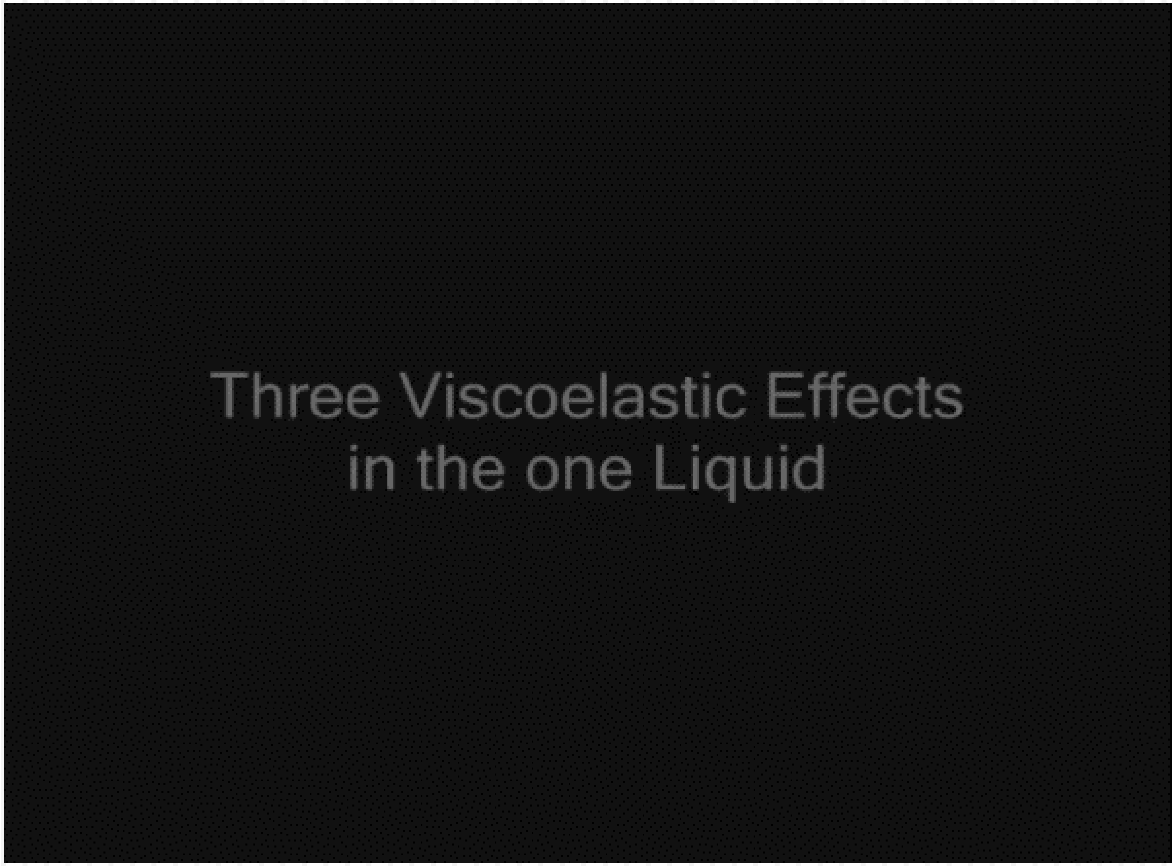
VISCOELASTICITY IN GLASS, RUBBER AND MELT PHASE

WHAT IS VISCOELASTICITY?

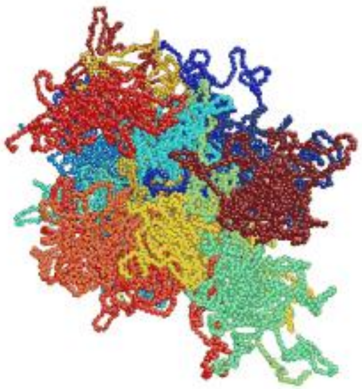
Elastic and viscous

- A viscoelastic material has at the same time both elastic and viscous properties.



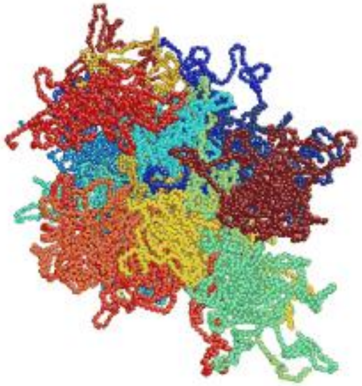
Cause of viscoelasticity

- Viscoelasticity is caused by entanglement of long particles.
- Any material that consists of long flexible fibre like particles is in nature viscoelastic.
  - Polymers are always viscoelastic.



Some viscoelastic materials

- A pile of snakes.
- Spaghetti.
- Tobacco.
- All fibre-like particles.



