Applications of Rheology to Polymers

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For TA Instruments
Eden Prairie MN
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Rheology Short Courses:

Stanford University, June 11-13, 2019

https://trainings.tainstruments.com/rheology-short-course/

KU Leuven, September 2-6, 2019, with lab

https://cit.kuleuven.be/smart/rheoschool

University of Minnesota, June 2020, with lab
https://rheology.cems.umn.edu/

Polymer Rheology

Molecular Structure

- MW and MWD
- Chain Branching and Cross-linking
- Thermosets
- Single or Multi-Phase Structure
- Solid polymers

Viscoelastic Properties

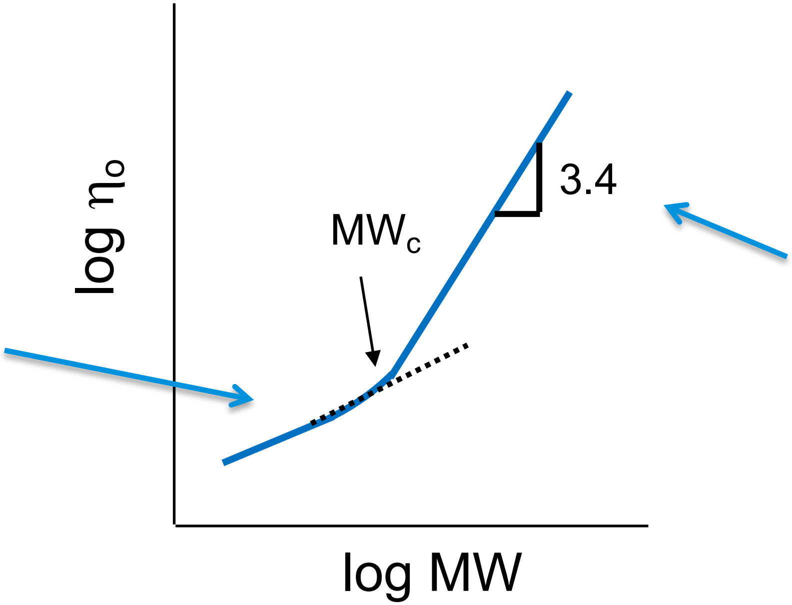
- Small strain (linear viscoelastic)
- Steady shearing
- Extension

Processability & Product Performance

Melt Rheology: MW Effect on Zero Shear Viscosity

- Sensitive to Molecular Weight, MW
- For Low MW (no Entanglements) η_0 is proportional to MW
- For MW > Critical MW_c, η_0 is proportional to $MW^{3.4}$

$\eta_0 = K \cdot Mw$

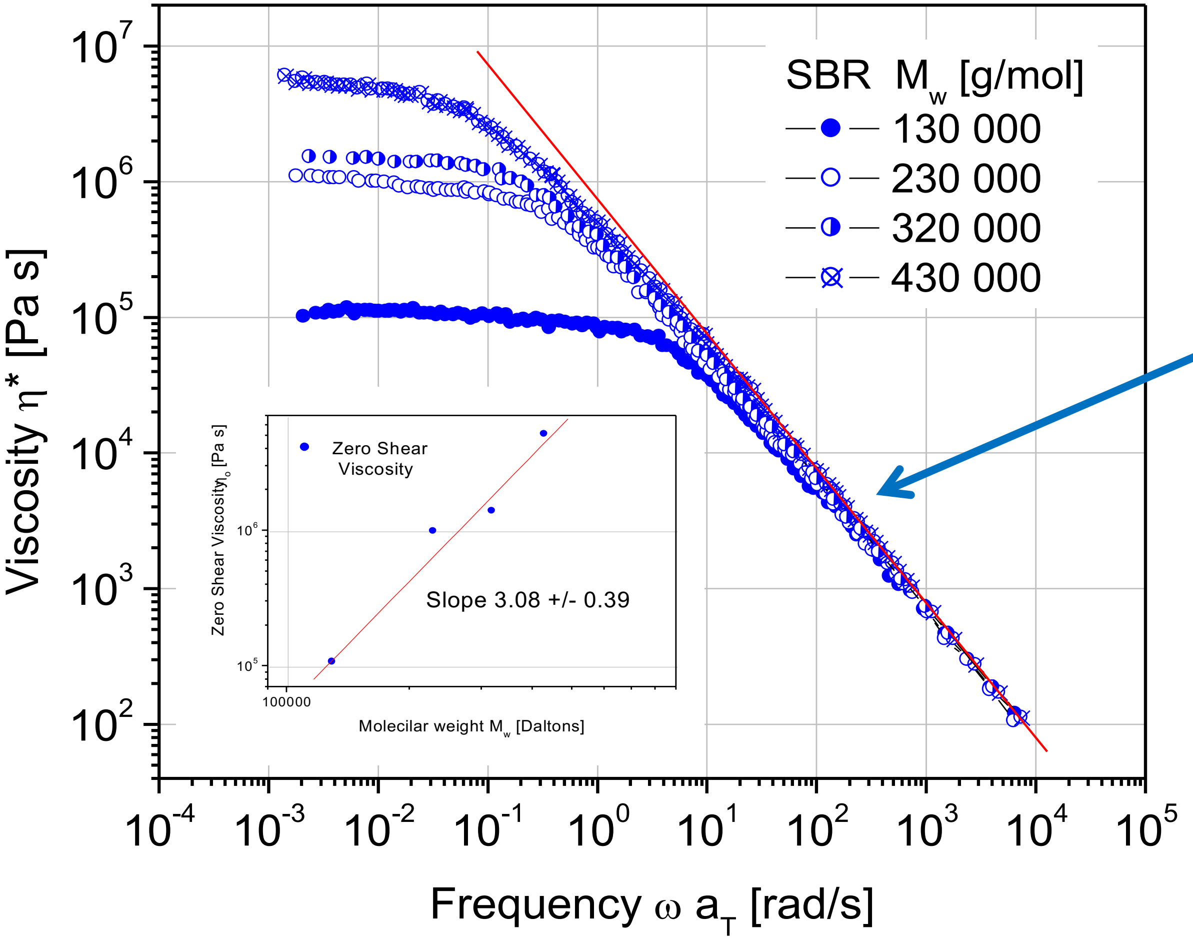


$\eta_0 = K \cdot Mw^{3.4}$

Ref. Graessley, Physical Properties of Polymers, ACS, c 1984.

Influence of MW on Viscosity

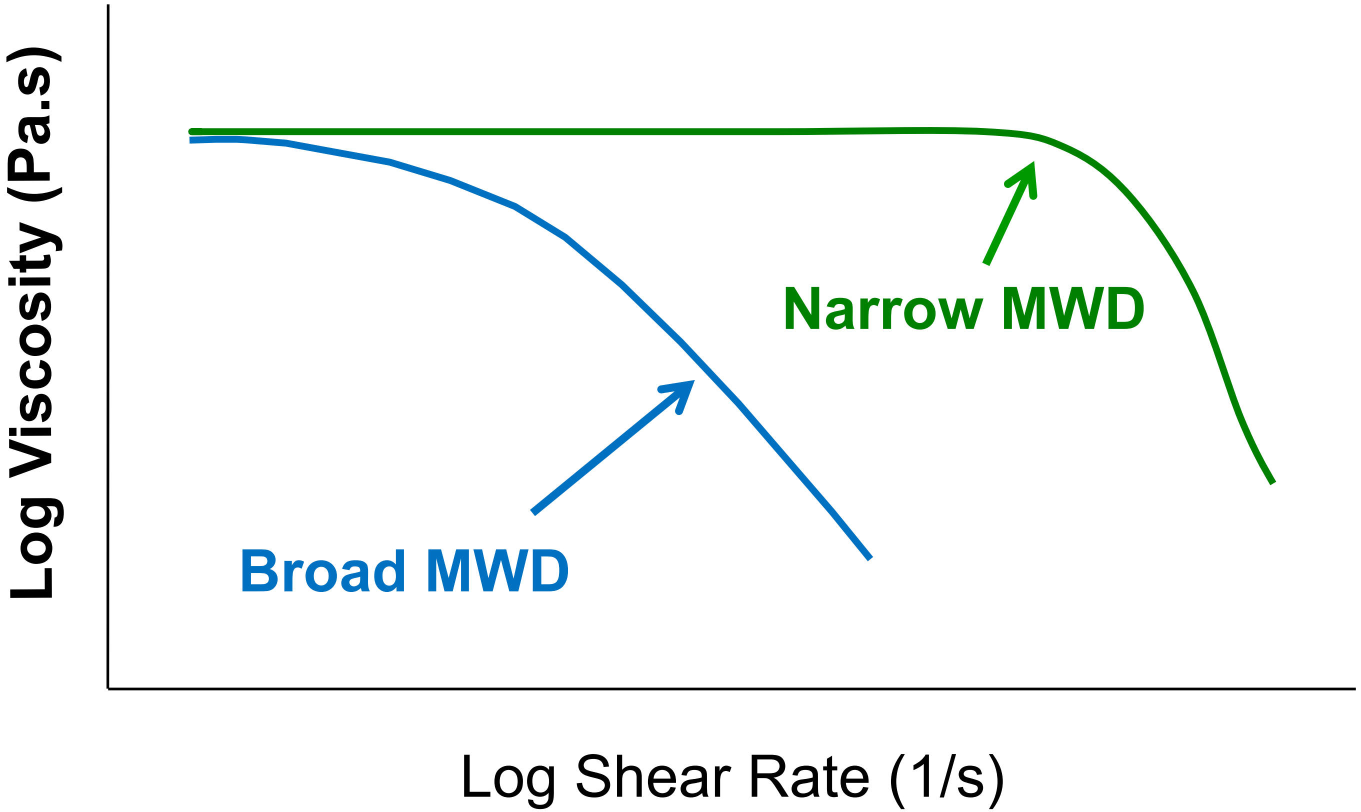
The zero shear viscosity increases with increasing molecular weight.
TTS is applied to obtain the extended frequency range.



The high frequency behavior (slope -1) is independent of the molecular weight

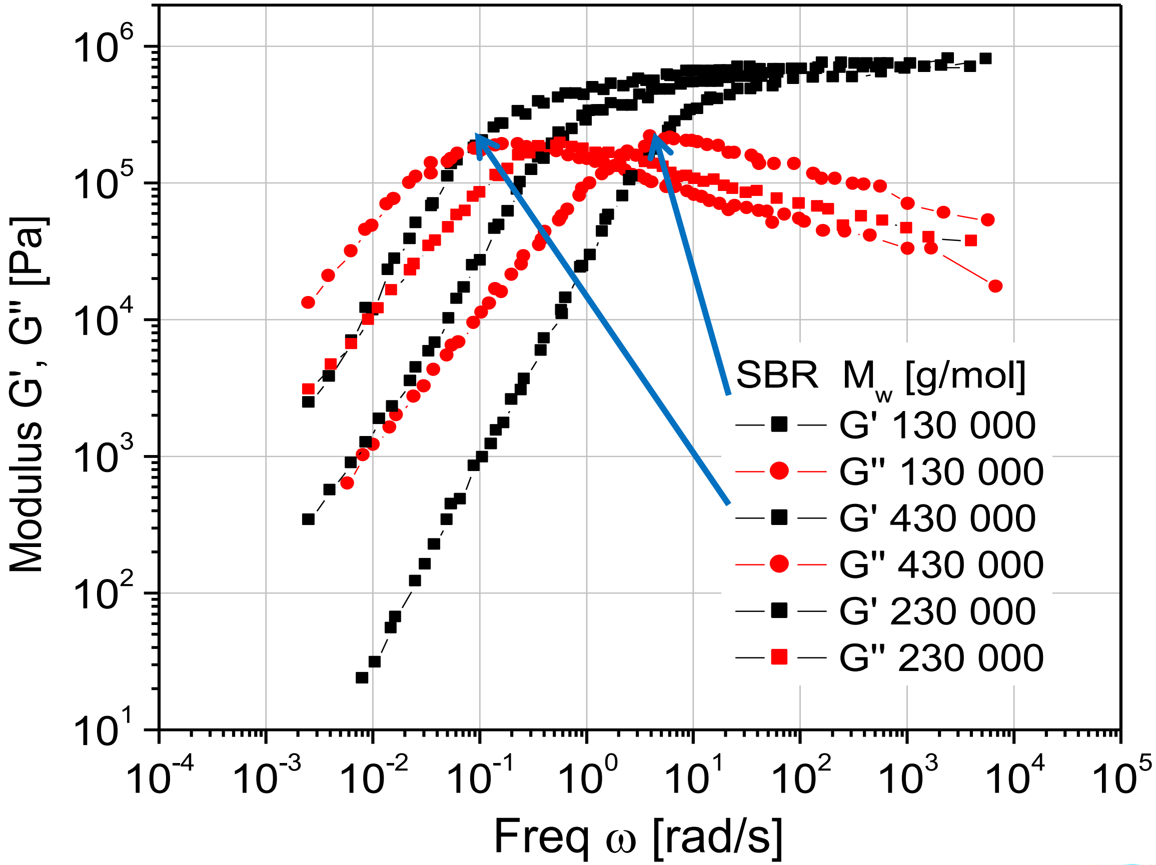
Influence of MWD on Viscosity

- A Polymer with a broad MWD exhibits non-Newtonian flow at a lower rate of shear than a polymer with the same η_0, but has a narrow MWD.

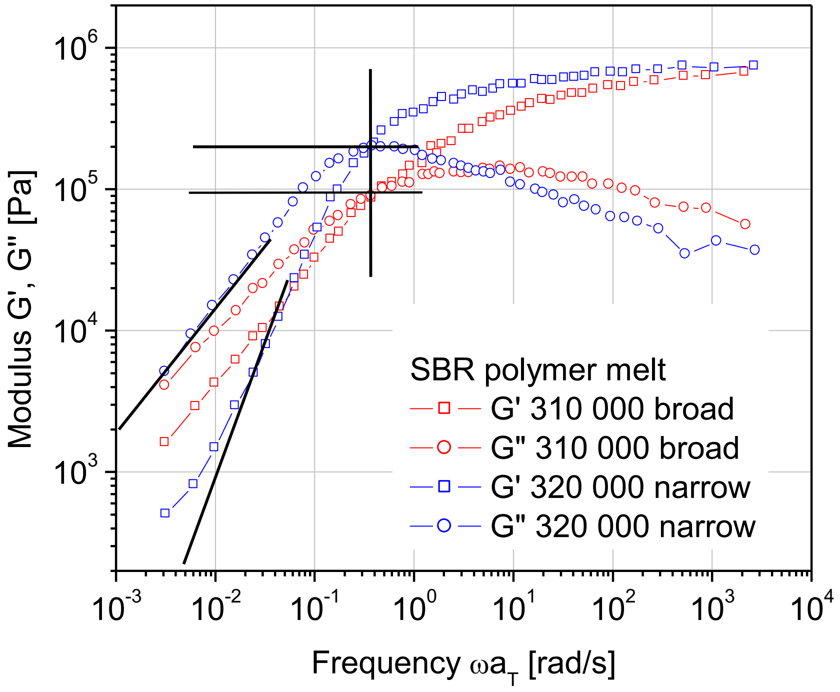


Influence of MW on G‘ and G“

The G‘ and G“ curves are shifted to lower frequency with increasing molecular weight.



Influence of MWD on G‘ and G“

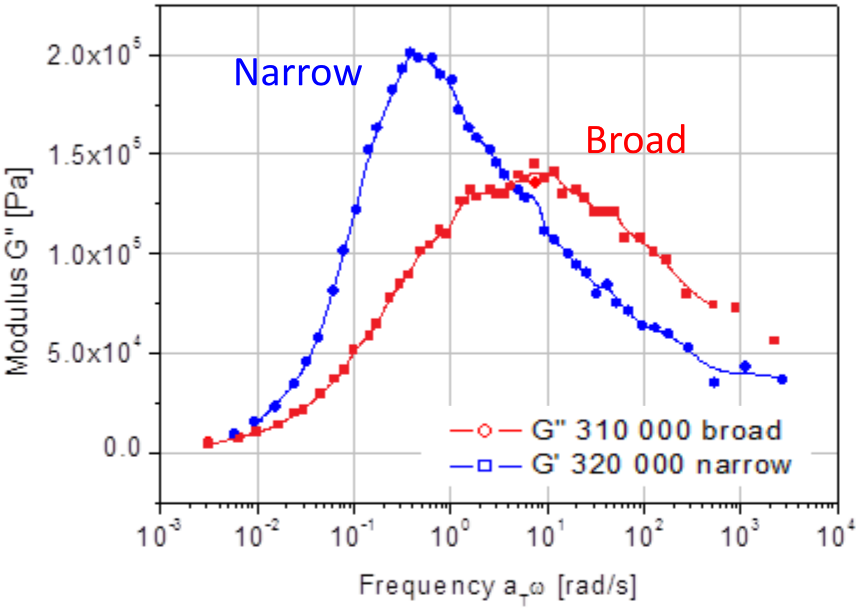


- The maximum in G“ is a good indicator of the broadness of the distribution

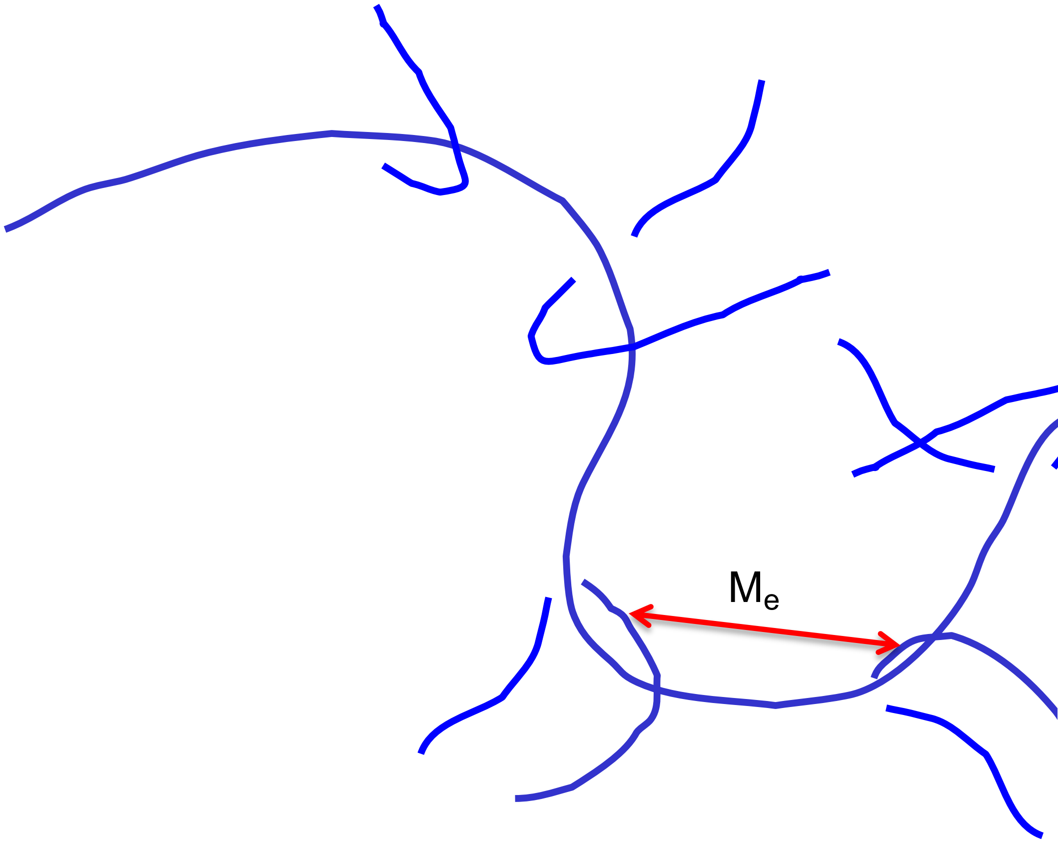
Higher crossover frequency : lower M_W

Higher crossover Modulus: narrower MWD

(note also the slope of G” at low frequencies – narrow MWD steeper slope)



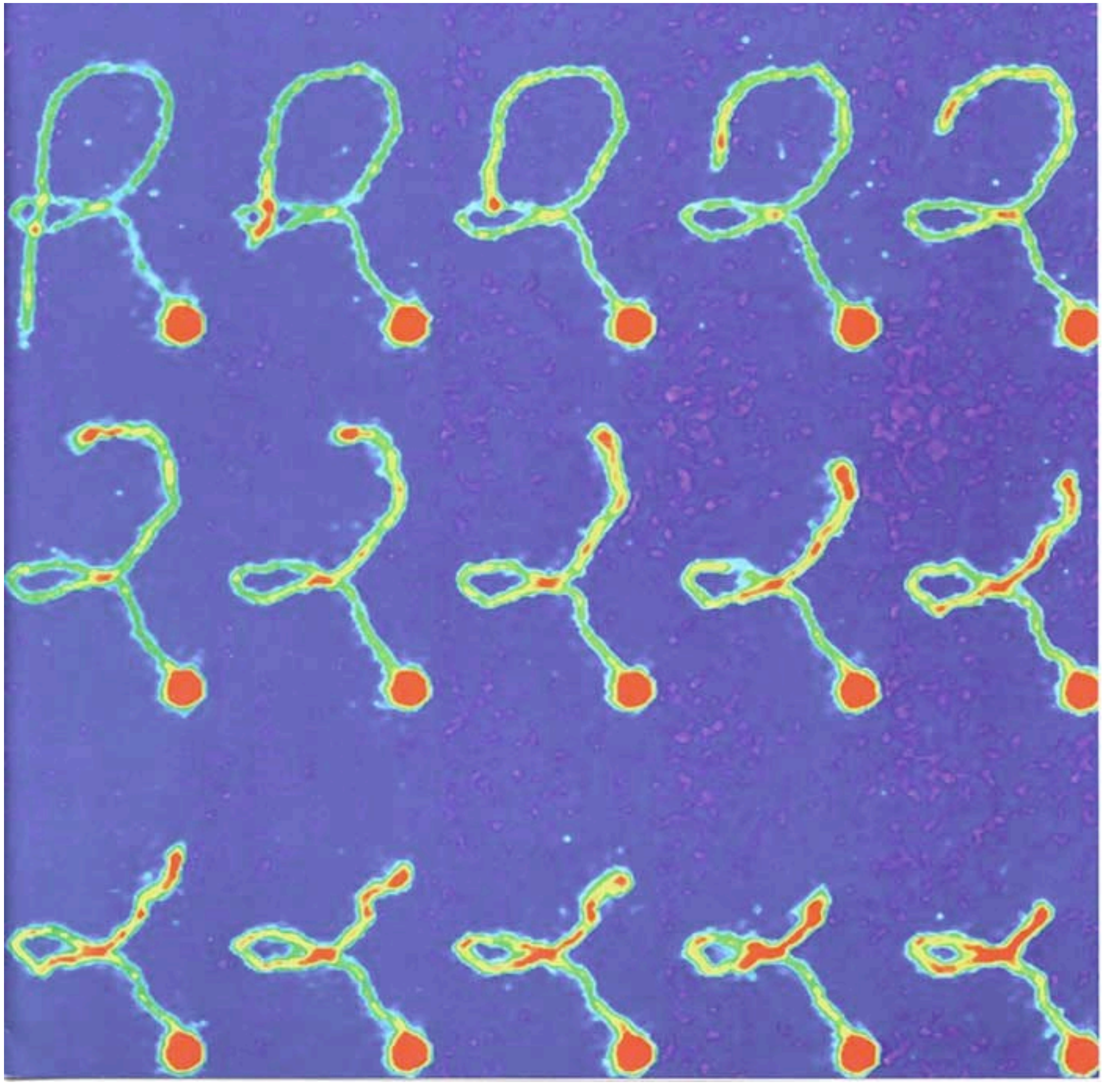
Mixture of Linear Homogeneous Chains



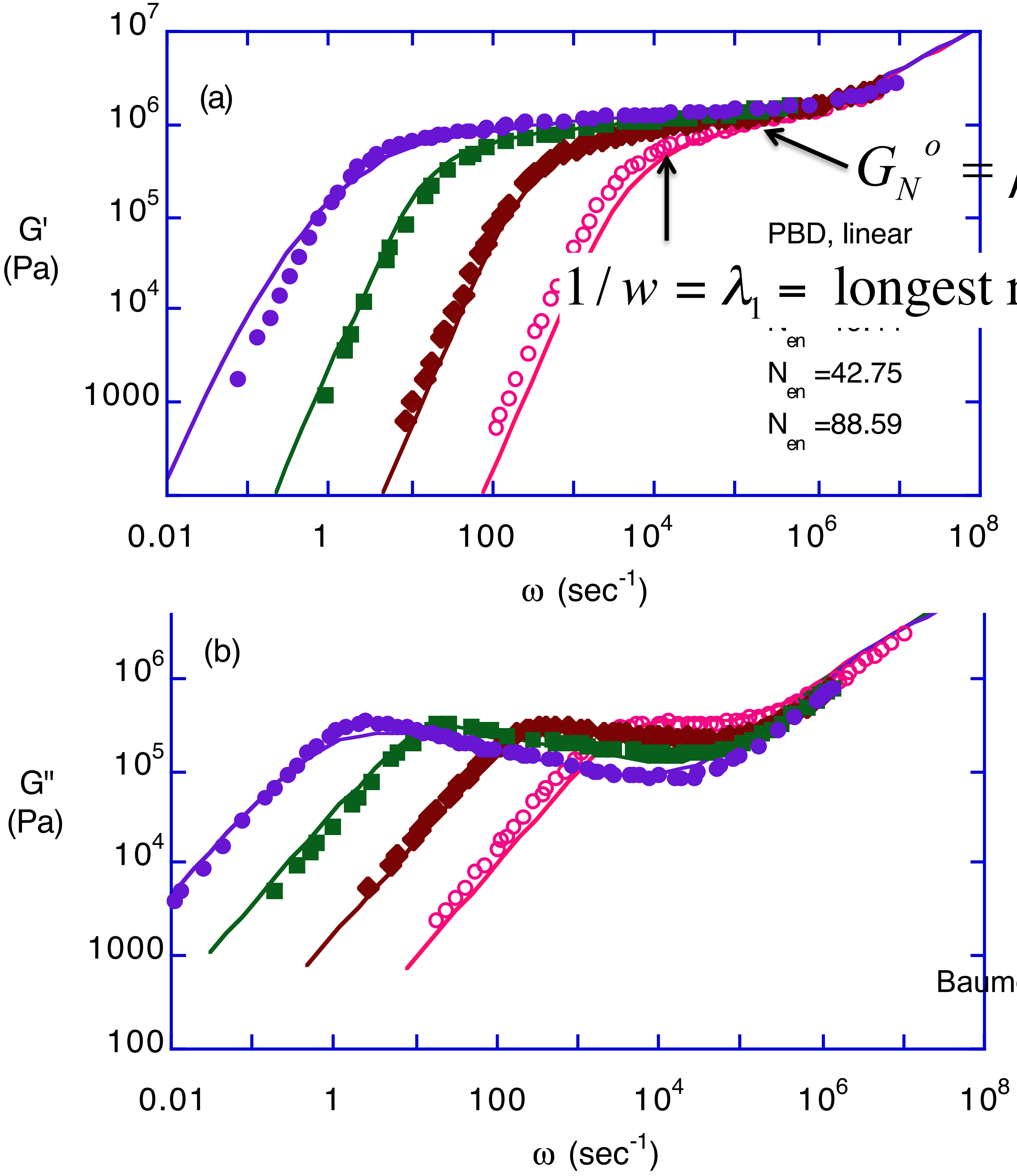
reptation – PG deGennes

Nobel Physics 1991

Fluorescent DNA attached to a PS bead in a sea of DNA



S. Chu et al. *Science,* **264**, 822 (1994)
Nobel Physics 1997

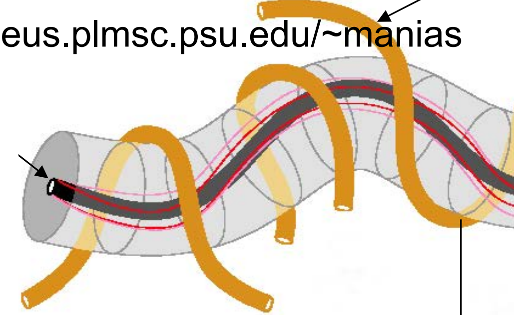


$G_N^{\,o} = \rho \mathrm{RT}/\mathrm{M_e}$

$1/w = \lambda_1 =$ longest relaxation

Baumgaertel, Schausberger, Winter
Rheol. Acta, **29**, 400 (1990)

zeus.plmsc.psu.edu/~manias



Single Reptation

$\lambda_1 =$ longest relaxation

$$\lambda_1 = \zeta \frac{b^2}{kT}\left(\frac{M}{M_o}\right)^2\left(\frac{M}{M_e}\right)^{1.4}$$

$$\log \zeta = \log \zeta_g - \frac{c_1^g\left(T - T_g\right)}{c_2^g + T - T_g}$$

segment friction

$$G(t) = G_N{}^o \exp(-t/\lambda_1)$$

$$G_N{}^o = \rho \mathrm{RT/M_e}$$

$$\eta = \int G(t)dt$$

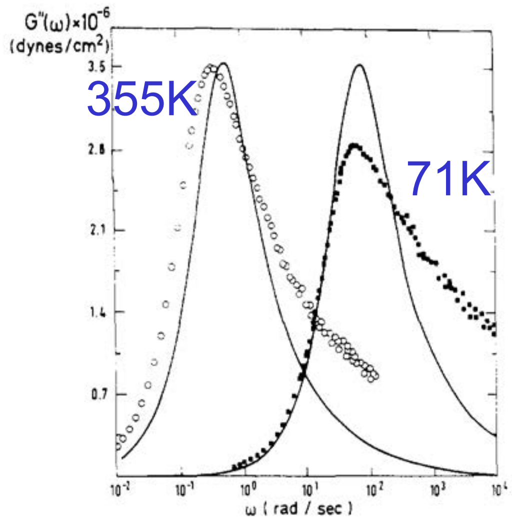
Double reptation, Tsenoglou mixing rule

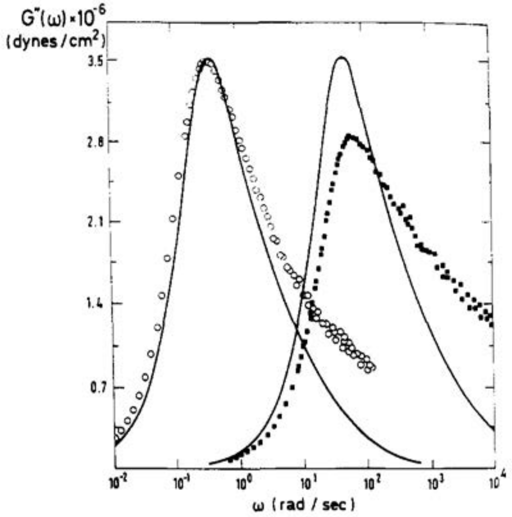
$$G(t) = (\Sigma_i \varphi_i G_i(t)^{1/2})^2$$

