



Polymer Rheology

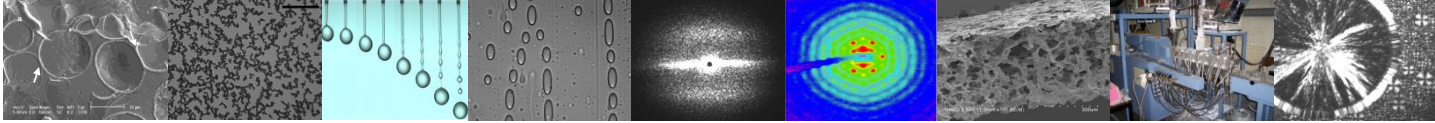
P. Moldenaers

August 21, 2019

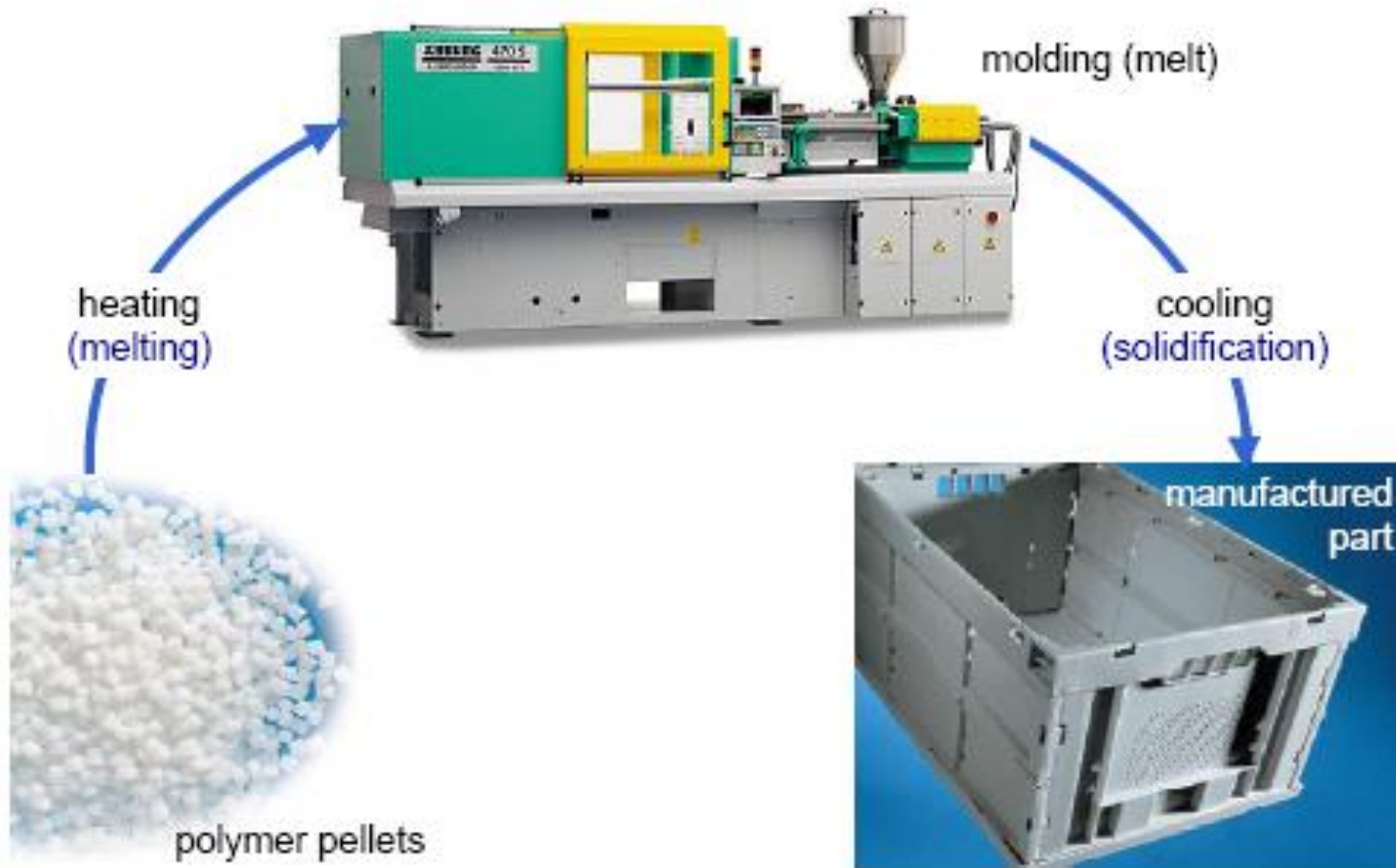
Soft Matter, Rheology and Technology (SMaRT)

Department of Chemical Engineering

KU Leuven, Belgium

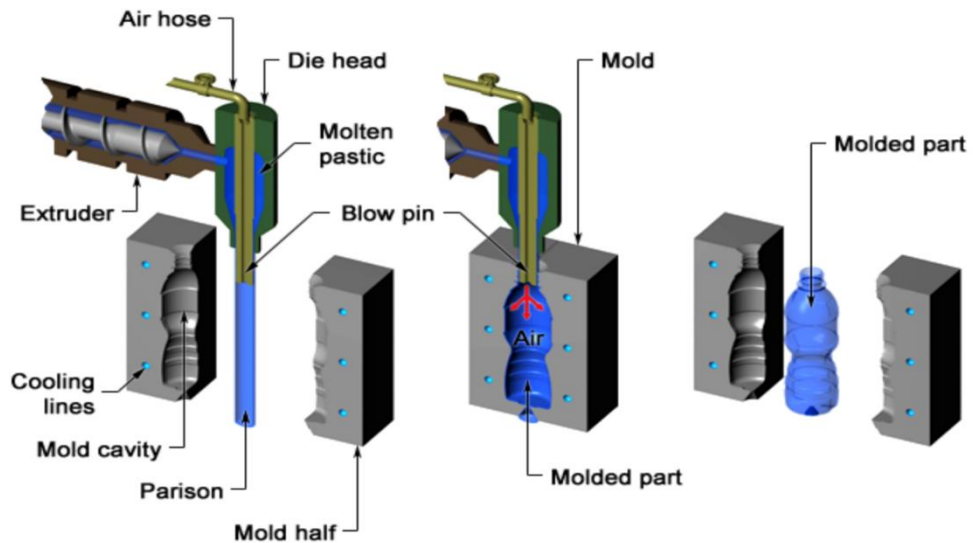


The context: Polymer processing operations



Complexity of processing operations

- e.g. extrusion blow moulding

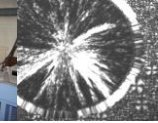
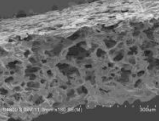
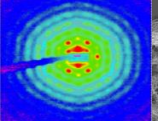
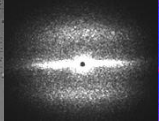
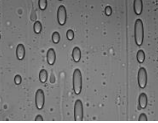
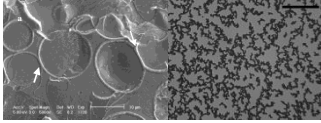


- extrusion** – shear viscosity
- parison** – die swell - sagging
- blowing** – extensional viscosity
- solidification** - crystallization

- processing behaviour to a large extent determined by the rheology

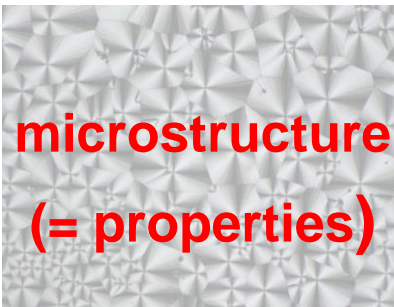
<https://www.youtube.com/watch?v=oY7hyuMHm68>

<http://www.custompartnet.com/wu/blow-molding>



Competition of time-scales

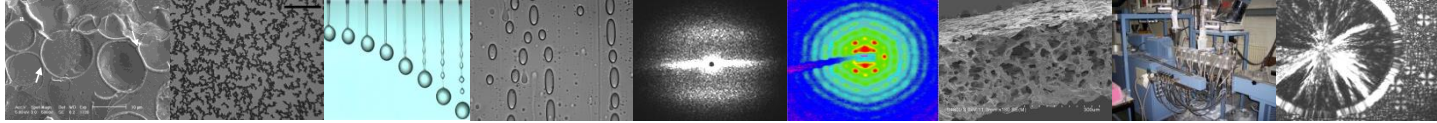
intrinsic material time-scale
(relaxation time spectrum)



processing time-scale
(flow rate, flow time)

thermal time-scale
(cooling rate)

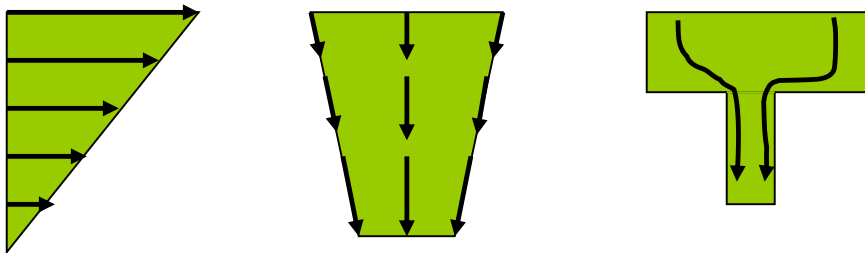




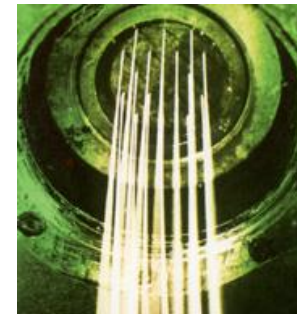
Polymer processing operations

- flow properties: melt is visco-elastic

→ shear flow and elongational flow (-> often combined)



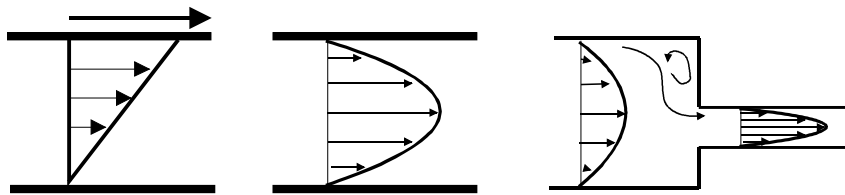
→ f (shear/elongational rate, temperature, pressure, molecular weight distribution, molecular architecture, ...)



Rheometry: classification

⇒ kinematics: shear versus elongational flows

⇒ homogeneous – non-homogeneous – complex flows



⇒ type of straining:

- small : $G'(\omega)$, $G''(\omega)$, $\eta(t)$, $G(t)$, σ_y

- large : $G'(\omega, \gamma)$, $G''(\omega, \gamma)$, $\eta(t, \gamma)$, $\eta(t, \gamma)$, $G(t, \gamma)$, $\eta(t, \varepsilon)$

- steady : $\eta(\text{shear rate})$, $\Psi_1(\text{shear rate})$

⇒ shear rheometry: drag versus pressure driven flows

Rheometry: classification

⇒ kinematics: shear versus elongational flows

Shear flow has received far more attention in literature than elongational flow

For shear flow wide range of experimental techniques is available to determine impact of flow on morphology (see further)

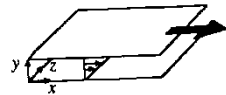
- Rheological
- Rheo-optical

Elongational flow is the dominant deformation mechanism in many processing operations

