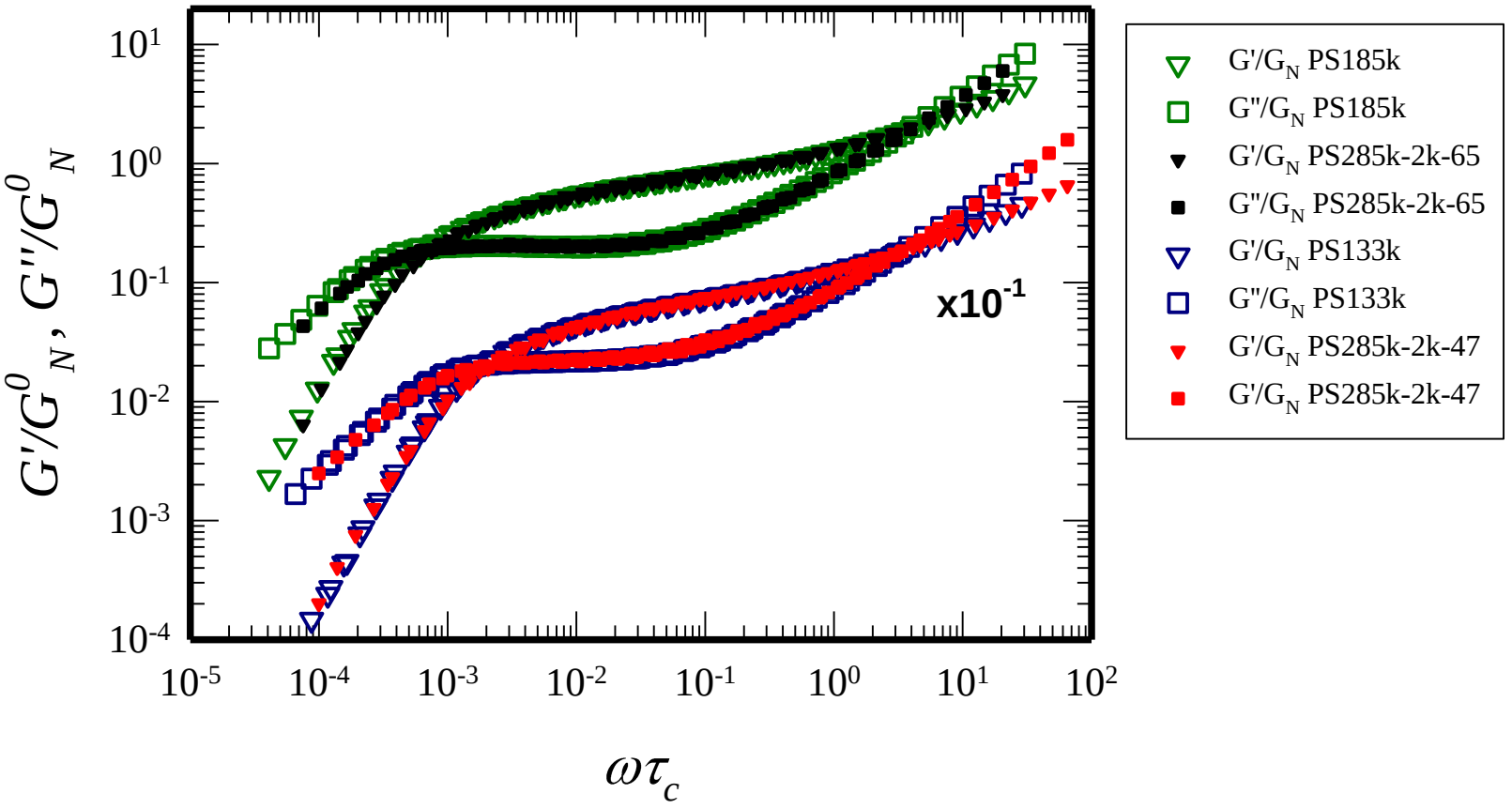
Sample handling





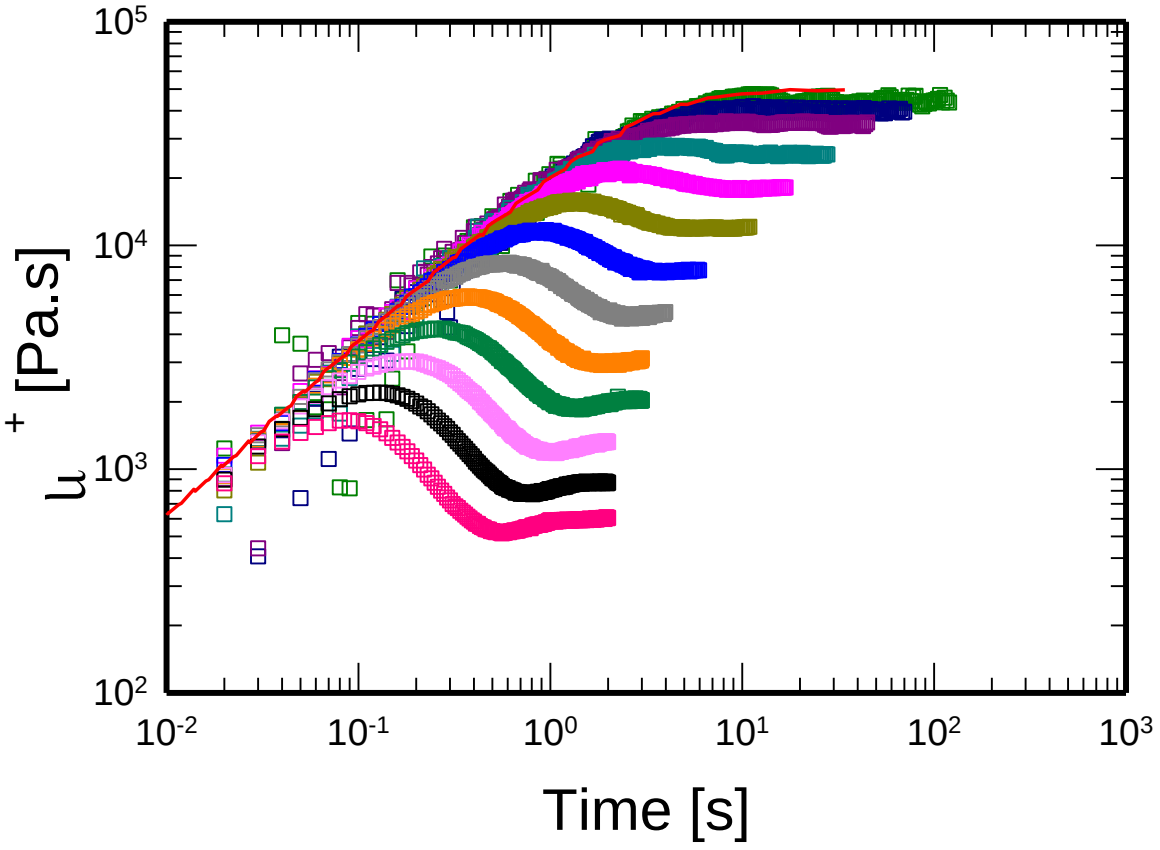
T_g is a determining factor

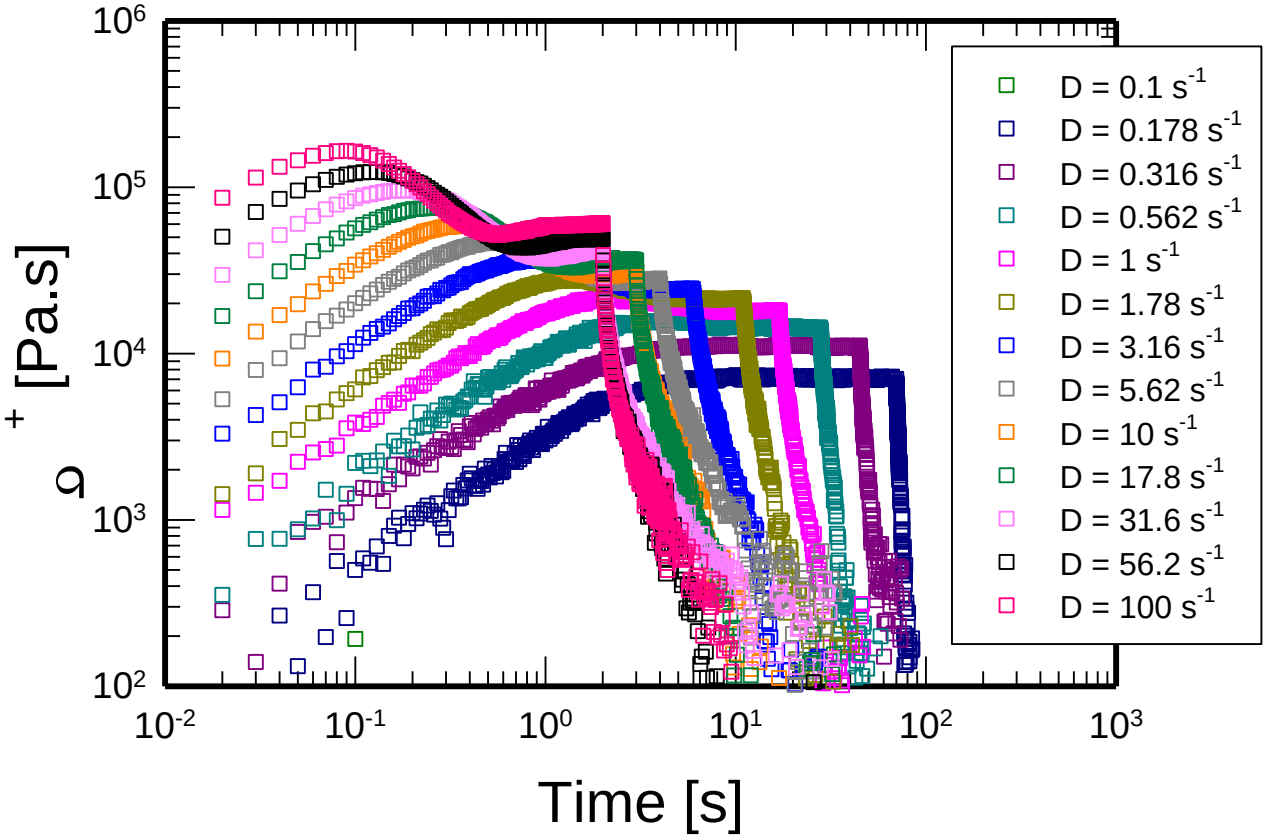
LVE scaling


G'/G^0_N, G''/G^0_N
$\omega\tau_c$
x10^{-1}
G'/G$_N$ PS185k
G"/G$_N$ PS185k
G'/G$_N$ PS285k-2k-65
G"/G$_N$ PS285k-2k-65
G'/G$_N$ PS133k
G"/G$_N$ PS133k
G'/G$_N$ PS285k-2k-47
G'/G$_N$ PS285k-2k-47

Start-up and relaxation in simple shear

PS285k-2k-47 @ 140°C

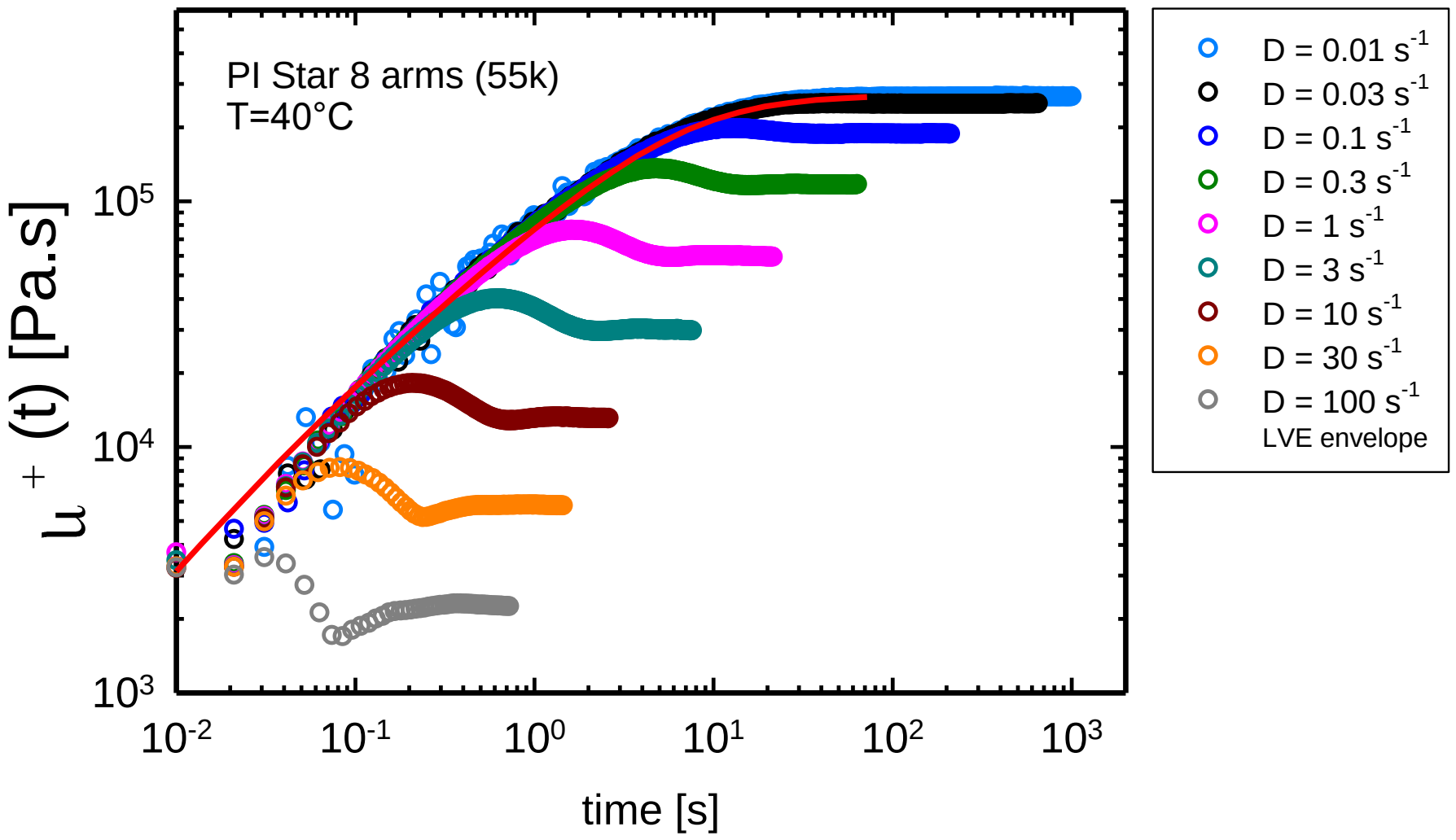




No steady state shear banding

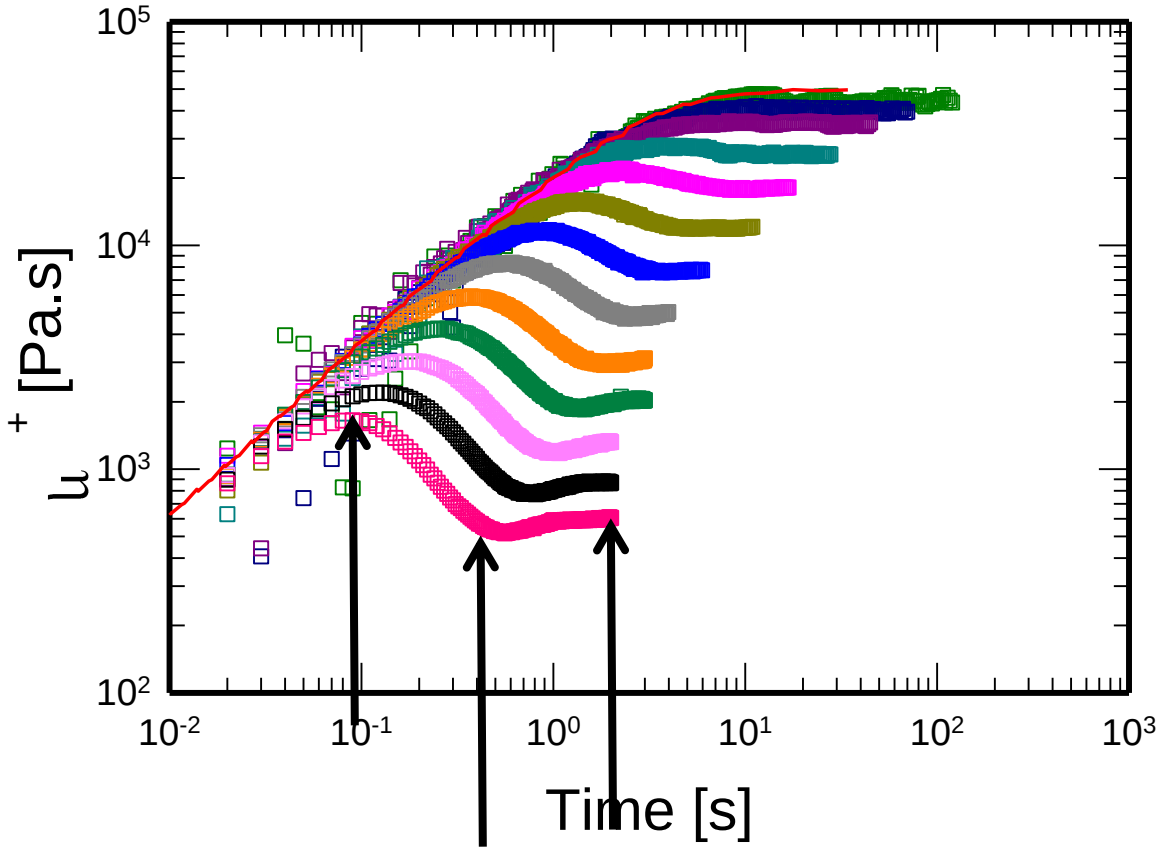
Undershoot at large shear rates

Costanzo et al., Macromolecules 2016


PI Star 8 arms (55k)
T=40°C
$\mu^+(t)$ [Pa.s]
10^5
10^4
10^3
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
time [s]
D = 0.01 s^{-1}
D = 0.03 s^{-1}
D = 0.1 s^{-1}
D = 0.3 s^{-1}
D = 1 s^{-1}
D = 3 s^{-1}
D = 10 s^{-1}
D = 30 s^{-1}
D = 100 s^{-1}
LVE envelope