MOBILITY OF POLYMER MOLECULES

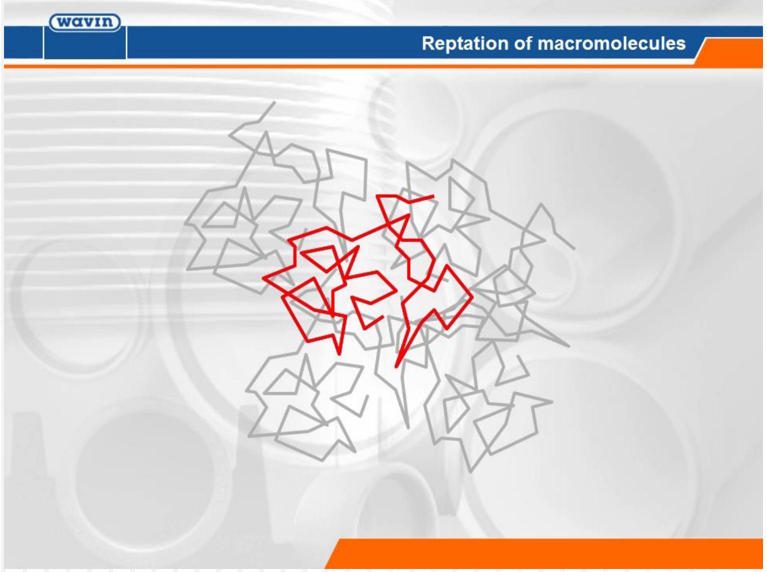
Movement possibilities of polymer molecules

Polymer molecules have two ways to move:

- Rotation of Kuhn segments = deformation
- Reptation of the entire molecule = displacement

Rotation

Reptation



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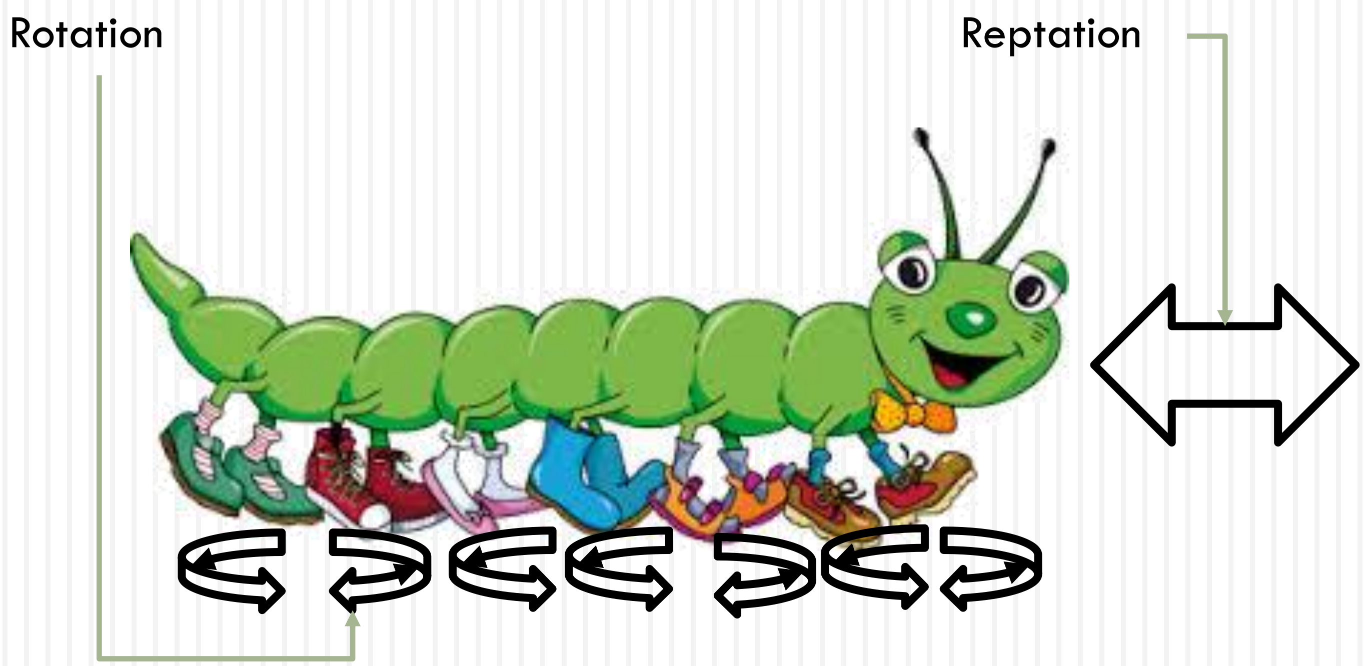

Movement possibilities of polymer molecules

Polymer molecules have two ways to move:

- Rotation of Kuhn segments = deformation
- Reptation of the entire molecule = displacement
  - Reptation is caused by the rotation of the Kuhn segments in random directions.

