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MULTIPLE SHEAR-BANDING TRANSITIONS IN SOLUTIONS OF A SUPRAMOLECULAR POLYMER

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Outline

- What are ***R****eversible* ***S****upramolecular* ***P****olymers*?
- The experimental system: “EHUT”
- Flow curves
  - 6 regimes, of which 3 with shear banding
    - birefringence
    - transients (stress relaxation after shear-rate increase)
    - velocity profiles
- Effect of temperature increase vs. “stopper” adition
- Conclusions

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What are ***Reversible Supramolecular Polymers (RSPs)*** ?

(*living polymers, equilibrium polymers, supramolecular polymers, reversible linear aggregates*)

Chains of small “bifunctional” units (molecules) linked together by reversible interactions.

Have much in common with ‘ordinary’ polymers, but there are interesting fundamental differences:

- chains are ‘dynamic’ (break/reassemble continuously)

- chain lengths assume equilibrium distribution . . .

- which responds to conditions (e.g.:concentration, presence of surfaces, hydrodynamic forces, . . .)

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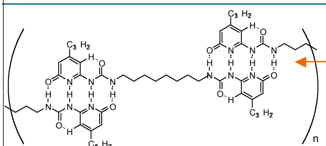
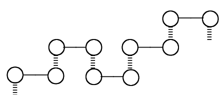
Some examples

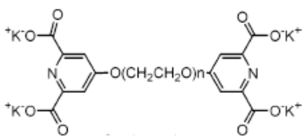


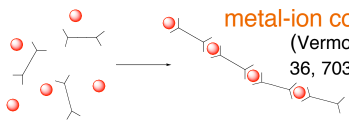
multiple hydrogen bonding



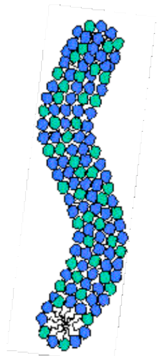
(Sijbesma et al, Science, 278: 1601-4,’97)

DNA-based stickers
Fogleman et al, Angew Chem. 41, 4026, ‘02





metal-ion complexation
(Vermonden et al, Macromolecules, 36, 7035-44,’03)



wormlike micelles formed by certain surfactants

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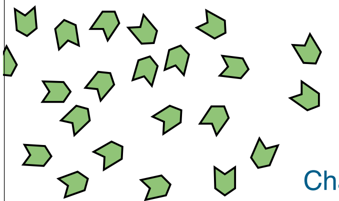
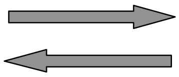
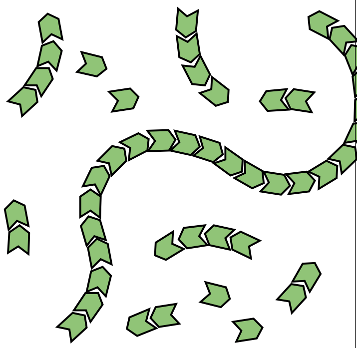
Bifunctional monomers → self-assemble into supramolecular chains







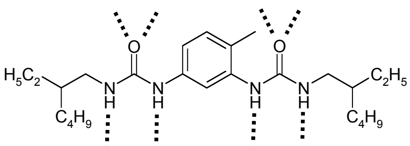
Chain-length distribution:

$$c(N) = \frac{C}{\langle N \rangle^2} \exp\left(-\frac{N}{\langle N \rangle}\right)$$

$$\text{with } \langle N \rangle \approx 2\sqrt{KC} \propto \sqrt{C} \exp\left(\frac{E}{2kT}\right)$$

N = degree of polymerisation
K = association constant
E = ‘scission energy’ = 2 x ‘end-cap energy’
C = overall monomer concentration

