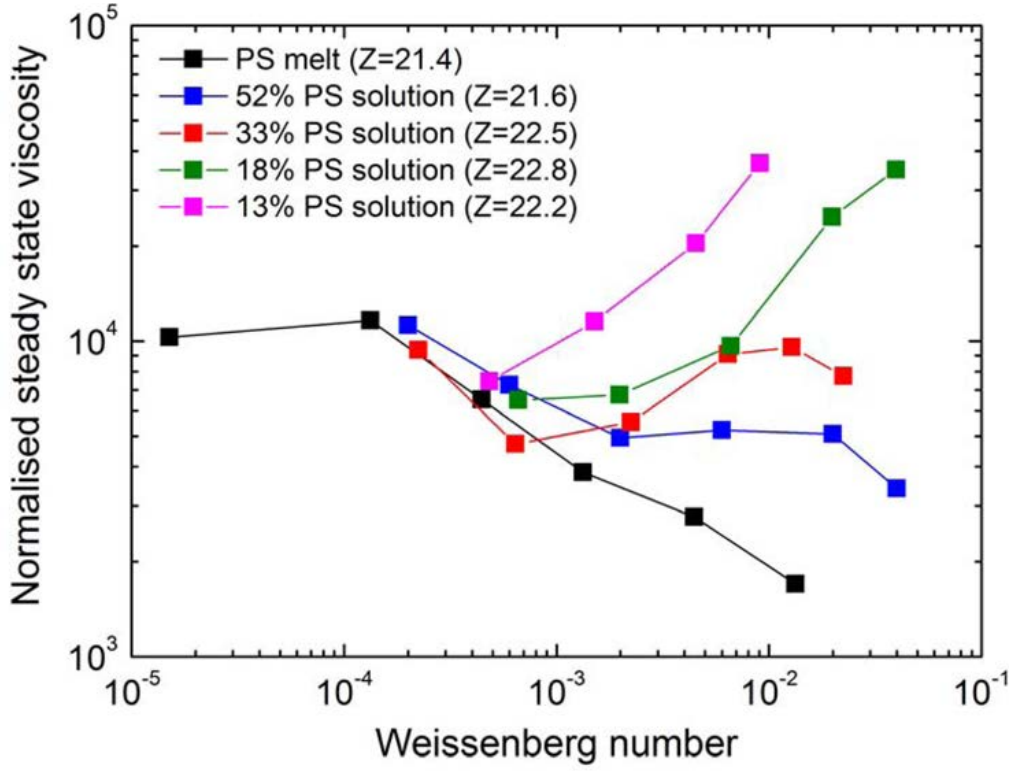
Extensional rheology of model polymers

Ole Hassager
Technical University of Denmark



Extensional rheology of model polymers

- Linear monodisperse polymers (solutions and melts)
- Branched commercial polymers (LDPE): Extensional viscosity
- Branched model polymers (stars): Extensional viscosity
- Branched model polymers (stars): Small Angle Neutron Scattering (SANS)
- Branched commercial polymers (LDPE): Stress maximum
- Branched commercial polymers (LDPE): Small Angle X-ray Scattering (SAXS)
- Linear commercial polymers: Flow-induced crystallization
- Fracture: The end of rheology?

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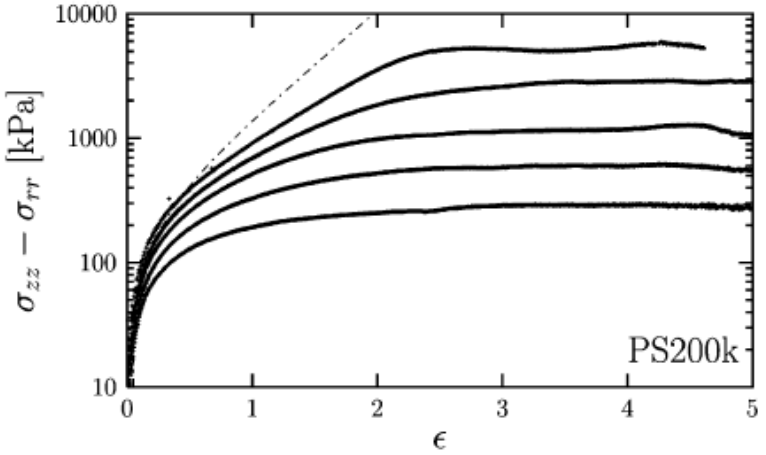
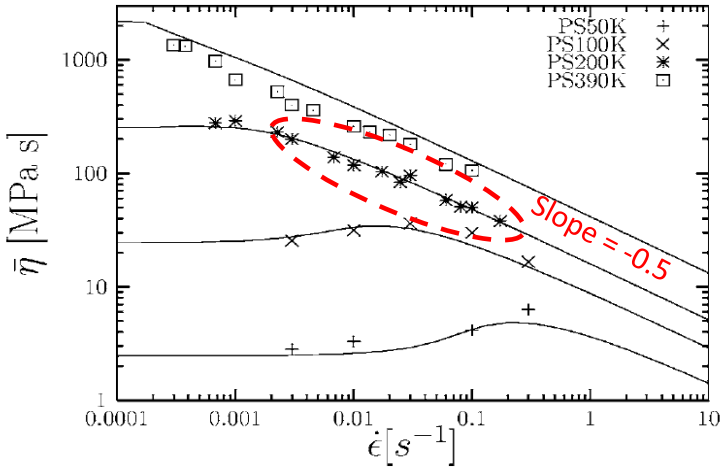
Linear monodisperse polymers: melts vs. solutions
The story of phase separation?

PS melts (130C)

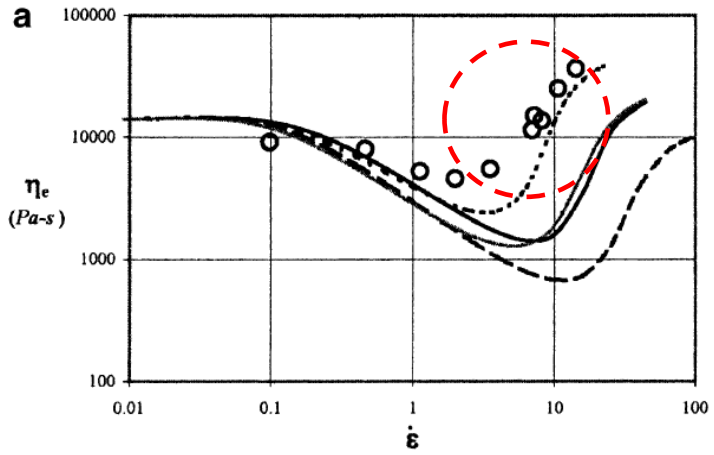




Bach et al., Macromolecules (2003) 34: 5174-6179

Similar number of entanglements

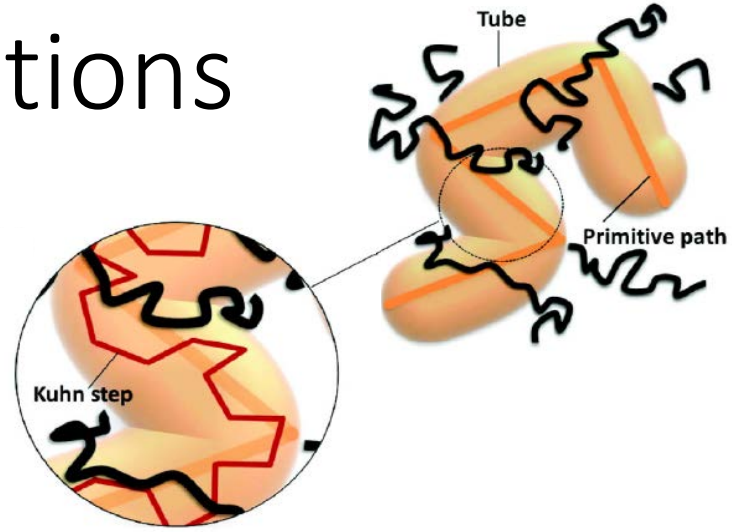
PS solutions (21C)



Bhattacharjee, Oberhauser, McKinley, Leal and Sridhar, Macromolecules (2002)

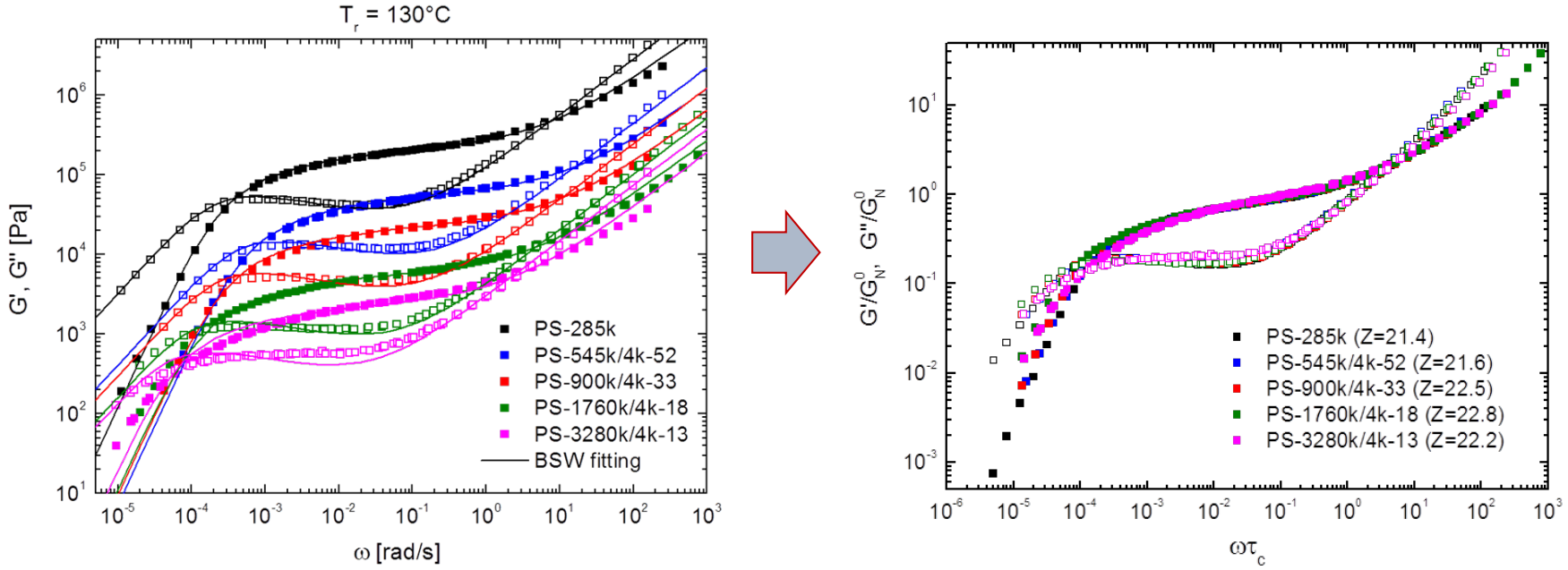
mol wt	polymer concn (wt %)	solvent
3 900 000	4.90	DOP
3 900 000	7.35	DBP
3 900 000	10.0	DEP
3 900 000	15.0	DEP
10 200 000	6.00	DBP

Linear polymers: melts vs. solutions



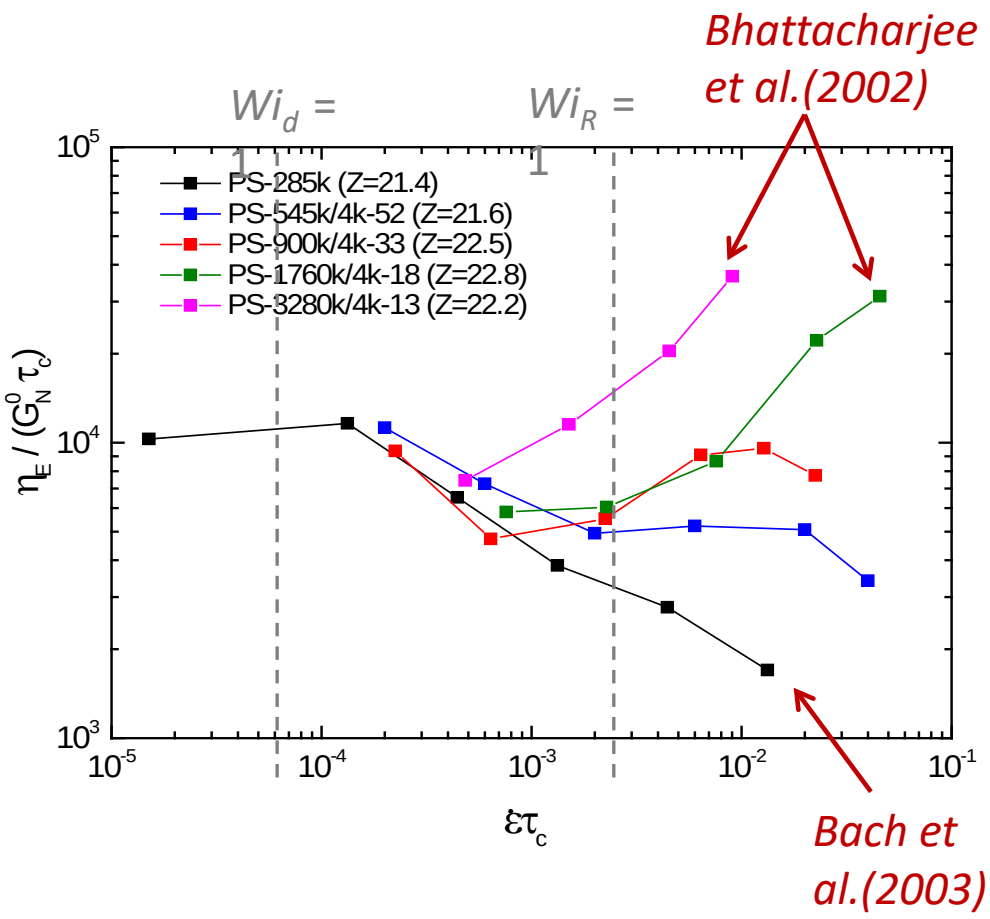
Tube model parameters:

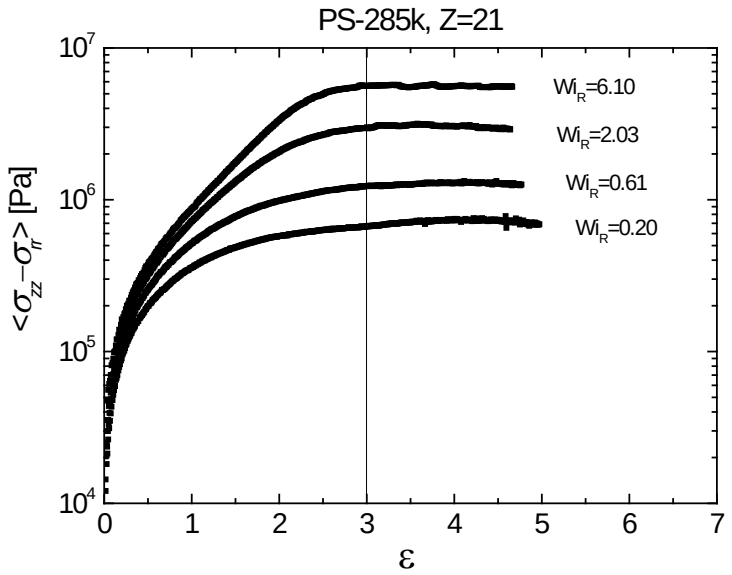
Number of entanglements per chain: Z
Number of Kuhn steps per entanglement: N_e
Entanglement Relaxation time: τ_e