C. Tsenoglou, *Macromolecules*, **24**, 1762 (1991)

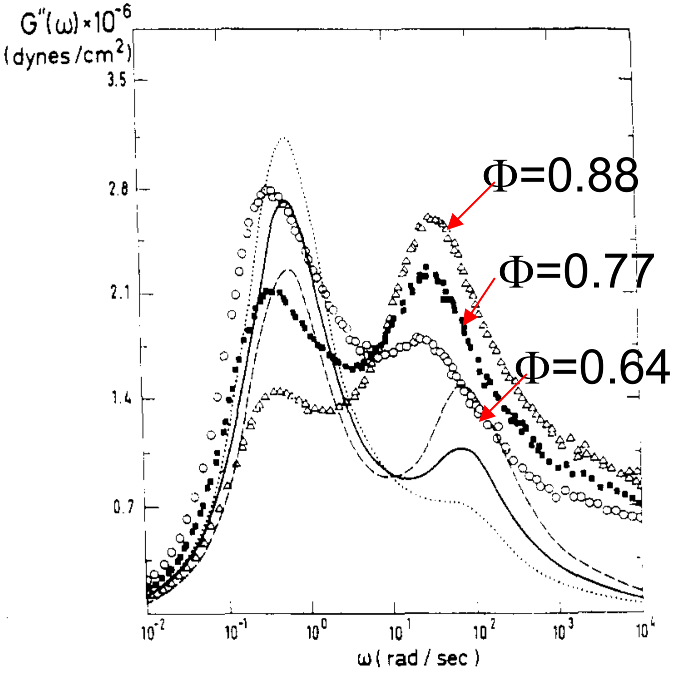
Single Reptation

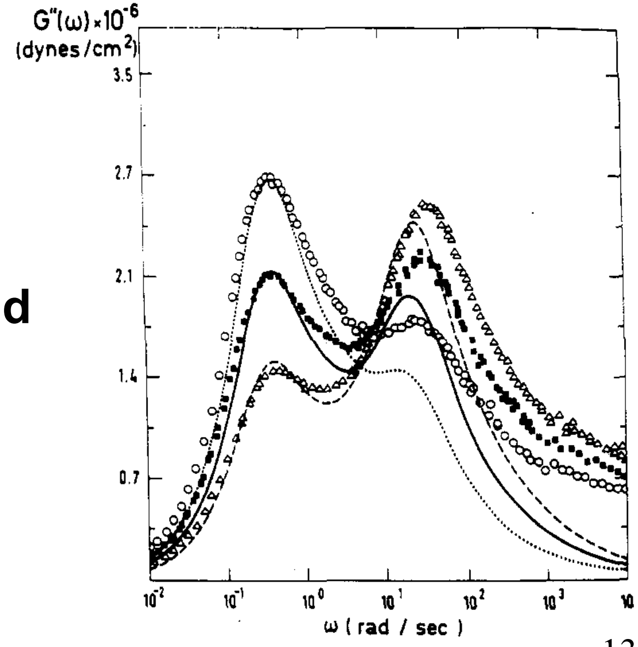
Double





Narrow MWD polybutadiene

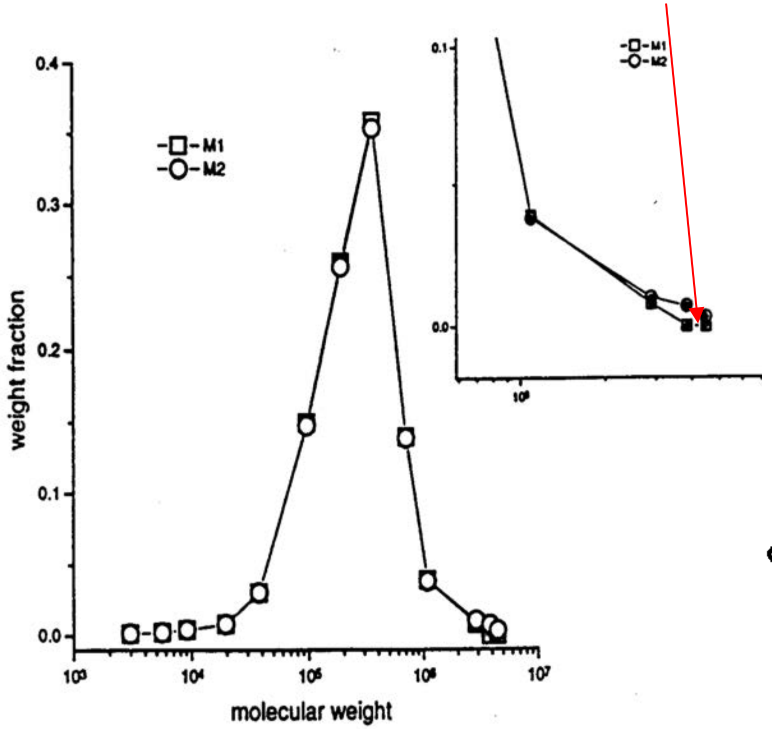


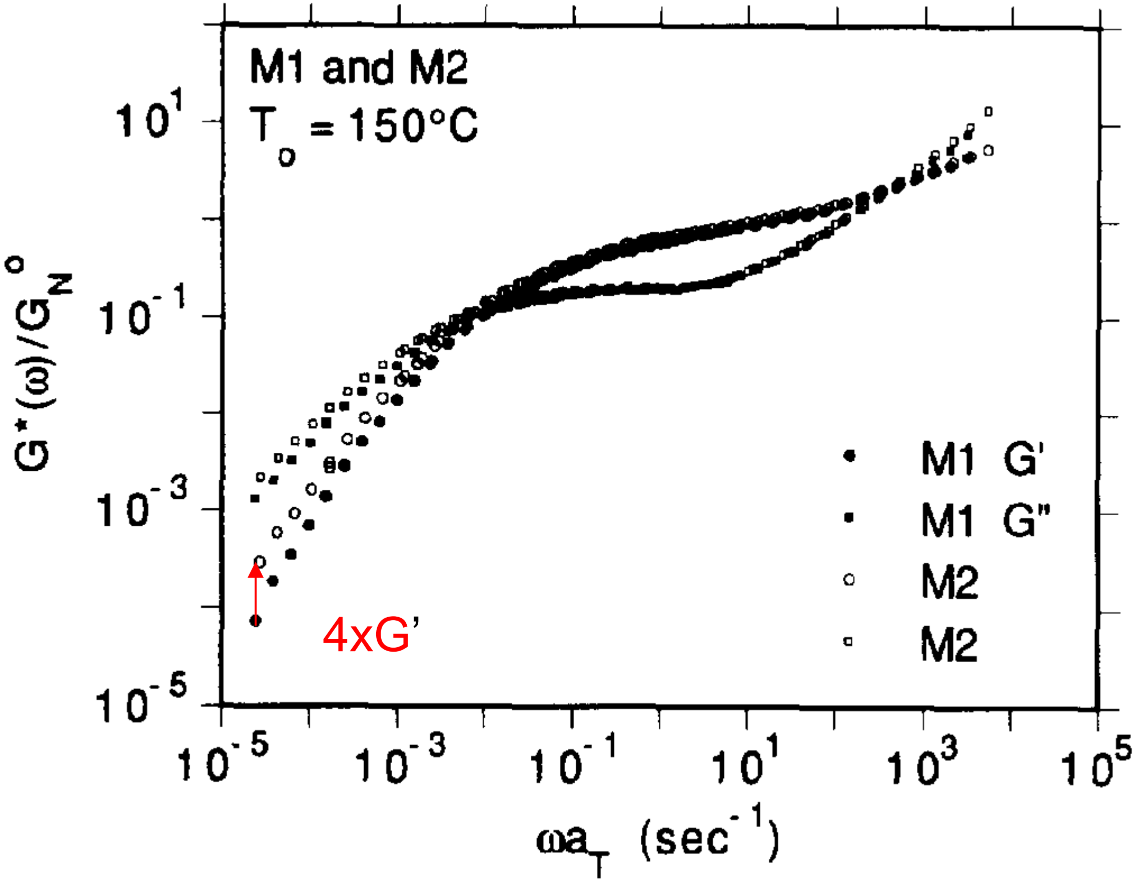


Bimodal blend

J. des Cloizeaux, *Macromolecules* **23**, 3992 (1990)

400K PS (M1) + 1% of 4,000K (M2)



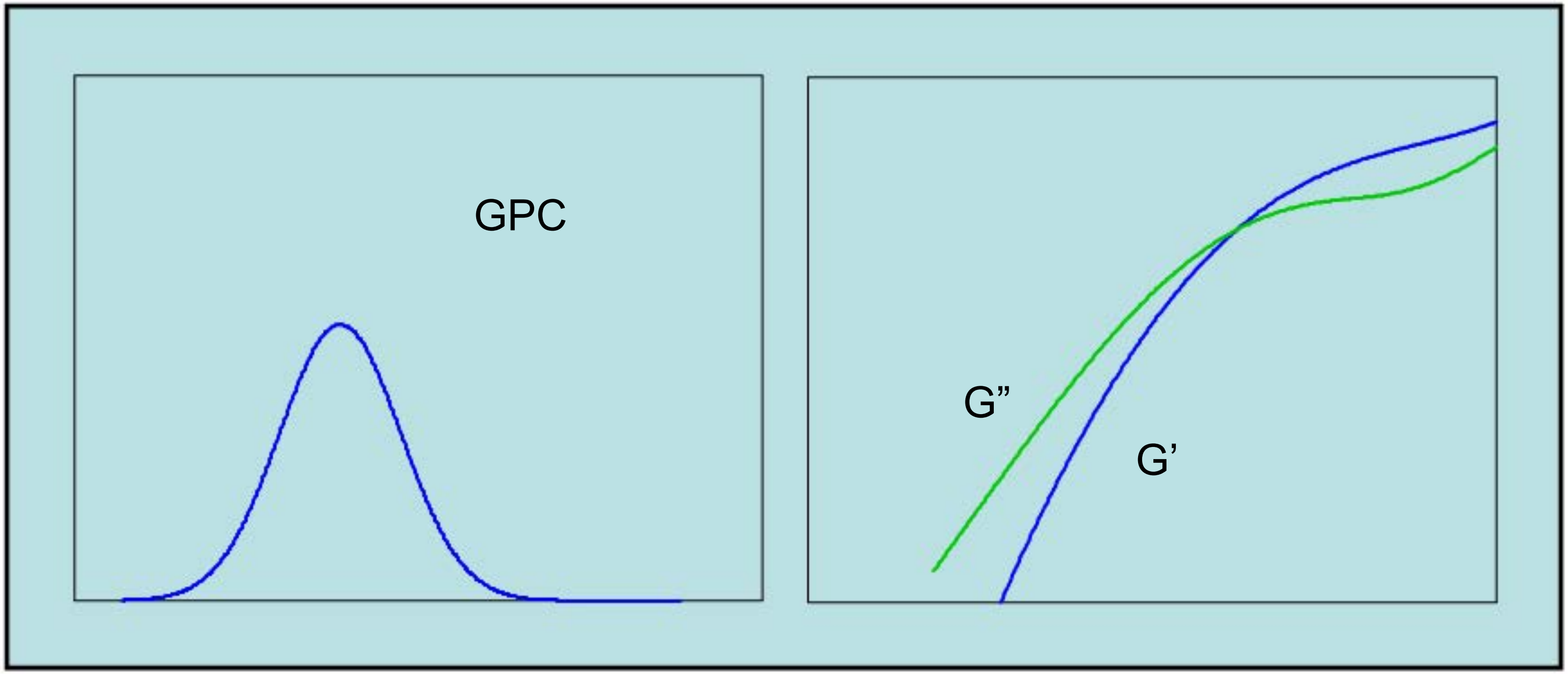


S. H. Wasserman and W. W. Graessley, J.
Rheol. **36**, 543 (1992)

Orchestrator: MWD from G’, G”

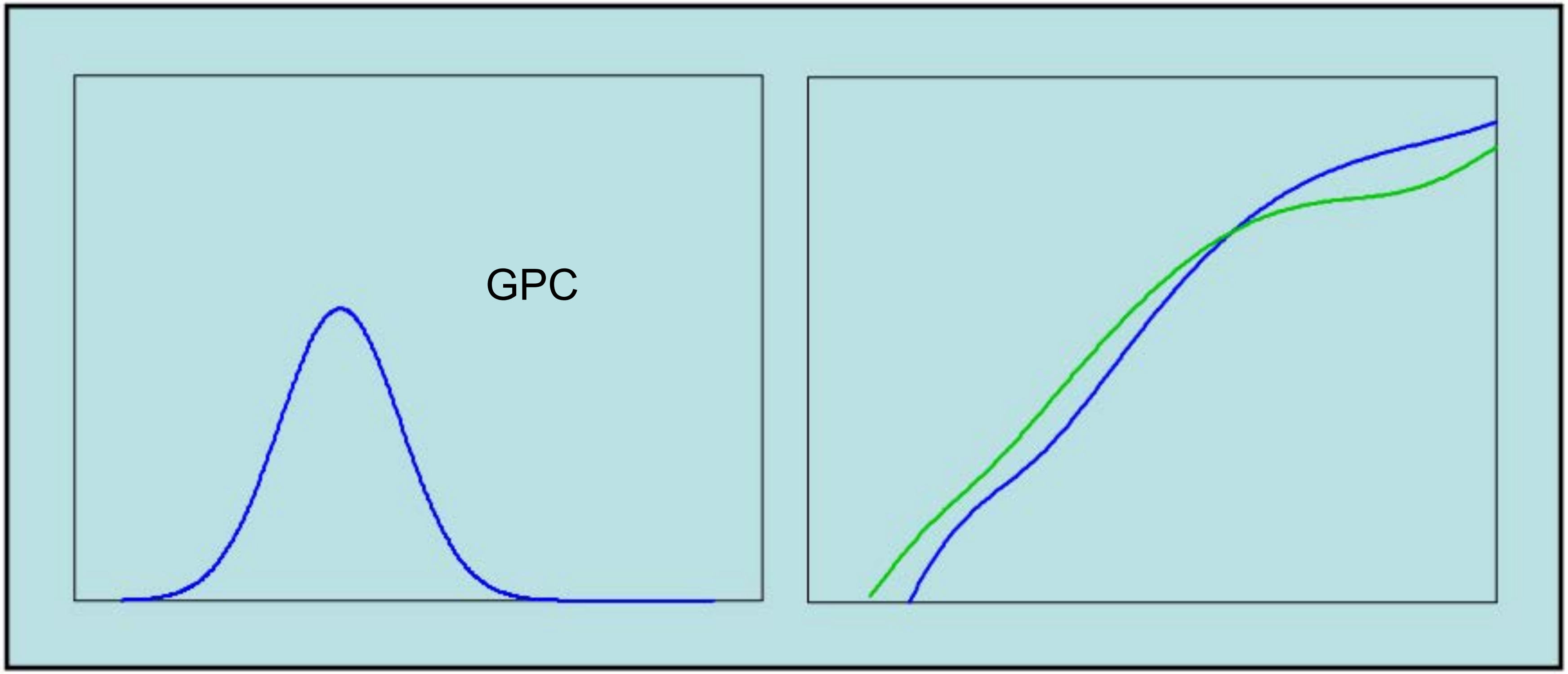
(or vice versa) via double reptation

400K PS



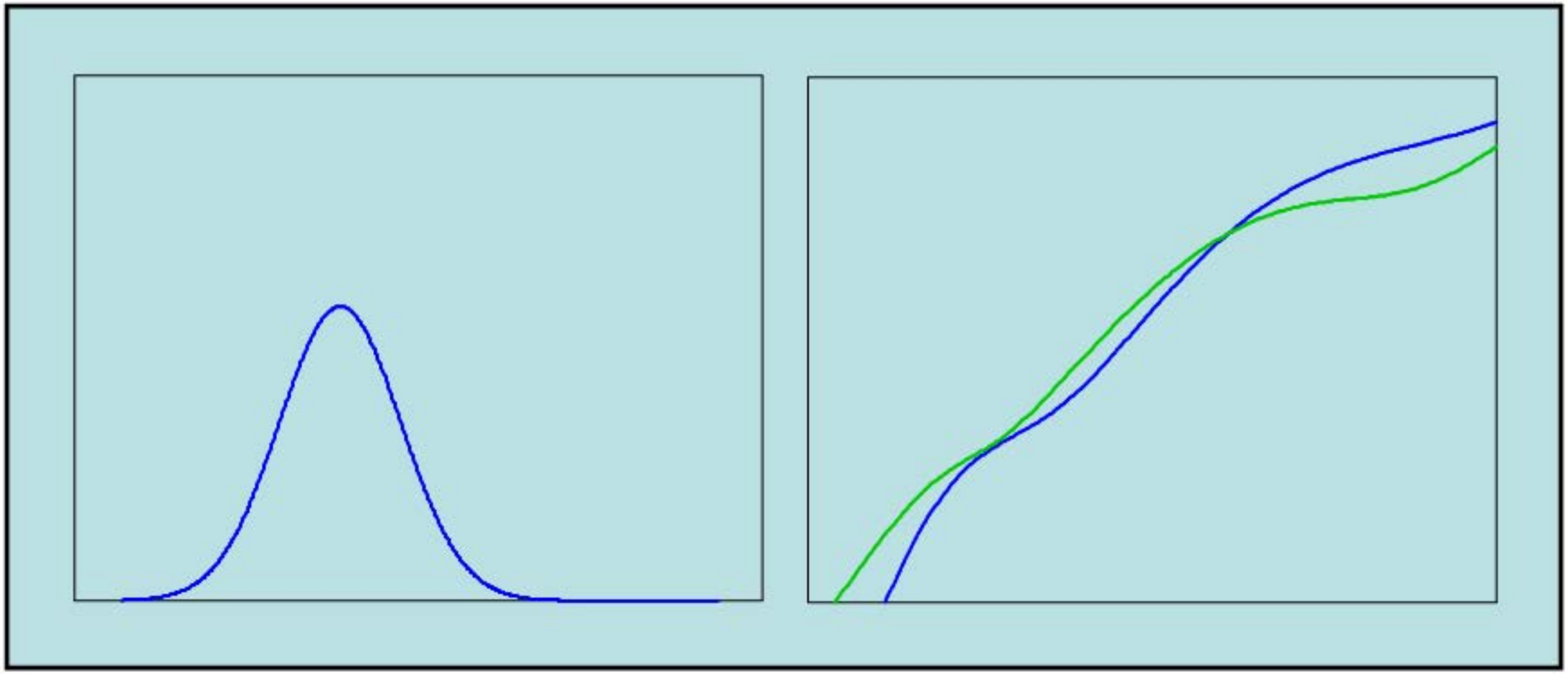
Orchestrator: MWD from G’, G” via double reptation

400K PS + 1% 12M



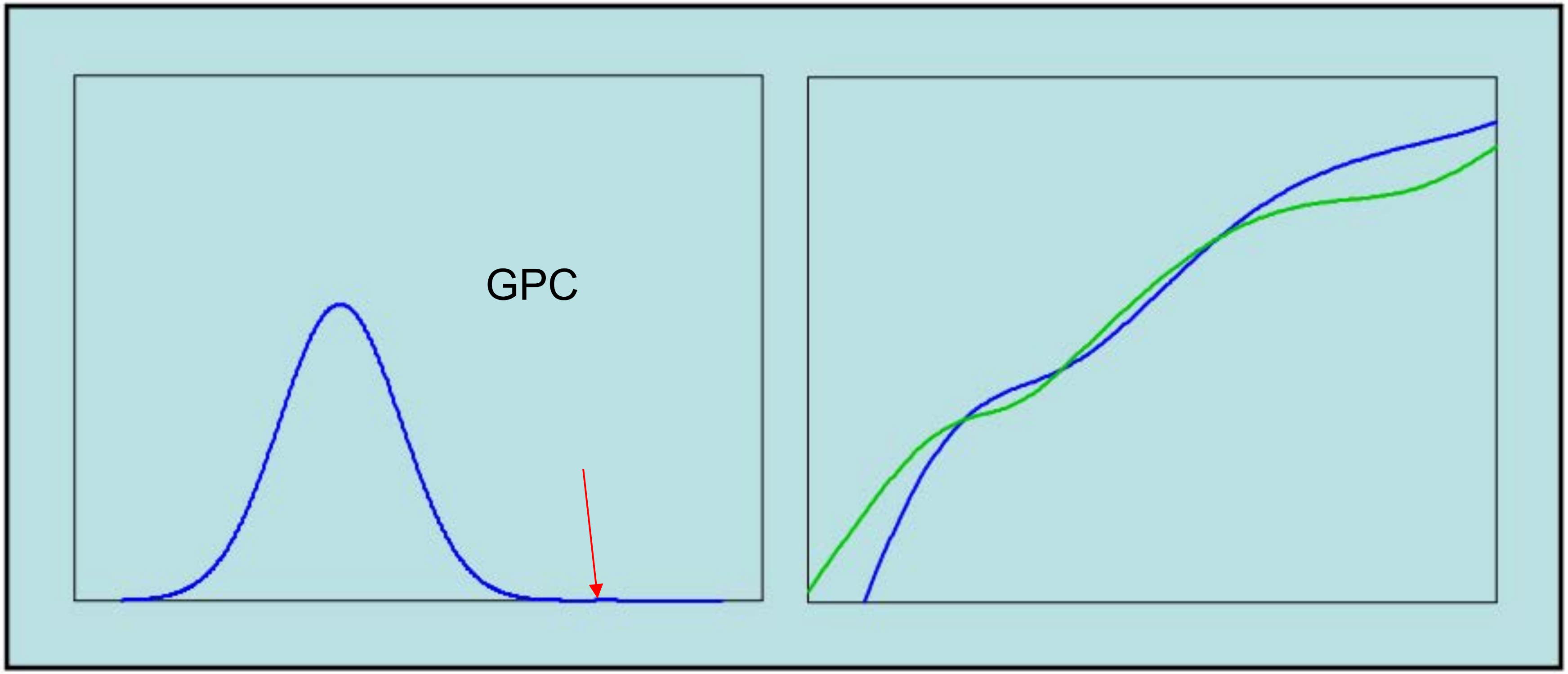
Orchestrator: MWD from G’, G” via double reptation

400K PS + 2% 12M

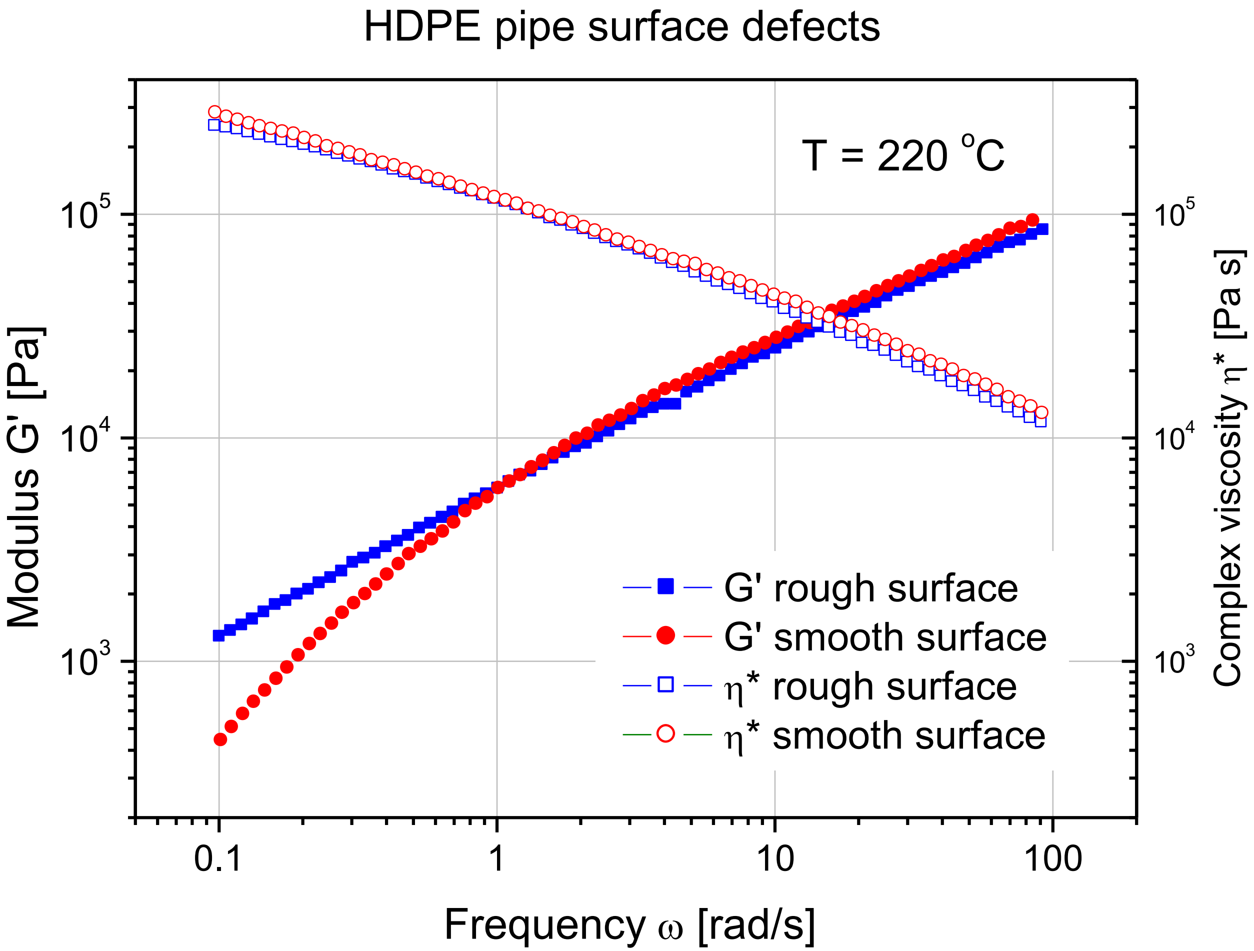


***Orchestrator*: MWD from G', G" via double reptation**

400K PS + 4% 12M



Extrusion of HDPE tubing



Extensive die swell,

high G' value at low frequency causes surface defects during extrusion of HDPE

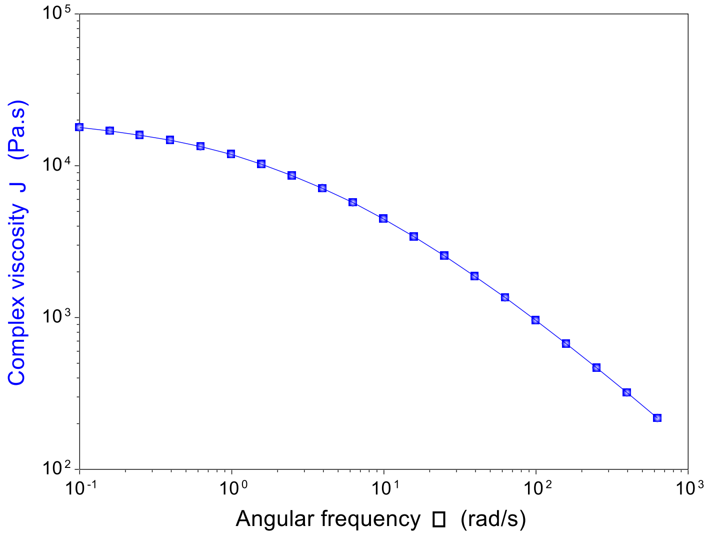
SEC or MFI measurements did not reveal the cause of the problem