Start-up and relaxation in simple shear

PS285k-2k-47 @ 140°C

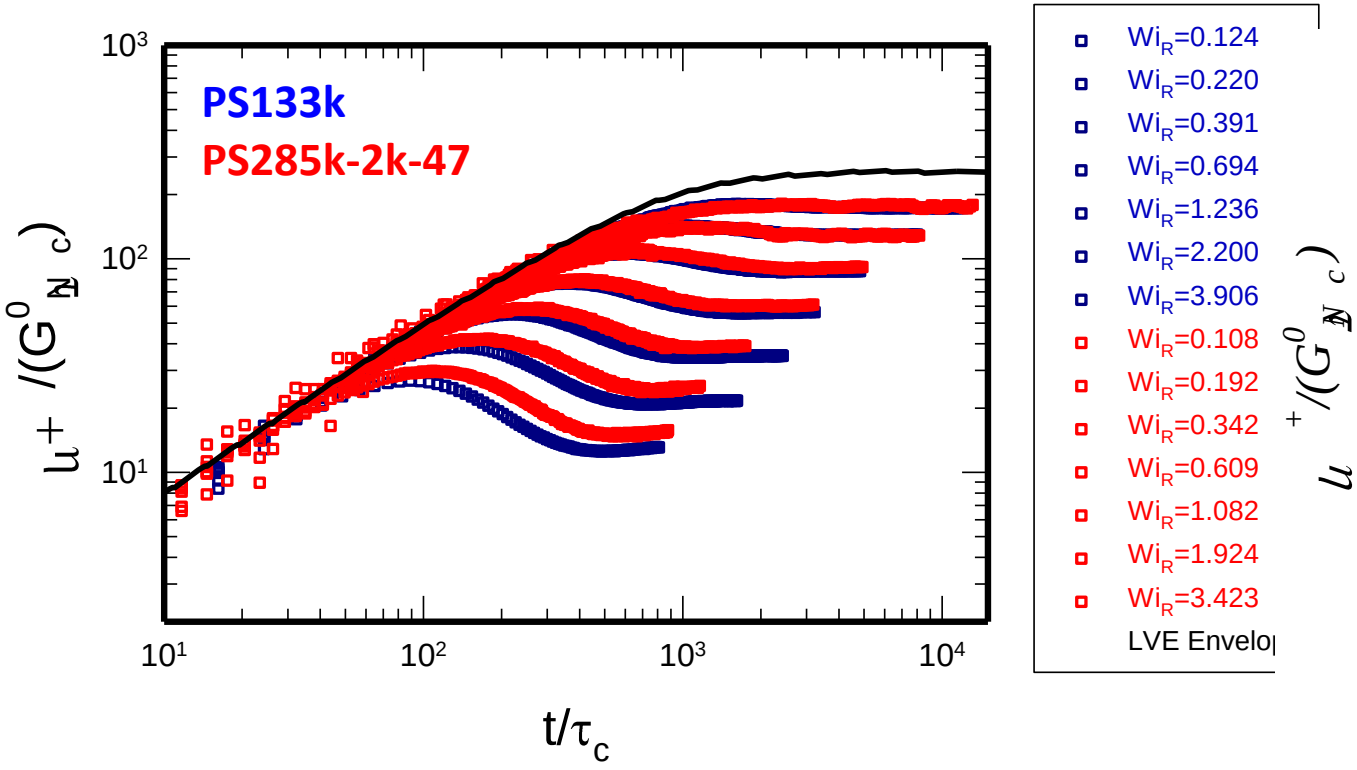


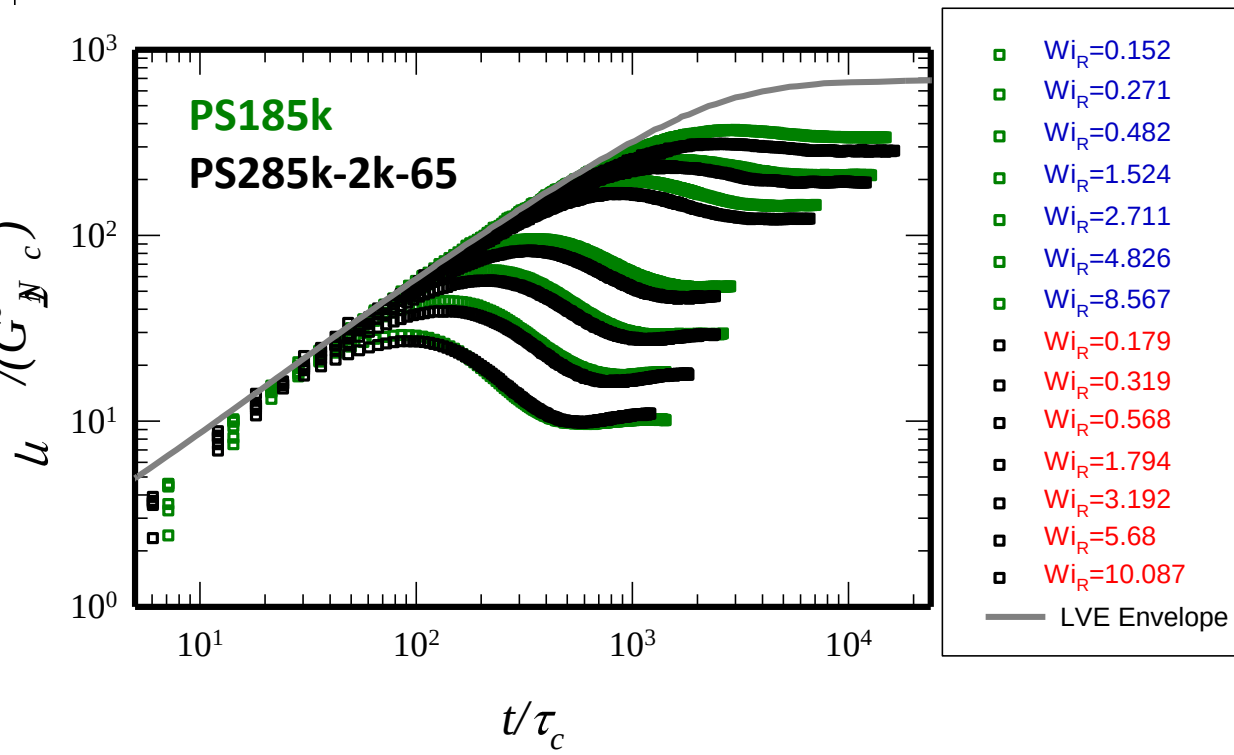
No steady state shear banding

Undershoot at large shear rates

Costanzo et al., Macromolecules 2016

Nonlinear Start-up shear flow: scaling

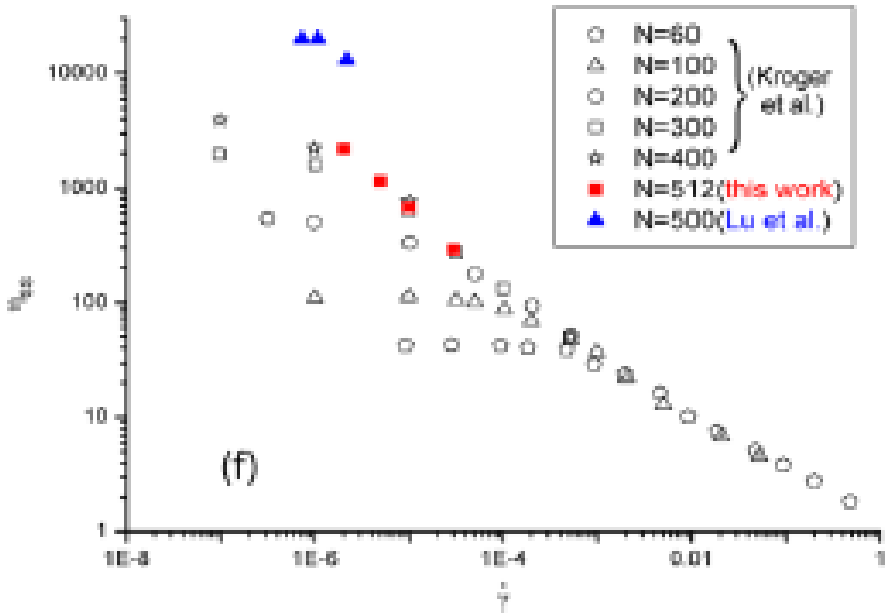


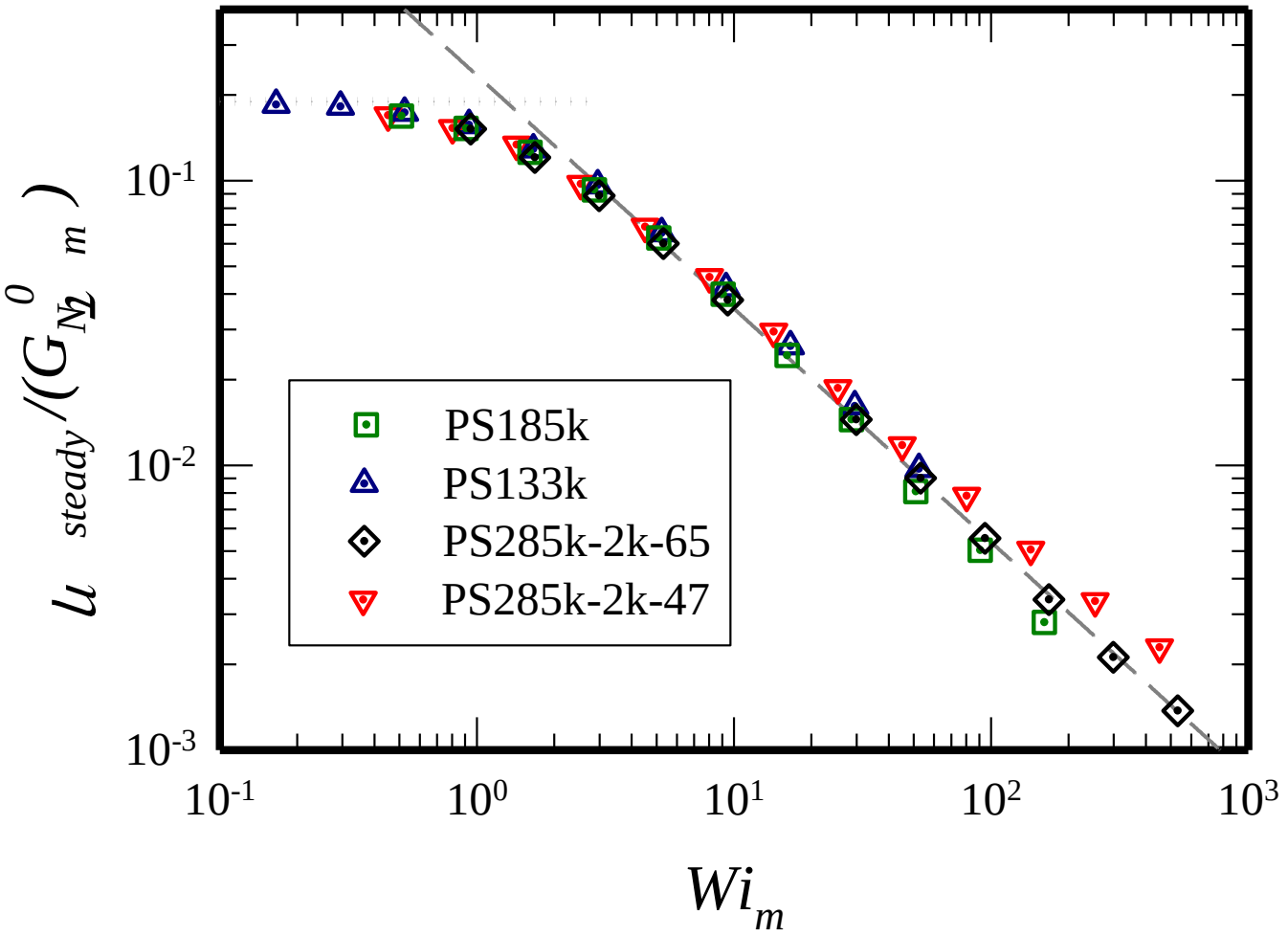


No difference between PS melts and solutions with the same Z

Steady shear flow

Thinning slope: -0.82

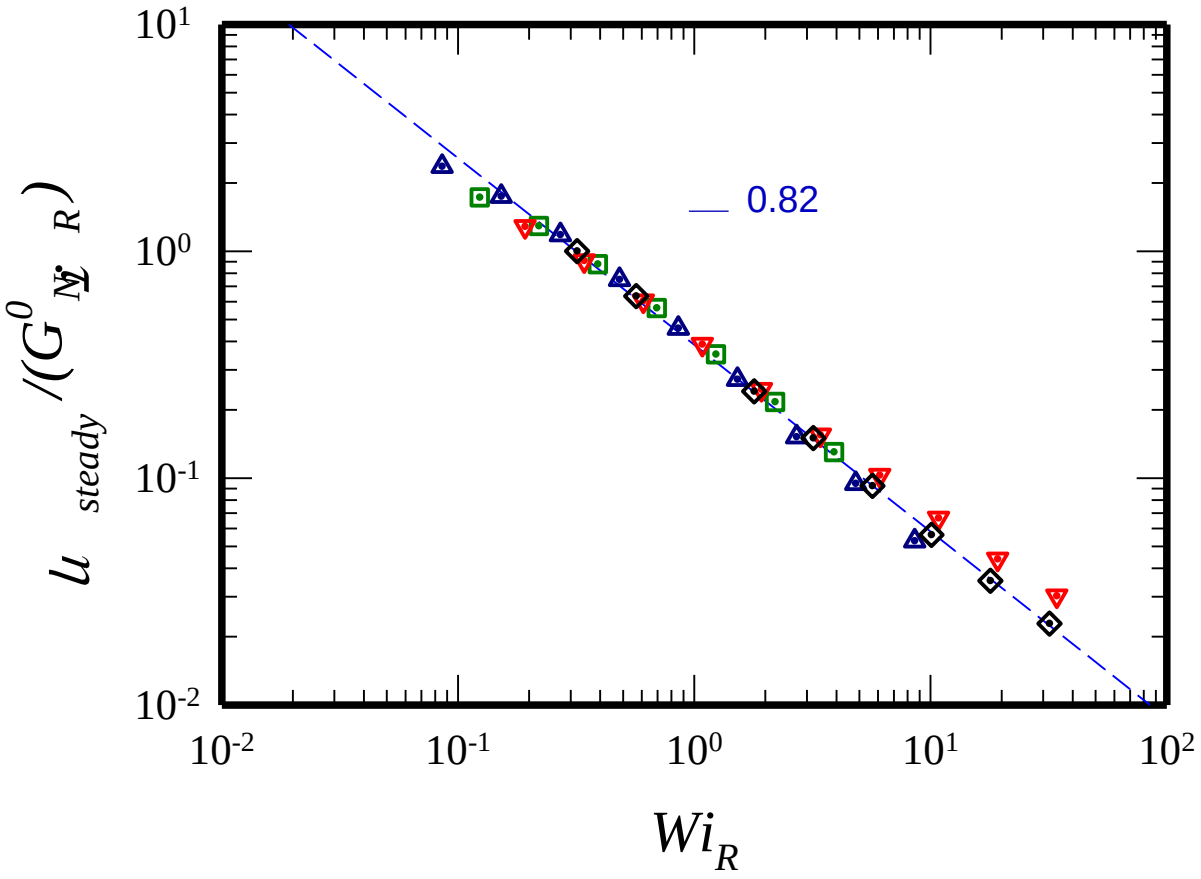


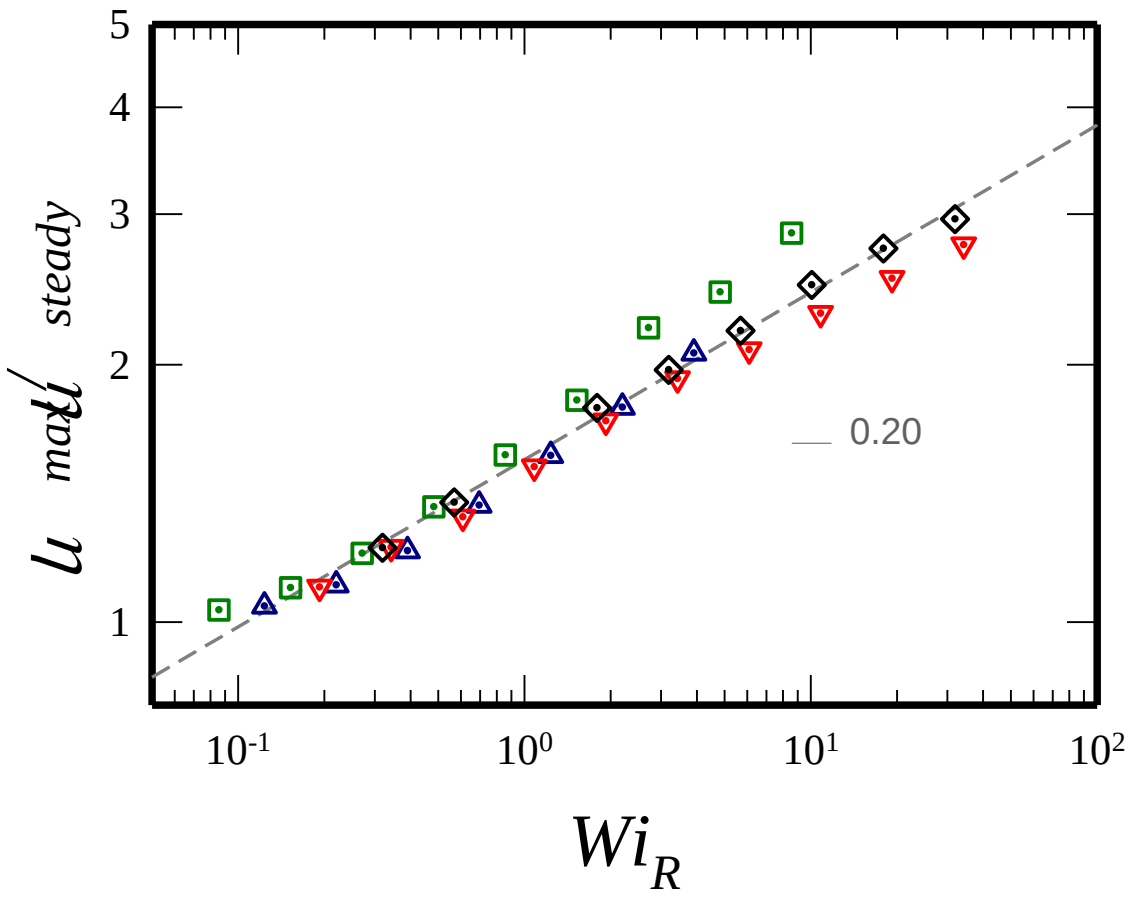


Cao and Likhtman, ACS Macro Lett. 2015
Kröger and Hess, PRL 2000

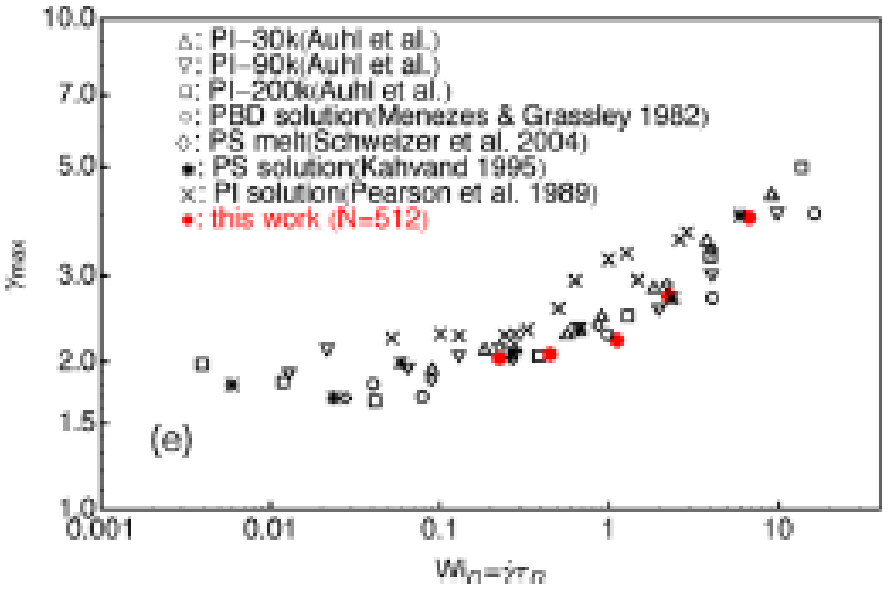
Costanzo et al., Macromolecules 2016

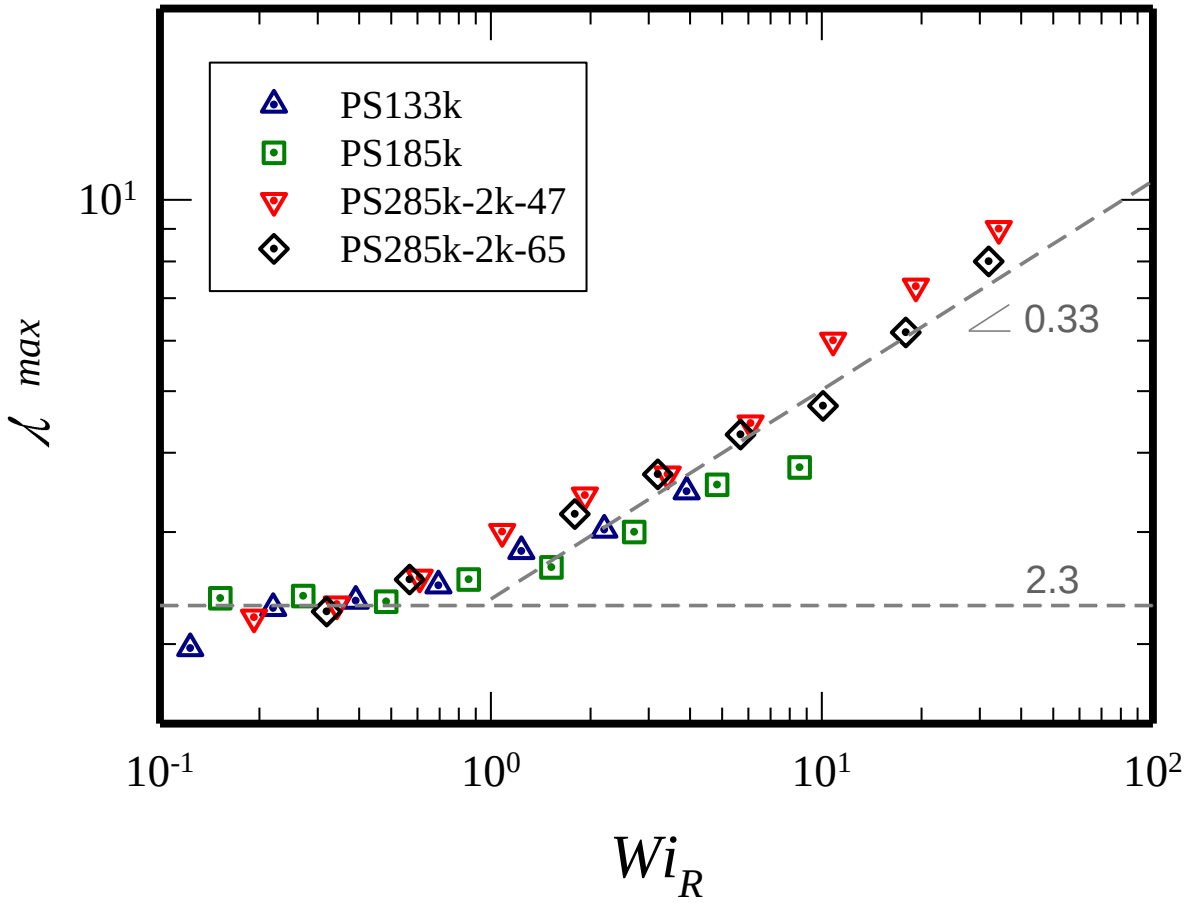
Shear viscosity: scaling





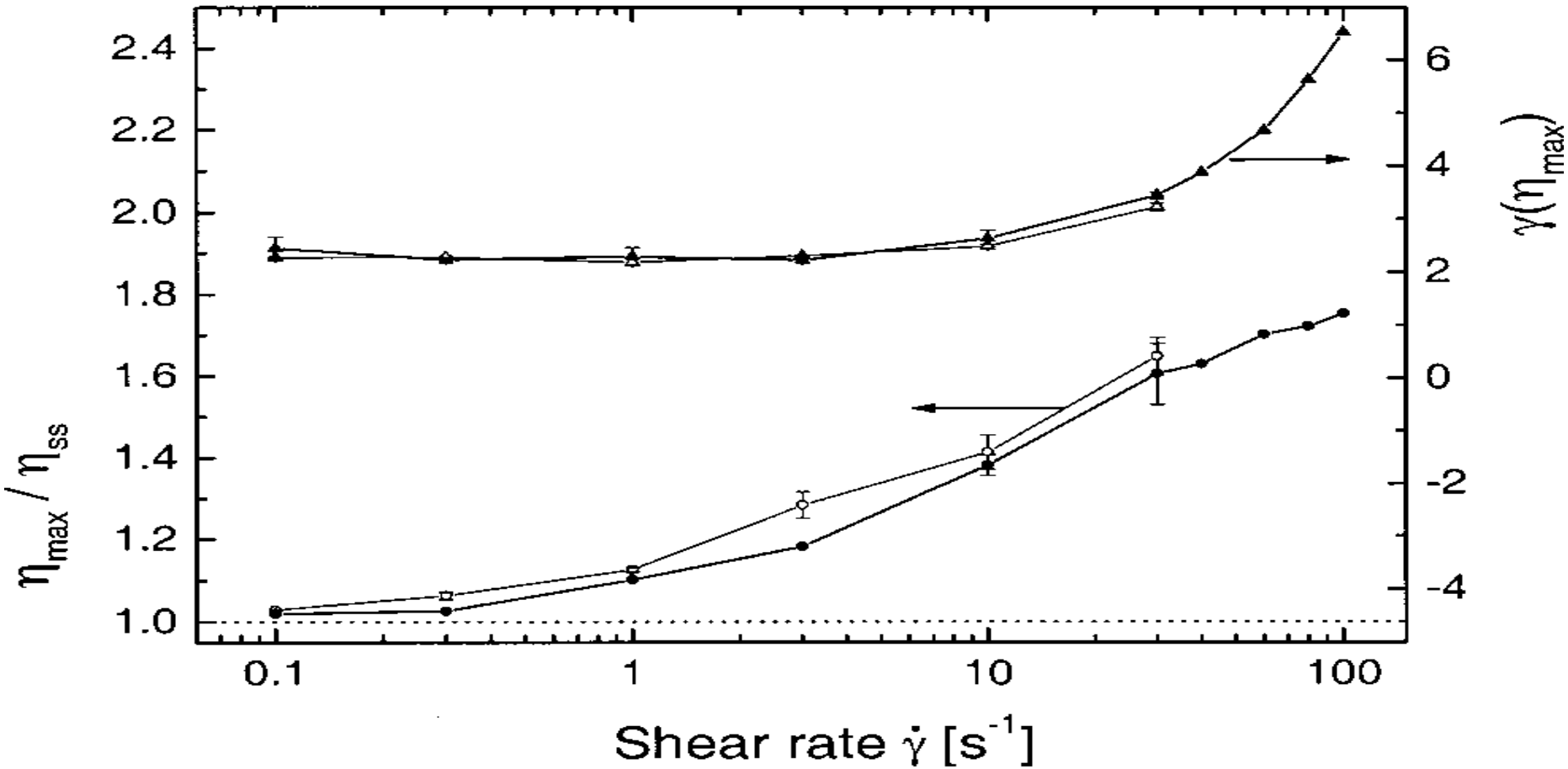
Peak strain: scaling





GLaMM: Graham et al., J. Rheol. 2003 (1)
K. S. Schweizer (2015) : retraction + internal force (1/3)
Cao and Likhtman , ACS Macro Lett. 2015 (1/3)
Auhl et al., J. Rheol. 2008