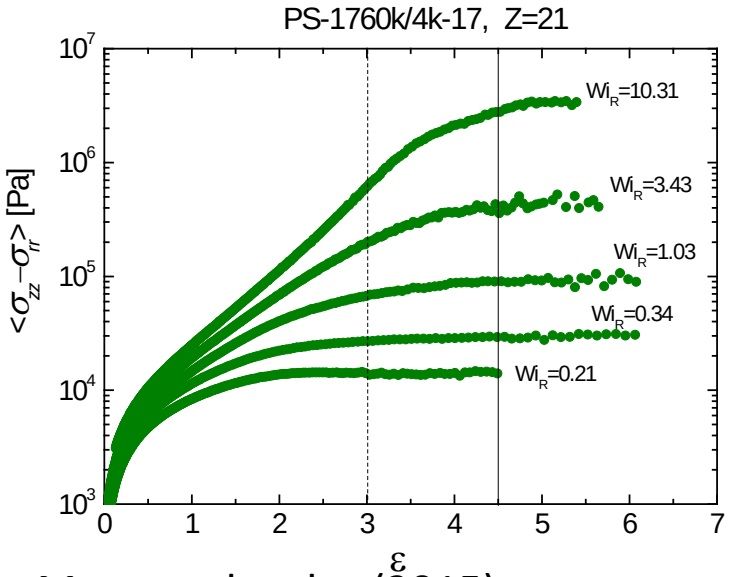


Huang et al., Macromolecules (2015)

Linear polymers: melts vs. solutions







Huang et al., Macromolecules (2015)

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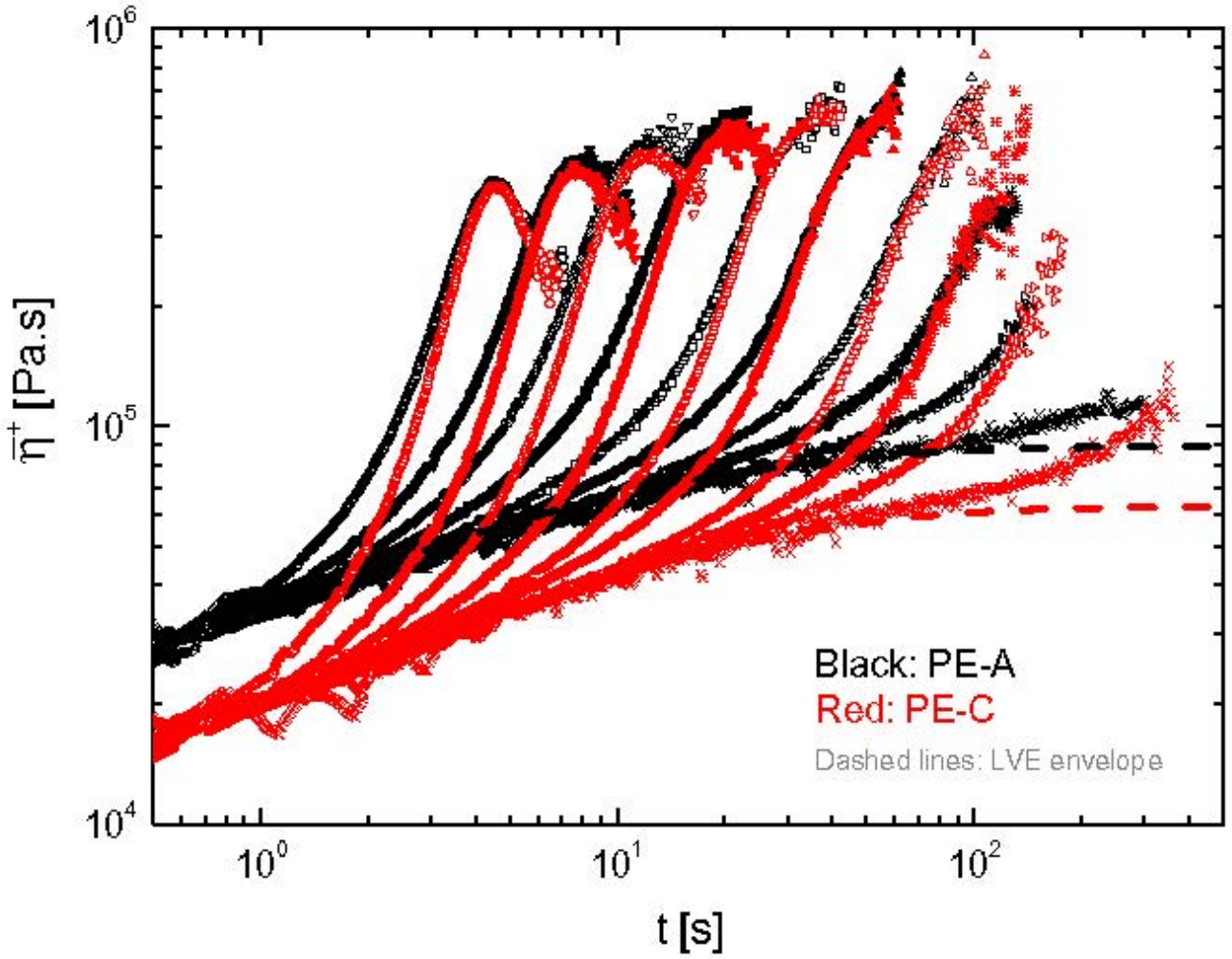
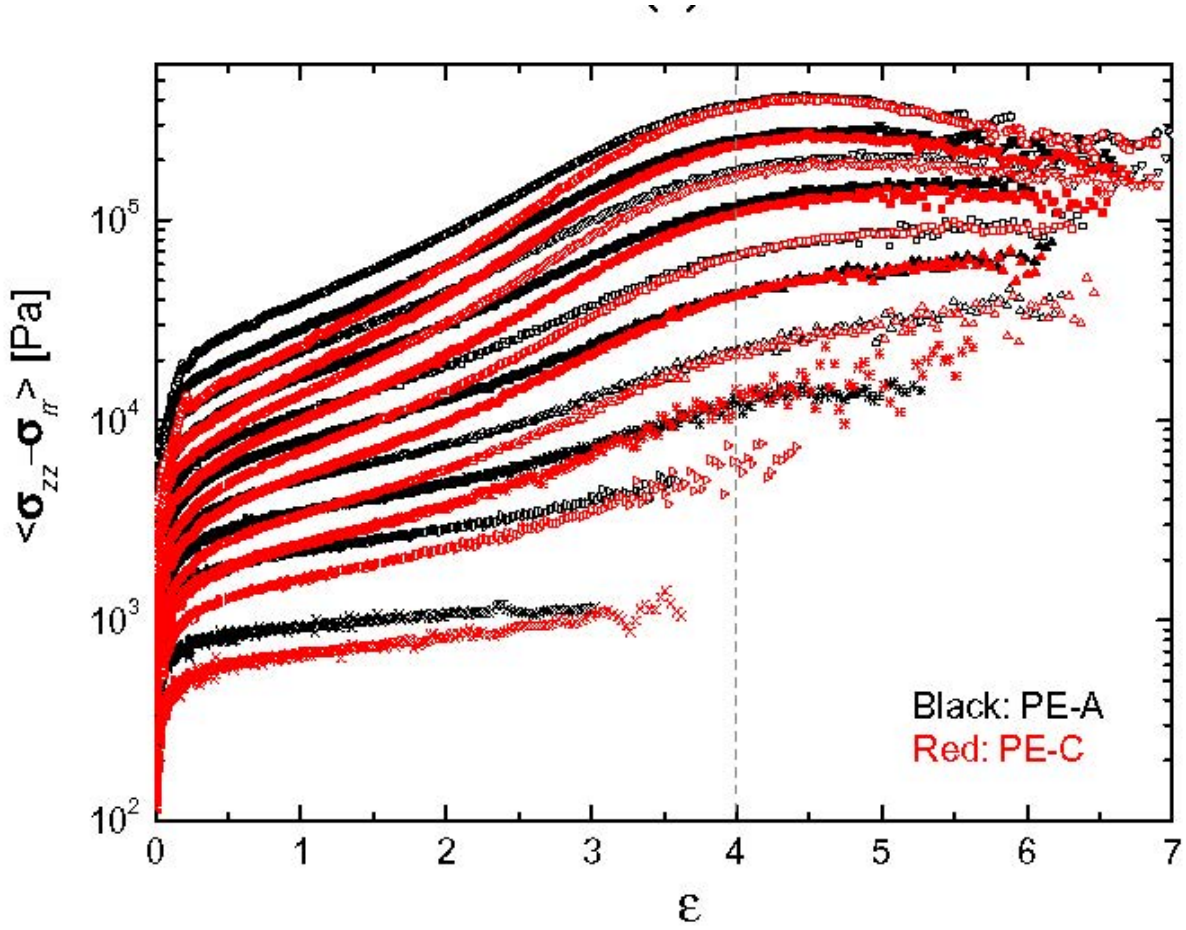
Comparison of two commercial polyethylene samples
(PE-A and PE-C) both at 150C.



Extensional stress growth coefficient as function of time. Strain rate (from left to right): 1.0, 0.6, 0.4, 0.25, 0.15, 0.1, 0.06, 0.04, 0.025, and 0.01 (1/s).

Q. Huang et al., Rheol. Acta (2016)

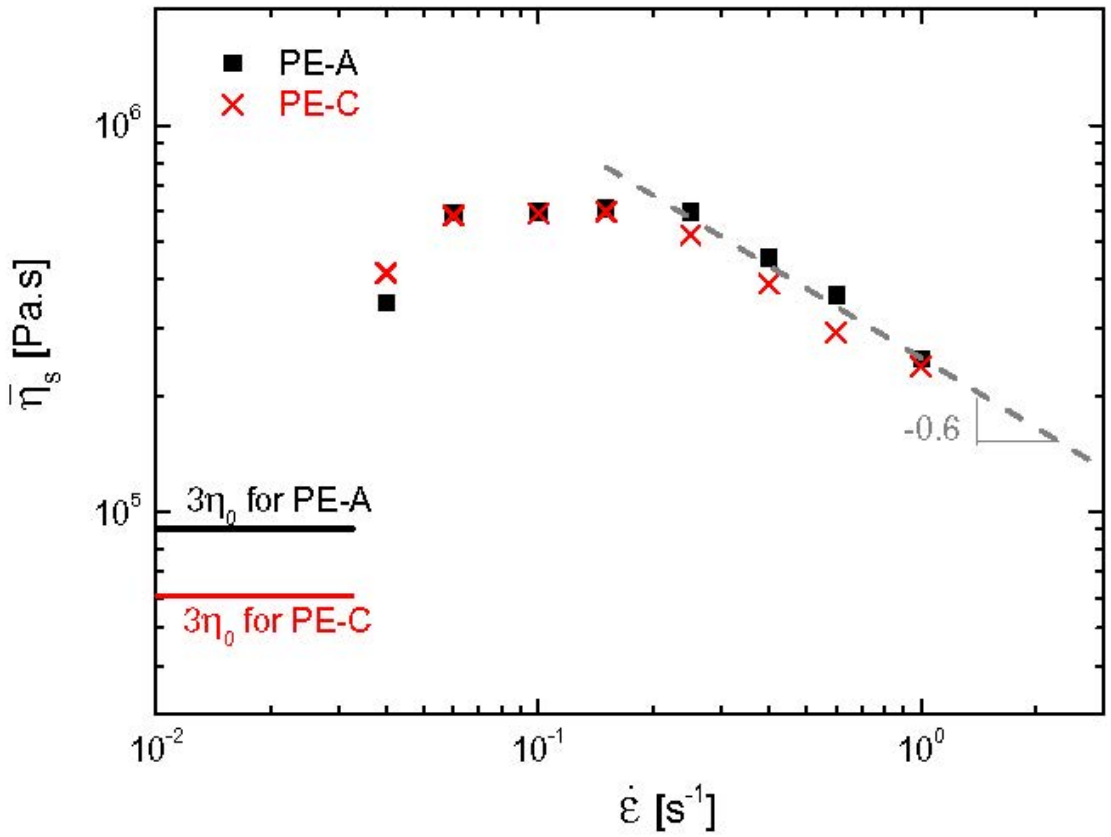
Comparison of two commercial polyethylene samples (PE-A and PE-C) both at 150C.



Extensional stress as function of strain. Strain rate (top to bottom): 1.0, 0.6, 0.4, 0.25, 0.15, 0.1, 0.06, 0.04, 0.025, and 0.01 (1/s).

Q. Huang et al., Rheol. Acta (2016)

Comparison of two commercial polyethylene samples (PE-A and PE-C) both at 150C. Steady viscosity:



Steady extensional viscosity (η_E) as function of strain rate $\dot{\epsilon}$.