TA Applications Note AAN013 *Understanding Rheology of Thermoplastics*

The Cox-Merz Rule

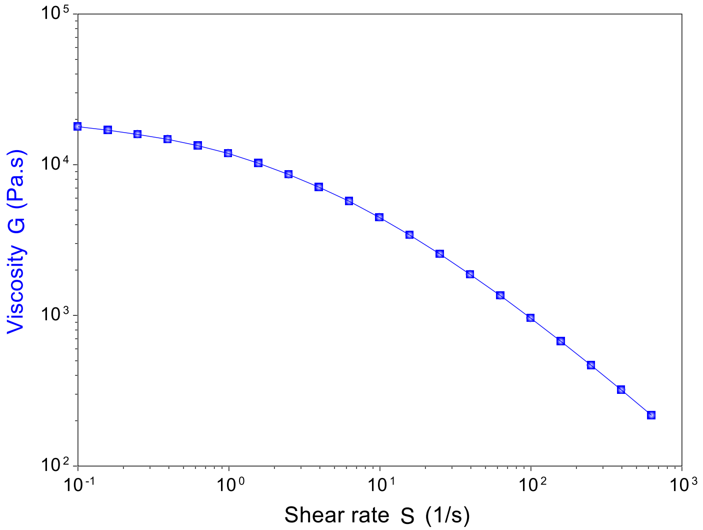
- For materials that exhibit wall slip or edge fracture, one alternative way to obtain viscosity information over shear is to use the Cox-Merz rule
- Cox-Merz “rule” is an empirical relationship. It was observed that in many polymeric systems, the steady shear viscosity plotted against shear rate is correlated with the complex viscosity plotted against frequency

Dynamic frequency sweep



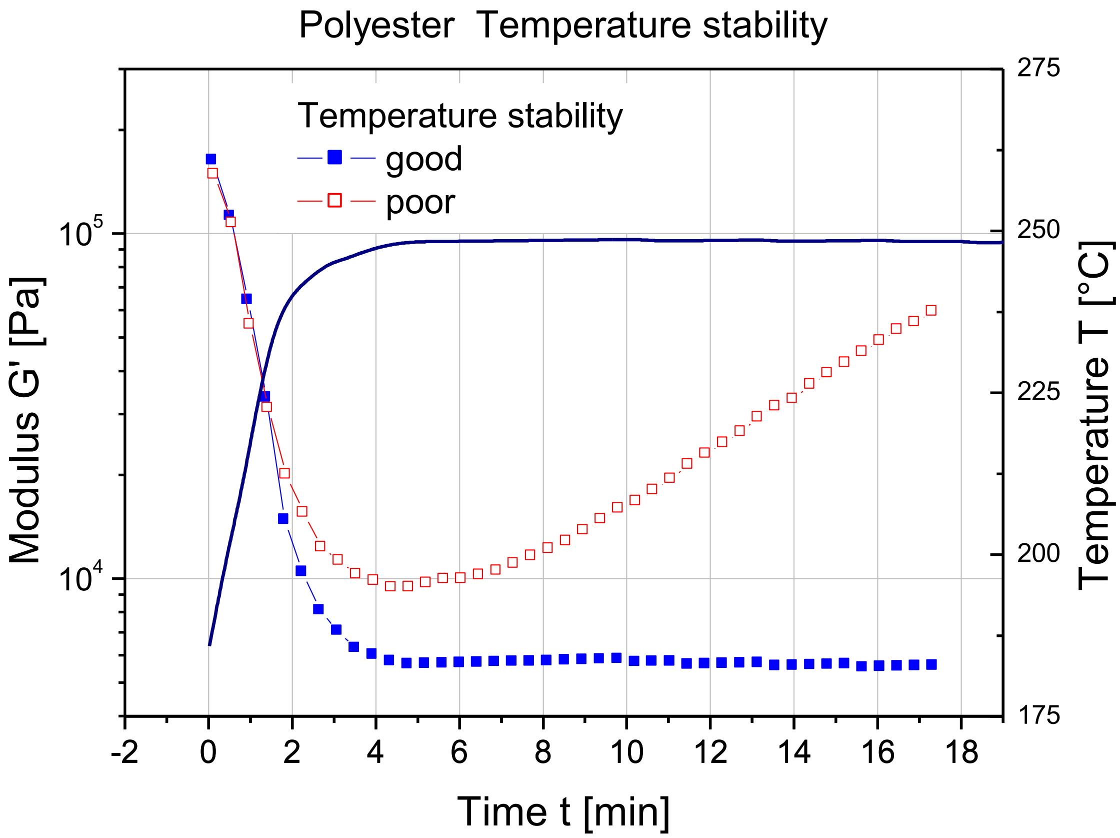
η^* (Pa.s)~ ω (rad/s)

Steady state flow



η (Pa.s)~ $\dot{\gamma}$ (1/s)

Polymer Melt Thermal Stability



Determines if properties are changing over the time of testing

- Degradation
- Molecular weight building
- Crosslinking

Important, but often overlooked!

Polymer Rheology

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MW and MWD
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Solid polymers

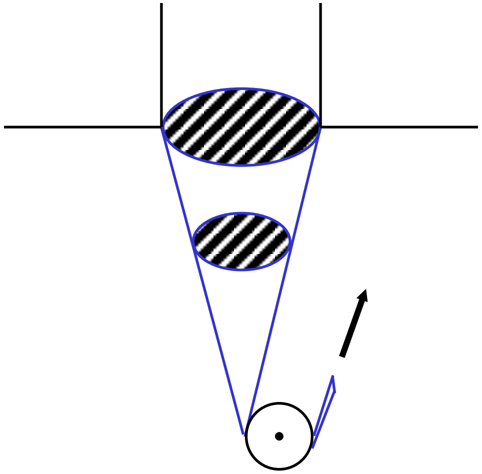
Viscoelastic Properties

Small strain (linear viscoelastic)
Steady shearing
Extension

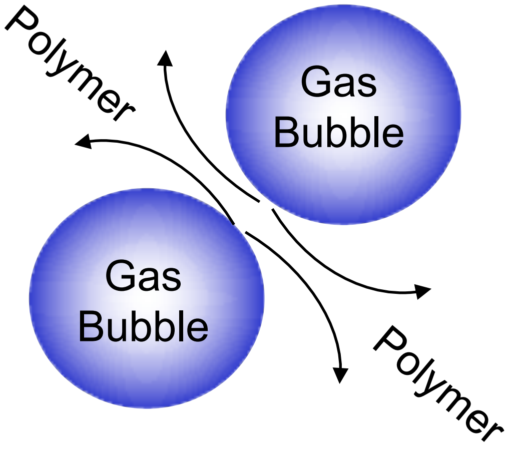
Processability & Product Performance

Extensional Flows

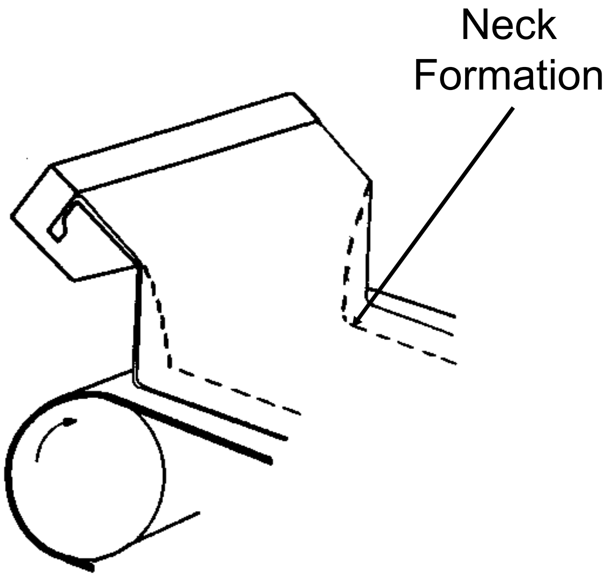
- Where do extensional flows occur?



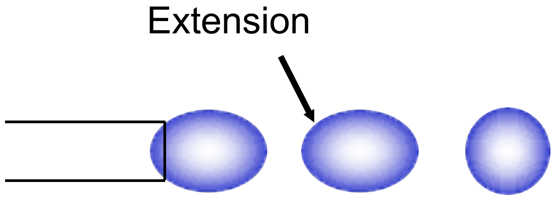
Fiber Spinning



Foaming



Coating



Droplet Formation
(Inkjet Printing, Atomization)

Complex flow during process –
shear + extensional flow

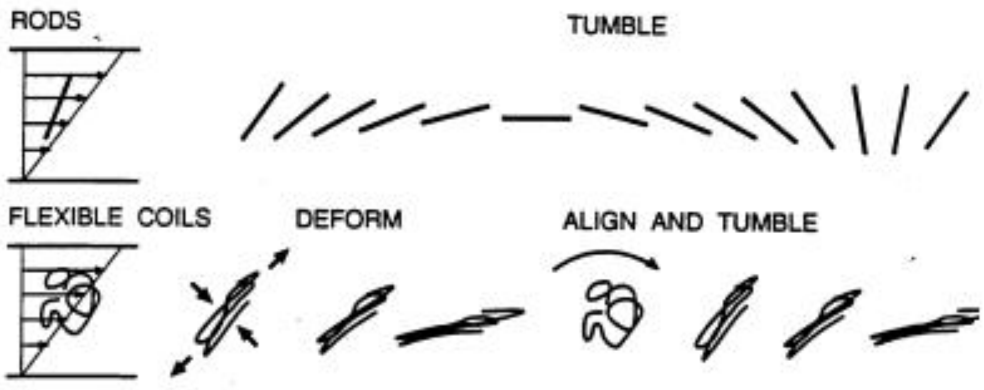
Flows with a High Extensional Component

Open-Syphon Flow

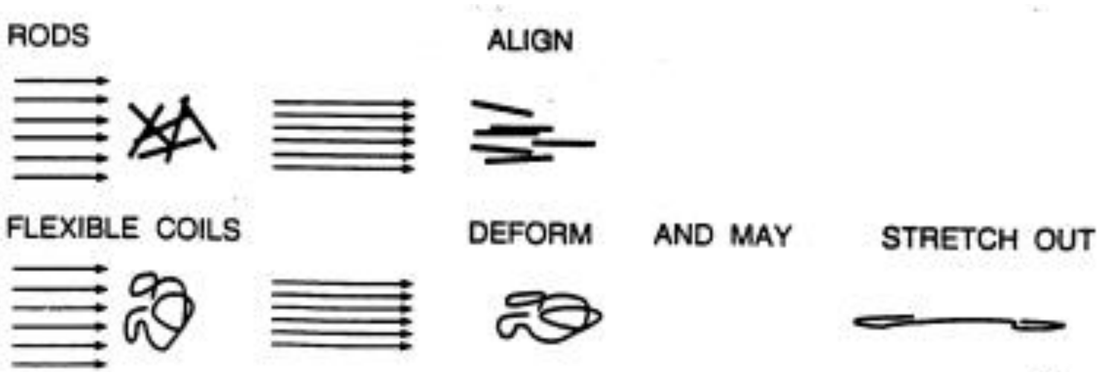
Extensional Flows

How are they different than shear ?

Shear



Extension

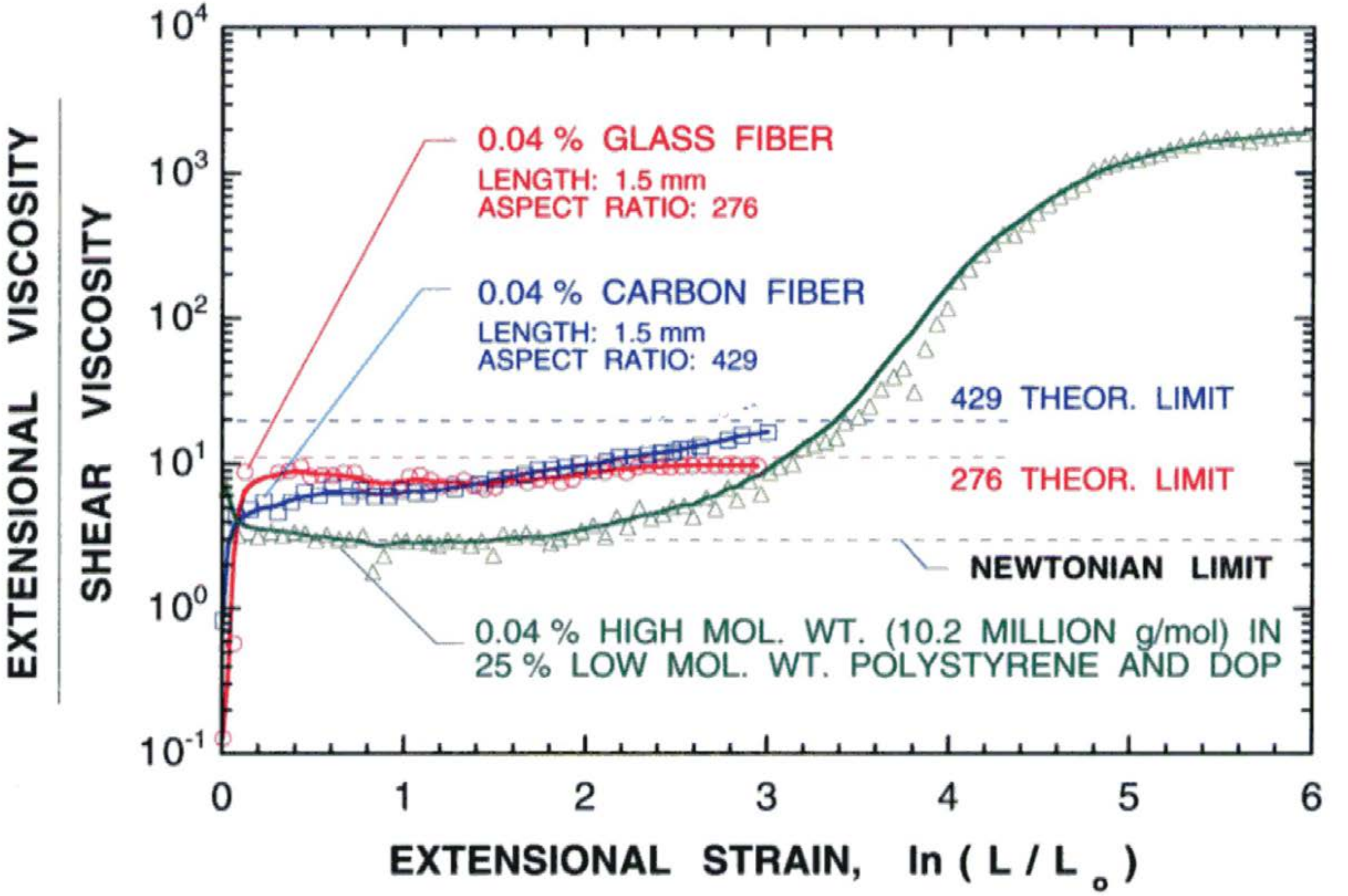


More alignment than shear

&

No rotation

Dilute Rods, Coils



Stiff particles orient at small strains

Flexible – high molecular weight polymers need larger strains to stretch and orient

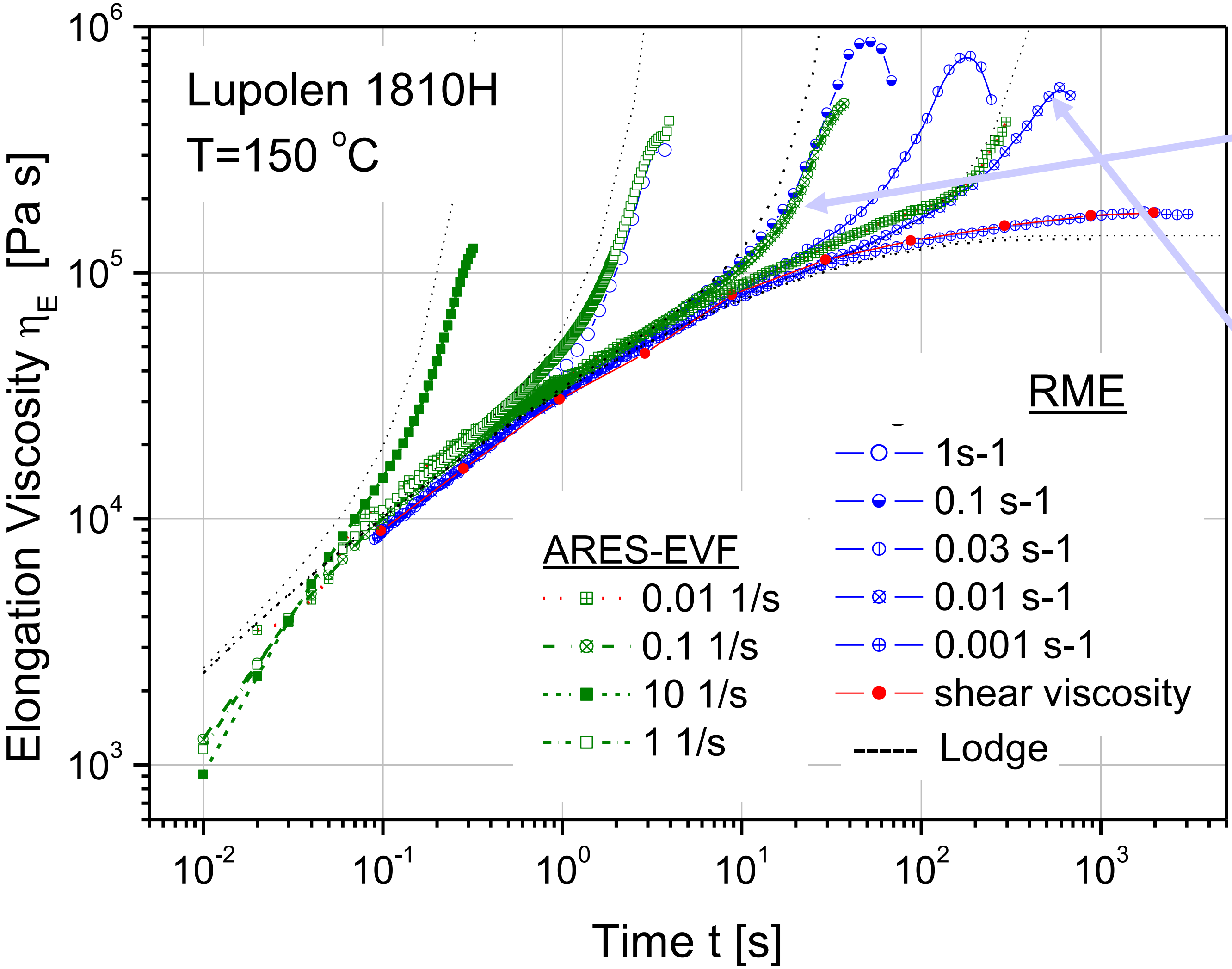
Gupta, Ngyen, & Sridhar (1998).

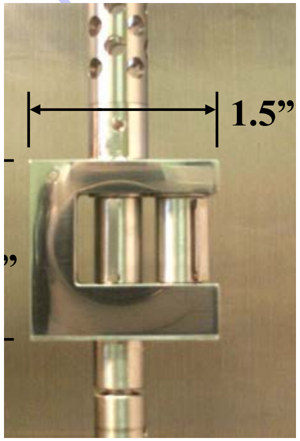
Extensional Viscosity Measurements

- Non linear elongation flow is more sensitive for some structure elements (e.g. branching) than shear flows

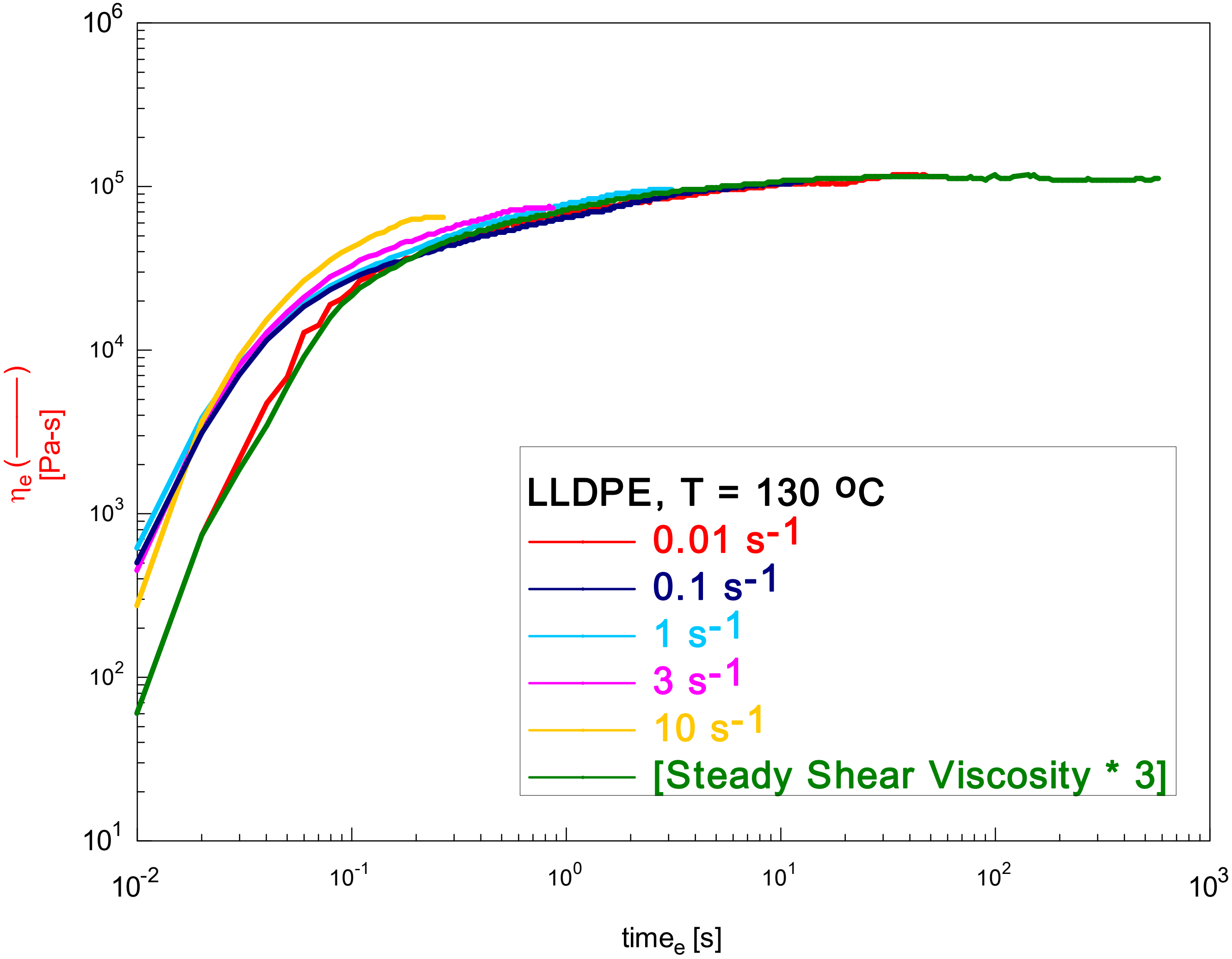
- Many processing flows are elongation flows. Extensional viscosity measurements can be used to help predict processability

EVF, SER - Extensional Viscosity Fixtures

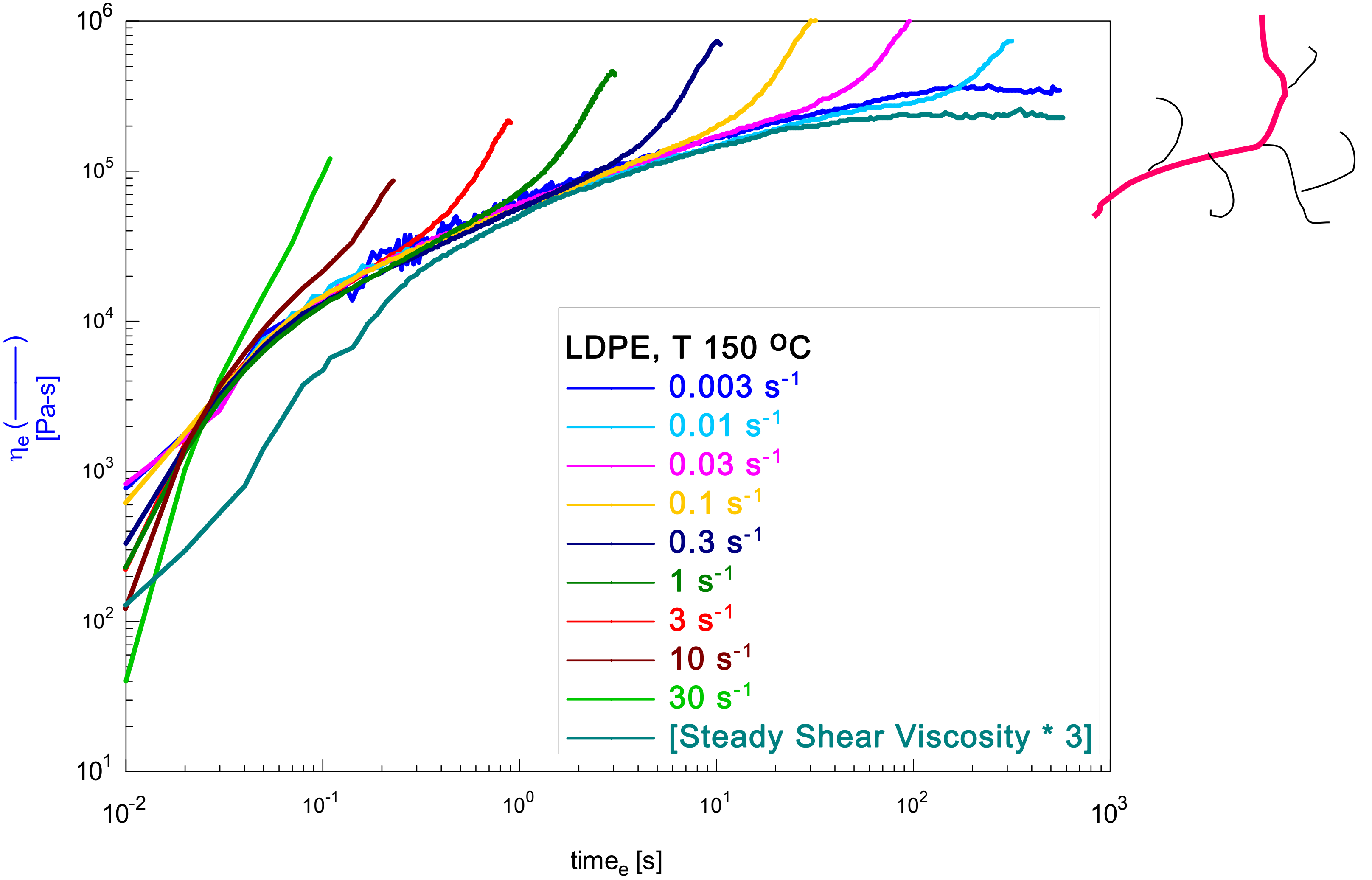




LLDPE (Low branching)

