



RHEOLOGICAL CHARACTERIZATION OF
POLYPROPYLENE MELTS OF VARIOUS DEGREES OF
BRANCHING

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Outline

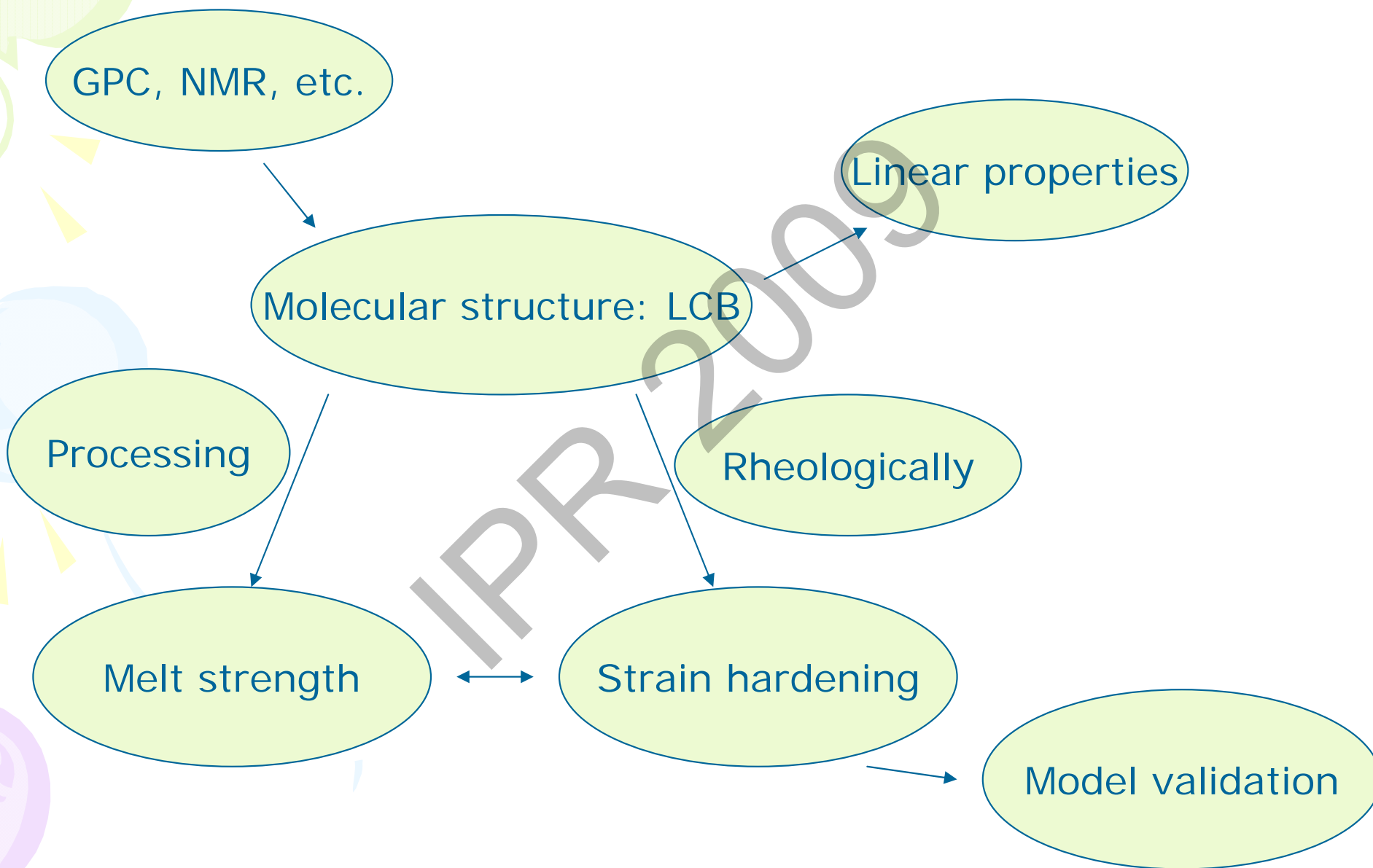
- Introduction
 - ▶ Rheological properties – molecular structure
 - Polymer processing
- Objectives
- Experiments and Results
 - ▶ Materials
 - ▶ Linear Properties
 - ▶ Nonlinear Properties
- Conclusions



Introduction

- Polyolefin processing
 - ▶ Film-blowing/fiber spinning
 - ▶ Thermoforming
 - Foaming
- Molecular structure
 - Molecular weight (chain length)
 - MWD
 - Long chain branching (LCB)
- Rheological Characterization
 - Linear properties: G' , G'' , $H(\dot{\tau})$,
 - Nonlinear: elongational viscosity

Introduction



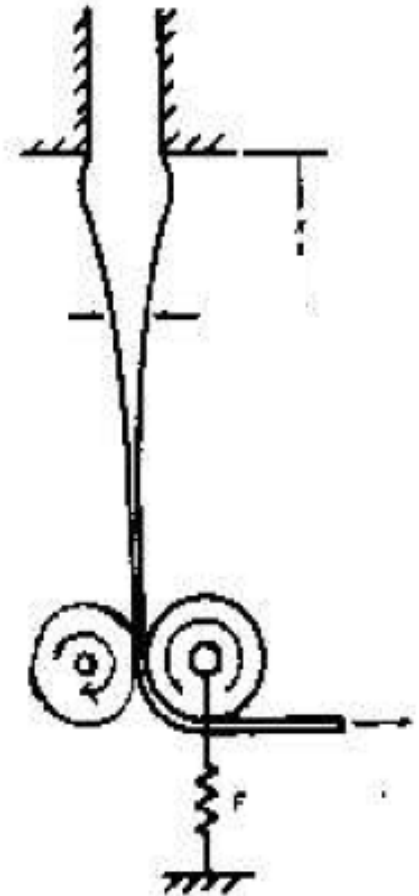
Introduction

- Melt strength
 - ▶ Constant speed
 - ▶ Draw ratio
 - ▶ One-point extensional viscosity
- Strain hardening
 - ▶ Exponential stretching
 - ▶ Planar elongations
 - ▶ Uniaxial elongations
 - ▶ Equibiaxial elongations

Gottfert Rheotens

Melt Tension (cN)

Velocity at Break (mm/sec)

