RHEOLOGICAL CHARACTERIZATION OF POLYPROPYLENE MELTS OF VARIOUS DEGREES OF BRANCHING

Shuihan Zhu and Costas Tzoganakis

Chemical Engineering Department
University of Waterloo

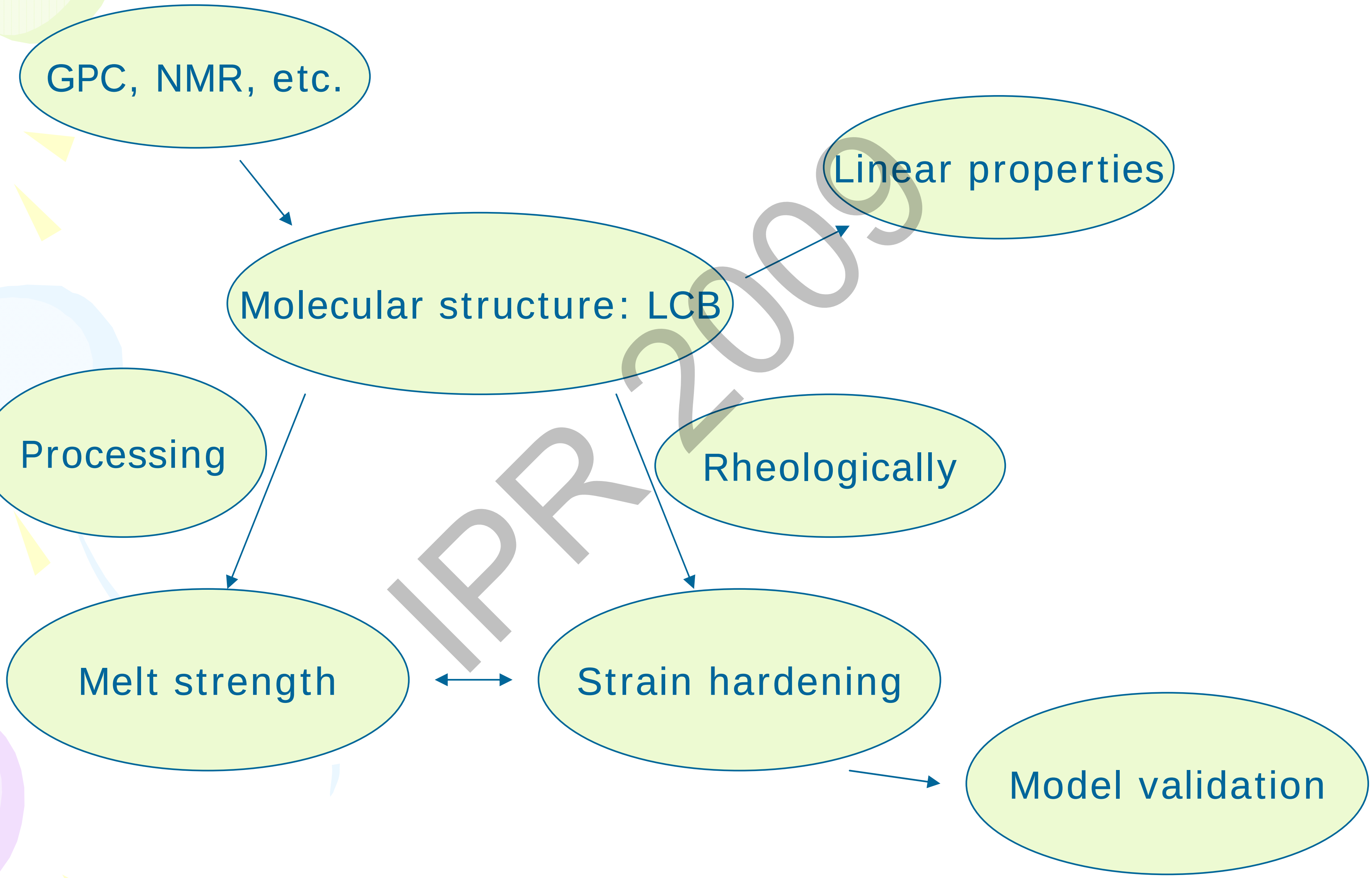
Outline

- 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(τ),
  - Nonlinear: elongational viscosity

Introduction



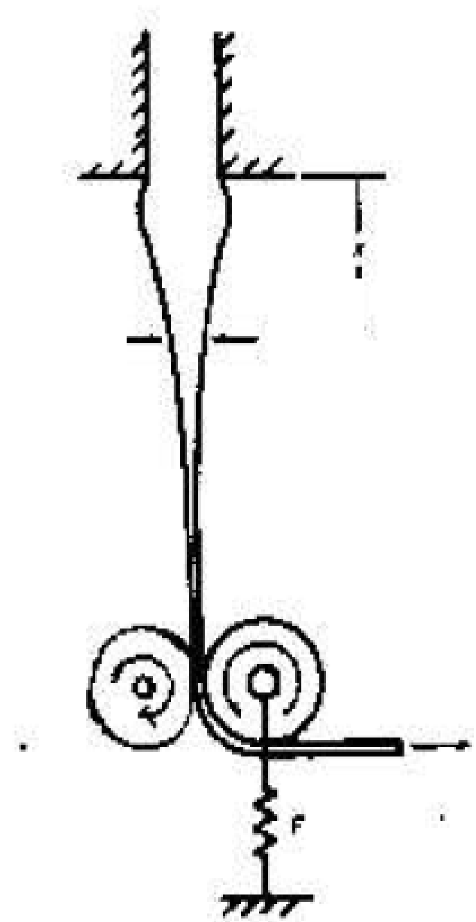
Introduction

- 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)

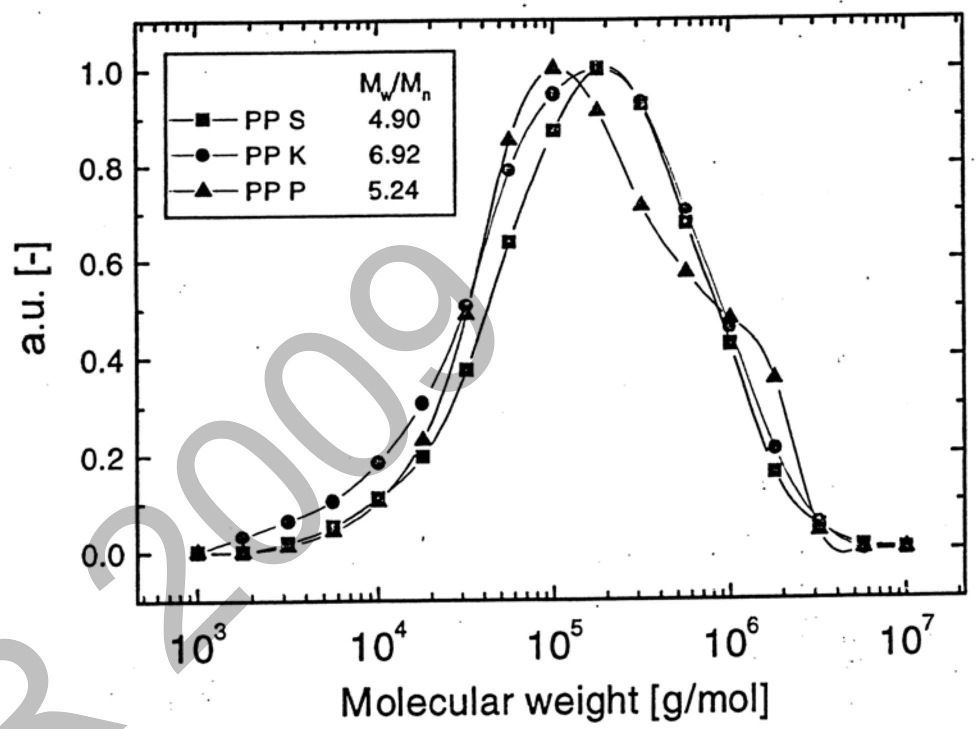
Velocity at Break (mm/sec)