Often part of more “complex” flows such as entrance flow in capillary die

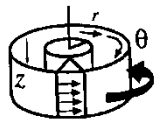
Rheometry: shear flow geometries

Sliding plates



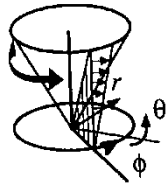
x y z

Couette



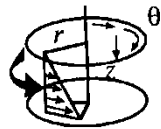
θ r z

Cone and Plate



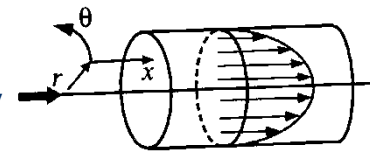
ϕ θ r

Parallel plates



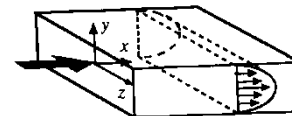
θ z r

Capillary



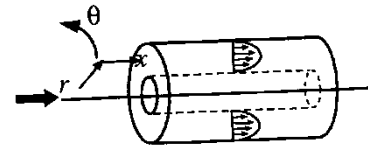
x r θ

Slit



x y z

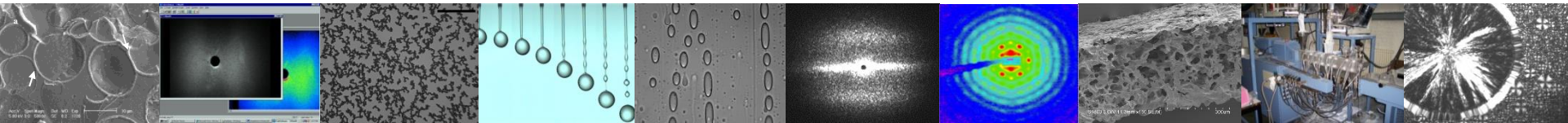
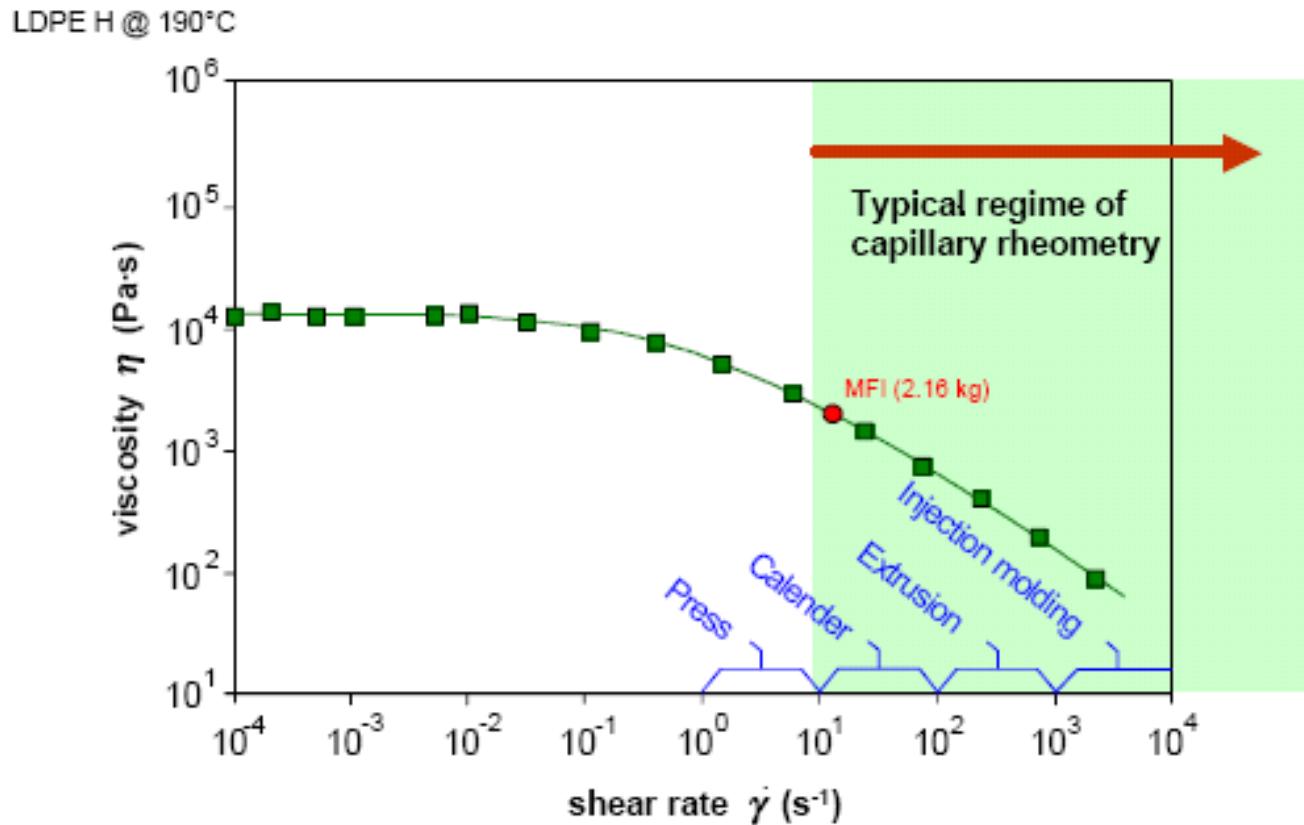
Annulus

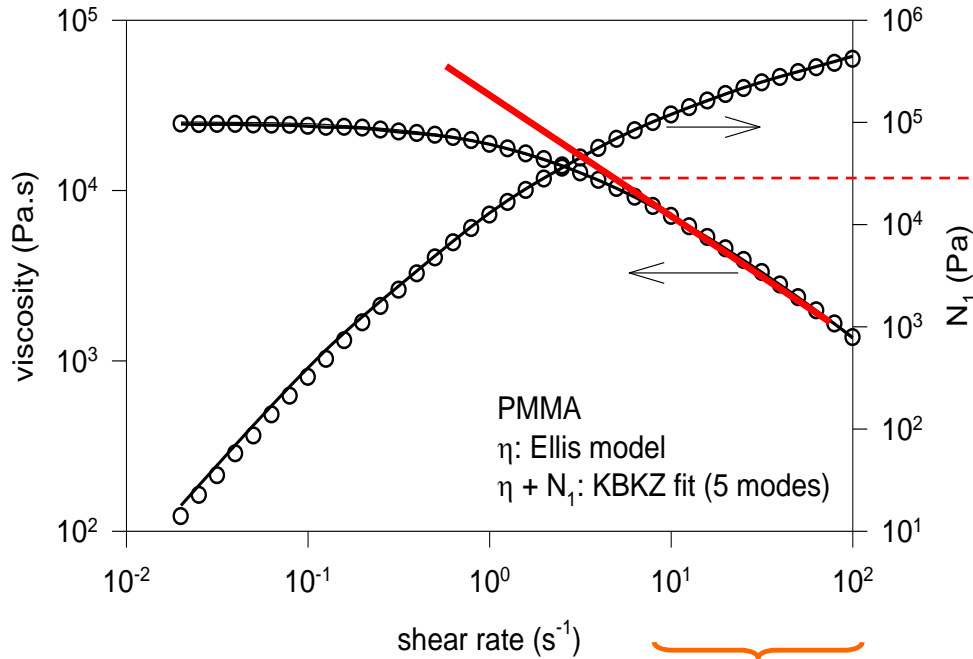


x r θ

Effect of shear rate

In polymer processing, **shear thinning** is well documented for polymeric melts under processing conditions



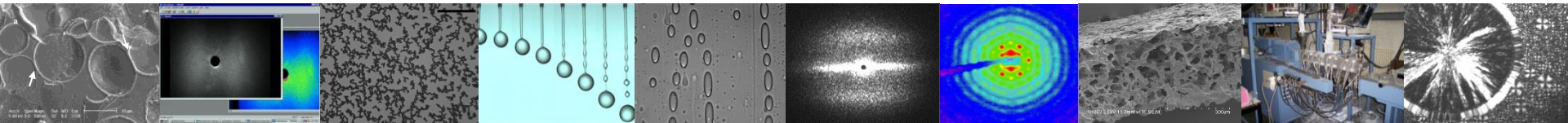


Various models:

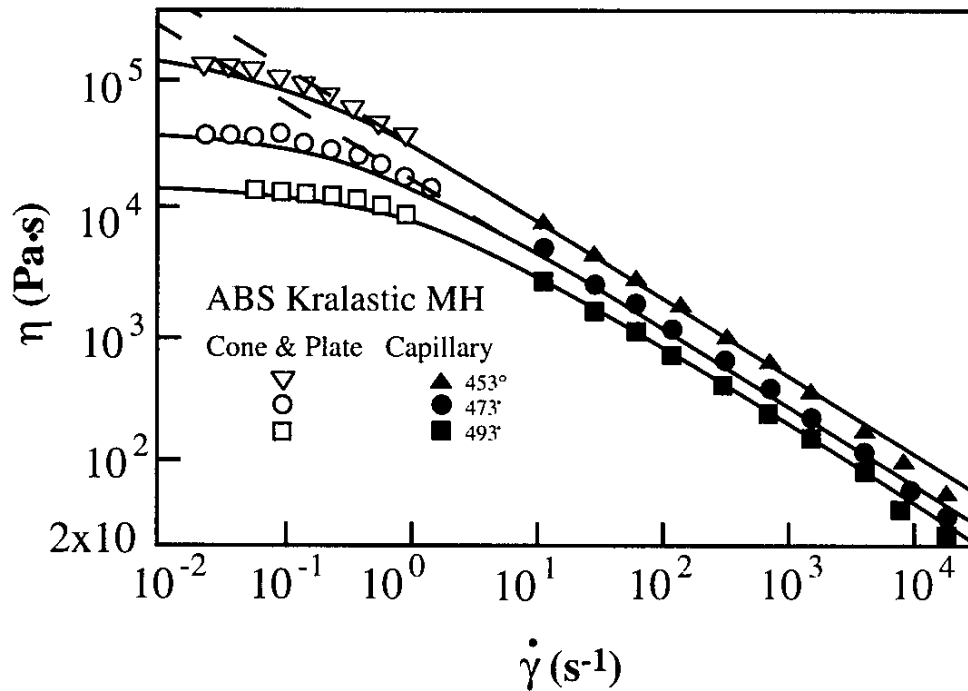
- power law: $\eta = m \cdot \dot{\gamma}^{n-1}$
- general (Ellis model):

$$\frac{\eta}{\eta_0} = \frac{1}{1 + k \cdot \dot{\gamma}^{1-n}}$$

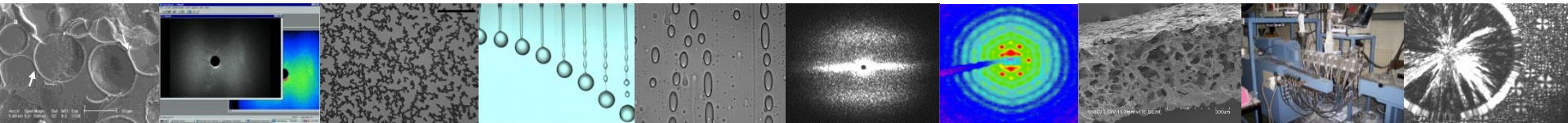
- typical processing shear rates
- injection moulding: 100-10000 s⁻¹
 - extrusion (barrel): 10-500 s⁻¹



Time-temperature superposition (WLF)



$$\log\left(\frac{\eta_{T_r} \rho_r}{\eta_r T \rho}\right) = \frac{-C_1(T - T_r)}{C_2 + T - T_r} = \log(a_T)$$



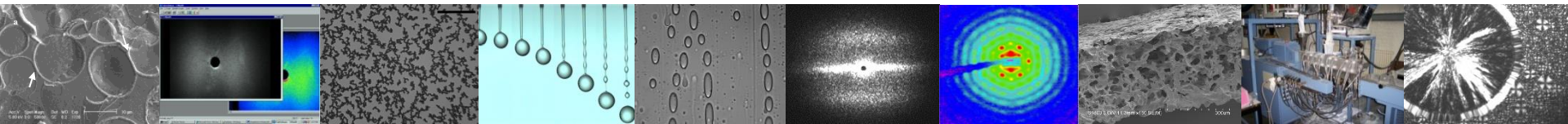
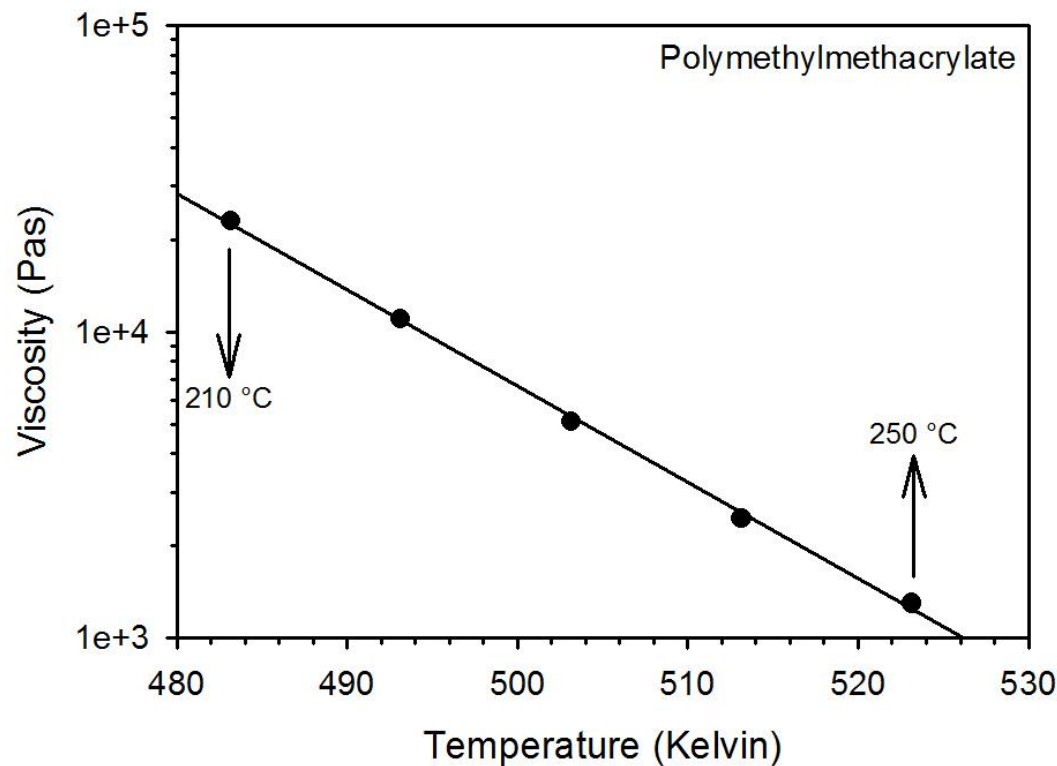
Temperature dependence of the zero-shear viscosity of polymeric melts can be described with the Arrhenius equation or with an exponential relation

Arrhenius equation:

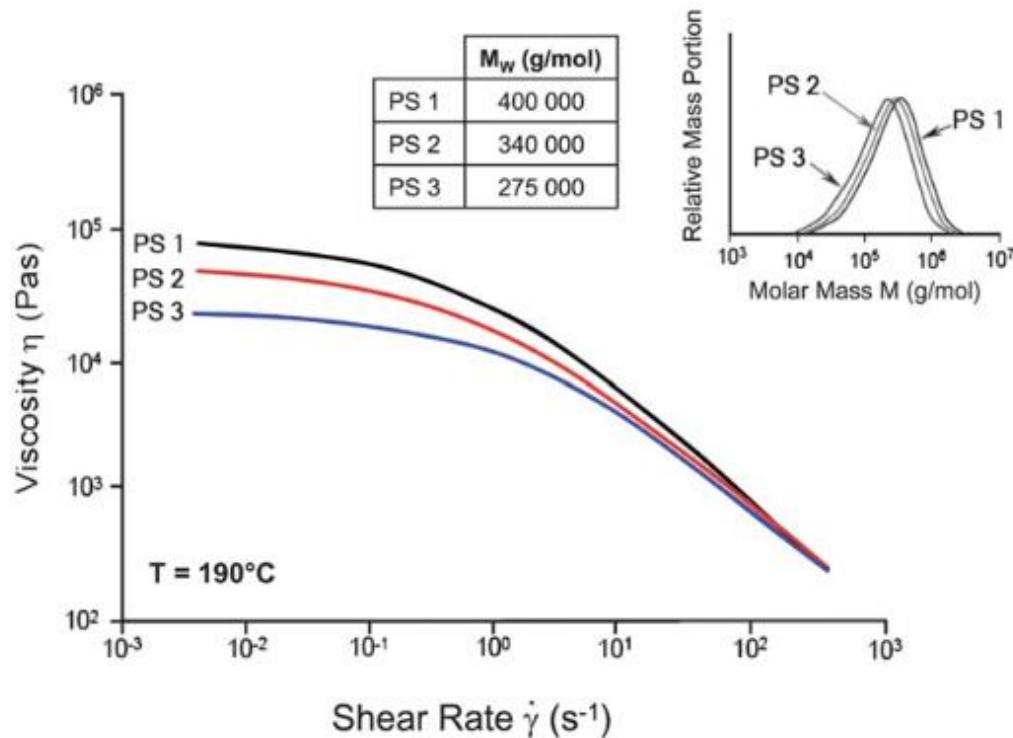
$$\eta = \eta_0 \cdot \exp\left(\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