Ravindranath and Wang, J. Rheol. 2008
Schweizer et al., J. Rheol. 2004
Snijkers and DV, J. Rheol. 2011
Costanzo et al., Macromolecules 2016



[Linear melt but

not monodisperse]

Comparing cone-partitioned plate and cone-standard plate shear rheometry of a polystyrene melt

Th. Schweizer[a)]

Institute of Polymers, ETH Zürich, CH-8092 Zürich, Switzerland

(Received 20 February 2003; final version received 14 April 2003)

Molecular modeling (Ianniruberto+Marrucci)

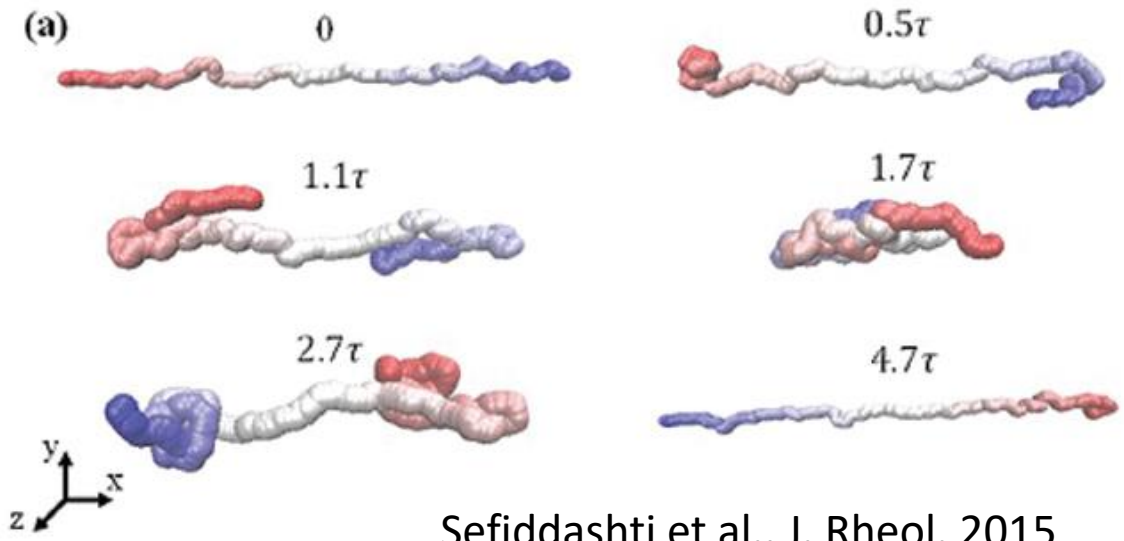
Decoupling stretch and orientation

$$\boldsymbol{\sigma}(t) = C_Q \lambda^2(t) \frac{f(\lambda)}{f_0} \sum G_i \boldsymbol{S}_i$$

Stretch ratio

Friction reduction in elongation

Tumbling function in shear

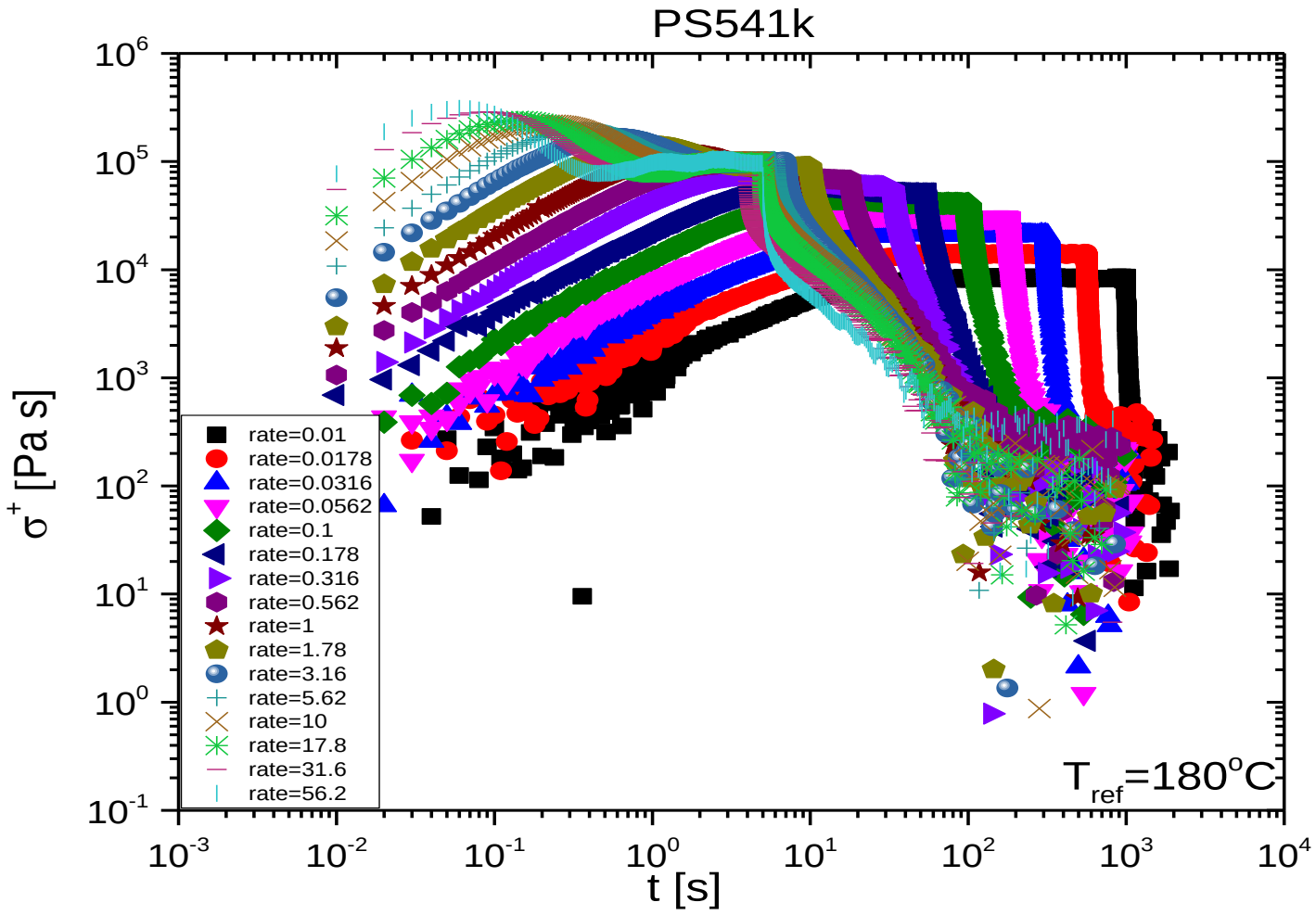


Sefiddashti et al., J. Rheol. 2015

Costanzo et al., Macromolecules 2016

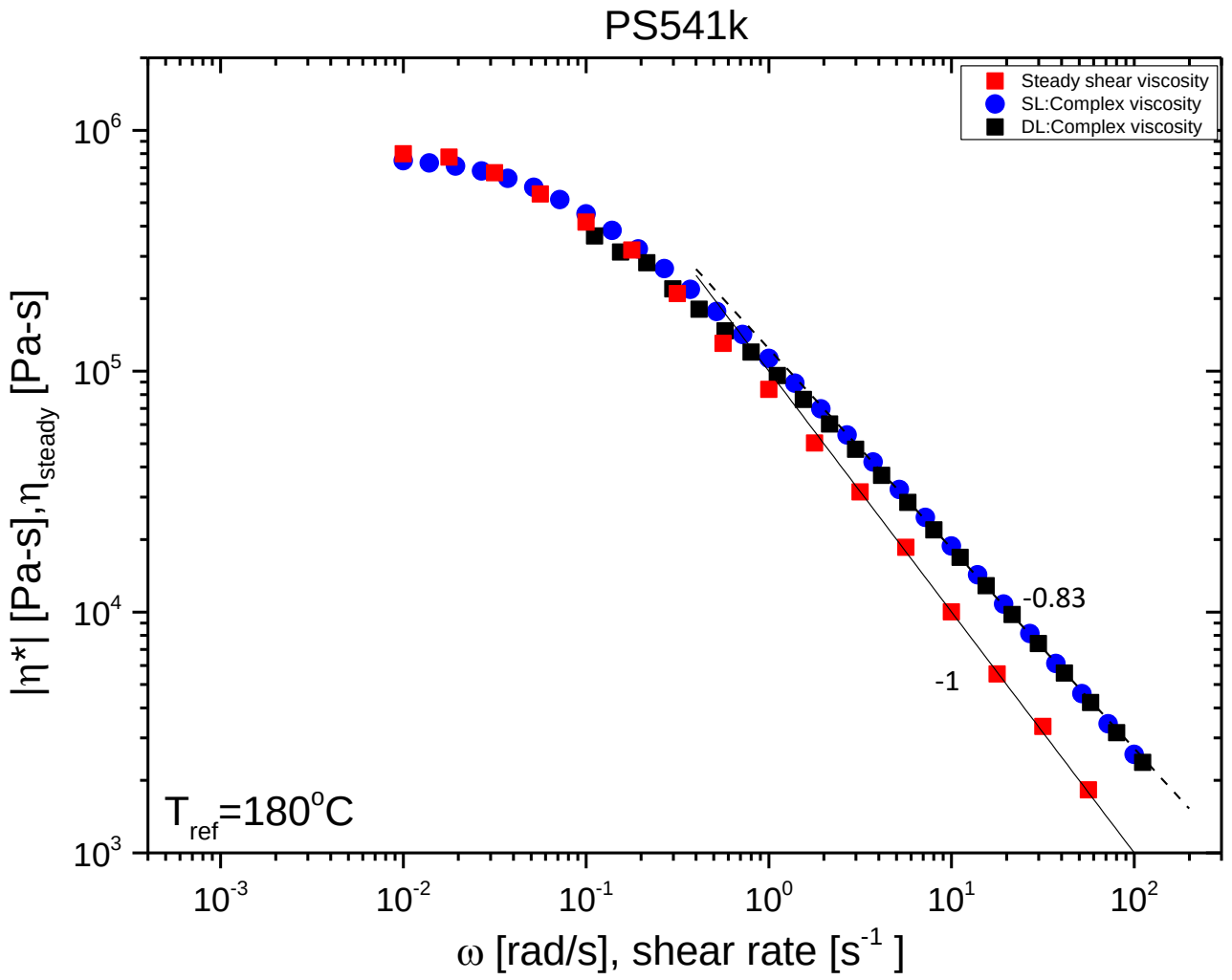
Ianniruberto , Macromolecules 2015

Careful: possible issues with data



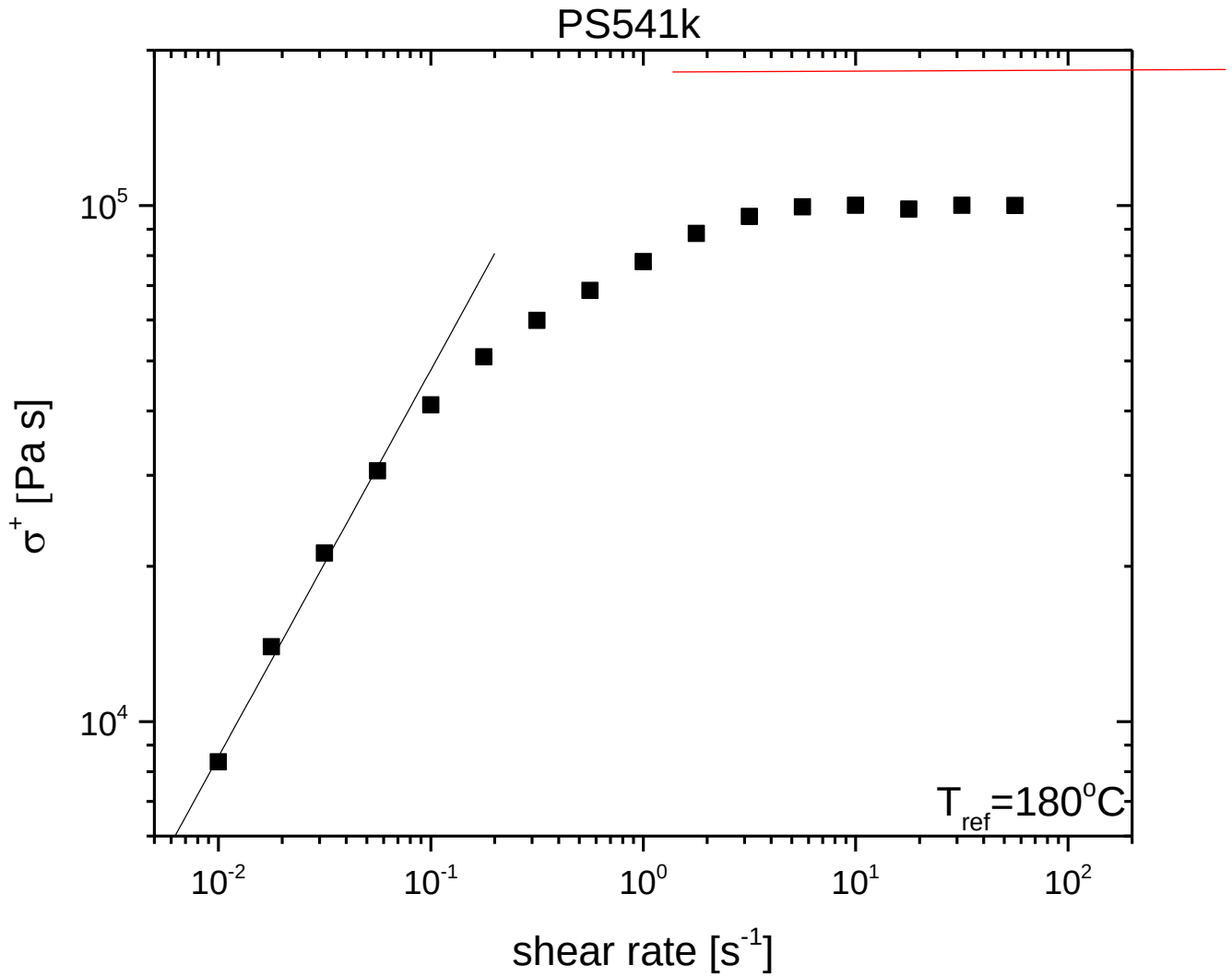
(tests: C. Pyromali)

Careful: possible issues with data



(tests: C. Pyromali)

Careful: possible issues with data



Shear banding

P. D. Olmstead
S. Fielding
W. J. Briels

(tests: C. Pyromali)

Olmstead, Rheol. Acta 2008

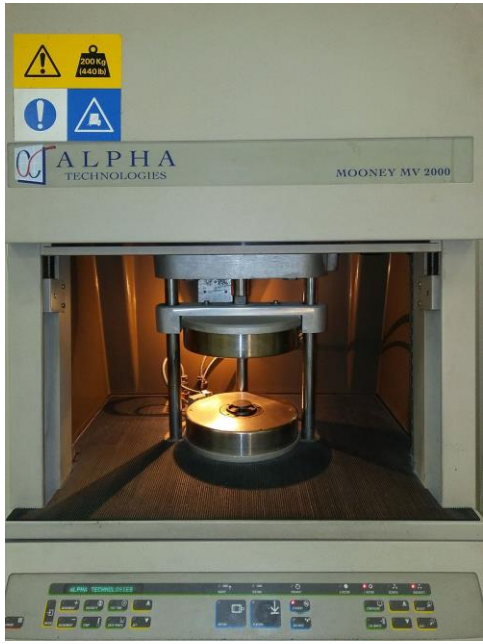
Higher rates

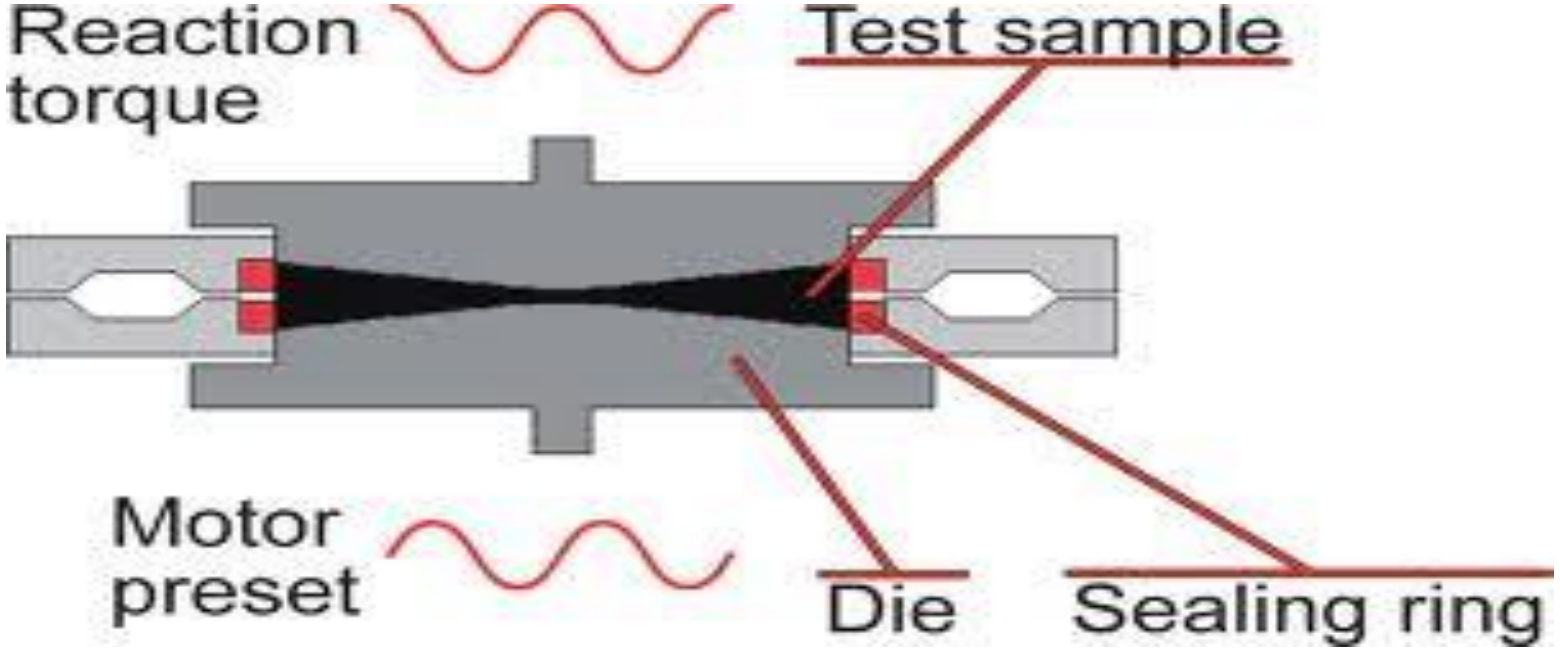
- Why do we need high rates? $[Wi_t > 10^3]$

- Above setups: Roughly ideal flow fields, but limited in rate, mainly due to instabilities especially for highly elastic samples but also due to technical limitations.
- How to reach higher rates?
  - Mooney viscometer
  - Capillary rheometer

  → Less ideal shear field... Hence more data analysis needed which includes sometimes dubious assumptions.