Objectives

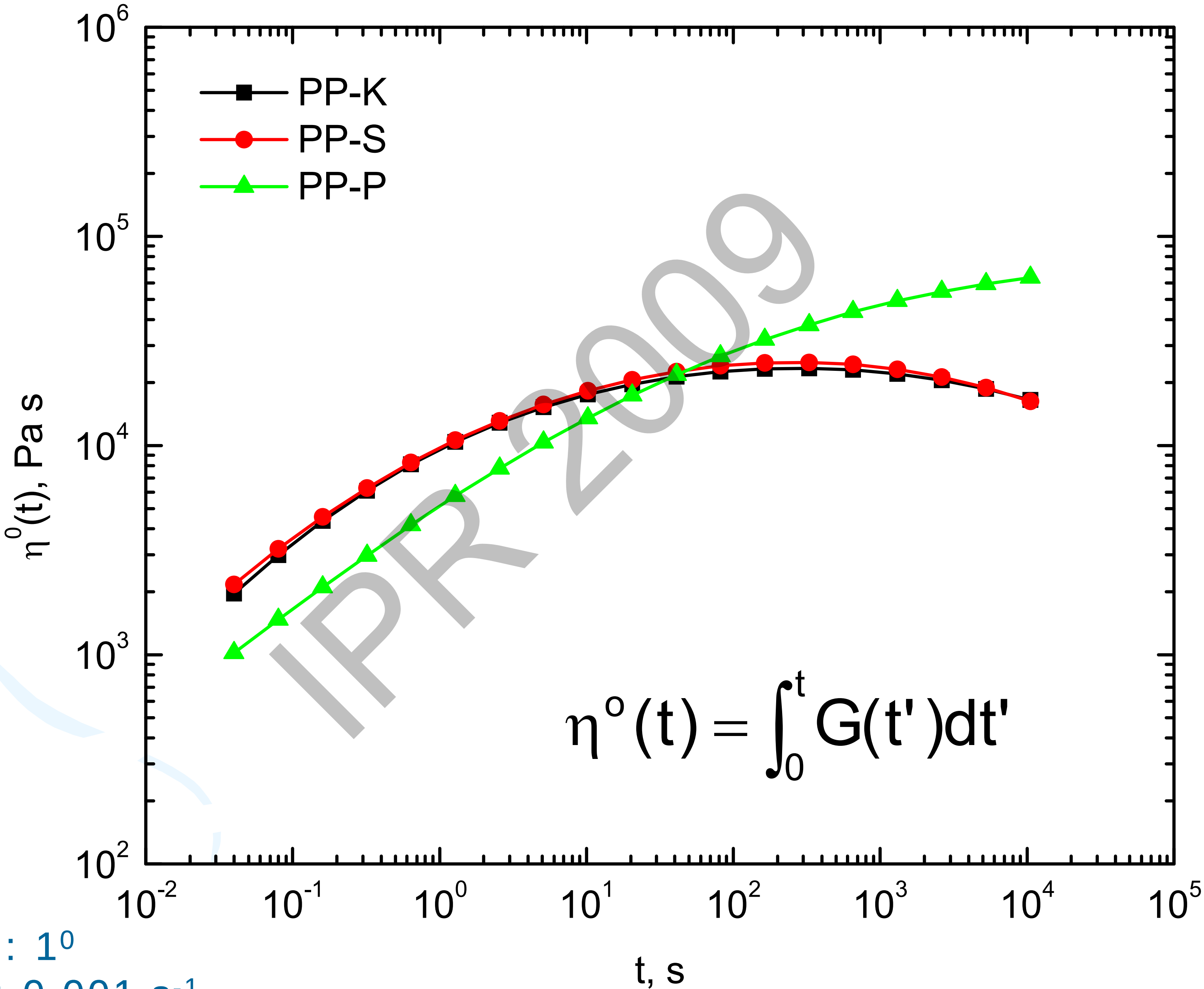
- Measure and calculate the linear rheological properties
- Acquire uniaxial and equibiaxial elongational viscosity
- Compare the results from linear vs nonlinear rheological properties
- Evaluate difference in uniaxial vs equibiaxial elongational flows
- Assess the different structures of PP melts

The molecular weights of
the three polypropylenes used.



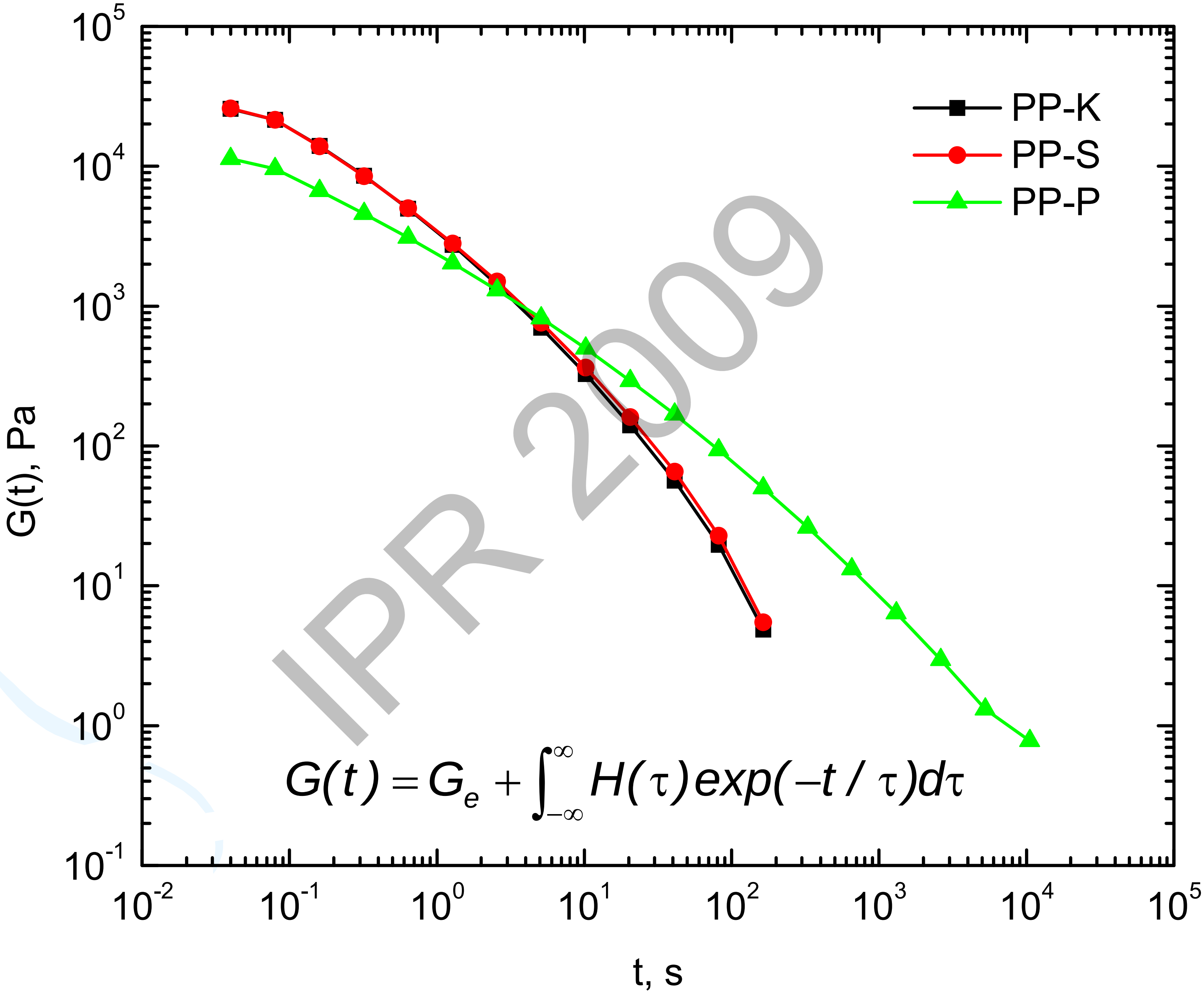
materials	M_n	M_w	M_z	d
PP-K	47100	326000	971100	6.92
PP-S	69800	342200	991500	4.90
PP-P	79300	384900	1135000	4.85

