Task 3: viscoelasticity, nonlinear rheology and mechanical properties

Task 3.1.: Diagnostic tests involving **linear viscoelastic measurements (LVE)** and in particular, oscillatory measurements. First, the thermal properties of the samples will be determined by differential scanning calorimetry (DSC) in order to establish the temperature range for rheological measurements. Since associating networks are essentially metastable systems, **dynamic time sweep tests** will be performed following thermal annealing or pre-shear in order to follow possible ageing and determine quasi-steady-state conditions, assess the sample's stability, and determine the proper protocol to use, which is necessary for comparing samples. **Strain amplitude sweeps** will be performed for determining the limits of the linear viscoelastic regime and, finally, **frequency sweep measurements** will provide important information about the relaxation time spectrum of a sample, which is of prime importance to understand and model their equilibrium dynamics, and will allow us to explore the influence of the structural and external parameters. Special attention will be paid to the reduction of degradation risks (by using of nitrogen or a special humidity-control chamber mounted on the rheometer).

The expected by-design distinct relaxation modes of DDNs will be decoded and their features (time, modulus, broadness) linked to molecular characteristics (molar mass, composition, strength of association). **Time-temperature superposition** will be tested and assessed (it is expected to fail due to different bonding interactions). Hence, to analyze the viscoelasticity, spectra over a very wide range of frequencies are needed, which will be achieved by **creep measurements**. To extend the spectra to higher frequencies a **piezo-rheometer will be used**. This setup has been recently developed by Partner P2. In conjunction with WP2, the latter insight will be cross-related to the complementary information from dynamic light scattering. With this method, we shall particularly focus on two modes: at long correlation times, we will look out for non-diffusive, viscoelastic modes of network relaxation and relate these to the low-frequency end of the elastic plateau in rheology. At short correlation-times, we will focus on diffusive modes of network-strand fluctuation and relate these to the high-frequency end and the level of this plateau.

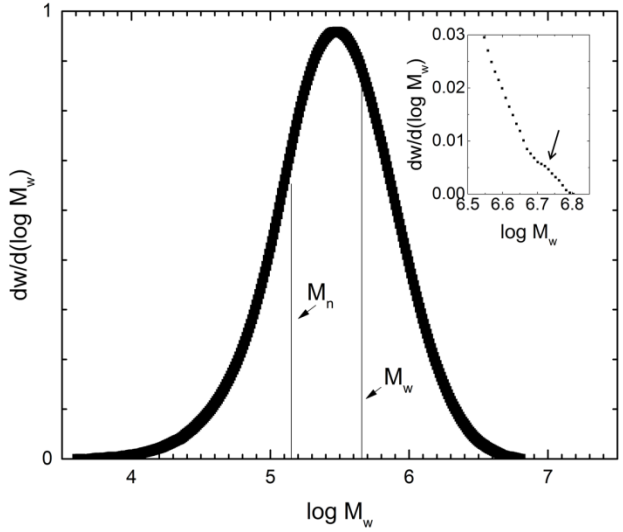
Task 3.2.: Step shear measurements of the DDNs will provide information about relaxation process and time of the dense network and how they are influenced by a nonlinear (out of equilibrium) deformation. By performing **measurements under constant (large) shear rates**, we shall obtain information about the shear thinning (or shear thickening) behavior in function of the lifetime of the two transient networks, and about important potential issues such as yielding, wall slip, and shear banding, in order to further understand the material response but also to determine guidelines for efficient processing of the networks. In order to avoid artifacts (primarily edge fracture), a customized cone-partioned plate fixture developed by Partner P2[17] will be implemented in a strain-controlled rheometer, which allows measuring both shear and **normal stresses** reliably. Further, to assess the elastic memory of the networks and self-healing potential, shear deformation will cease at different levels of stress during its transient response and their relaxation will be analyzed and compared against its linear response and DLS in WP2. The long-time relaxation will be examined to detect possible residual stresses associated with the metastable nature of the DDNs and possible heterogeneities. In this direction, we'll take advantage of structural information obtained from in-situ light scattering experiments or selected rheo-SANS experiments (in conjunction with task 2.3). Results will be compared against those obtained by means of light scattering (task 2.1).

Task 3.3.: Nonlinear creep tests at stresses above yielding will be performed and analyzed, to discern internal partial break of the network or loss of entanglements, i.e. loss of macroscopic cohesion. They will be also compared against step shear measurements.

Tasks (with specific DDNs from WP1):

LVE (TTS, creep, creep, piezo)
NLVE shear (CPP, N1-N2, transients, creep-relaxation thixotropy, banding)

Example: semi-crystalline high-MW polyethylene



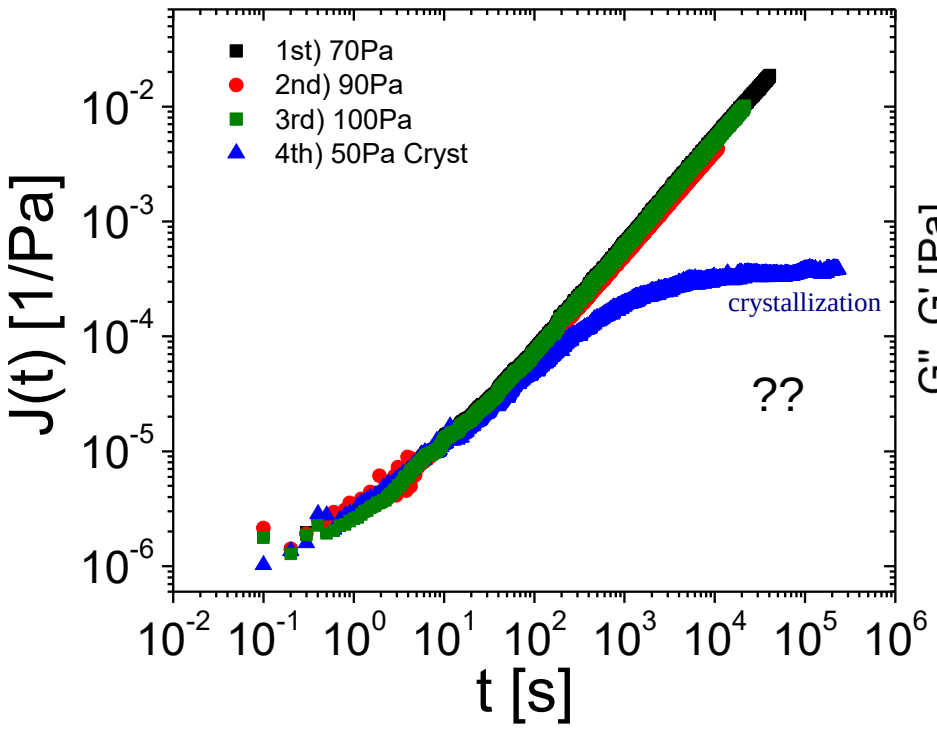
SAMPLE "PE-460k":