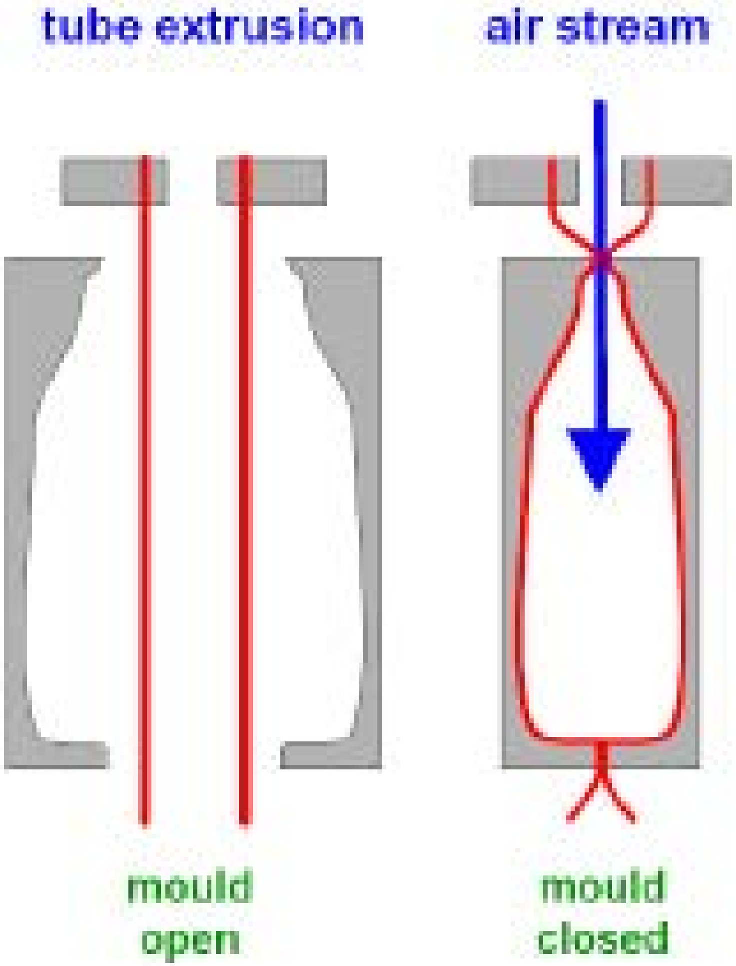


LDPE (High branching)



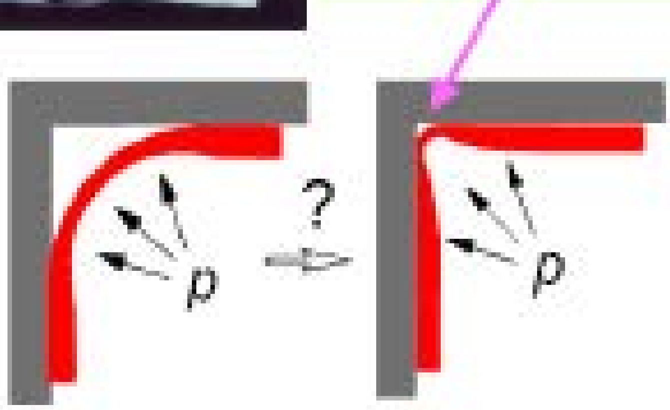
Elongational flow

⇨ importance of high elongational viscosity



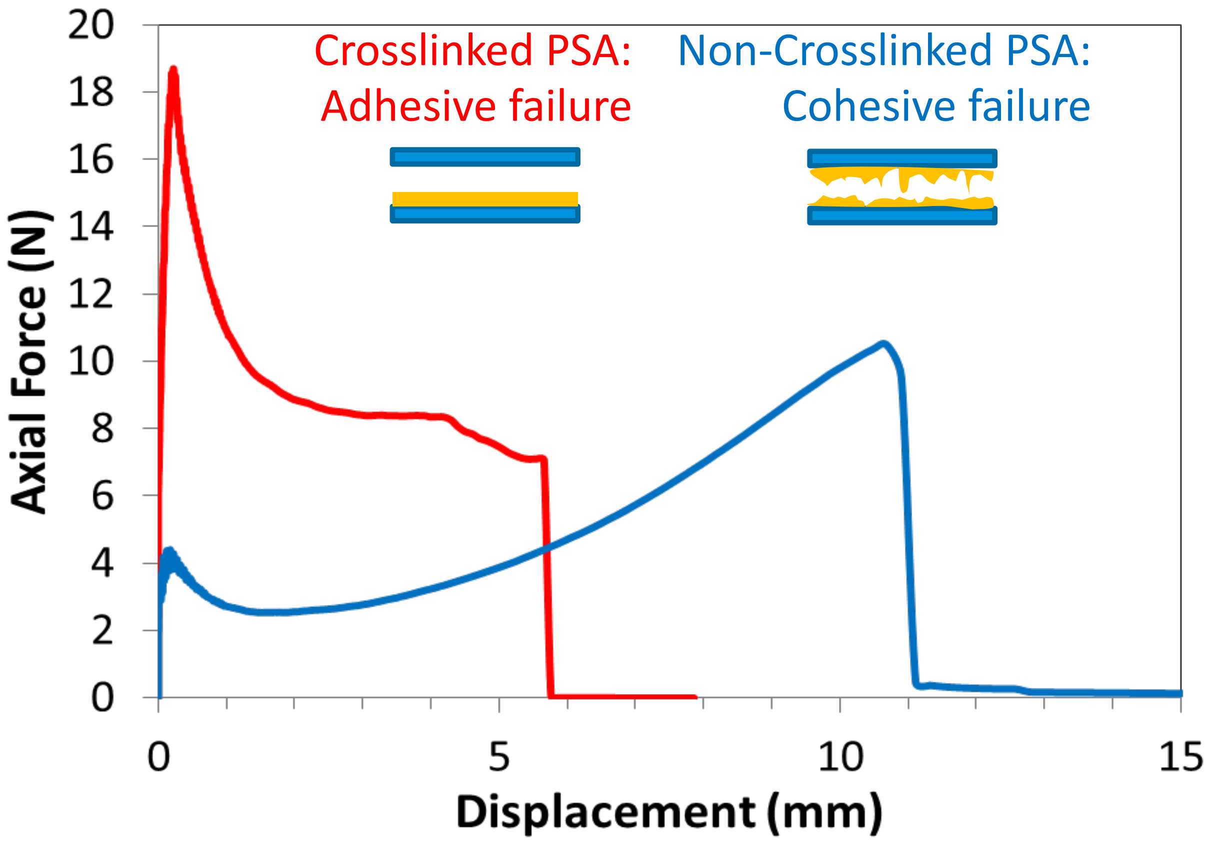
Blow moulded bottle.

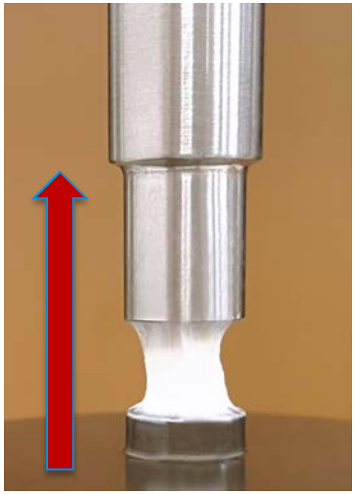
High elongational viscosity required at corner to keep thickness reduction small !



Adhesive Tack Testing

- Tack testing method: ASTM D2979
- Use 8mm parallel plate, axial tensile at 0.1mm/sec
- The maximum force required to pull the plate away is defined as the sample's tackiness.





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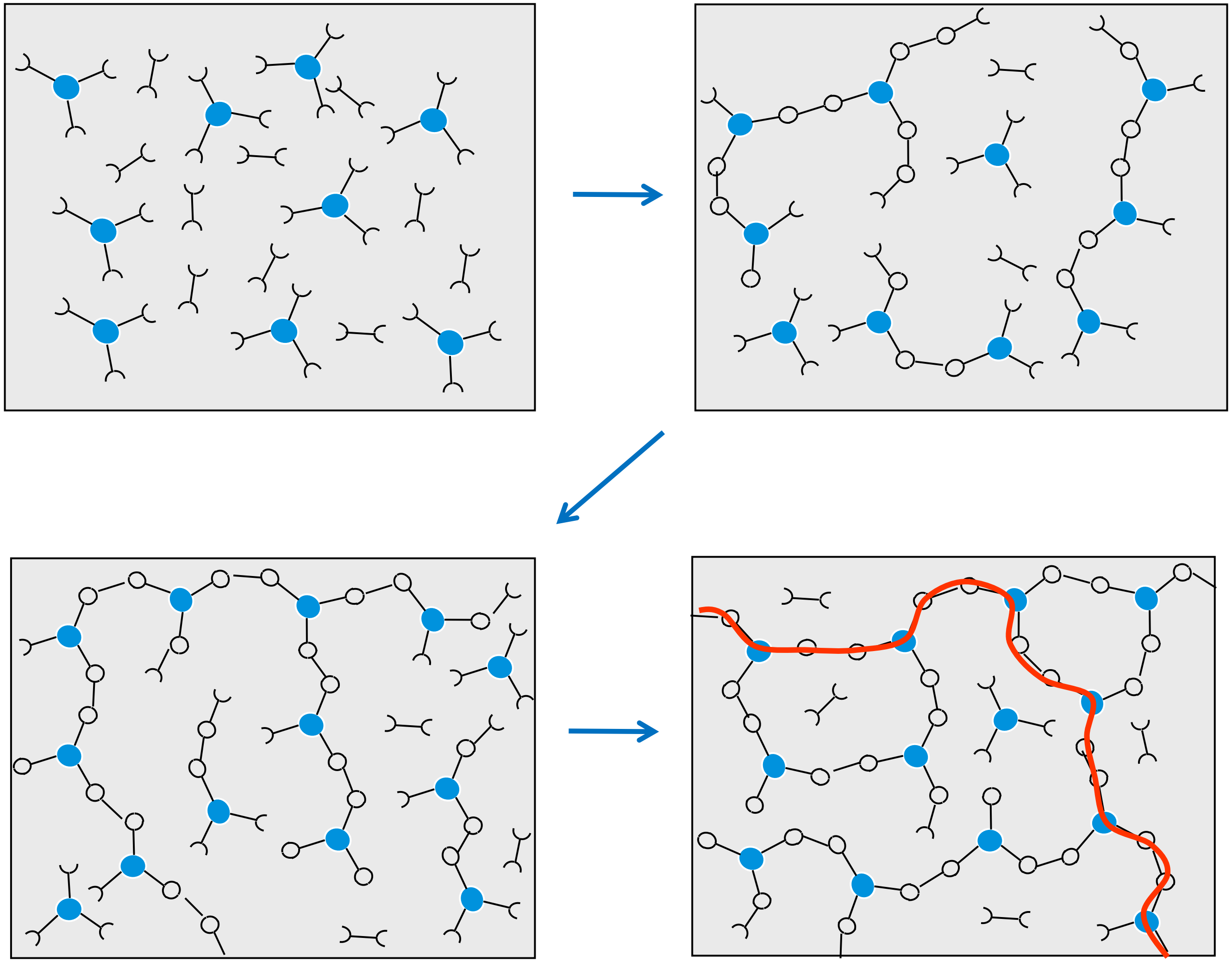
Thermosetting Polymers

- Thermosetting polymers are perhaps the most challenging samples to analyze on rheometers as they challenge all instrument specifications both high and low.

- The change in modulus as a sample cures can be as large as 7-8 decades and change can occur very rapidly.

Structural Development During Curing



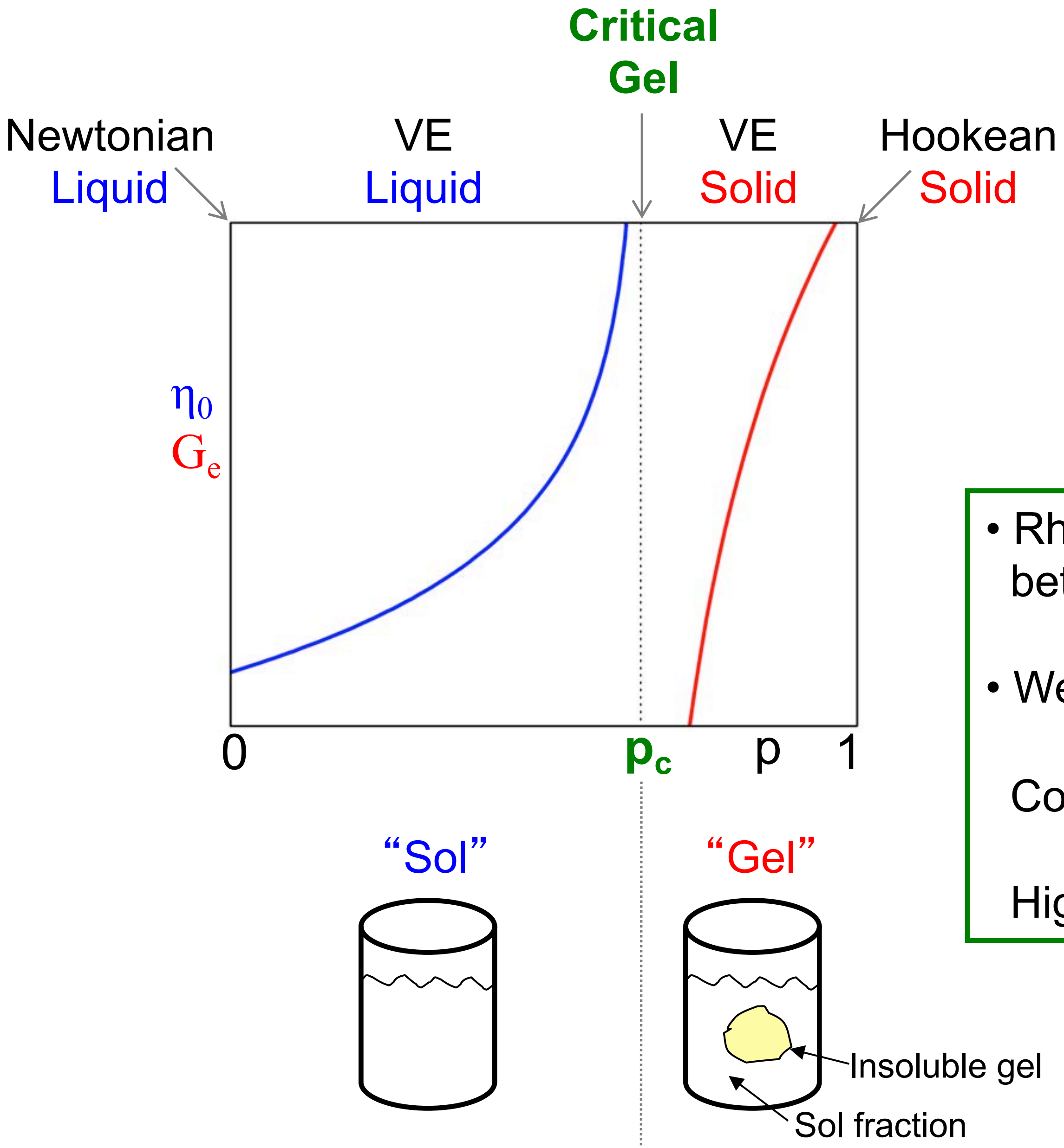
Gel point

At the Gel Point

- Molecular weight M_w goes to infinity
- System loses solubility
- Zero shear viscosity goes to infinity
- Equilibrium Modulus is zero and starts to rise to a finite number beyond the gel point

Note: For most applications, gel point can be considered as when G’ = G” and tan δ = 1

Measuring the gel point



$$\eta_0 : (p_c - p)^{-s}$$

$$G_e : (p - p_c)^{z}$$

s, z predicted from theory

C. P. Lusignan et al. (1999)

@ GP

- Rheological properties intermediate between liquid and solid
- Wetting properties of the liquid

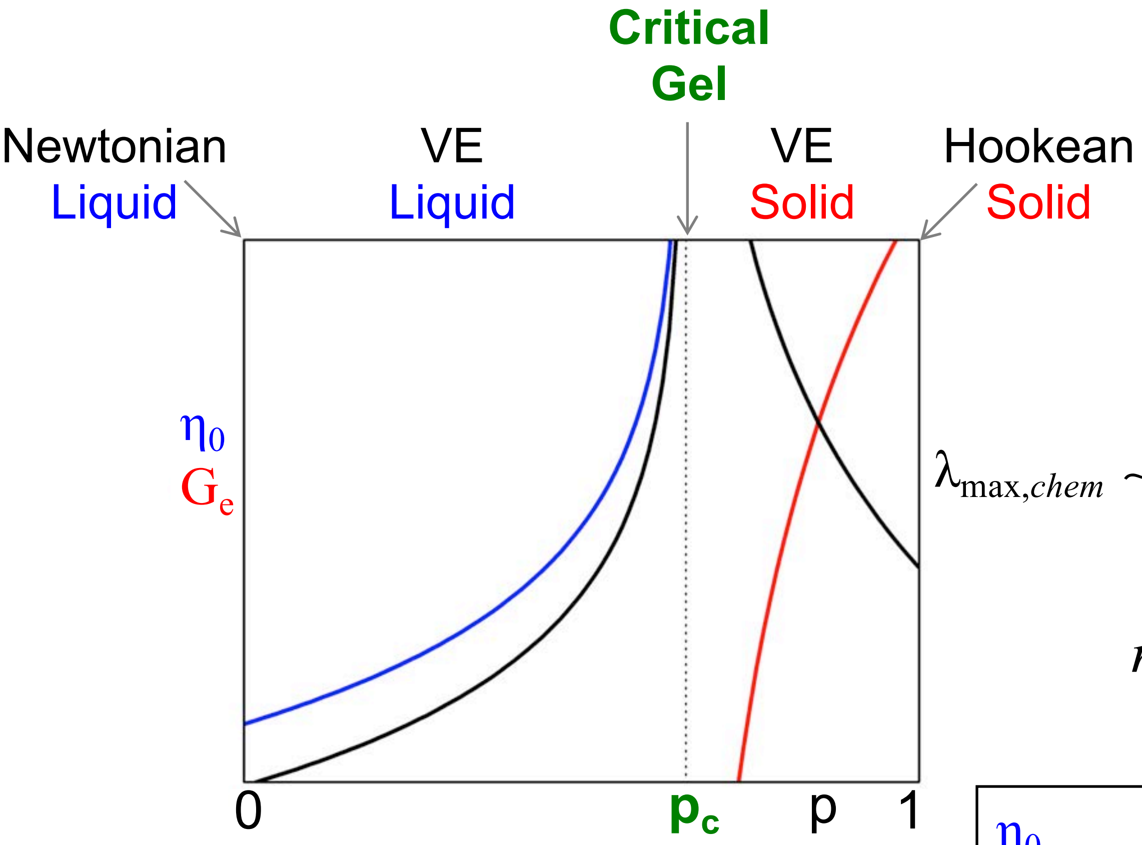
  \+

  Cohesive strength of the solid

  =

  High adhesion strength (**tackiness**)

Steady State measurements difficult



$$\eta_0 : (p_c - p)^{-s}$$

$$G_e : (p - p_c)^{z}$$

s, z predicted from theory

C. P. Lusignan et al. (1999)

$$\lambda_{\max,chem} \sim \begin{cases} (p-p_c)^{-s/(1-n_c)} & \text{for} \quad p < p_c \\ (p_c - p)^{-z/n_c} & \text{for} \quad p_c < p \end{cases}$$

$$n_c = \frac{z}{z+s}$$

assuming symmetry

(typo in H. H. Winter (2003))

η_0, G_e

- ∞ **time to reach steady state**, need to extrapolate

e.g. nanocomposites

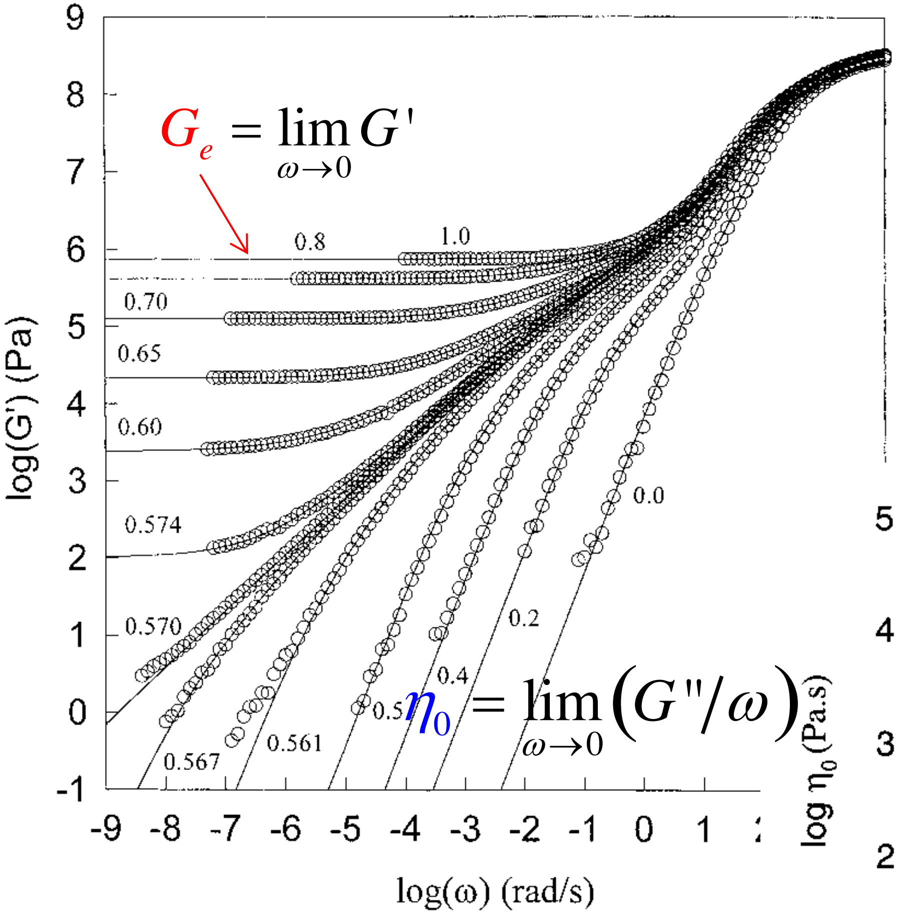
η_0

- Network gets broken
  - ⟶ apparent gelation delay or RG
  - ⟶ apparent gelation point

G_e

- Detection limit

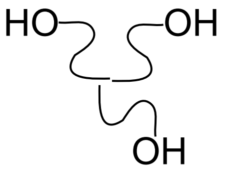
Crosslinking Polymerization to form Polyurethane



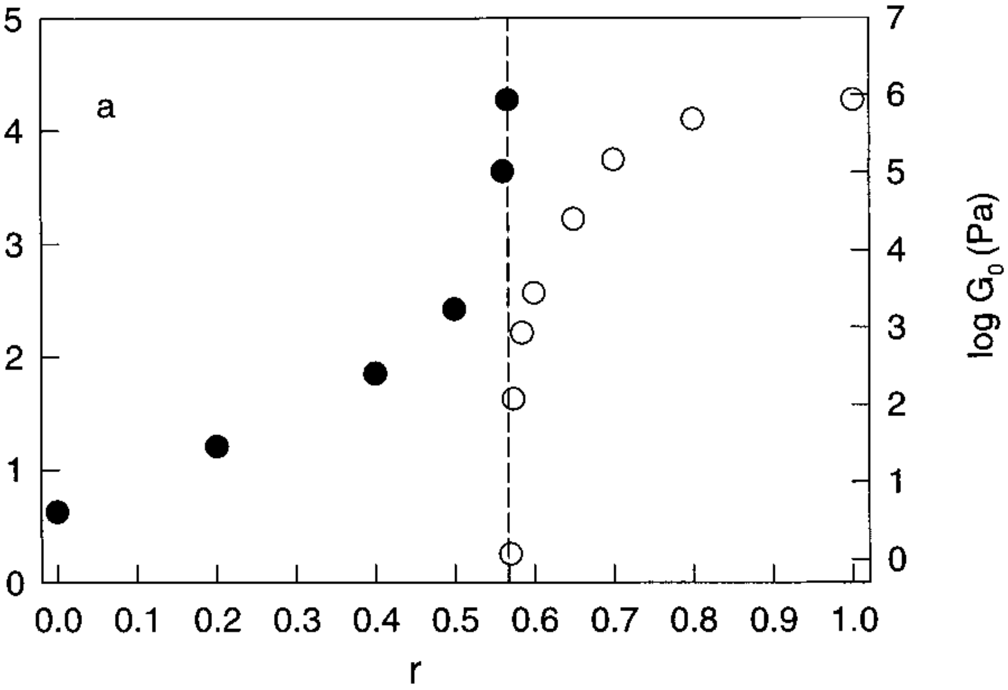
$$G_e = \lim_{\omega \to 0} G'$$

$$\eta_0 = \lim_{\omega \to 0} \left(G''/\omega \right)$$

OCN—NCO +



r = [NCO]/[OH]
= stoichiometric imbalance
(assume complete conversion)