Mooney viscometer



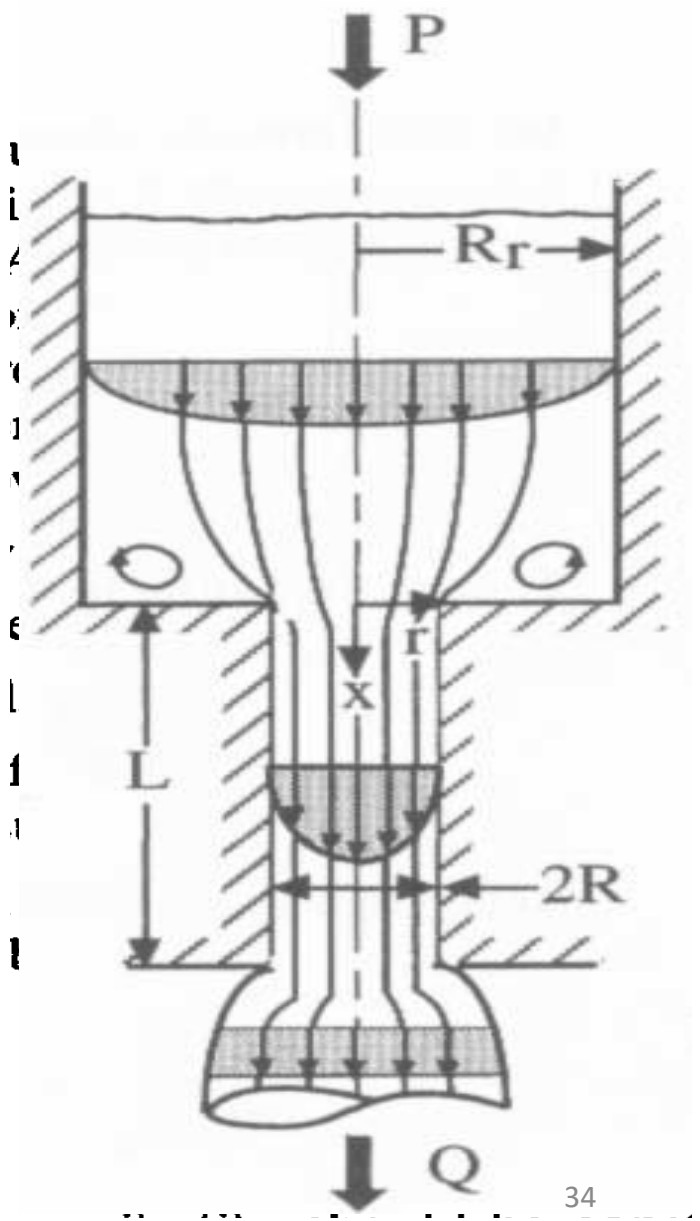


- Biconical shape
- Closed chamber
- Under pressure (→ less instabilities)
- Typical for rubber testing (mainly industry)

Macosko 1994

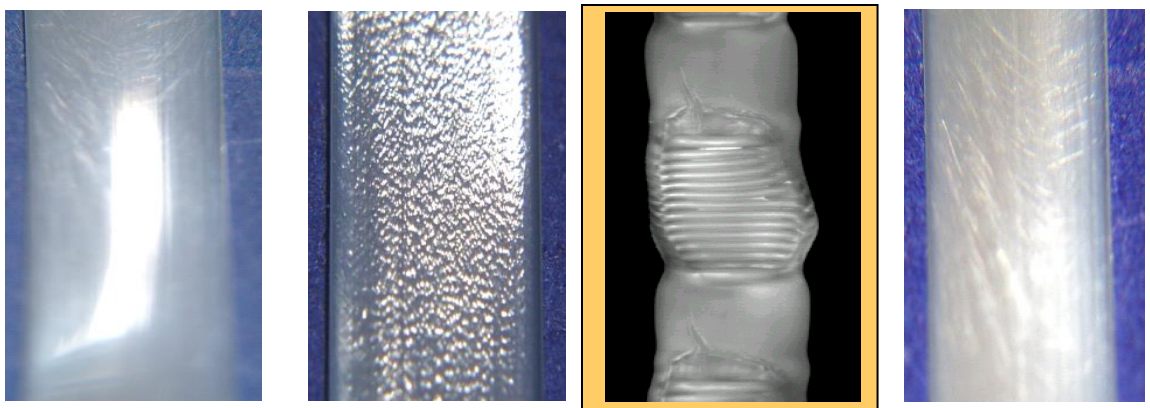
Capillary rheometry

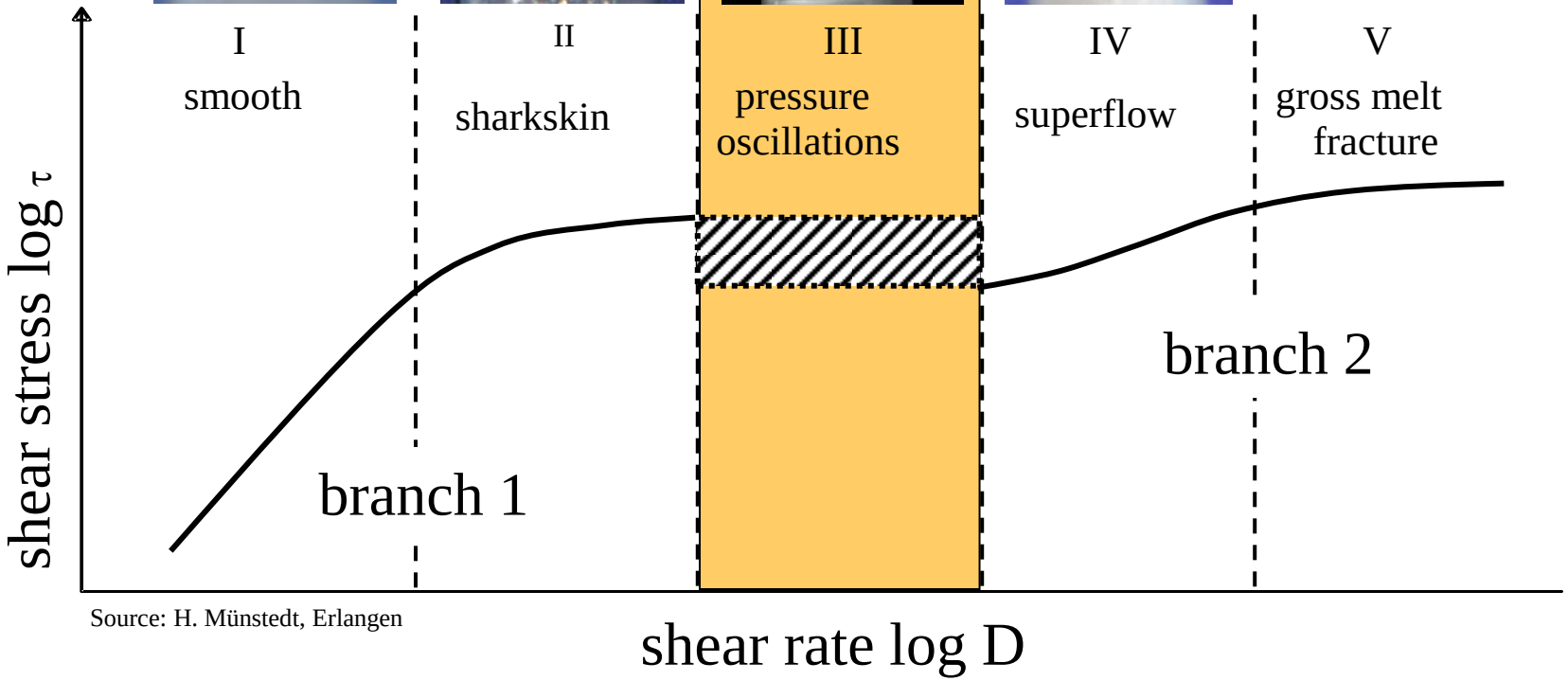
- Poiseuille flow (not simple shear) – parabolic profile
- Entrance and exit effects (Bagley)
- Very high rates
- Pressure effects
- Only steady properties
- Also possible instabilities



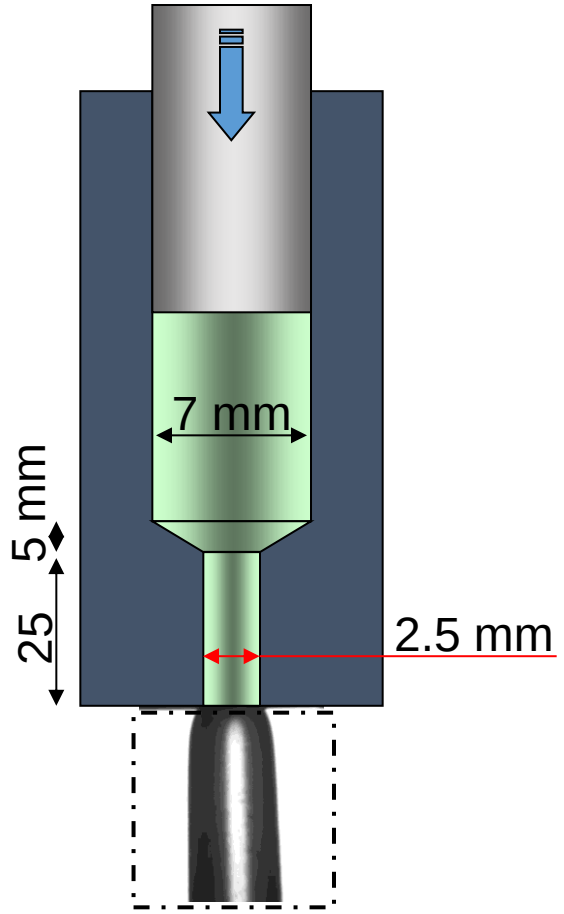
Macosko 1994

Examples of melt fracture for an HDPE





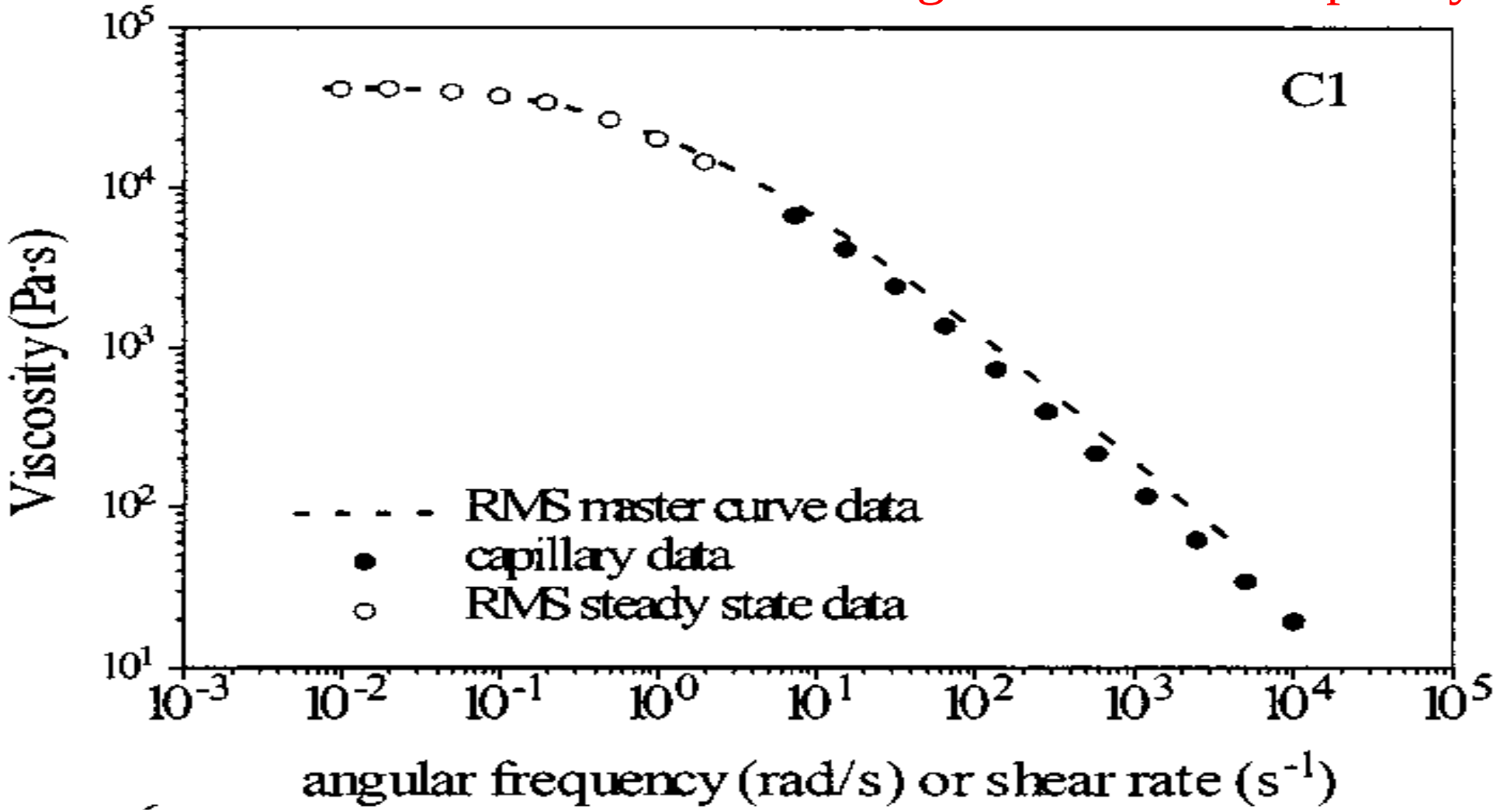
Source: H. Münstedt, Erlangen



(D. Auhl)

Example: Linear PS, M_W = 300K, PDI = 1.8

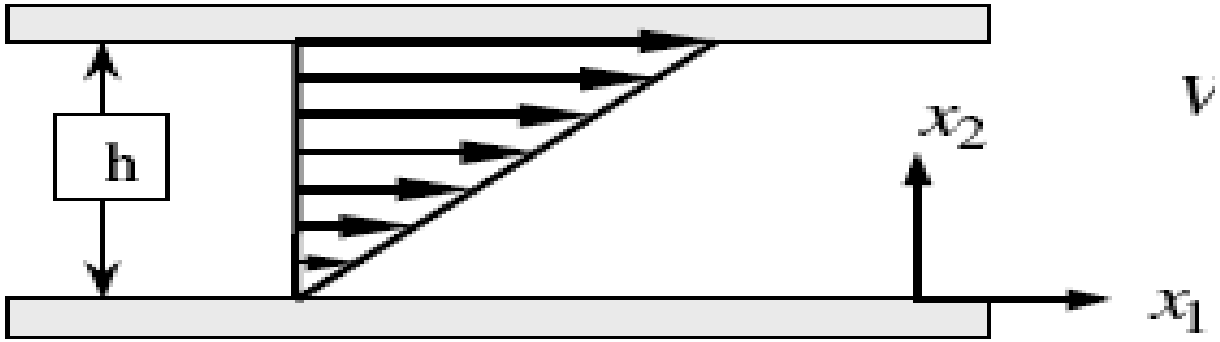
Higher rates with capillary rheometer



Ferri and Lomellini, JOR (1999)

Behavior of polymers in simple steady shear flow

Basic observations



Observation 1: Polymers are shear-thinning

h_o

$\frac{1}{t_o}$

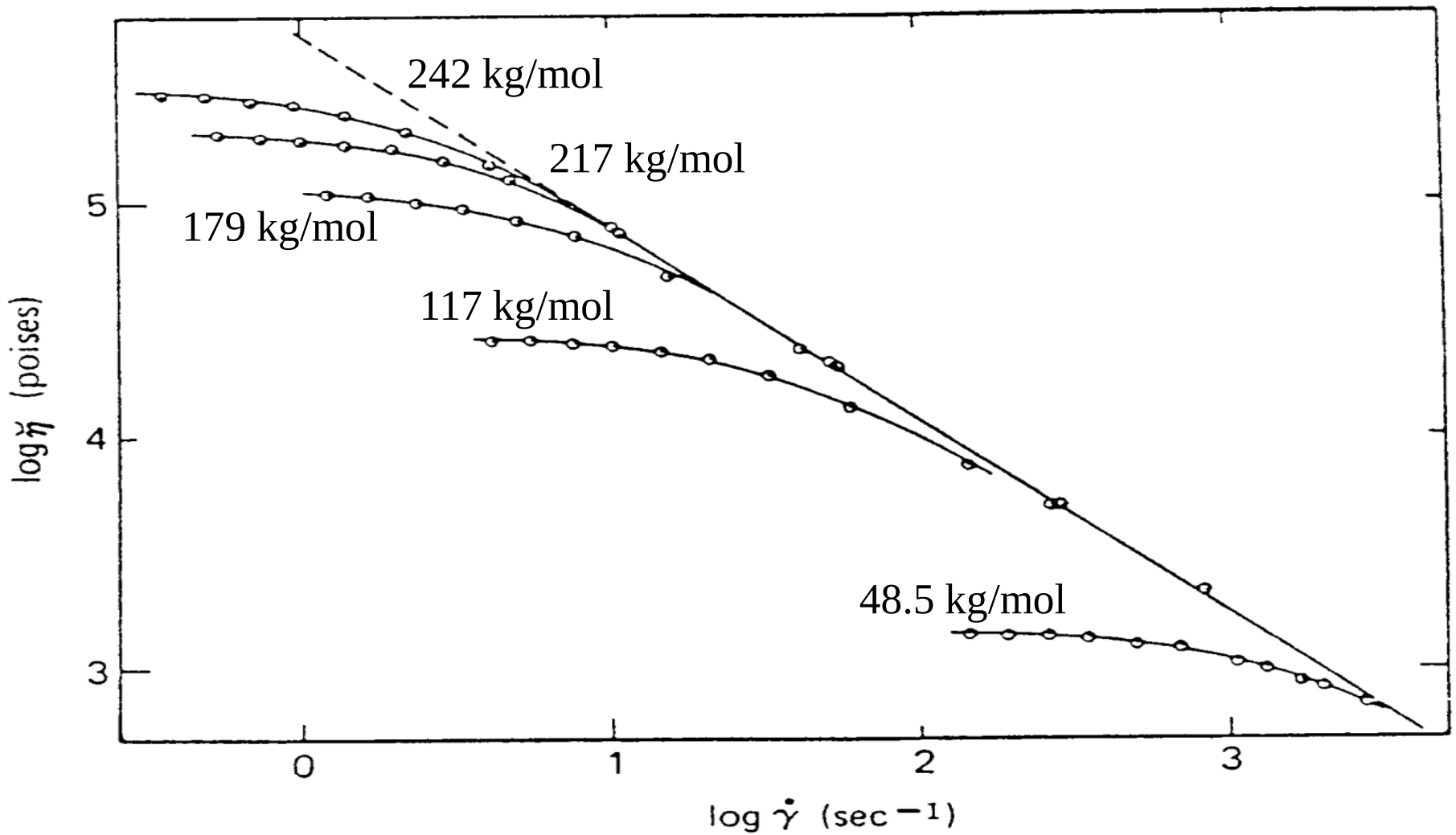
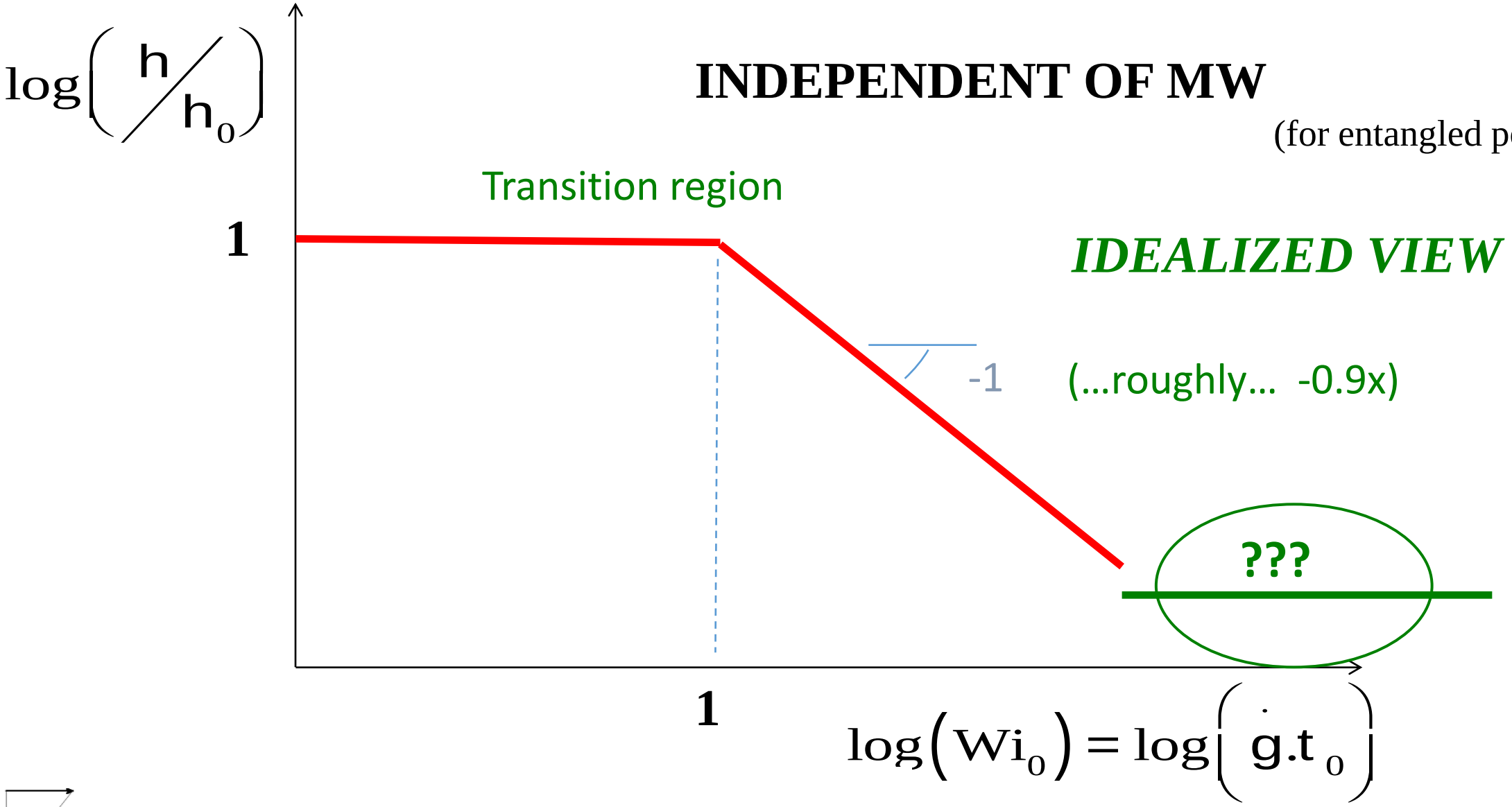
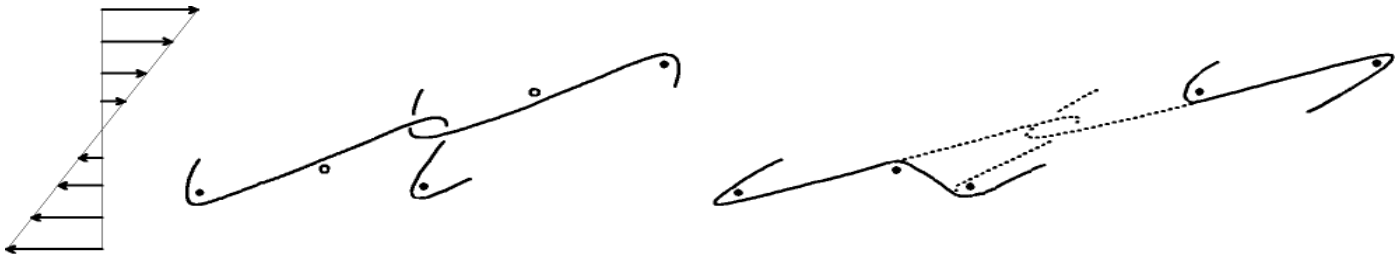


FIG. 13-9. Non-Newtonian viscosity η plotted against shear rate, for narrow-distribution polystyrenes.[45] Molecular weights from top to bottom, $\times 10^{-4}$: 24.2, 21.7, 17.9, 11.7, 4.85.