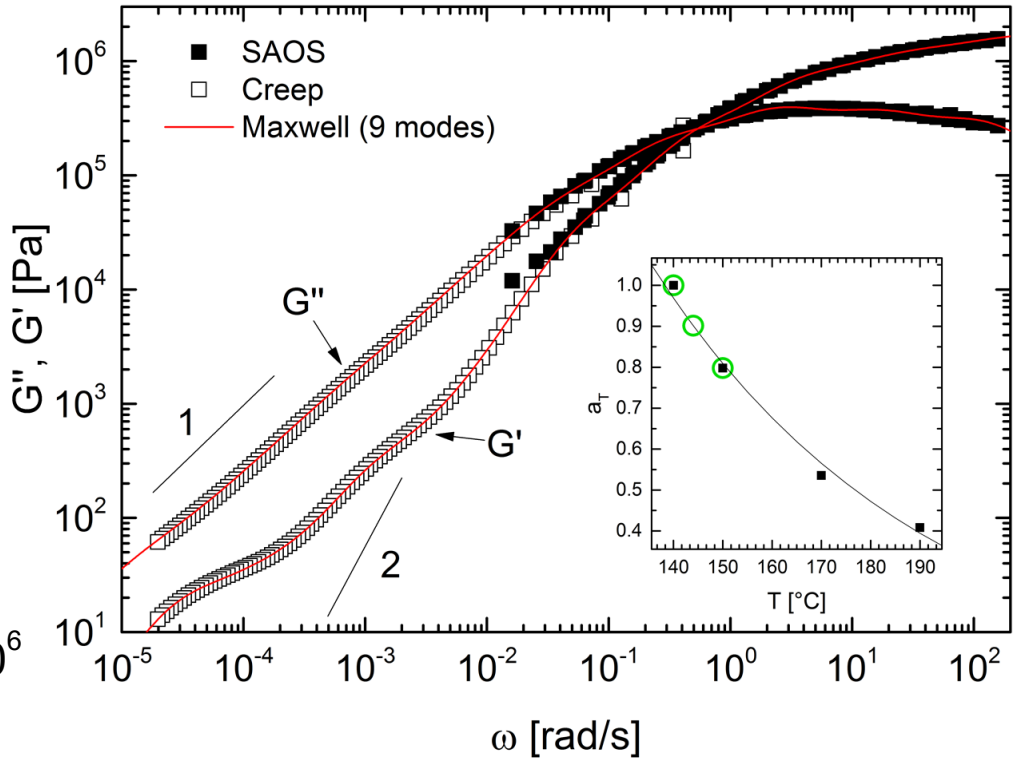
HDPE: CP00416-021 from Chevron Philips

T_m = 138.0 °C

M_w = 460 kg/mol

PDI=2.7

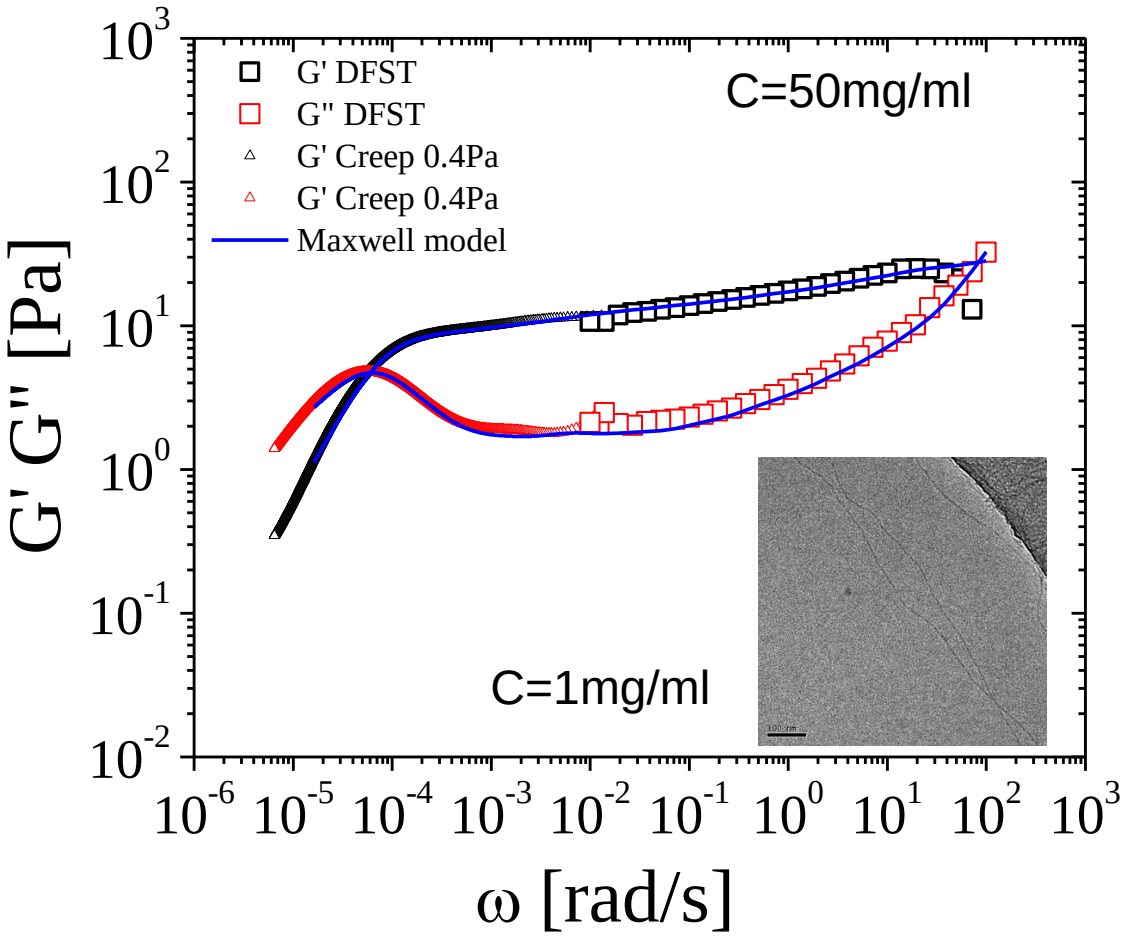




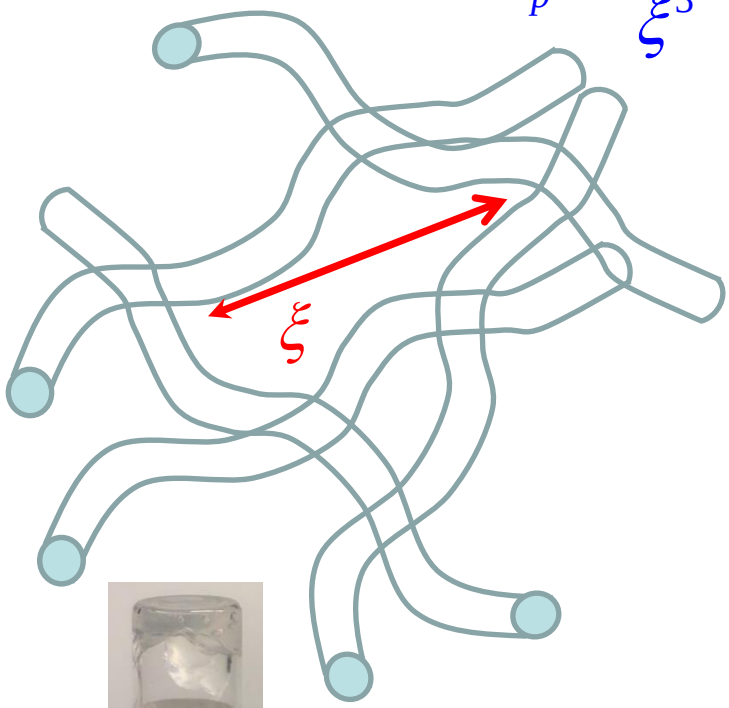
with S. Wingstrand, O. Hassager

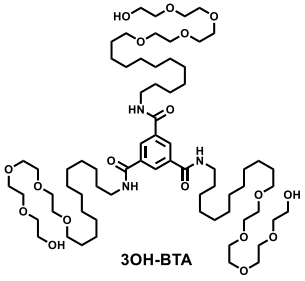
Example: hydrogels

with E. W. Meijer



$$G_p \approx \frac{kT}{\xi^3}$$



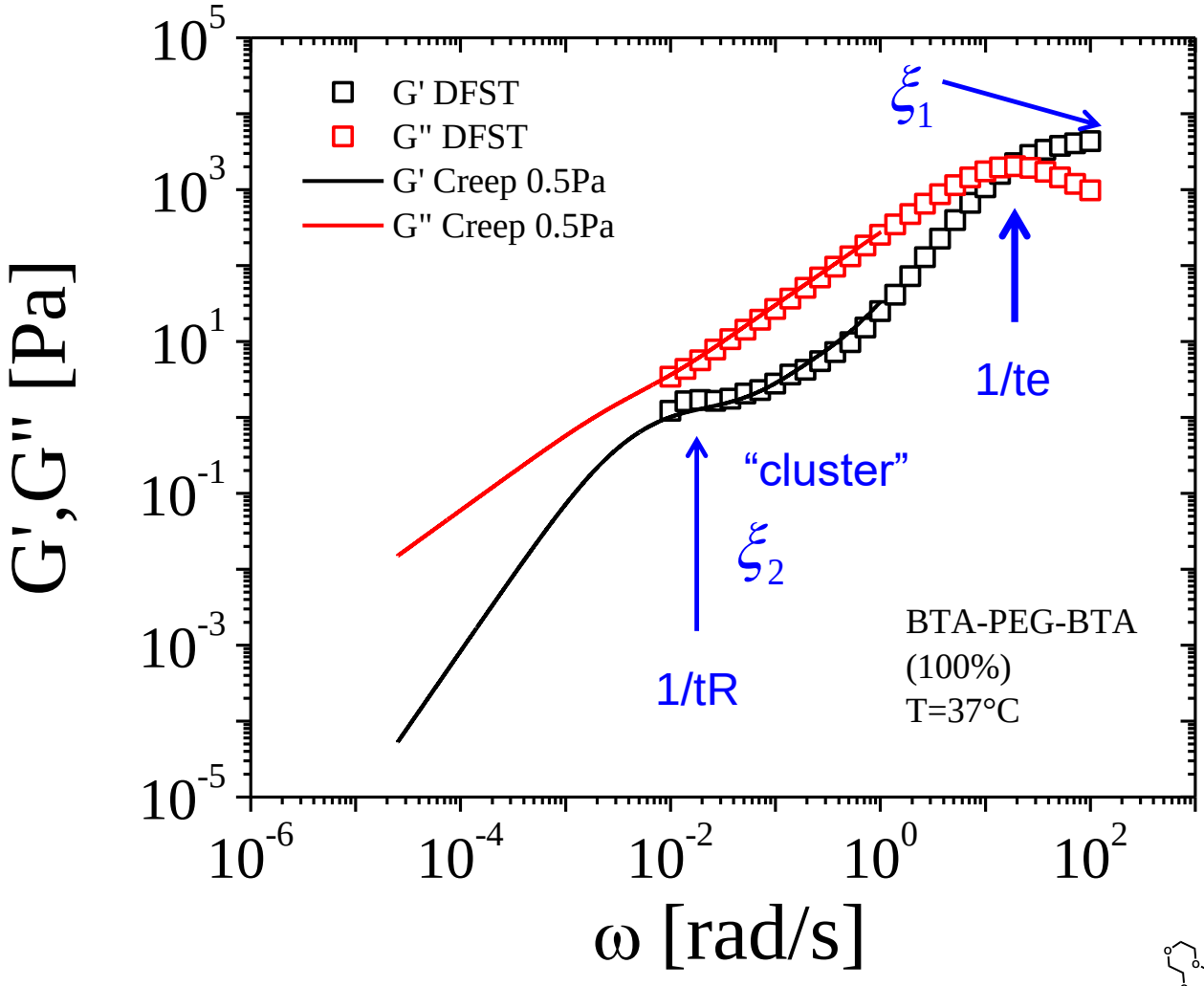