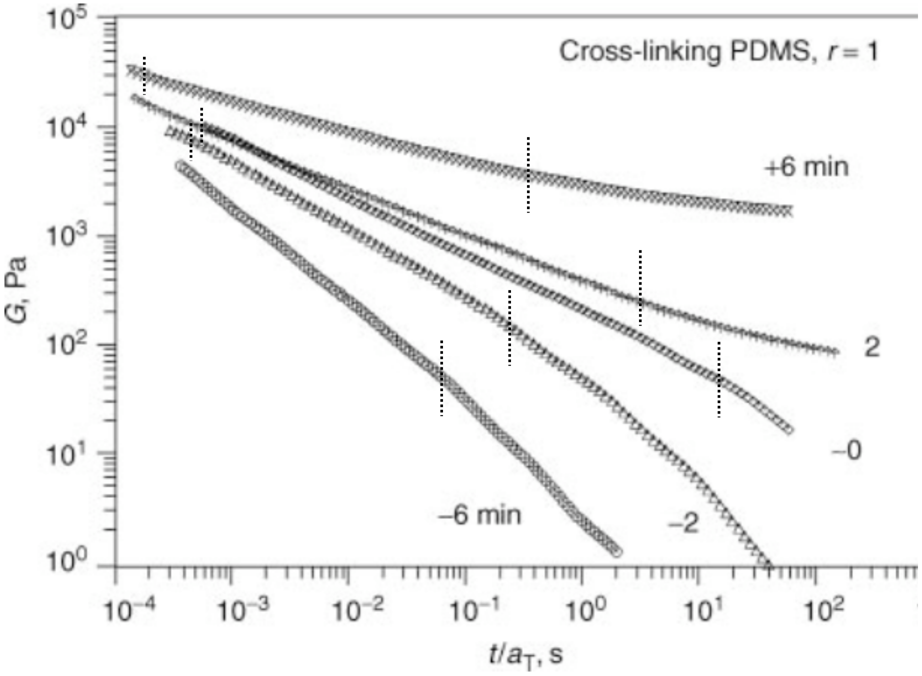


T. Nicolai, H. Randrianantoandro, F. Prochazka, and D. Durand, *Macromolecules Sci*, 30 (1997), 5897.

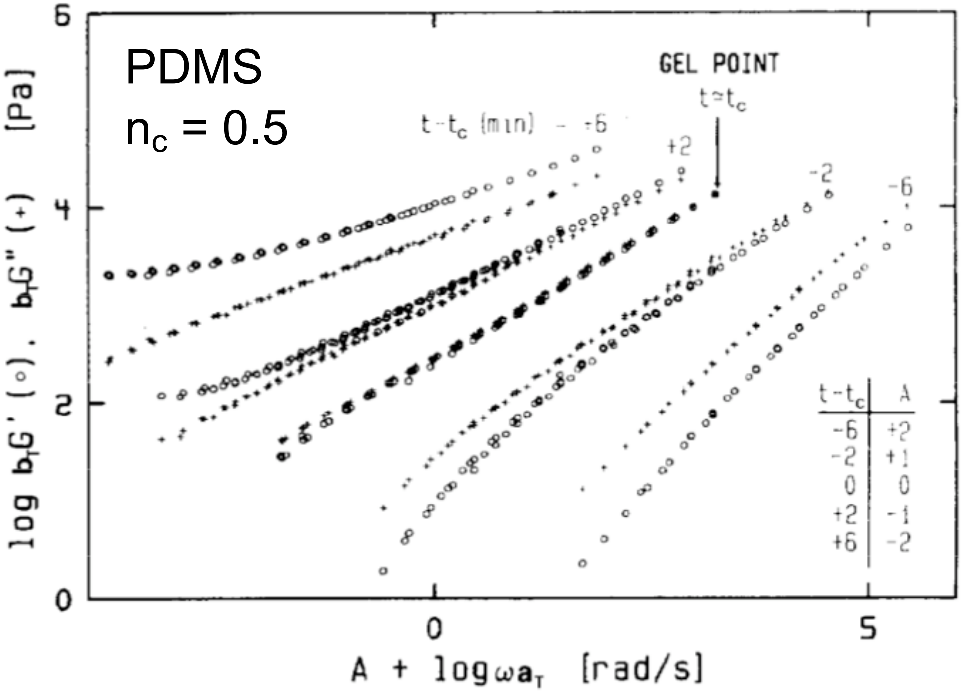
Power Law Behavior

$$G(t) = S t^{-n_c} \quad \text{for} \quad \lambda_{0,chem} \le t \le \infty \text{ (infinite sample)}$$ chemical gels

$$G(t) = S t^{-n_c} \quad \text{for} \quad \lambda_{0,phys} \le t \le \lambda_{\max,phys}$$ physical gels



H. H. Winter (2003)

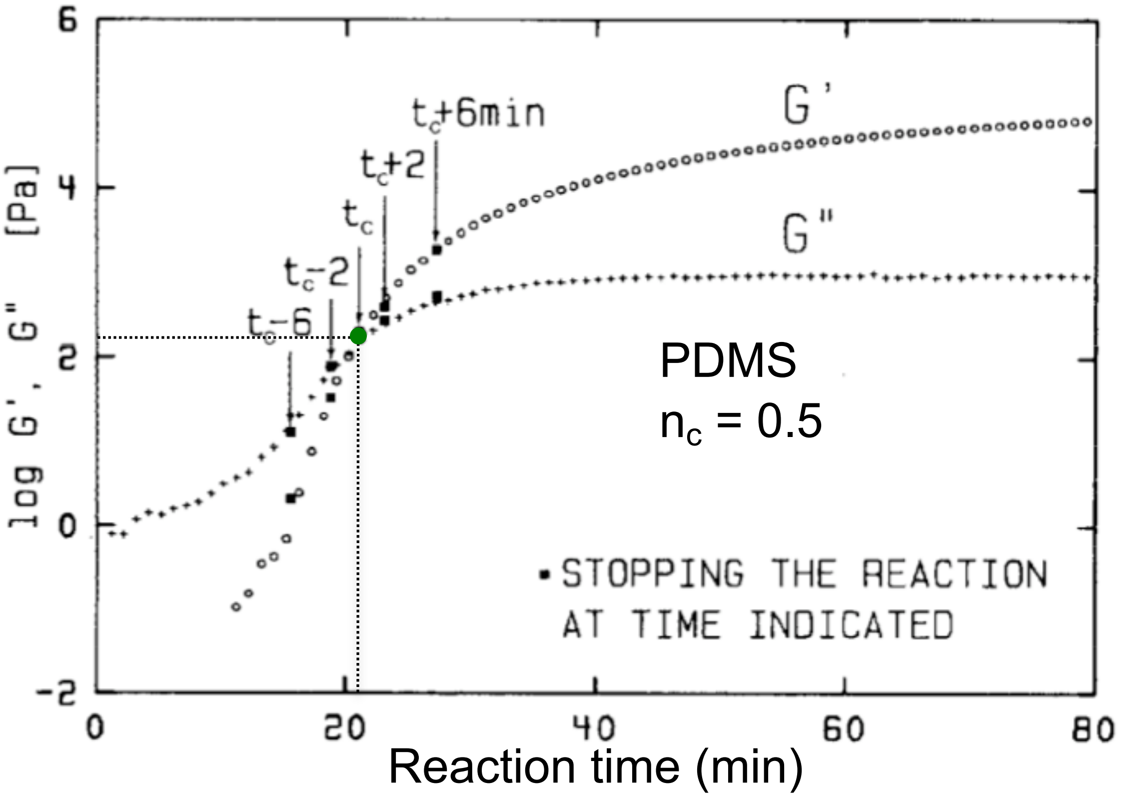


H. H. Winter and F. Chambon (1986)

$G' = G''$ only when $n_c = 0.5$

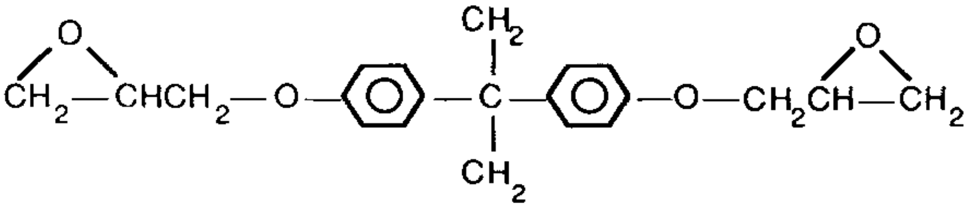
$G' = G''$

empiricism of Y. M. Tung and P. J. Dynes (1982)

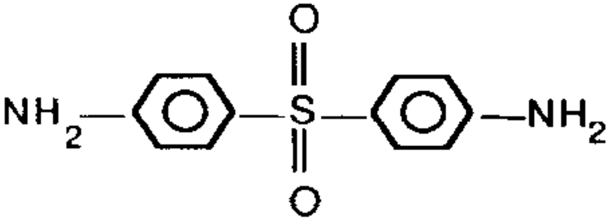


F. Chambon and H. H. Winter (1985)

Epoxy-Amine Crosslinking: Monomers



diglycidyl ether of bisphenol A
(DGEBA)



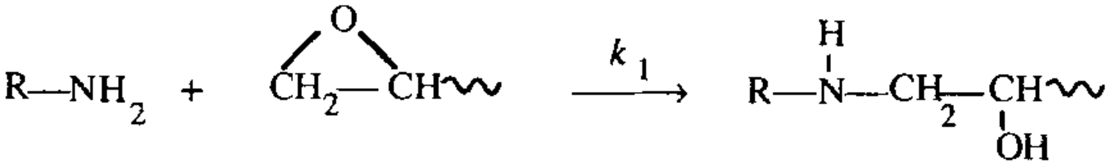
diamino-diphenyl sulfone
(DDS)

application: F-117 radar invisibility

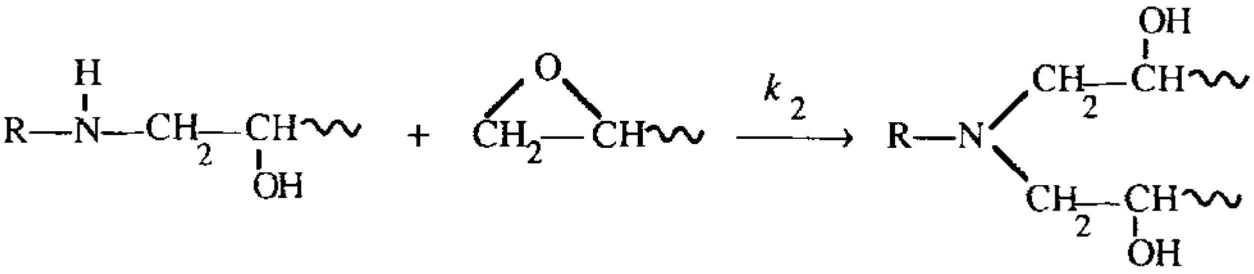
Bidstrup and Macosko, *J Polym Sci*, 28 (1990), 691.

Epoxy-Amine Chemistry

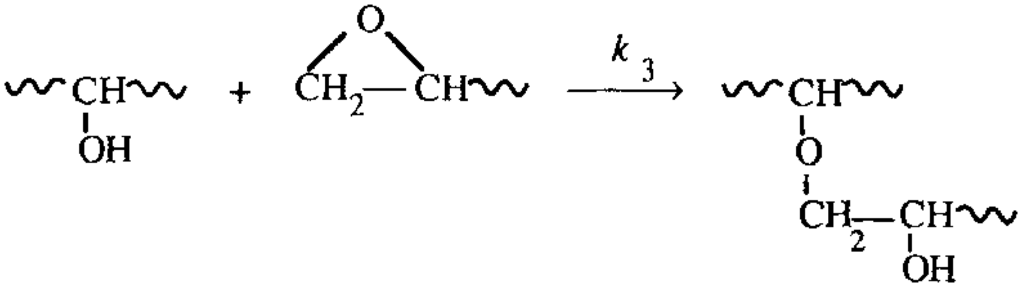
Reaction with an epoxide group to form a secondary amine



Reaction with another epoxide group to form a tertiary amine

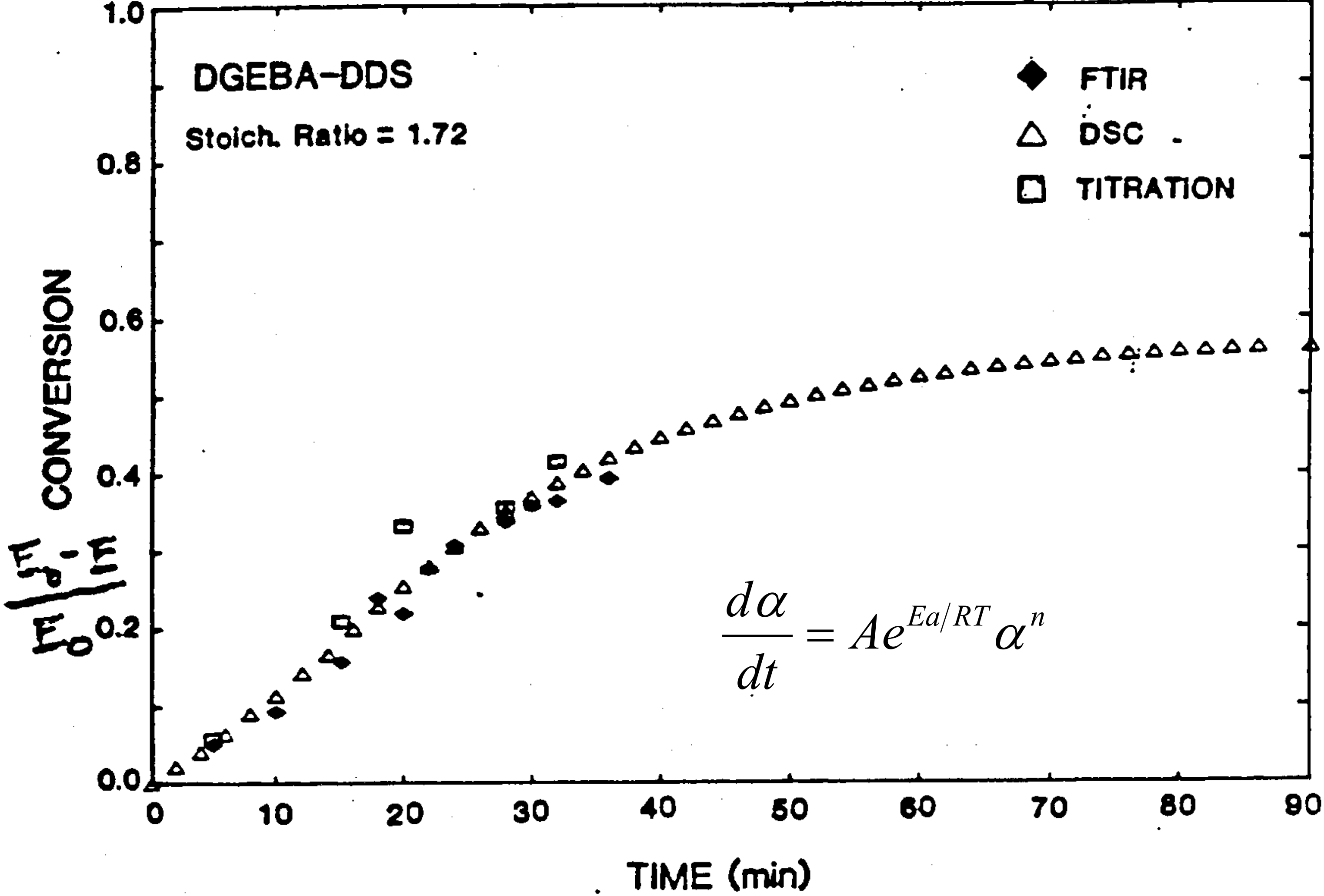


Reaction of the formed hydroxyl with an epoxide group



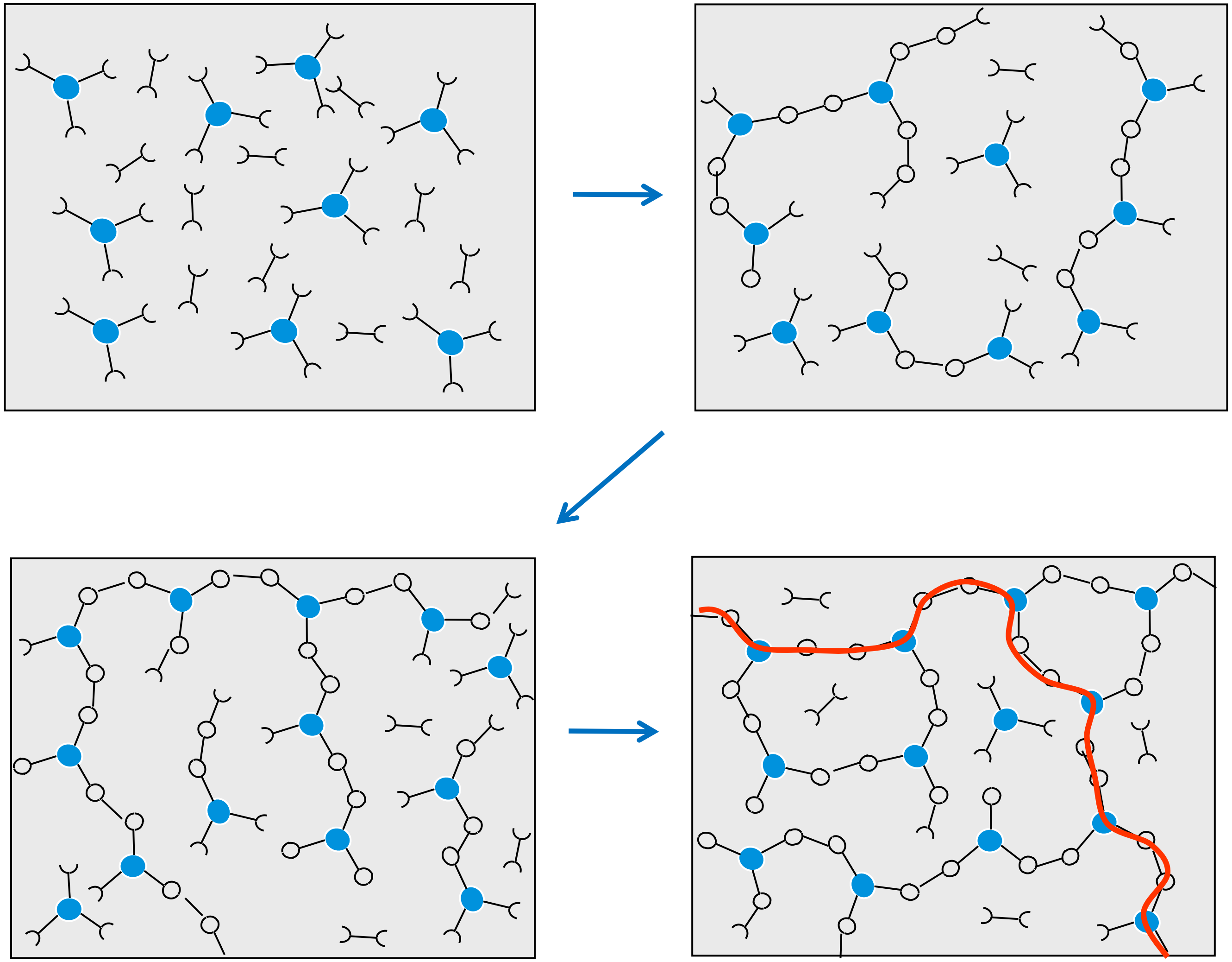
Measure Epoxy-Amine Kinetics

conversion of epoxy groups



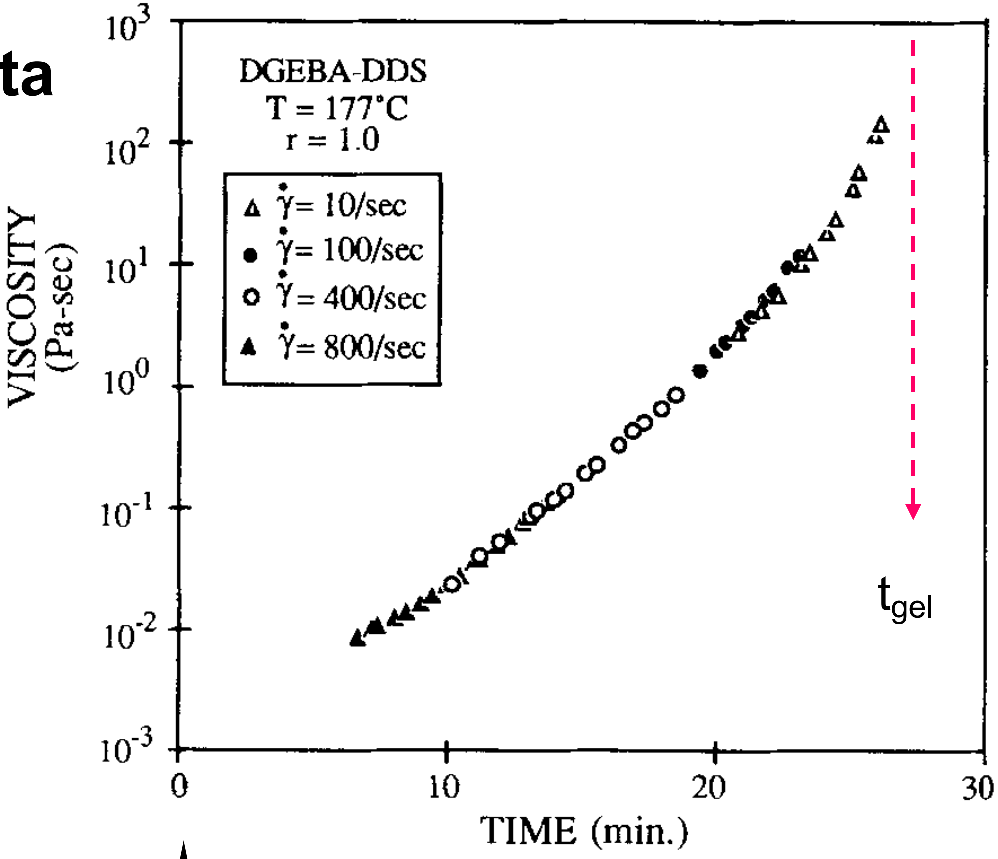
$$\frac{d\alpha}{dt} = Ae^{Ea/RT}\alpha^{n}$$

Structural Development During Curing



Gel point

Typical Steady Shear Data



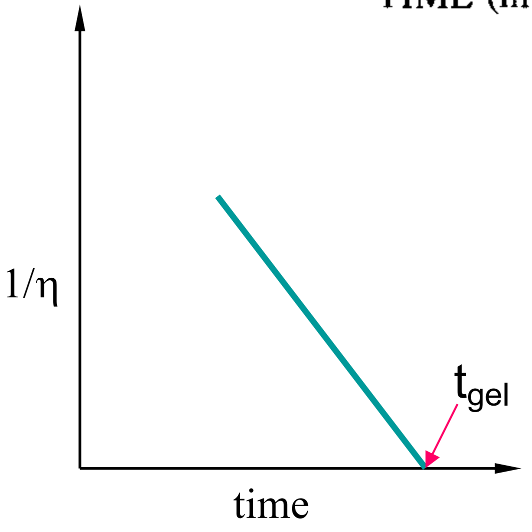
Data obtained from four experiments, each set measured at a different shear rate

How find gel time?

$\eta > 10^4$ Pa·s

or

$1/\eta \to 0$



Bidstrup and Macosko, *J Polym Sci*, 28 (1990), 691.

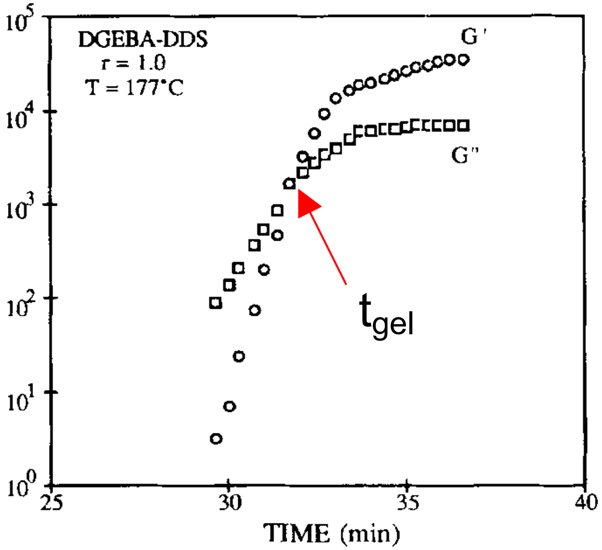


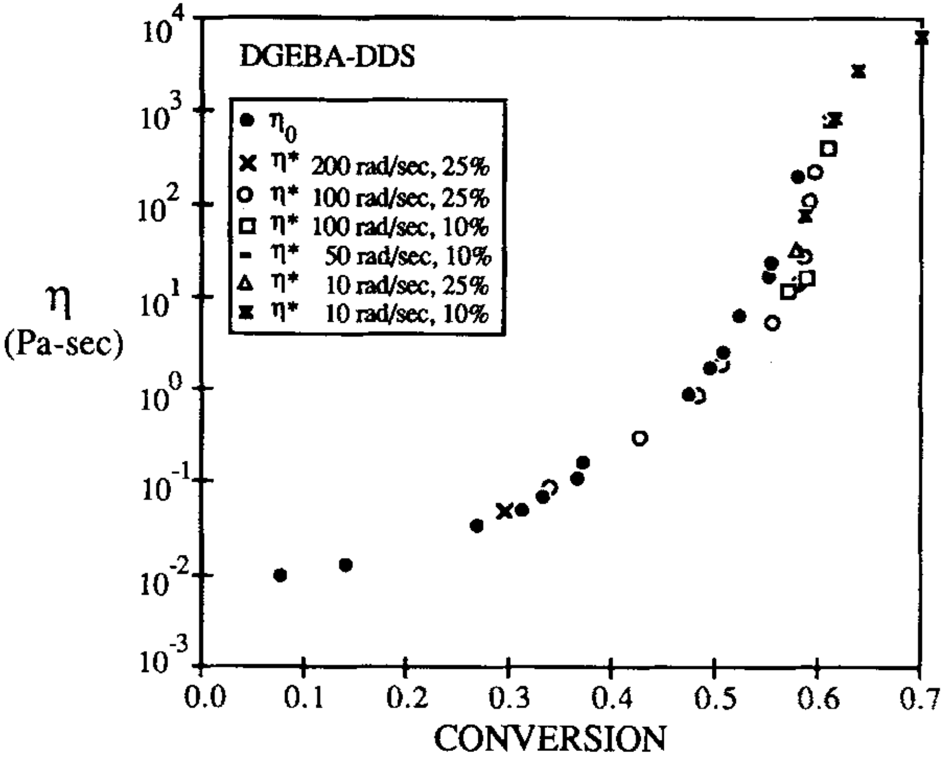
Fig. 11. The loss and storage moduli versus cure time for the DGEBA-DDS system at balanced stoichiometry. The cure temperature is 177°C. The frequency of oscillation is 10 rad/s, and the strain is 10%.

Gel Time from

G' = G"

Comparison of Dynamic η* and Steady η_o Viscosities

$$\left|\eta^*\right| = (G'^2 + G''^2)^{1/2} / \omega$$



Bidstrup and Macosko, *J Polym Sci*, 28 (1990), 691.