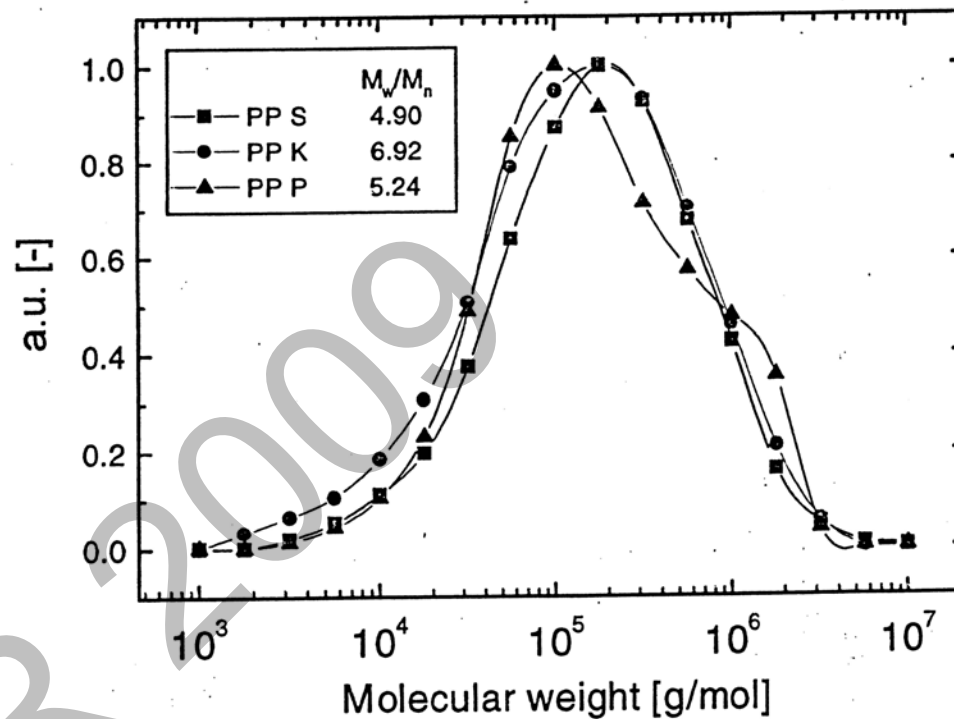




Objectives

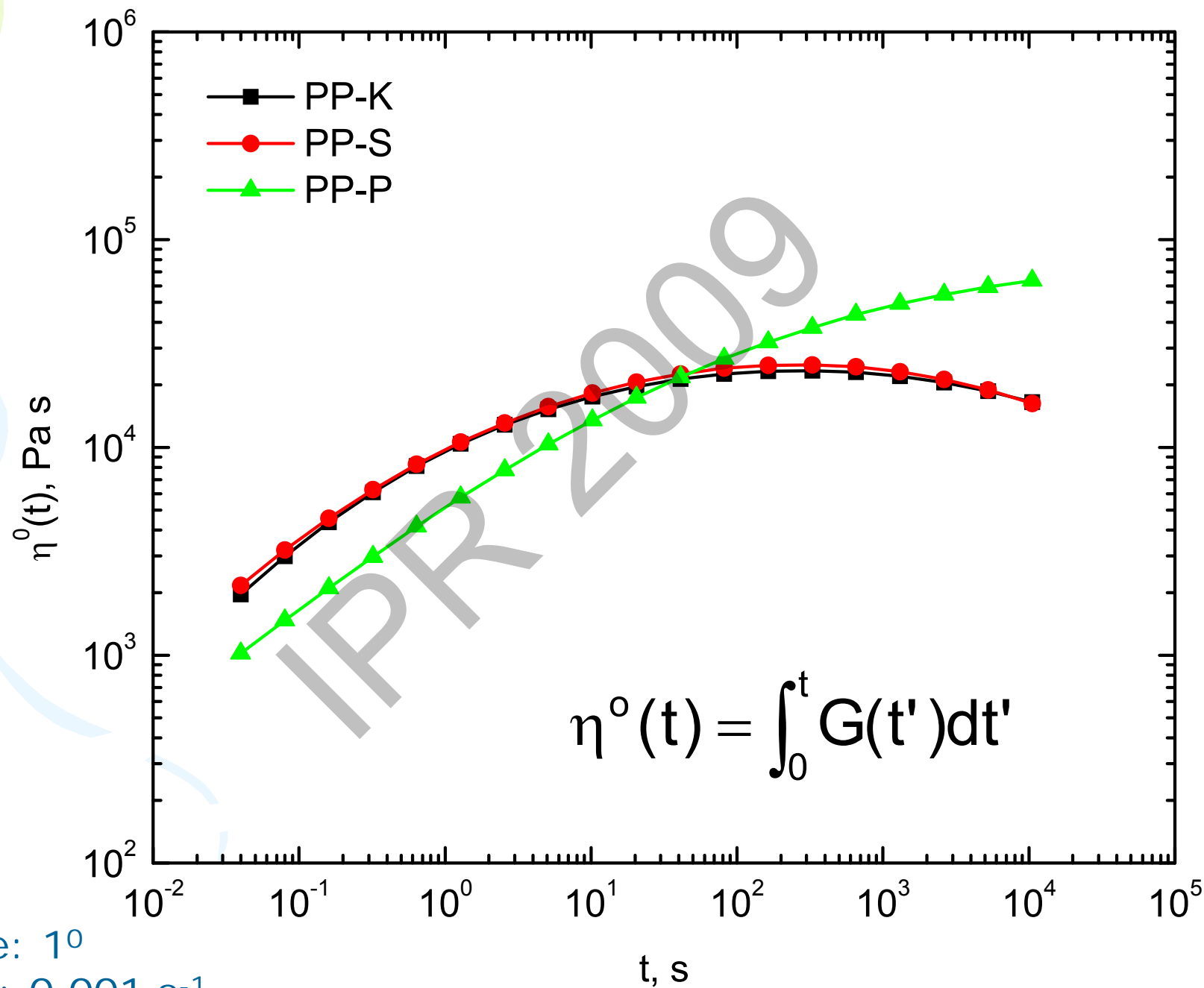
- Measure and calculate the linear rheological properties
- Acquire uniaxial and equibiaxial elongational viscosity
- Compare the results from linear vs nonlinear rheological properties
- Evaluate difference in uniaxial vs equibiaxial elongational flows
- Assess the different structures of PP melts

The molecular weights of the three polypropylenes used.



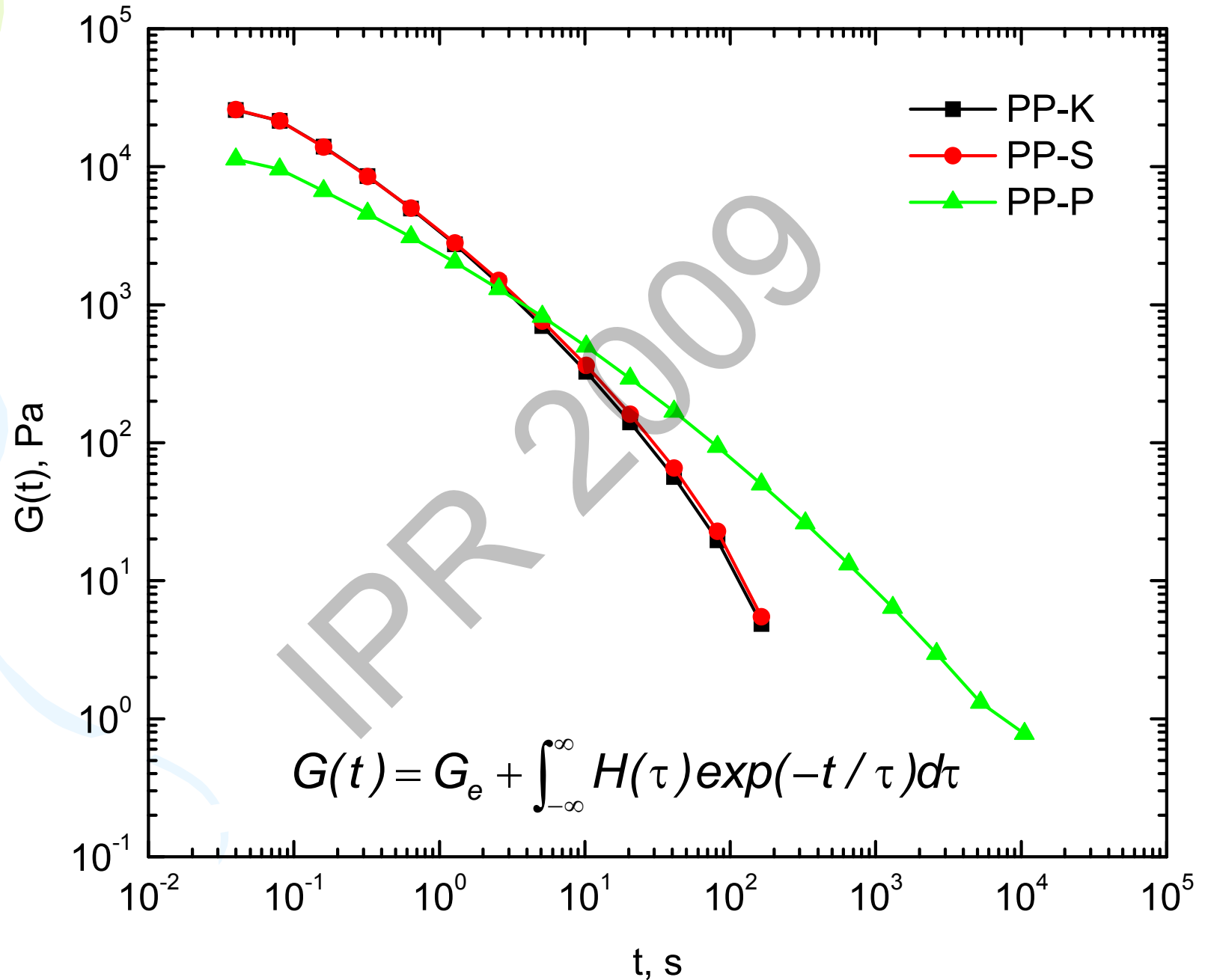
| materials | M_n | M_w | M_z | d |
|-----------|-------|--------|---------|------|
| PP-K | 47100 | 326000 | 971100 | 6.92 |
| PP-S | 69800 | 342200 | 991500 | 4.90 |
| PP-P | 79300 | 384900 | 1135000 | 4.85 |