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

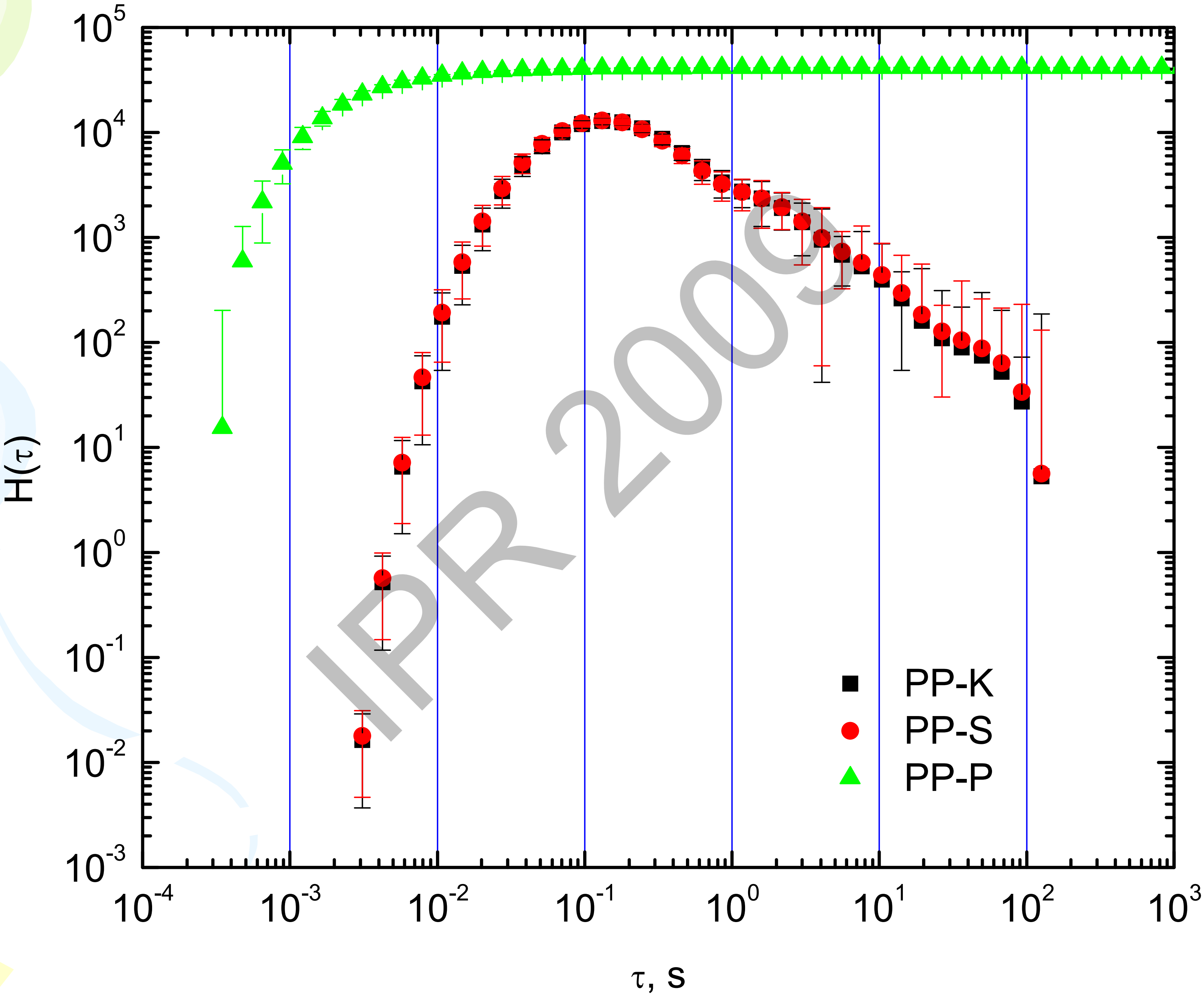


175 ^{0}C
Cone angle: 1^0
Shear rate: 0.001 s^{-1}
RMS800, Rheometrics

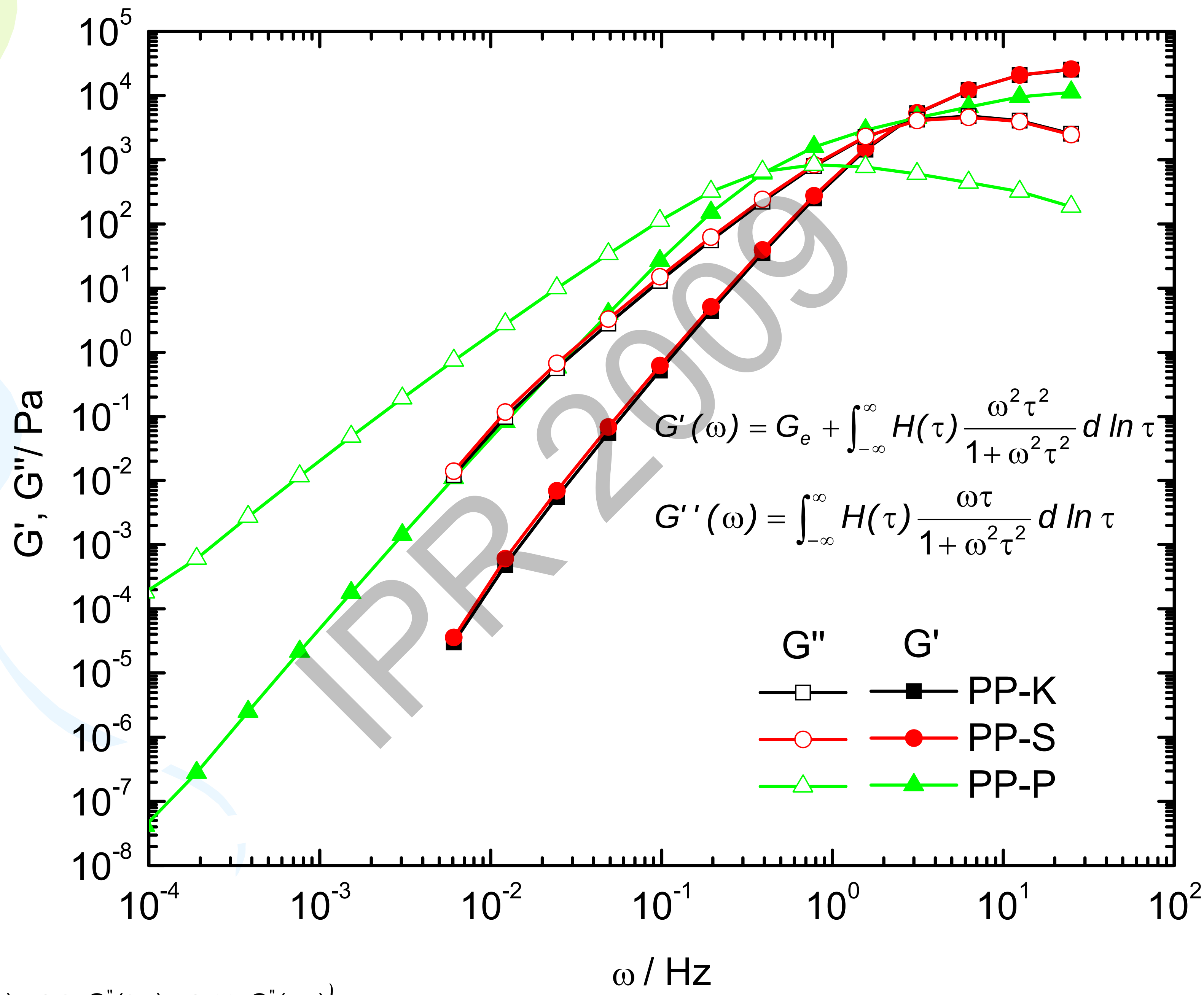
Relaxation modulus as a function of time calculated.



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

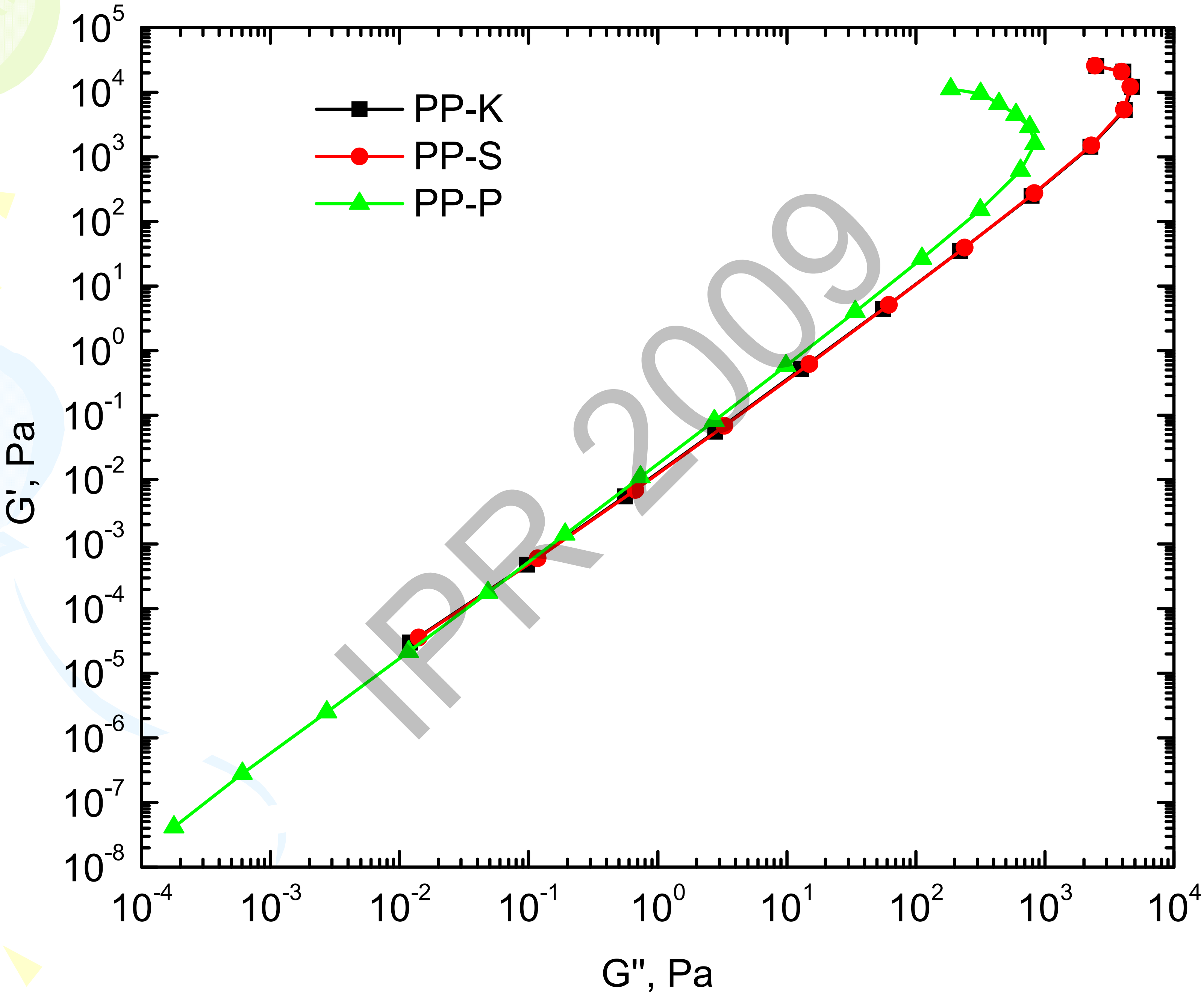


Other linear rheological properties: G’ and G’’