Exponential relation:

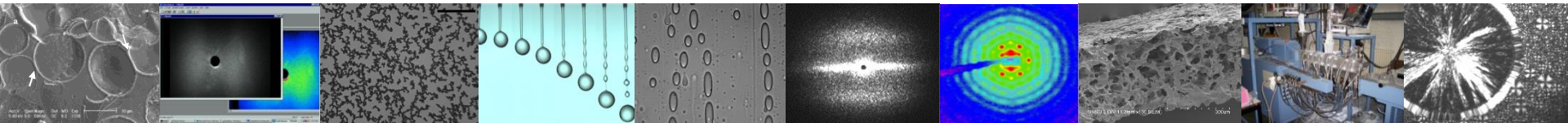
$$\eta = \exp(\varepsilon(T_{ref} - T))$$



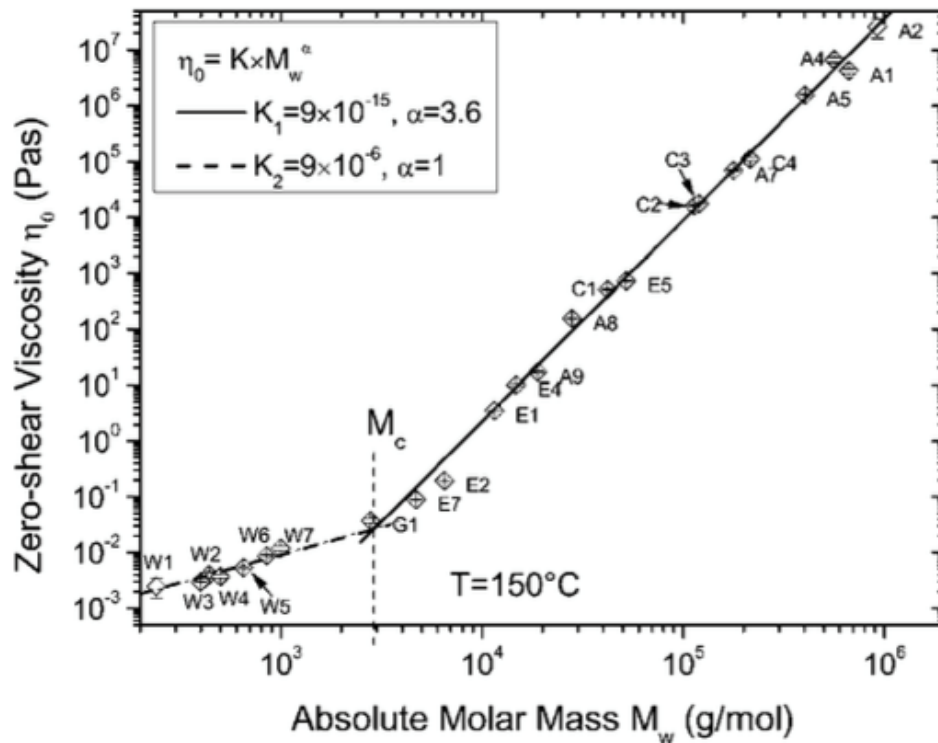
Effect of **weight average molecular weight** on the viscosity curves
(Polystyrene with similar molecular weight distribution)



Münstedt, *Soft Matter*, 2011, 7, 2273-2283

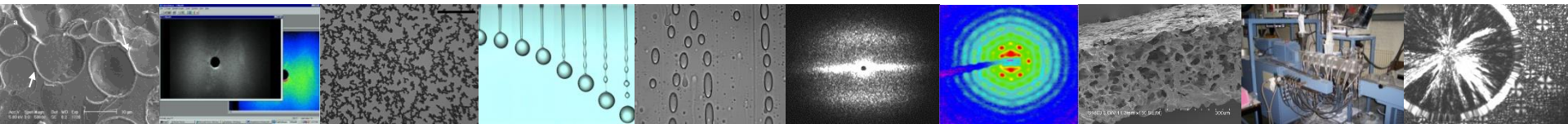


Effect of weight average molecular weight on the zero-shear viscosity (linear polyethylenes)

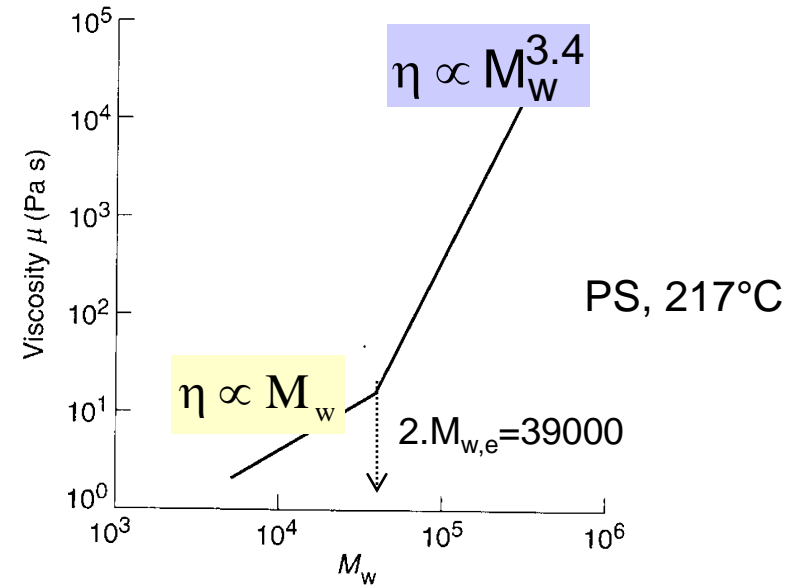
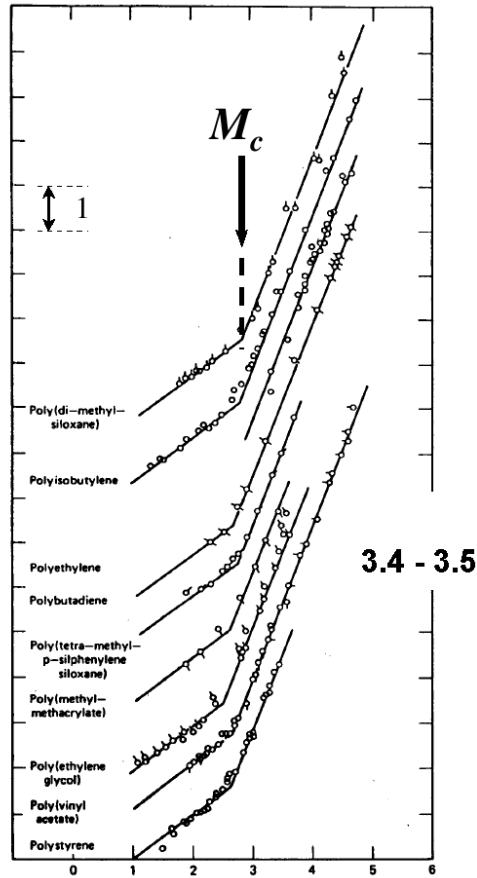


	$M_w/\text{g mol}^{-1}$	M_w/M_n	Remarks
G1	2800	2.9	
E7	4700	2.5	
E2	6500	2.1	
E1	11 500	1.8	
E4	14 800	2.5	
A9	19 000	6.5	
A8	28 000	7.8	Bimodal
C1	42 000	3	Low M -sh.
E5	52 000	2	
C2	114 000	16	High and low M -sh.
C3	120 000	2	
A7	178 000	4	Bimodal
C4	224 000	3	High M -sh.
A5	403 000	2.6	High M -sh.
A1	665 000	3.5	
A4	564 000	4.3	
A2	923 000	3.8	

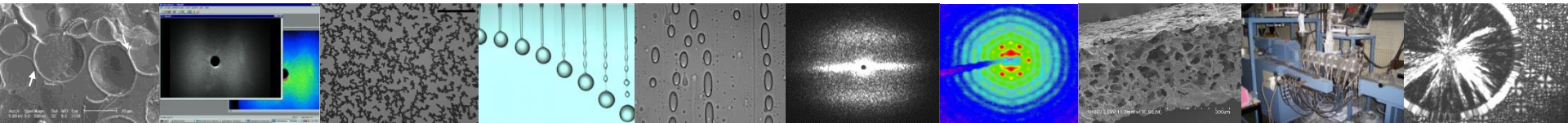
Münstedt, *Soft Matter*, 2011, 7, 2273-2283, see also Stadler et al., *Rheologica Acta*, 2006, 45, 755-764



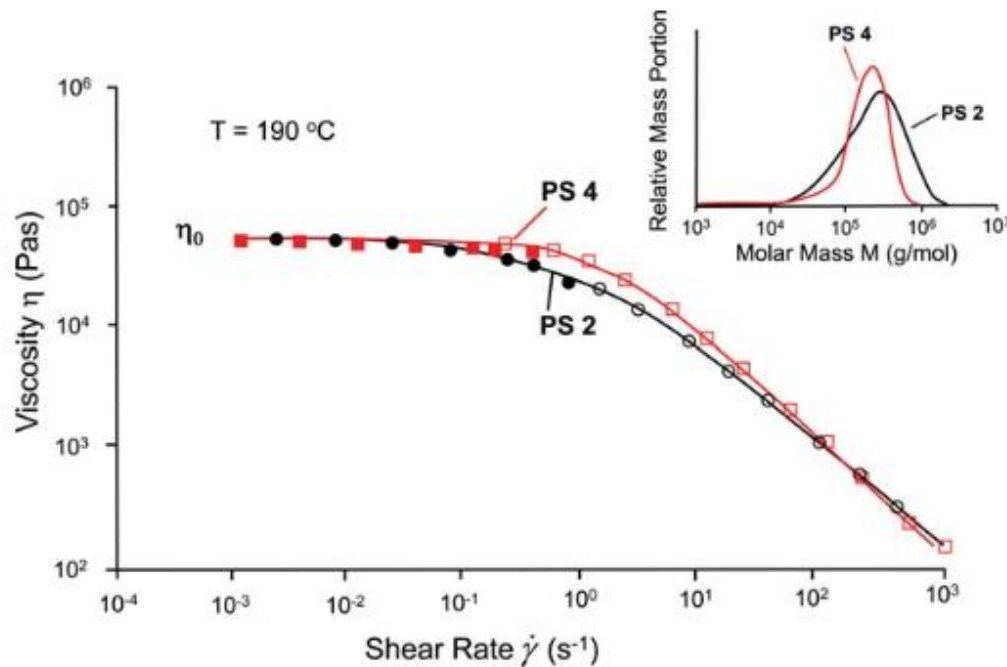
Effect of **weight average molecular weight** on the zero-shear viscosity for a series of linear polymers



Using the melt viscosity of polystyrene at 217°C, we can

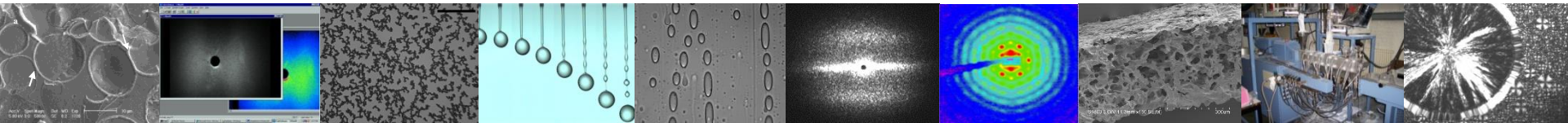


Effect of **molecular weight distribution** on the viscosity curves
(Polystyrene with similar weight average molecular weight, hence same zero-shear viscosity)



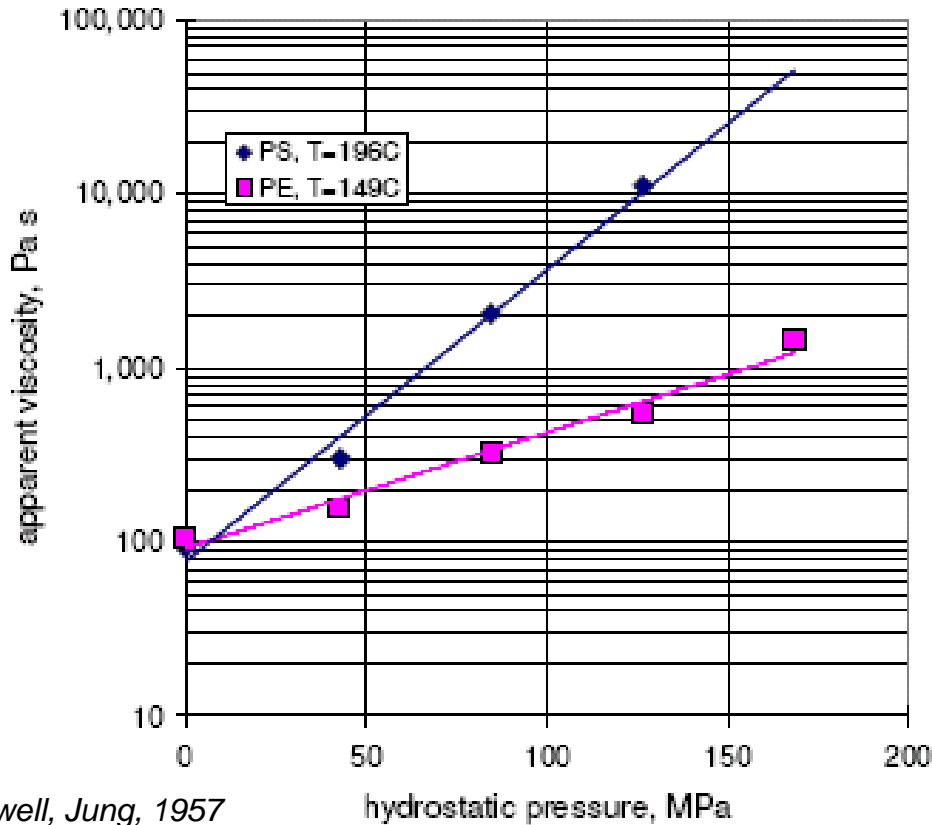
full symbols: rotational data
open symbols: capillary data

Münstedt, *Soft Matter*, 2011, 7, 2273-2283



Pressure dependence of the viscosity of polymeric melts can be substantial, but is often neglected.