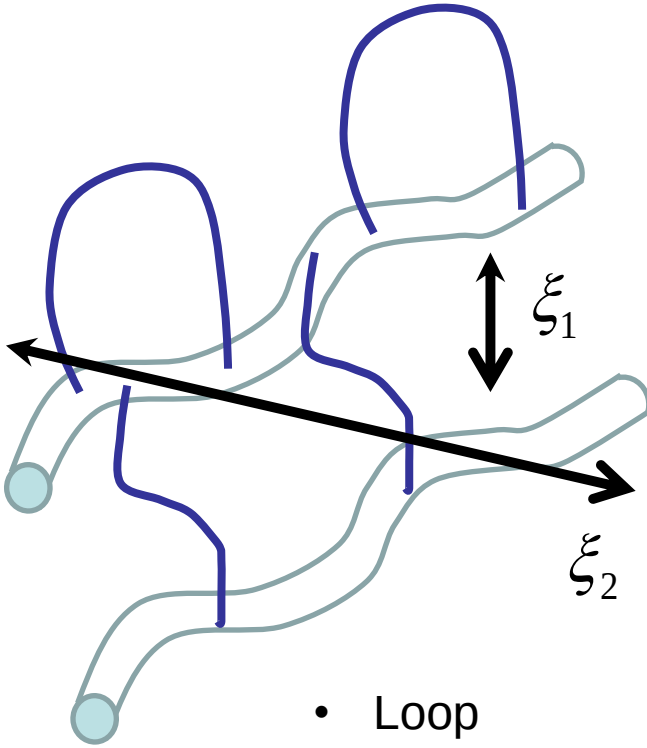
Weak gel, akin to entangled polymer network, with:
Modulus Gp=13Pa
Relaxation time tR=1.8x10^4 s
Correlation length (mesh size of gel network) =69 nm

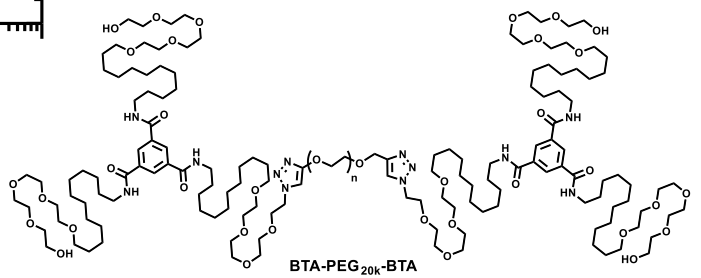
Note: Very dilute DLS studies reveal wormlike chains with persistence length of ~180 nm, contour L~4500 nm and bending stiffness ~180 kTnm, ie, about 5 times larger and surfactant micelles