Q. Huang et al., Rheol. Acta (2016)

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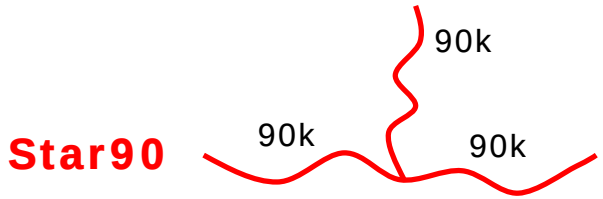
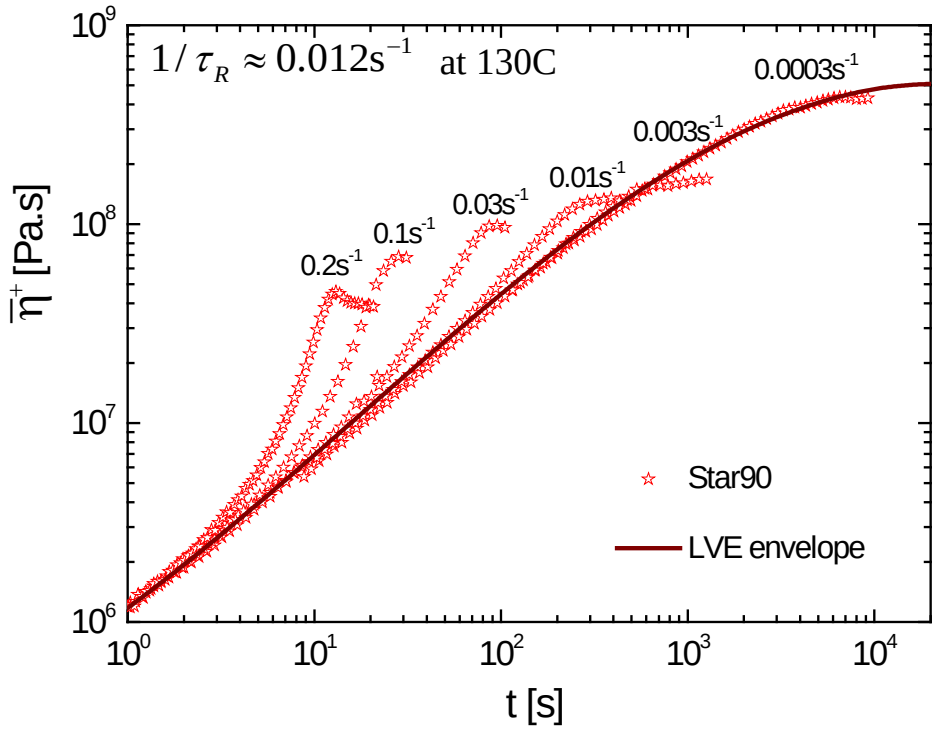
Polymer melts: linear vs. star

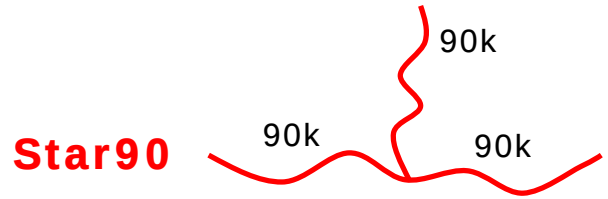


M_w = 289k, PDI = 1.03



Synthesized by **Serena Agostini**
at Durham University

Polymer melts: linear vs. star



M_w = 289k, PDI = 1.03

M_w = 187k, PDI = 1.02

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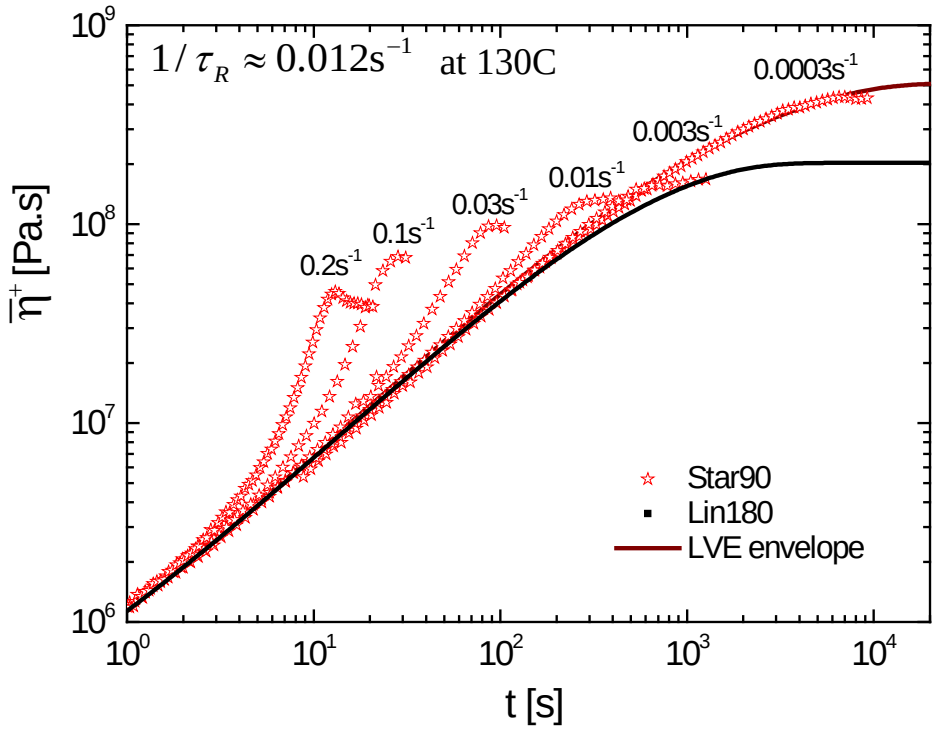
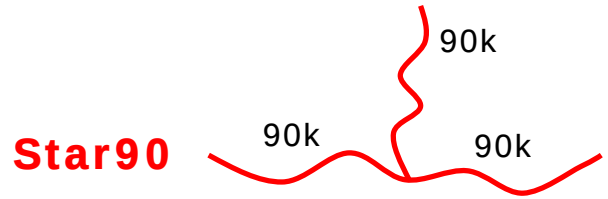


Polymer melts: linear vs. star



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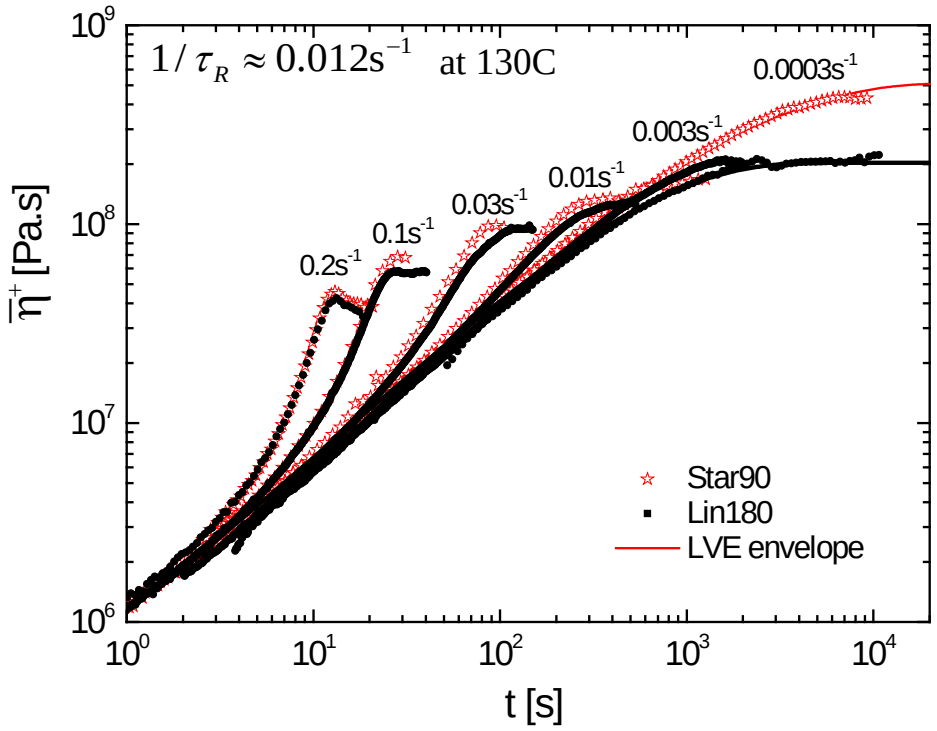

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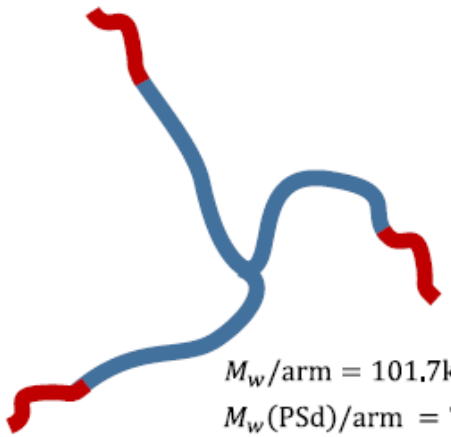
SANS for star PS

3-Arm Polystyrene Star-Polymer
Each arm has end-block of deuterated monomers

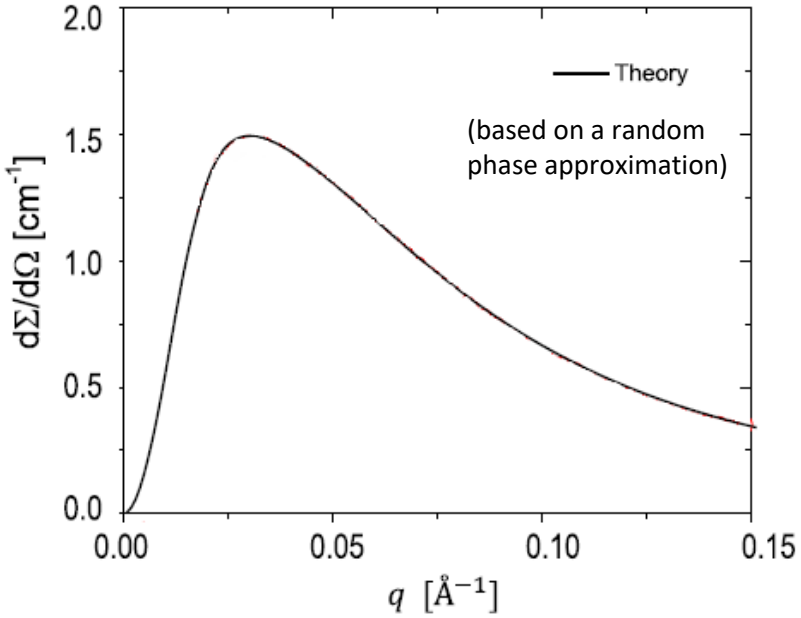


M_w/arm = 101.7kg/mol
M_w(PSd)/arm = 7.7kg/mol

Mass fraction of deuterated PS: f = 0.075

M_w = 309k, PDI = 1.3

Synthesized by **Andriy Dorokhin**
at DTU Nanotech



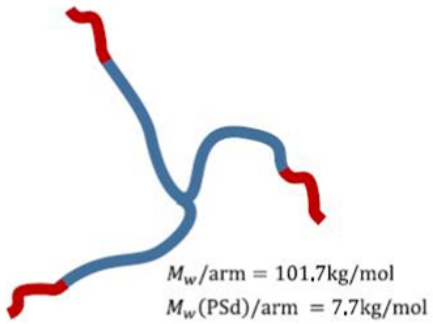
$$I(q) = \frac{N}{S/W - 2\chi N} \qquad (1)$$

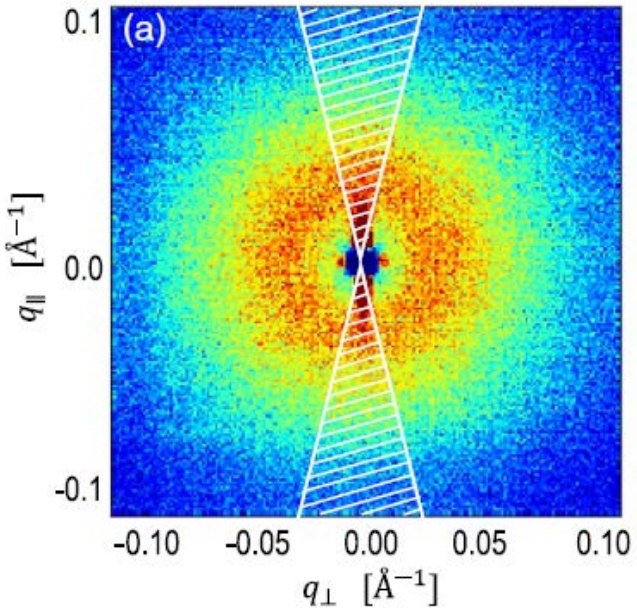
$$S = S_{AA} + S_{BB} + 2S_{AB} \qquad W = S_{AA}S_{BB} - S_{AB}^2$$

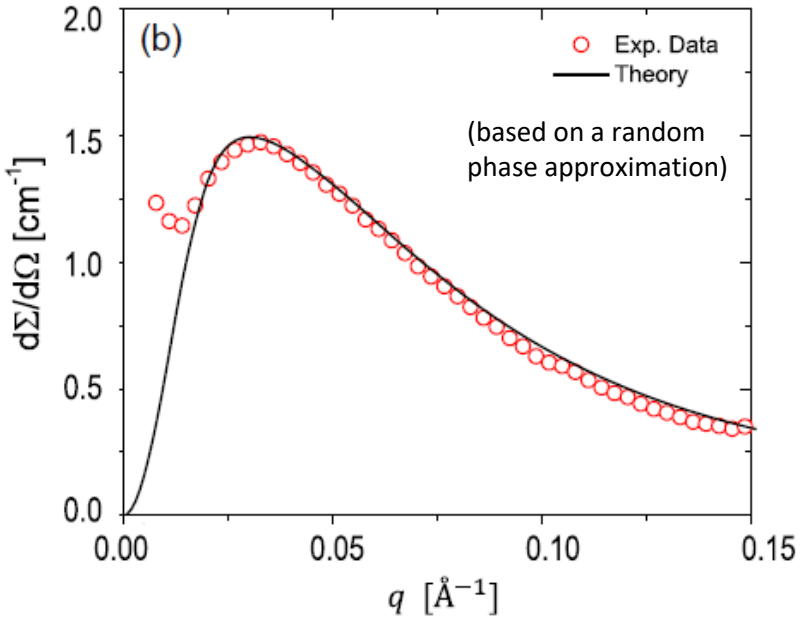
$$\begin{aligned} S_{AA} &= -3h[(1-f)/3] + 3h[2(1-f)/3] \\ S_{BB} &= 3\{h(f/3) + h(2/3) + h[2(1-f)/3] \\ &\quad - 2h[(2-f)/3]\} \\ S_{AB} &= 3/2h[(1-f)/3] - 3/2h(1/3) - 3/2h(f/3) \\ &\quad + 3\{h[(2-f)/3] - h[2(1-f)/3]\}, \end{aligned} \qquad (2)$$

$$h(x) = 2/(qR_{g,N})^4\{x(qR_{g,N})^2 + \exp(-x(qR_{g,N})^2) - 1\} \qquad (3)$$

SANS for star PS







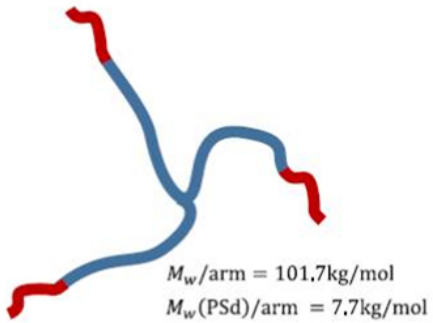
SANS measurements and data analysis were carried out by **Anine Borger and Kell Mortensen** from Copenhagen University

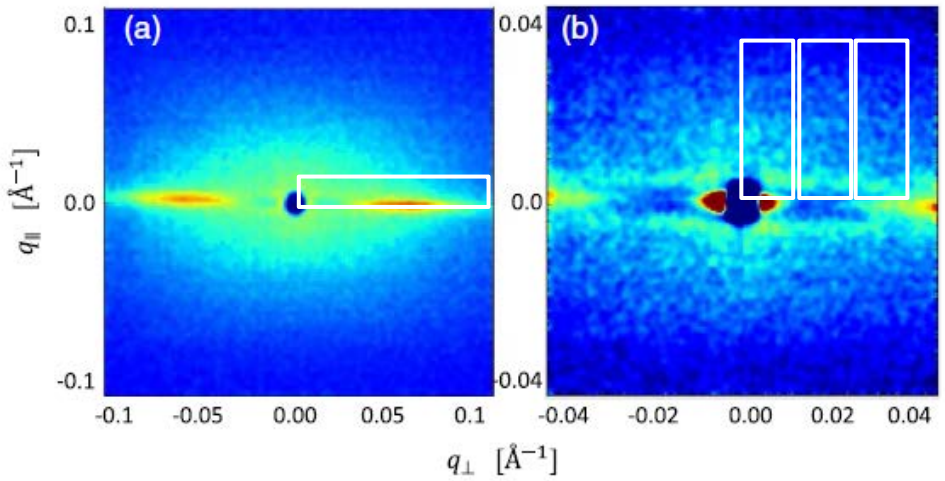
SANS data were obtained using the Quokka at ANSTO, Australia.