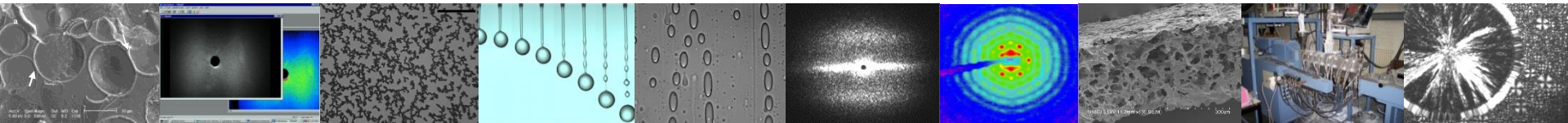
Classical data by Maxwell and Jung (1957)



Maxwell, Jung, 1957

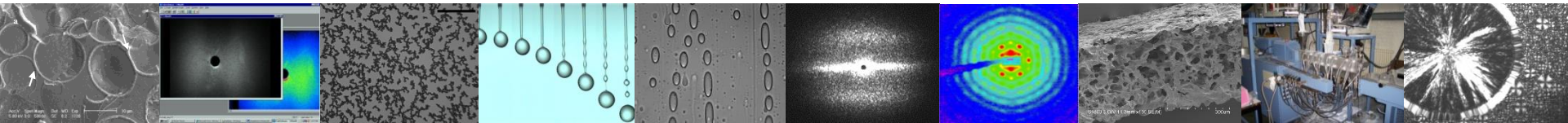
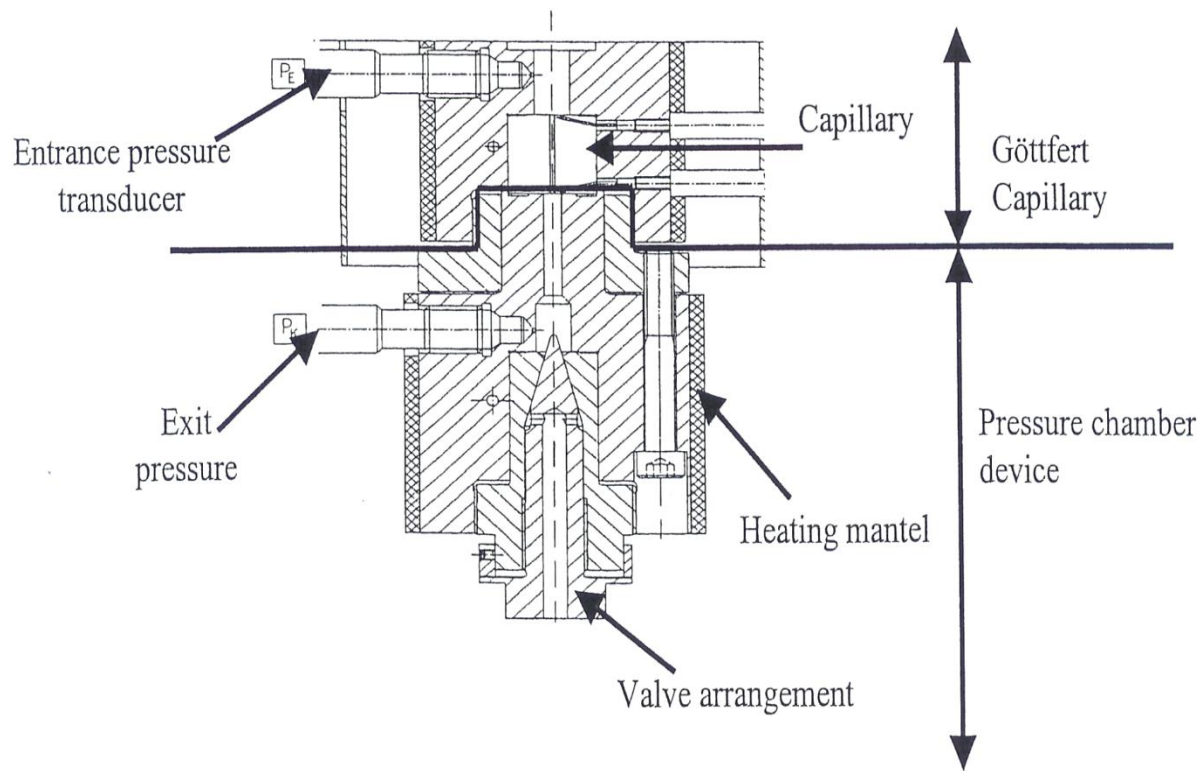
$$\eta = \eta_0 \cdot \exp(\beta(P - P_0))$$

$$\beta = \left(\frac{d \ln \eta}{dP} \right)_{T,i}$$



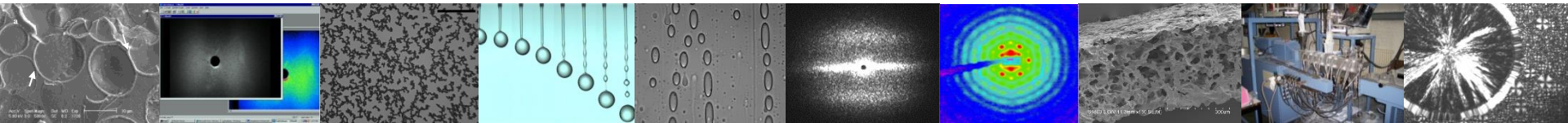
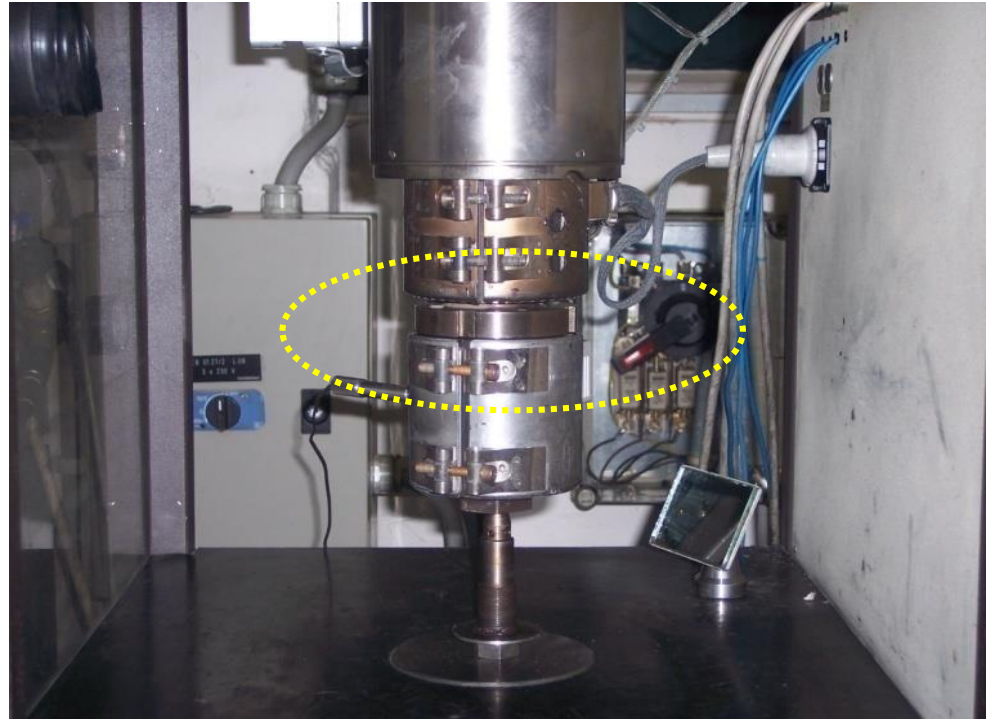
Effect of pressure: enhanced exit pressure

Example: using special devices to enhance the exit pressure
Can be used as 'add-on' to traditional capillary rheometer

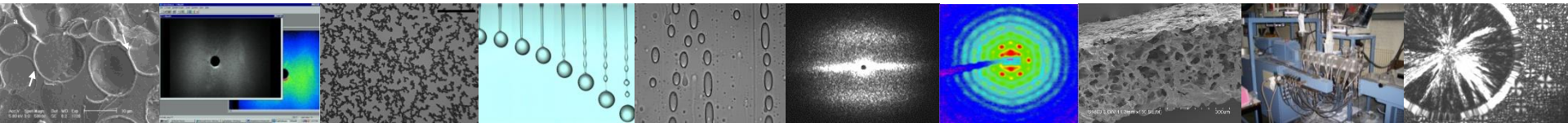
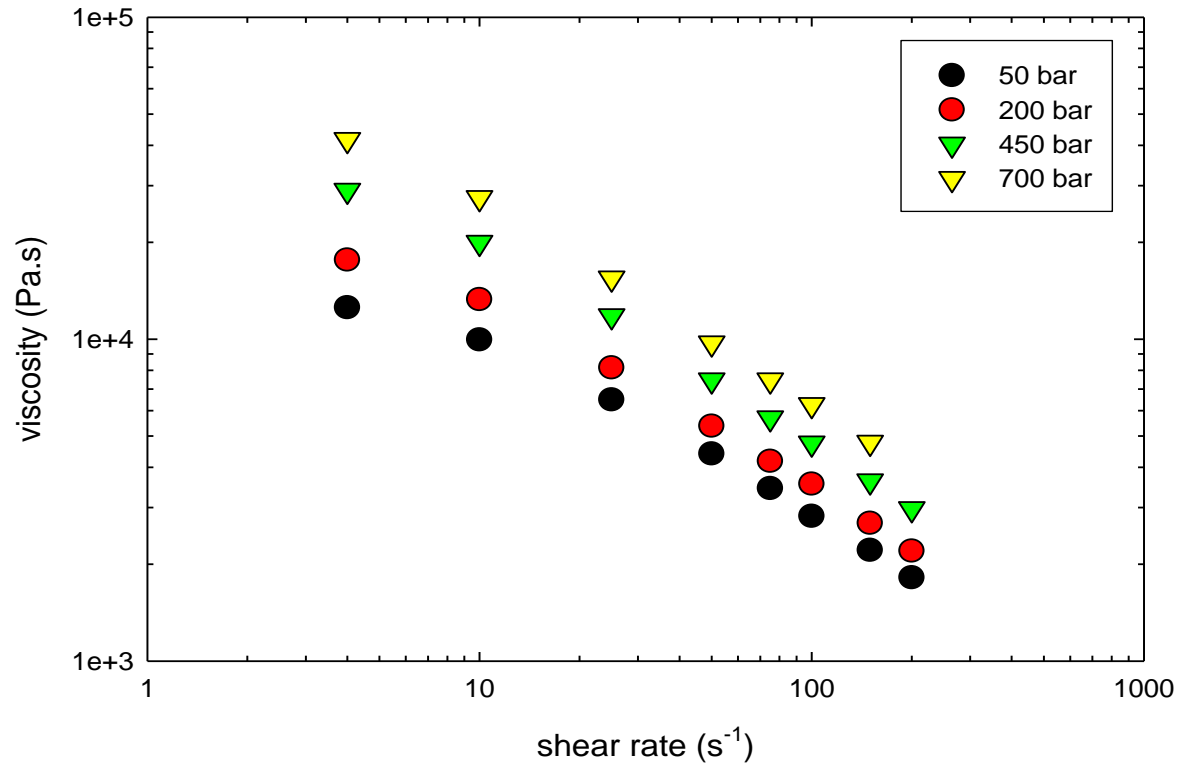


Effect of pressure: enhance exit pressure

Average hydrostatic pressure is approximated by linear average between entrance pressure and pressure in pressure chamber. The error in doing so $\sim 5\%$ if nonlinearities of pressure profile remain small



Example: PS at 200 °C (data Oosterlinck et al., 2000)

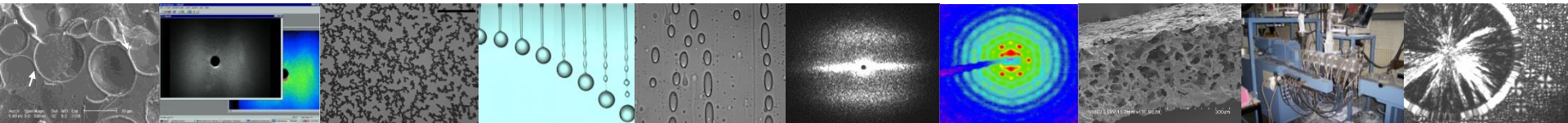
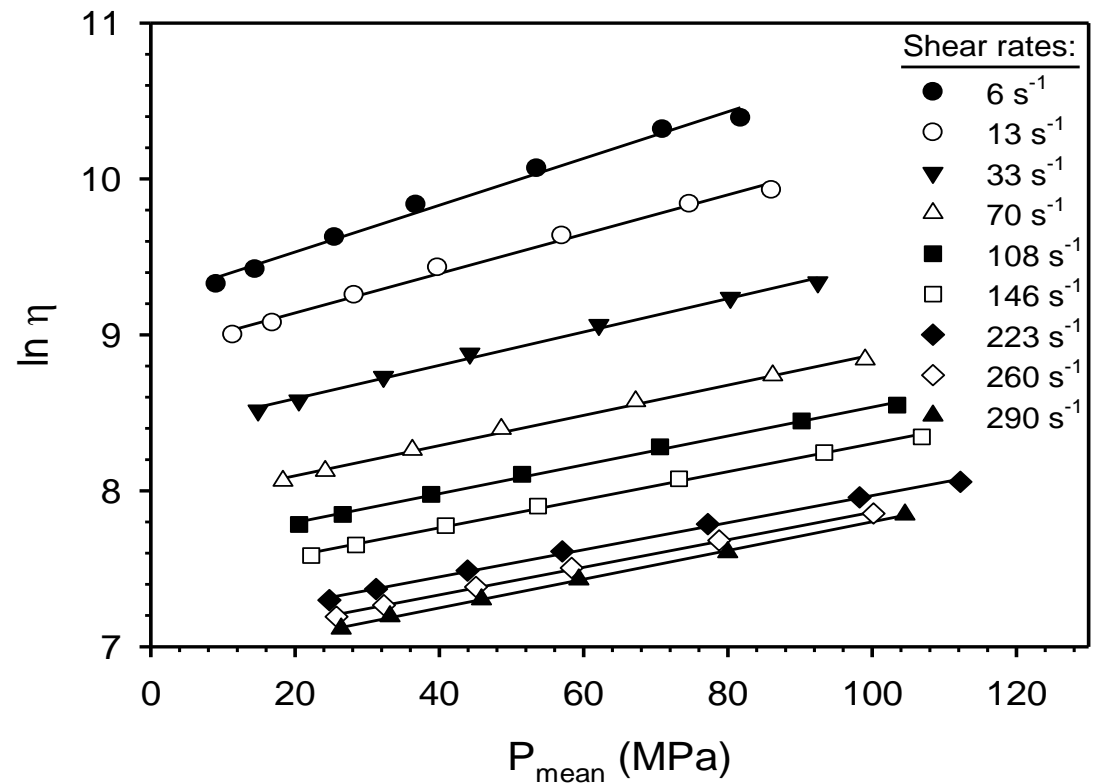


Example: PMMA at 2010 °C.