INDEPENDENT OF MW

(for entangled polymers)





Convective constraint release

Marrucci, JNNFM (1996) ; ; Ianniruberto JoR 2016

Ianniruberto + Marrucci JoR 2015

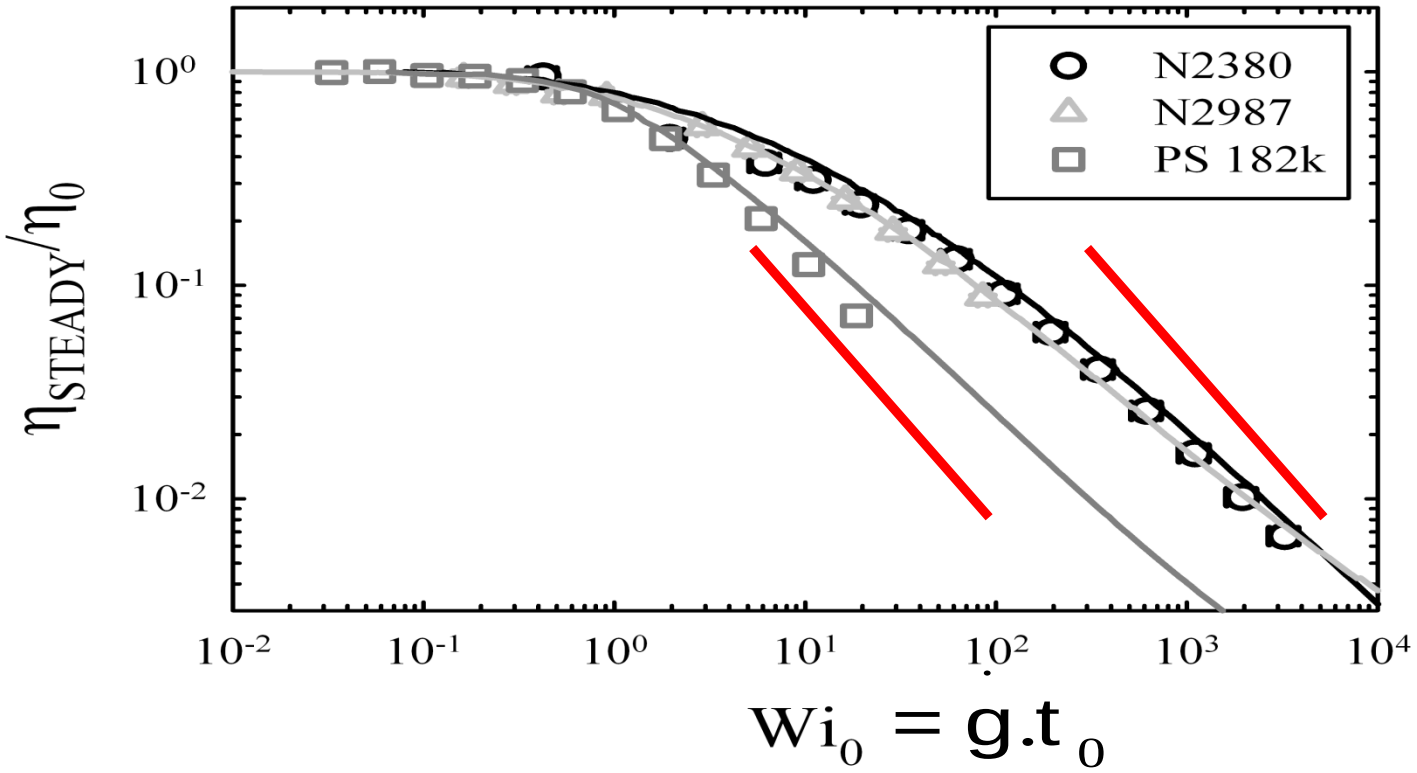
Observation 1: Polymers are shear-thinning

Observation 2: Linear polymers obey the empirical Cox-Merz rule

Cox-Merz (1958) rule:

$$\eta(\dot{\gamma}) = \eta^*(\omega)\Big|_{\omega=\dot{\gamma}}$$

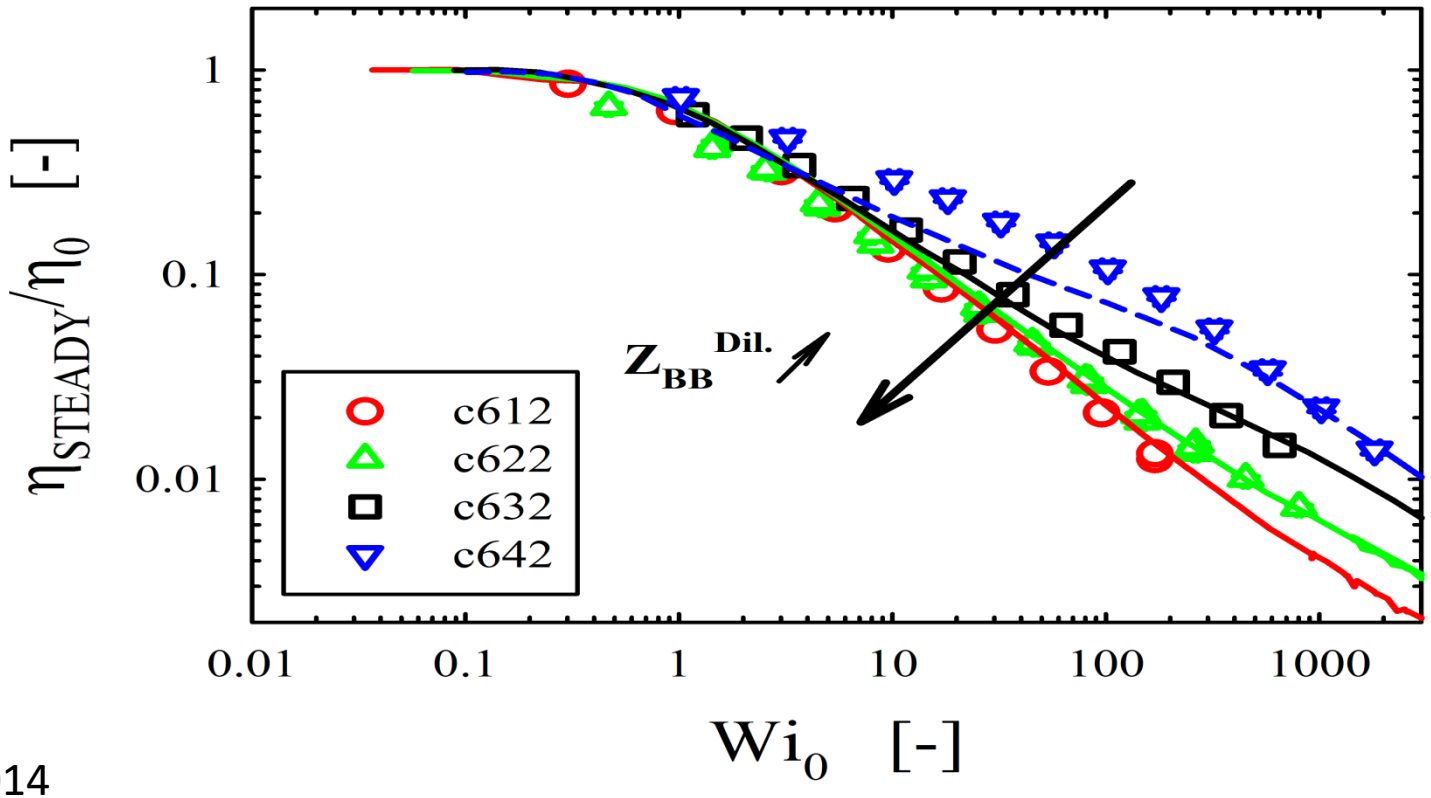
Observation 3: Higher levels of polydispersity → less thinning.



PS 182k: Linear, monodisperse PS
(M_w=182kg/mol, PDI < 1.1)
N2380: Linear, polydisperse PS
(M_w=275kg/mol, PDI < 2.1)
N2987: Linear, polydisperse PS
(M_w=124kg/mol, PDI < 1.9)

SAMPLE	M_{TOT}	M_{BB}	M_{Br}	q
PS c612	477	275	6.5	31
PS c622	626	275	11.7	30
PS c632	918	275	25.7	25
PS c642	1640	275	47	29

Observation 4: Like polydispersity, also branching decreases thinning (and leads to failure of Cox-Merz rule).



Snijkers, DV, Rheol. Acta 2014

Observation 5: Polymers exhibit normal forces

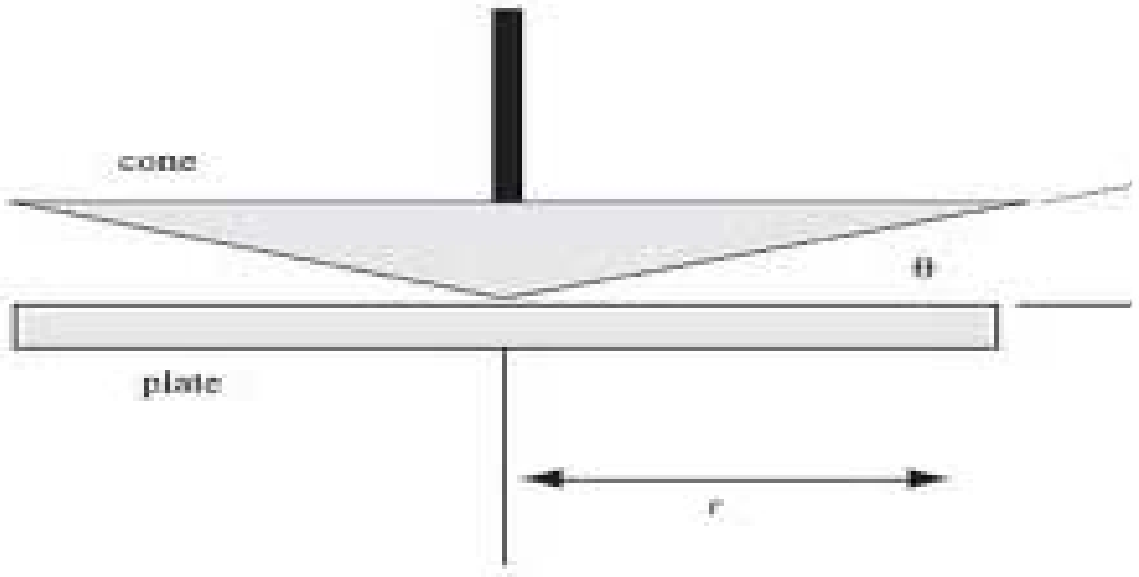
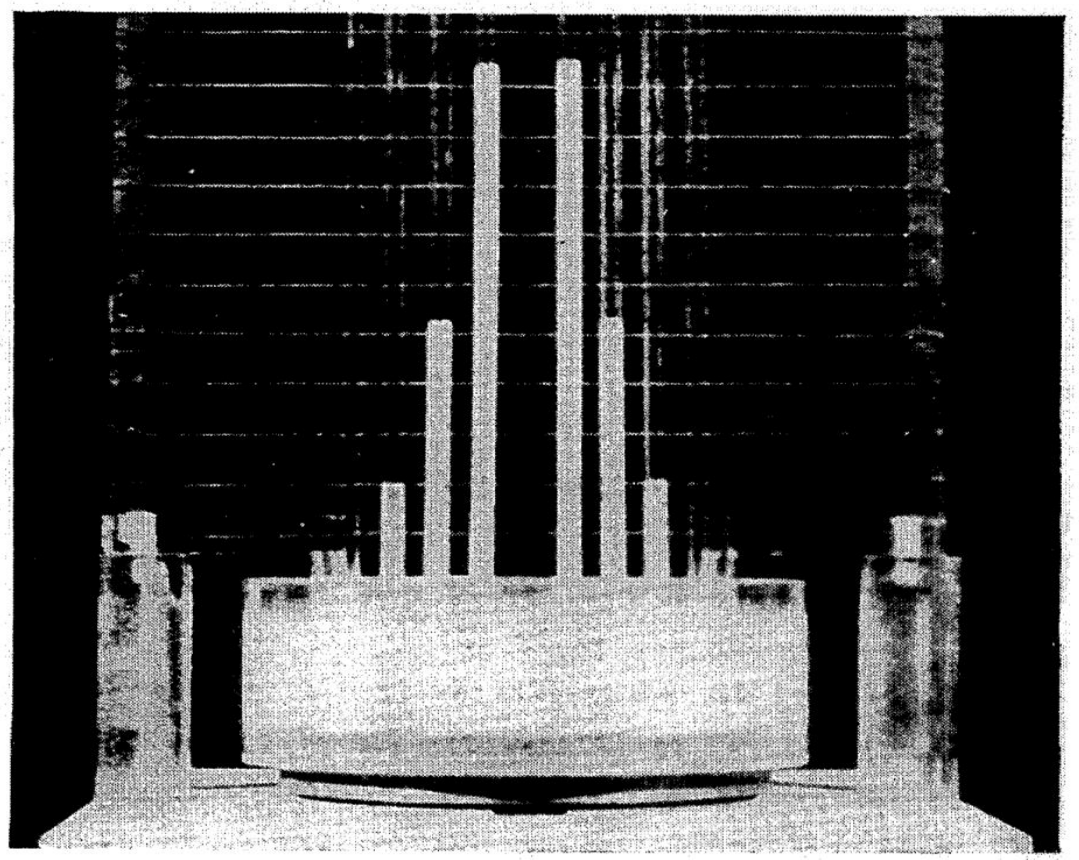
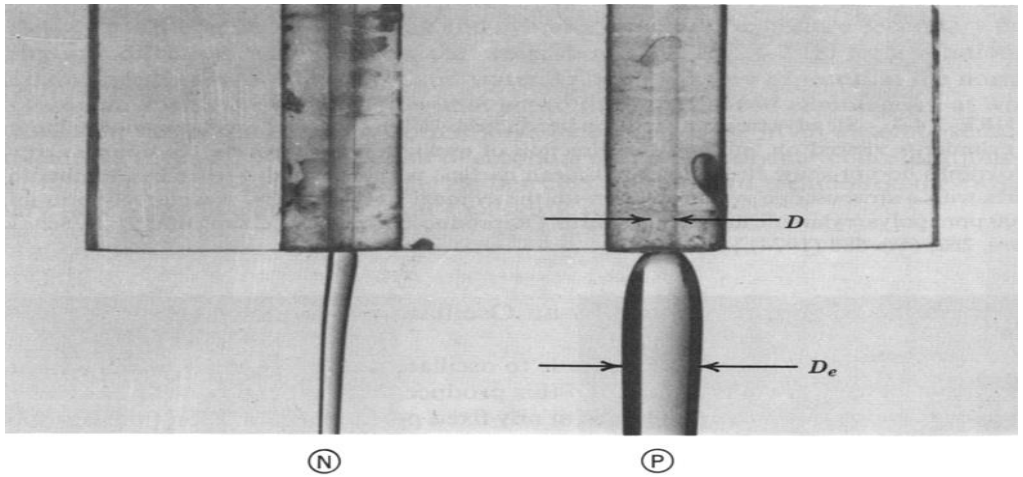


Figure 2. Schematic diagram of the cone and plate rheometer. θ, is angle between cone and plate and r, is the radius of the cone (and well).

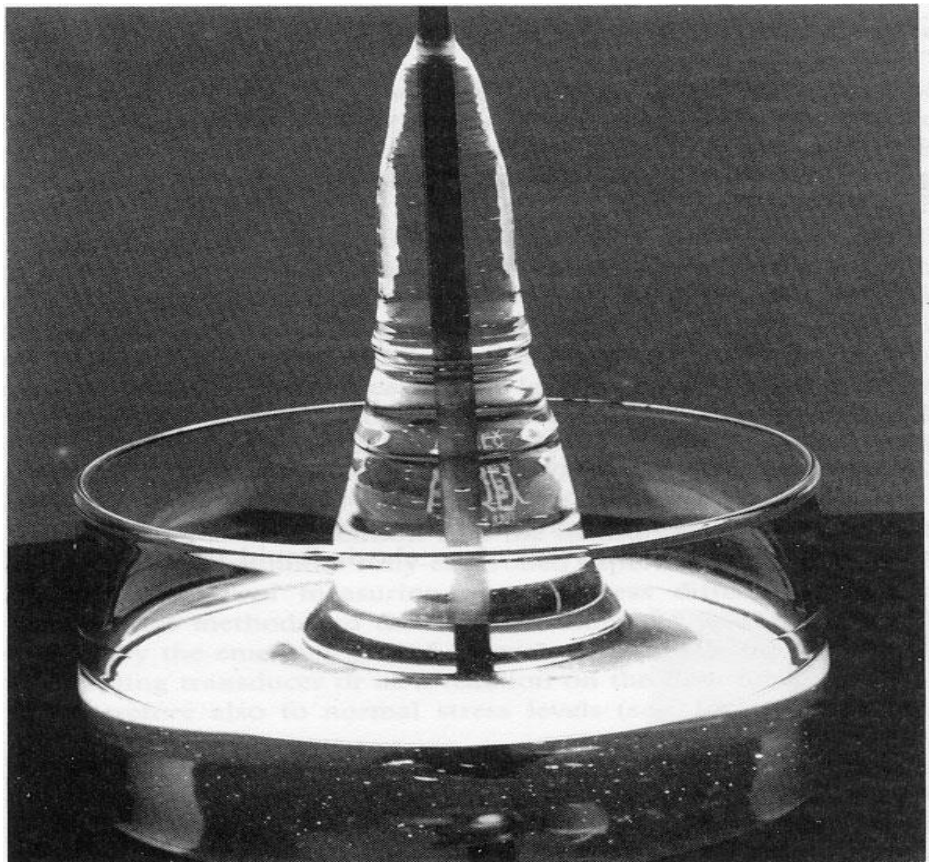


Karl Weissenberg, 1945

Extrudate swell



Rod climbing (Weissenberg)



Observation 5: Polymers exhibit normal forces

$$\Psi_1 = \frac{N_1}{\dot{\gamma}^2}$$

N_1 = First normal stress [Pa]

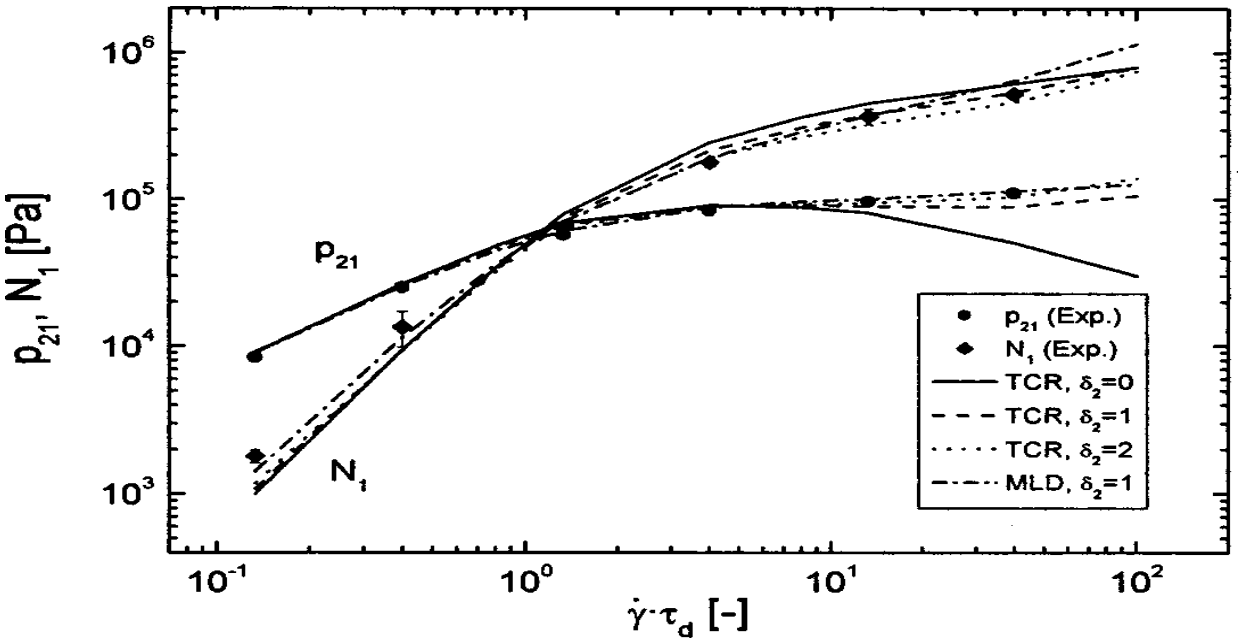
Ψ_1 = First normal stress coefficient [Pa.s^2]

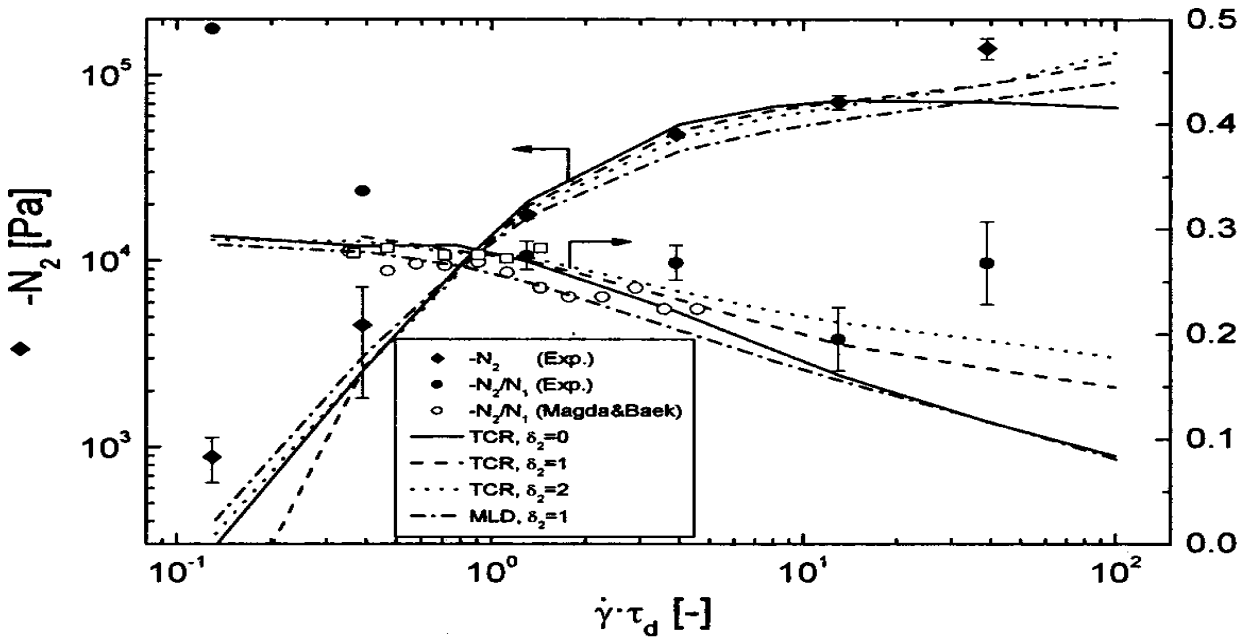
Same for N_2

N_2<0 for polymer melts

Monodisperse PS 200kg/mol ; Schweizer et al., JOR (2004)

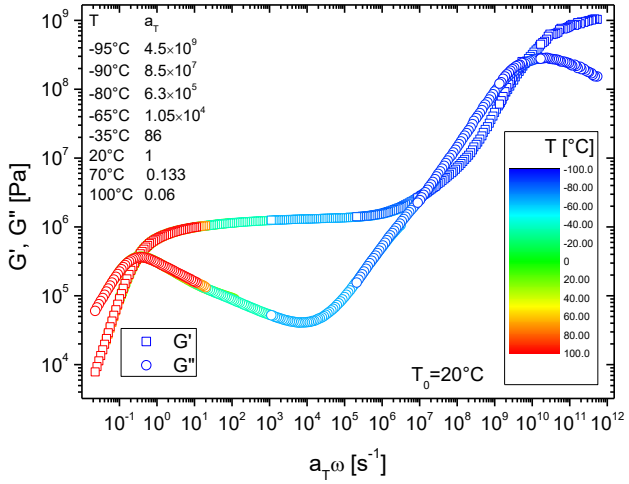
$N_2 \ll N_1$





Bird et al. DPL vol.1, Wiley 1987 ; Laun, JNNFM (1978)