5 Å neutrons with 10% wavelength resolution

SANS for star PS

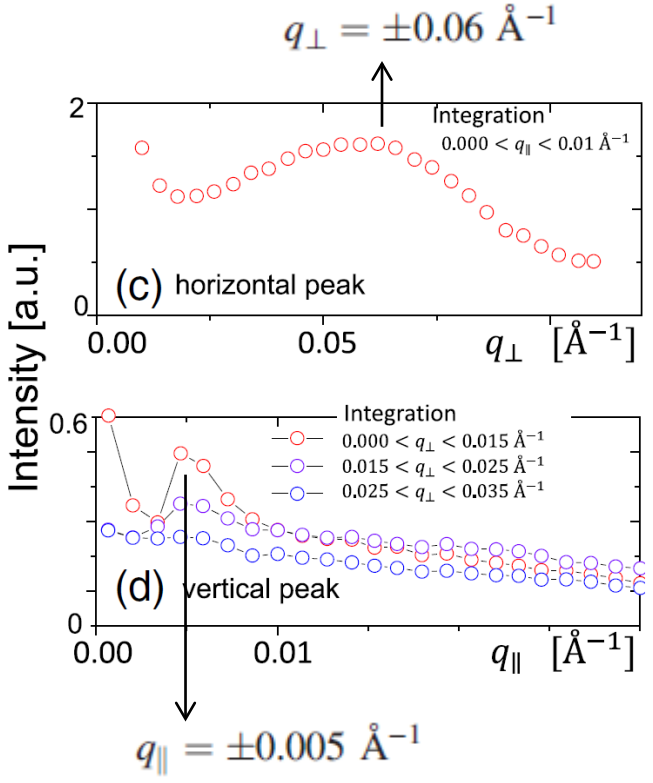
Stretched at 0.06s^{-1} at 125C to Hencky strain 3 (steady stress) and quenched (<3s)
Rouse time 450s





10m collimation length and 5m sample-to-detector distance
q range: $0.01 - 0.15$ Å^{-1}

14m collimation length and 14m sample-to-detector distance
q range: $0.004 - 0.06$ Å^{-1}



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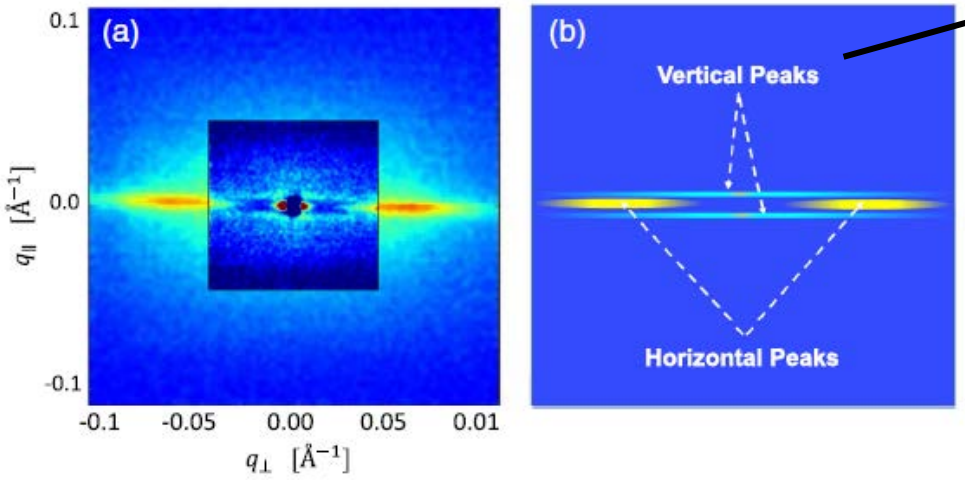


Two elongated scattering domains aligned in the flow direction will have exactly such characteristics with the peak-width being confined in the direction parallel to flow

Two types of peaks do not merge - not part of a common ellipsoidal (or other simple) correlation ring

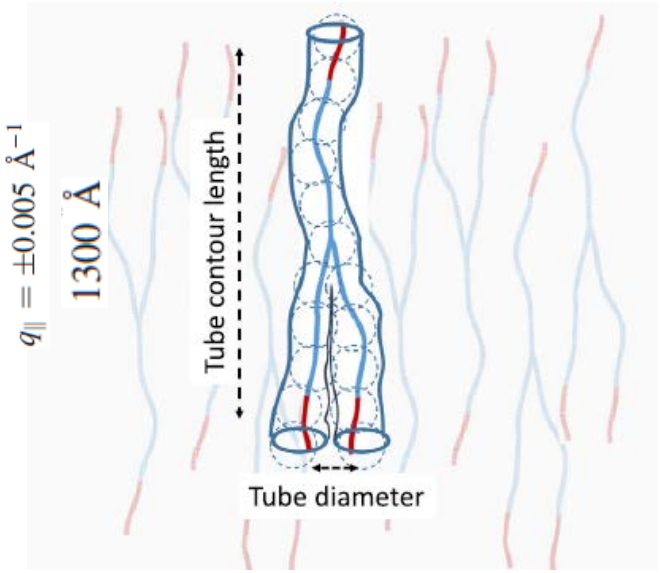
SANS for star PS

Stretched at 0.06s^{-1} at 125C to Hencky strain 3 (steady stress) and quenched (<3s)
Rouse time 450s

Fully *oriented* length: 1020 Å

Fully *stretched* length: 4860 Å

Tube diameter: 85 Å



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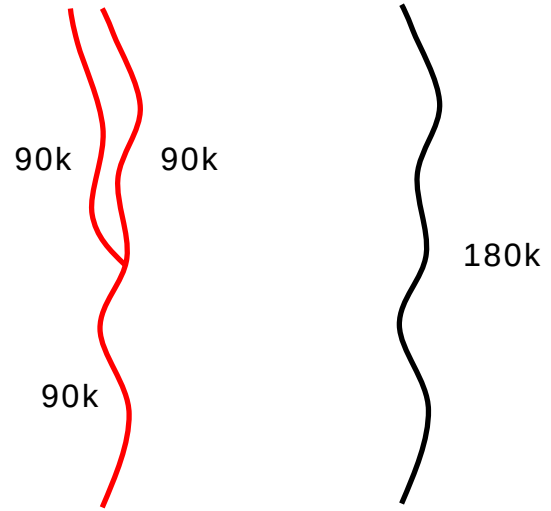

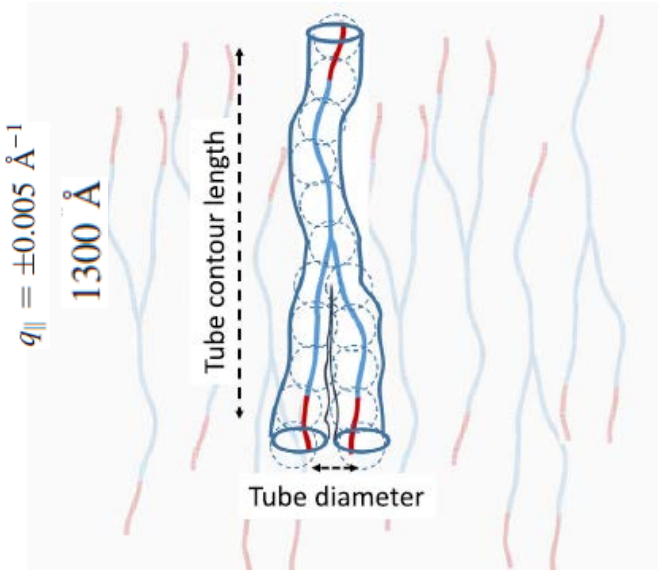

$q_{\perp} = \pm 0.06$ Å^{-1}
100 Å

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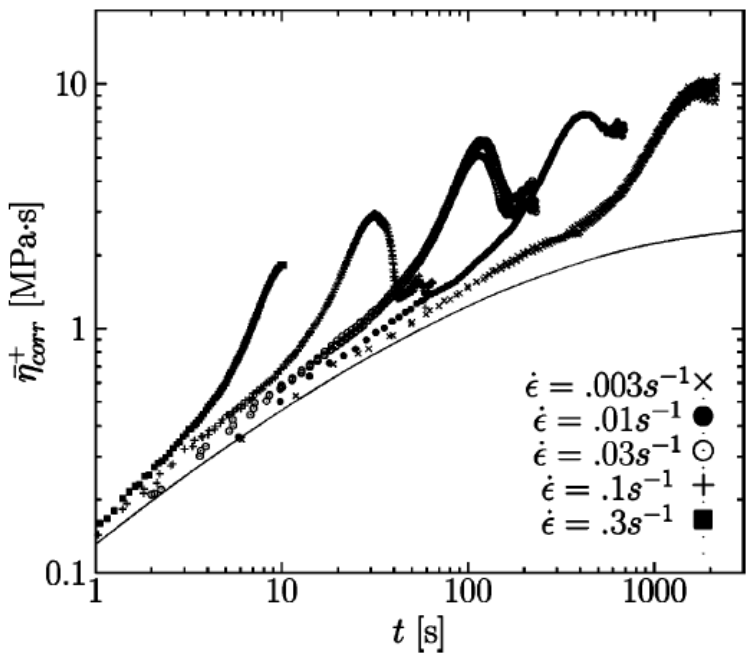
Stress growth coefficient for BASF Lupolen 1840D and 3020D observed with first feedback loop on plate motion:



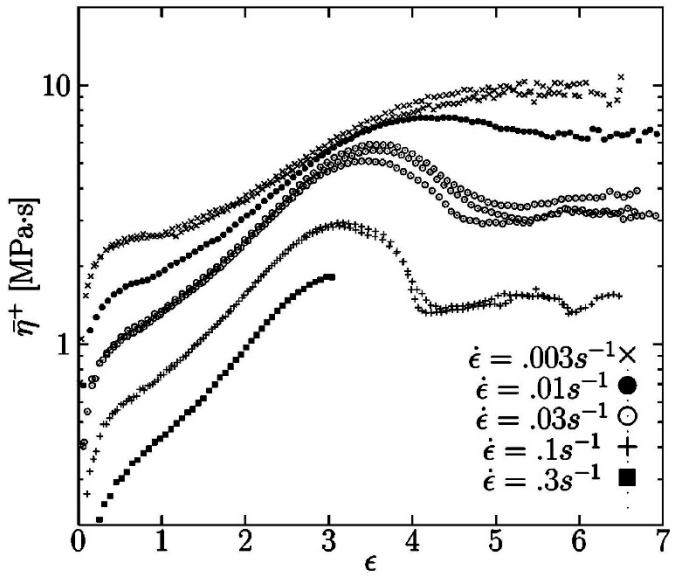


FIG. 1. The uncorrected transient elongation viscosities $\bar{\eta}^+$ of Lupolen 3020D measured at 130 °C, using Eq. (3), shown as a function of the Hencky strain, ϵ. $\bar{\eta}^+$ are measured at five different elongational rates $\dot{\epsilon}$ as shown in the figure.

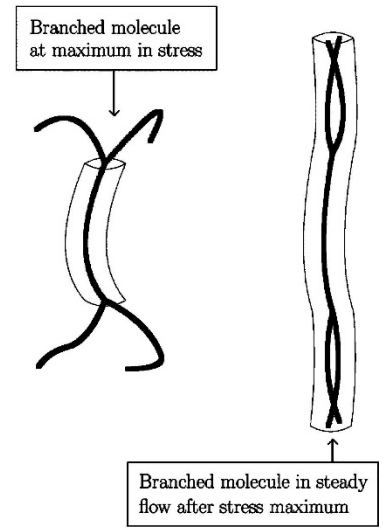
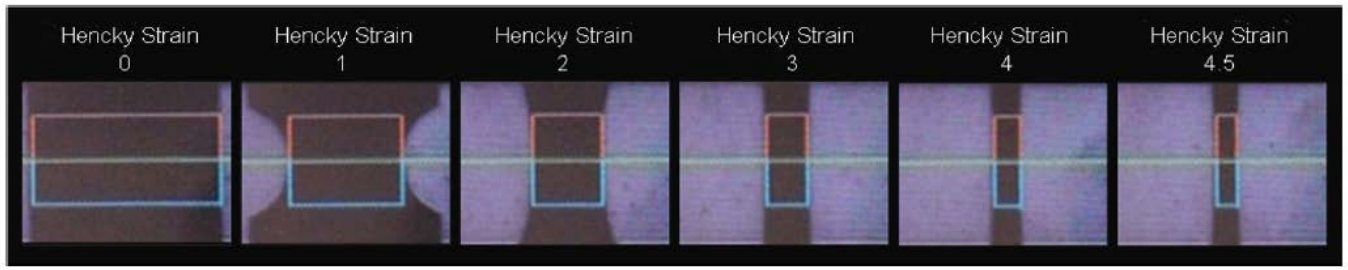


FIG. 6. Interpretation of reduction in stress in terms of Pom-Pom picture. At the maximum in stress, the arms contribute to the tension in the backbone. At steady state, the molecule becomes effectively a linear polymer without arms.



Viscosity overshoot in the start-up of uniaxial elongation of low density polyethylene melts, by H.K. Rasmussen, Nielsen, Bach and Hassager, J. Rheol. (2005)

Creep Measurements Confirm Steady Flow after Stress Maximum in Extension of Branched Polymer Melts

Nicolas J. Alvarez, José Manuel Román Marín, Qian Huang, Michael Locht Michelsen, and Ole Hassager*

FIG. 1. Polyethylene sample before (bottom, diameter 9 mm) and after (top) stretching. The midplane deformation corresponds to a Hencky strain of 6.7. The Hencky strain in the filament midplane is measured on-line by a laser micrometer during the experiment.