Movement possibilities of polymer molecules

Polymer molecules have two ways to move:

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Rotation

- Parts of the chain rotate; the molecule itself is not displaced
- The rotation time θ_{rot} is strongly dependent on temperature.
- Rotation is important for the glass phase properties:
  - Glass transition temperature
  - Yield stress
  - Glass stress relaxation

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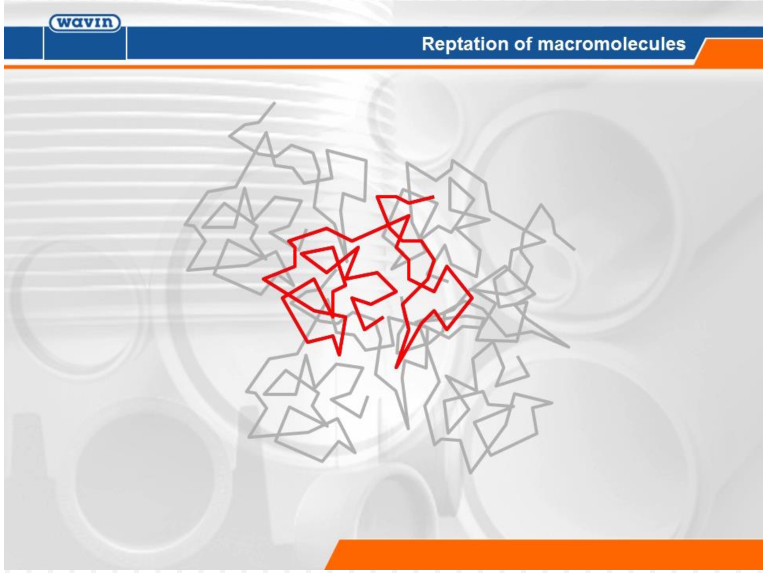

Reptation

- The molecule moves into another position.
- The reptation time is proportional to the rotation time ($\theta_{rep} = \alpha\ \theta_{rot}$) with $\alpha = 10^4 - 10^8$.
- Reptation is important for the fluid properties:
  - Viscosity
  - Elasticity
  - Rubber stress relaxation

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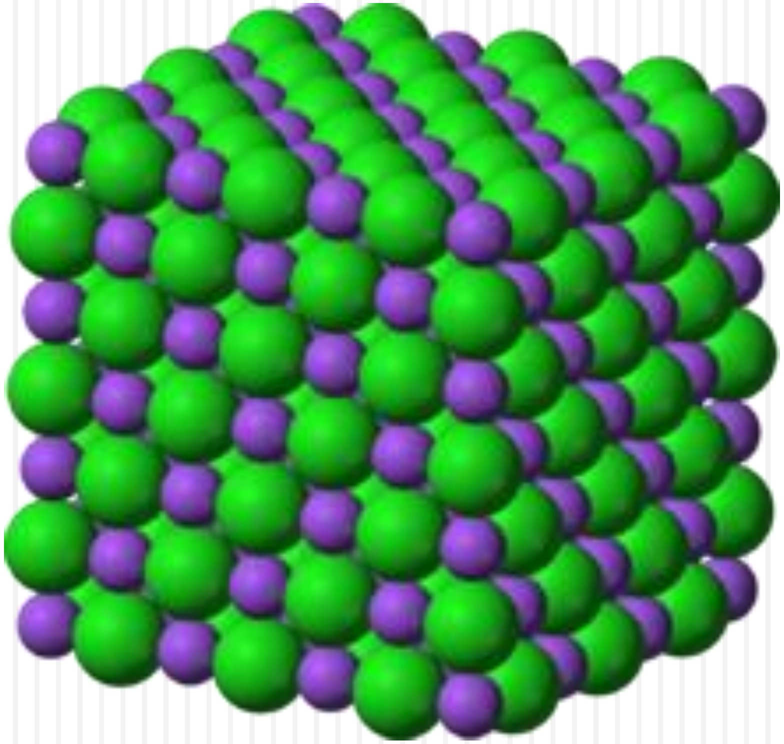
Rotation of Kuhn segments

- The polymer feels stiff when the rotation time is much more than 1 second (glass phase).
- The polymer feels flexible when the rotation time is much shorter than 1 second (rubber and melt phase).
- The glass transition temperature T_g is the temperature at which the rotation time of the Kuhn segments is 1 second.