Present experimental system



EHUT

stiff supramolecular chains $l_p > 200$ nm
~ 2 monomers / repeat unit

dodecane

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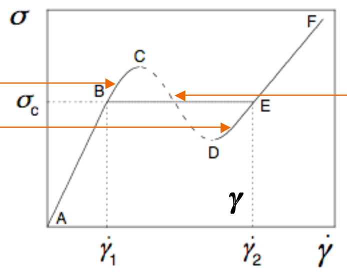
‘Standard picture’ of shear banding (gradient direction)



schematic constitutive relation
- $\dot\gamma_1 < \dot\gamma < \dot\gamma_2$ coexistence of bands 1 and 2
- $\dot\gamma_1$ and $\dot\gamma_2$ constant
- fraction of gap with $\dot\gamma_2$ increases upon increasing $\dot\gamma$
- horizontal stress plateau (BE)

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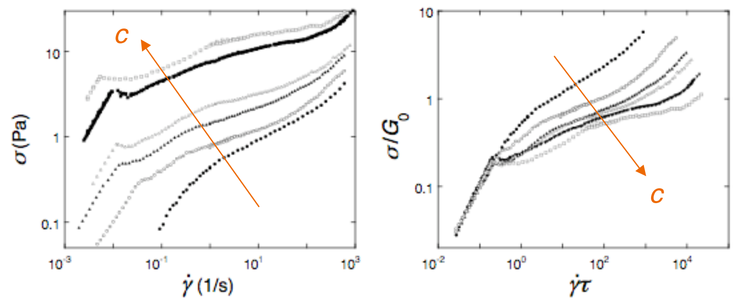
flow curves (controled shear rate)

20°C, concentrations: 0.75, 1.4, 2.0, 3.1, 5.9, 6.4 g/l (all > entanglement conc.)



each curve renormalised by “Maxwellian” plateau modulus and relaxation time

J. van der Gucht e.a., Phys. Rev. Lett, 97 (2006) 108301

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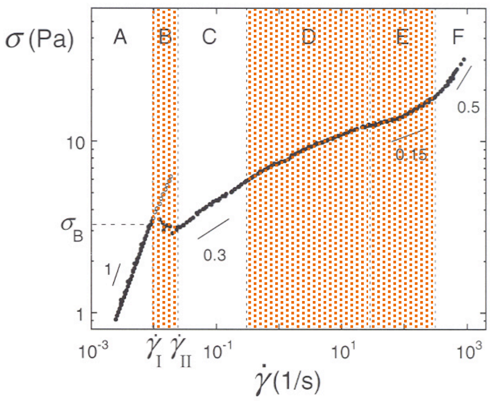
flow curve (example at 5.9 gr/l)



6 regimes: overview

A - linear regime
B - shear banding, stress overshoots, slow transients, metastability,
C - no shear banding, stress overshoots, fast transients
D - shear banding, slow oscilatory transients, birefringent textures
E - shear banding, faster transients, birefringent textures
F - no shear banding, birefringence

black symbols: stable steady states
open symbols: metastable points, increasing shear rate

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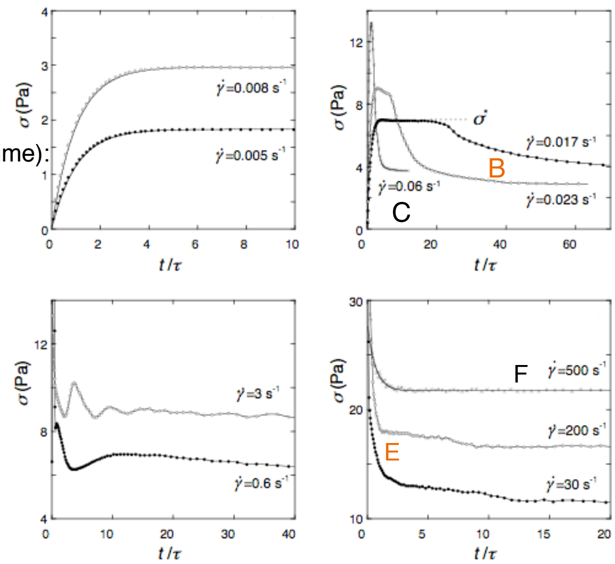
transients

A (linear regime): exponential relaxation



B (1st s.b): 'metastable' states

C: overshoots, fast relaxation

D (2nd s.b.): oscilatory transients, 'tumbling' (?)