Shear viscosity at a low shear rate in a c/p rheometer

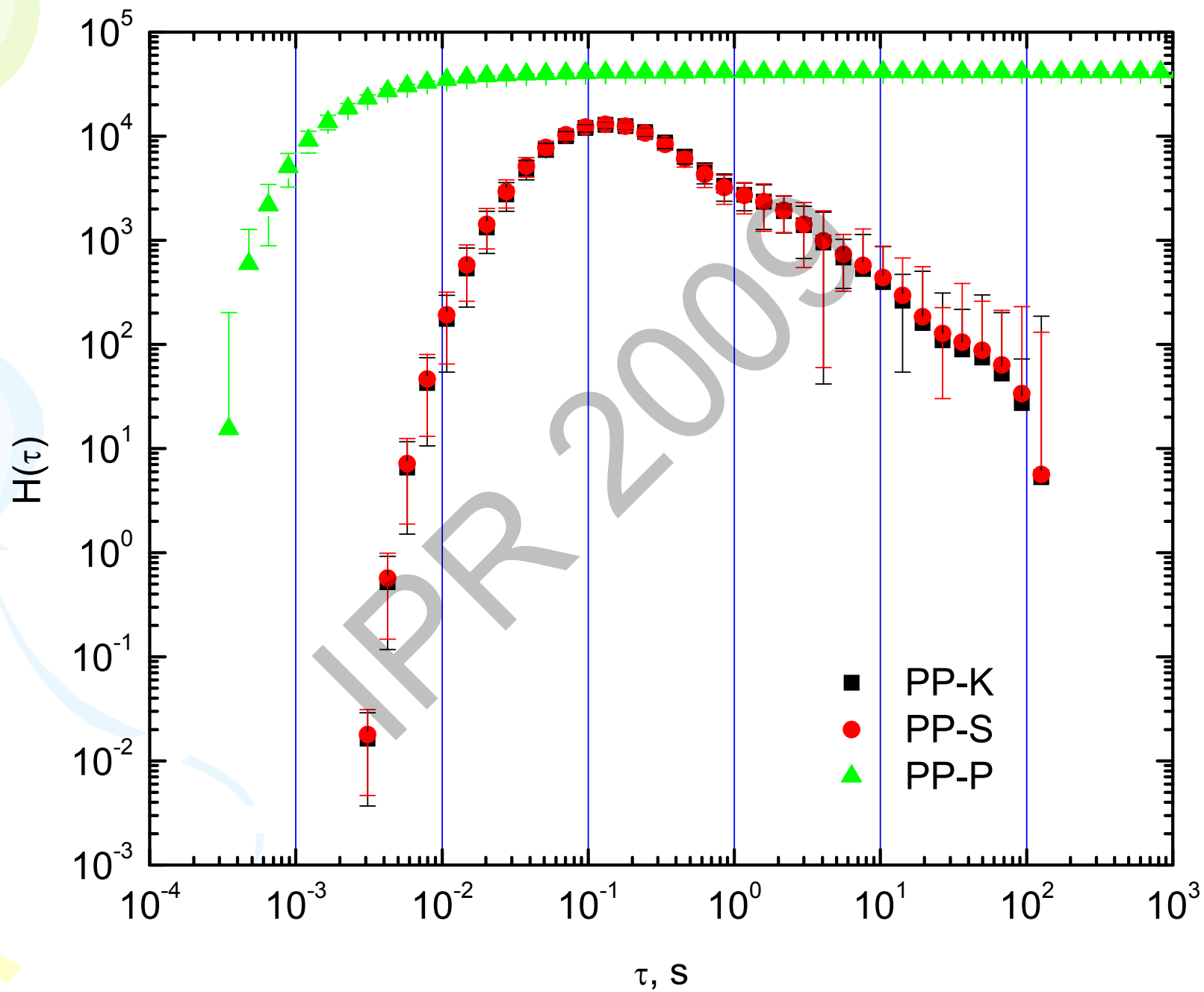


175 °C
Cone angle: 1°
Shear rate: 0.001 s^{-1}
RMS800, Rheometrics

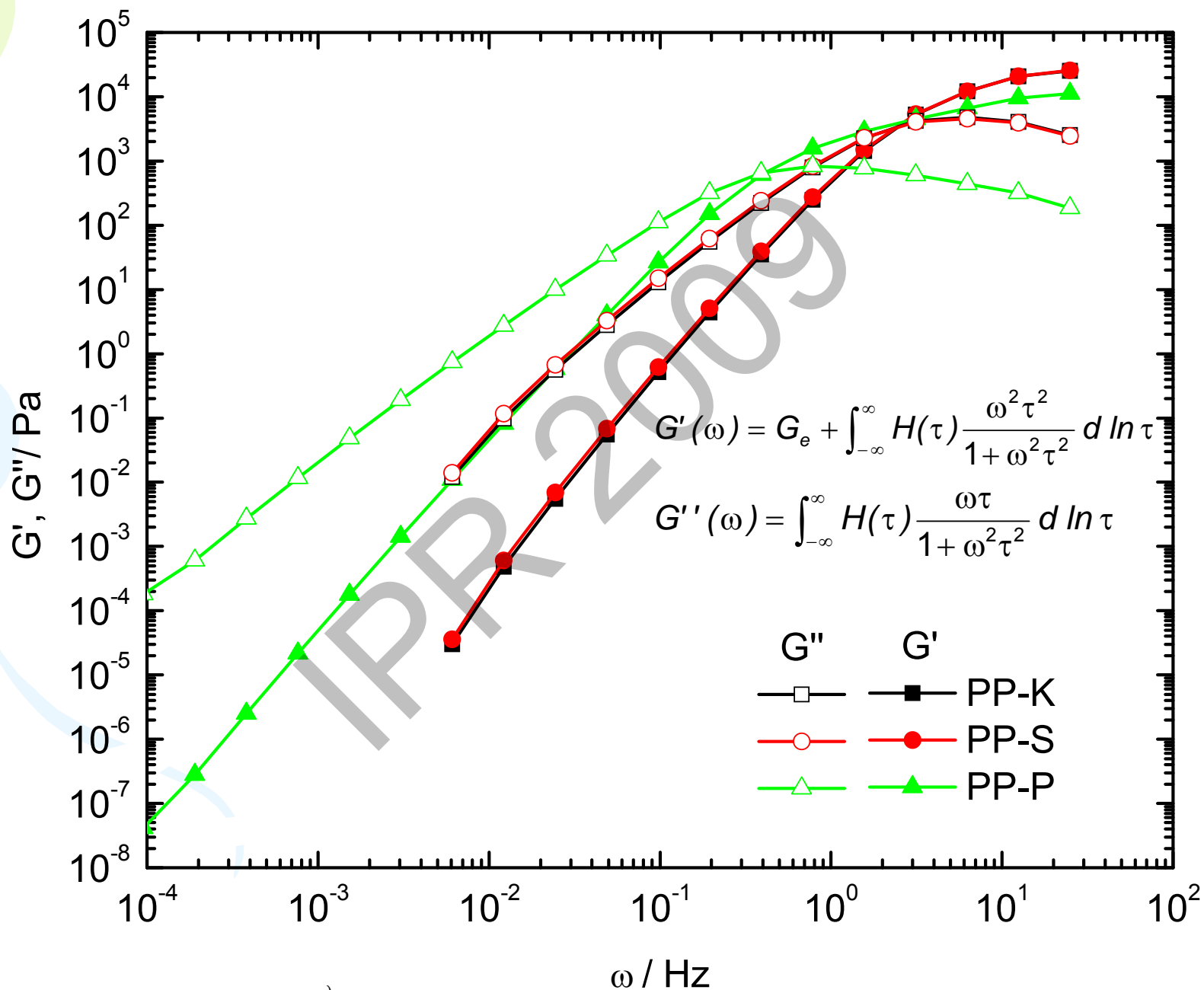
Relaxation modulus as a function of time calculated.



Relaxation spectra of 3 PPs calculated from $G(t)$ vs t .

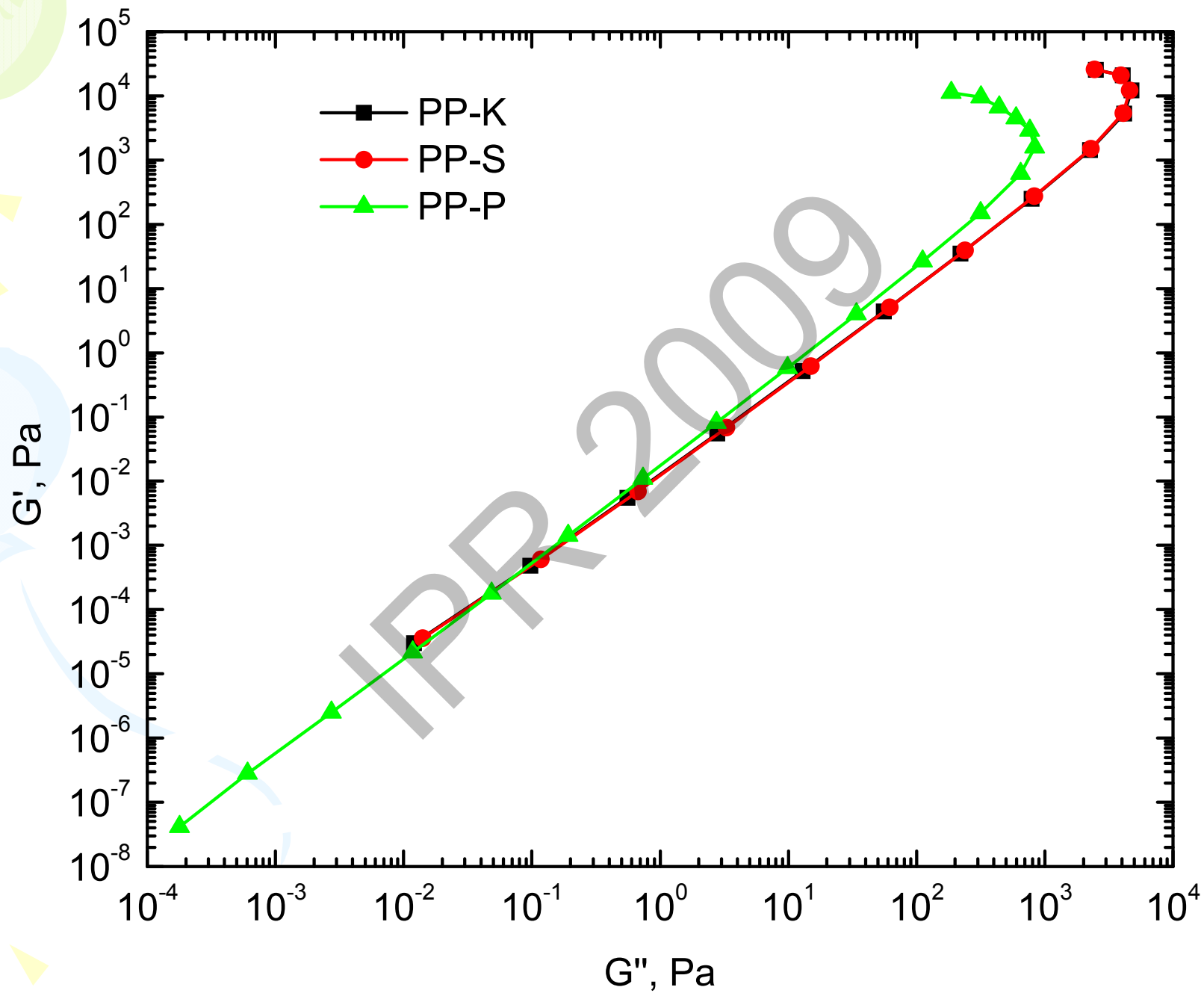


Other linear rheological properties: G' and G''



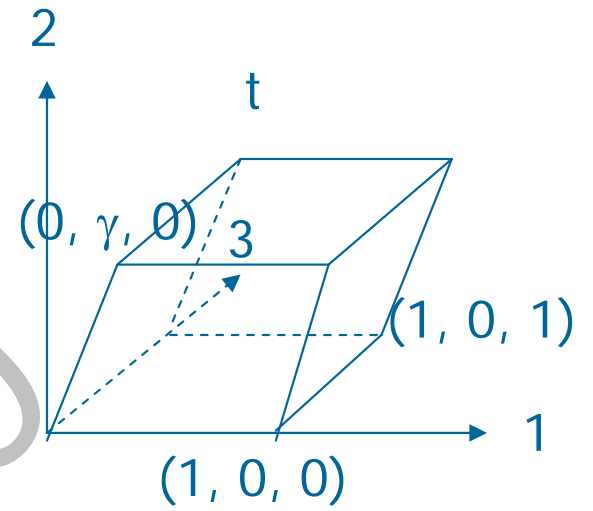
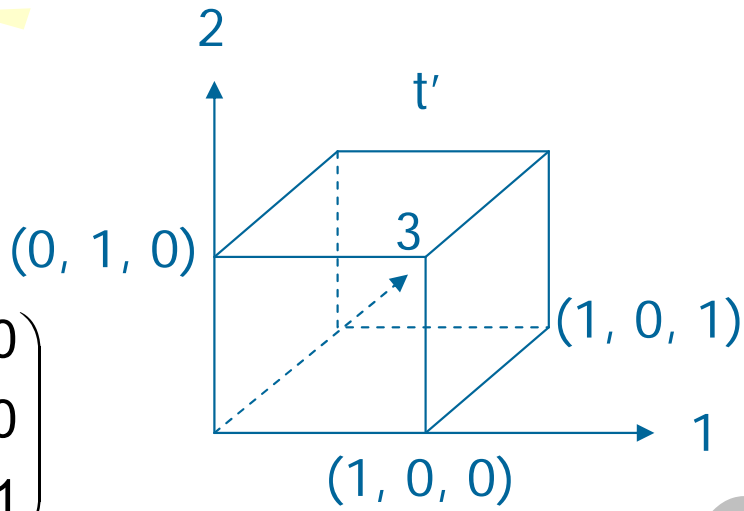
$$\eta^0(t) = \left\{ G'(\omega) + 0.27G''(2\omega) + 0.115G''(4\omega) \right\}_{\omega=1/t}$$