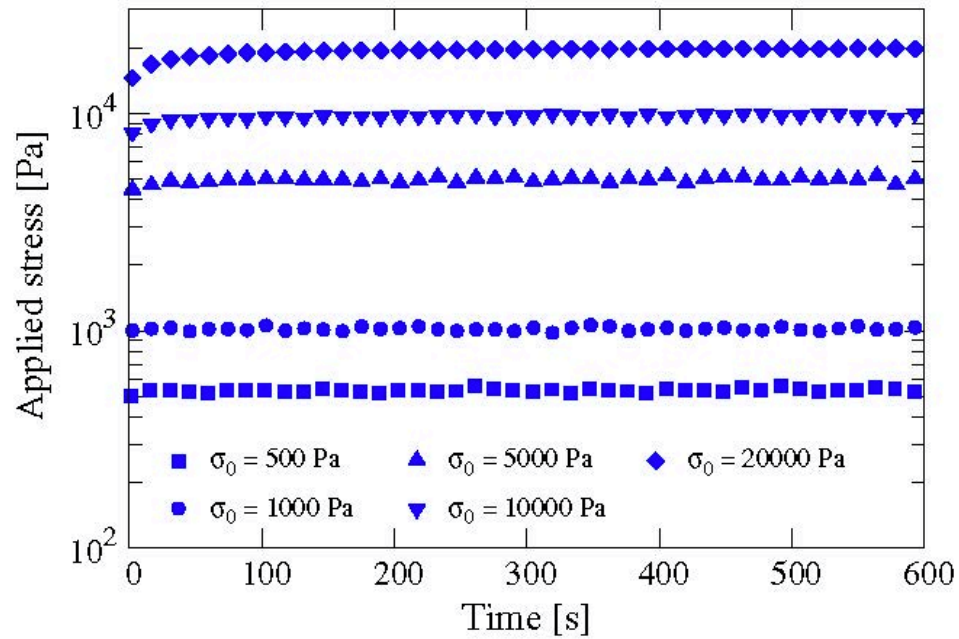
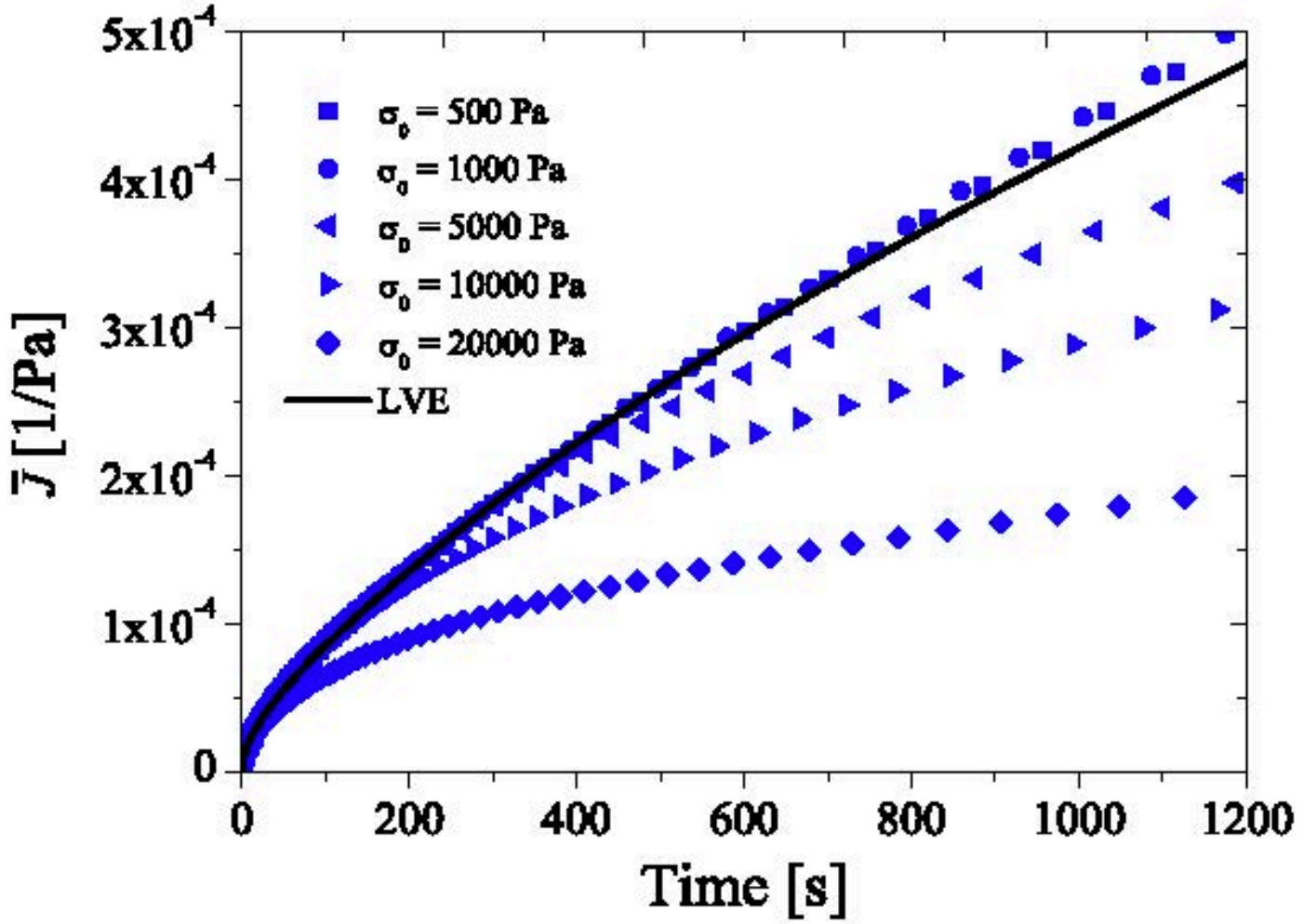


FIG. 2 (color online). Stress in the filament midplane measured as a function of time for five predefined stress levels.

Creep compliance: $J(t) = \epsilon(t)/\sigma$



Compliance: Comparison shear vs. extension:

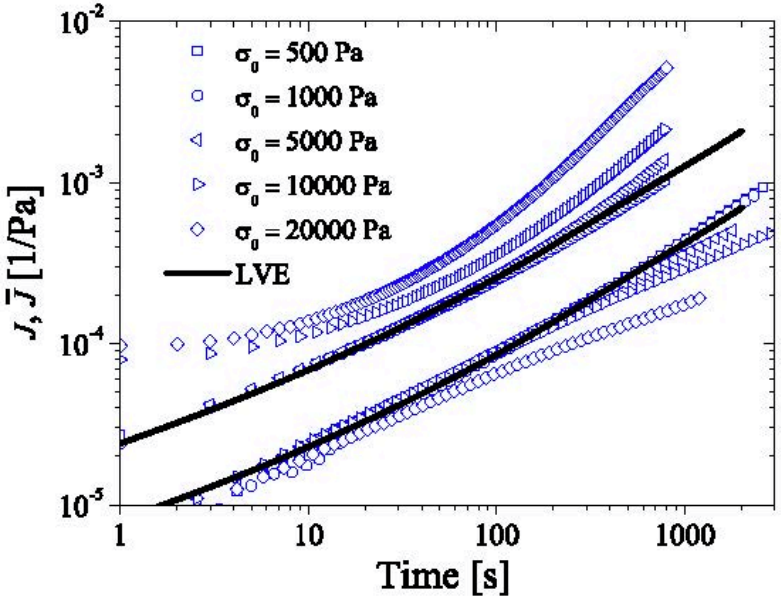


FIG. 3 (color online). Top: Extensional compliance $\bar{J}$ versus time at five applied stresses. Bottom: Comparison of shear compliance (top curves) and extensional compliance versus time for five applied stresses (log-log scales). The solid lines in both graphs correspond to the predicted LVE compliance from Eq. (3).

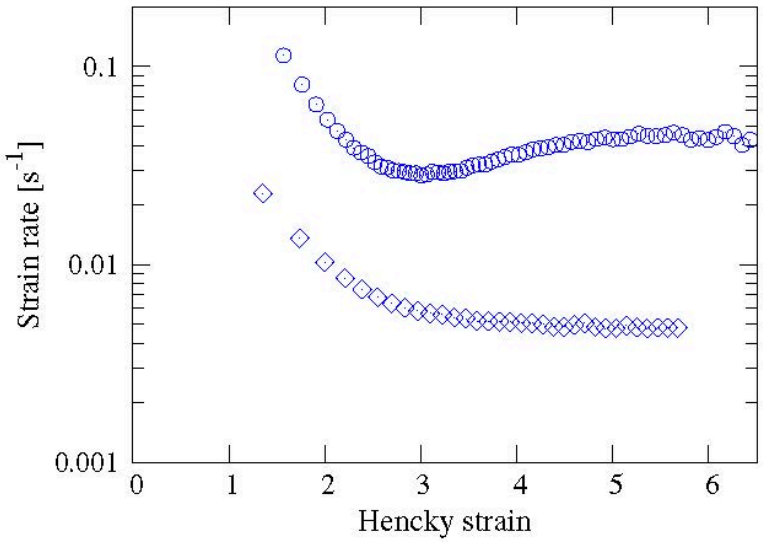


FIG. 4 (color online). Hencky strain rate $\dot{\epsilon}$ as a function of Hencky strain ϵ for constant applied σ_0 equal to 40 kPa (diamonds, bottom) and 150 kPa (circles, top). For σ_0 larger than approximately 80 kPa, the strain rate goes through a minimum before reaching a steady state value.

Comparison constant stress (creep) vs. constant strain rate:

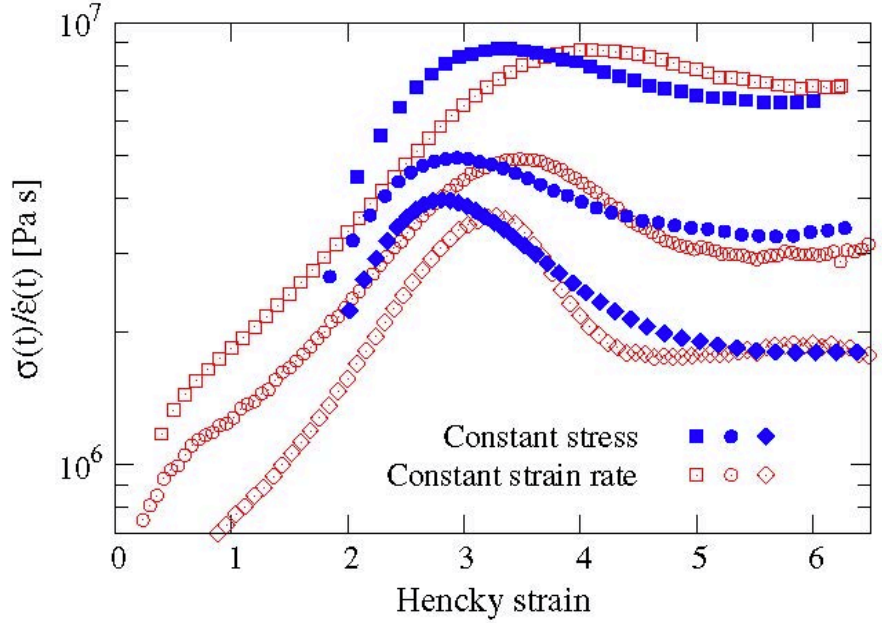


FIG. 5 (color online). $\sigma/\dot{\epsilon}$ as a function of Hencky strain ϵ for constant stress (closed symbols) and constant strain rate (open symbols) experiments. The constant stress experiments correspond to (filled squares) 80, (filled circles) 100, and (filled small diamonds) 200 kPa. The constant strain-rate experiments correspond to (squares) 0.01, (circles) 0.03, and (big diamonds) 0.1 s^{-1}.

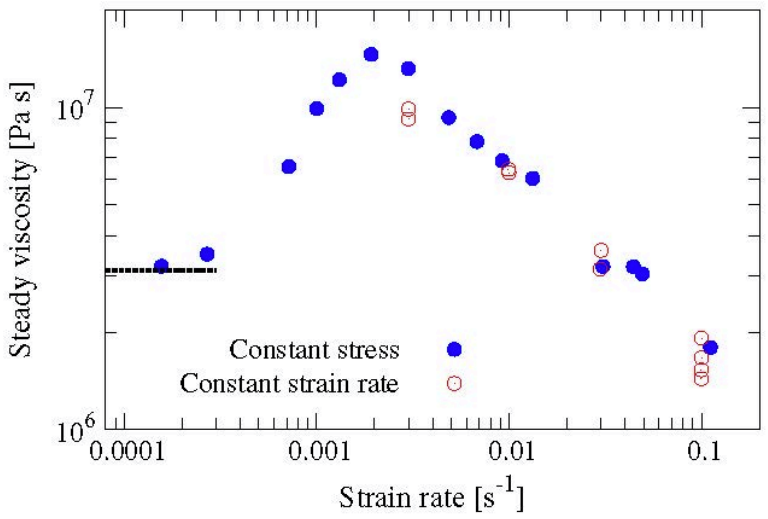


FIG. 6 (color online). Steady viscosity as a function of Hencky strain rate $\dot{\epsilon}$ for constant stress (closed symbols) and constant strain-rate (open symbols) experiments [4]. The dashed line represents the zero shear rate viscosity determined from the LVE.

Alvarez et al., Physical Review Letters, (2013).

Extensional rheology of model polymers

- Linear monodisperse polymers (solutions and melts)
- Branched commercial polymers (LDPE): Extensional viscosity
- Branched model polymers (stars): Extensional viscosity
- Branched model polymers (stars): Small Angle Neutron Scattering (SANS)
- Branched commercial polymers (LDPE): Stress maximum
- Branched commercial polymers (LDPE): Small Angle X-ray Scattering (SAXS)
- Linear commercial polymers: Flow-induced crystallization
- Fracture: The end of rheology?