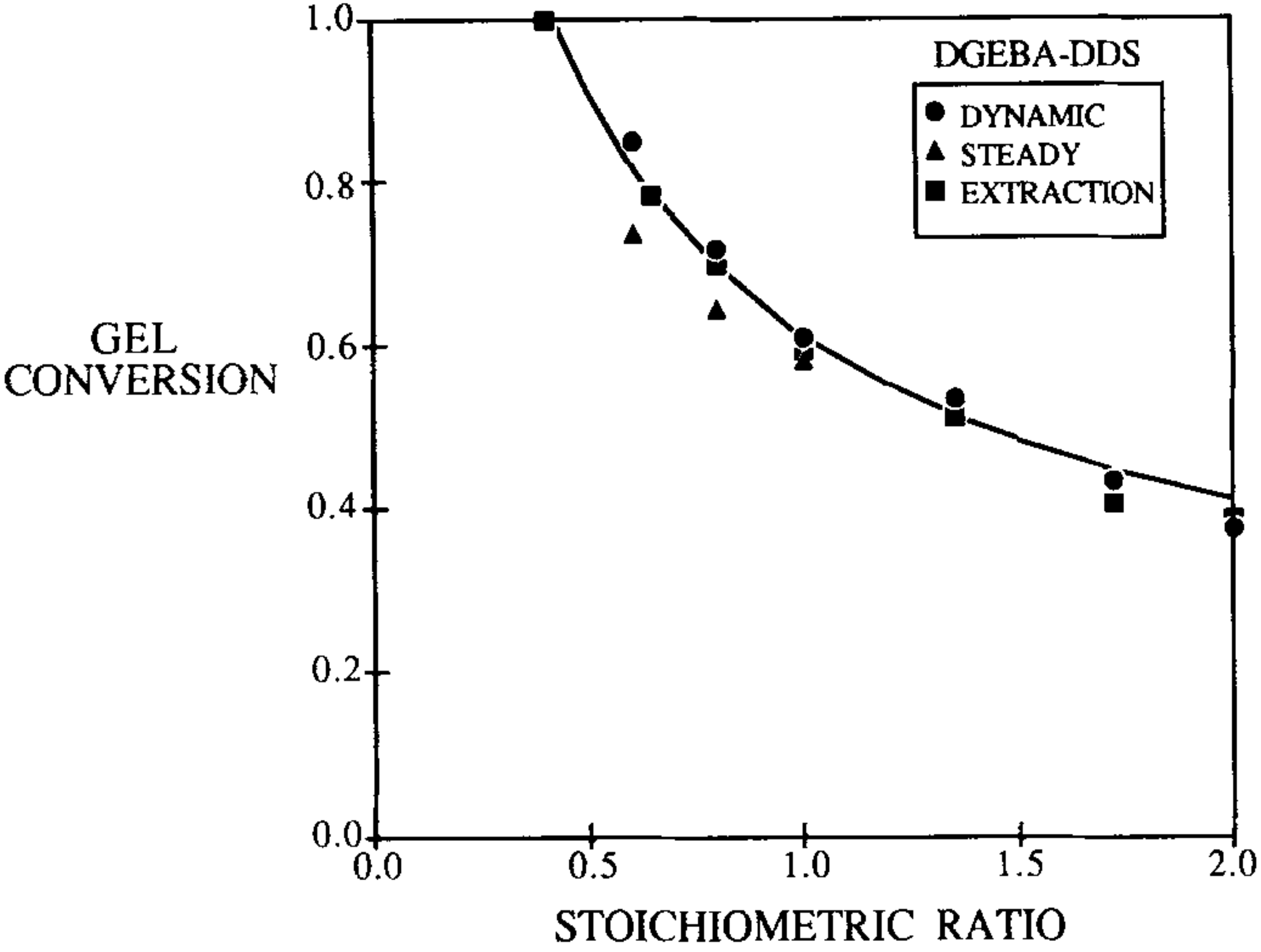
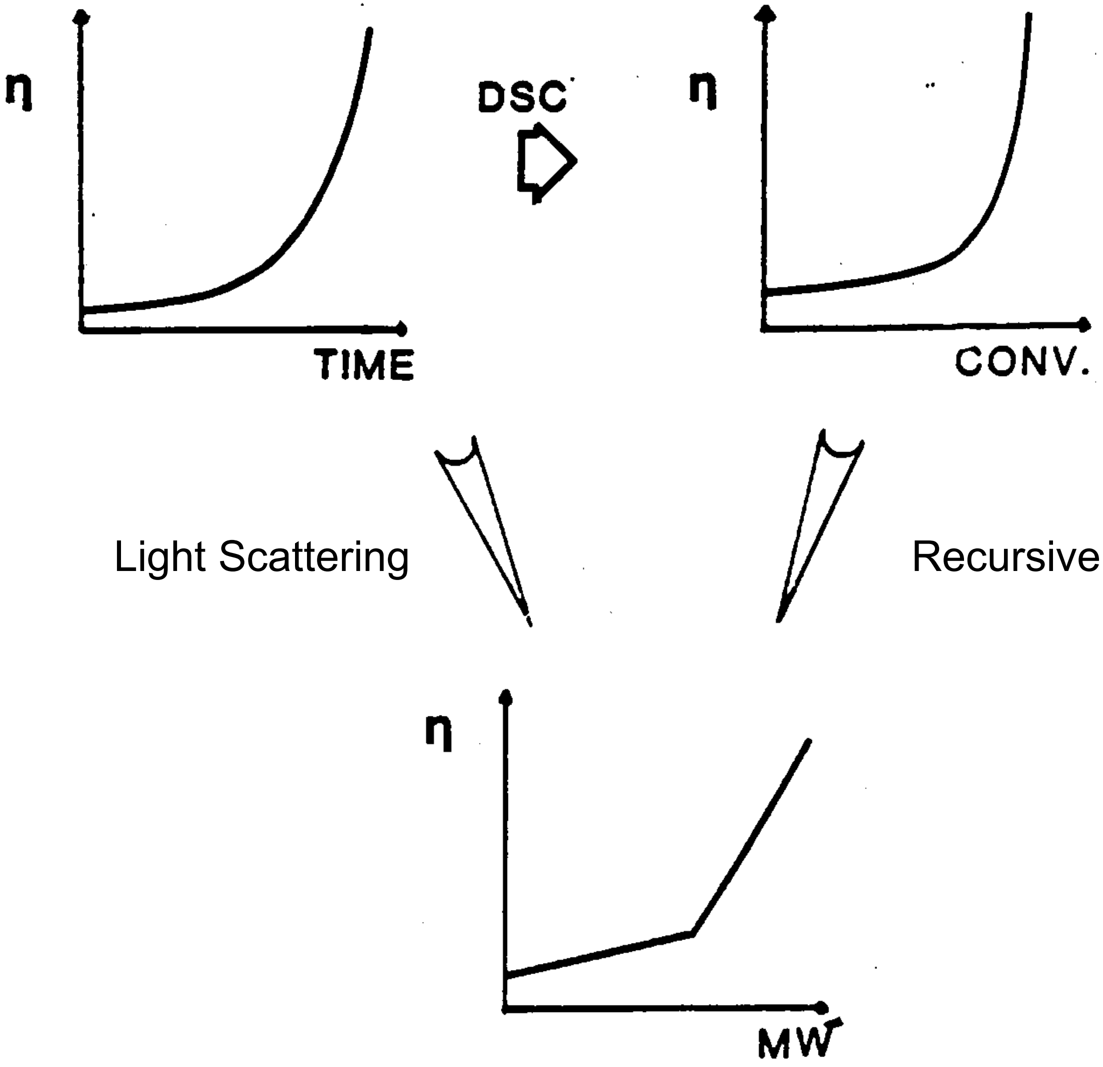


Fig. 14. Epoxy conversion at the modulus crossover point (●) compared with the gel conversion predicted by the recursive theory (solid line). The gel conversions obtained by extrapolation of the steady shear viscosity data (▲) and the extraction data (■) are also shown.

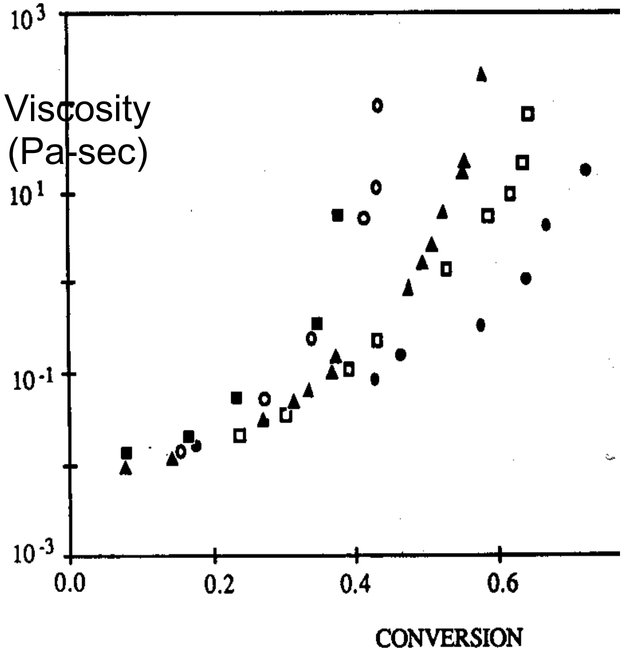
Bidstrup and Macosko, *J Polym Sci*, 28 (1990), 691.

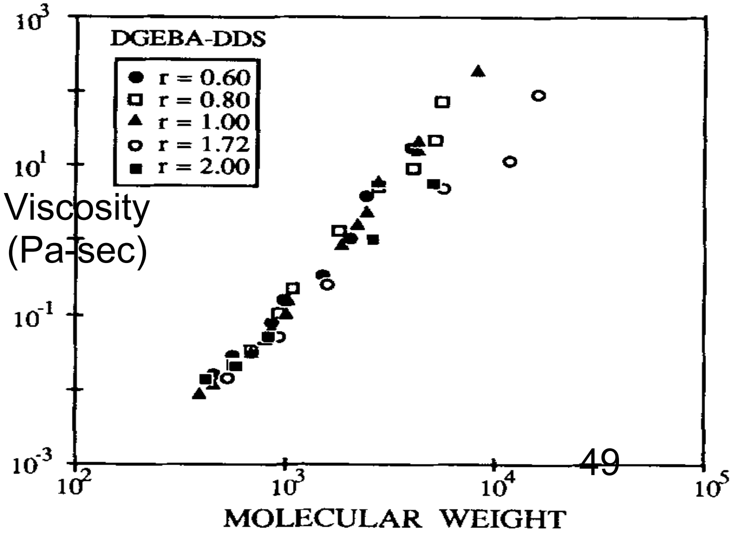
Correlation of Viscosity with Structure

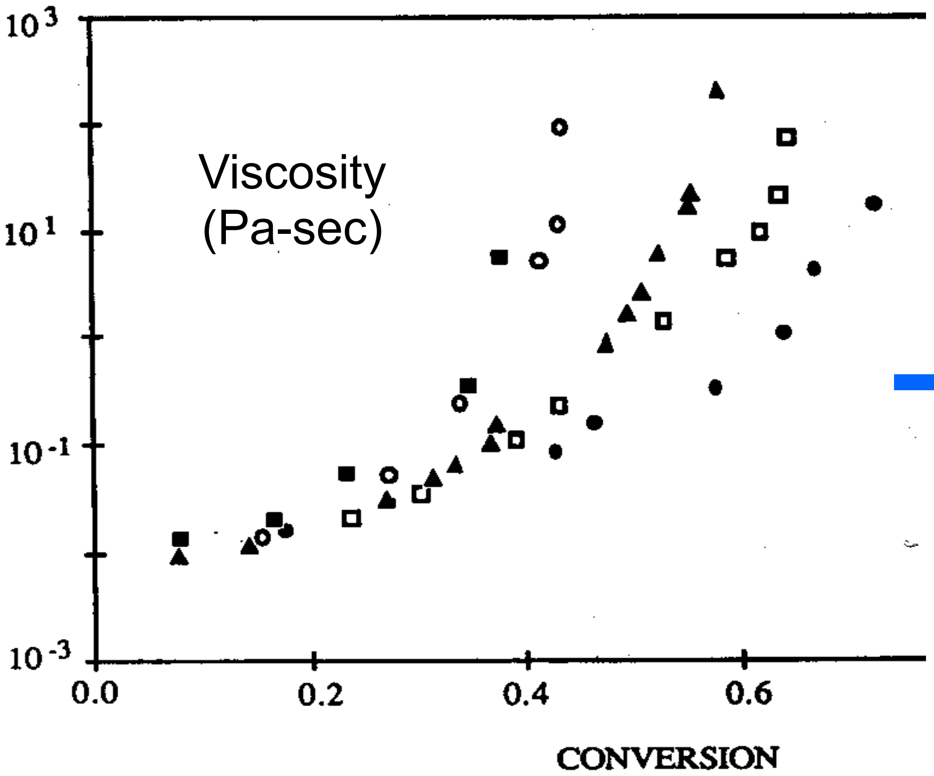


Light Scattering

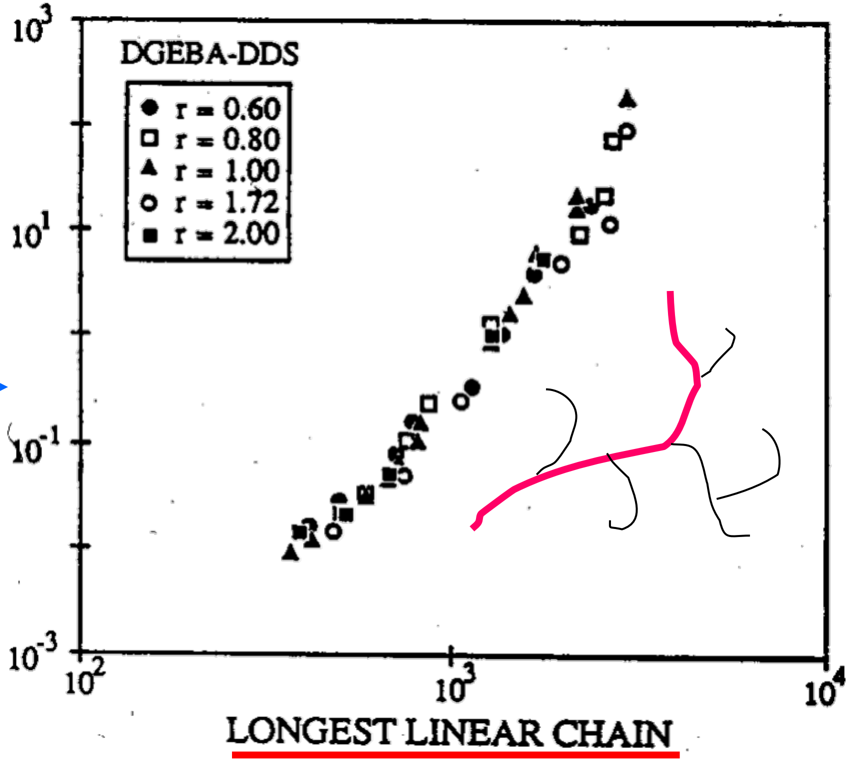
Recursive Theory







Viscosity rise versus conversion of epoxide groups at stoichiometric ratios ranging from 0.6 to 2.0.



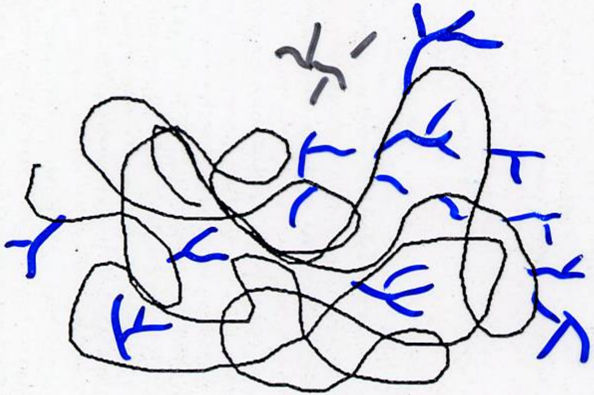
Viscosity rise vs. molecular weight of the average longest linear chain at stoichiometric ratios ranging from 0.6 to 2.0. The molecular weight of the longest linear chain is calculated using the recursive theory assuming α = 0.2.

Bidstrup and Macosko, *J Polym Sci*, 28 (1990), 691.

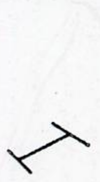
VISCOSITY = (STRUCTURE FACTOR) (FRICTION FACTOR)

Stiffness

SIZE



INHERENT FRICTION PER SEGMENT



Temperature
Tg

$$\eta = \zeta \underline{M_w}^{1 \rightarrow 3.4}$$

friction/segment

$$\zeta = \zeta_o \exp\left[\frac{B}{f_g + \alpha_1 \underline{(T-Tg)}}\right]$$

WLF eq

$T_g = f(\alpha)$

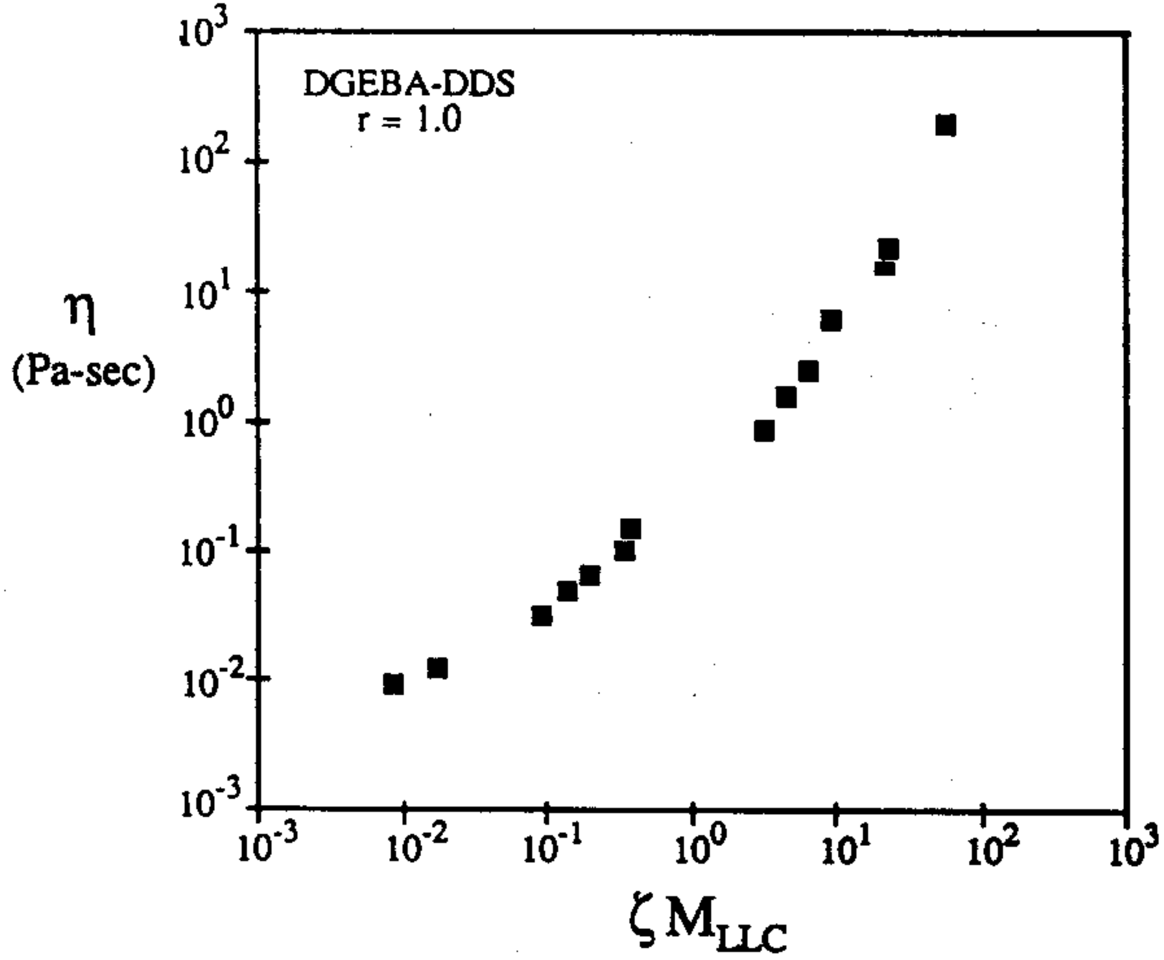
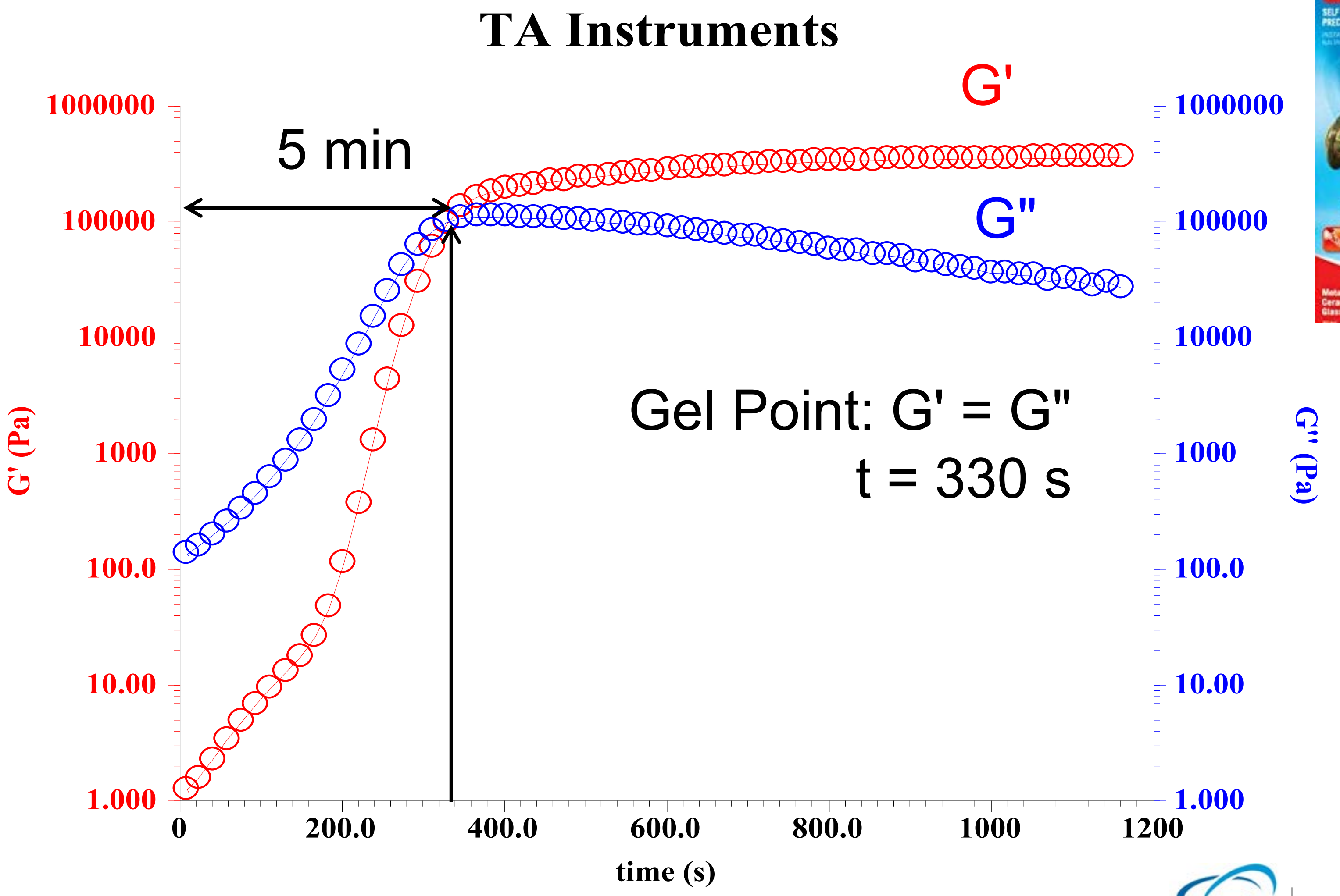


Figure 14. Viscosity rise versus the product of the friction factor and the molecular weight of the average longest linear chain for the DGEBA-DDS system at balanced stoichiometry.

Bidstrup and Macosko, *J Polym Sci*, 28 (1990), 691.