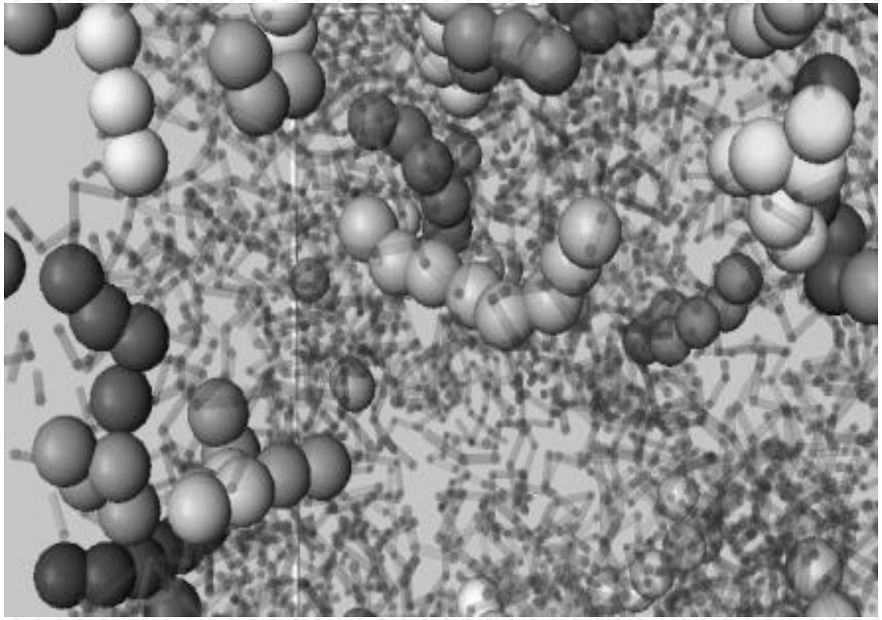
Rotation of Kuhn segments

- All molecules attract each other.
  - Below the melting temperature they form a regular crystalline structure.



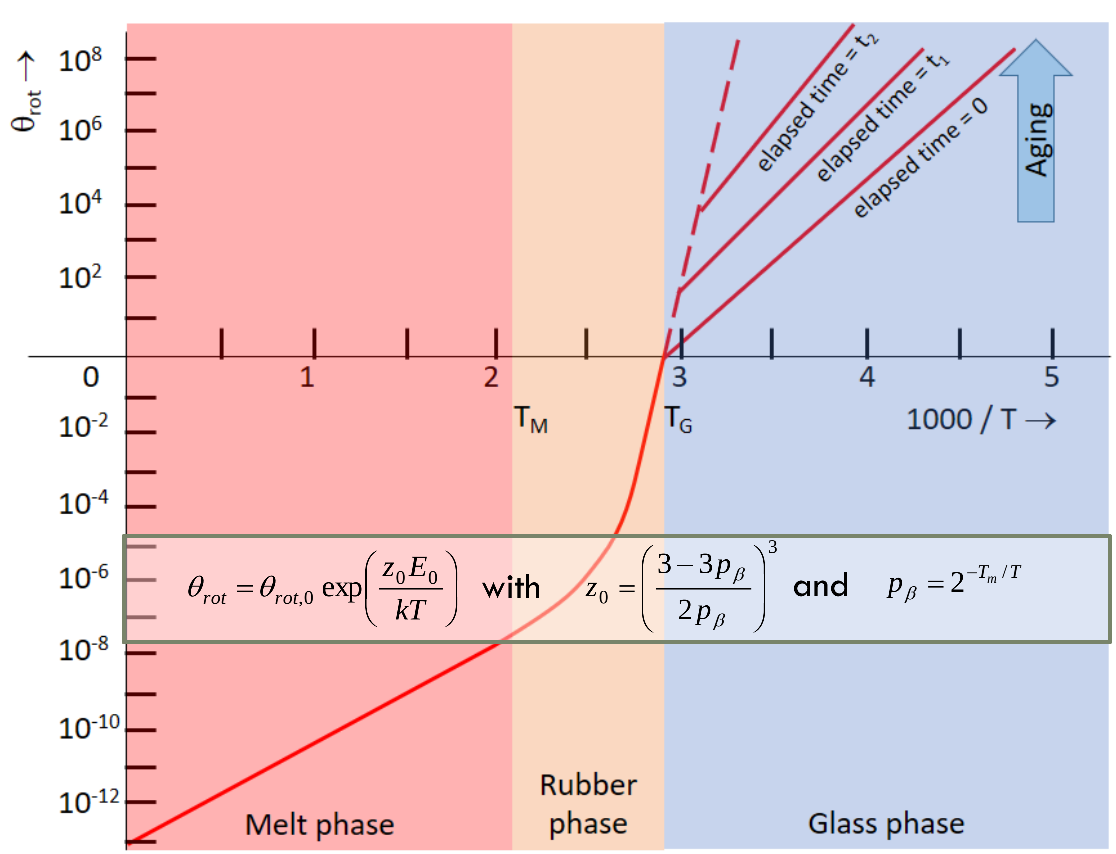
Rotation of Kuhn segments

- The repeat units in a polymer also attract each other.
  - Below the melting temperature the formation of a crystalline structure is difficult due to the limited mobility of the repeat units.
  - They cluster together in cooperatively rearranging regions (CRR's).
  - The seriously hinders the rotation of the Kuhn segments.