Small Angle X-ray Scattering (SAXS) top showing overall ”shish-kebab” crystallite structures
Wide Angle X-ray Scattering (WAXS) bottom showing crystal detail

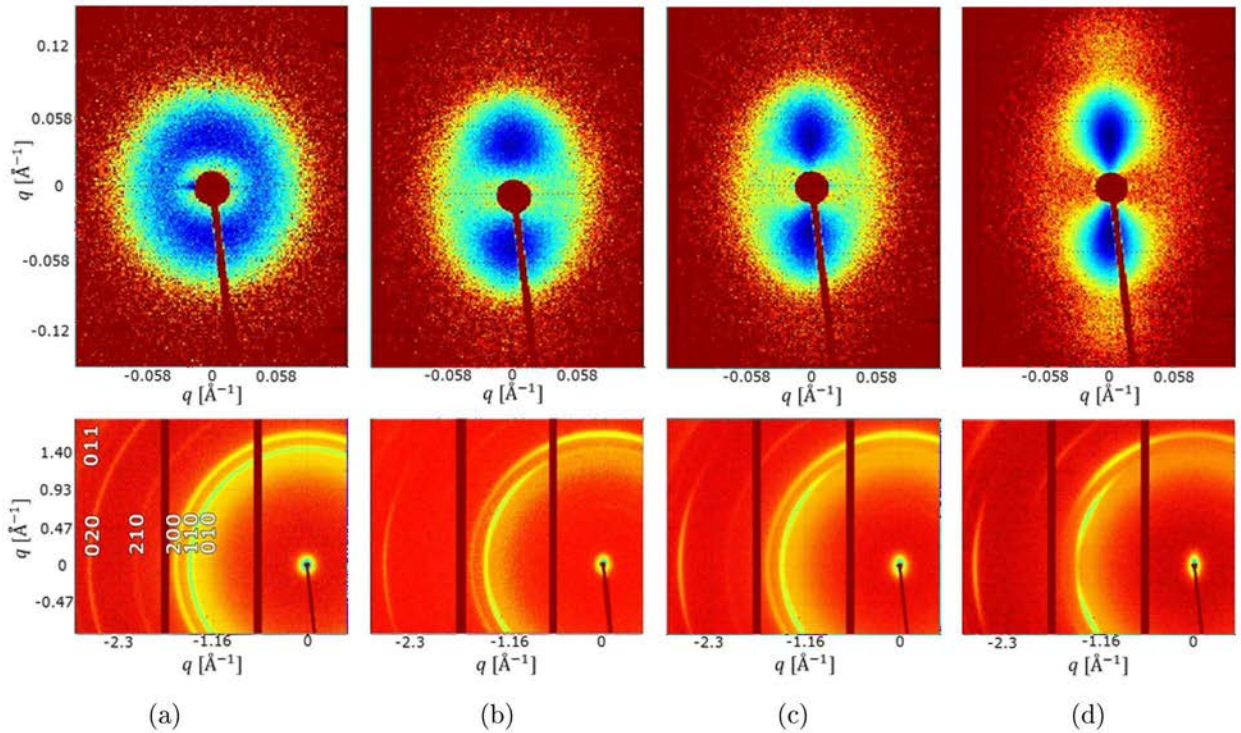
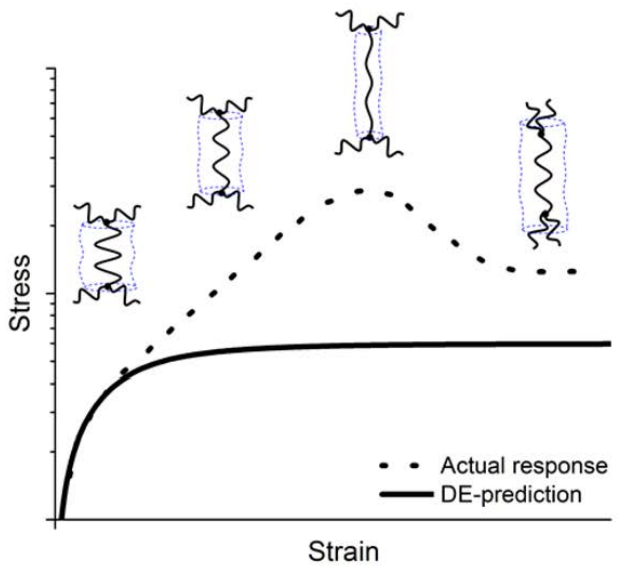
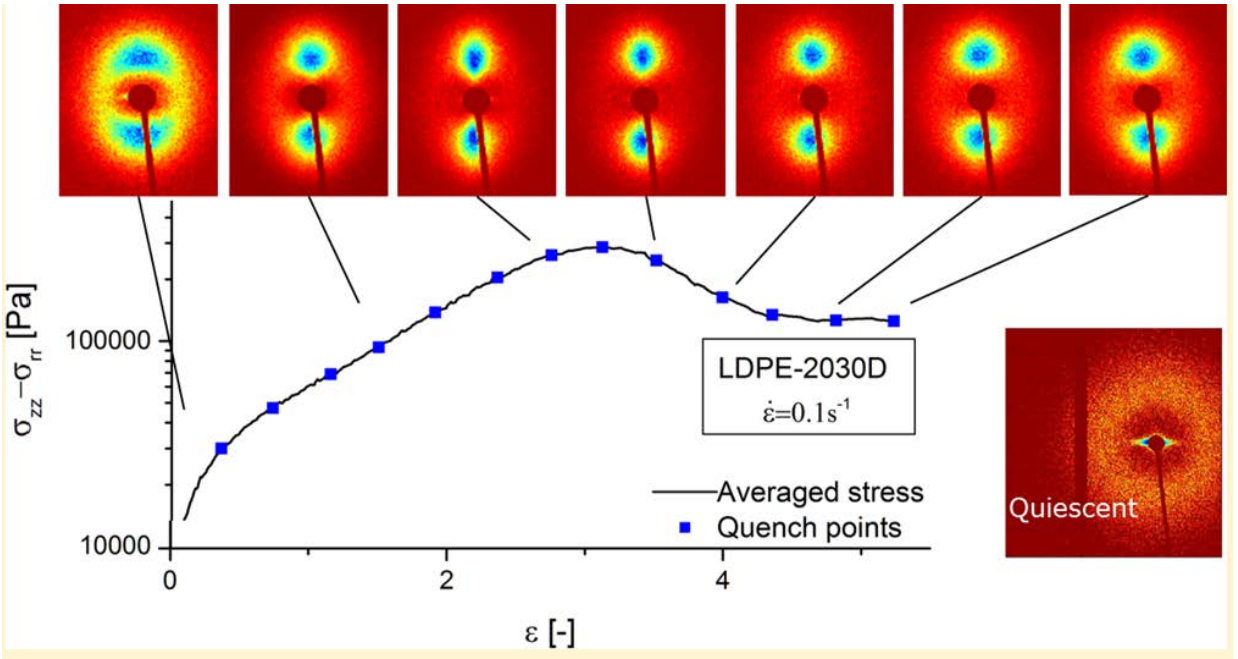


Figure 3. SAXS (top) and WAXD (bottom) patterns of LDPE filaments quenched at various stress (a) 30, (b) 126, (c) 262, and (d) 518 kPa. All filaments have been elongated at T = 130 °C, and flow direction is vertical.

Wingstrand et al., Macromolecules (2017)

SAXS patterns showing maximum crystalline orientation at maximum stress





Wingstrand et al., Macromolecules (2017)

Extensional rheology of model polymers

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- Branched commercial polymers (LDPE): Small Angle X-ray Scattering (SAXS)
- Linear commercial polymers: Flow-induced crystallization
- Fracture: The end of rheology?

Extensional flow can lead to crystallization 26C above equilibrium melting temperature.

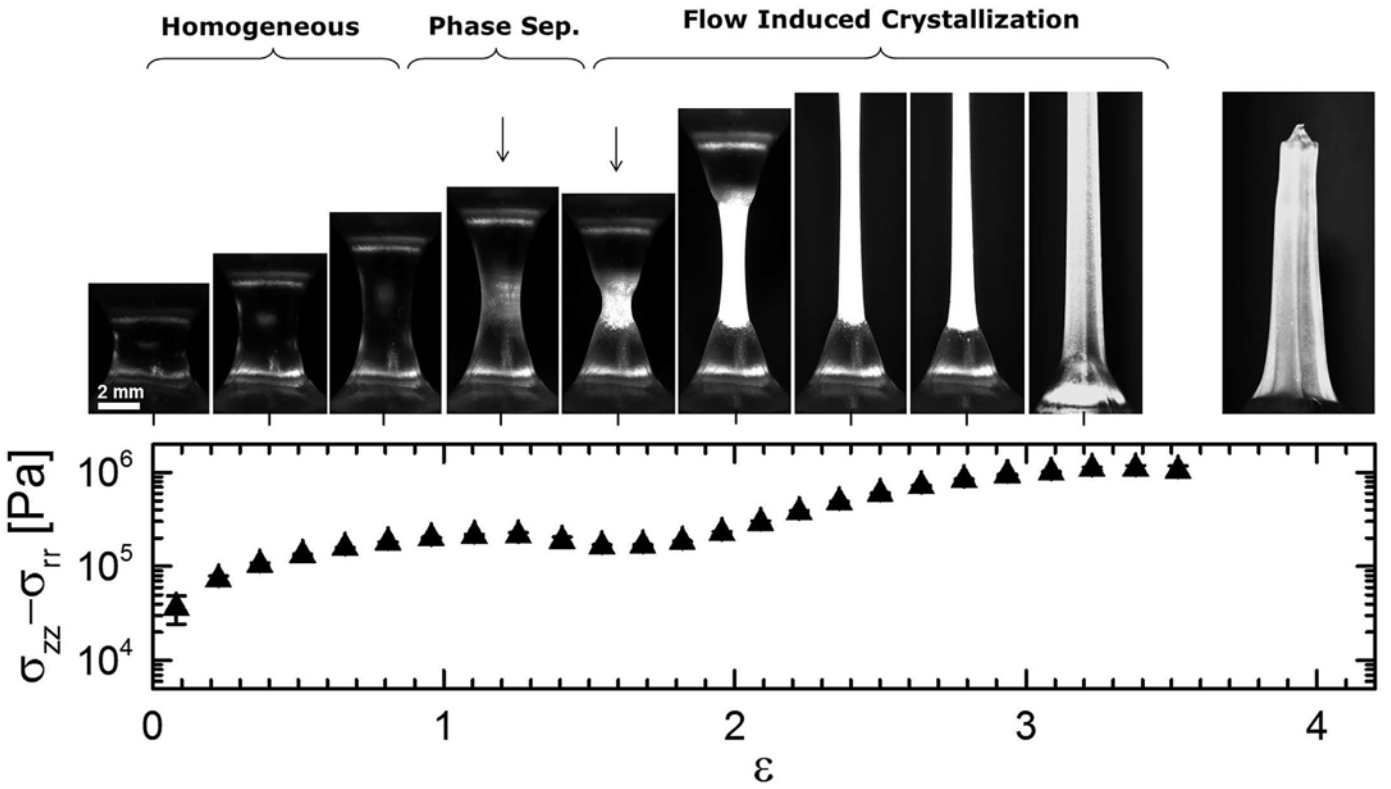


Fig. 8. Example of FIC for stretch experiments performed at 150 °C. The sample is PE/PO-29 stretched at $\dot{\varepsilon} = 0.1\ s^{-1}$. Images are collected through crossed polarizers with light source and camera on the same side. Arrows above image 4 and 5 indicate the strain range in which the onset of FIC occurs. The two images to the far left are taken from a replica of the stretch.

Extensional rheology of model polymers

- Linear monodisperse polymers (solutions and melts)
- Branched commercial polymers (LDPE): Extensional viscosity
- Branched model polymers (stars): Extensional viscosity
- Branched model polymers (stars): Small Angle Neutron Scattering (SANS)
- Branched commercial polymers (LDPE): Stress maximum
- Branched commercial polymers (LDPE): Small Angle X-ray Scattering (SAXS)
- Linear commercial polymers: Flow-induced crystallization
- Fracture: The end of rheology?

Definition of Fracture of a fluid by Ligoure and Mora:

« the fracture of a fluid due to mechanical deformation, including flow, can be understood as a dissipation of ***bulk*** elastic energy into breaking of physical or chemical bonds." This definition excludes the hydrodynamic instabilities observed also in inviscid or Newtonian fluids. »

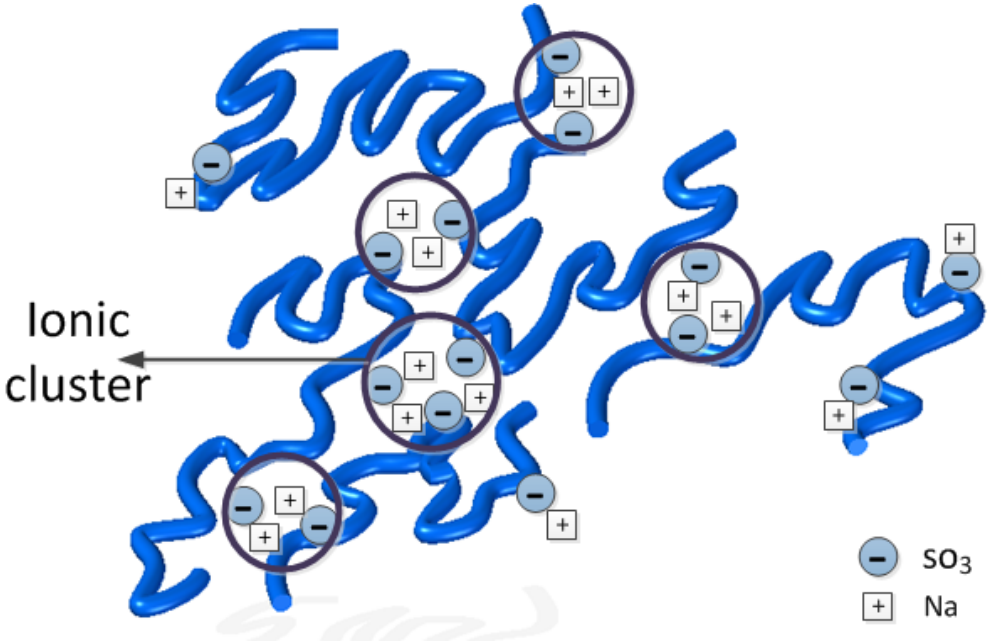
Fractures in complex fluids : the case of transient networks » Christian Ligoure and Serge Mora**,** Rheologica Acta, **52**, p 91-114 (2013)

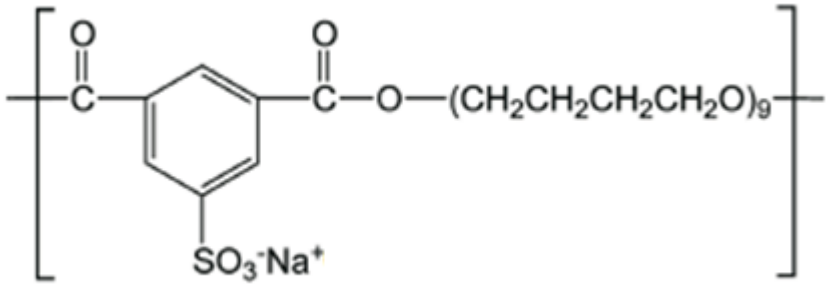
As opposed to necking, fracture is:

- Not axisymmetric
- Not predictable from linear stability analysis
- Local and fast
- Not described by the conservation equations and constitutive equations alone, but requires some ansats on conditions in front of crack tip.

Example 1: (ionomers)

- Ionic groups attached to the polymer backbone.
- Bulk properties governed by ion-clusters.
- Strong dipolar interaction between the ion-pairs results in the formation of ionic aggregrates.