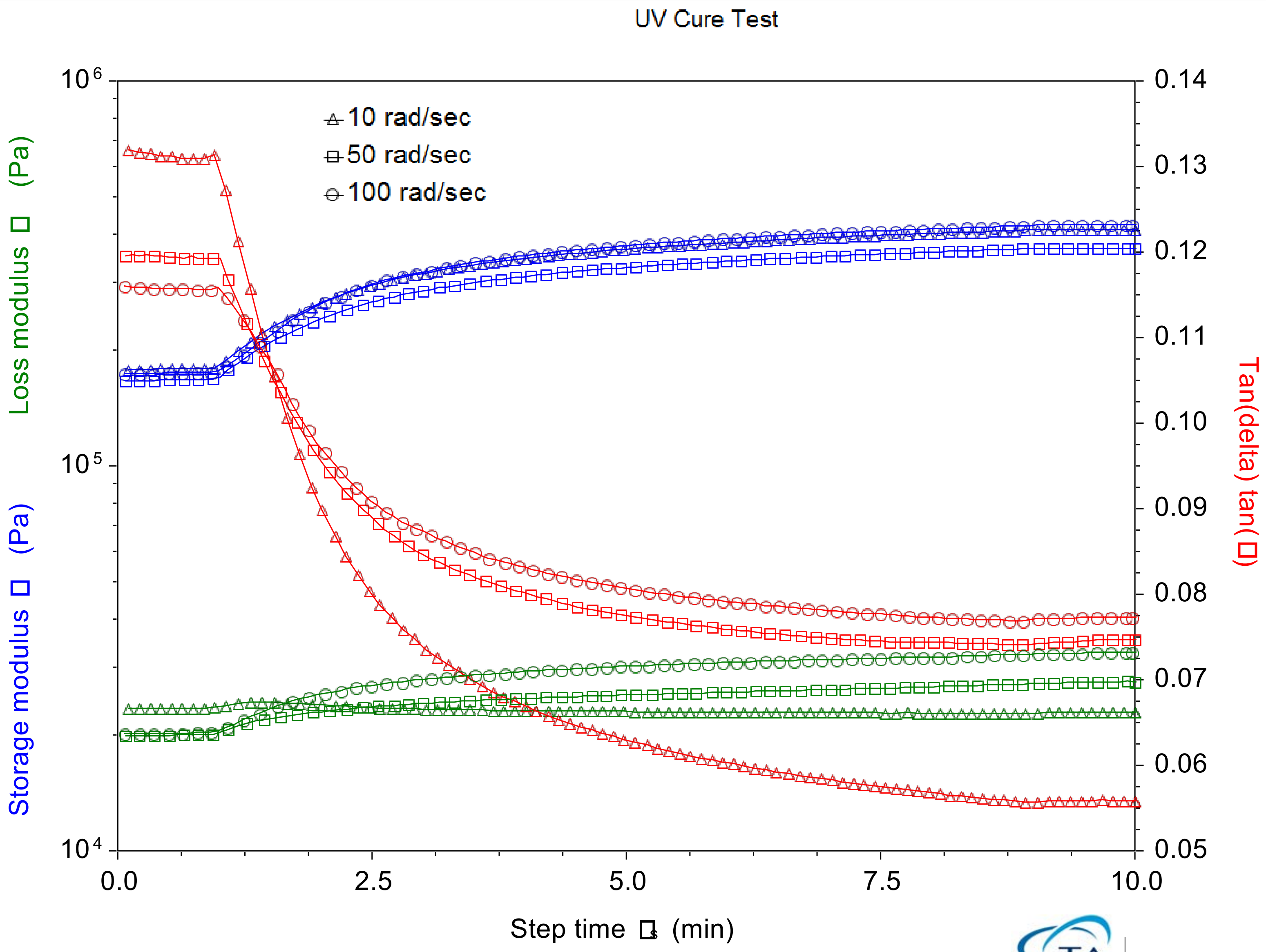
Curing Analysis: Isothermal Curing



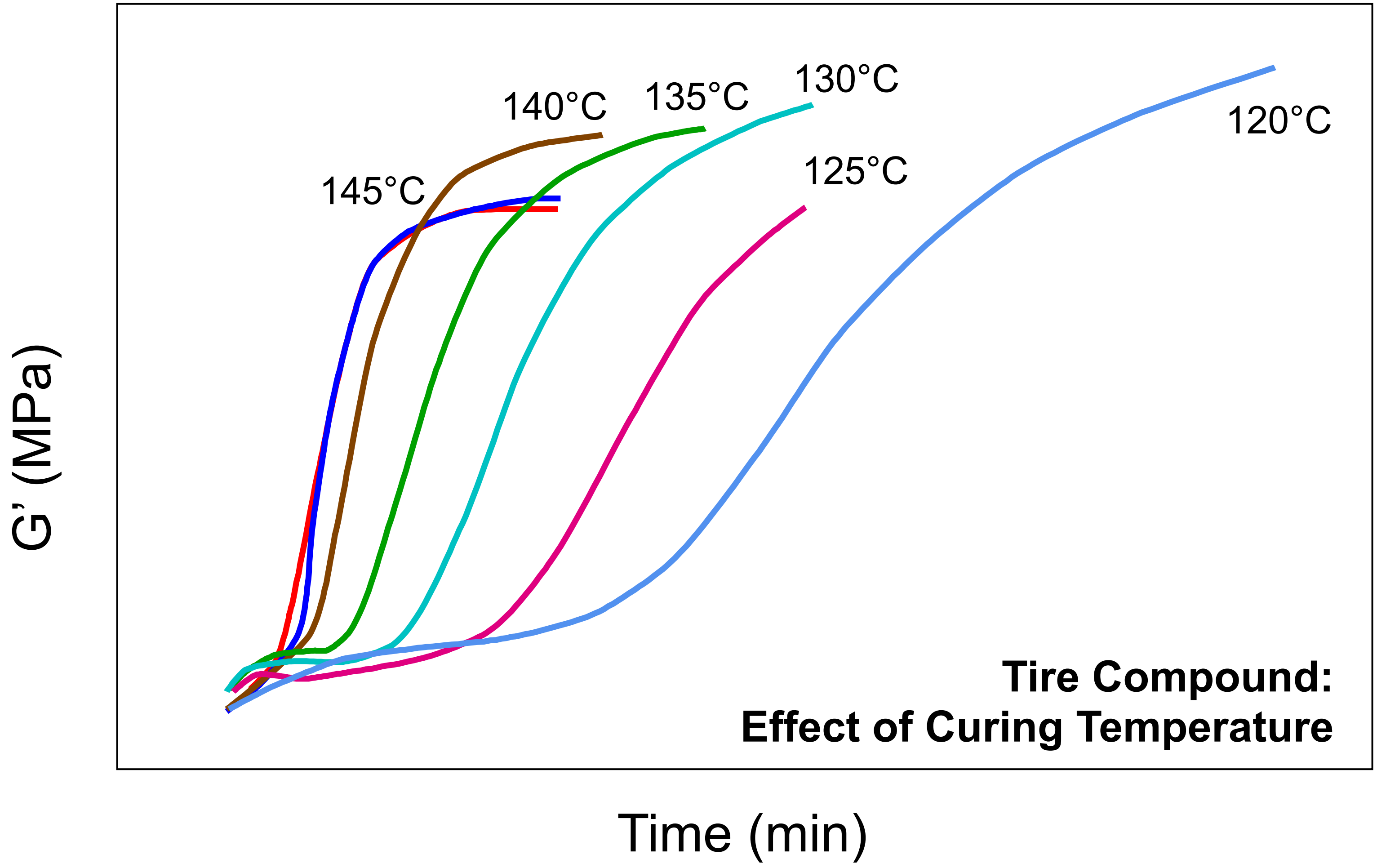
5 min

Gel Point: G' = G''
t = 330 s

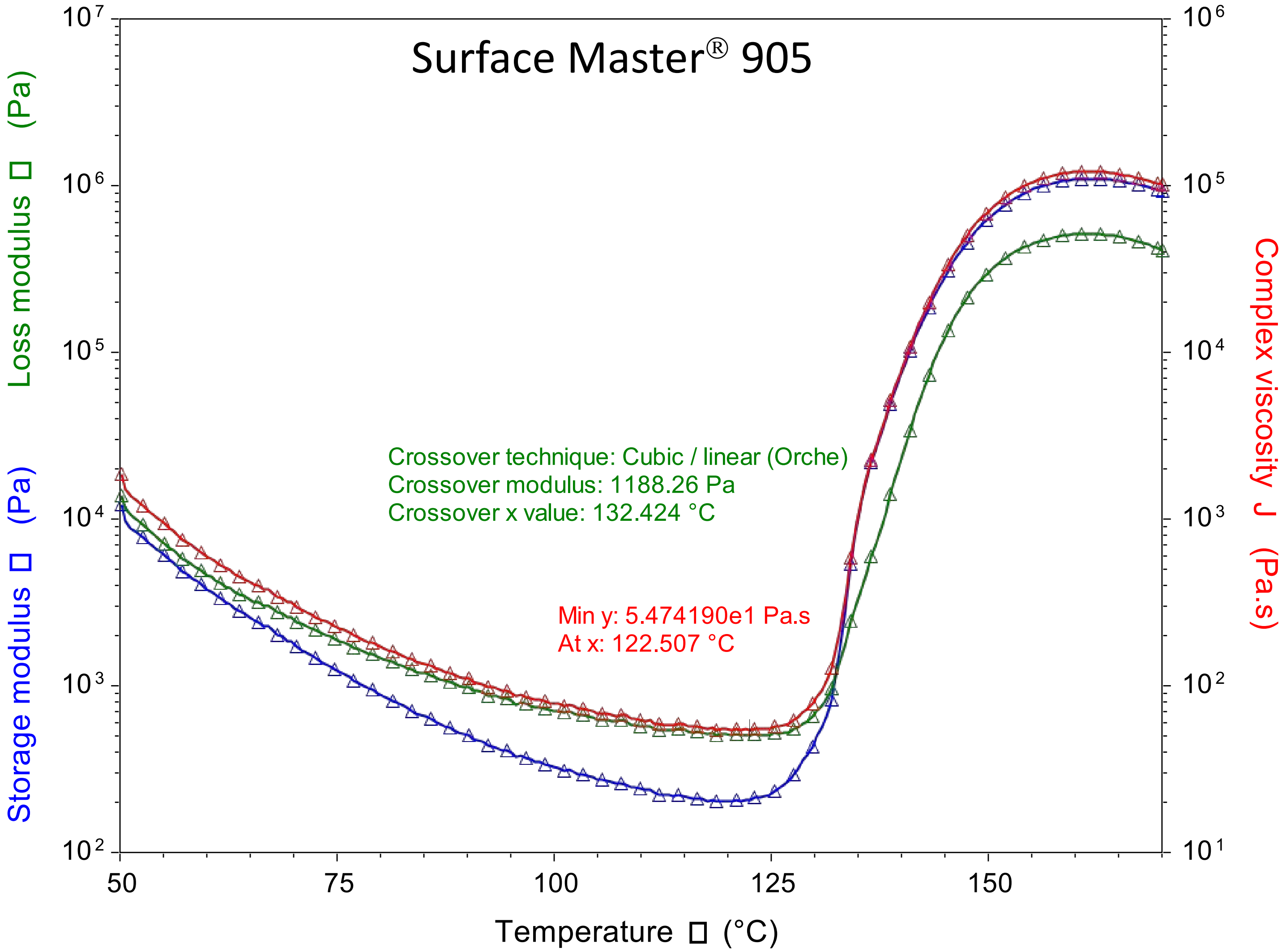
Gel Point using Tan Delta



Isothermal Curing



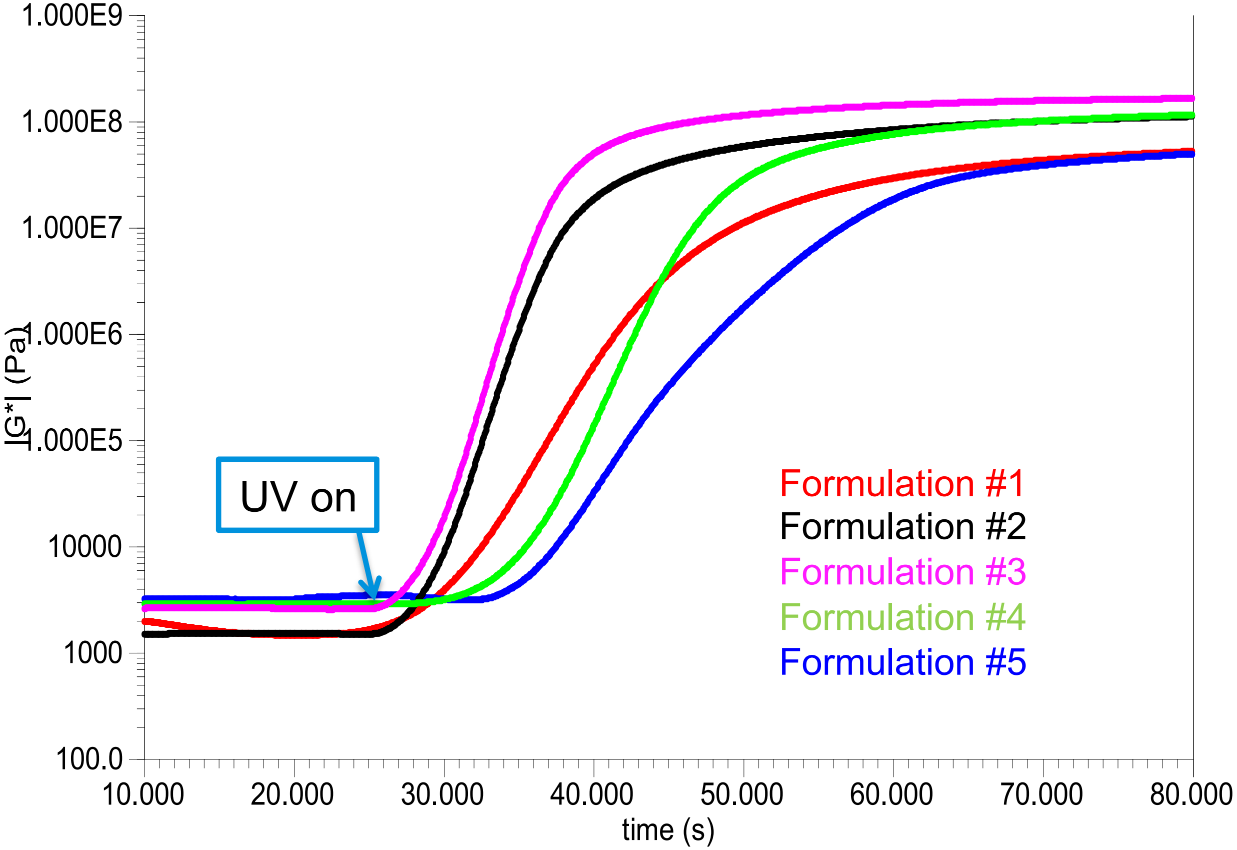
Temperature Ramp Curing



TAINSTRUMENTS.COM

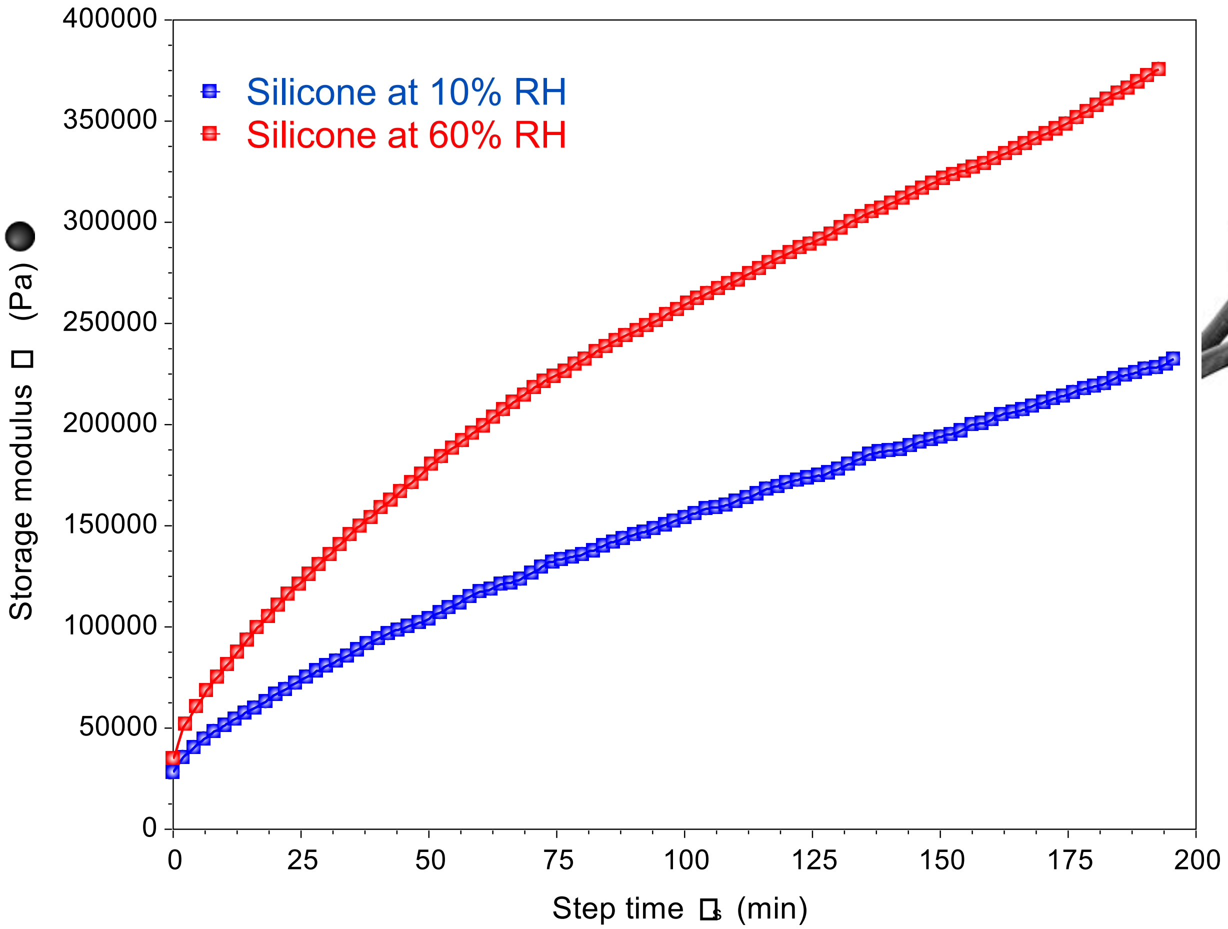
UV Curing

- Monitor UV curing: Dynamic time sweep
- Measure curing time with different formulations, UV intensity and temperature
- Measure cured adhesive modulus



Curing with Controlled Humidity

- Silicone adhesive curing under 25°C and 10%; 60% relative humidity
  - Higher humidity, faster curing



Polymer Rheology

Molecular Structure

MW and MWD
Chain Branching and Cross-linking
Thermosets
Single or Multi-Phase Structure
Solid polymers

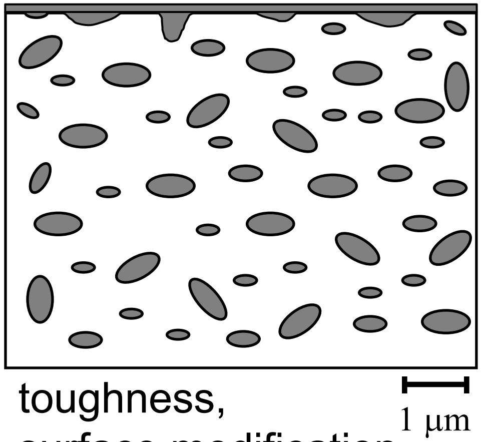
Viscoelastic Properties

Small strain (linear viscoelastic)
Steady shearing
Extension

Processability & Product Performance

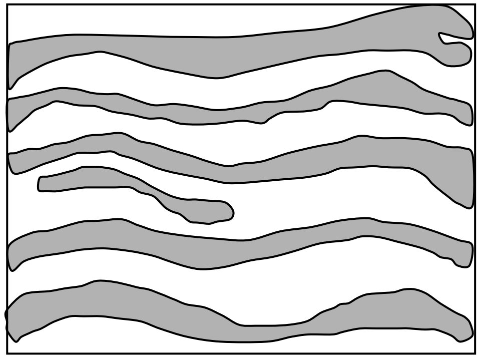
Immisible Blends: Useful Morphologies

Drops



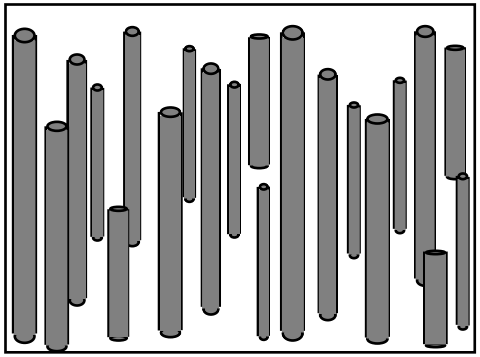
toughness,
surface modification

Laminar



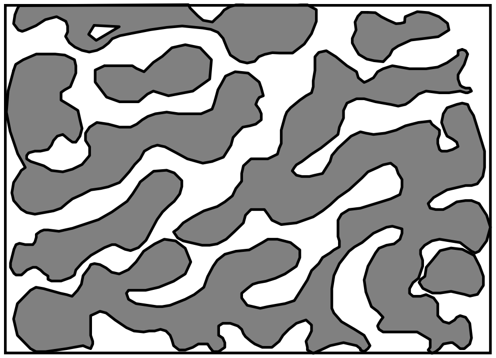
barrier

Fibers



strength, thermal expansion

Cocontinuous



high flow, adsorbents
electrical conductivity,
toughness, stiffness

"Morphology without rheology is zoology"

Richard Stein
U Mass.

Macosko, *Macromol. Symp.* **149**, 171 (2000)

Most polymer pairs are immiscible

But two-phase systems can have desirable properties

- ***Surface modification***

Dynamar (Dyneon)	**PE/PTFE, 1%**
MB (Dow Corning)	**PP/PDMS**

- ***Toughness***

HIPS	**styrene polymerized with PB**
ABS	**SAN/PB latex**
“super tough nylon” (Dupont)	**PA6,6/EPR**

- ***Gas barrier***

Selar (Dupont)	**PE/PA6,6**

- ***Processibility***

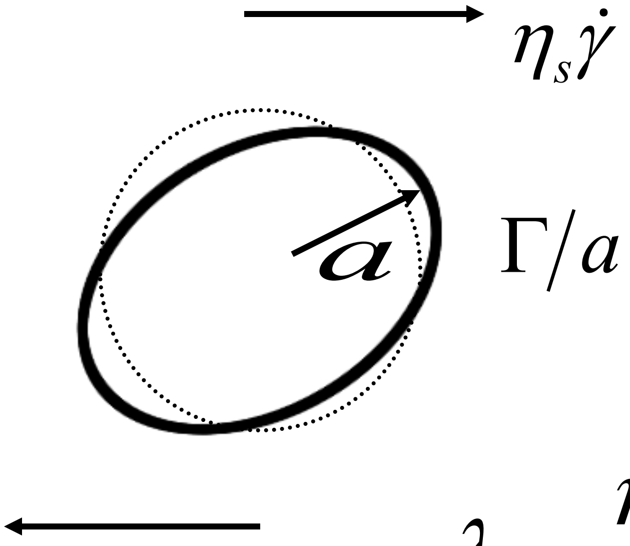
Noryl GTX (Sabic)	**PA6/PPO/SB**
TPO (ExxonMobil, others)	**PP/EP**

- ***Thermal expansion***

Vectra	**PET/LCP**

Macosko, *Macromol. Symp.* **149**, 171 (2000)

Deformable Spheres



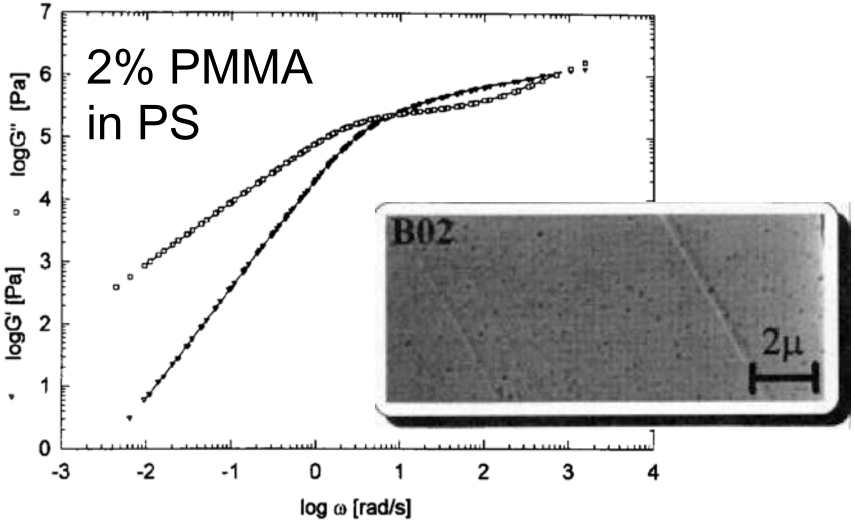
$$\lambda = \frac{\eta_s a}{\Gamma}$$

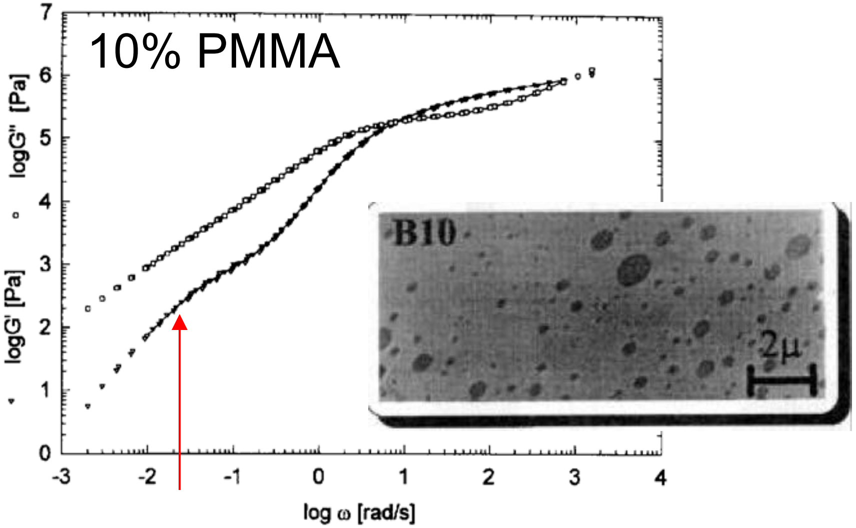
$$G' = G'_s\left[\frac{1+3\phi H}{1-2\phi H}\right]$$

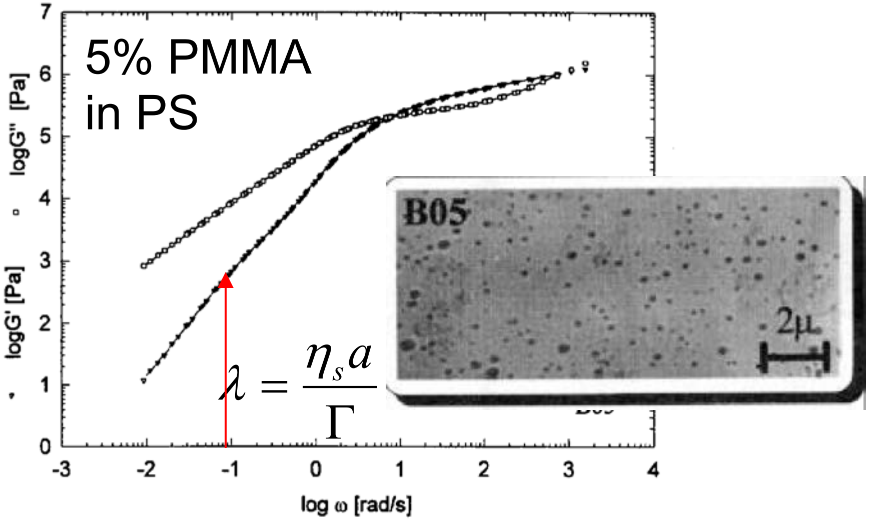
$$H = \frac{4(\Gamma/a)(5G'_d + 2G'_s) + (G'_d - G'_s)(19G'_d + 16G'_s)}{40(\Gamma/a)(G'_d + G'_s) + (2G'_d + 3G'_s)(19G'_d + 16G'_s)}$$

$$= H(\Gamma/a, G'_d, G'_s)$$

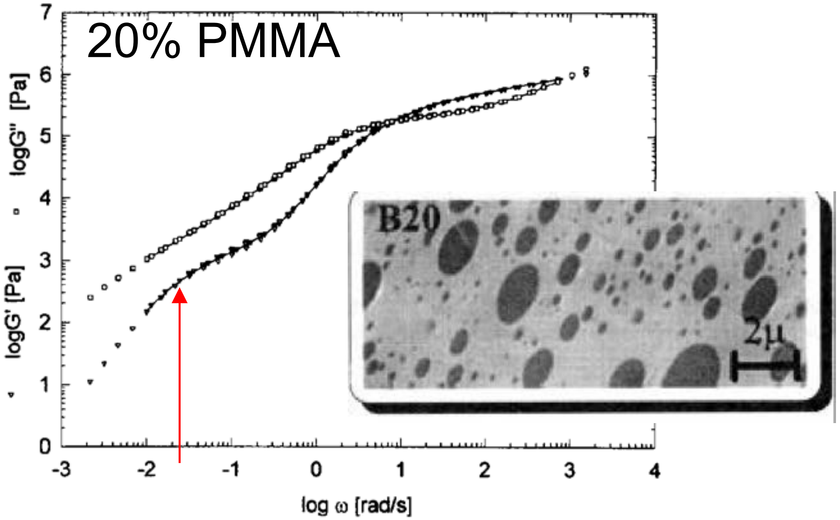
Palierne, *Rheol. Acta,* **29**, 204 (1990)


2% PMMA
in PS


10% PMMA

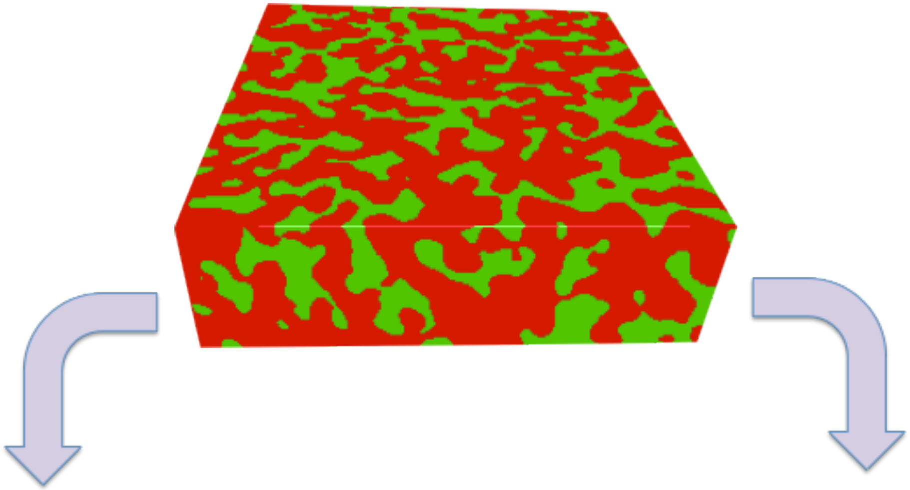

5% PMMA
in PS

$$\lambda = \frac{\eta_s a}{\Gamma}$$


20% PMMA

Ch. Friedrich et al, *J. Rheol.* **39**,1411 (1995)