Example: hydrogels

with E. W. Meijer



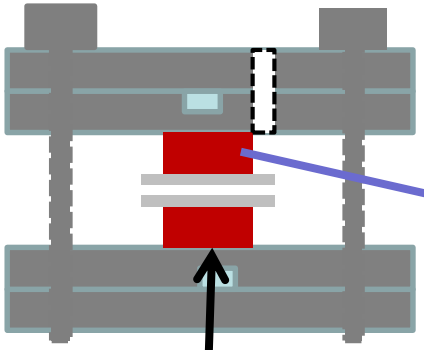


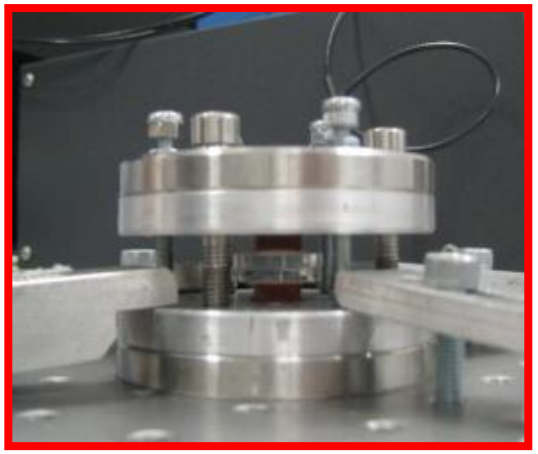


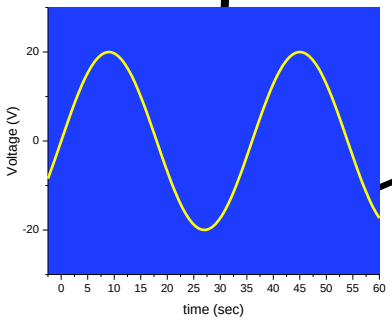
High-frequency modulus Gp1=8000Pa, Gp2=1.7Pa
Long relaxation time tR=278 s
Short relaxation time te=0.06 s
Correlation length (ξ) 1: 8 nm ; 2: 136 nm

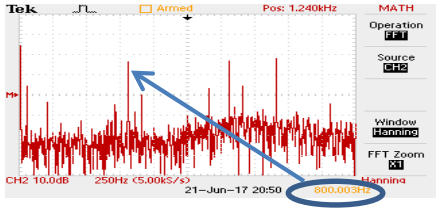
Very different response than 3OH-BTA
Correlated liquid – clusters?
No low-frequency (gel) plateau
G'' slope ~ -1 (flow)

Example: high-frequency (piezo)rheometry [2 kHz]



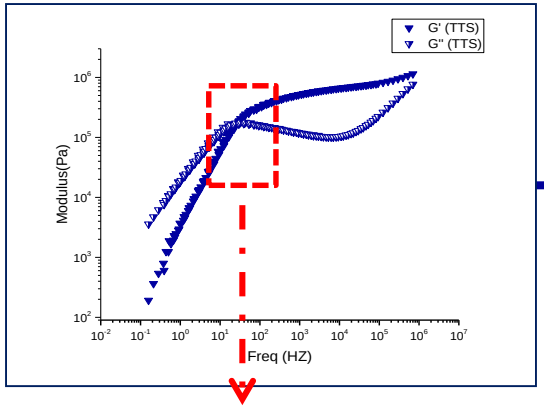






Lock-In
Phase Sensitive
Detection

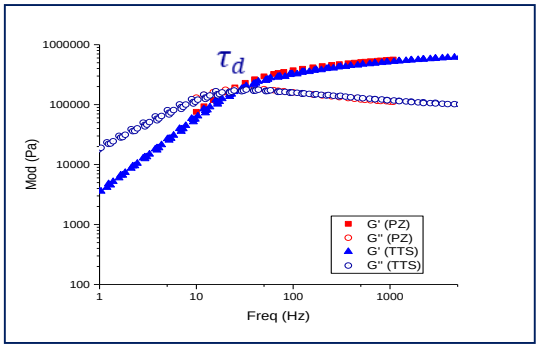
with G. Petekidis

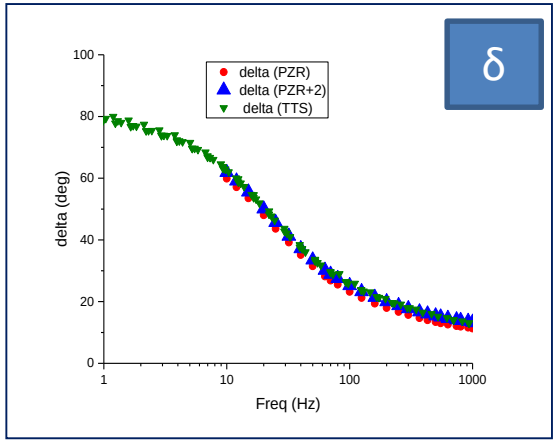


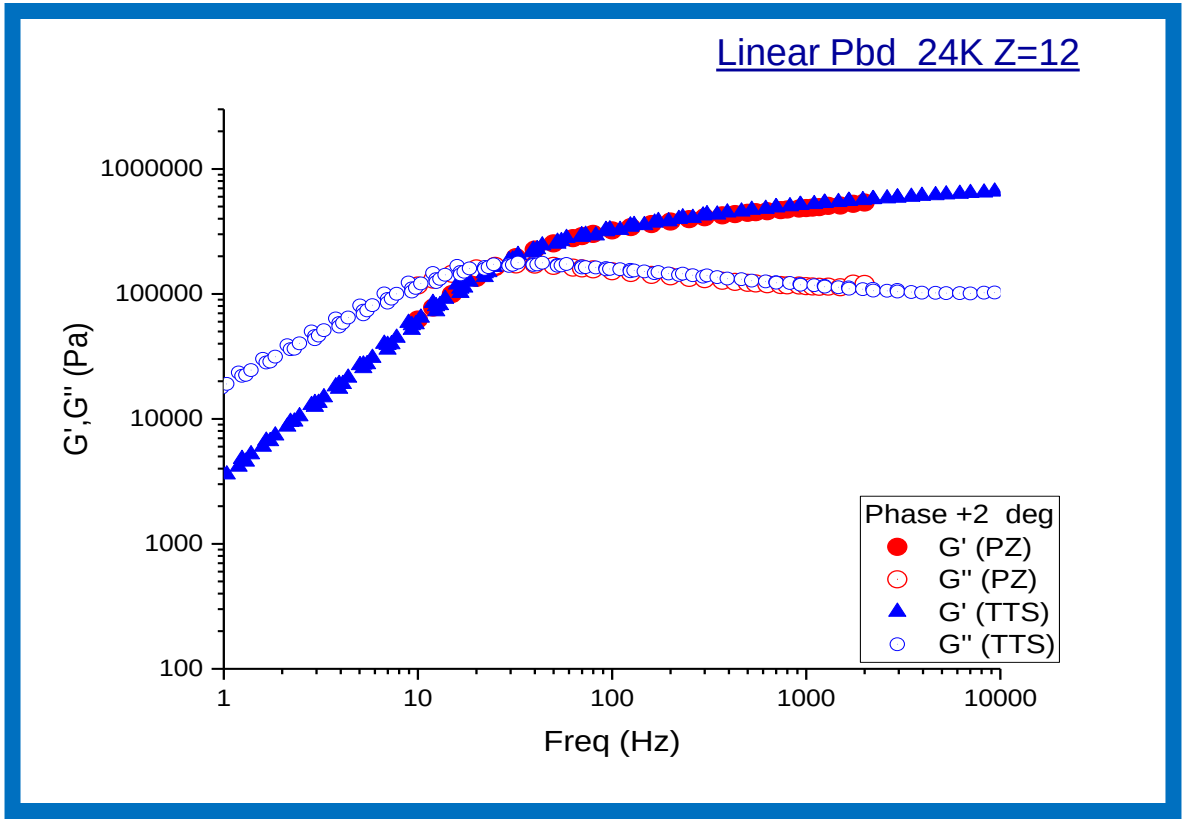
Example:
compare TTS and piezorheometry with entangled polymers