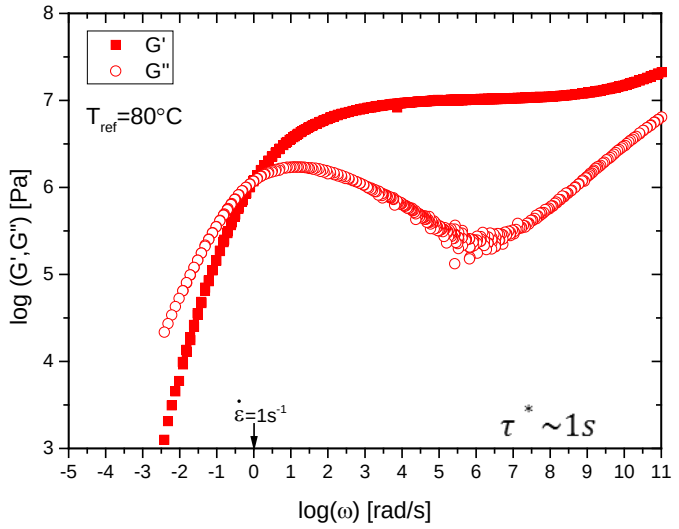


PTMO ionomer supplied by Ralph Colby

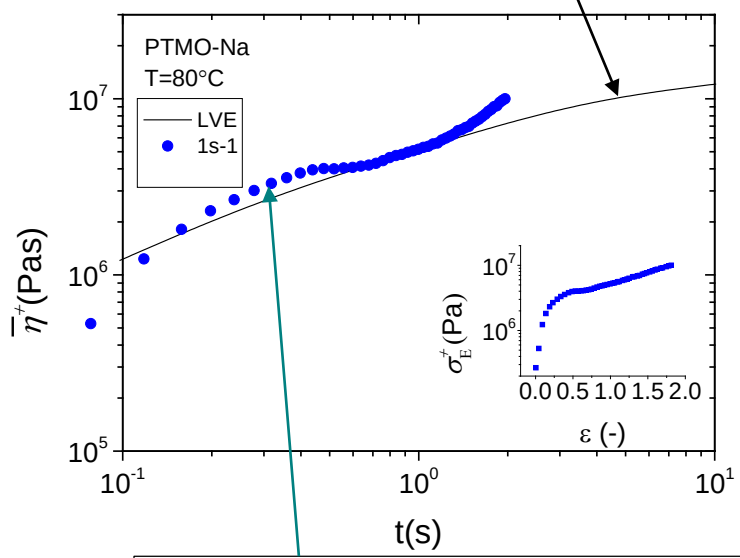
Chen et al., Macromolecules 2014, 47, 3635−3644

The linear viscoelastic envelope:

$$\boldsymbol{\sigma}(t) = \int_{t'=-\infty}^{t} G(t-t')\,\dot{\boldsymbol{\gamma}}(t')dt'$$



Small Amplitude Oscillatory Shear



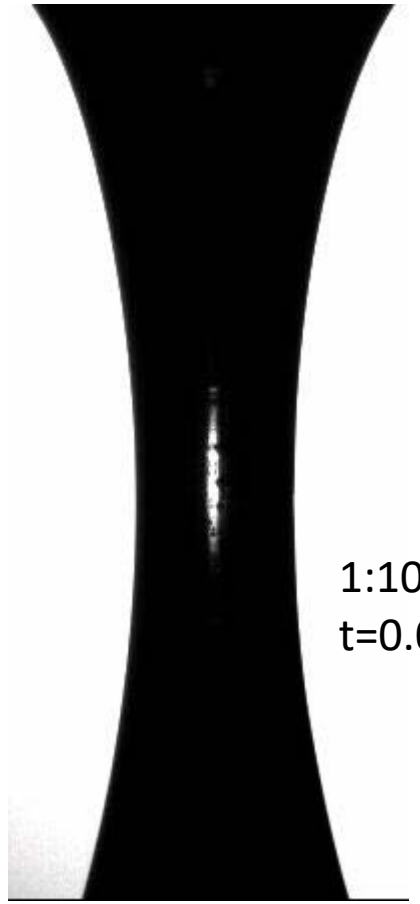
Extensional stress growth coefficient

Rheological data 80C

Brittle fracture in Ionomer melt

1:5
t=0.45s

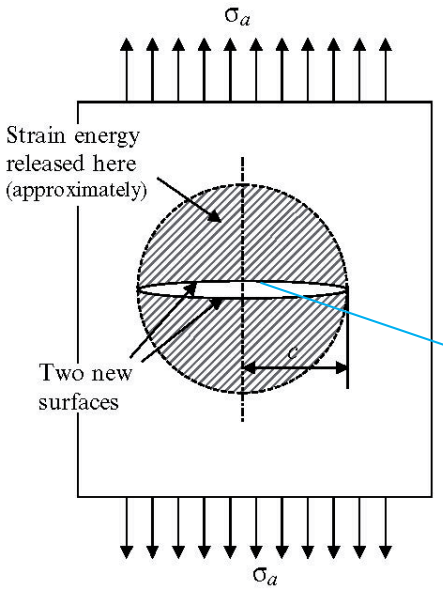
PTMO-Na, T=60C
Extensional rate 1s-1.



1:10000
t=0.0086s

PTMO-Na supplied by Ralph Colby

Griffith energy balance for solids:

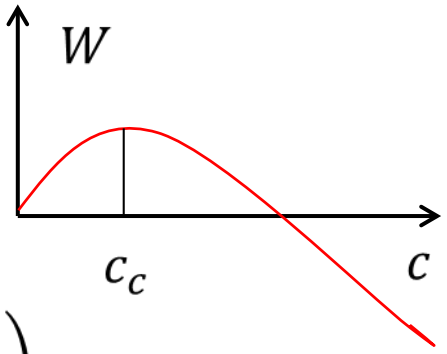


Energy balance per crack tip:

$$W = W_s - W_e$$

$$= 2\,F_s c - \frac{\pi\sigma^2 c^2}{2\,E}$$

$$= 2\,F_s c - (\pi c^2)\left(\frac{\sigma^2}{2\,E}\right)$$



Strain energy density

$$\frac{dW}{dc} = \frac{dW_s}{dc} - \frac{dW_e}{dc} = 0 \quad \text{for} \quad c_c = \frac{2\,F_s\,E}{\pi\,\sigma^2}$$

The Griffith length.

$$\frac{dW_e}{dc} \stackrel{\text{def}}{=} G$$

The strain energy release rate per crack tip

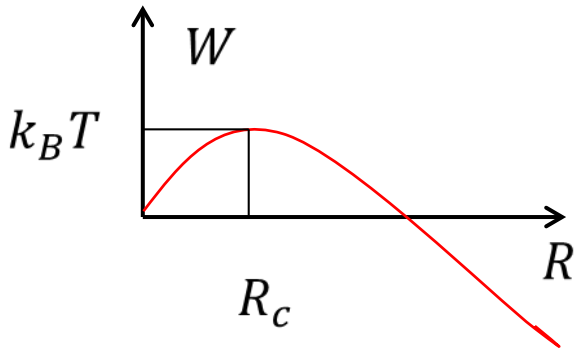
Griffith-Pomeau energy condition:

3D disk-like crack radius R:

$$W = \frac{\pi}{2} R^2 F_s - \frac{\pi R^3}{3}\left(\frac{\sigma^2}{2E}\right)$$

Strain energy density:

$$\frac{\sigma^2}{2E} = r \int_0^{\epsilon_c} (\sigma_{zz} - \sigma_{rr}) d\varepsilon = rA$$



$$F_S = (2\, k_B T (rA)^2)^{1/3}$$

$$R_c = \frac{F_S}{rA}$$

Now the critical energy input becomes a material property!

Pomeau, C.R. Acad. Sci. Ser. II 314, 553 (1992)

H. Tabuteau et al. Phys. Rev. Lett., 102, 155501 (2009)

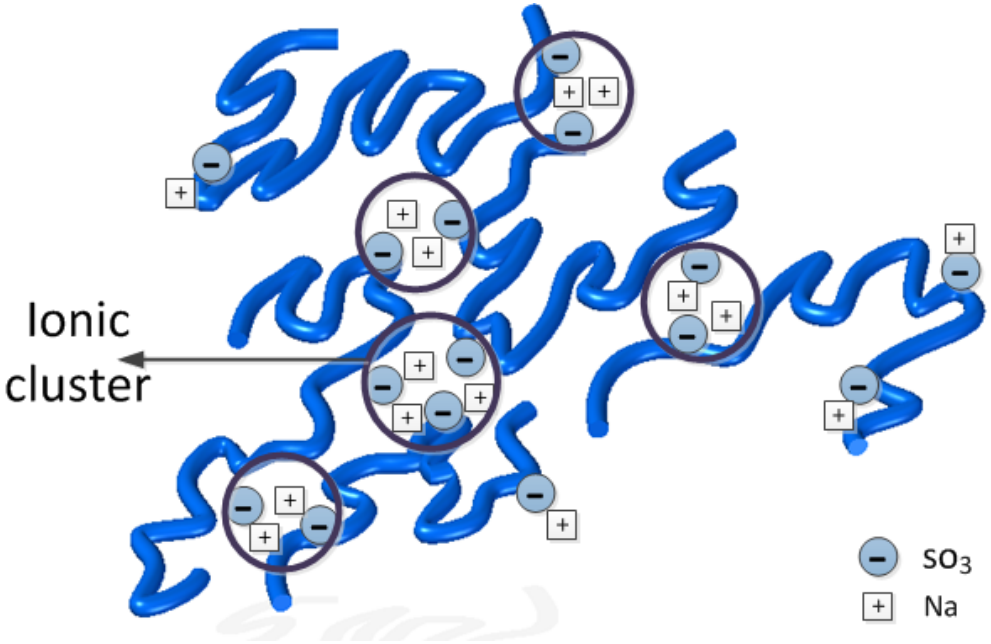
Griffith-Pomeau theory of brittle fracture

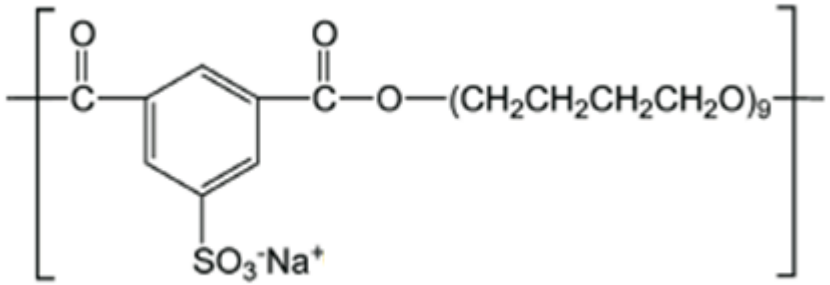
PTMO-Na ionomer

60C		80C	
Kb	1.38065E-23	Kb	1.38E-23
T	333K	T	353K
r	0.923356447	r	0.659699
E	7005357.425Pa	E	9827835Pa
Fs	0.007308988Jm^{-2}	Fs	0.007464Jm^{-2}
Rc	1.13nm	Rc	1.15nm

(ionomers – again:)

- Ionic groups attached to the polymer backbone.
- Bulk properties governed by ion-clusters.
- Strong dipolar interaction between the ion-pairs results in the formation of ionic aggregrates.