Rotation of Kuhn segments

- The rotation time θ_{rot} of the Kuhn segments increases strongly with reducing temperature.

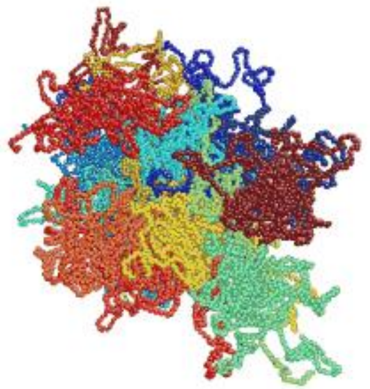


$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{z_0 E_0}{kT}\right) \quad \text{with} \quad z_0 = \left(\frac{3-3p_\beta}{2p_\beta}\right)^3 \quad \text{and} \quad p_\beta = 2^{-T_m/T}$$

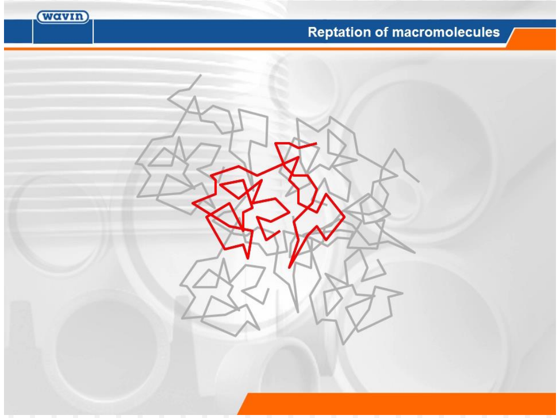
Reptation of the macromolecule

- At times longer than the reptation time the polymer behaves like a fluid.
- At times shorter than the reptation time the polymer behaves like a rubber.