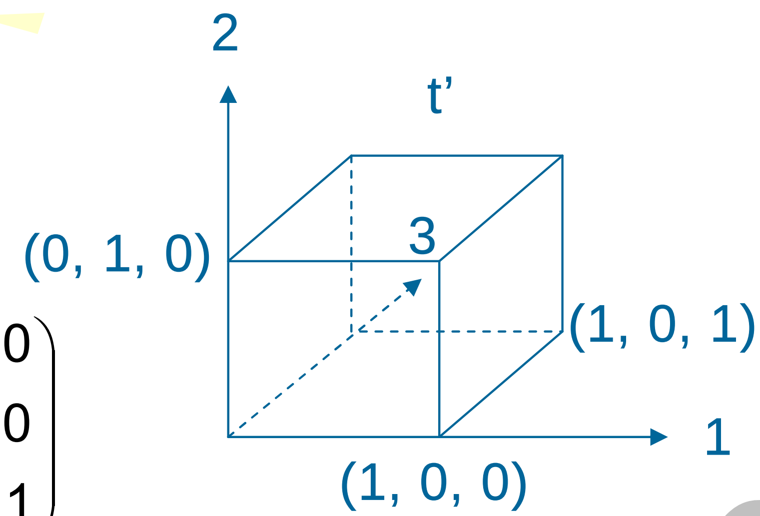
$$\eta^{o}(t) = \left\{G'(\omega) + 0.27G''(2\omega) + 0.115G''(4\omega)\right\}_{\omega=1/t}$$

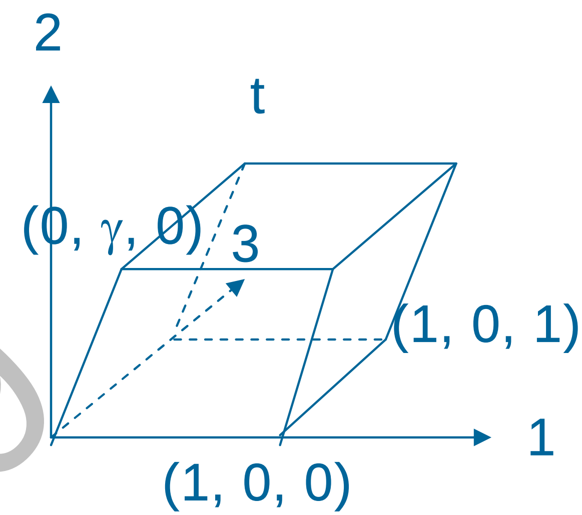
Cole-Cole plot of the PP



Simple shear

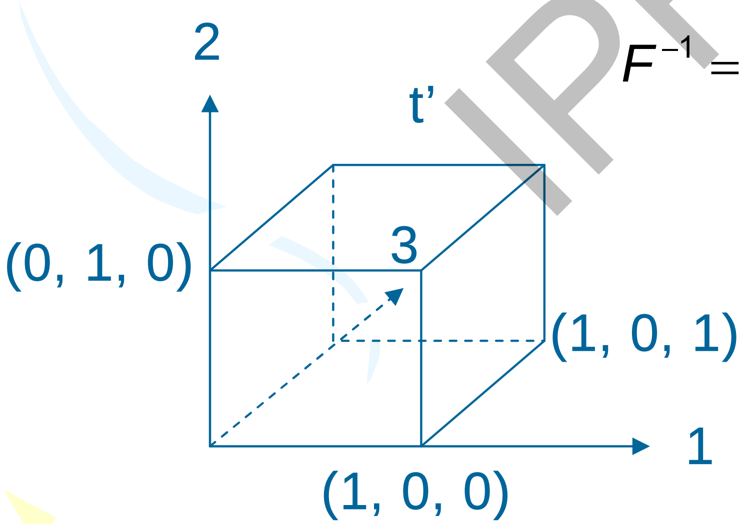
$$F^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

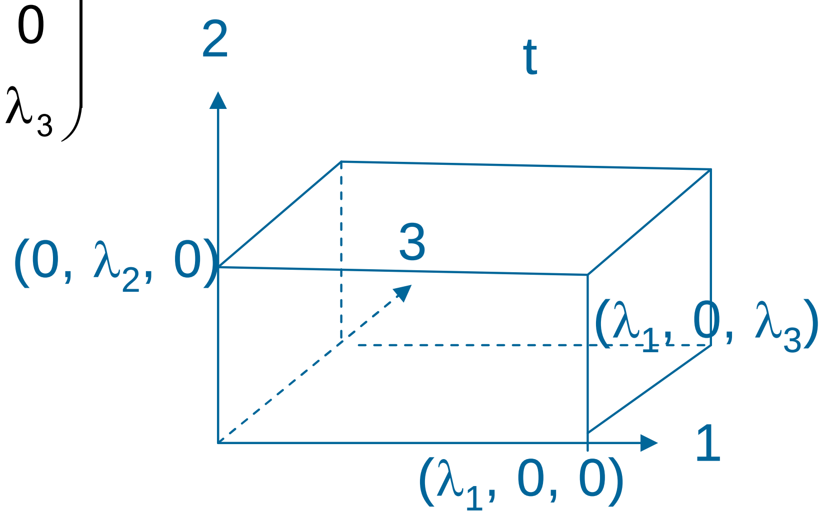




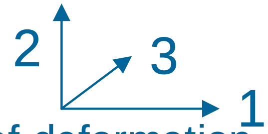
Elongations

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





Velocity gradient



Deformation gradient

Finger tensor

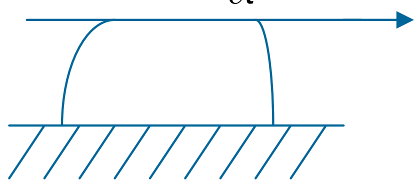
$C^{-1}=(F^{-1})^{T}F^{-1}$

Simple shear

Rate of deformation

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

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



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

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

Uniaxial elongation

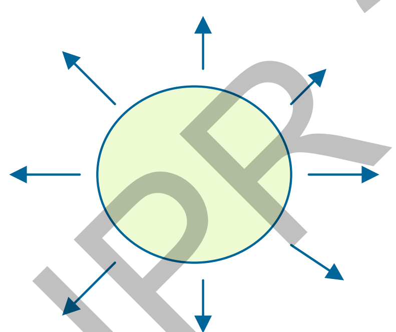
$$\nabla V=\begin{pmatrix}\dot{\varepsilon}&0&0\\ 0&-\frac{1}{2}\dot{\varepsilon}&0\\ 0&0&-\frac{1}{2}\dot{\varepsilon}\end{pmatrix}$$

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

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

Equibiaxial elongation

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

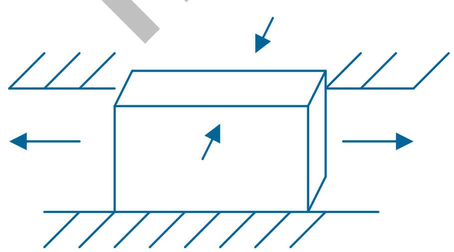


$$F^{-1}=\begin{pmatrix}\lambda&0&0\\ 0&-2\lambda&0\\ 0&0&\lambda\end{pmatrix}$$

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

Planar elongation

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



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

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

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

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

- Strain invariant I_1, I_2, I_3

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

$$I_2 = (tr(C^{-1}))^2 - tr(C^{-1})^2$$

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

- Flow strength:

  Strong flow - exponential in material line

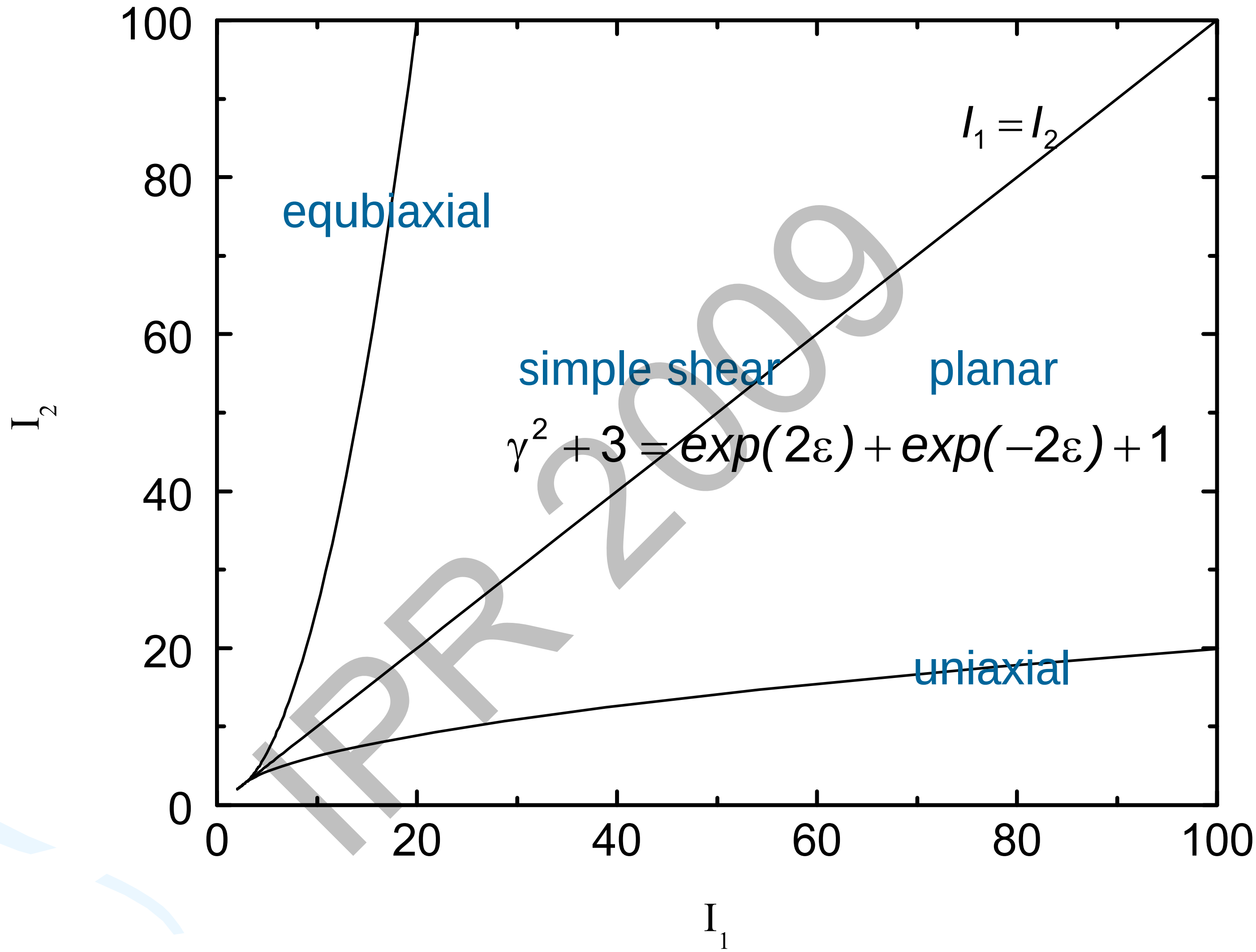
  weak flow - linear

- Alignment strength:

  Strongly aligning: $I_1 - I_2 > 0$

  neutrally $I_1 - I_2 = 0$

  weakly $I_1 - I_2 < 0$



100
80
60
40
20
0
0
20
40
60
80
100
$I_1 = I_2$
equbiaxial
simple shear
planar
$\gamma^2 + 3 = exp(2\varepsilon) + exp(-2\varepsilon) + 1$
uniaxial
I_2
I_1

Deformation gradient tensor:

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

uniaxial m=-1/2
equibiaxial elongation m=1

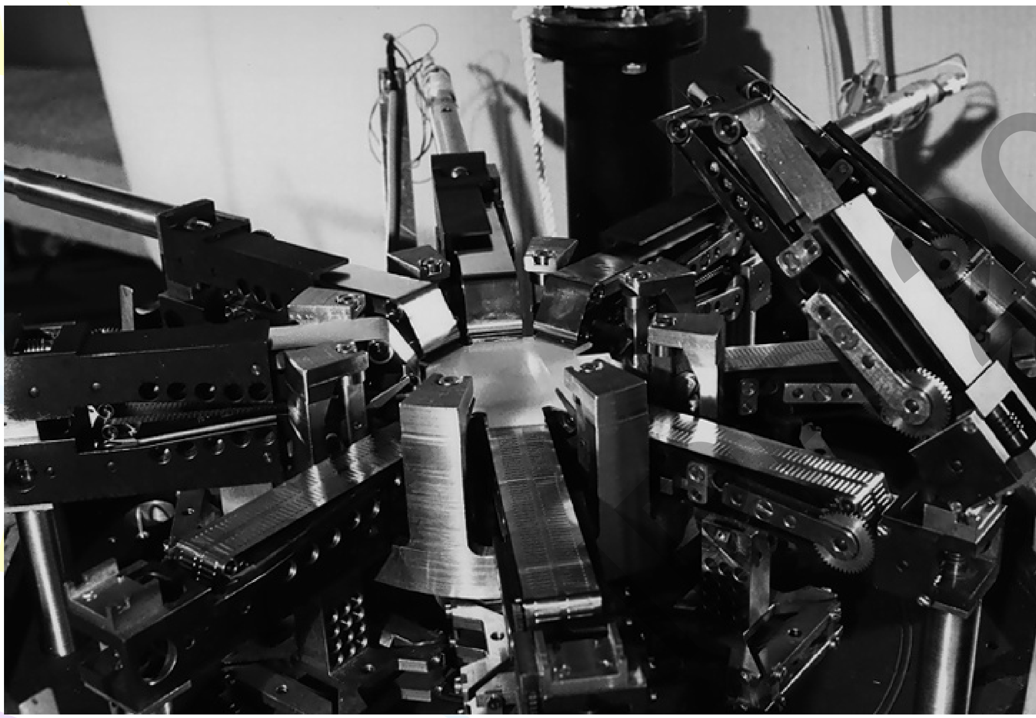
$\dot{\varepsilon}$ is the Hencky strain rate.

Viscosity:

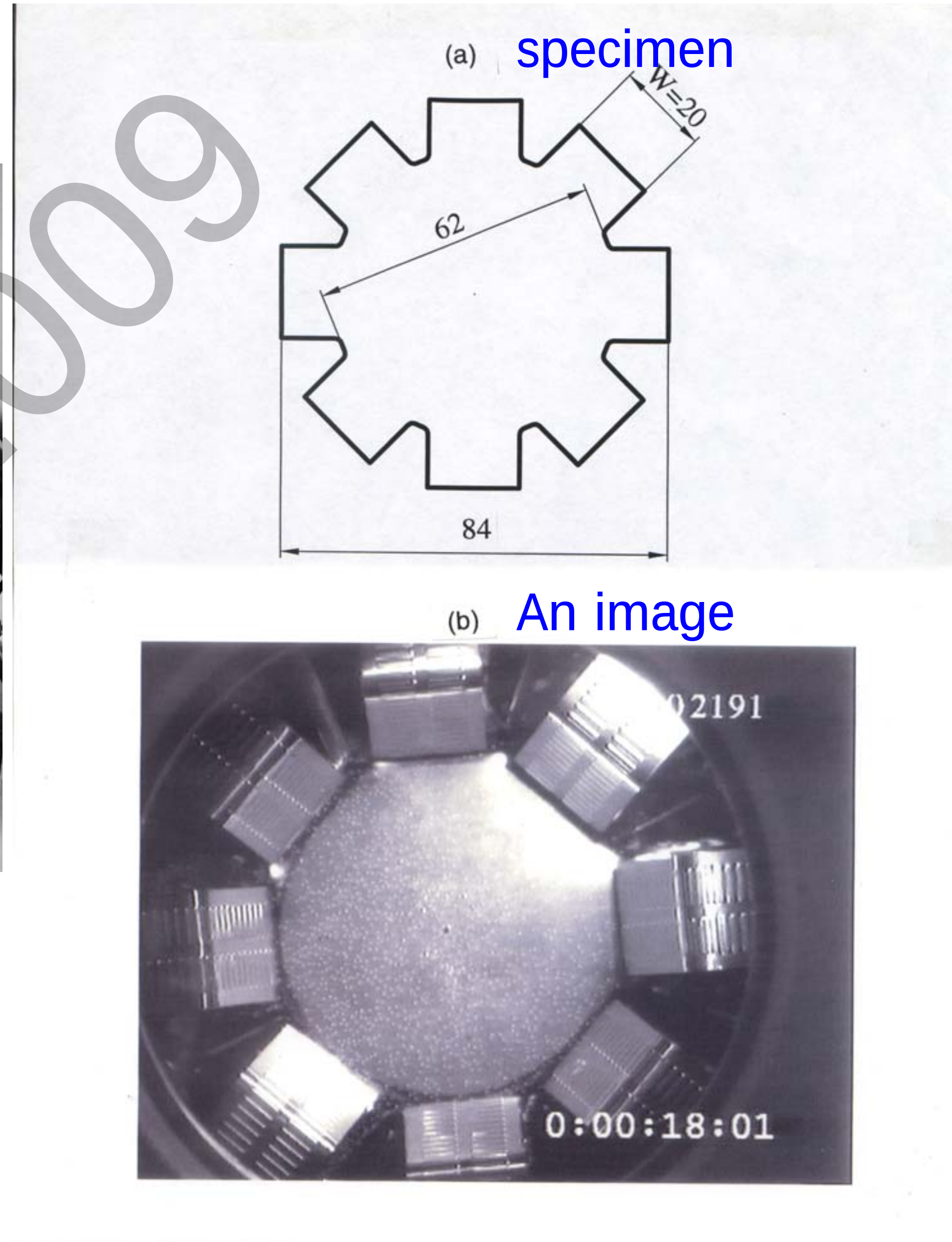
$$\mu_i(t) = \frac{1}{2(2+m)} \frac{(\sigma_{11} - \sigma_{22})}{\dot{\varepsilon}}$$