Obtaining the pressure coefficients at constant shear rate:

(Cardinaels et al., Rheol. Acta, 2007)

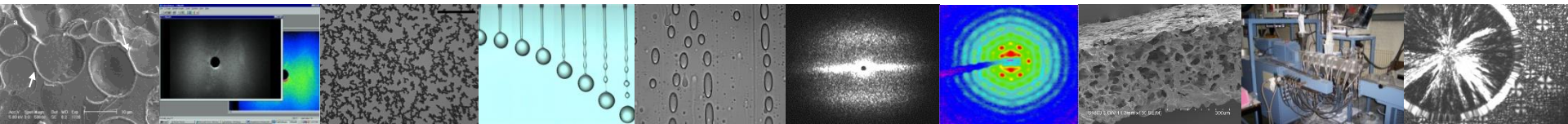
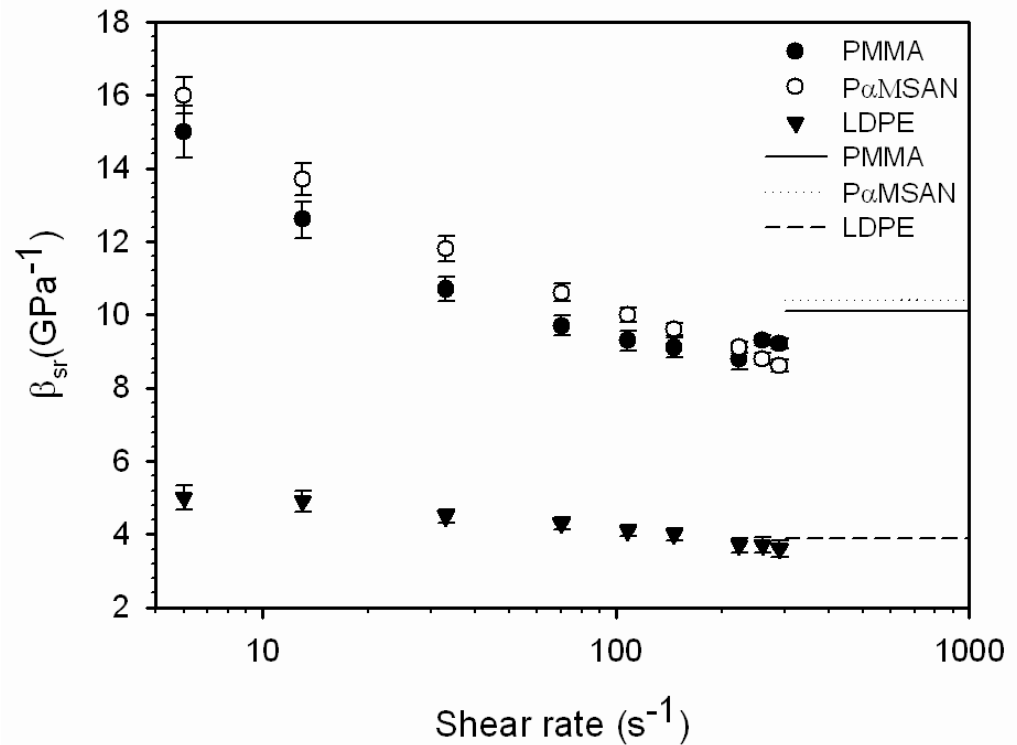
$$\beta = \left(\frac{d \ln \eta}{dP} \right)_{T, \dot{\gamma}}$$



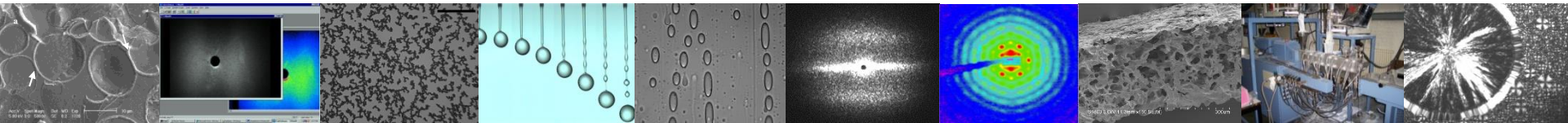
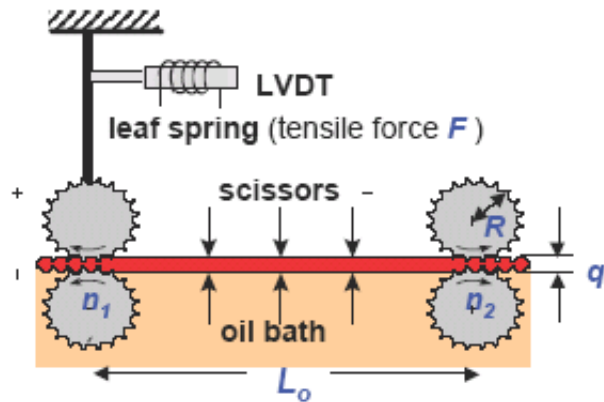
Obtaining the pressure coefficients at constant shear rate:

(Cardinaels et al., Rheol. Acta, 2007)

$$\beta = \left(\frac{d \ln \eta}{dP} \right)_{T, \dot{\gamma}}$$

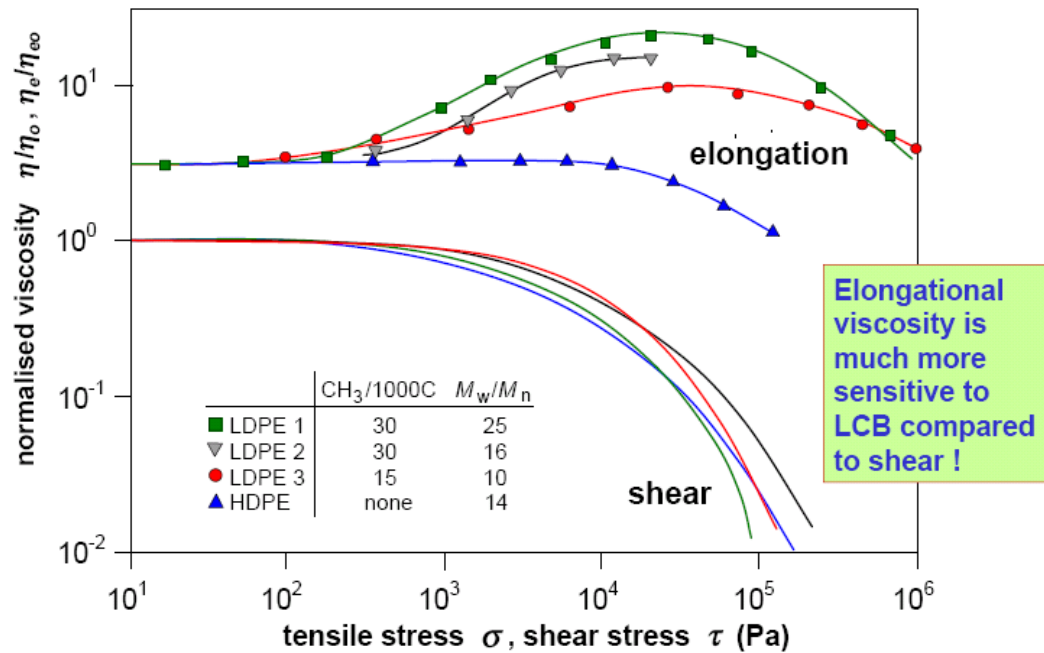
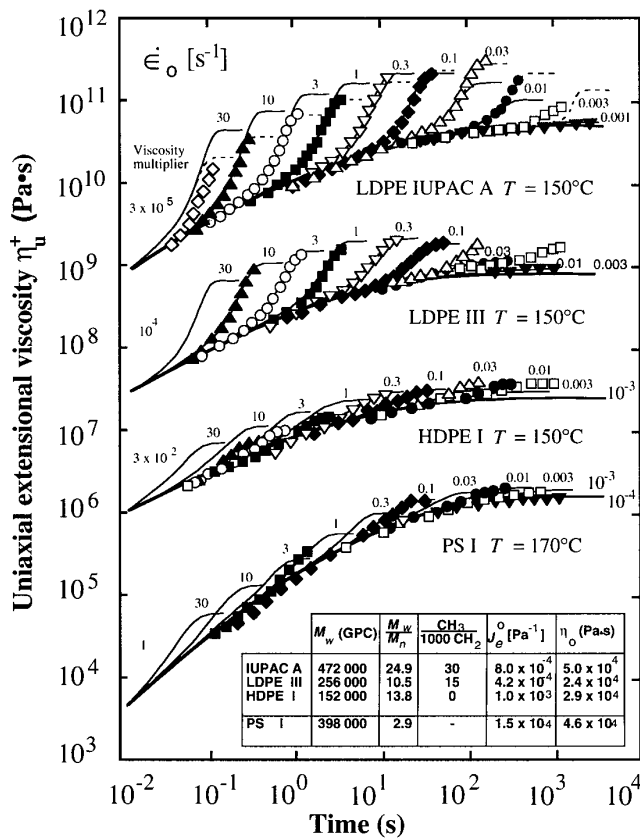


A variety of devices exist, but elongational experiments are in general difficult. For Newtonian liquids or in the linear regime, it can be shown that: the extensional viscosity = 3 x the shear viscosity (Trouton ratio)

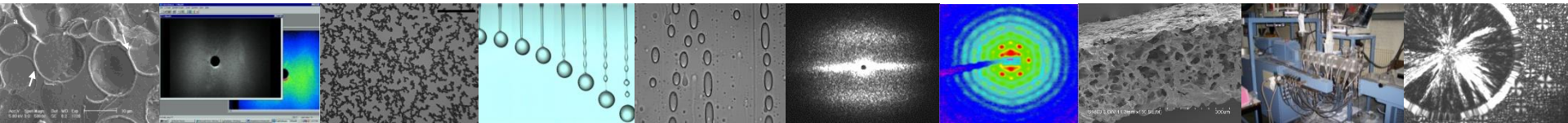


Elongational flows: effect of branching

The elongational viscosity is much more sensitive to long chain branching, as compared to the shear viscosity



Elongational viscosity is much more sensitive to LCB compared to shear!



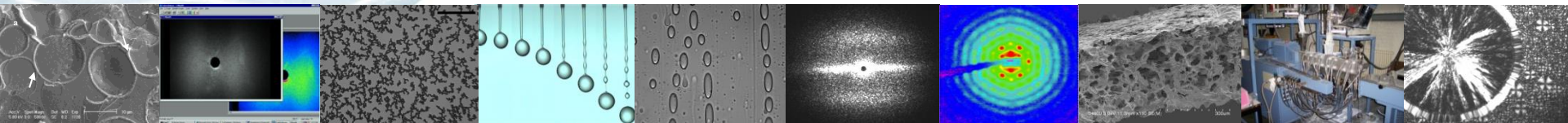
A case study: mixtures of linear and branched PP

Two polypropylenes have been used:

- **branched high melt strength PP** (HMS PP),
 - supplied by Borealis (PP Daploy WB 135 HMS)
 - tensile modulus 2000 MPa
- **linear PP**,
 - supplied by Total (PPH 4070)
 - tensile modulus of 1950 Mpa

+ antioxidants Irgafos 168 (0.08 wt%) and Irganox 1010 (0.02 wt%),
supplied by Ciba

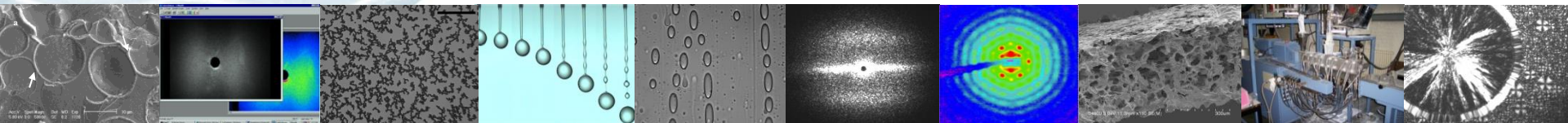
+ chemical blowing agent (azodicarboramide) (3 wt%),
supplied by Lanxess



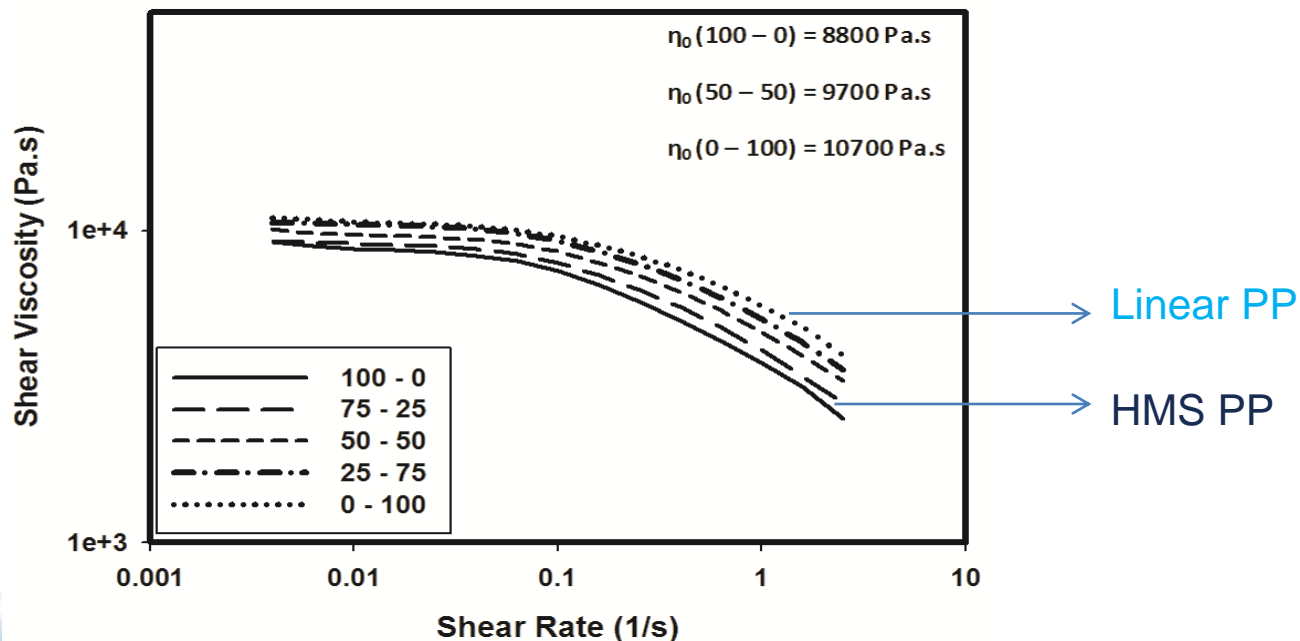
Five blends of HMS PP and linear PP have been prepared, varying the ratio HMS PP/Linear PP:

- with a co-rotating twin-screw extruder (L/D = 24, 80 rpm)
- at 190 °C

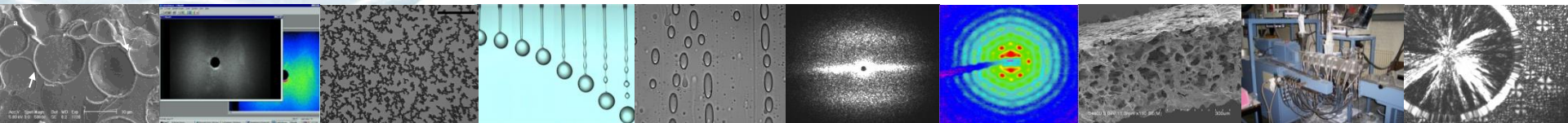
Sample	T _m (°C)	T _c (°C)	ΔT (°C)
100 - 0	161.44	123.65	37.79
90 - 10	160.99	122.29	38.70
75 - 25	161.50	121.97	39.53
50 - 50	163.32	120.95	42.37
25 - 75	164.10	121.36	42.74
10 - 90	165.51	119.10	46.41
0 - 100	166.40	119.41	46.99



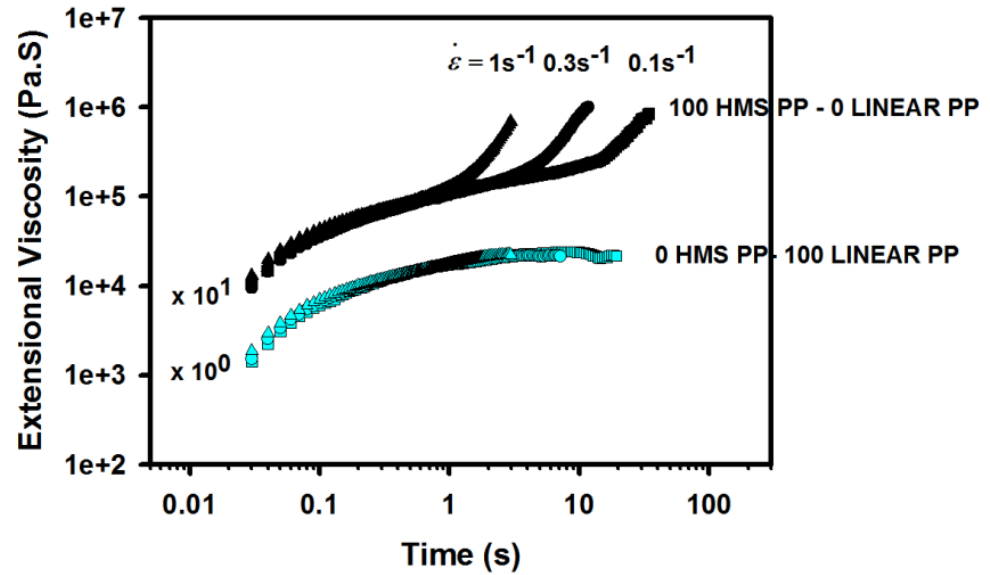
Results: rheological characterization in shear



- The polymers and blends behave as expected:
 - Newtonian plateau + shear thinning
 - In shear the seven materials behave very similarly

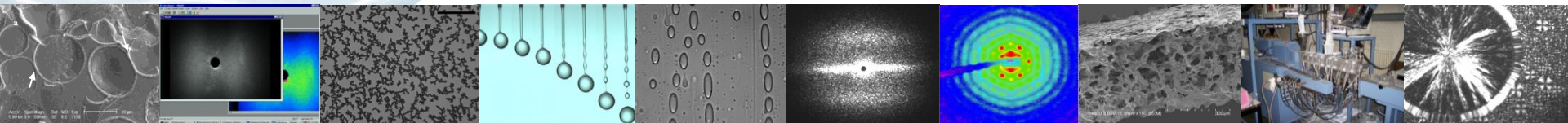


Results: rheological characterization in extension

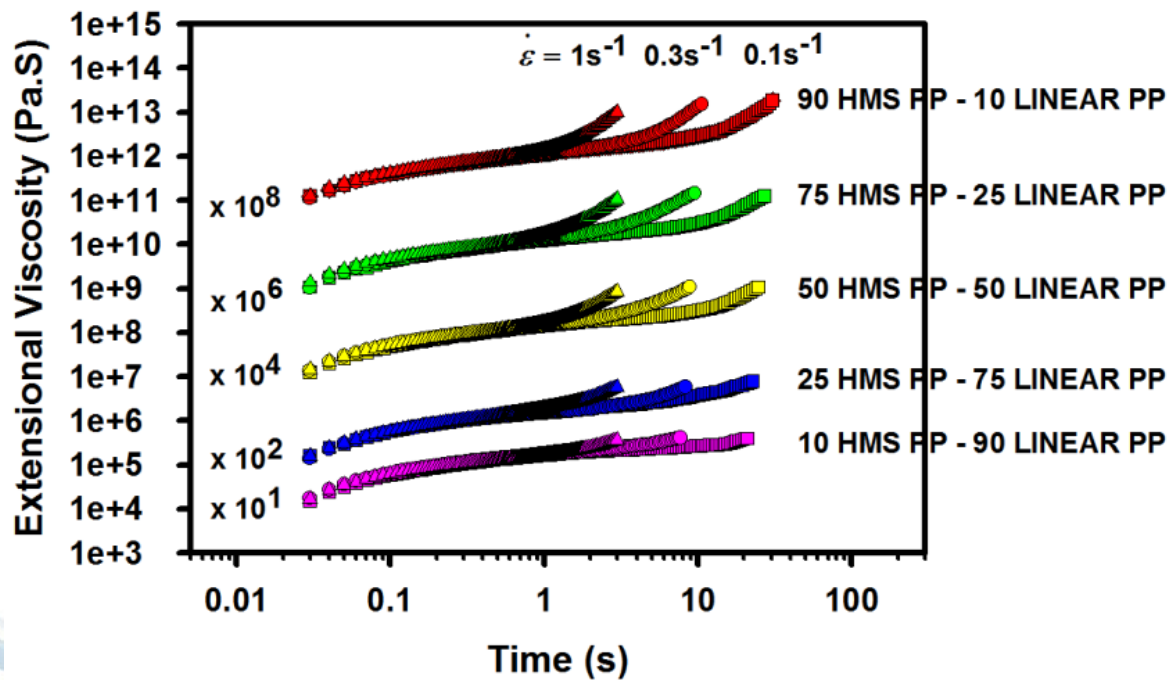


EVF = extensional viscosity fixture

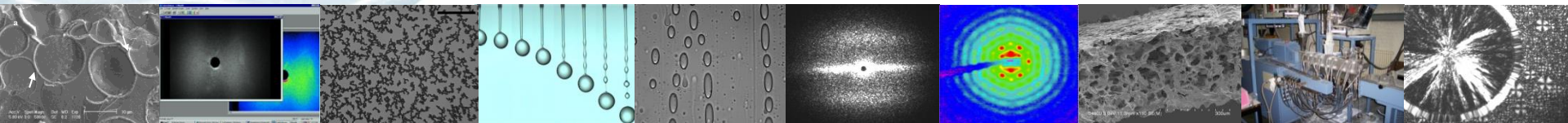
- The linear PP shows no strain hardening
- The branched, HMS PP shows substantial strain hardening



Results: rheological characterization in extension



There is a gradual increase in degree of strain hardening as the amount of branched HMS PP increases

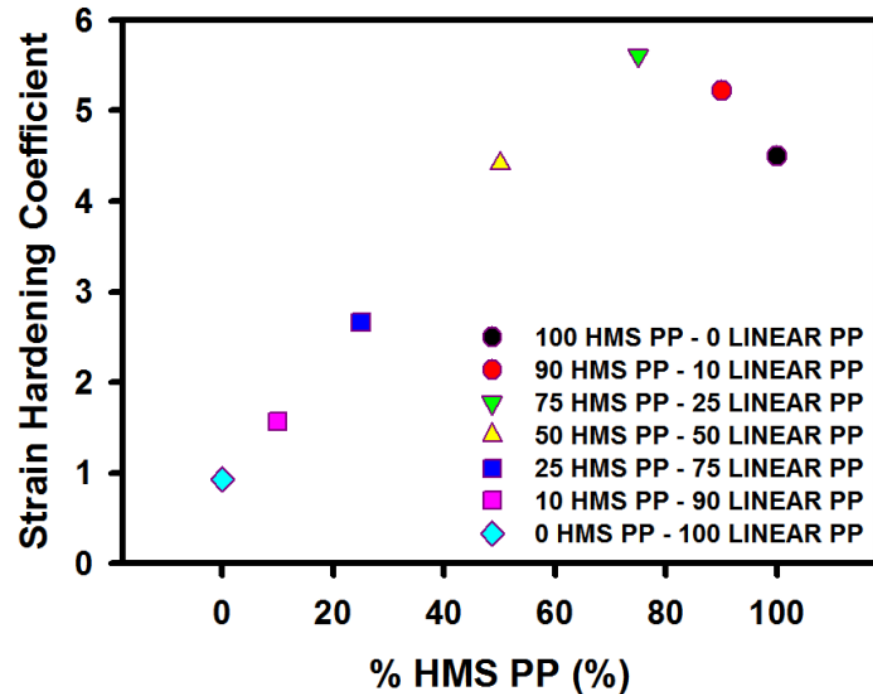


To quantify strain hardening: the strain hardening coefficient

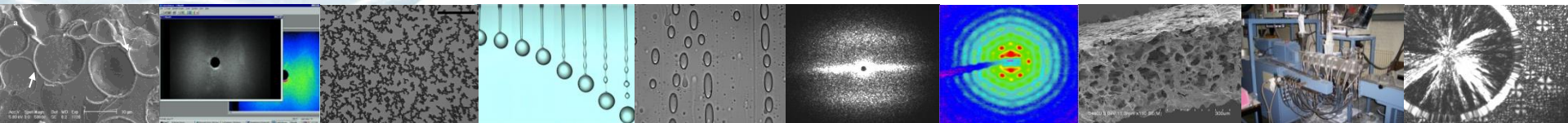
$$S = \frac{\eta_E^+(t, \dot{\epsilon}_0)}{\eta_{E0}^+(t)}$$

Here S was determined at:

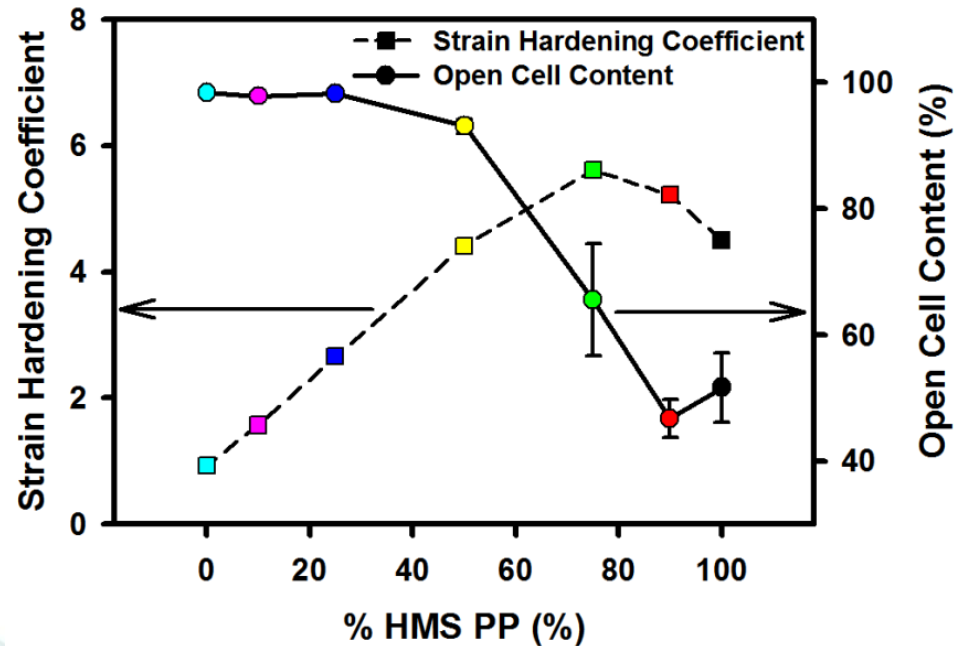
- A strain rate of 1 s⁻¹
- After 3 seconds



- Linear PP has a strain hardening coefficient of 1
- The strain hardening coefficient increases with amount of branched PP
- At high concentrations of branched PP the situation is less clear

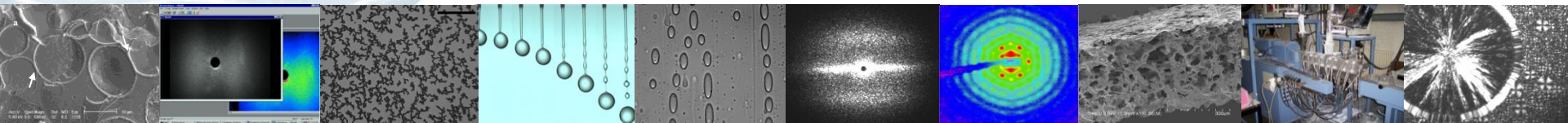


What is the relation with the microstructure of the foam?