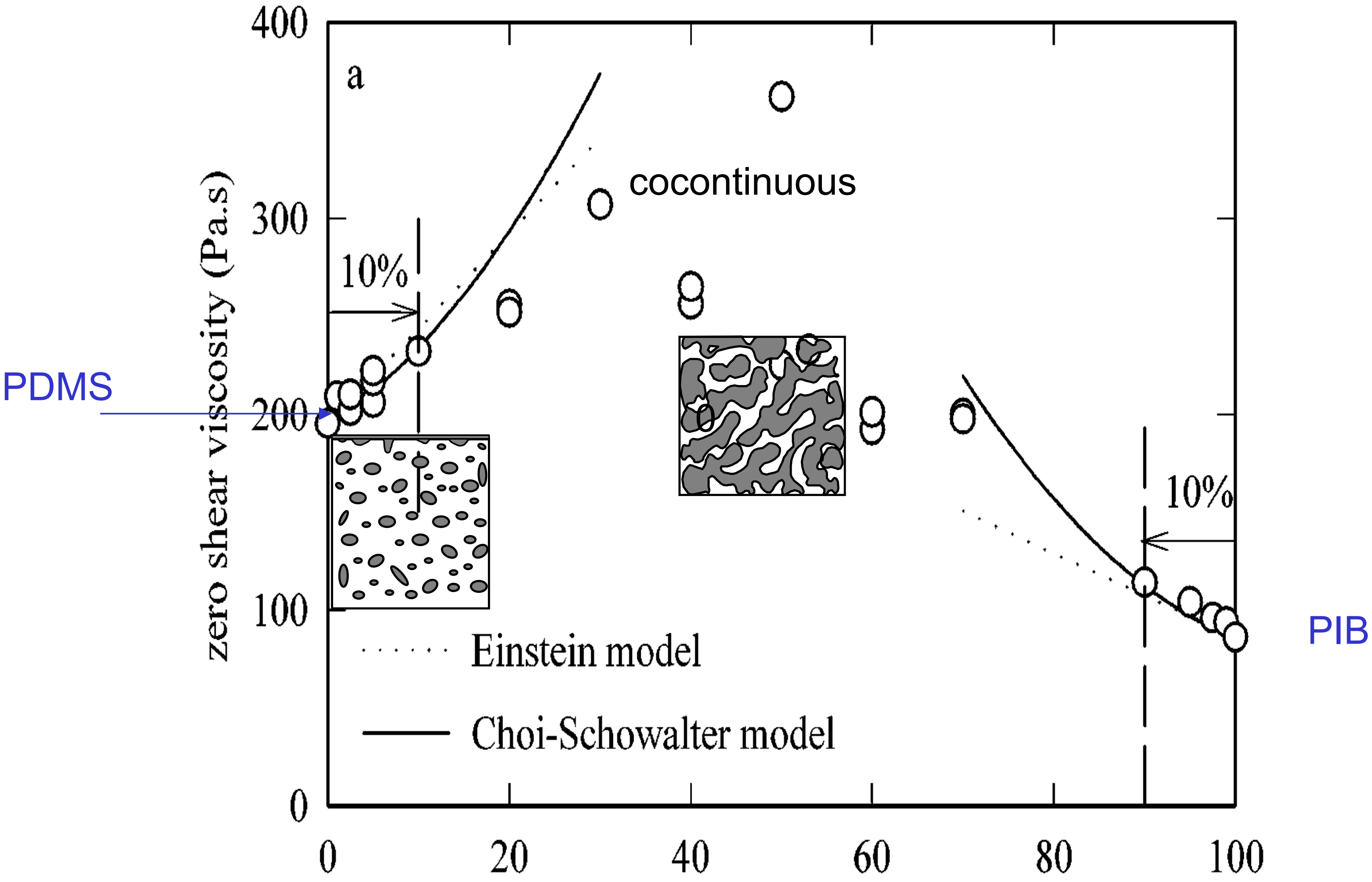
Cocontinuous Blends



- non-equilibrium
- melt processing

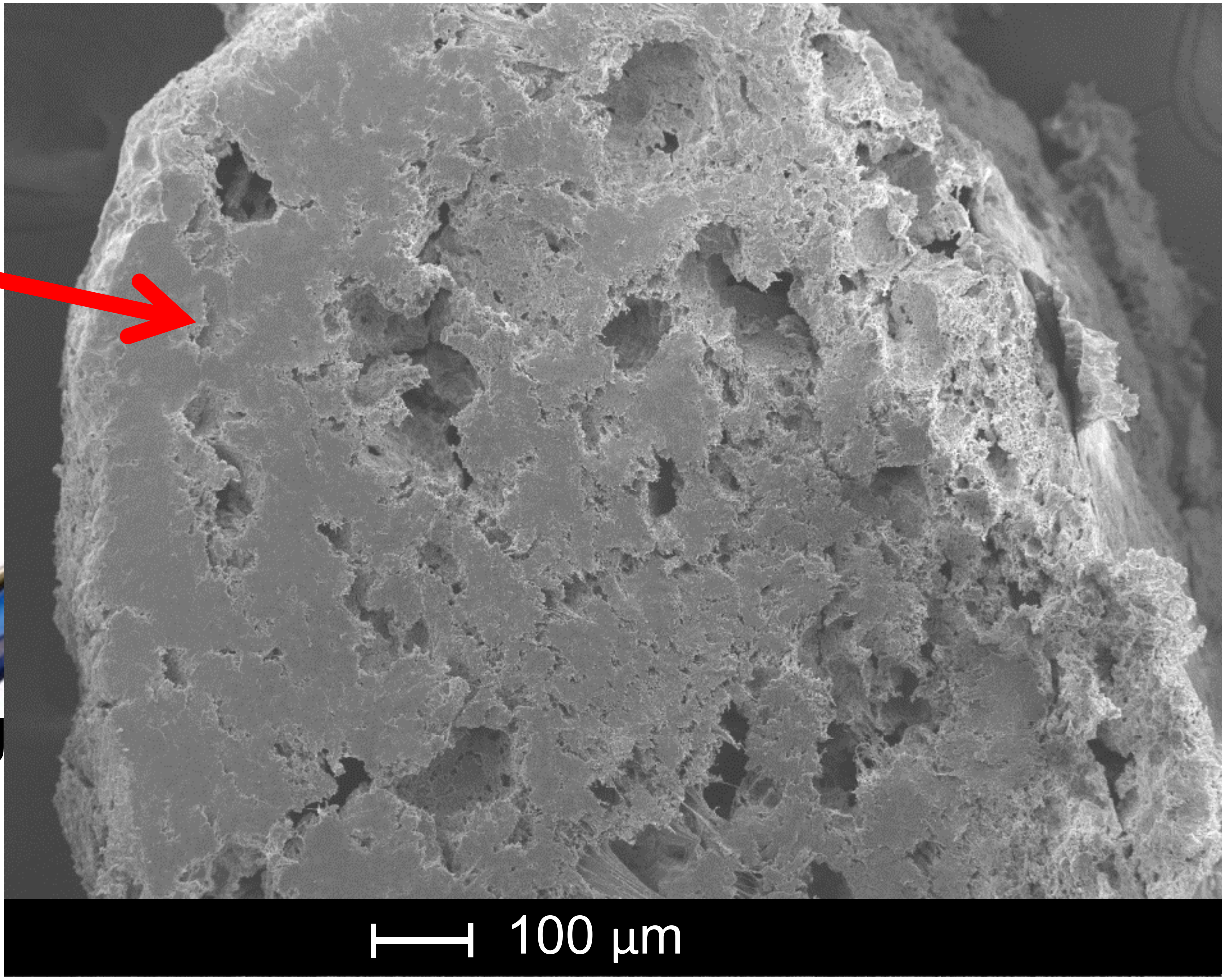
- phase size: ~1-10 μm
- phase extraction yields porous matrix

Lopez-Barron, Macosko *Langmuir* 2009, 2010



Vinckier et al., *Colloid and Surfaces. A:* **150,** 217 (1999)

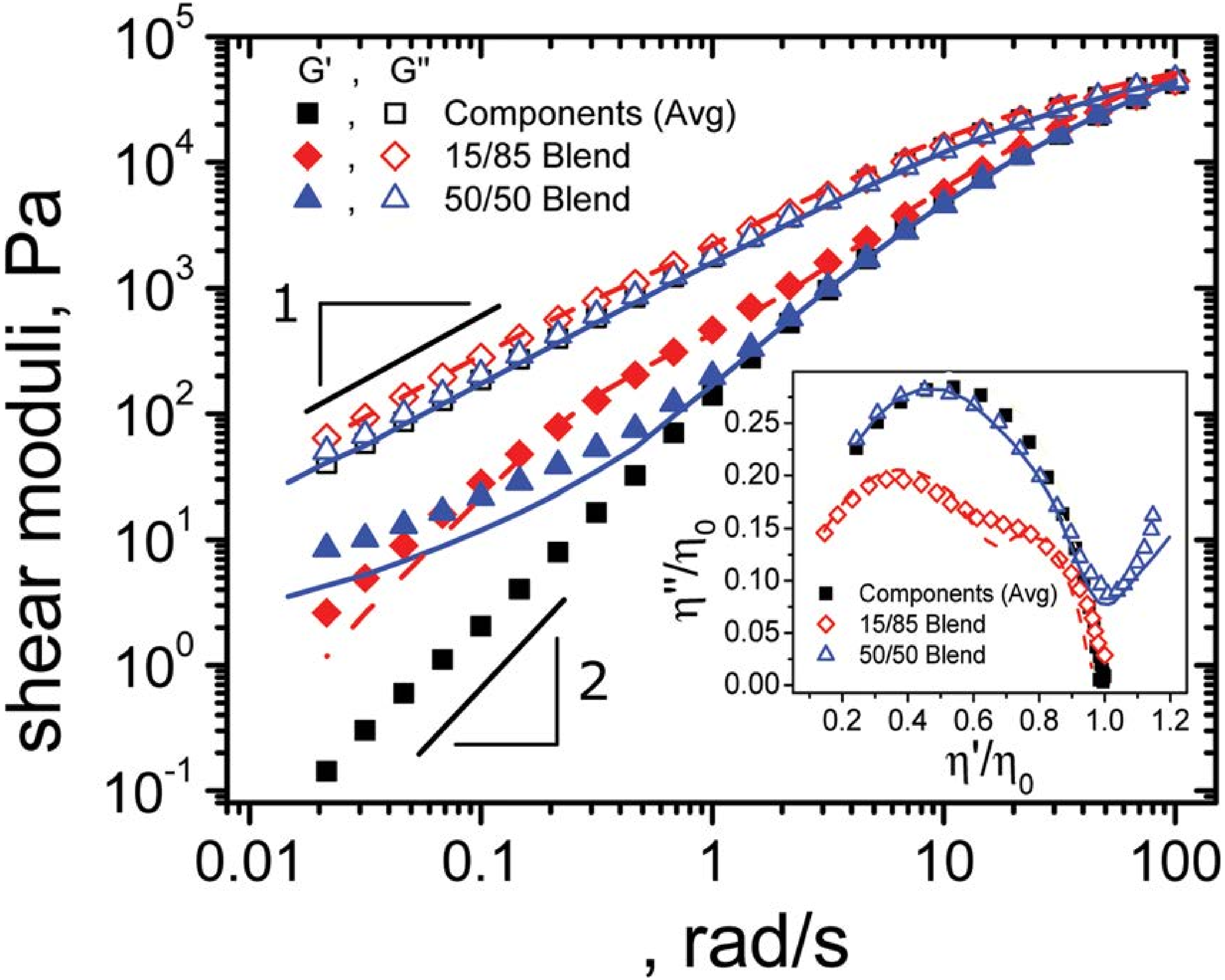
Application: Lubricating Strips



Cocontinuous structure, containing polyethylene oxide as lubricating agent.

Razor image from Proctor and Gamble
“Lubricious polymer blends comprising polyethylene oxide, polyethylene and a polylactone.” US Patent #5589545 A

Droplet-matrix vs. cocontinuous



Lopez-Barron; Macosko, *J.Rheol.* **56,**1315 (2012)

Polymer Rheology

Molecular Structure

MW and MWD
Chain Branching and Cross-linking
Thermosets
Single or Multi-Phase Structure
Solid polymers

Viscoelastic Properties

Small strain (linear viscoelastic)
Steady shearing
Extension

Processability & Product Performance

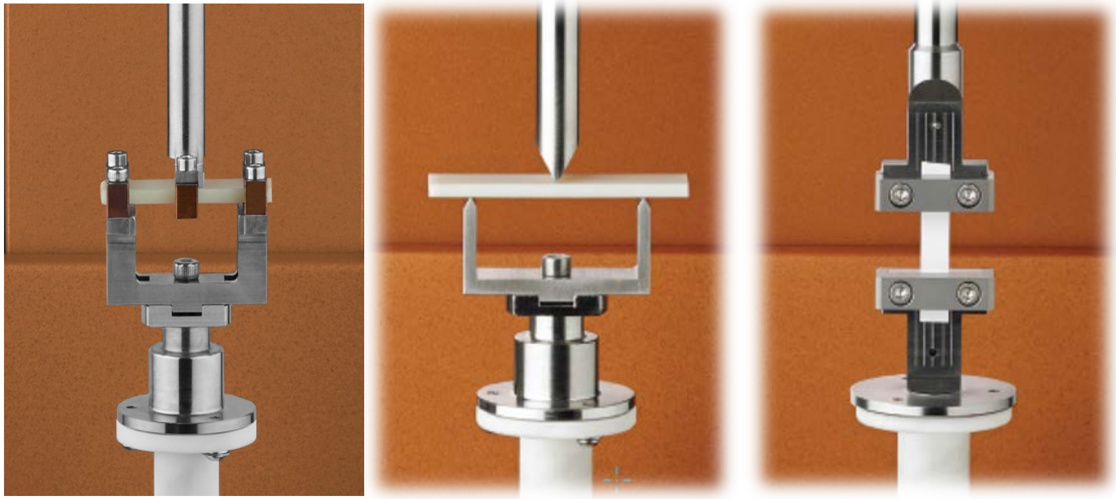
Testing Solids: Torsion and DMA

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment
  - Torsion measures G’, G”, and Tan δ
  - DMA measures E’, E”, and Tan δ
    - DMA mode on ARES G2 (max 50 μm amplitude)
    - DMA mode on DHR (max 100 μm amplitude)

$$E = 2G(1 + \nu)$$

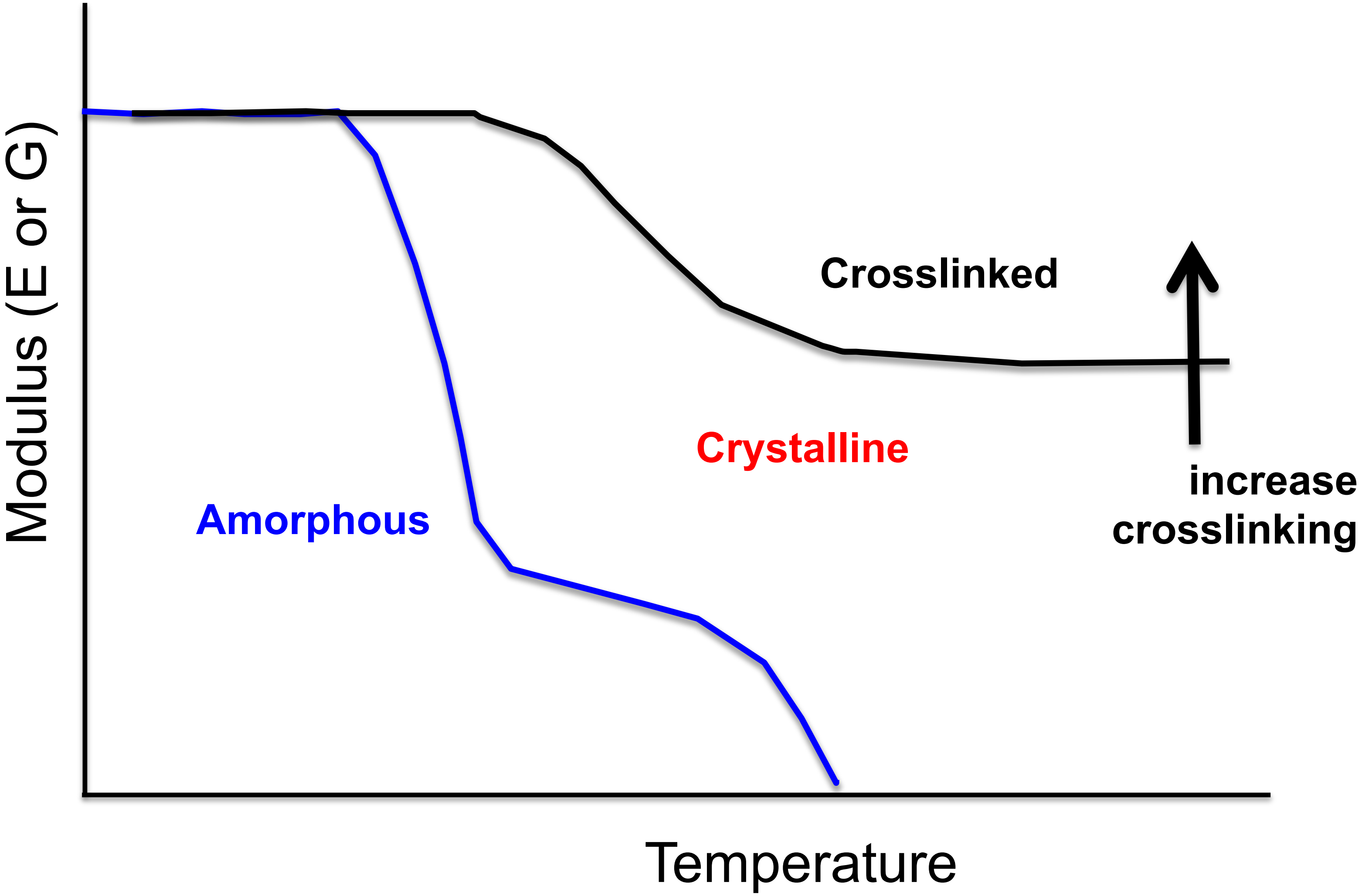
ν : Poisson’s ratio

Torsion rectangular and cylindrical clamps



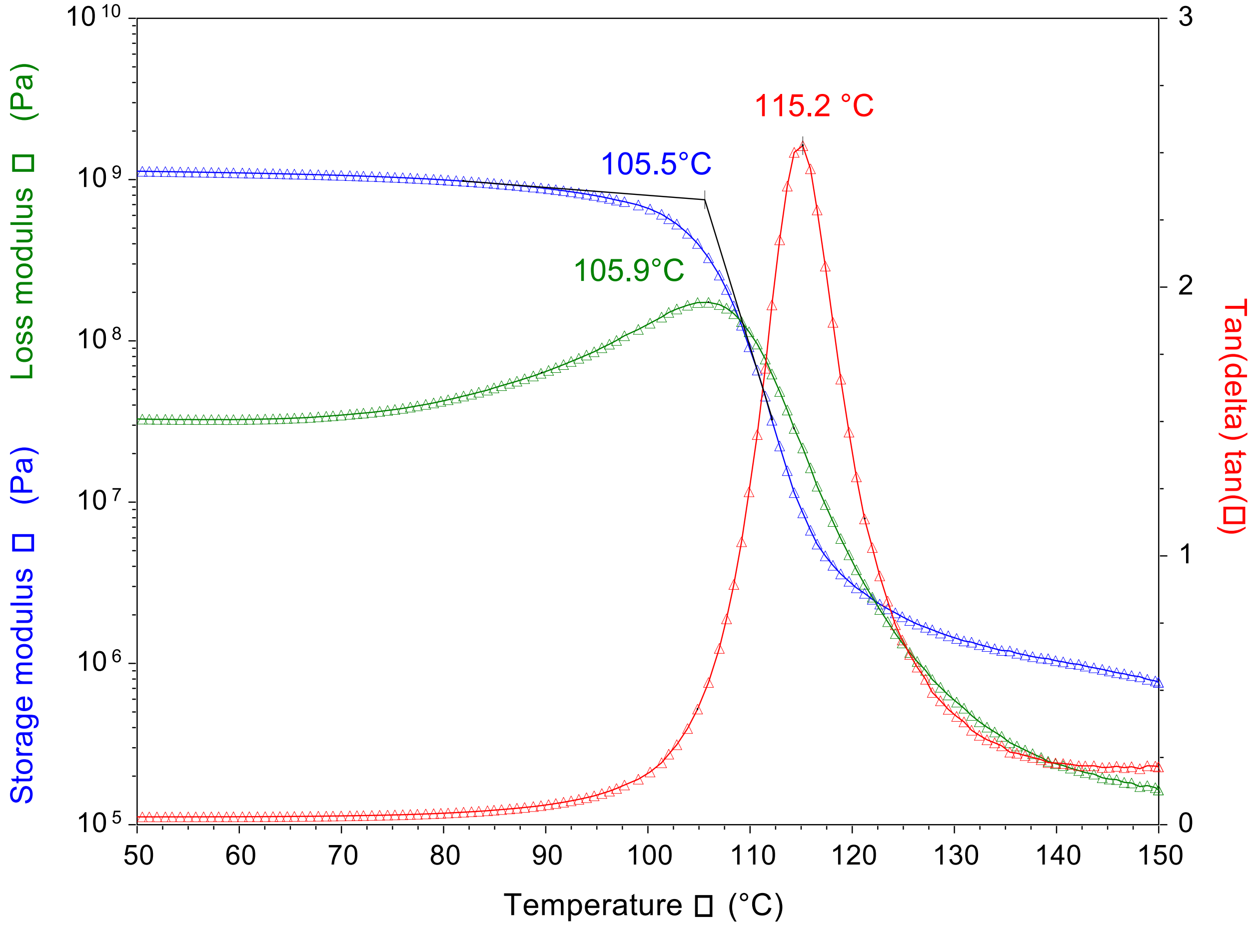
DMA cantilever, 3-point bending and tension clamps

Amorphous, Crystalline and Crosslinked Polymers



Dynamic Temp Ramp Test

- Measure moduli, tan δ and transitions



How to Measure Glass Transition

G' Onset: Occurs at lowest temperature - Relates to mechanical failure

G" Peak: Occurs at middle temperature - more closely related to the physical property changes attributed to the glass transition in plastics. It reflects molecular processes - agrees with the idea of T_g as the temperature at the onset of segmental motion.

tan δ Peak: Occurs at highest temperature - used historically in literature - a good measure of the "leatherlike" midpoint between the glassy and rubbery states - height and shape change systematically with amorphous content.

Reference: Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 980.

The Glass & Secondary Transitions

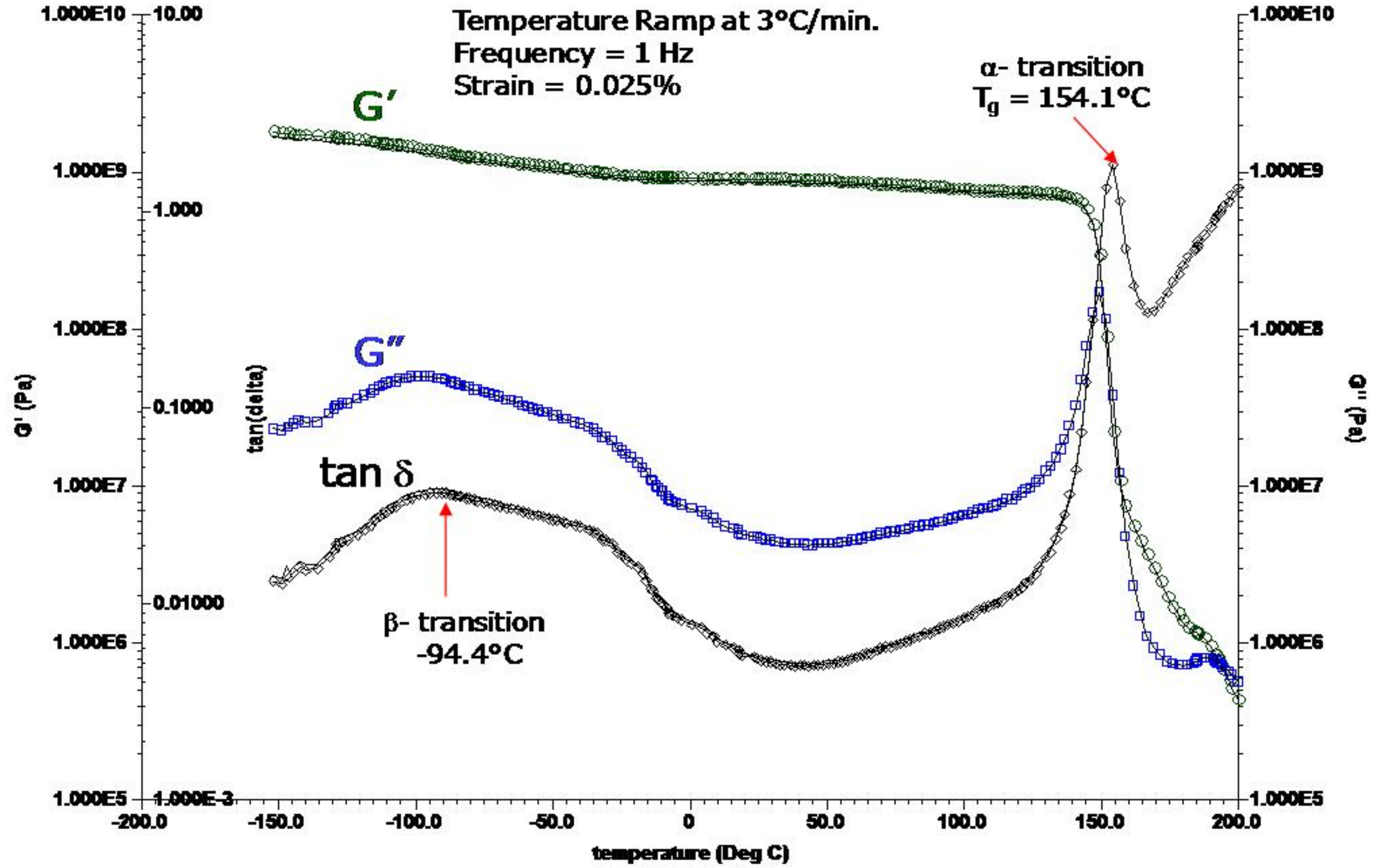
Glass Transition - Cooperative motion among a large number of chain segments, including those from neighboring polymer chains

Secondary Transitions

- Local main-chain motion - intramolecular rotational motion of main chain segments four to six atoms in length
- Side group motion with some cooperative motion from the main chain
- Internal motion within a side group without interference from side group
- Motion of or within a small molecule or diluent dissolved in the polymer (e.g. plasticizer)

Reference: Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 487.

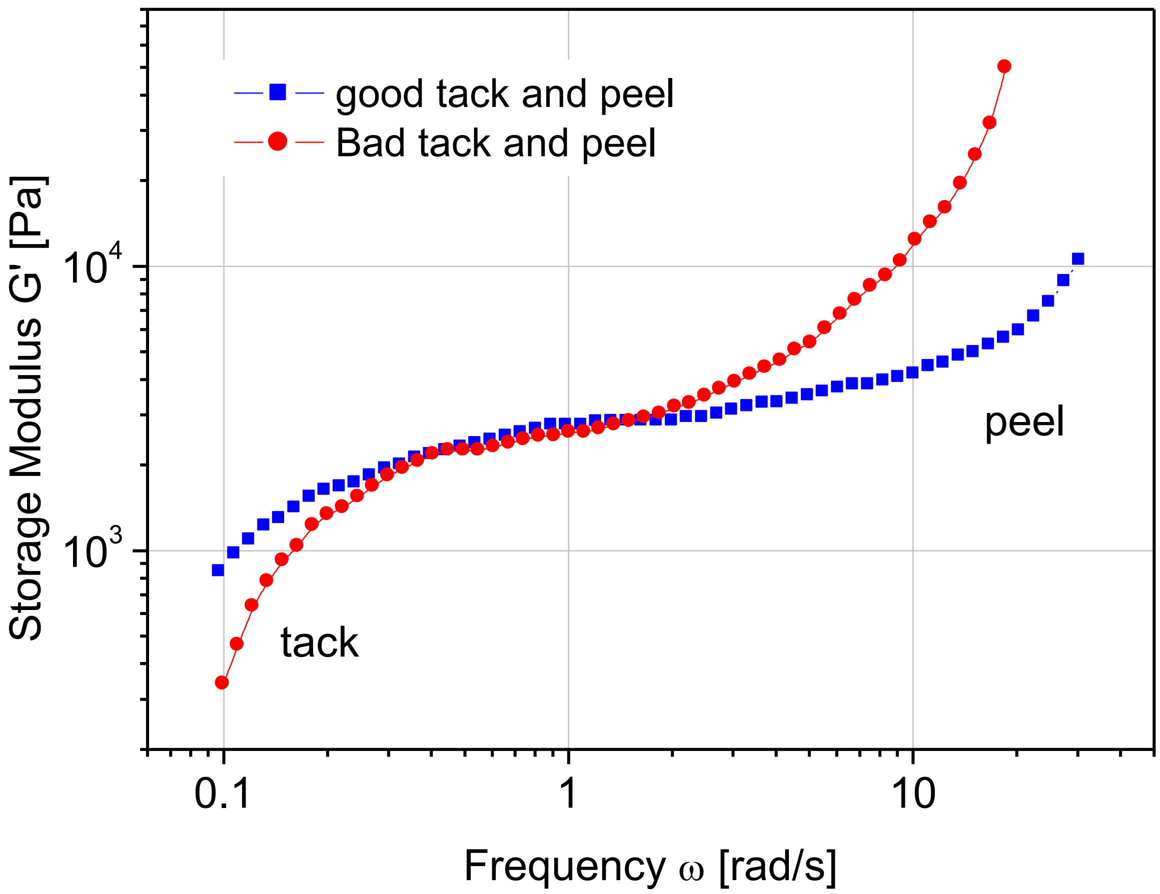
Polycarbonate in Torsion



Tack and Peel of Adhesives

- Bond strength is obained from peel (fast) and tack (slow) tests
- It can be related to the viscoelastic properties at different frequencies

Tack and Peel performance of a PSA



Tack and peel have to be balanced for an ideal adhesive

Rheology Short Courses:

Stanford University, June 11-13, 2019

https://trainings.tainstruments.com/rheology-short-course/

KU Leuven, September 2-6, 2019, with lab

https://cit.kuleuven.be/smart/rheoschool

University of Minnesota, June 2020, with lab
https://rheology.cems.umn.edu/