What about monodisperse linear polymers? → Doi-Edwards



1. $\dot{\gamma} < 1/\tau_D$ σ and N_1 increase monotonically to SS

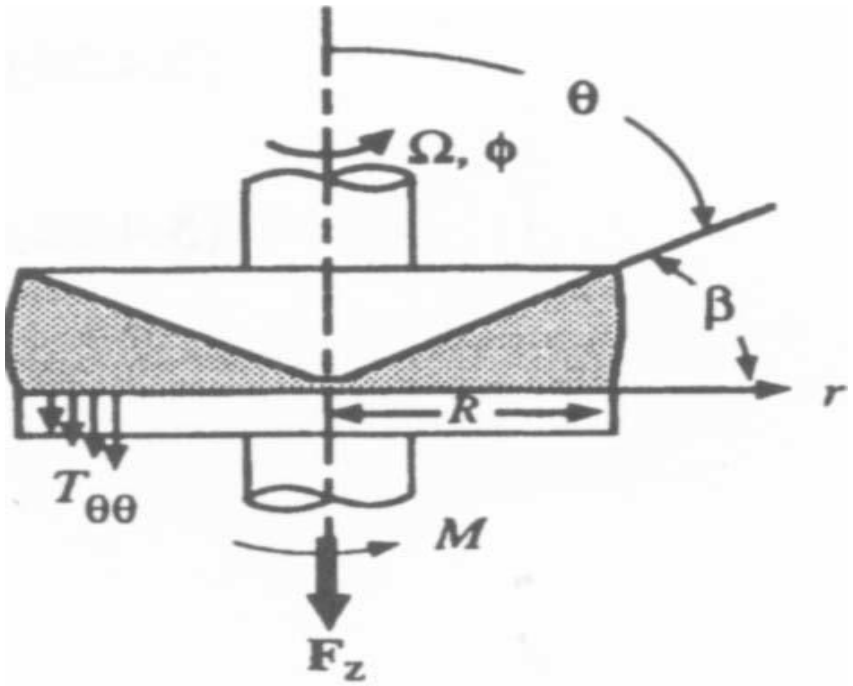
2. $1/\tau_D < \dot{\gamma} < 1/\tau_R$ Max in σ at γ = 2.3

   N_1 monotonic (DE → tube orientation)

3. $1/\tau_R < \dot{\gamma}$ Max in σ shifts to higher γ Asymptote: $\gamma \approx \dot{\gamma}\tau_R$

   Max in N_1 appears (DE → chain stretch)

Measure N1 and N2



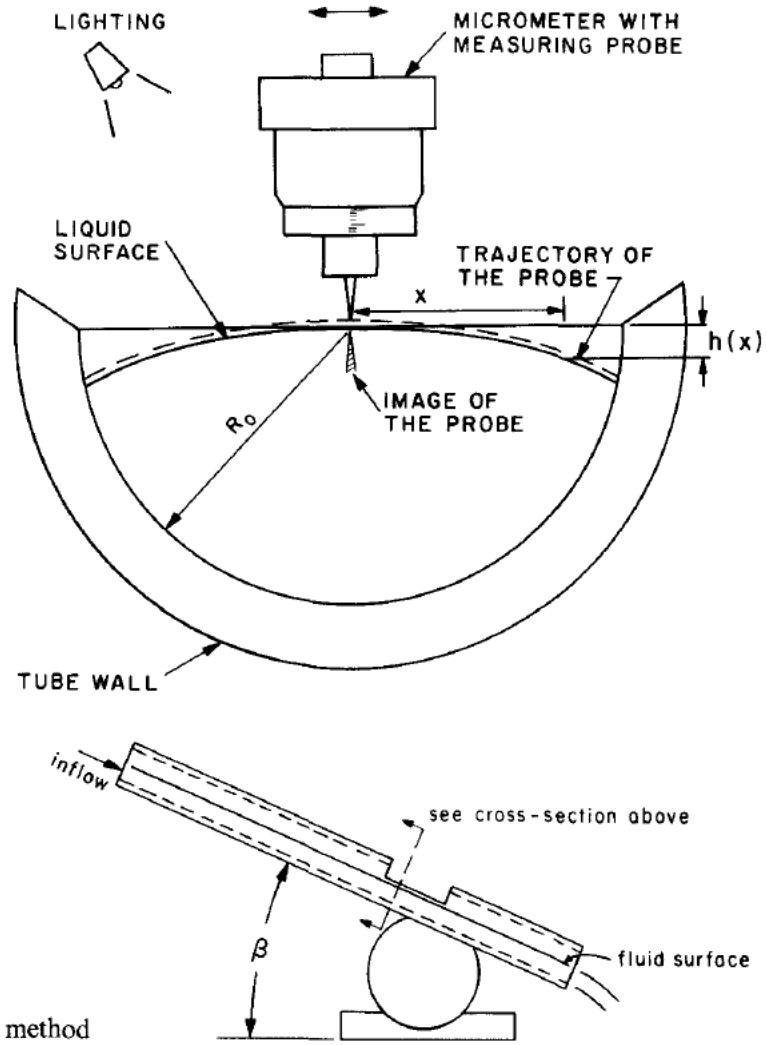
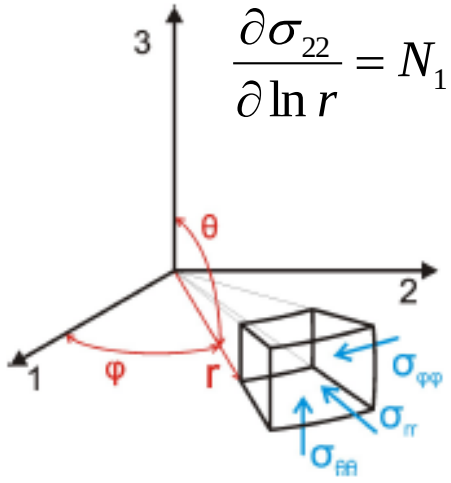


Fig. 1. The channel geometry and the measuring method

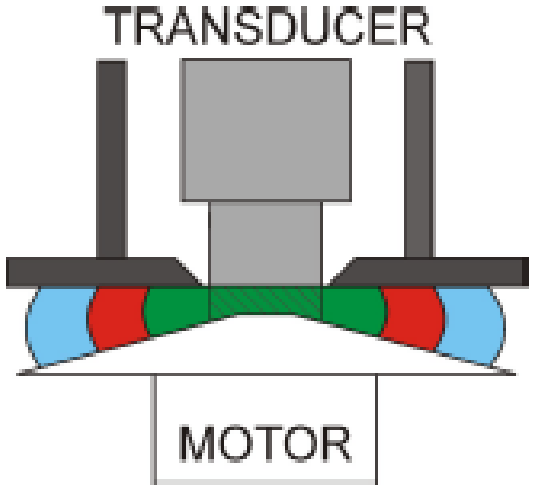
Tanner, Rheol. Acta 1974
Schweizer, Rheol. Acta 2002

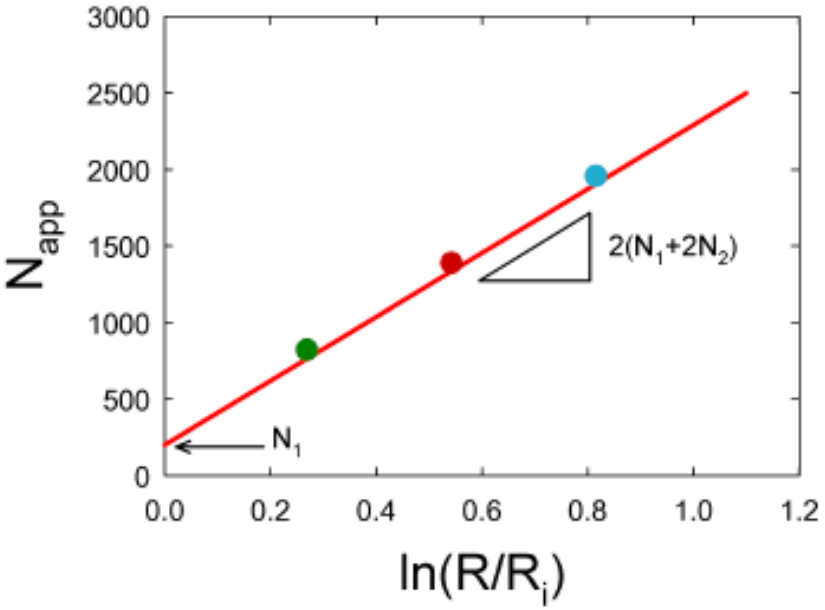
N1 and N2 from separate shear measurements with CPP

CPP: initial shape of sample (edge) matters (Schweizer, Denn, Fielding)



$$\frac{\partial \sigma_{22}}{\partial \ln r} = N_1 + 2N_2$$





$$N_1 = \sigma_{\phi\phi} - \sigma_{\theta\theta}$$
$$N_2 = \sigma_{\theta\theta} - \sigma_{rr}$$

Fixed inner partition/Different external diameters
(*n* measurements with fixed CPP2)

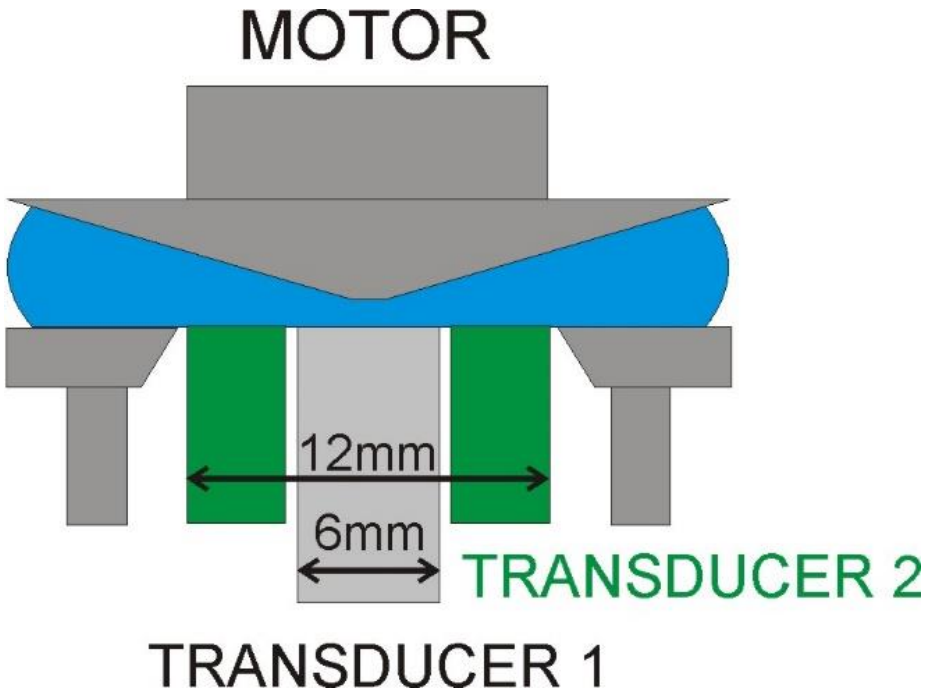
$$N_{app} = \frac{2F_i}{\pi R_i^2} = N_1 + 2(N_1 + 2N_2)\ln\left(\frac{R}{R_i}\right)$$

Schweizer, Rheol. Acta 2002

Experimental limitations (multiple measurements for a single shear rate)

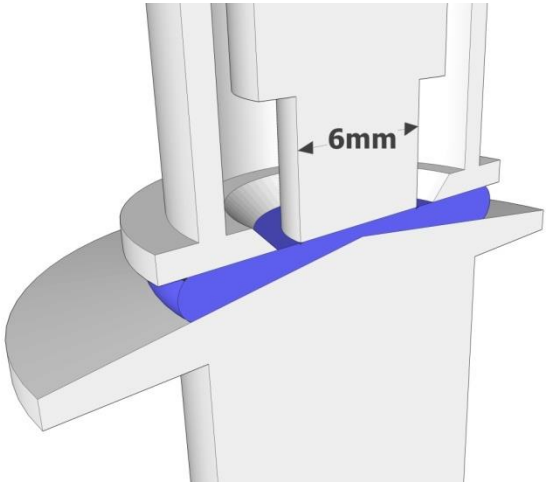
Alternative (and better) ways to measure N1 and N2

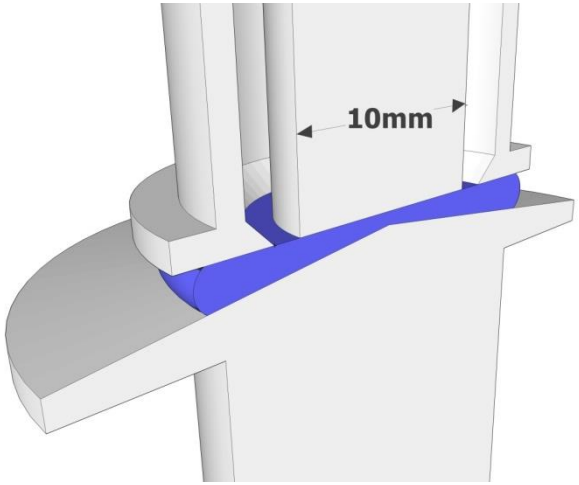
CPP: initial shape of sample (edge) matters (Schweizer, Denn, Fielding)



Fixed external diameter/Two different inner radii
(single measurement with double CPP)

Schweizer and Schmidheiny, JoR 2013

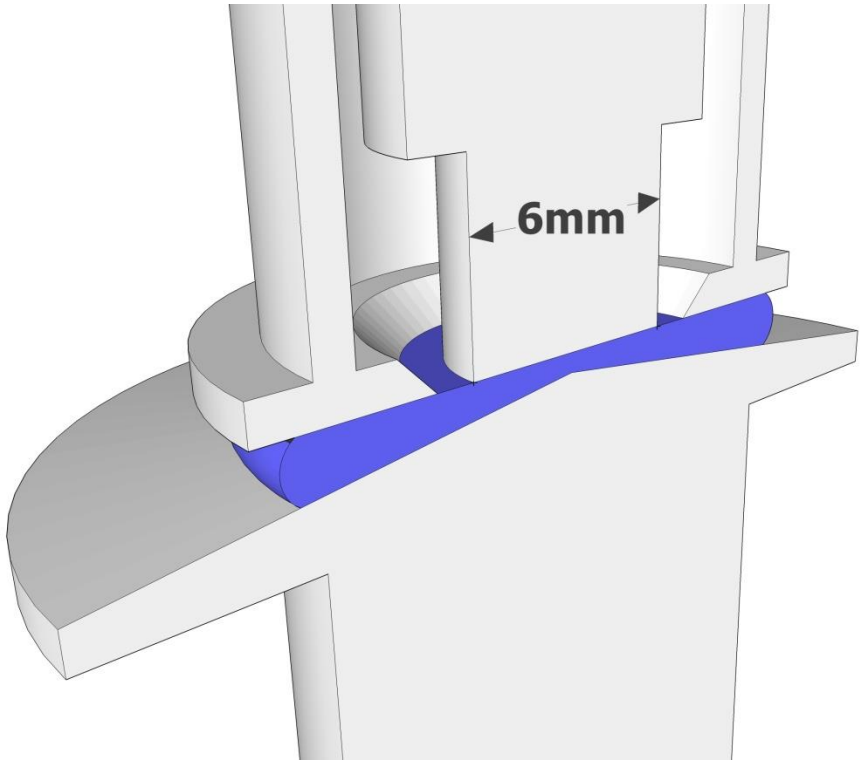


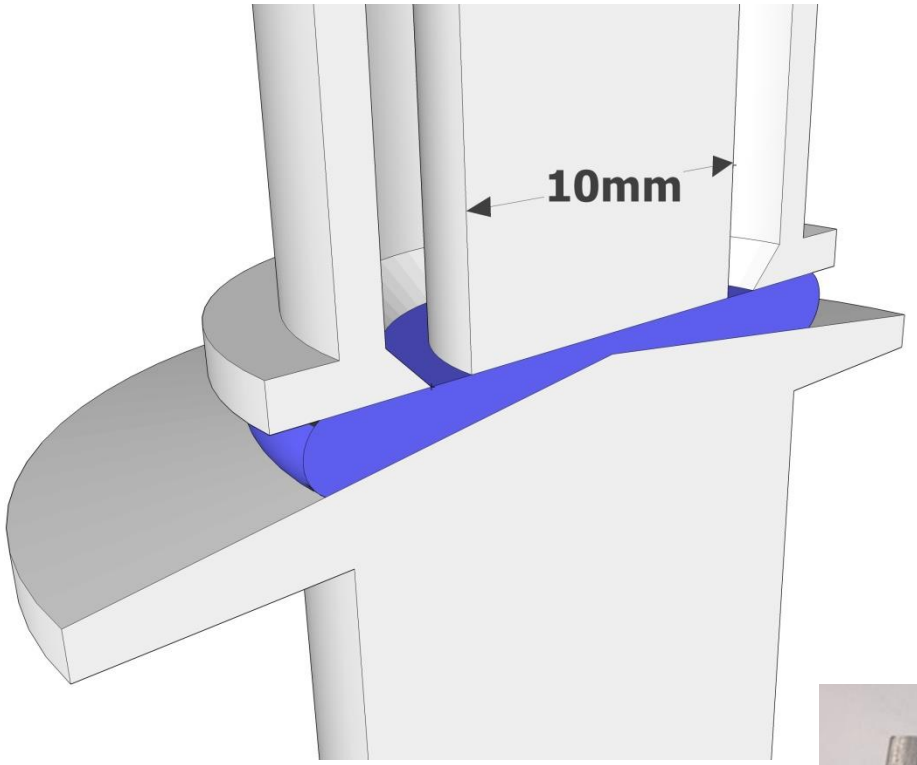


Fixed external diameter/Two different inner radii
(two measurements with two CPPs):

Costanzo, Iannirubertо, Marrucci, DV, Rheol. Acta 2018

Modular CPP: N1 and N2 from two shear measurements

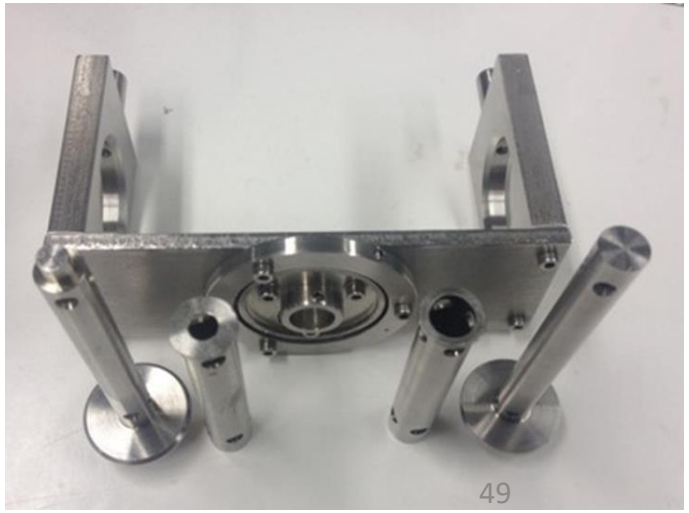




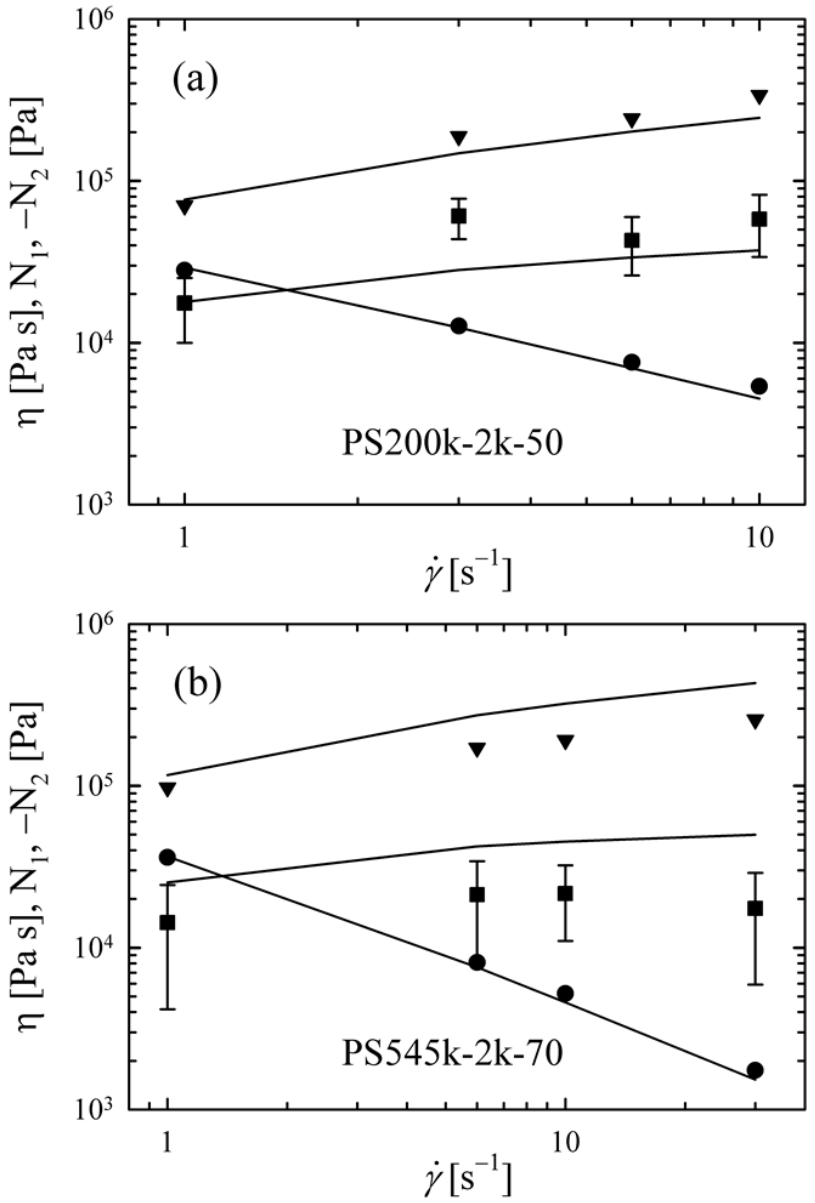
Fixed external diameter/Two different inner radii
(two measurements with CPP2):

$$N_{app} = \frac{2F_1}{\pi R_1^2} = N_1 + 2(N_1 + 2N_2)\ln\left(\frac{R}{R_1}\right)$$