Test Parameters Master-Curve :
ARES MELT γ=3%
Tref=25C

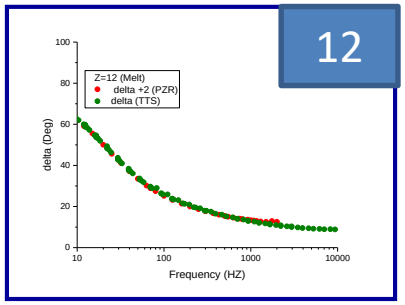
Test Parameters PZR 1
γ=10^-3 %
T=25C

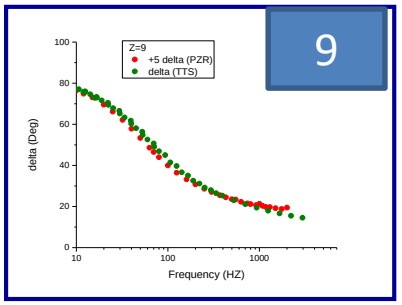


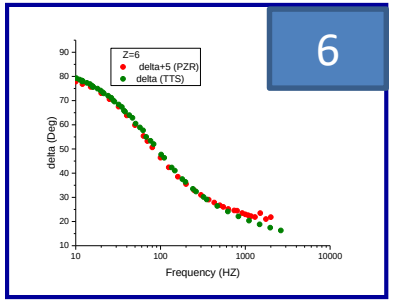


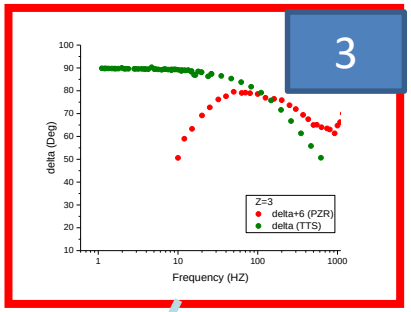


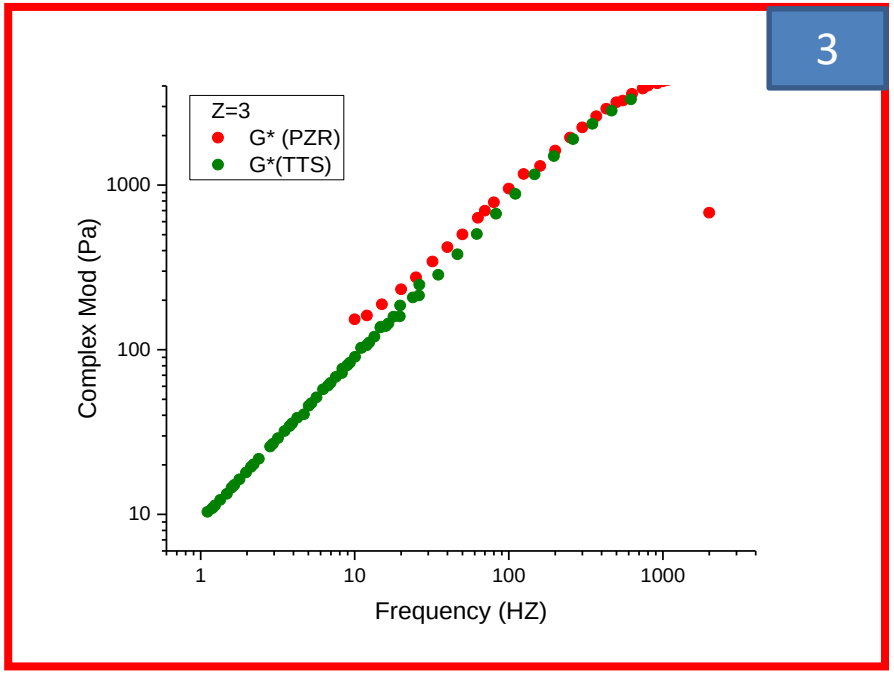
Vary number of entanglements Z from 3 to 12