rubber



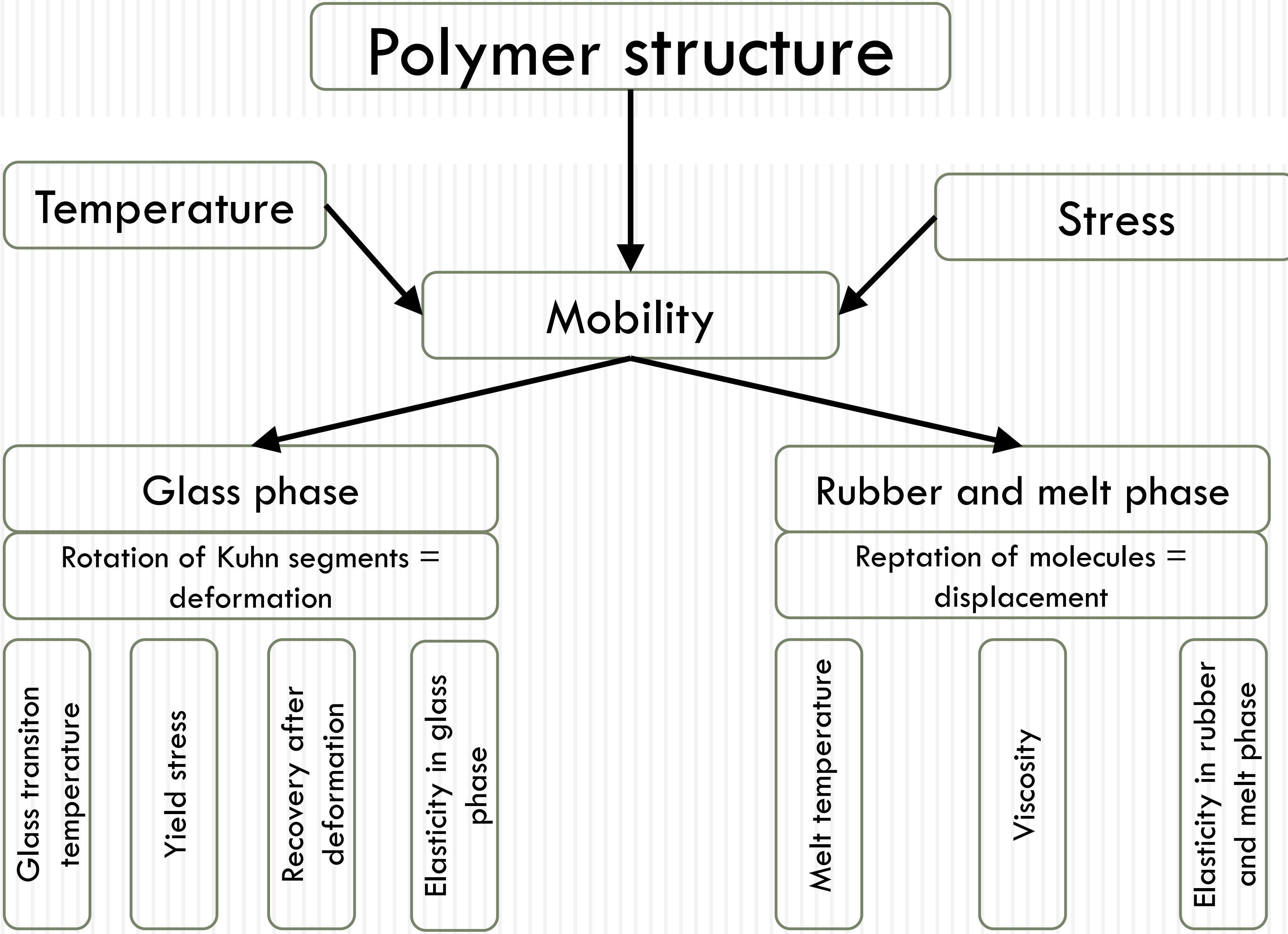
fluid



Reptation of the macromolecule

- The reptation time is proportional to the rotation time.
- The proportionality strongly depends on the number of Kuhn segments N_K in the macromolecule:
  - 1 Kuhn segment: + or - give step $-l_K$ or $+l_K$ during θ_{rot}.
  - 2 Kuhn segments: ++ or -- give step step $-l_K$ or $+l_K$
    +- and -+ give no displacement
    $\rightarrow$ Step $-l_K$ or $+l_K$ takes $2\theta_{rot}$.
  - N_K Kuhn segments: Step $-l_K$ or $+l_K$ takes $N_K\theta_{rot}$.
  - Reptation over N_K Kuhn segments takes N_K^2 steps:

$$\theta_{rep} = N_K^2 N_K \theta_{rot} = N_K^3 \theta_{rot}$$


Polymer structure
Temperature
Stress
Mobility
Glass phase
Rotation of Kuhn segments = deformation
Rubber and melt phase
Reptation of molecules = displacement
Glass transiton temperature
Yield stress
Recovery after deformation
Elasticity in glass phase
Melt temperature
Viscosity
Elasticity in rubber and melt phase

GLASS, RUBBER AND MELT PHASE

Glass phase (short term)

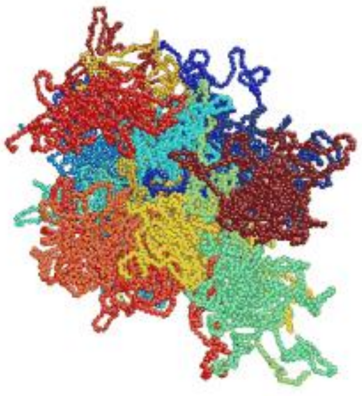
- Kuhn segments have a rotation time of (much) more than 1 second.
  - The plastic is rigid on a human time scale (observation time is a few seconds).
- The polymer is difficult to deform:
  - Chain segments can only bend a little bit. The macromolecules are rigid.
  - An applied force will only result in a small deformation of the plastic.

Glass phase (long term)

- Kuhn segments have a rotation time of (much) more than 1 second.
  - The plastic is rigid on a human time scale (observation time is a few seconds).
- A force applied for a **long time** is still able to deform the polymer in the glass phase.
  - The time should be longer than the time that the Kuhn segments need to rotate.
  - This slow deformation is called creep.
  - The polymer now behaves like a rubber.

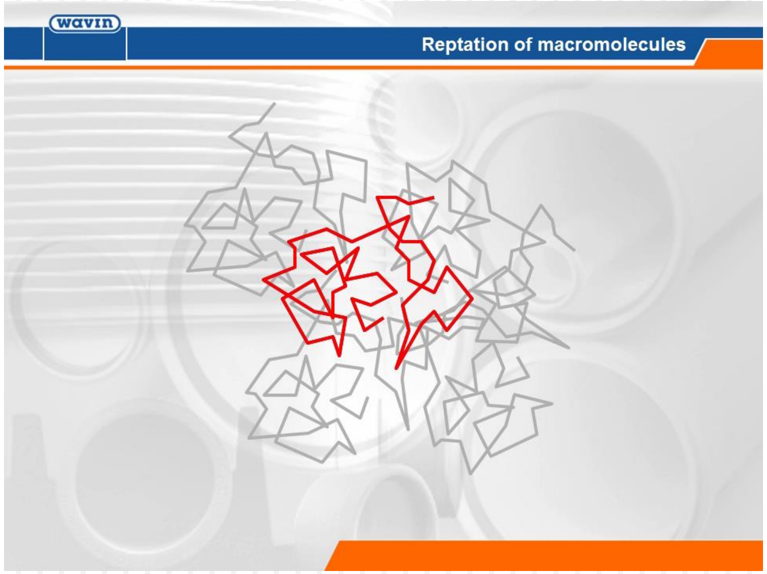
Rubber phase

- In the rubber phase the Kuhn segments rotate in a time less than 1 second.
  - The plastic is flexible.
- The reptation time of the macromolecules is much higher than 1 s.
  - The relative position of the macromolecules will not change.