Degree of strain hardening = $\mu_i(t)/\eta^o(t)$ ($\eta^o(t)$: linear shear viscosity)

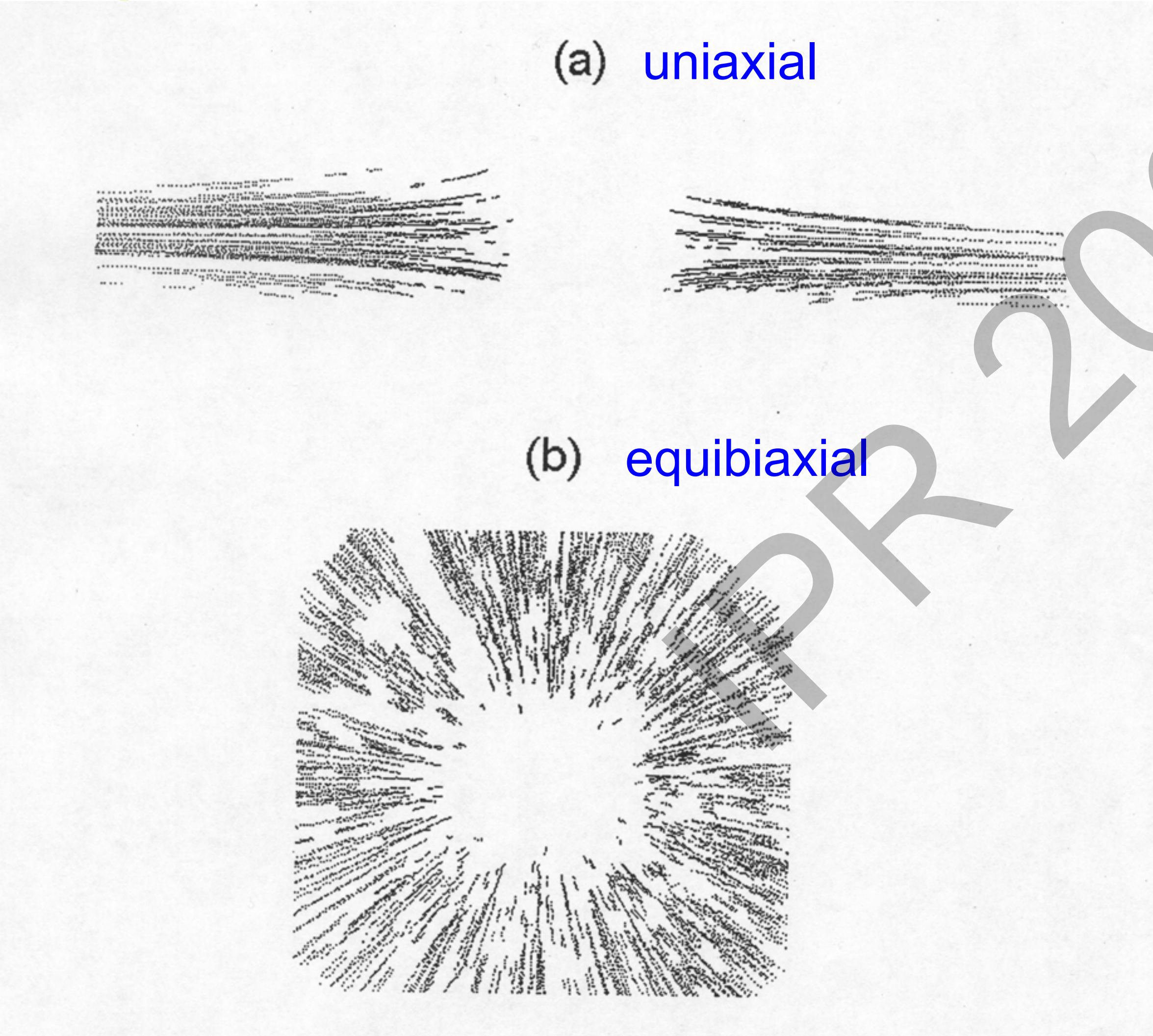
Experimental set-up for equibiaxial elongational rheometer