Costanzo et al., Rheol. Acta 2018



Summary of the results: (a) PS200k-2k-50 ; (b) PS545k-2k-70



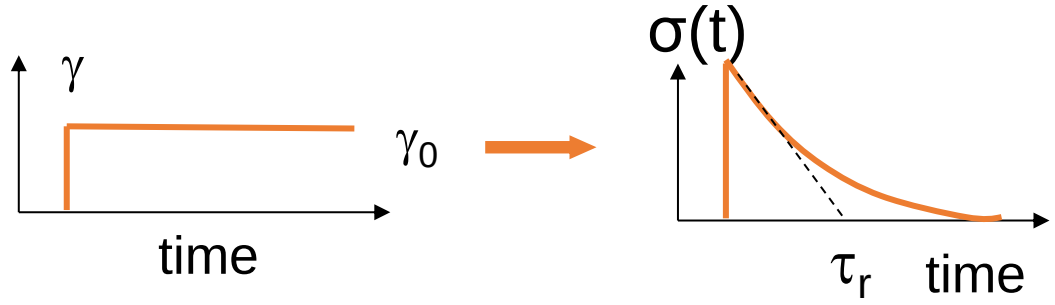
$Wi_R = 40$

Costanzo et al., Rheol. Acta 2018

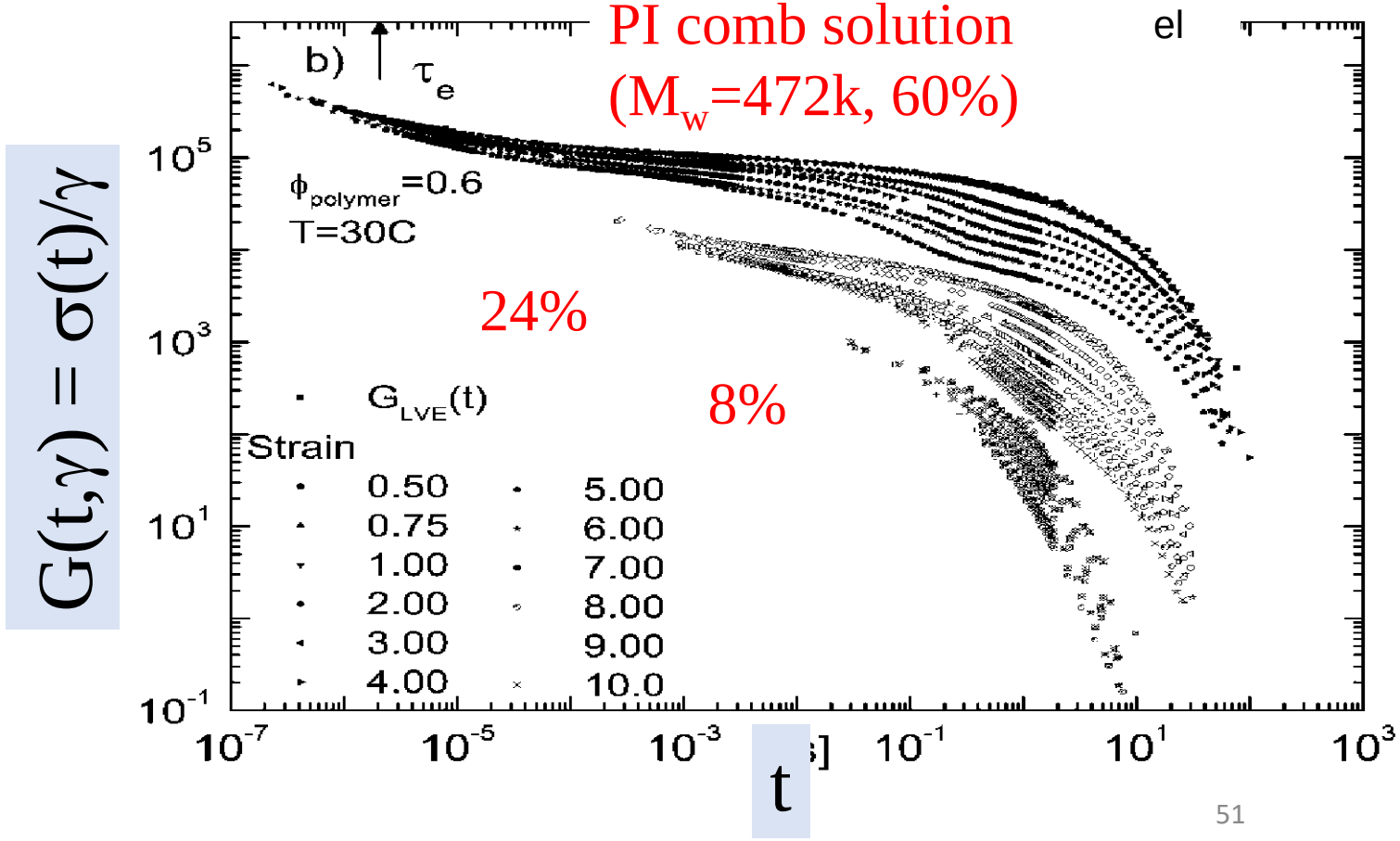
Behavior of polymers in step-strain shear

Sudden imposition of a fixed strain at t=0

Monitor the stress upon relaxation at t>0



Cone and plate



Time-Strain Separability

At long times:

$$G(t,\gamma) = G(t).h(\gamma)$$

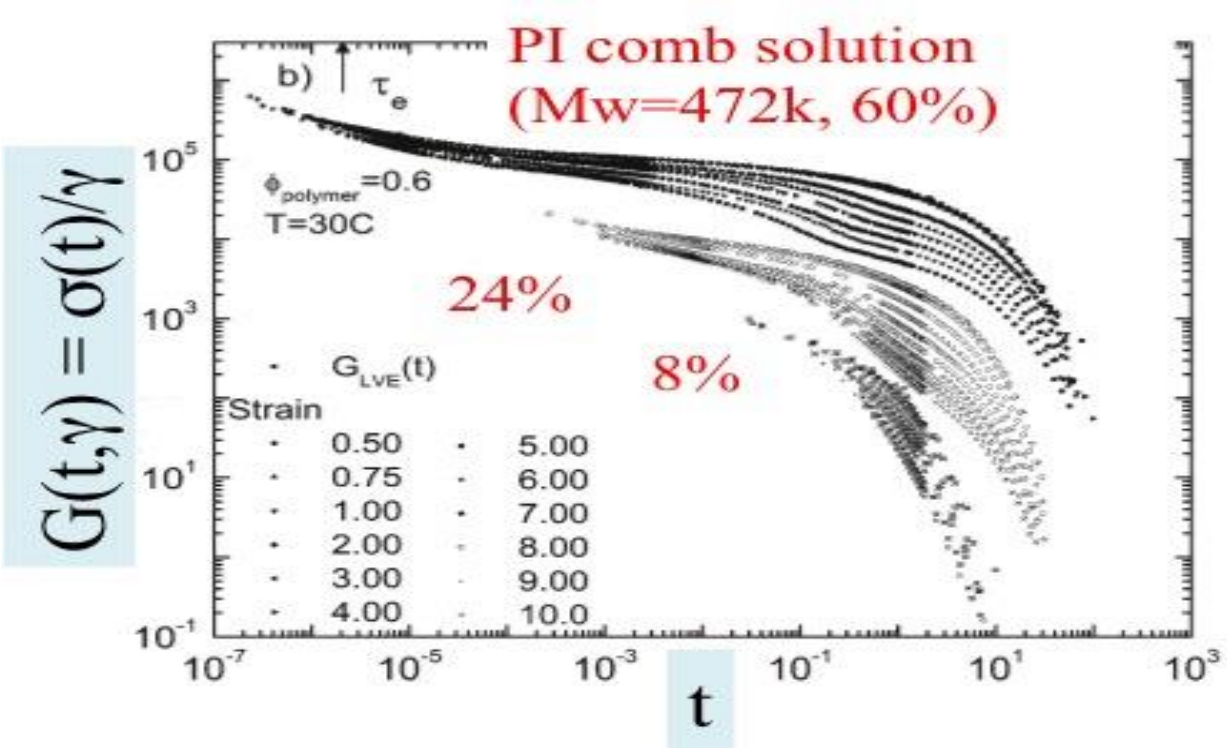
h(γ): Damping function

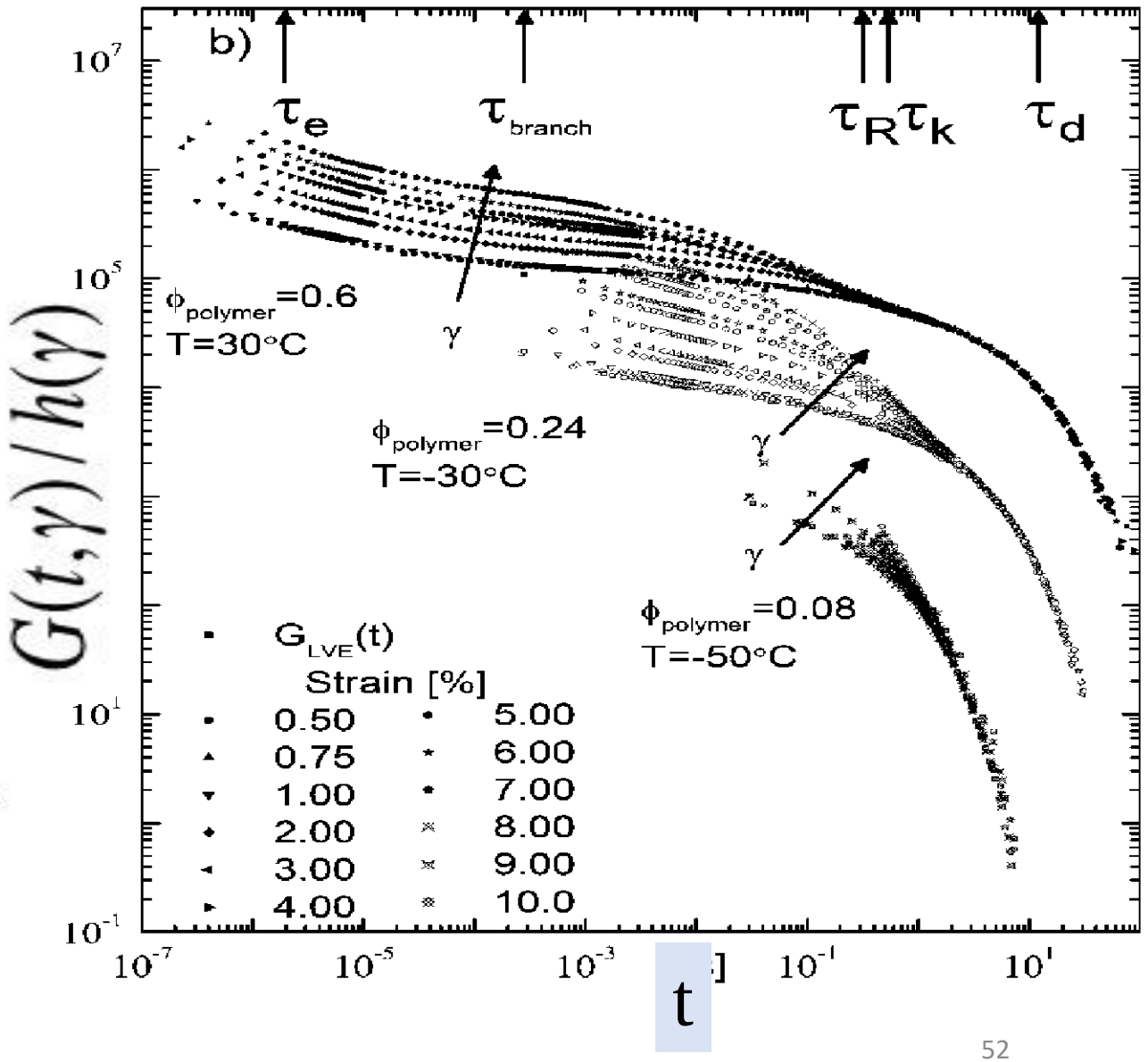
Kirkwood et al., Macromolecules (2009)

At long times:

$$G(t,\gamma) = G(t).h(\gamma)$$

h(γ): Damping function





Kirkwood et al., Macromolecules (2009)

$$G(t,\gamma) = G(t).h(\gamma)$$

h(γ): Damping function

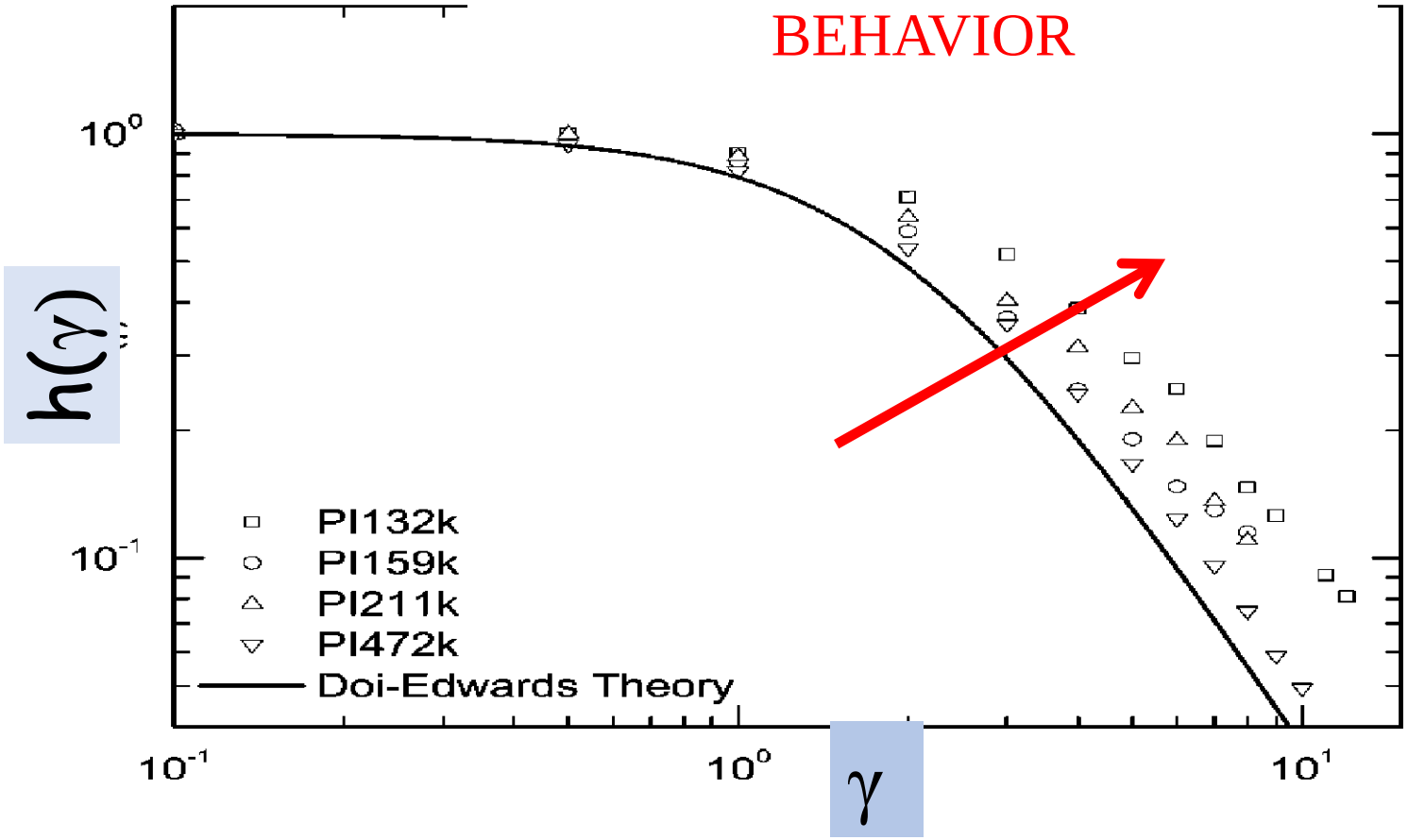
Theory for linear, monodisperse polymers (Doi-Edwards):

$$h(\gamma) = \frac{1}{1+\frac{4}{15}\gamma^2}$$

Polydisperse linear polymers have identical h(γ); IF molar mass of "all components" is high enough

Ye and Sridhar, Macromolecules (2005)

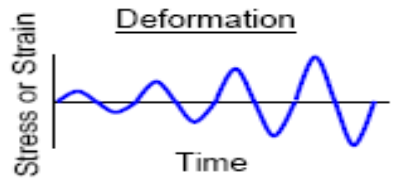
BRANCHING LEADS TO A WEAKER DAMPING BEHAVIOR



Kirkwood et al., Macromolecules (2009)

Large amplitude oscillatory shear (LAOS)

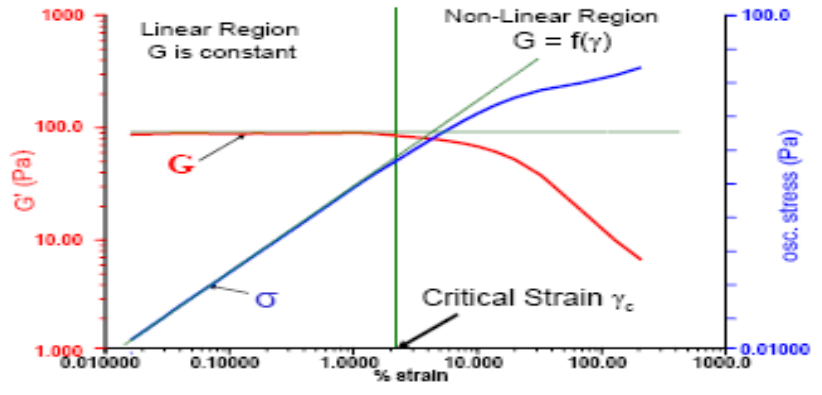
Dynamic Stress or Strain Sweep (Torque Ramp)



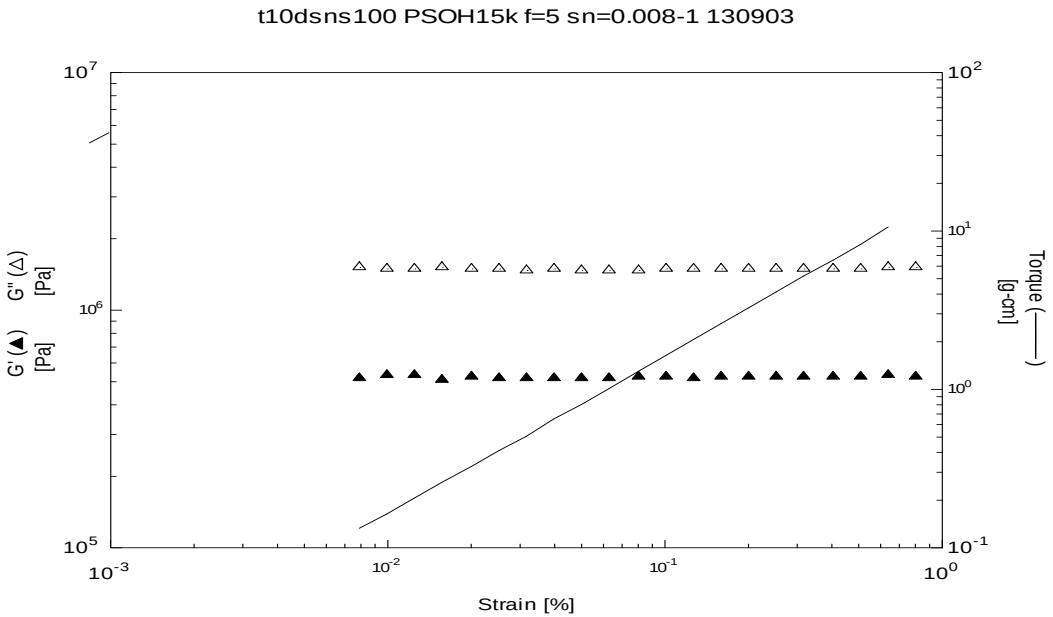
- The material response to increasing deformation amplitude (stress or strain) is monitored at a constant frequency and temperature.

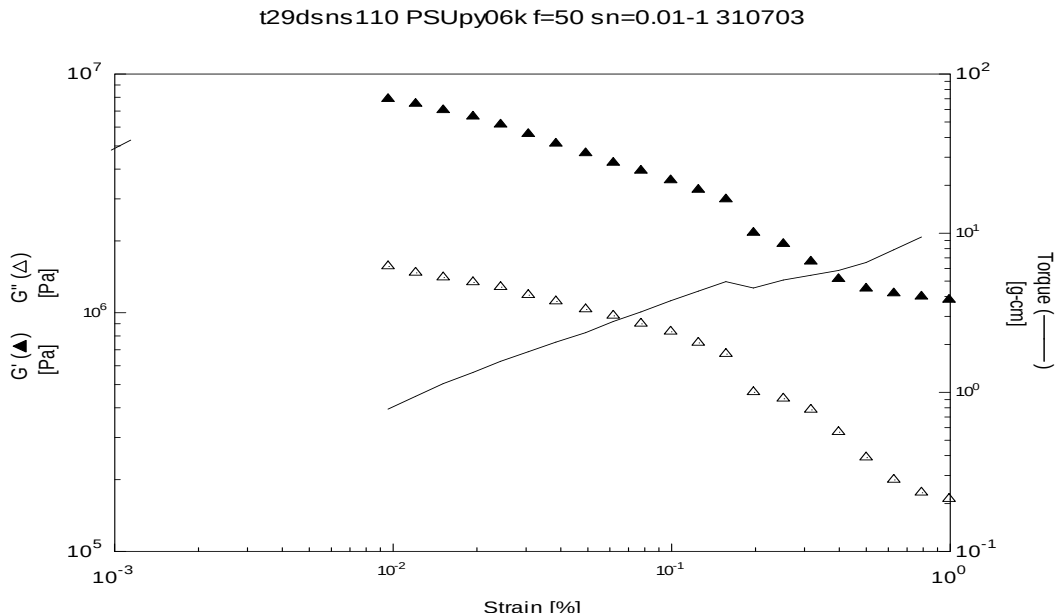
- USES
  - Identify Linear Viscoelastic Region
  - Strength of dispersion structure - settling stability
  - Resilience