- When the strain hardening coefficient is low, the open cell content is 100%
- With increasing strain hardening the open cell content decreases

PS: Open cell content was determined quantitatively with a gas pycnometer (ASTM D1622-08)



A case study: immiscible polymer blends

Motivation:

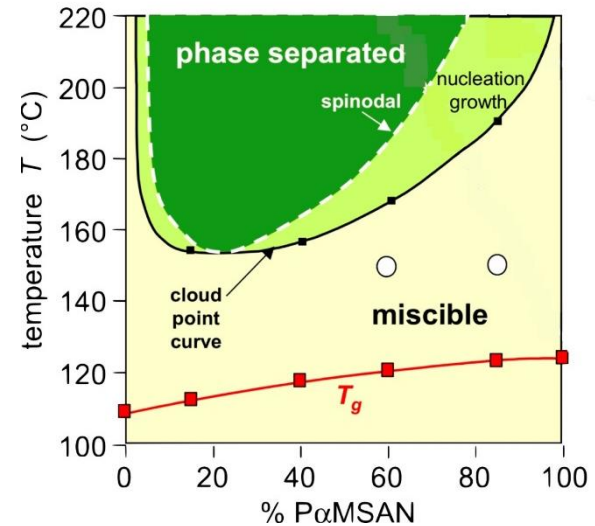
multiphasic materials are omnipresent



Thermodynamics:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

- miscible
- immiscible
- partially miscible

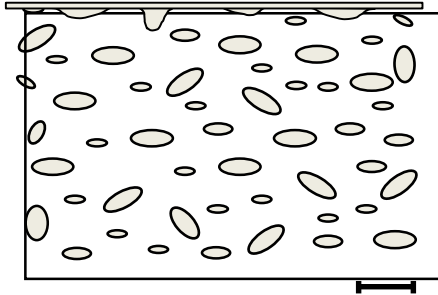


Laun H.M., 1998

Polymer blends can have different morphologies

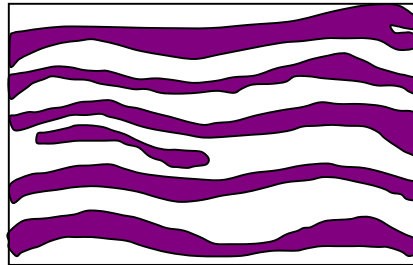
Different phase morphologies:

Drops



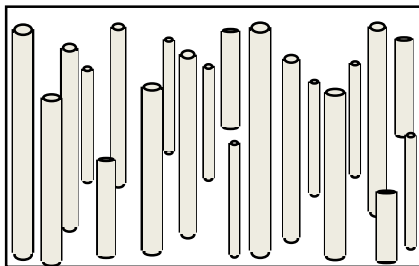
toughness

Lamellar



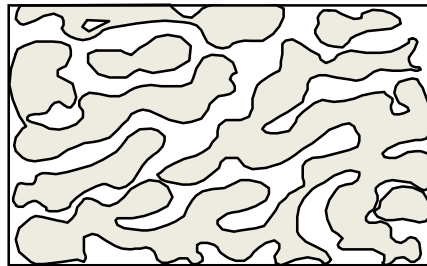
barrier properties

Fibers



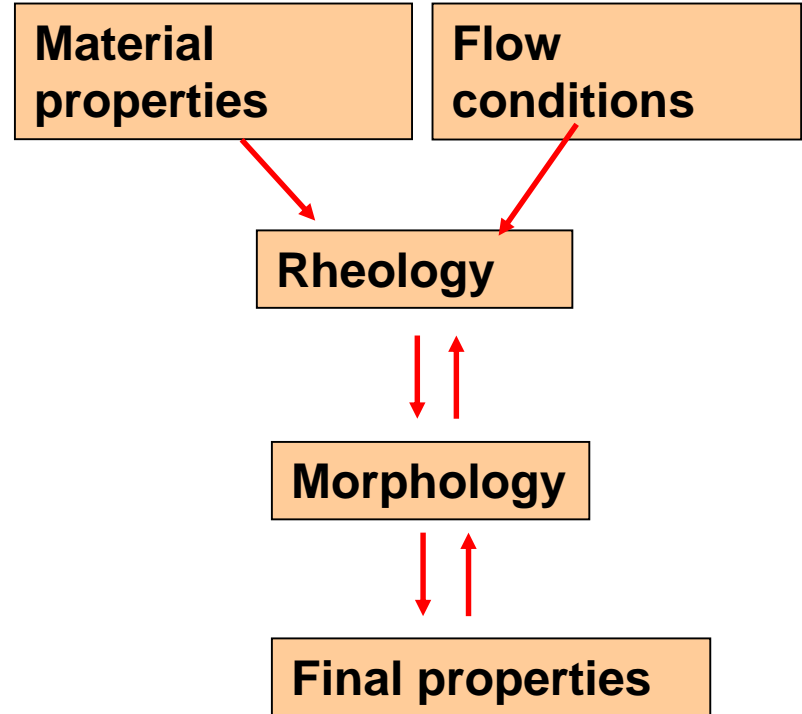
strength

Cocontinuous



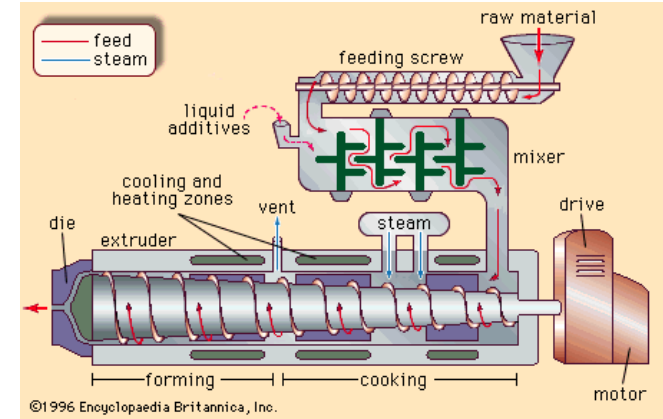
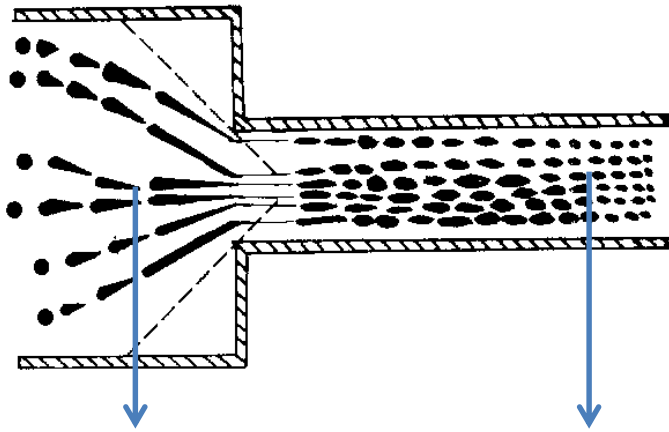
electrical conductivity,
toughness

The interplay:

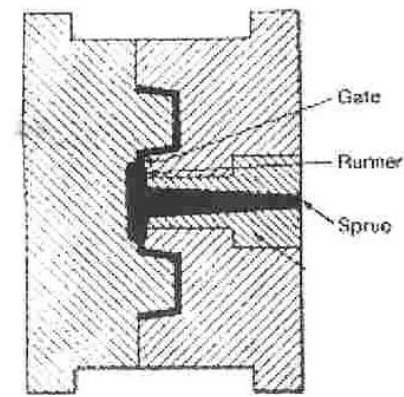
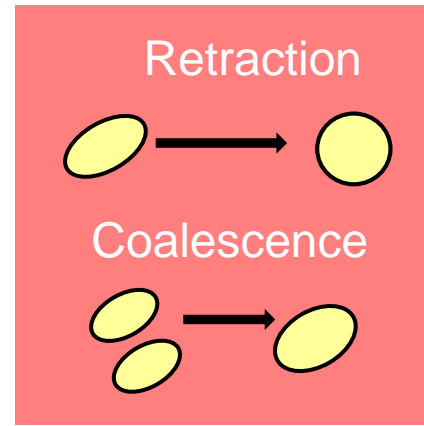
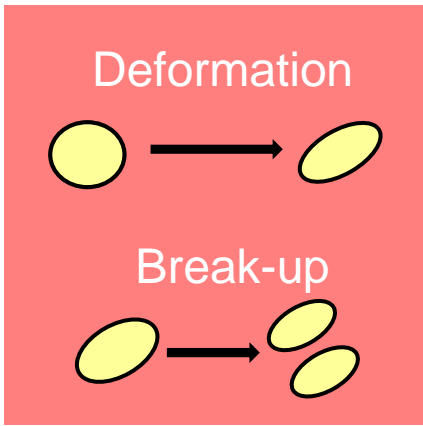


The morphology is generated during processing

Morphological processes occur simultaneously



© 1996 Encyclopaedia Britannica, Inc.



(Principles of polymer engineering, McCrum, Buckley, Bucknall Oxford Science Publications)



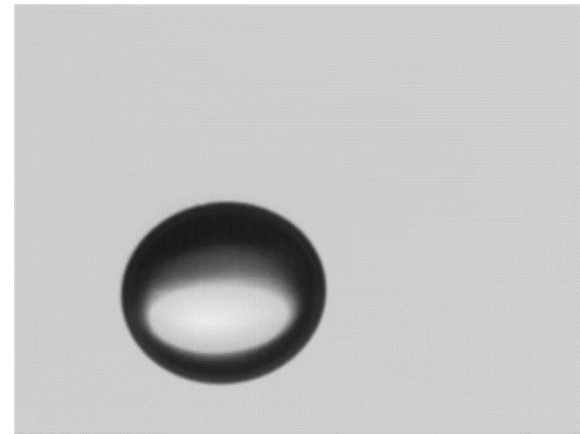
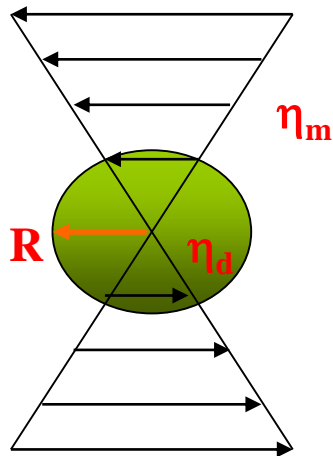
An example: deformation and break-up in shear flow

Deformation and break-up: - hydrodynamic stress: $\eta_m \dot{\gamma}$

- interfacial stress: α/R

⇒ Capillary number: $Ca = \eta_m \dot{\gamma} R / \alpha$

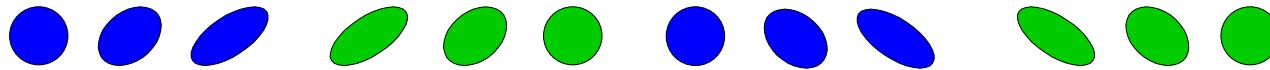
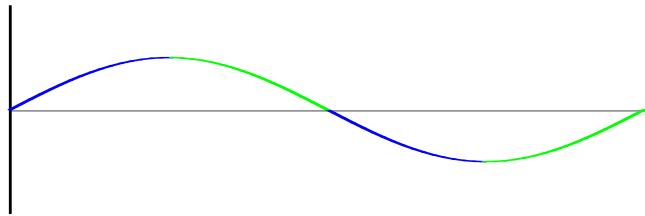
⇒ Viscosity ratio: $\rho = \eta_d / \eta_m$



Morphology: link with linear visco-elastic rheology

For small deformations: oscillatory shear

Measure storage modulus (G') and loss modulus (G'') as function of frequency.

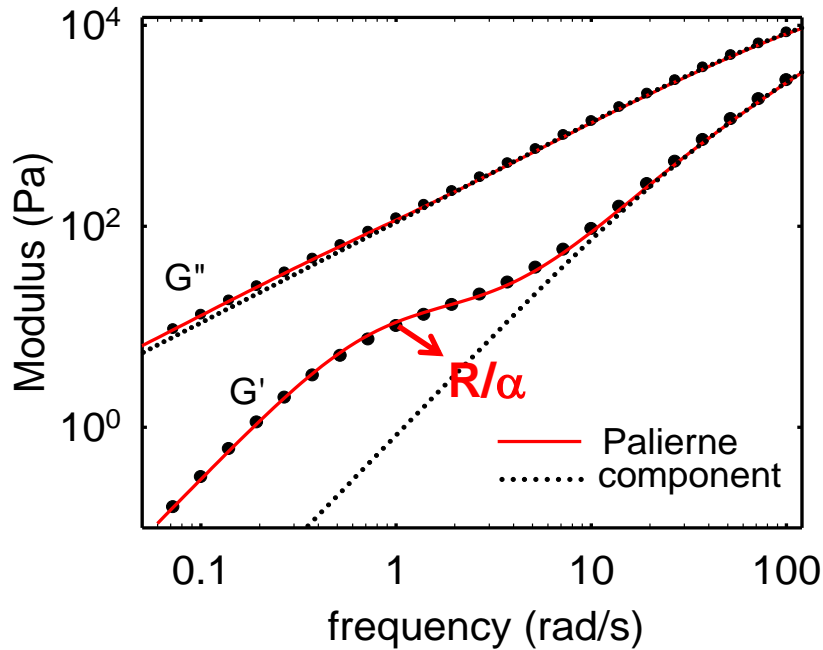


Interface = storage and release of elastic energy

⇒ excess storage modulus $G' = f(\Phi, R/\alpha)$

Palierne model: $G^* = G_m^* \left(\frac{1 + 3\phi H}{1 - 2\phi H} \right)$ with $H(\alpha/R, G_d^*, G_m^*)$