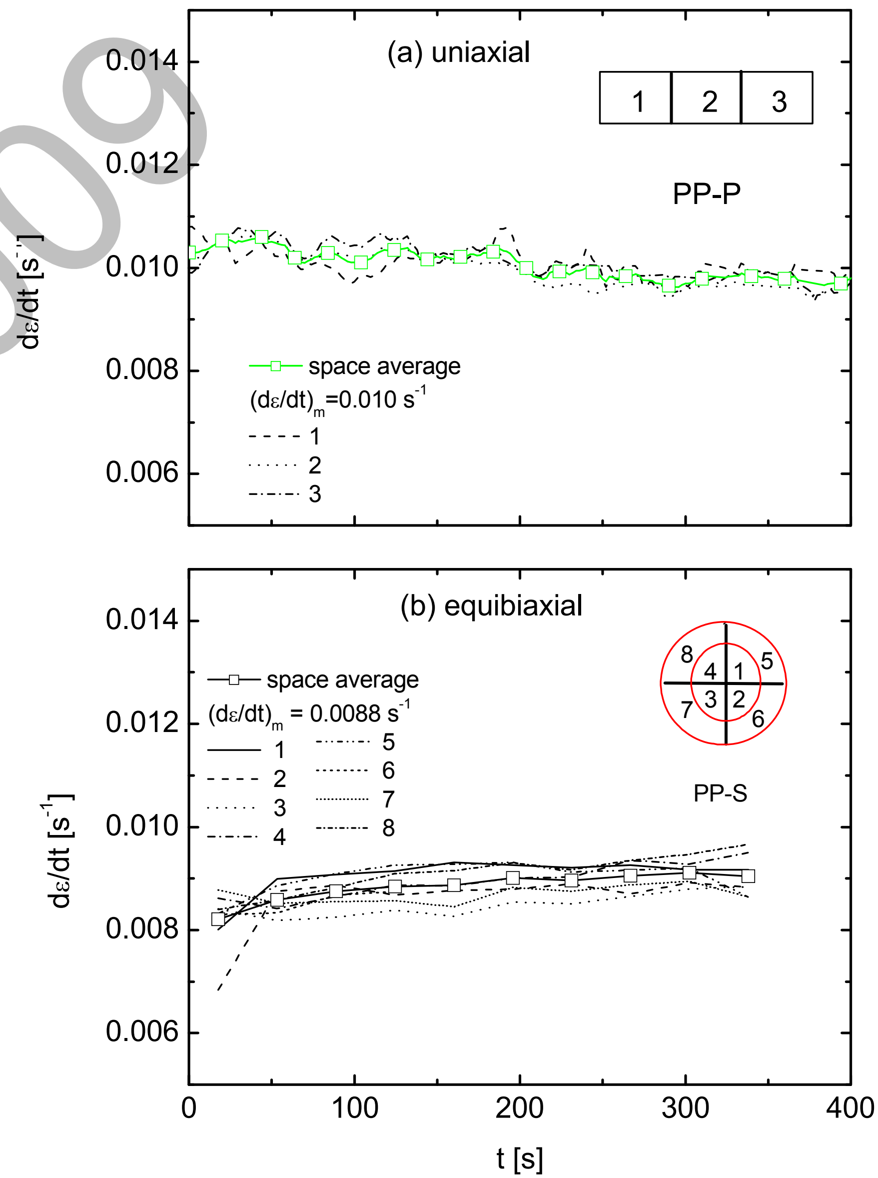
The instrument



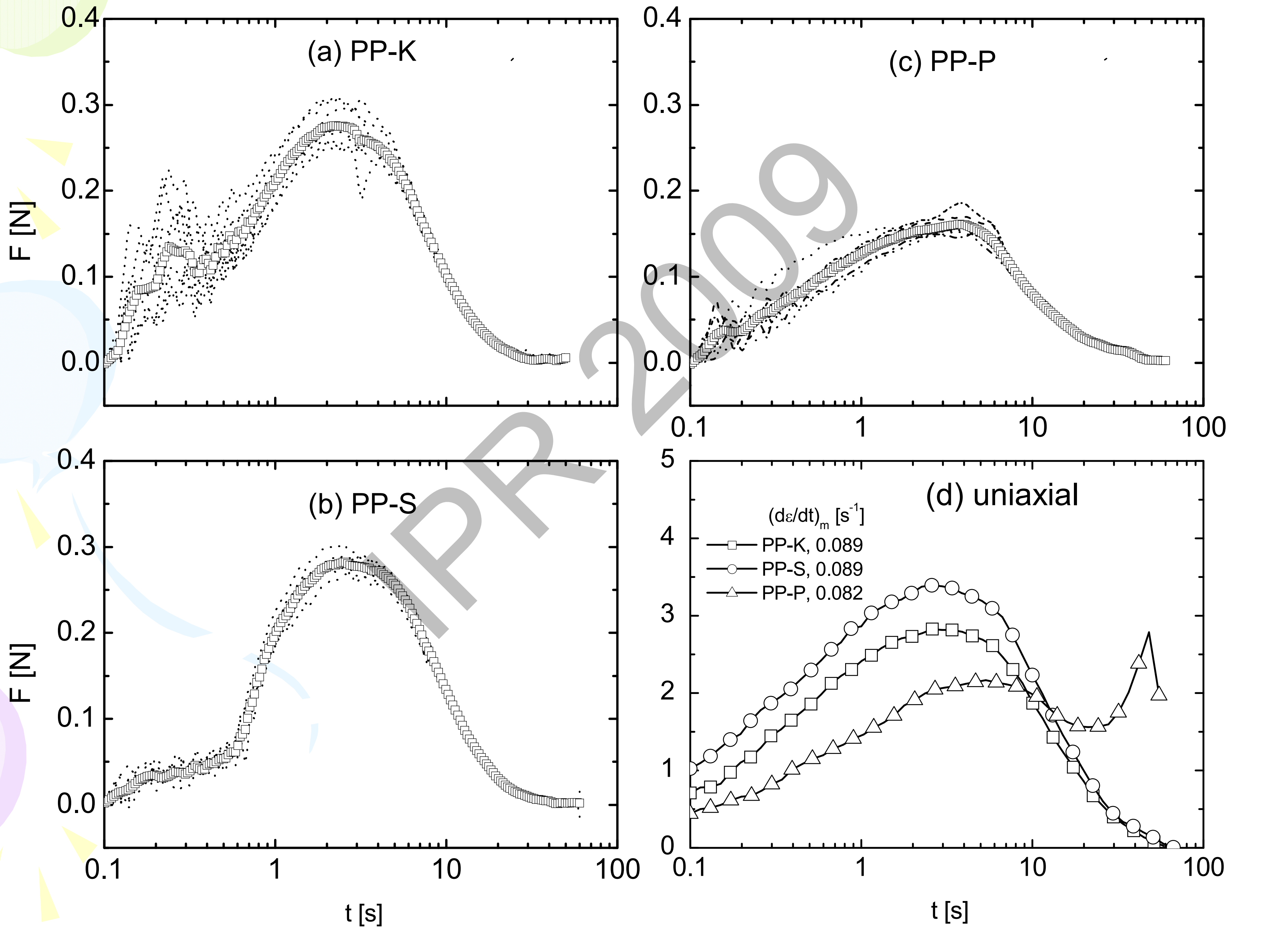
The pathlines of tracers on the specimen surface during uniaxial and equibiaxial elongations



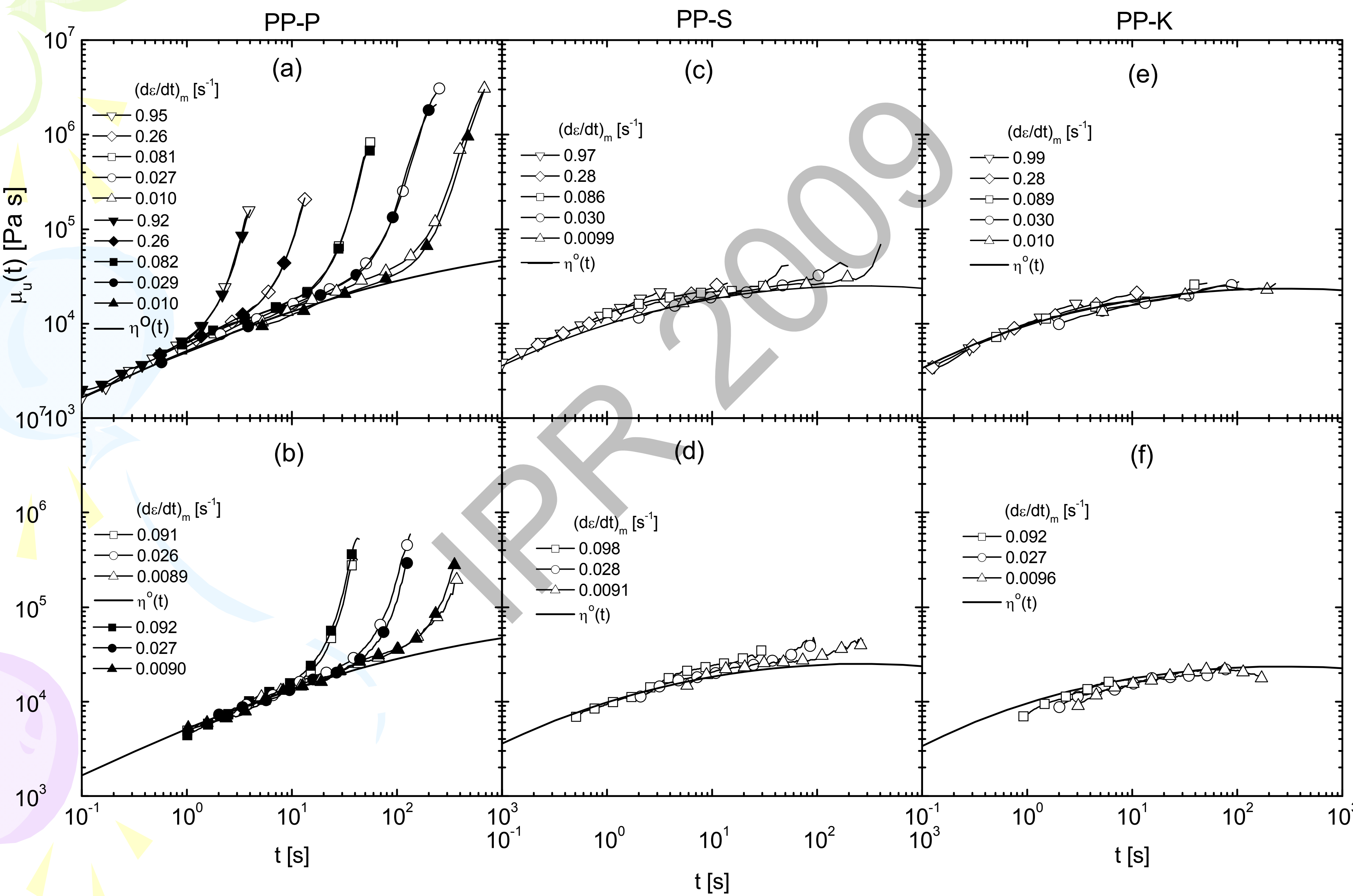
The strain rates measured at different locations on the specimen surface during uniaxial and equibiaxial elongations



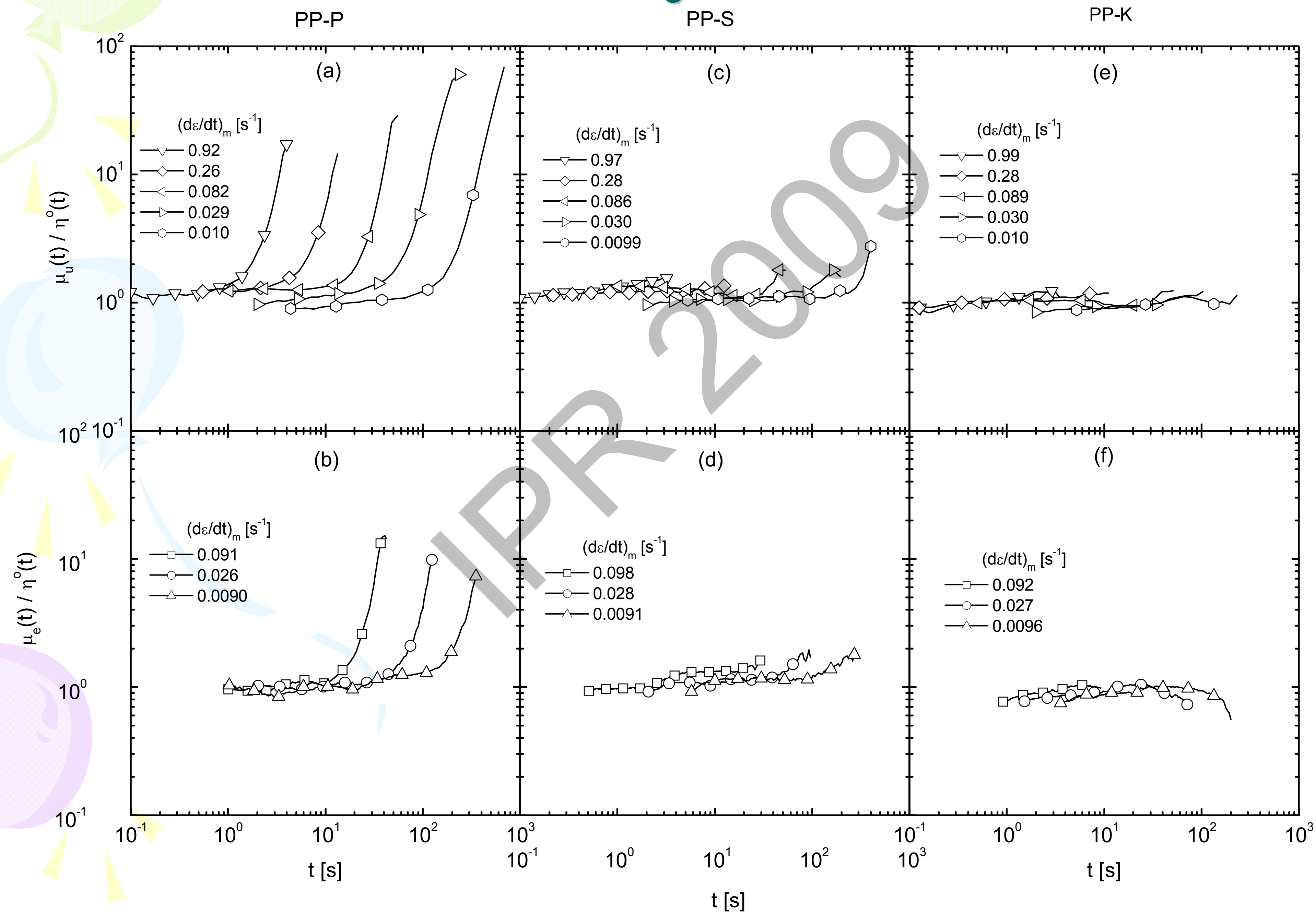
The force curves of the three PP melts during equibiaxial (a, b, c) and uniaxial (c) elongations.