E (3rd s.b.): overshoots, slow irregular relaxation

F: overshoots, fast relaxation

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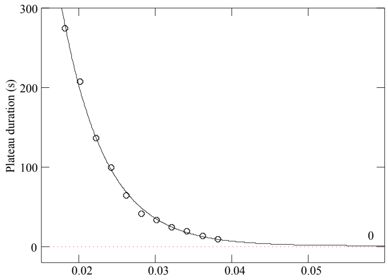
transients (regime B)

- Life-time of metastable stress 'plateau' vs. shear rate



$\dot{\gamma}$ 1/s

$$\Delta t \approx A \exp(-B\dot{\gamma})$$
$$A \approx 6.6\ 10^{3}\ \mathrm{s}^{-1}$$
$$B \approx 176\ \mathrm{s}^{-1}$$

- Decrease of stress during life-time of 'plateau' is constant $(\Delta\sigma \approx -0.04\ \mathrm{Pa})$

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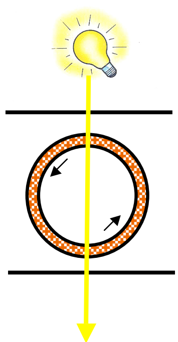
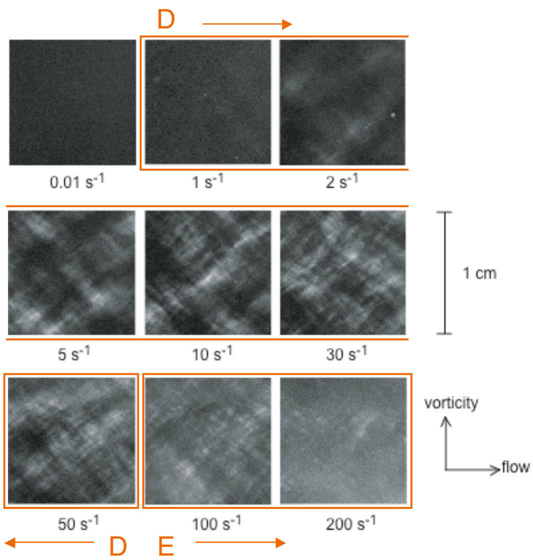
birefringence





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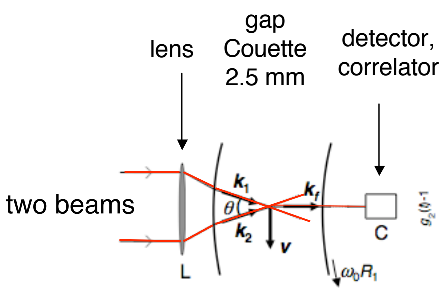
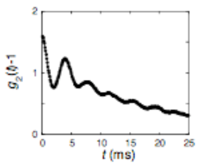
velocity profiles

direct measurement by
heterodyne dynamic light scattering / laser Doppler velocimetry
(setup at Jülich)