Melt phase

- In the melt phase the reptation time of the macromolecules is less than 1 second.
  - The macromolecules can change their relative position.
- In this condition the plastic can be shaped into products by means of extrusion, injection moulding or blow moulding.



Glass, rubber and melt phase

	Rotation time	Reptation time
Glass phase	> 1 s	>> 1 s
Glass transition temperature	1 s	>> 1 s
Rubber phase	< 1 s	> 1 s
Rubber – melt transition temperature	<< 1 s	1 s
Melt phase	<< 1 s	< 1 s

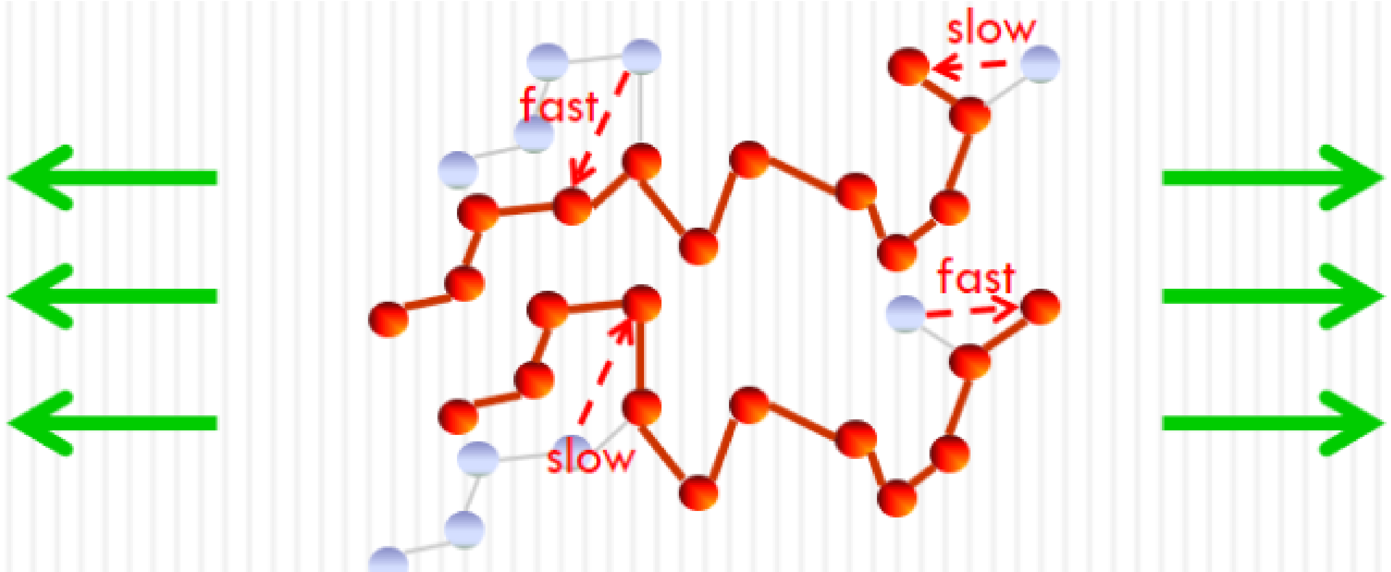
Glass, rubber and melt phase

- Relaxation of stress in the glass phase is caused by rotation of the Kuhn segments.
- Relaxation of stress in the rubber and melt phase is caused by reptation of the macromolecules