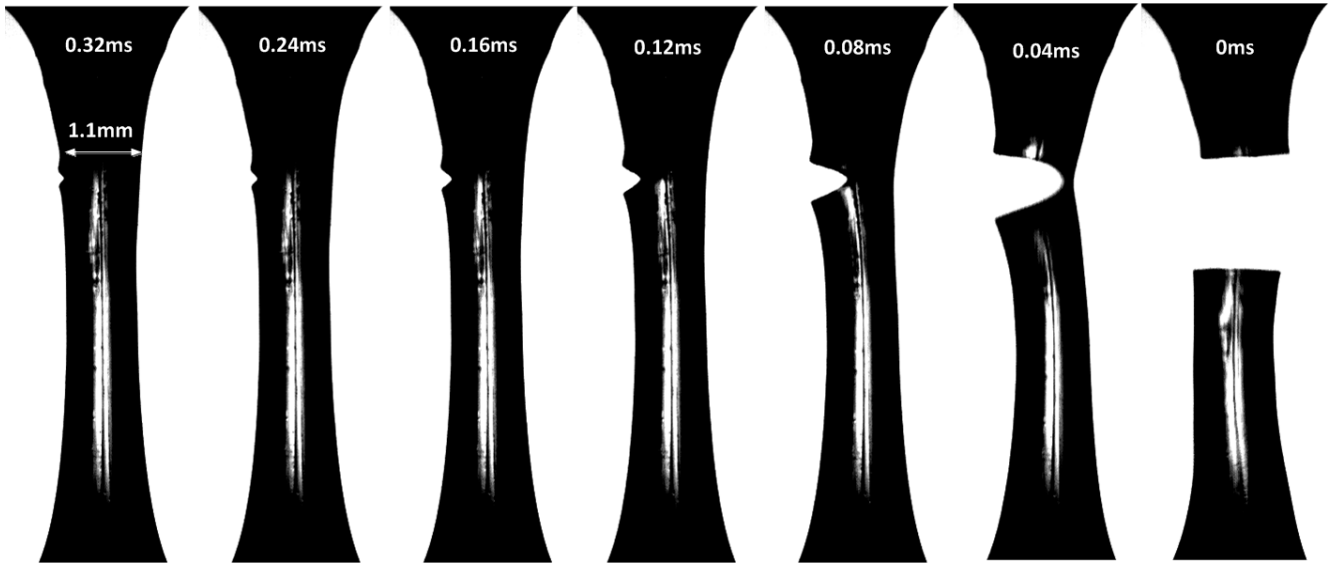


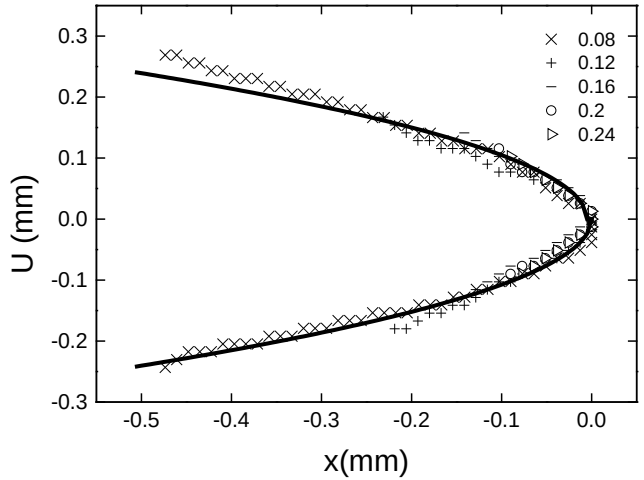


PTMO ionomer supplied by Ralph Colby

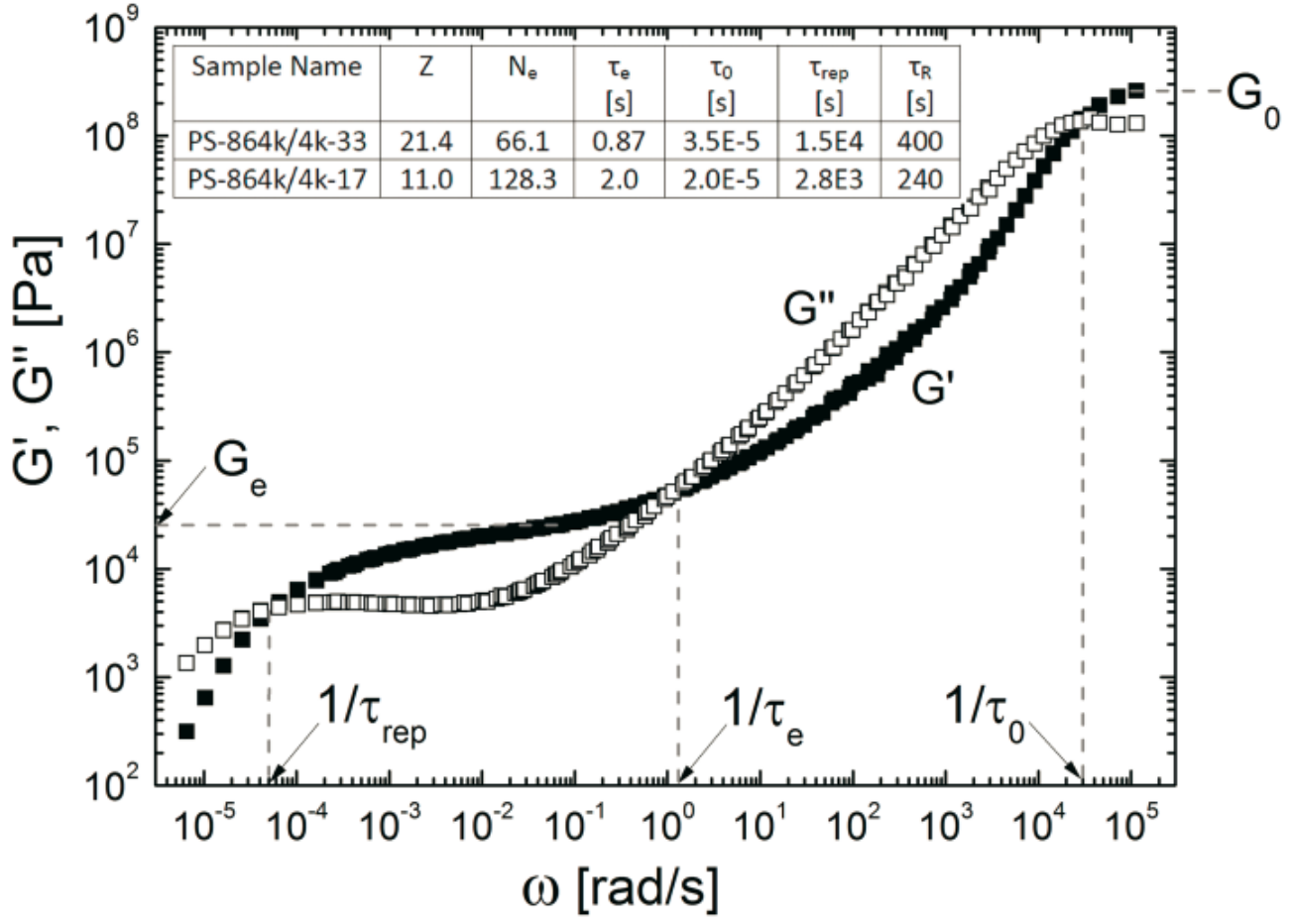
Chen et al., Macromolecules 2014, 47, 3635−3644

Fracture profile at 80C



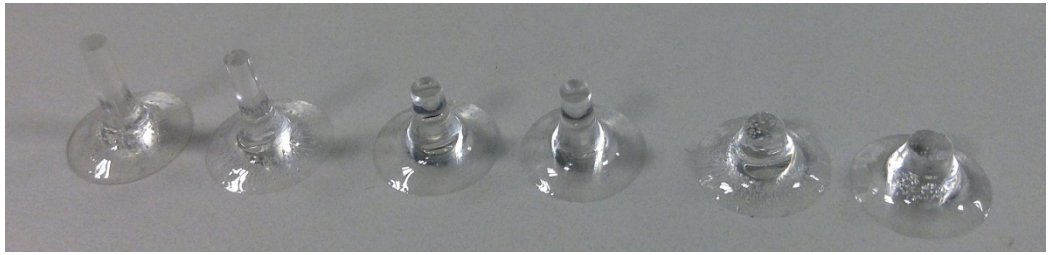


Example 2:
Fracture in mono-disperse polymer systems.

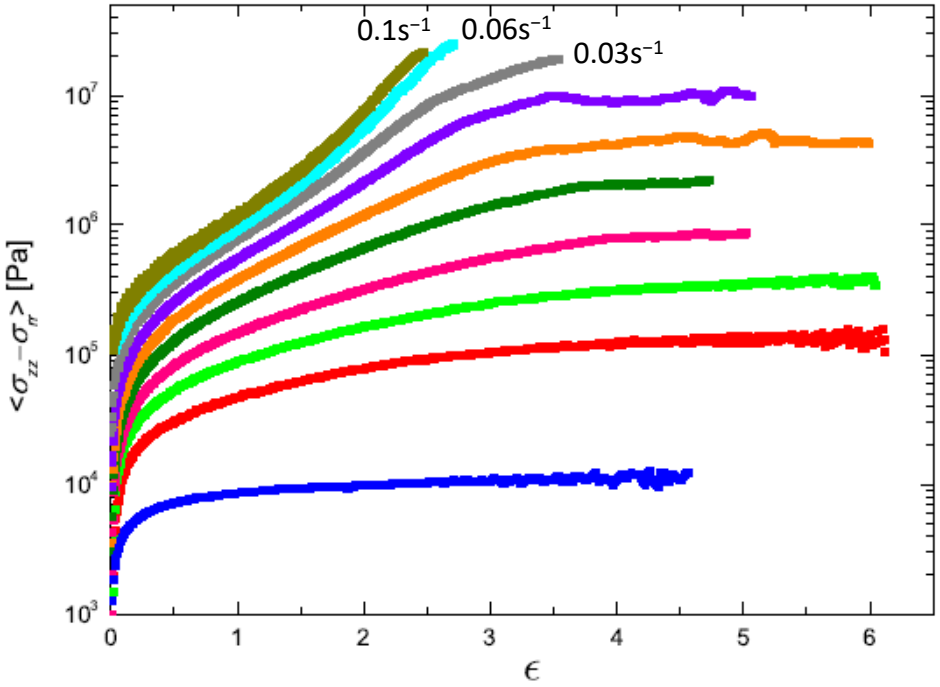


PS Melt – CAS 0993-53-6 (M_w=230k, *PDI*=3.7)

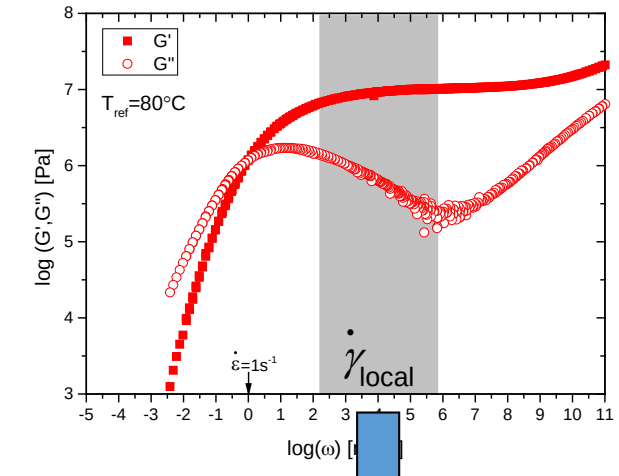
Stretch rate at 120°C (from left to right): 0.03, 0.06, 0.1s^{-1}

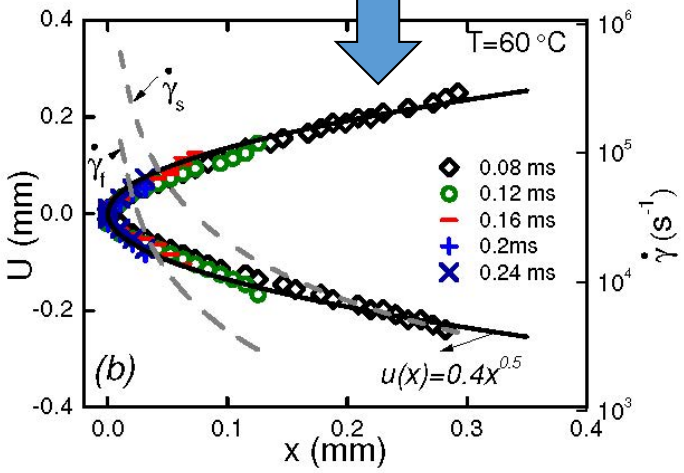


FSR extension at 120°C:

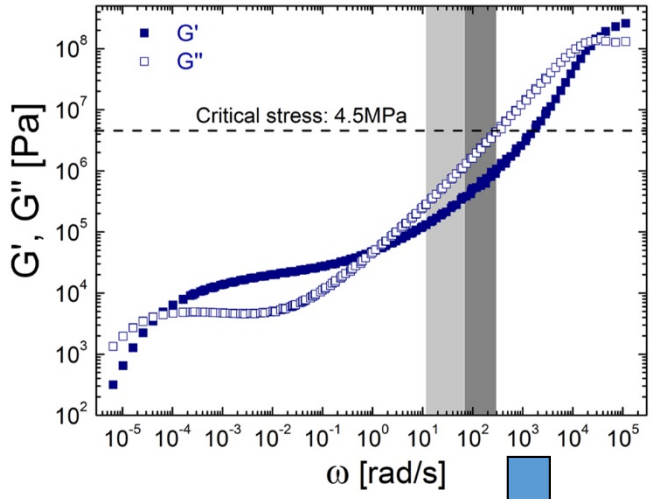


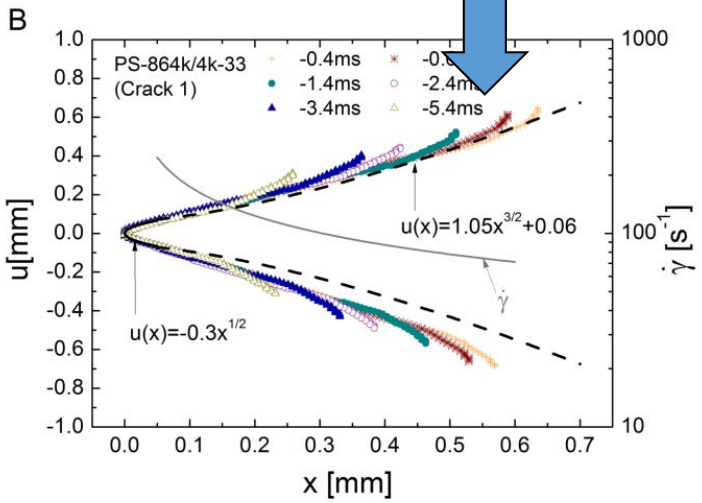
Ionomer





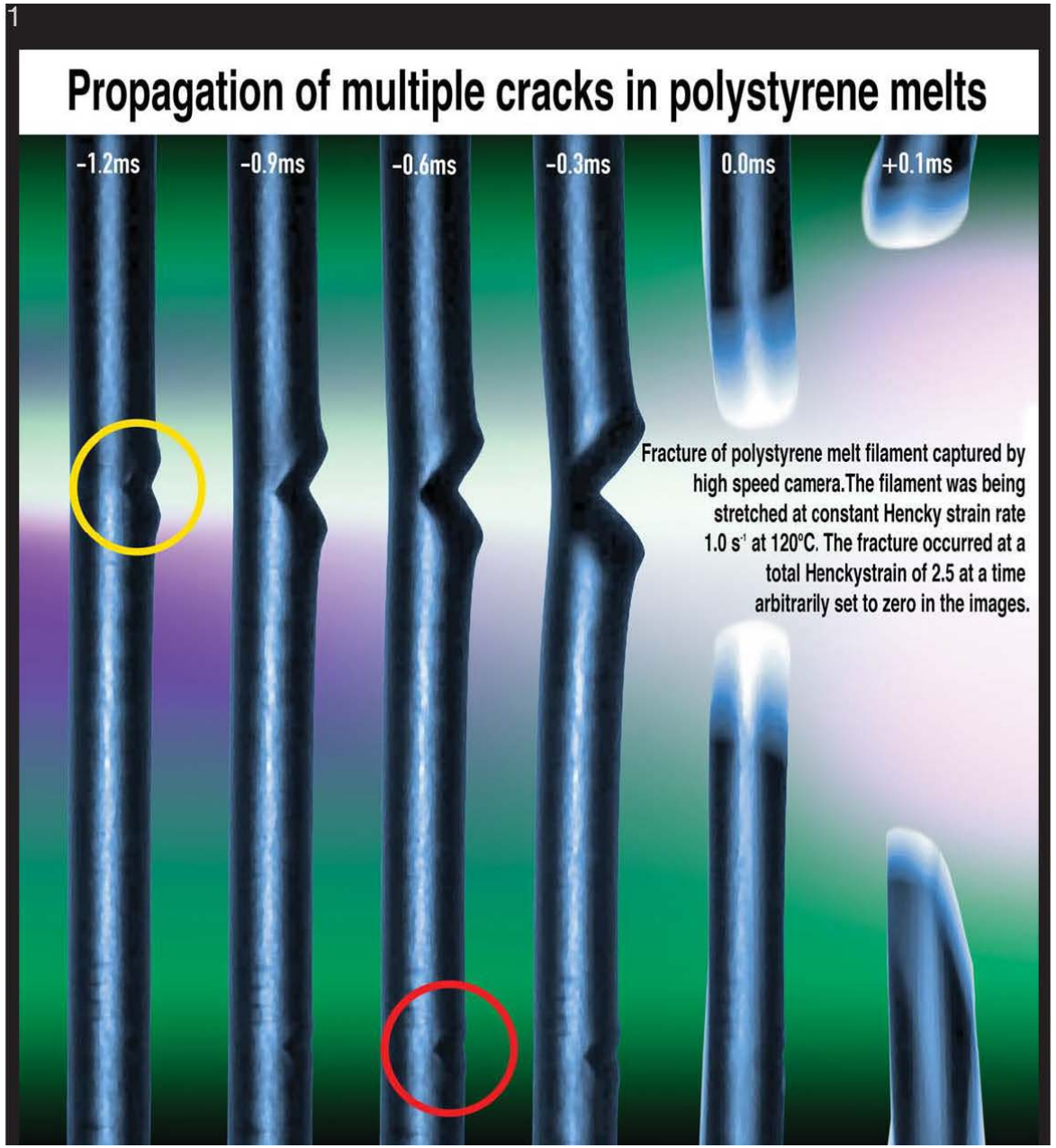
Entangled Polymer Solution





Huang et al, Physical Review Letters (Aug. 15, 2016)

Shabbir et al., Soft Matter, 2016, DOI: 10.1039/C6SM01441K



The observation of simultaneous fracture at two different spatial points is nearly impossible in a "weakest link" scenario.
Fineberg, *Physics* (2016)

Huang et al., poster, SoR Denver (2017)
Huang et al., PRL (2016)