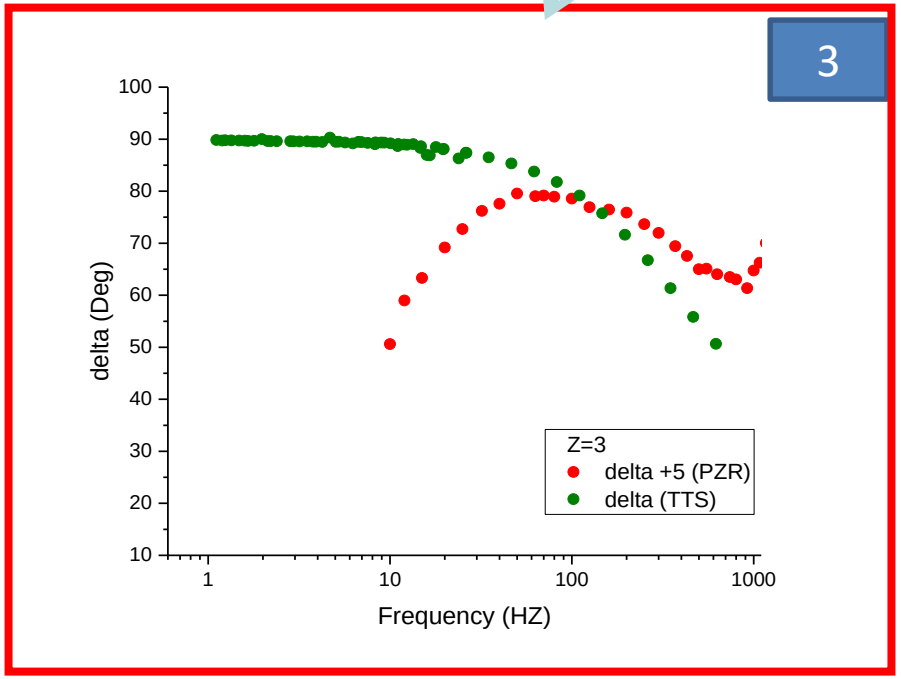




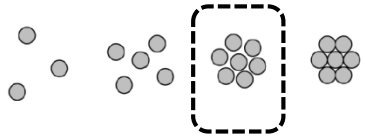






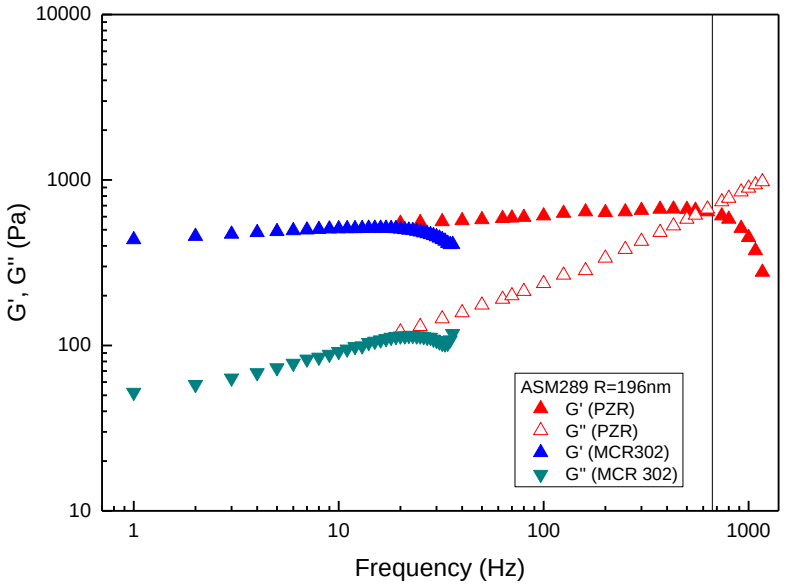


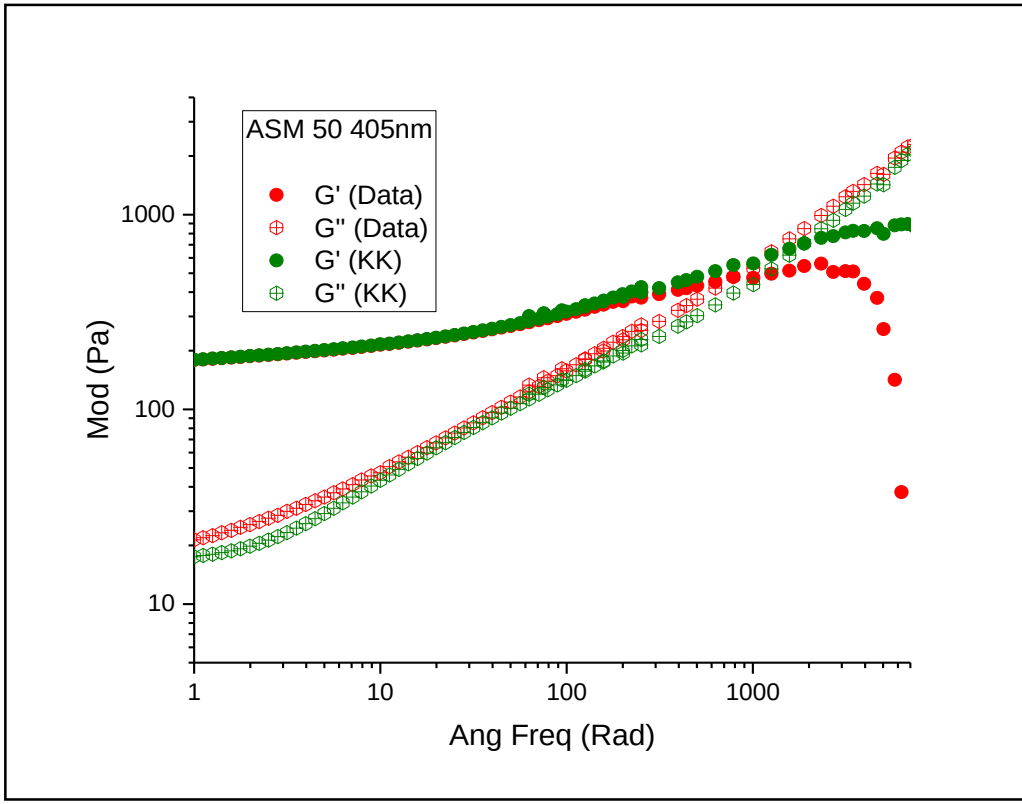
Example: dynamically arrested system (colloidal glass)



PMMA
R=196nm
φ = 0.624

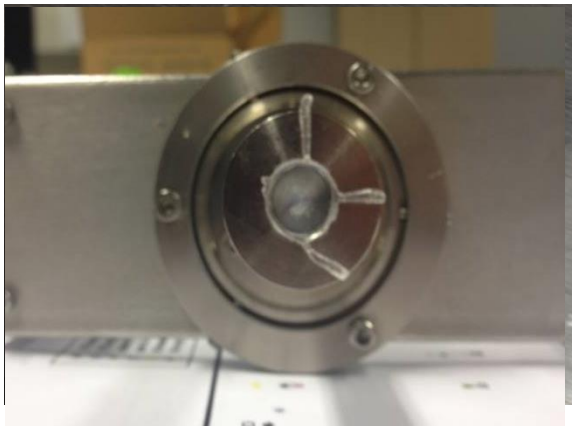
660 Hz=4,144 rad/s

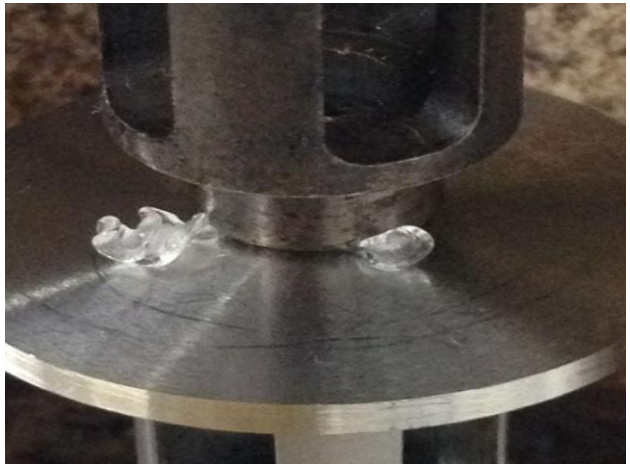




Example: edge fracture instabilities (N2 dominated)

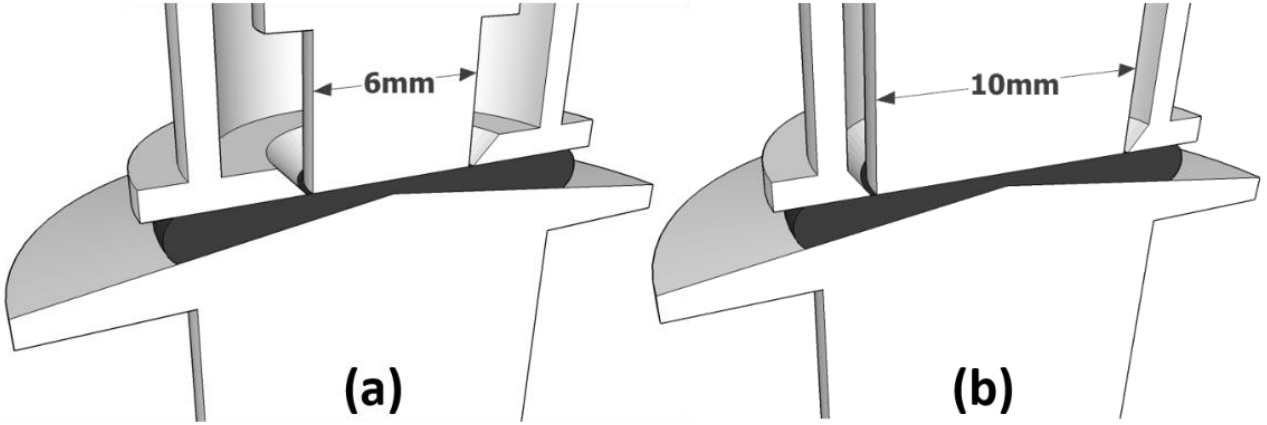
SUPOLEN

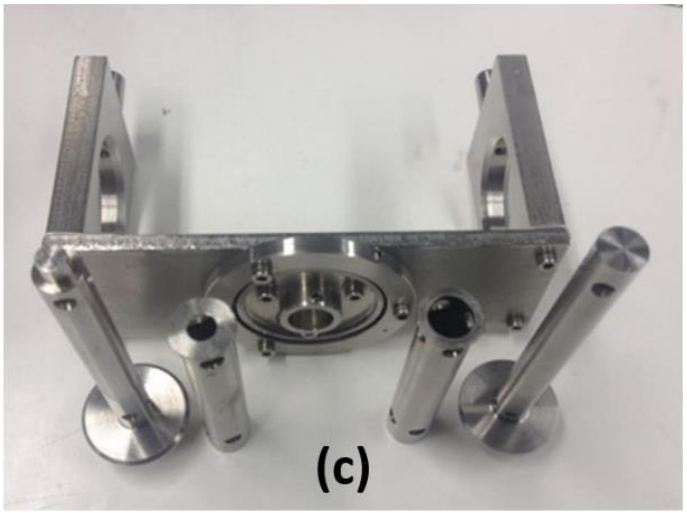


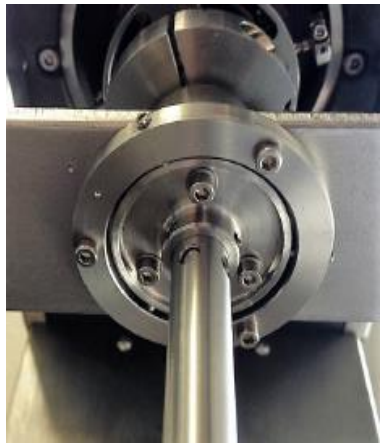


Example: cone-partitioned plate geometry (CPP)