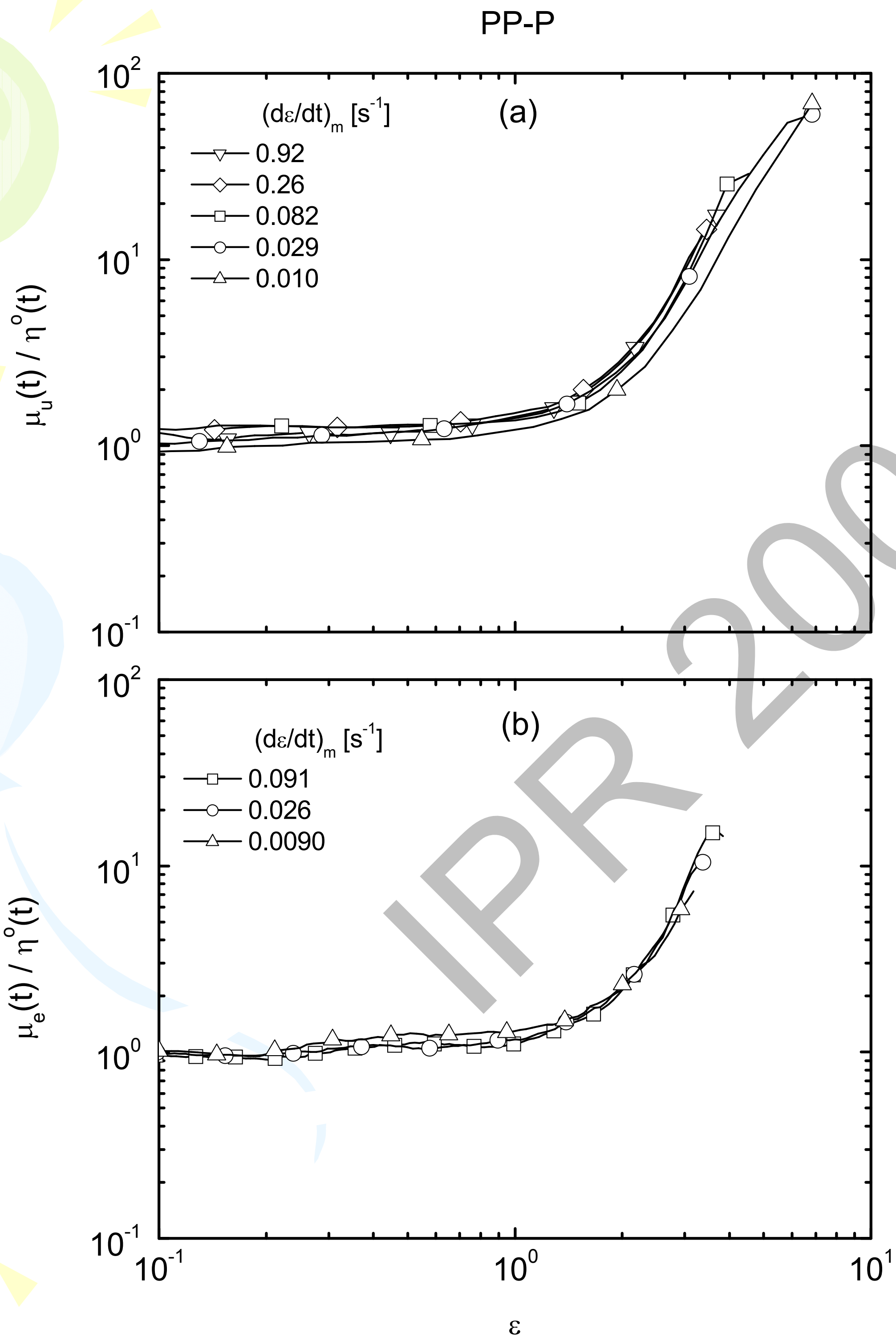


Comparison of elongational viscosities in equibiaxial and uniaxial elongations



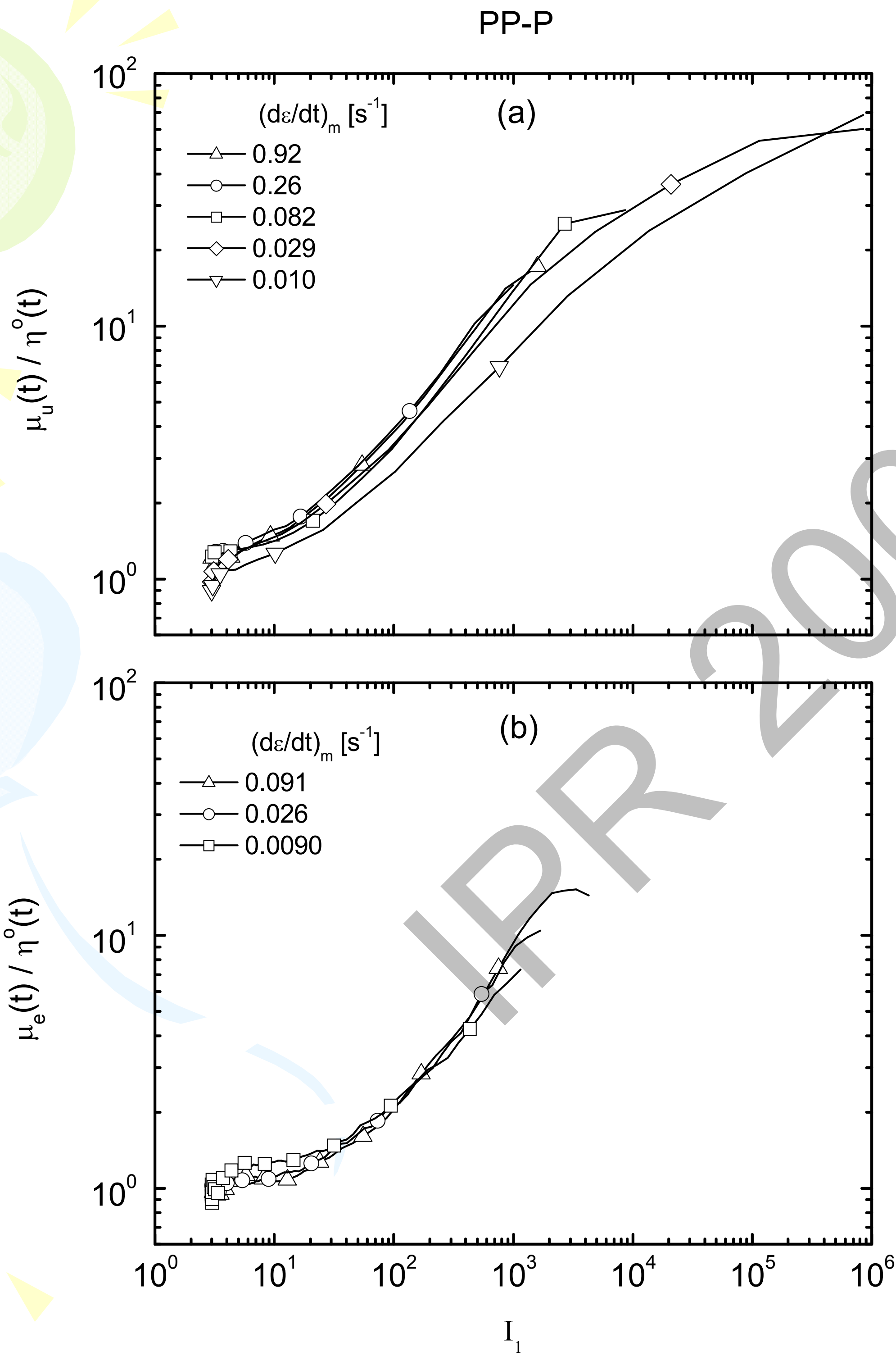
Comparison of strain hardening in equibiaxial and uniaxial elongations





Uniaxial: $\varepsilon_c \sim 1$

Equibiiaxial: $\varepsilon_c \sim 1$



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.

Thanks for your attention!

Questions ?