Cole-Cole plot of the PP

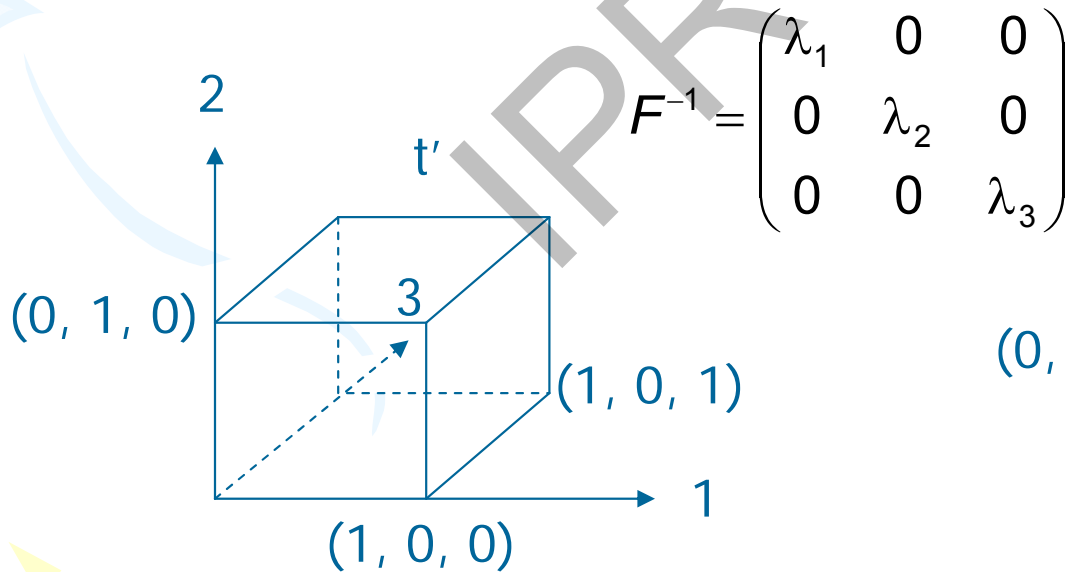


Simple shear

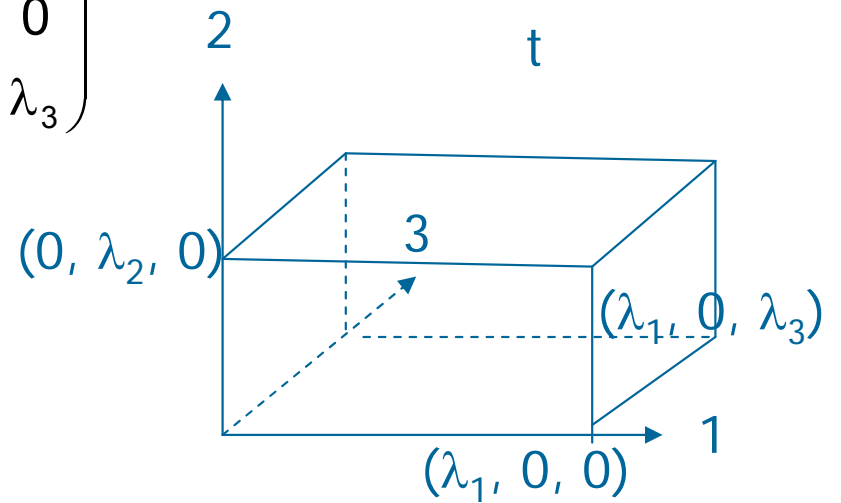
$$F^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



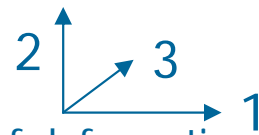
Elongations



$$F^{-1} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}$$



Velocity gradient



Deformation gradient

Finger tensor

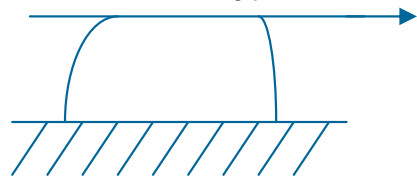
$$C^{-1} = (F^{-1})^T F^{-1}$$

Simple shear

$$\nabla V = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Rate of deformation

$$D = \frac{1}{2}(\nabla V + (\nabla V)^T) = \frac{\partial F^{-1}}{\partial t} = F^{-1} \nabla V$$



$$F^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$C^{-1} = \begin{pmatrix} 1 + \gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Uniaxial elongation

$$\nabla V = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\frac{1}{2}\dot{\epsilon} & 0 \\ 0 & 0 & -\frac{1}{2}\dot{\epsilon} \end{pmatrix}$$

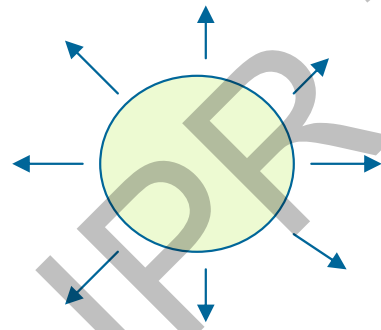


$$F^{-1} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & -\frac{1}{2}\lambda & 0 \\ 0 & 0 & -\frac{1}{2}\lambda \end{pmatrix}$$

$$C^{-1} = \begin{pmatrix} \lambda^2 & 0 & 0 \\ 0 & \lambda^{-1} & 0 \\ 0 & 0 & \lambda^{-1} \end{pmatrix}$$

Equibiaxial elongation

$$\nabla V = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -2\dot{\epsilon} & 0 \\ 0 & 0 & \dot{\epsilon} \end{pmatrix}$$

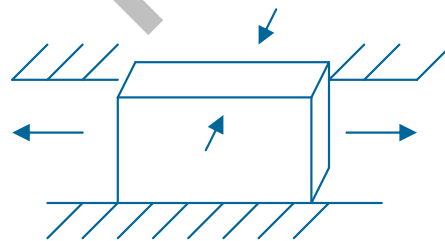


$$F^{-1} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & -2\lambda & 0 \\ 0 & 0 & \lambda \end{pmatrix}$$

$$C^{-1} = \begin{pmatrix} \lambda^2 & 0 & 0 \\ 0 & \lambda^{-4} & 0 \\ 0 & 0 & \lambda^2 \end{pmatrix}$$

Planar elongation

$$\nabla V = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\dot{\epsilon} \end{pmatrix}$$



$$F^{-1} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & -\lambda & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$C^{-1} = \begin{pmatrix} \lambda^2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \lambda^{-2} \end{pmatrix}$$

Elongation ratio $\lambda = \exp(\dot{\epsilon}t) = \exp(\epsilon)$

Hencky strain rate $\epsilon = \dot{\epsilon}t$

$$I_1 = \text{tr}(C^{-1})$$

- Strain invariant I_1, I_2, I_3 $I_2 = (\text{tr}(C^{-1}))^2 - \text{tr}(C^{-1})^2$

$$I_3 = \det(C^{-1})$$

- Flow strength:

Strong flow - exponential in material line

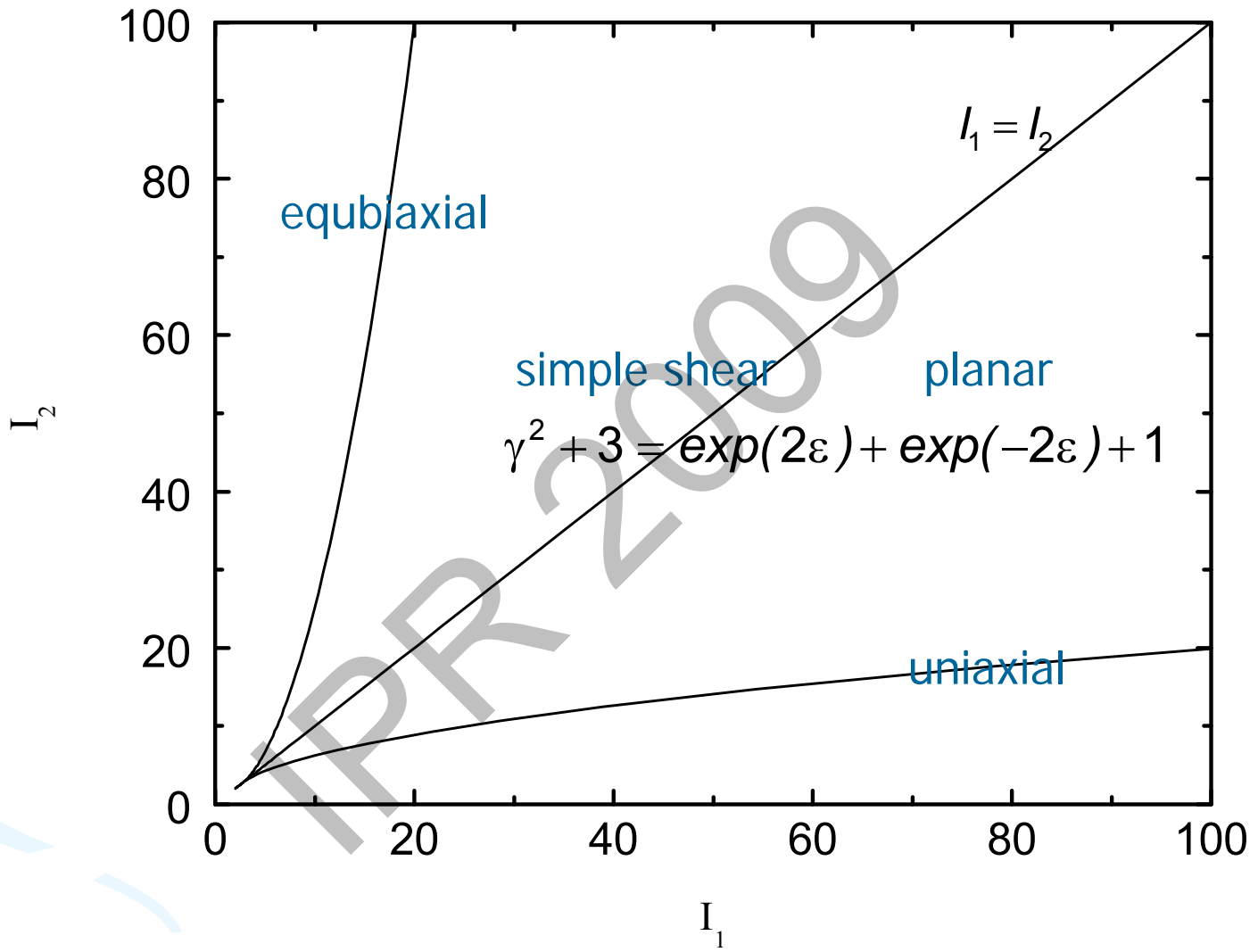
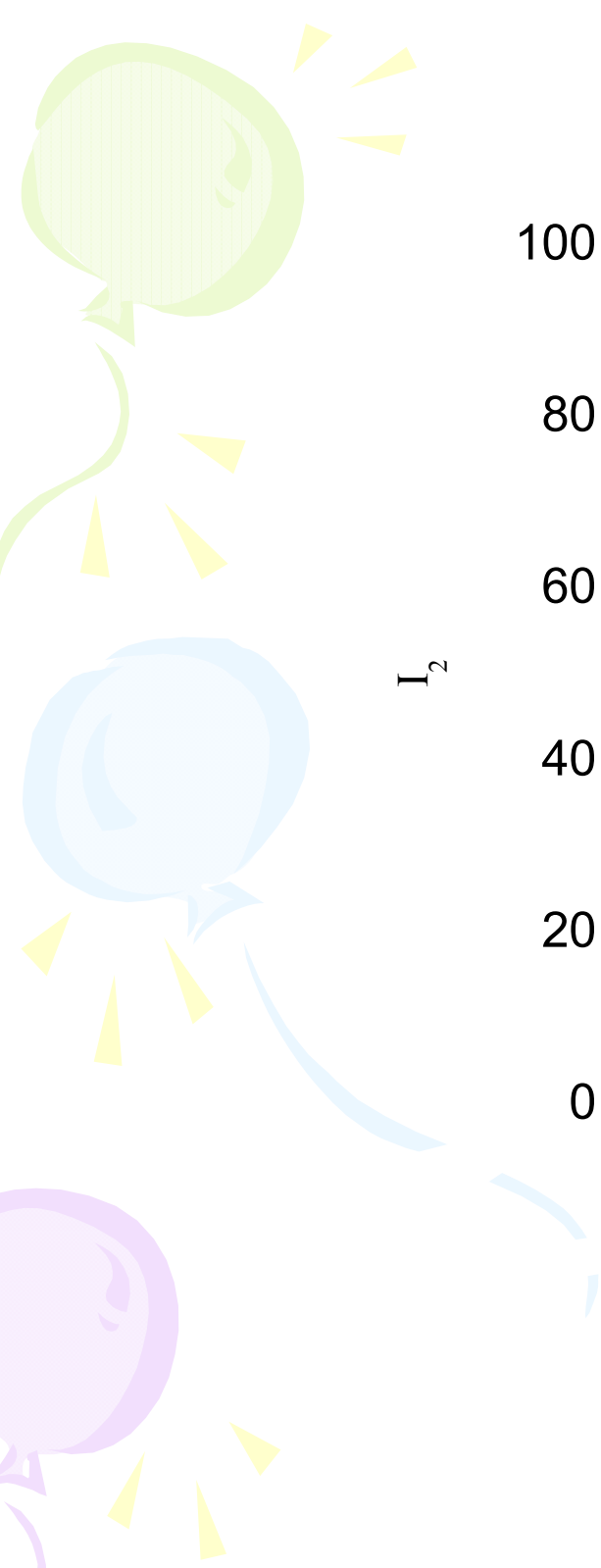
weak flow - linear

- Alignment strength:

Strongly aligning: $I_1 - I_2 > 0$

neutrally $I_1 - I_2 = 0$

weakly $I_1 - I_2 < 0$



Deformation gradient tensor:

$$F^{-1} = \begin{pmatrix} \text{Exp}(\dot{\varepsilon}t) & 0 & 0 \\ 0 & \text{Exp}(m\dot{\varepsilon}t) & 0 \\ 0 & 0 & \text{Exp}(-(1+m)\dot{\varepsilon}t) \end{pmatrix}$$

uniaxial $m=-1/2$

equibiaxial elongation $m=1$

$\dot{\varepsilon}$ is the Hencky strain rate.

Viscosity:

$$\mu_i(t) = \frac{1}{2(2+m)} \frac{(\sigma_{11} - \sigma_{22})}{\dot{\varepsilon}}$$

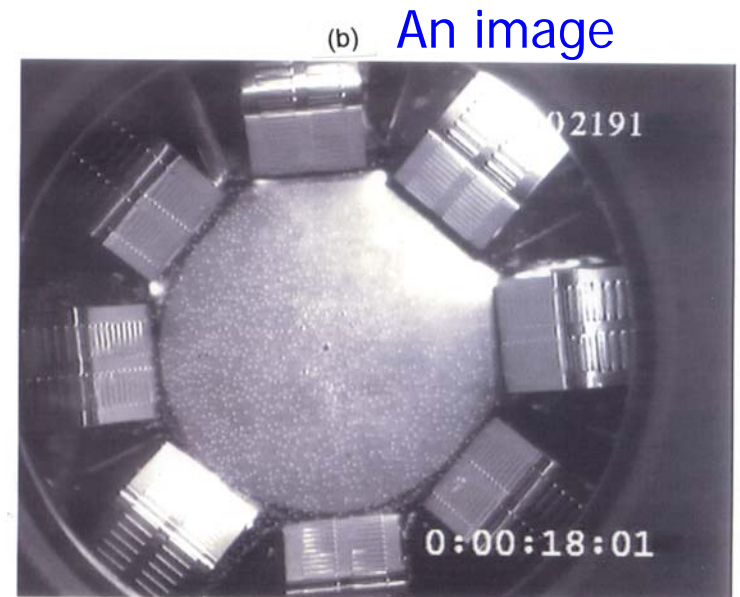
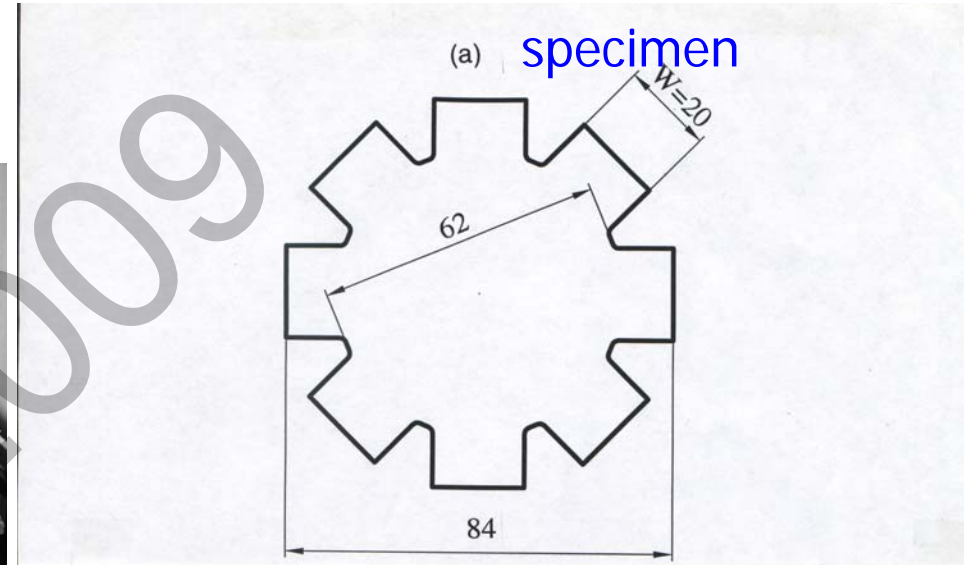
Degree of strain hardening = $\mu_i(t)/\eta^o(t)$

($\eta^o(t)$: linear shear viscosity)