SUPOLEN



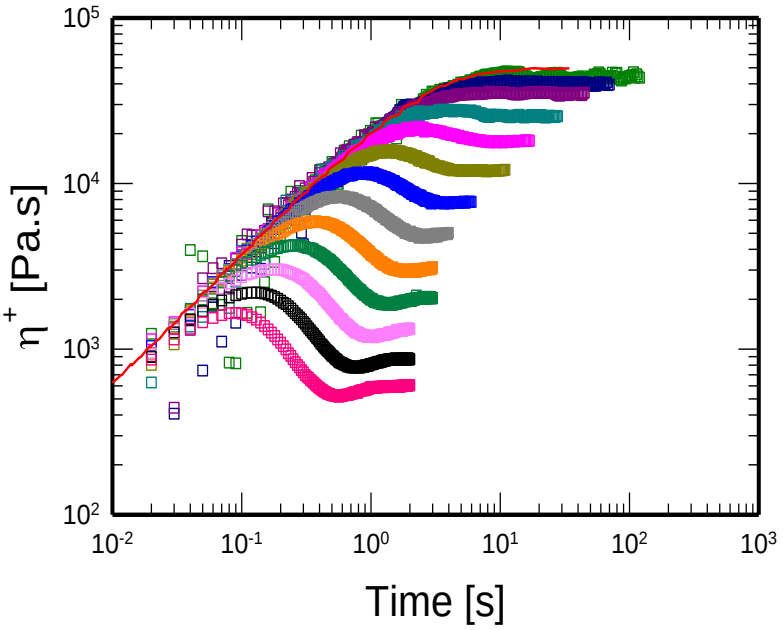


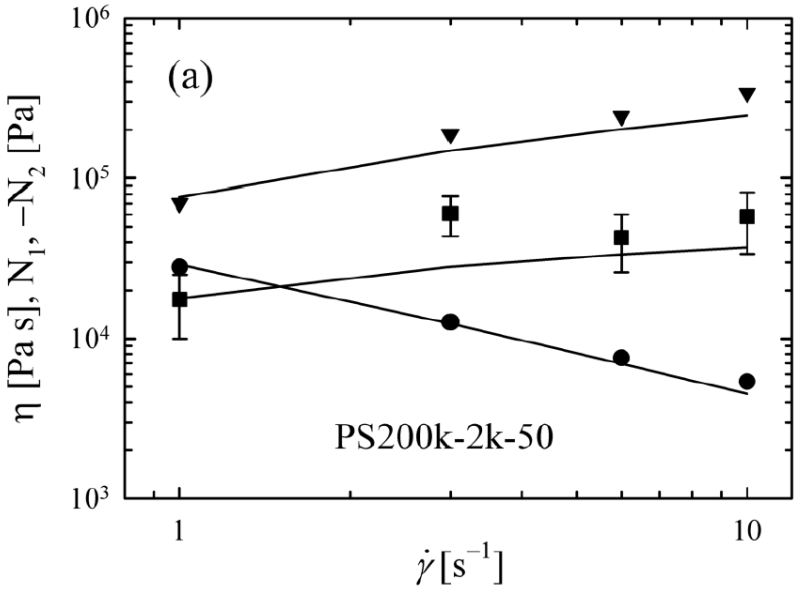


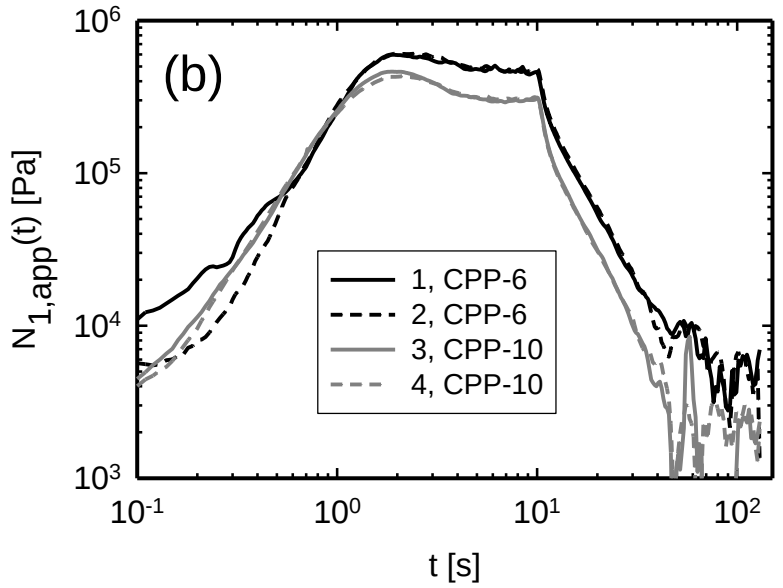
Example: CPP measurements

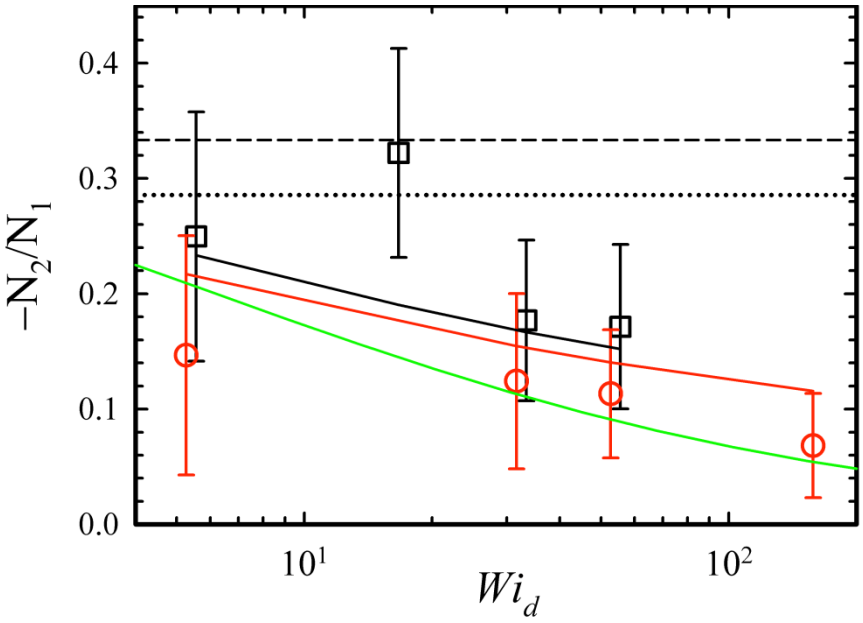
PS melt

SUPOLEN







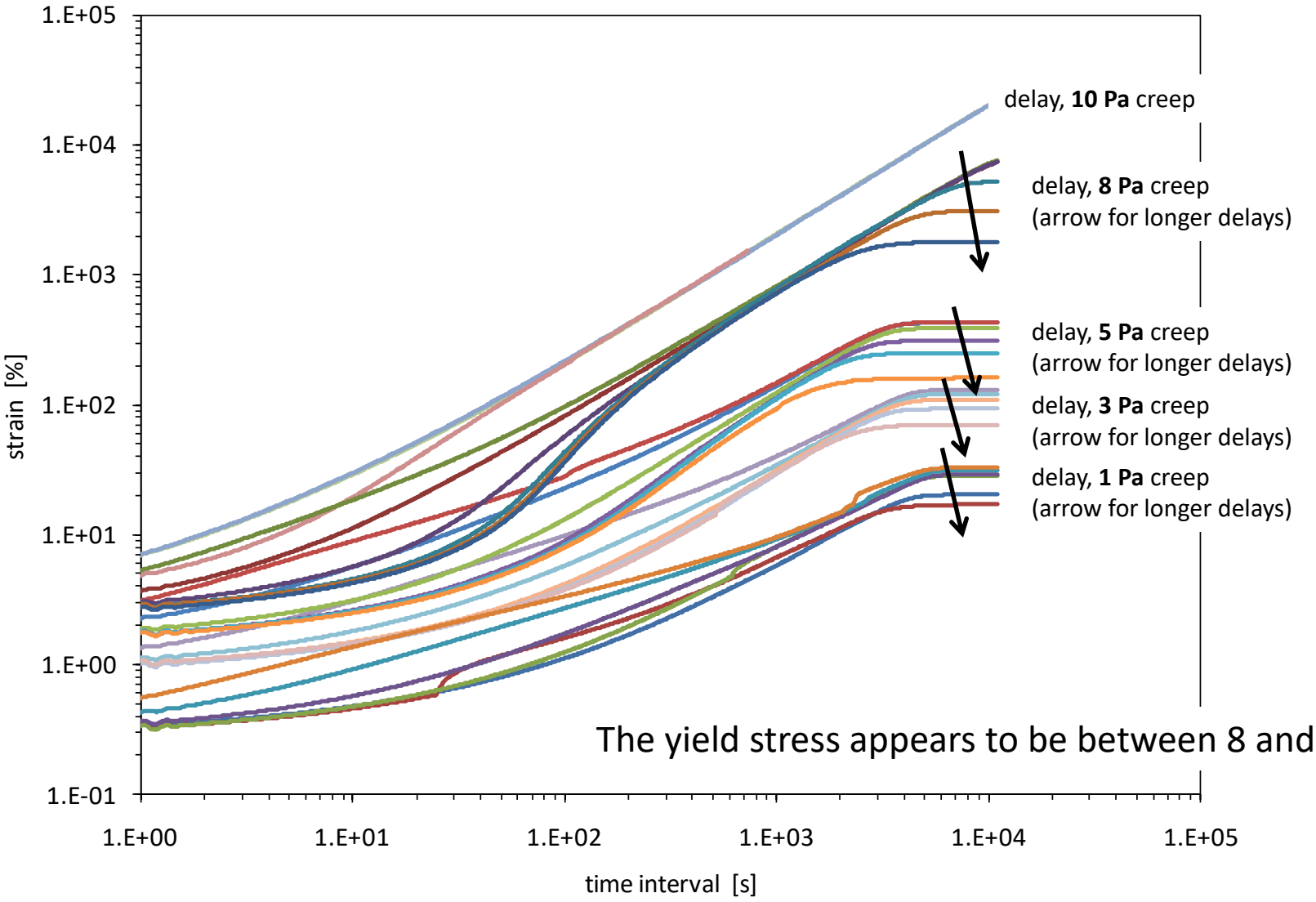


with G. Iannirubertо, G. Marrucci

Example: nonlinear creep

with M. Cloitre

a. pre-shear stress of 100 Pa applied for 50 s
b. varied time delay with zero stress: (0.1, 1), (2), 10, 100, 500, 1000, 2000 s
c. stress applied for creep experiment: 1, 3, 5, 8, or 10 Pa



The yield stress appears to be between 8 and 10 Pa.

Example: Rheo-optics

Microscopy, LS, DLS-echo, imaging (shape of fractured surface)

Example: biaxial deformation (bubble inflation)

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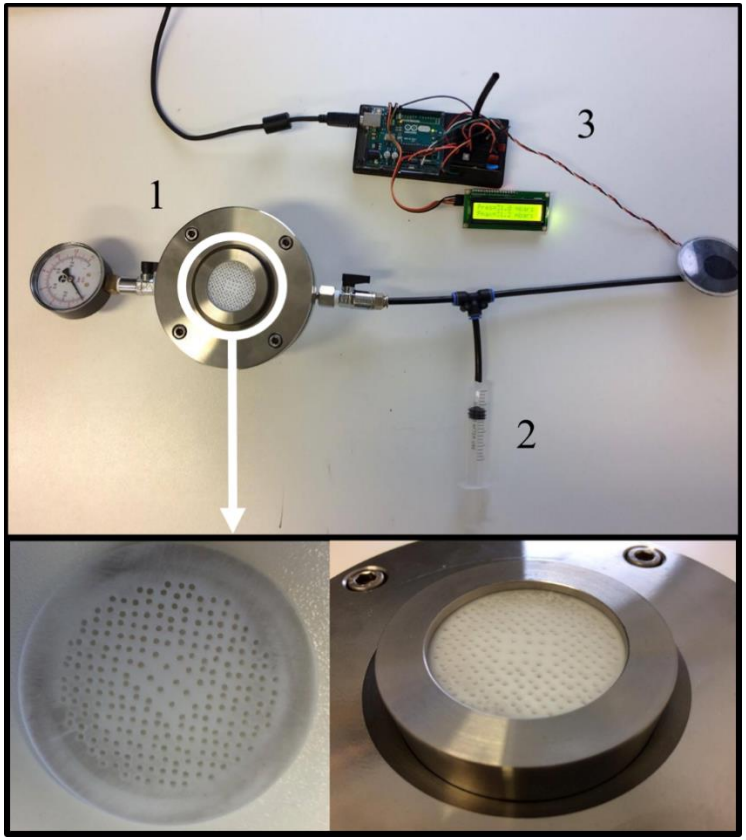