typical intensity correlation function
frequency of oscilations ~ velocity

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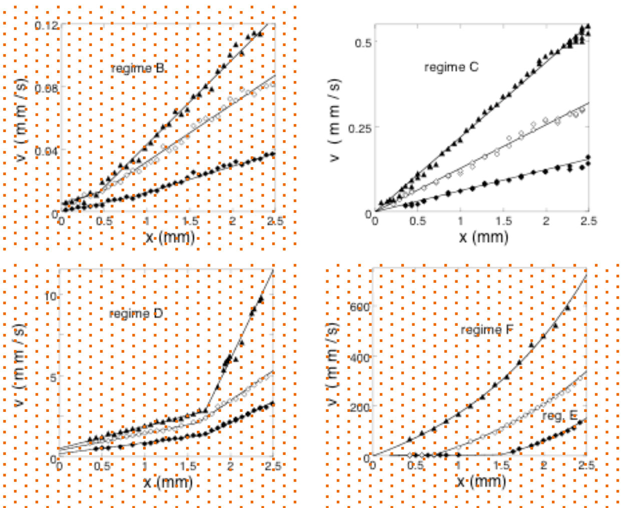
velocity profiles



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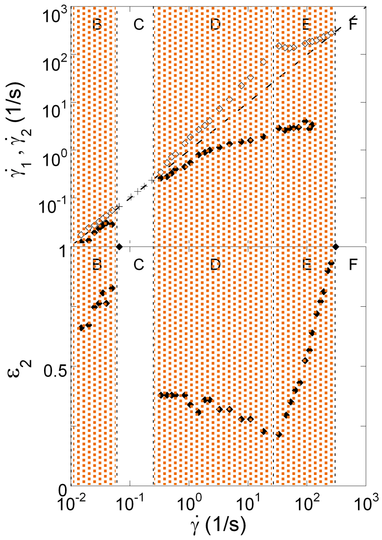
avarage shear rates in each of the two bands

fraction of gap occupied by high-shear-rate band



'standard picture' does not apply

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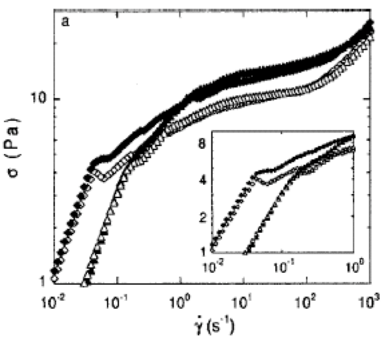
Effect of temperature / "stoppers"



(5 g/l EHUT)

reduce viscosity η by
- increasing the temperature (*filled markers*)
- adding "stoppers" (*open markers*)

("stoppers" = monofunctional monomers which reduce average chain length number of stoppers determines number of chain ends and hence average chain-length)

relaxation times & non-linear rheology: different for cases where η was reduced by either T-increase or stopper addition

W. Knoben e.a., J. Chem. Phys., 126, (2007) 024907

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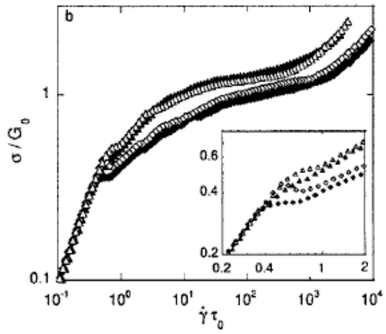
Effect of temperature / “stoppers”



relaxation time reduced more strongly
by temperature increase than
by stopper addition

Solution	S_{T1}	S_{x1}	S_{T2}	S_{x2}
T (°C)	30	20	40	20
x (−)	0	0.005	0	0.015
η_0 (Pa s)	71	67	31	34
τ_0 (s)	4.5	6.0	1.8	3.0

- Reduced flow curves are largely the same for cases where η was reduced to the same vallue by either T-increase or stopper addition,
- But not for the shear-banding regime B

At shear banding regime B: coupling between flow and reversible polymerisation

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Conclusions

- The RSP “EHUT” exhibits complex non-linear rheology
  - three shear-banding regimes
  - with peculiar dependencies upon average shear rate (shear rates within separate bands, position of interface, no stress plateau)

- 1st shear-banding regime (B) probably associated with a mechanical instability (no birefringence / alignment of chains)

- 2nd and 3rd shear-banding regimes (D&E) probably associated with ‘nematic’ alignment (birefringent textures, oscilatory transients)

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