Experimental set-up for equibiaxial elongational rheometer

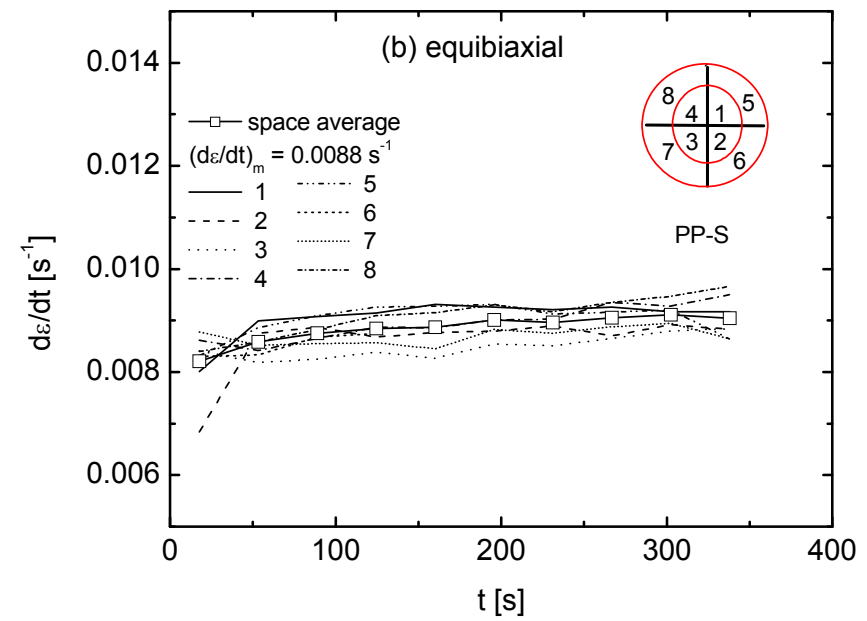
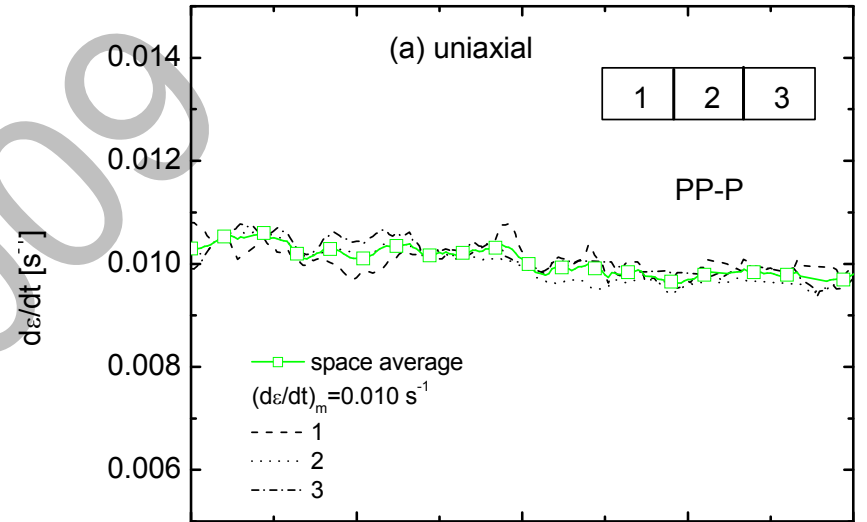
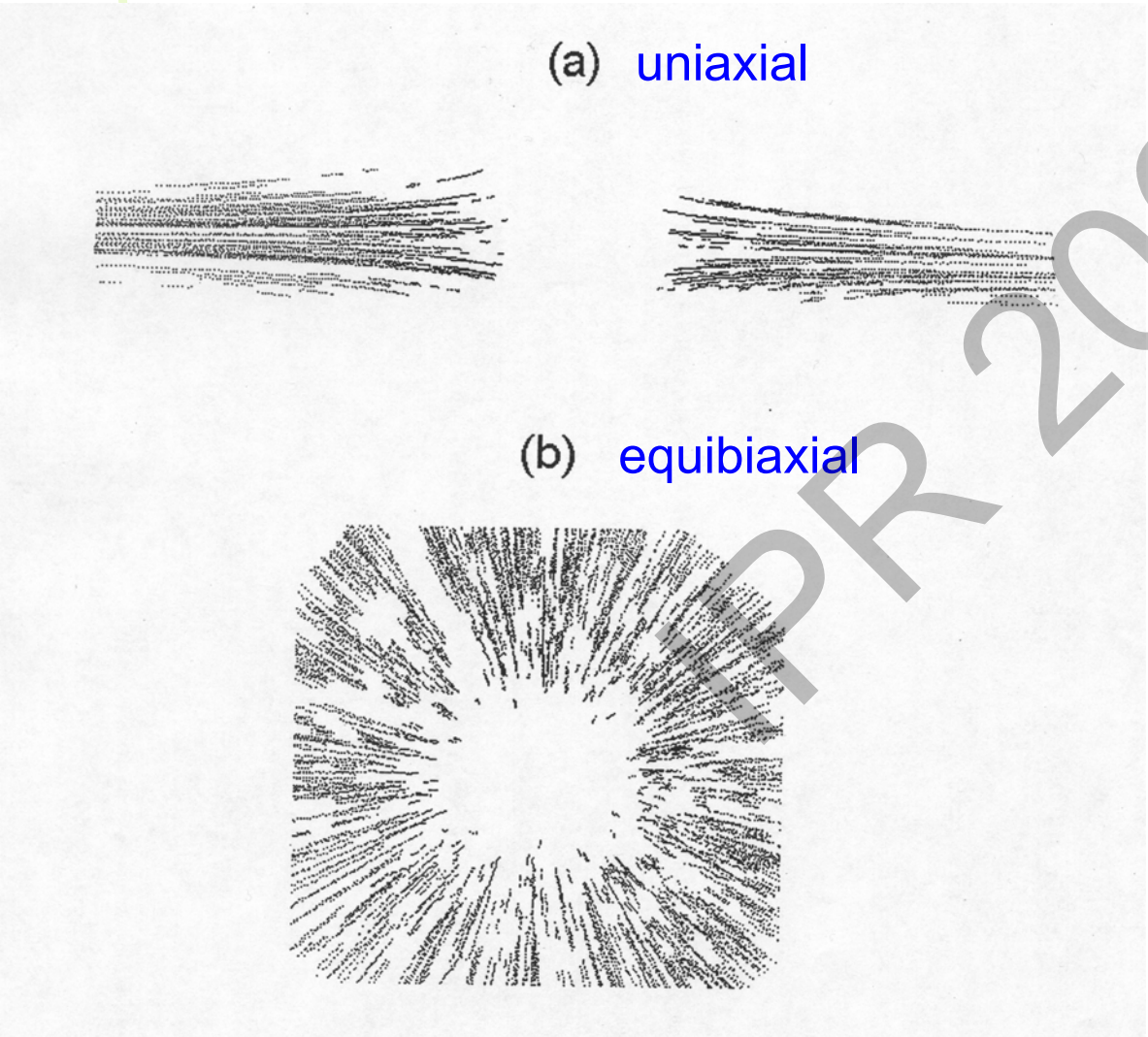


The instrument

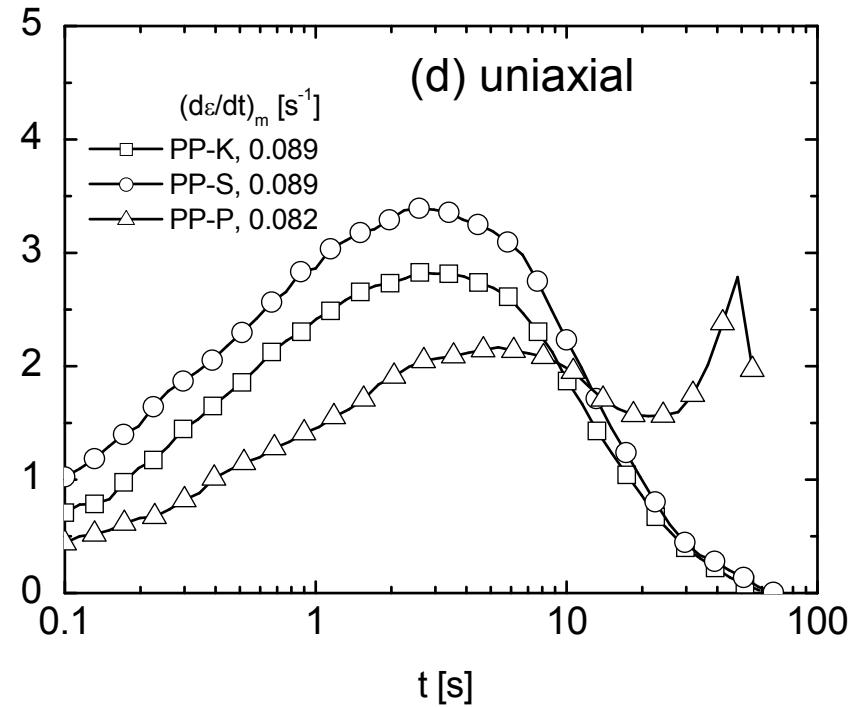
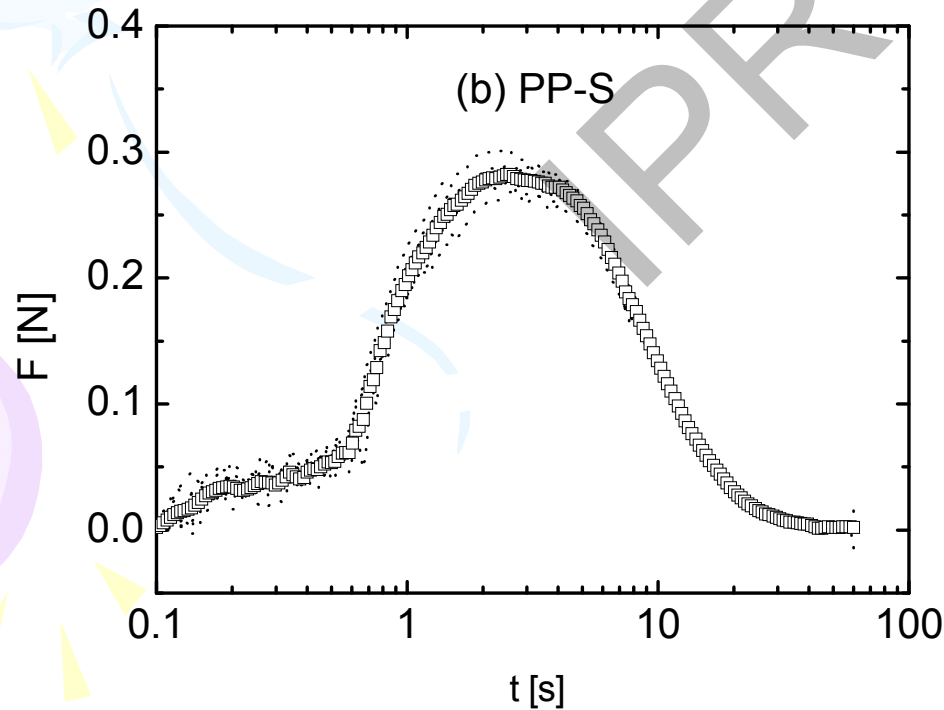
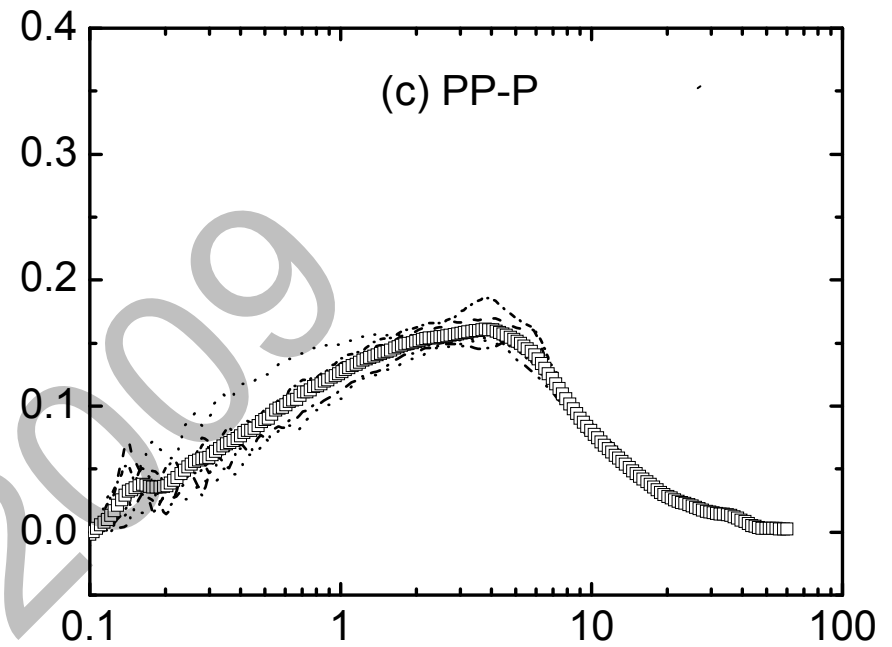
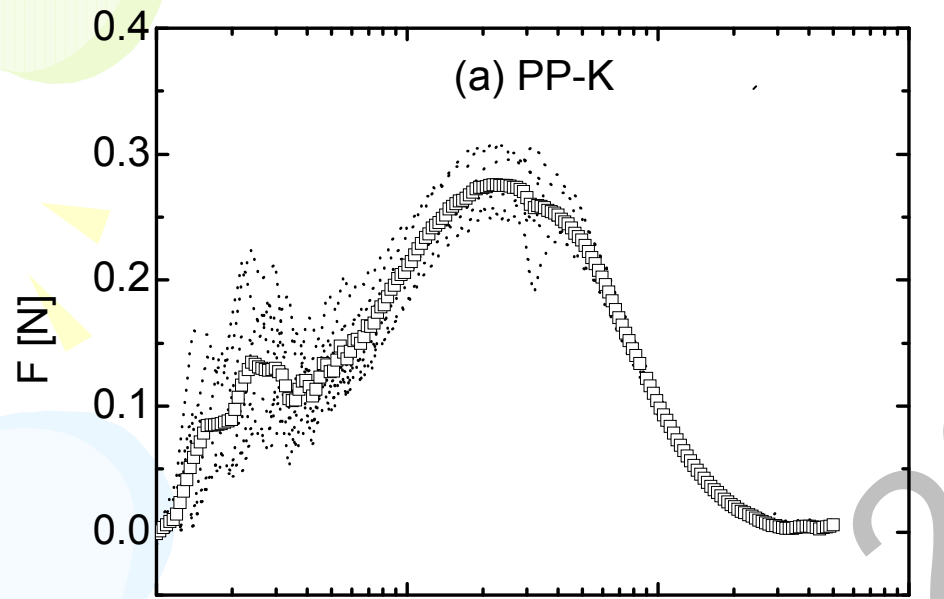