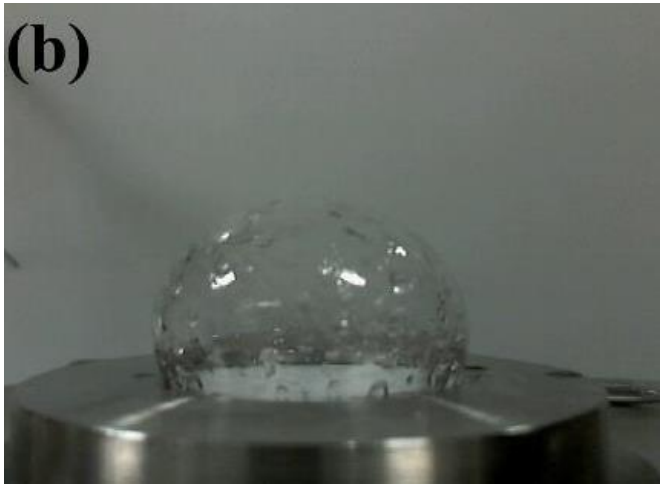

Envisaged collaborations (not finalized):

UCL (systems, modeling)
ESPCI (systems, rheo-microscopy/velocimetry, fracture-"solid")
CNRS (fracture-"liquid")
DTU (elongational deformation)
UM (FCS, FRAP)
UN (modeling)

Start (~ first year)

Development (improve CPP N1/N2, piezorheometry, biaxial deformation for weak gels)
Test rheo-optical setups (back to polarimetry, echo, EWDLS-slip)
Slow dynamics
Polymeric systems (continue from Supolen) and hydrogels
'Starting' systems?

Unfinished collaborative projects from Supolen
NLVE of telechelics based on metal-ligand interactions (UCL)
Spreading of viscoelastic sheets (CNRS)
Compare nonlinear shear and extension (DTU)
Modeling dynamics of telechelic stars (UCL)
Normal stresses (UN)
Unusual stress relaxation (KUL, ESPCI)