Morphology: link with linear visco-elastic rheology



Shoulder in $G' \equiv$ drop relaxation

Palierne model:

$$G^*_{\text{blend}} = f(G^*_{\text{comp.}}, \phi, R/\alpha)$$

R/α is used to fit the moduli

α known \Rightarrow get R

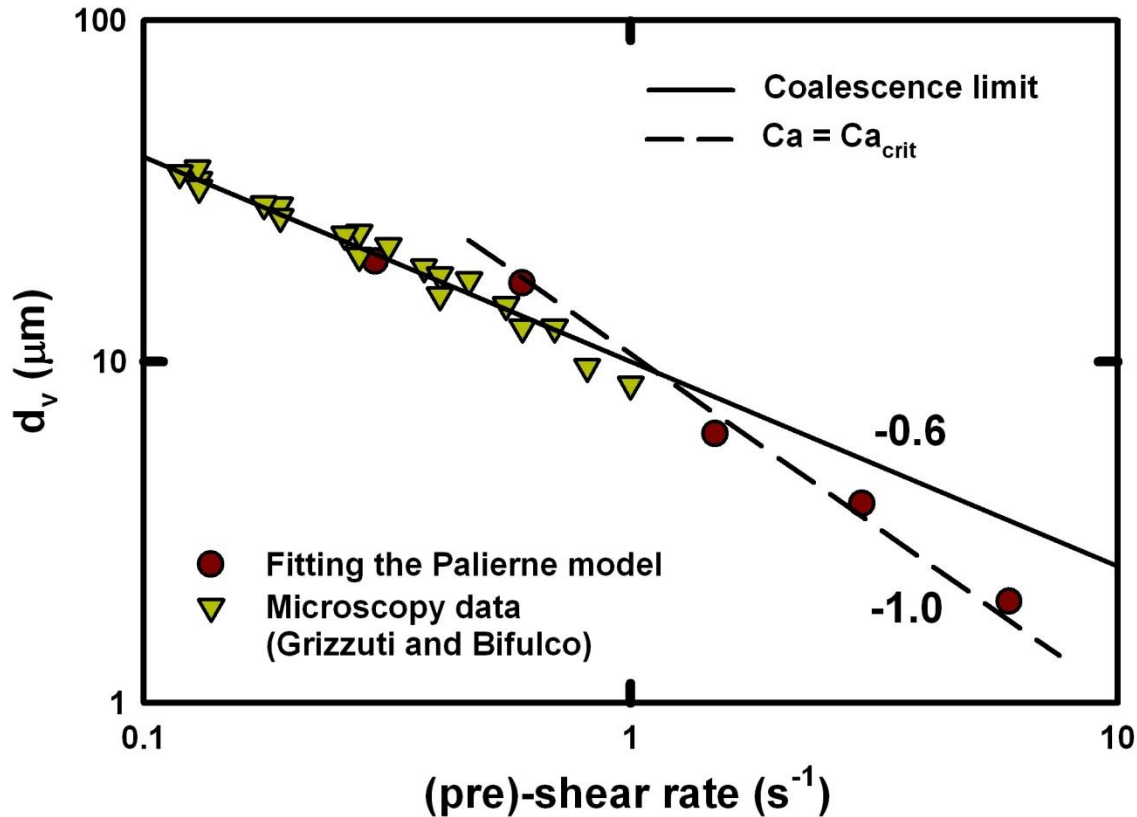
Alternatively: describe with a shape relaxation time τ_f :

$$\tau_f = \frac{R\eta_m}{4\alpha} \frac{(19p + 16)(2p + 3 - 2\phi(p - 1))}{10(p + 1) - 2\phi(5p + 2)}$$

Morphology: link with linear visco-elastic rheology

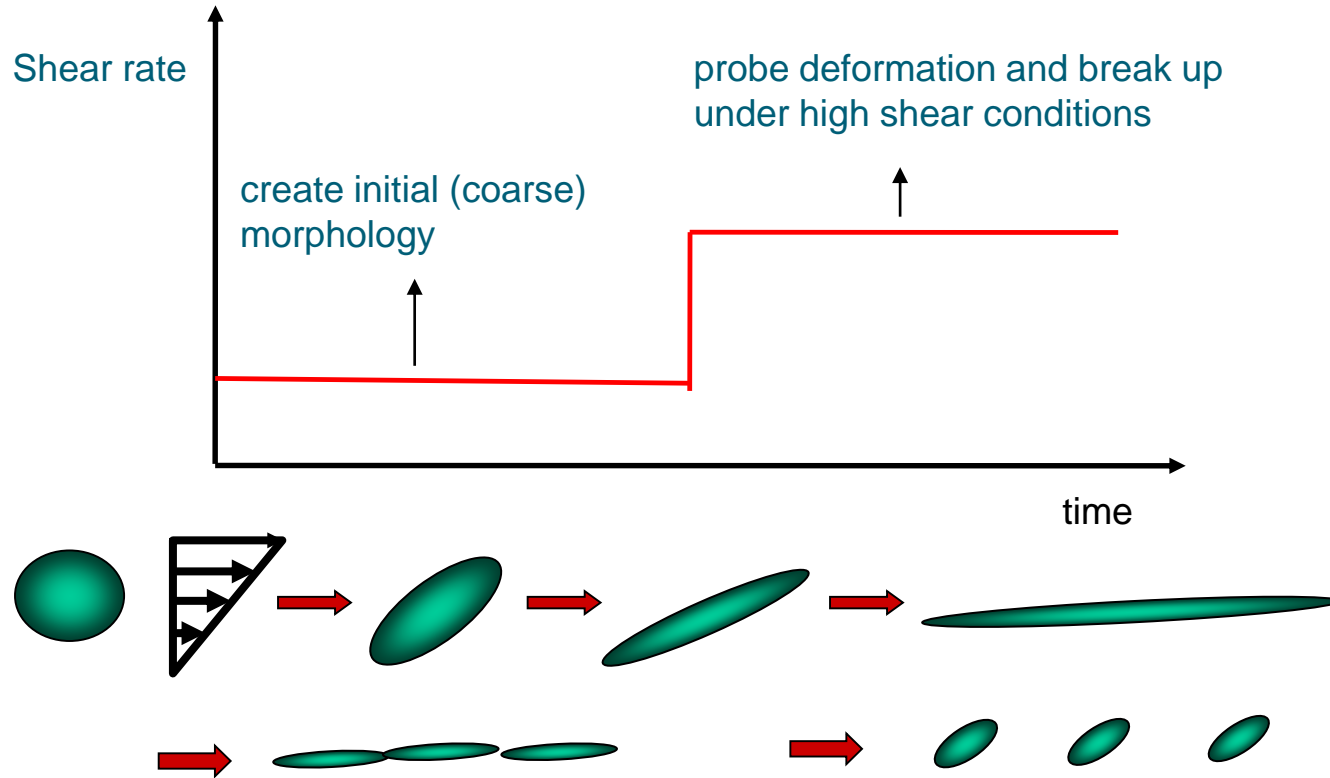
Example of using the Palierne model

(10% PIB in PDMS with $p = 0.45$)

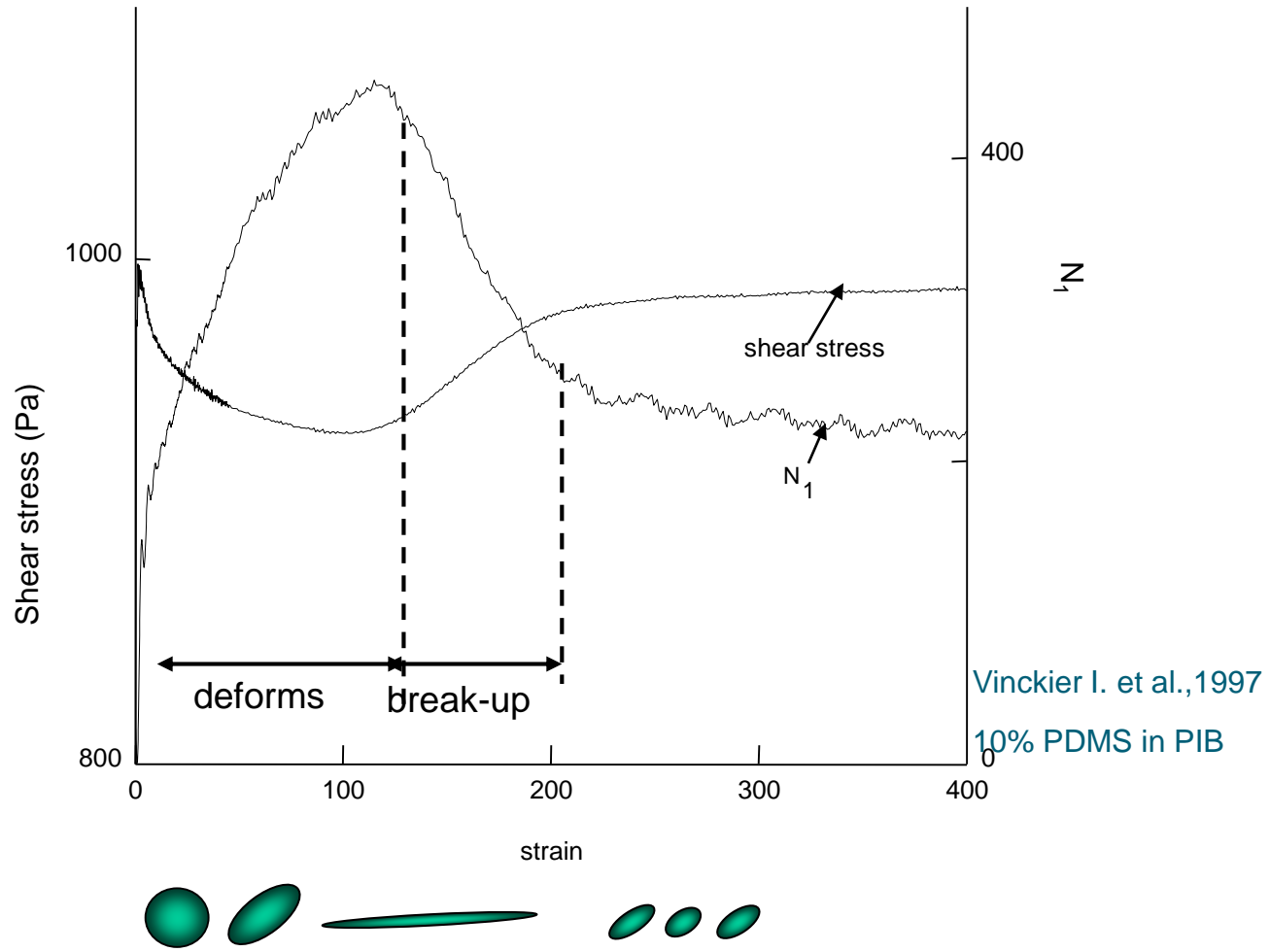


Morphology: link with shear flow

For **large deformations**: e.g. step-up in shear rate



Morphology: link with shear flow

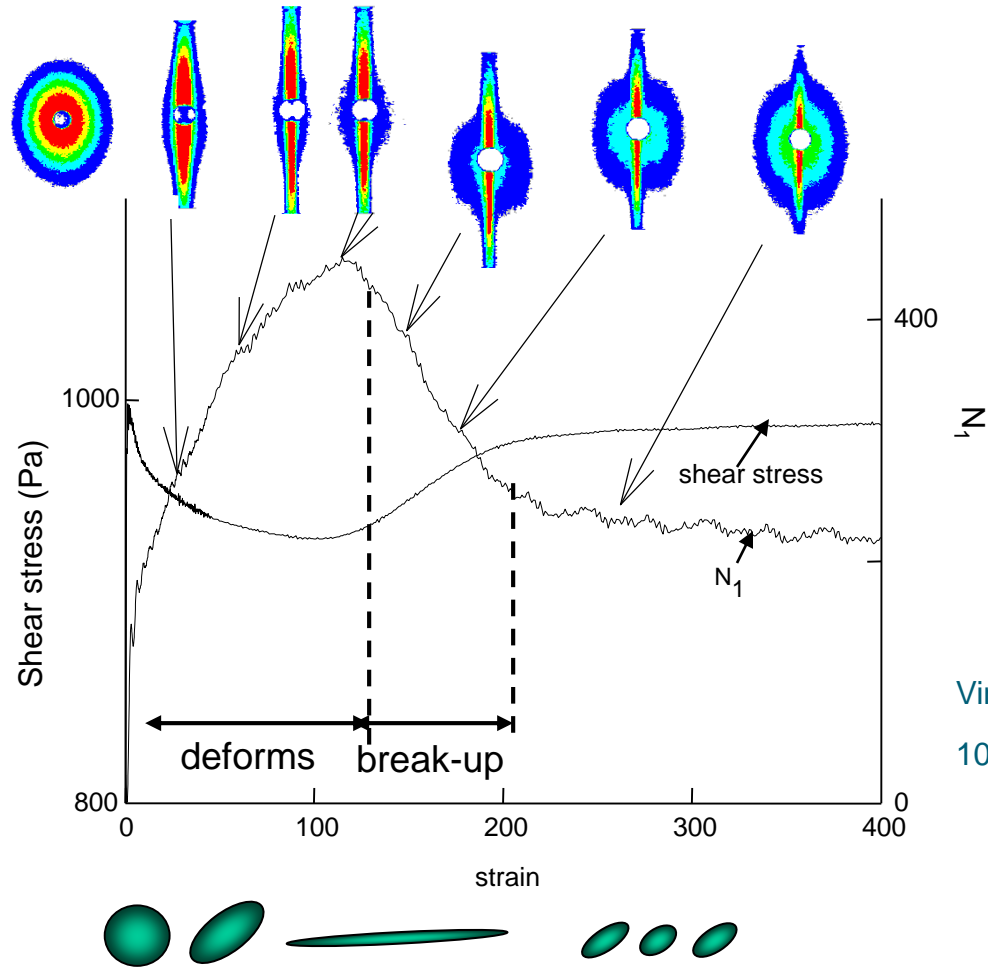


Vinckier I., Moldenaers P. and Mewis J., J. Rheol., 41, 705-718 (1997)

Tucker III C.L. and Moldenaers P., Ann. Rev. of Fluid Mech., 34, 177-210 (2002) (review)



Morphology: link with shear flow



Vinckier I. et al., 1997

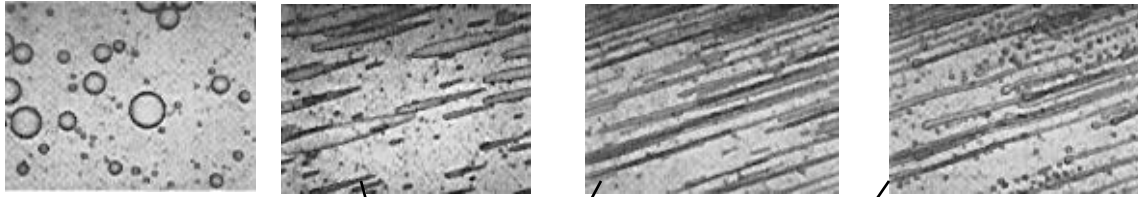
10% PDMS in PIB

Vinckier I., Moldenaers P. and Mewis J., *J. Rheol.*, 41, 705-718 (1997)

Tucker III C.L. and Moldenaers P., *Ann. Rev. of Fluid Mech.*, 34, 177-210 (2002) (review)



Morphology: link with shear flow



Iza and Bousmina M., (2000)