The pathlines of tracers on the specimen surface during uniaxial and equibiaxial elongations

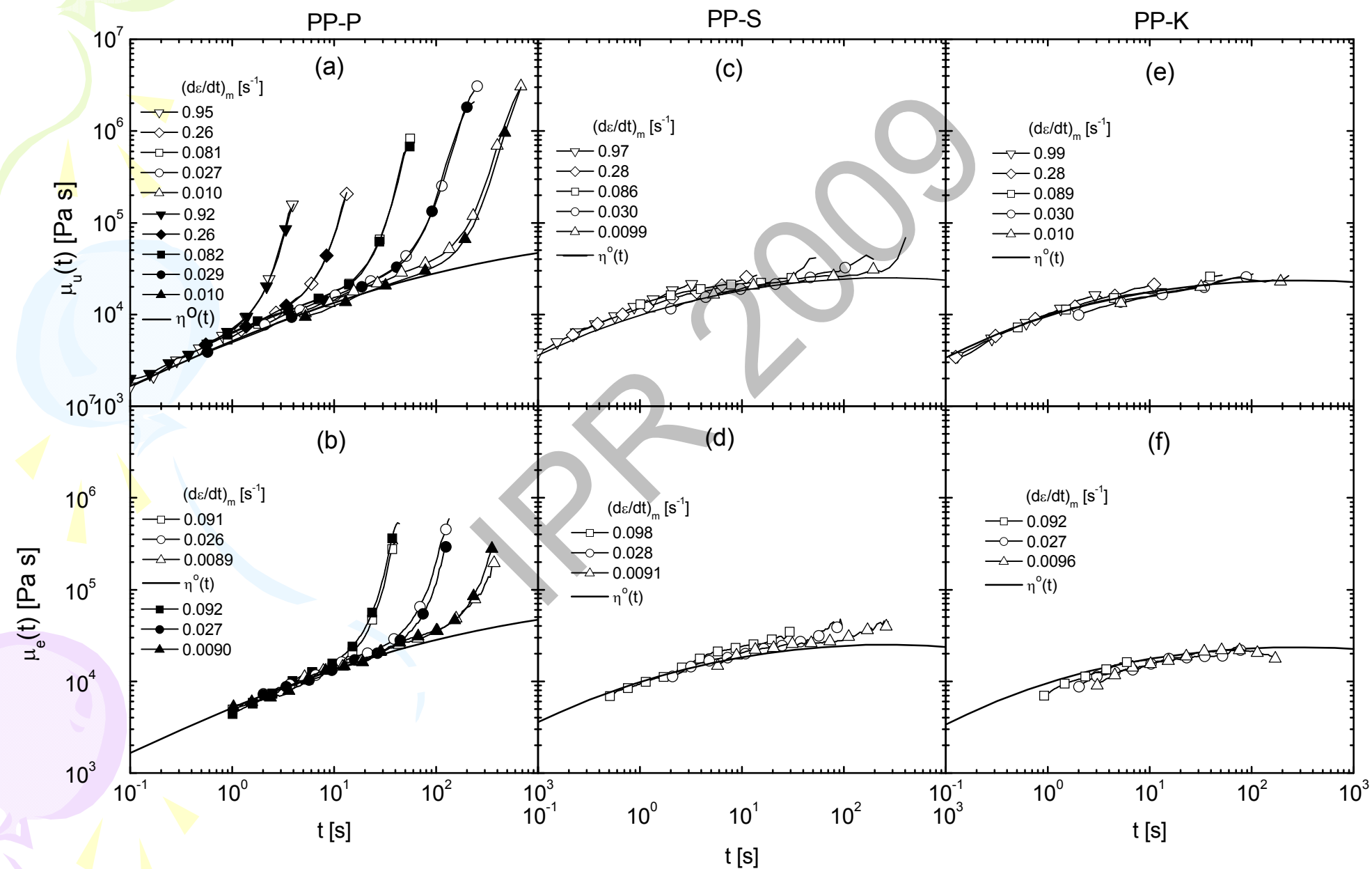
The strain rates measured at different locations on the specimen surface during uniaxial and equibiaxial elongations



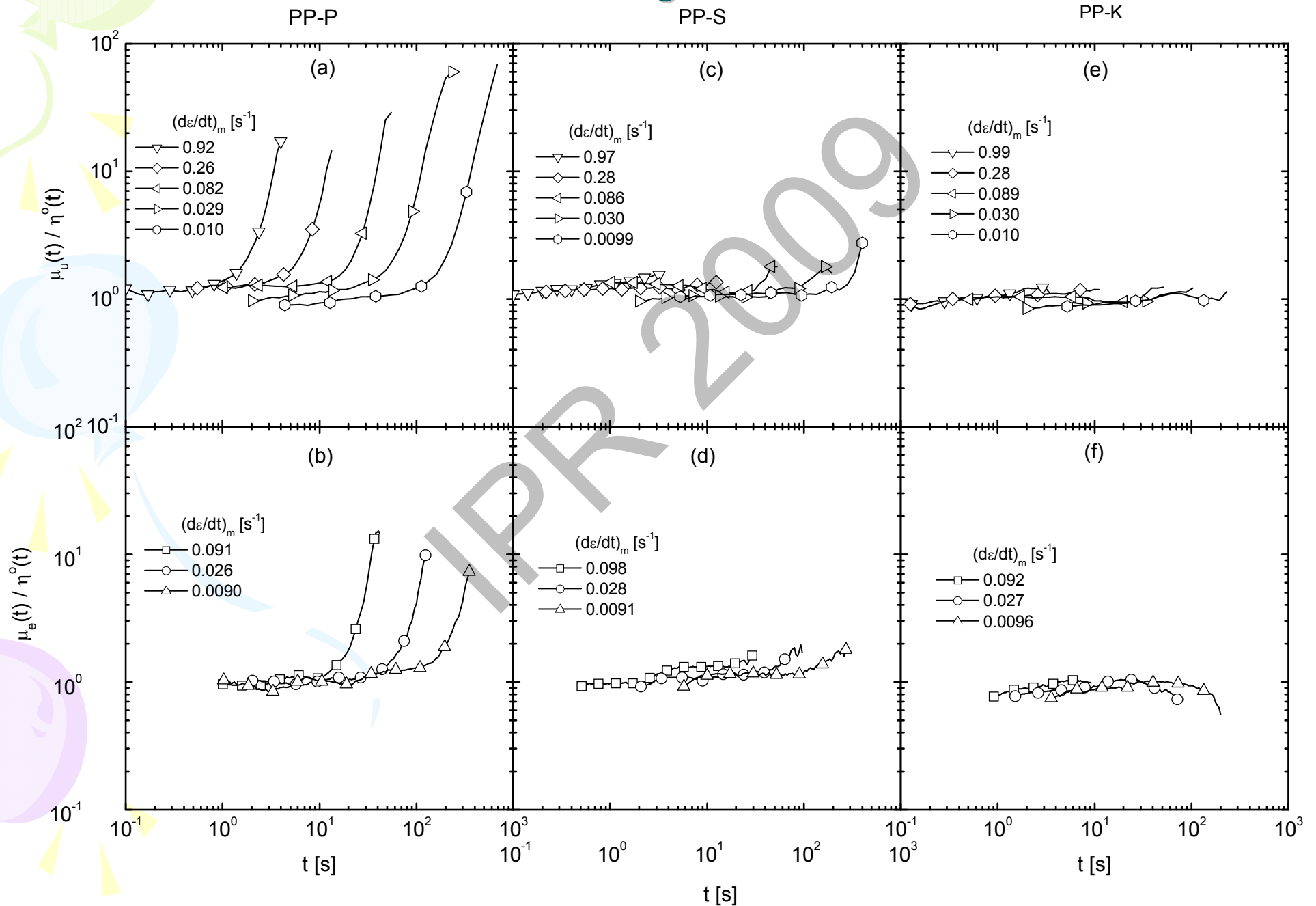
The force curves of the three PP melts during equibiaxial (a, b, c) and uniaxial (c) elongations.