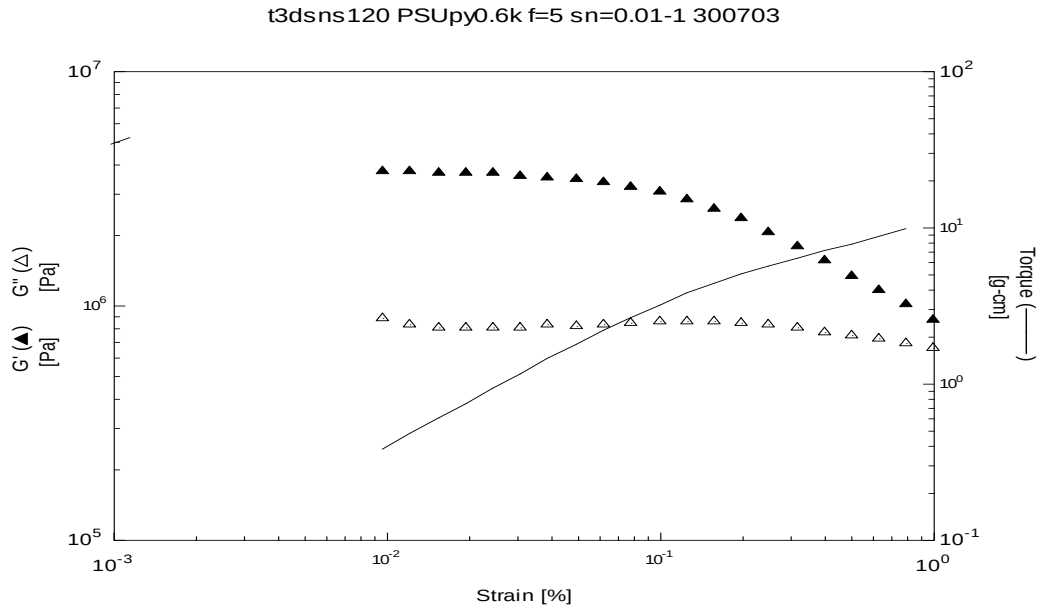
Dynamic Strain Sweep: Material Response

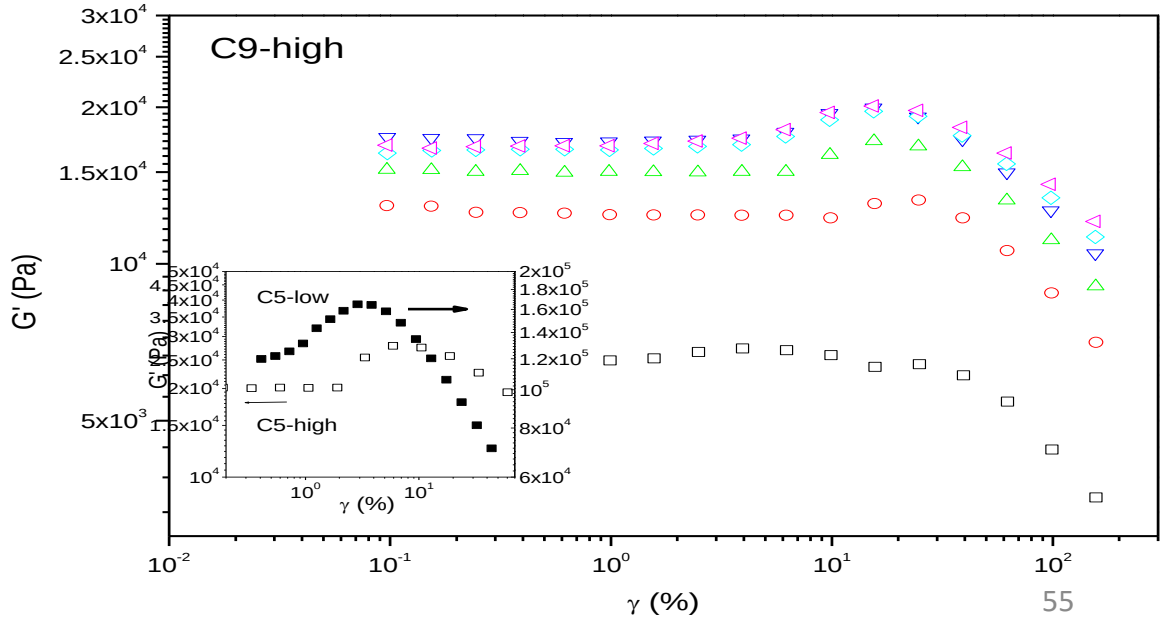


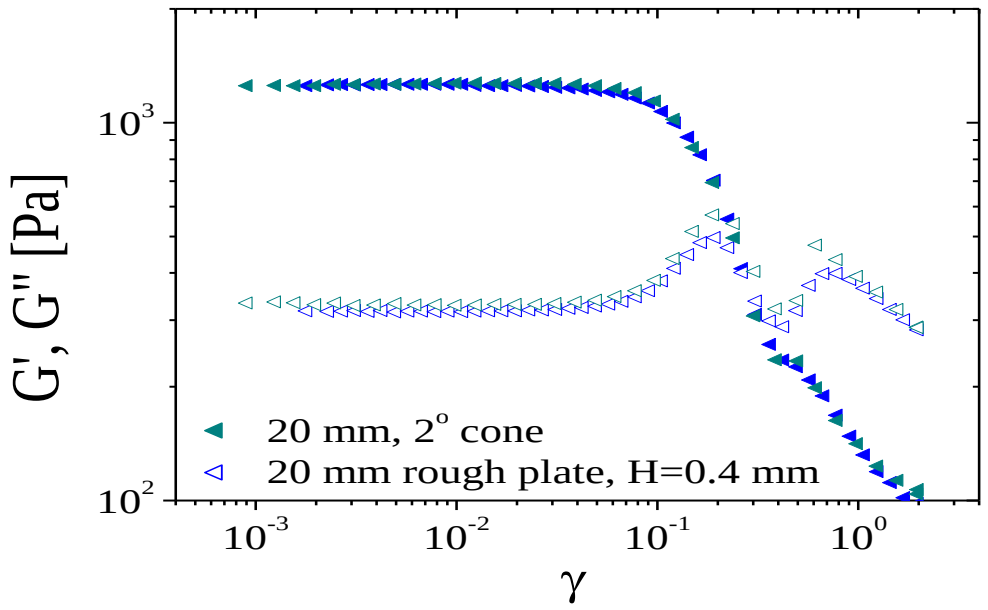
Linear and SCLC polymers

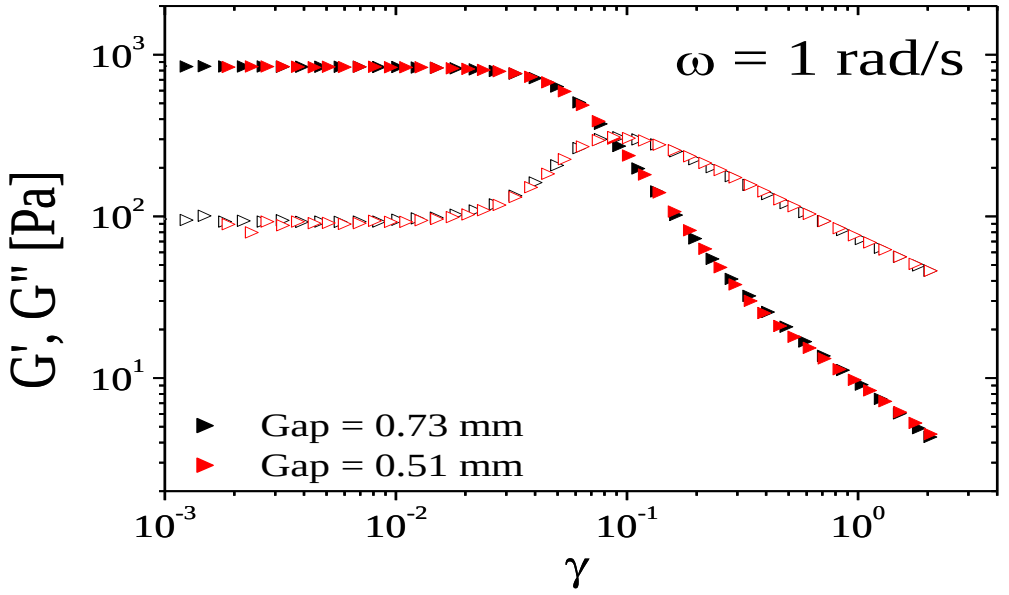


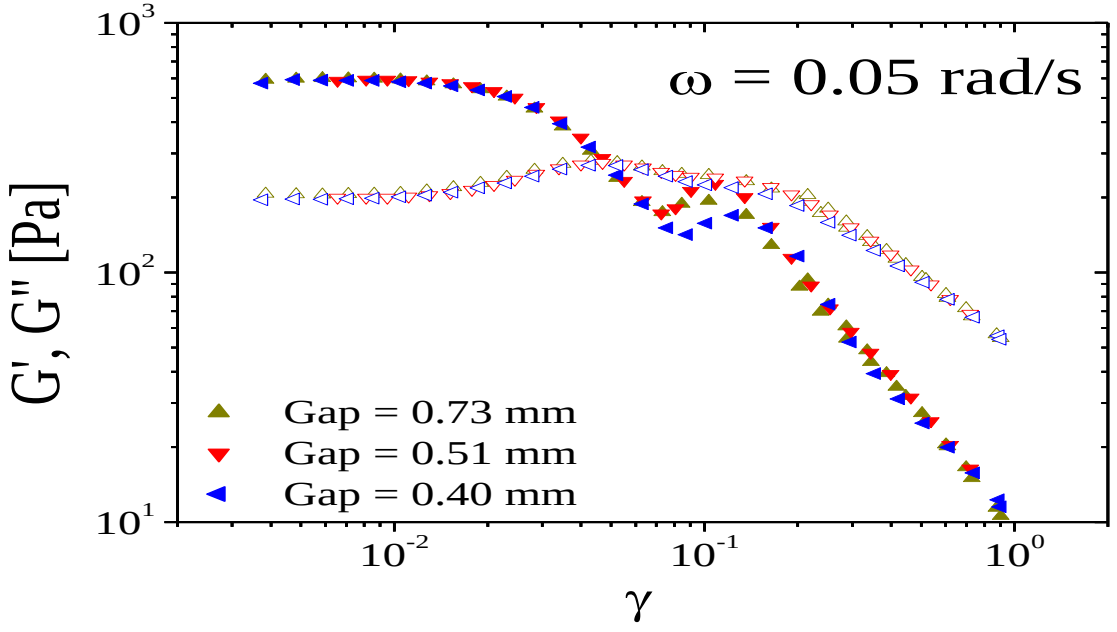


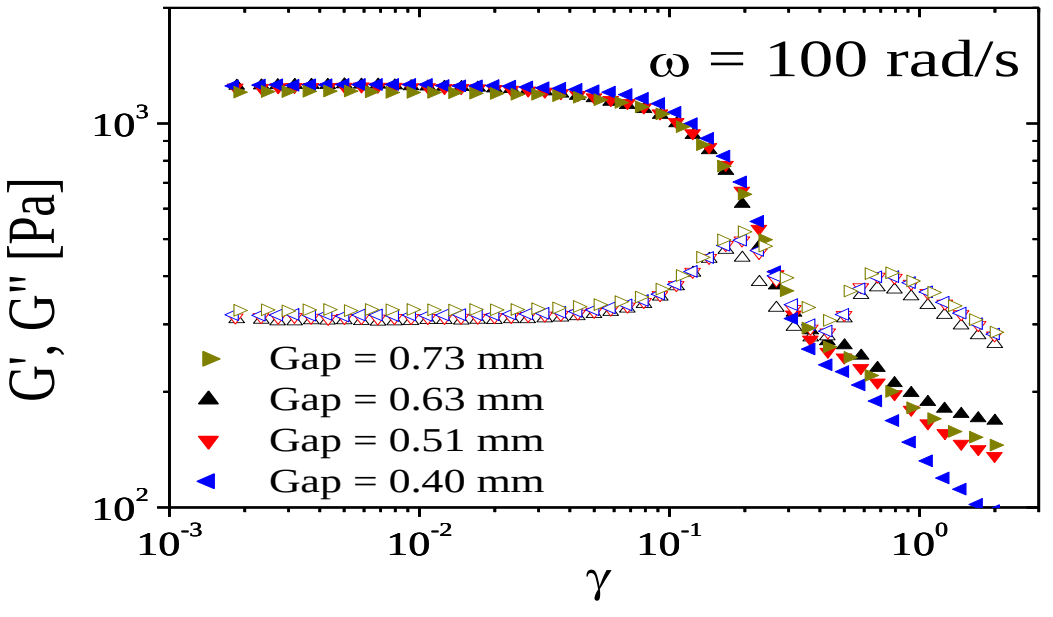





G', G'' [Pa]
γ
20 mm, 2° cone
20 mm rough plate, H=0.4 mm


ω = 1 rad/s
G', G'' [Pa]
γ
Gap = 0.73 mm
Gap = 0.51 mm

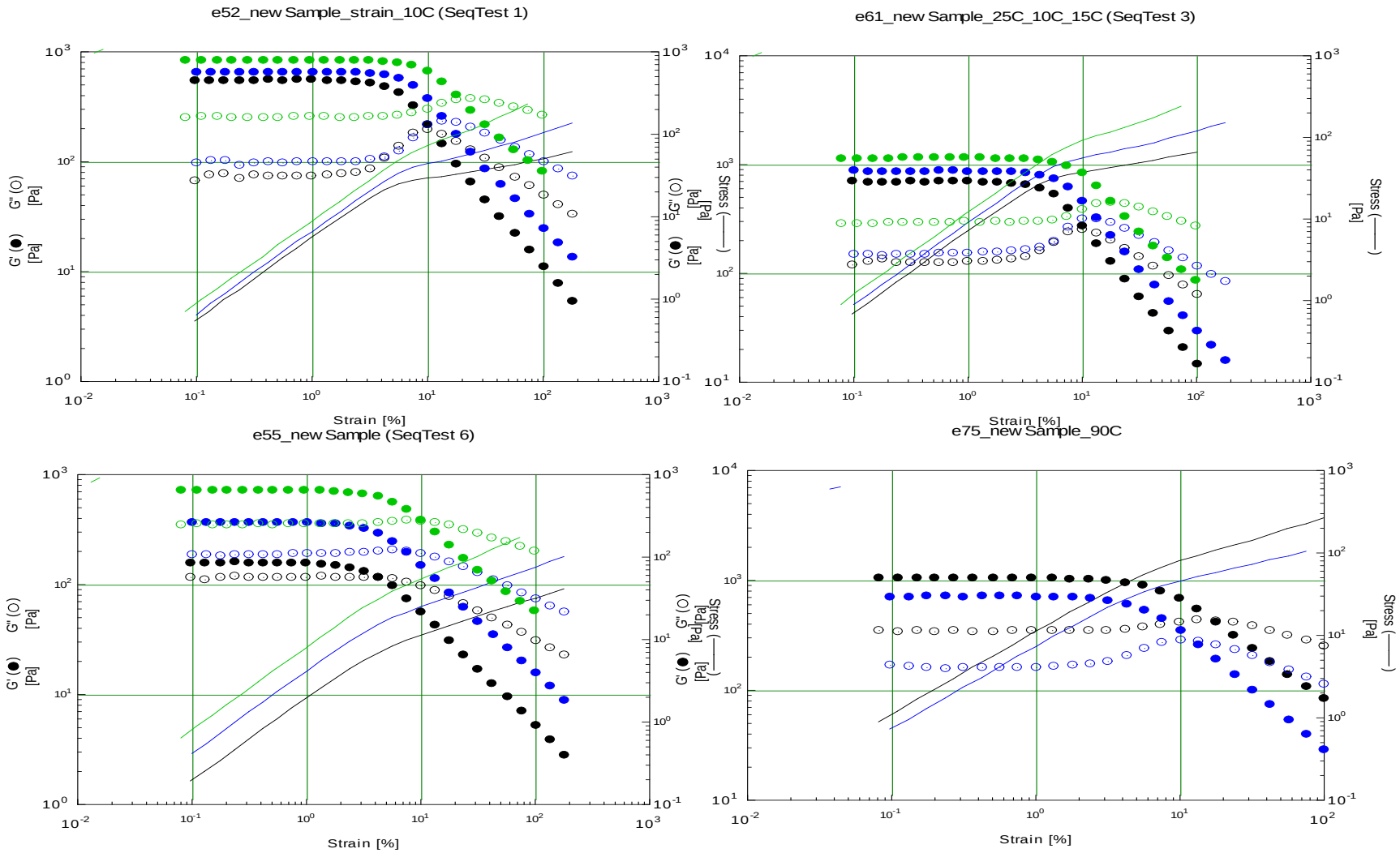

ω = 0.05 rad/s
G', G'' [Pa]
γ
Gap = 0.73 mm
Gap = 0.51 mm
Gap = 0.40 mm


ω = 100 rad/s
G', G'' [Pa]
γ
Gap = 0.73 mm
Gap = 0.63 mm
Gap = 0.51 mm
Gap = 0.40 mm

Tunable micelles, E. van Ruymbeke et al., 2007

1 rad/s, 10rad/s or 100 rad/s

2c*:



10C

25C

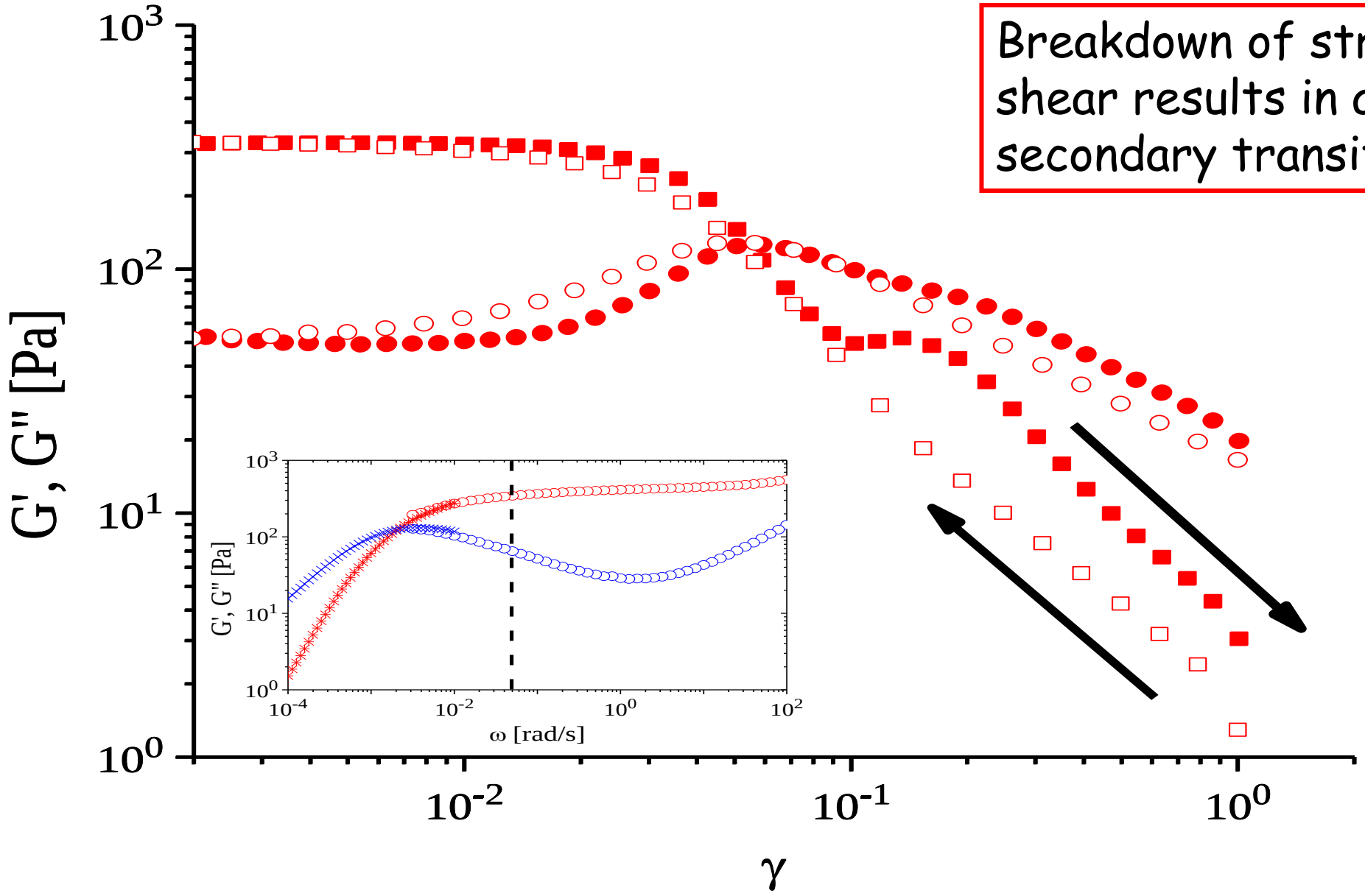
50C

90C

10 and 100 rad/s

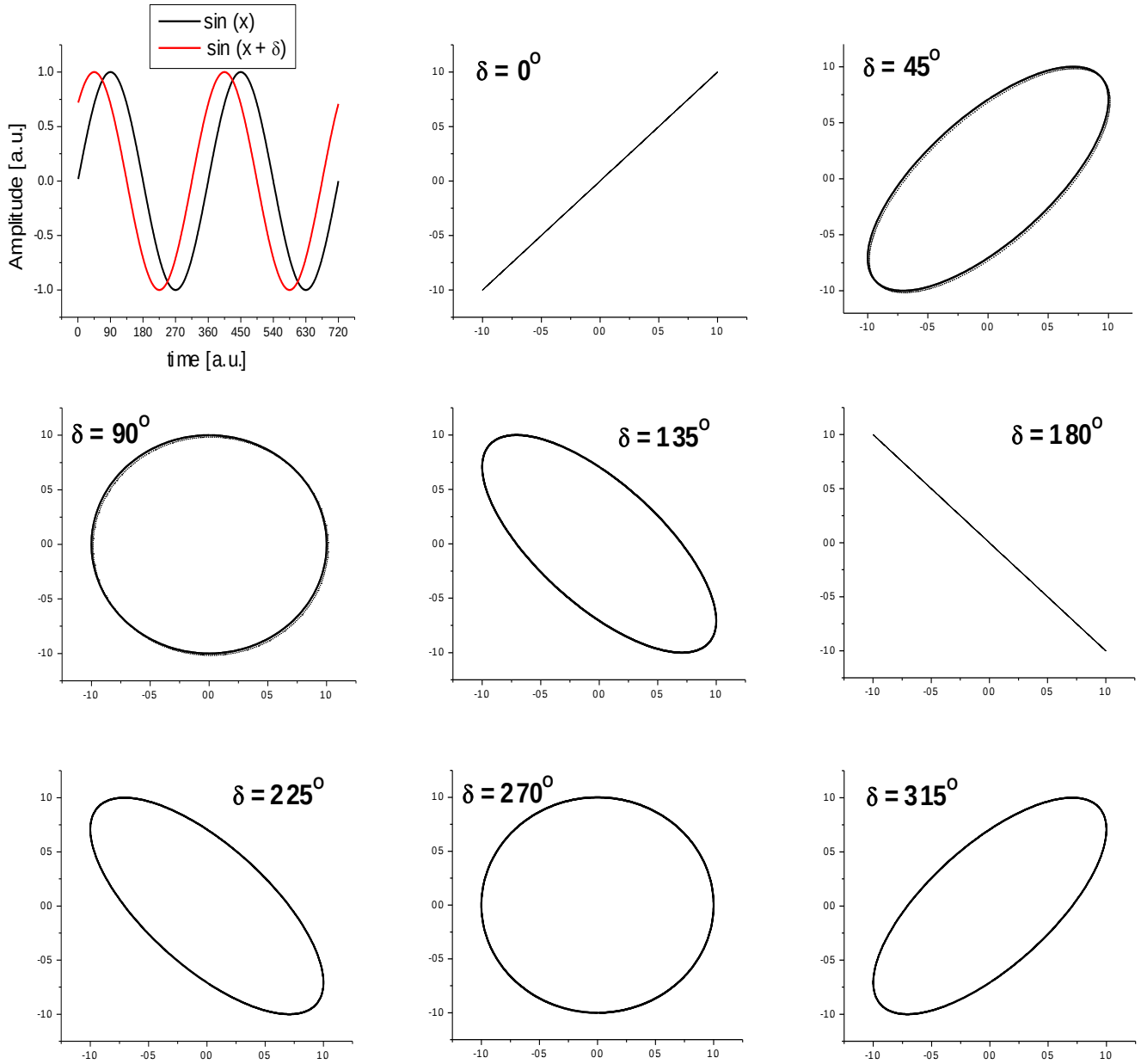
Van Ruymbeke et al. SM 2010

Thixotropic behavior



Breakdown of structure under high shear results in annealing of secondary transition

Lissajous-Bowditch plots



Steady vs oscillatory shear:
Which one is a better (more straightforward)
probe of (i) LVE and (ii) NLVE ?

LAOS and MAOS with polymers (and other soft matter systems):

Dealy, Giacomin
(sliding plate rheometry)

Recent advances:

R. Ewoldt, S. Rogers, Univ. of Illinois @ Urbana-Champaign