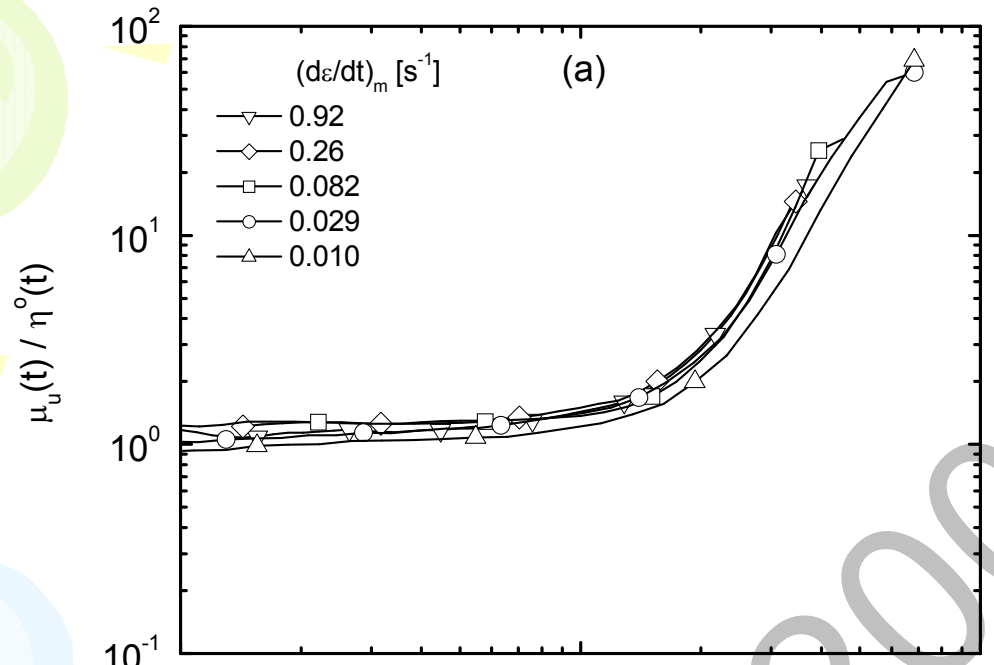
Comparison of elongational viscosities in equibiaxial and uniaxial elongations



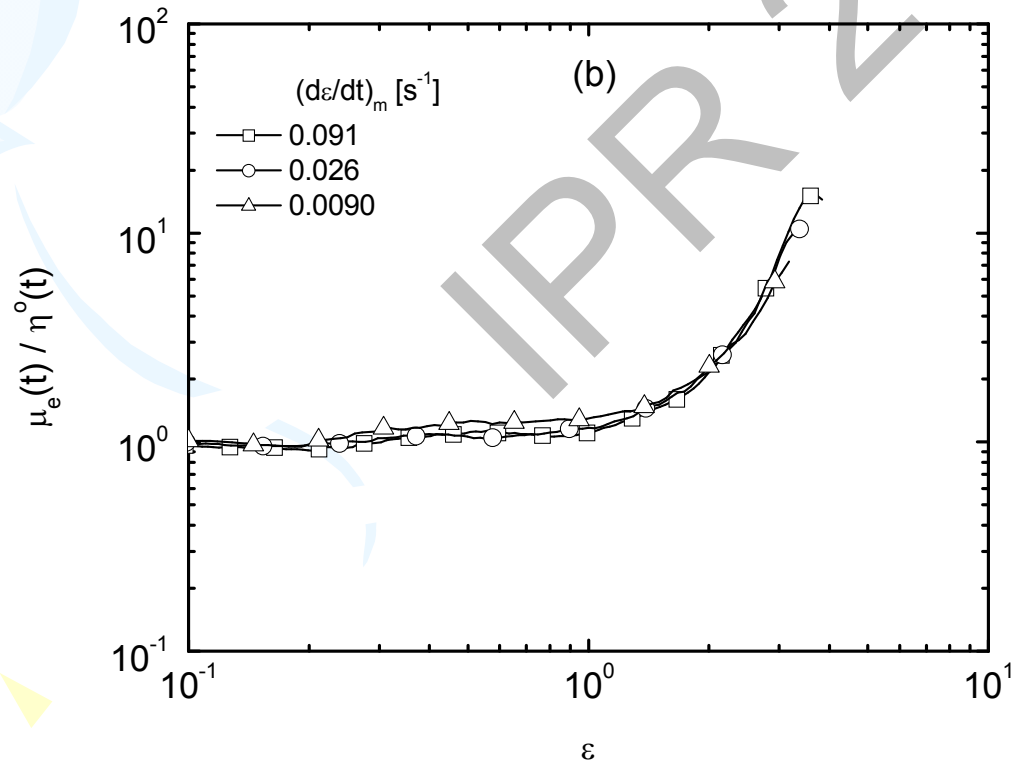
Comparison of strain hardening in equibiaxial and uniaxial elongations



PP-P

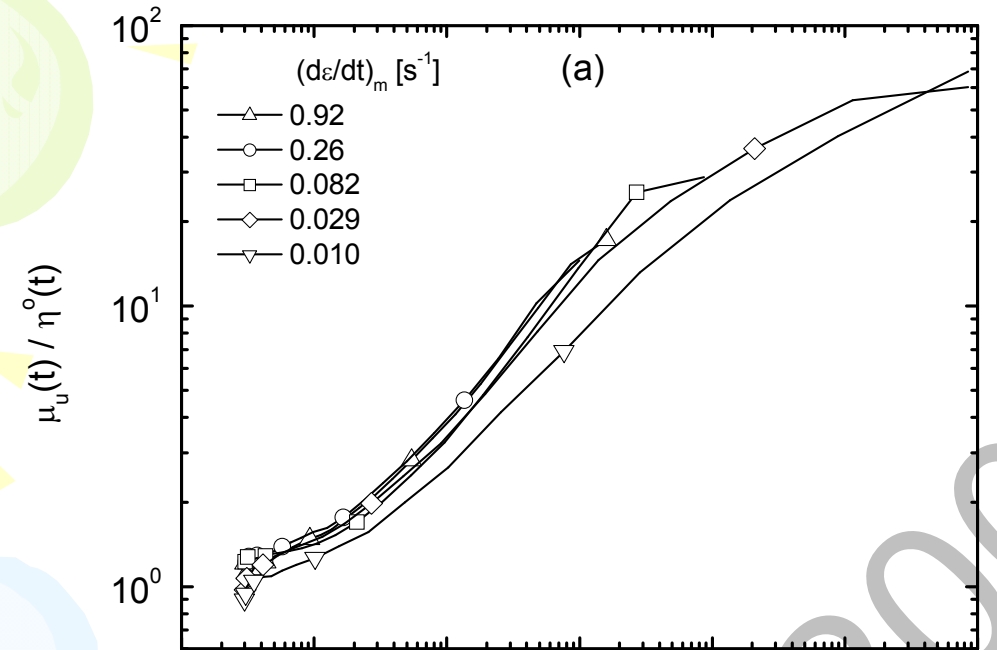


Uniaxial: $\epsilon_c \sim 1$



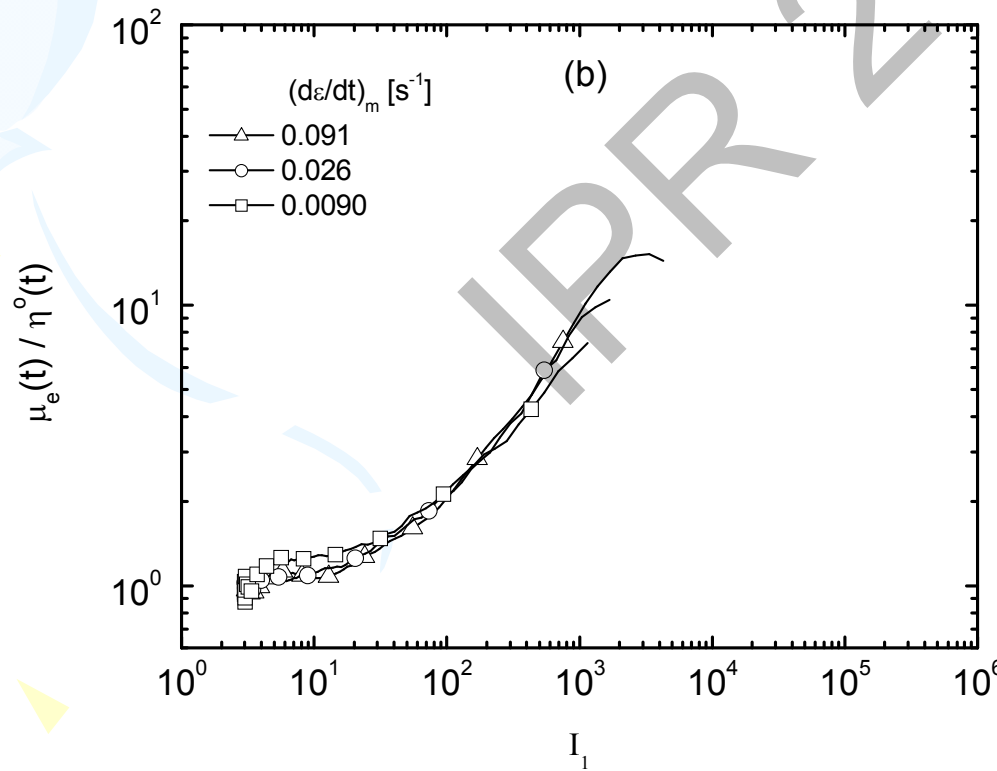
Equibiaxial: $\epsilon_c \sim 1$

PP-P



Uniaxial:

$I_{1c} \sim 10$




Equibiaxial:

$I_{1c} \sim 20$



Conclusions

- Linear rheological properties can distinguish large difference in the molecular structure, more details are revealed from the elongational viscosities.
 - Relaxation spectra explain the strain hardening behavior.
 - The bimodal PP melt show strong strain hardening, whilst the other two exhibit only moderate and no strain hardening.
 - The three PP have similar trends in equibiaxial and uniaxial elongations.
 - The bimodal PP melt shows nonlinear strain hardening at a critical strain of 1 for all the strain rates in uniaxial and equibiaxial elongations. The same values differ on the I_1 axis in uniaxial and equibiaxial elongations.
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Thanks for your attention!

Questions ?

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