INFLUENCE OF STRESS ON RELAXATION TIME

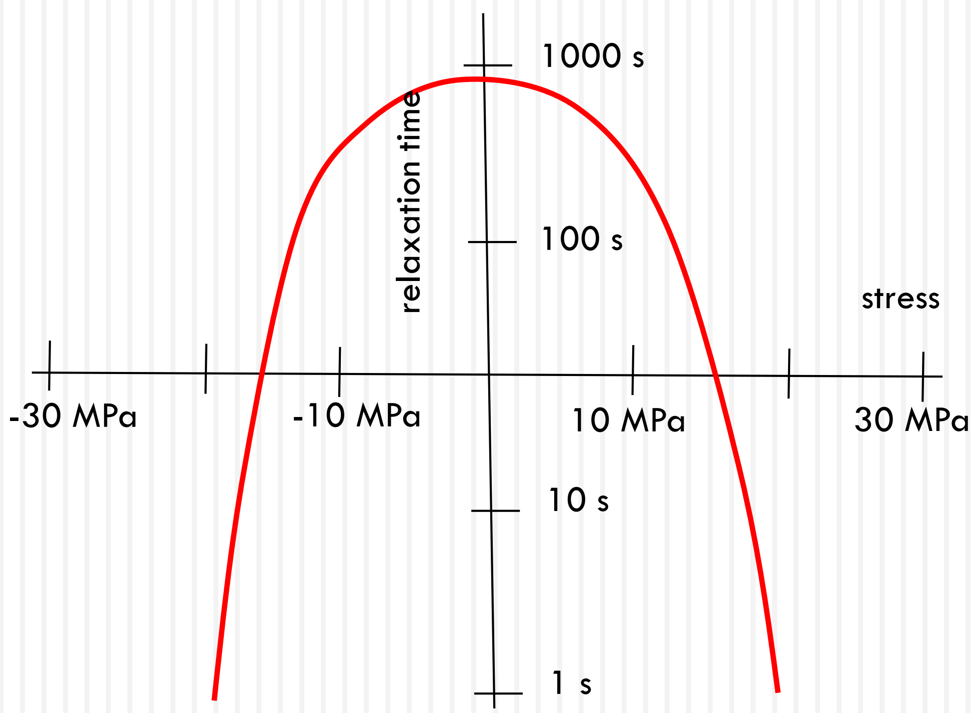
Stress and relaxation time

- Relaxation of stresses in the glass phase is caused by rotation of the Kuhn segments.
- Rotations that reduce the stress will speed up.
- Rotations that increase the stress will slow down.



Stress and relaxation time

- Nett result: The relaxation time decreases exponentially with the applied stress.



Stress and relaxation time

- The rotation time decreases with stress:

$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{V_{rot}\sigma_{gla}}{kT} \bigg/ \sinh\left(\frac{V_{rot}\sigma_{gla}}{kT}\right)$$

- The reptation time is proportional to the rotation time:

$$\theta_{rep} = N_K^3 \theta_{rot}$$

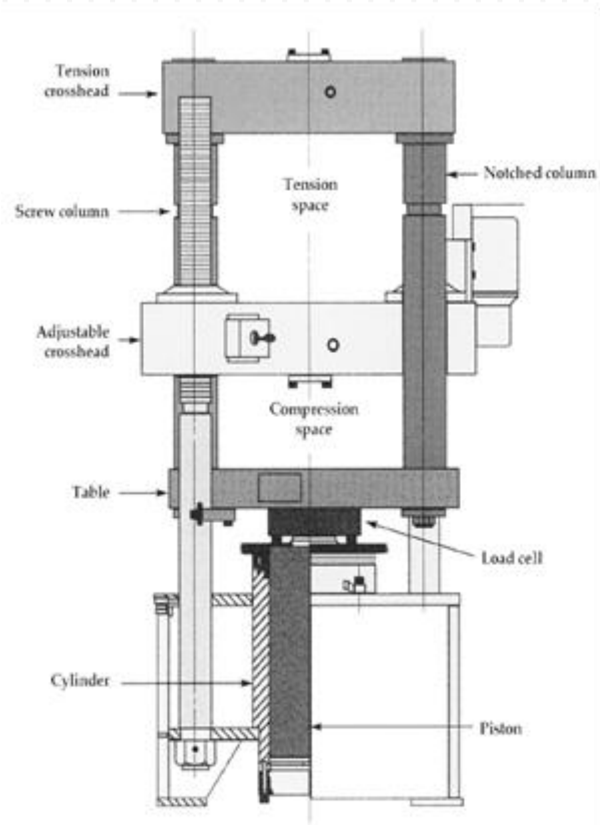
- Therefor the reptation time also decreases with stress:

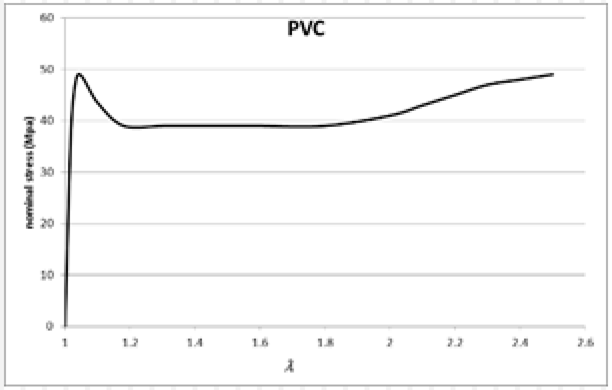
$$\theta_{rep} = \theta_{rep,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{V_{rep}\sigma_{rub}}{kT} \bigg/ \sinh\left(\frac{V_{rep}\sigma_{rub}}{kT}\right)$$

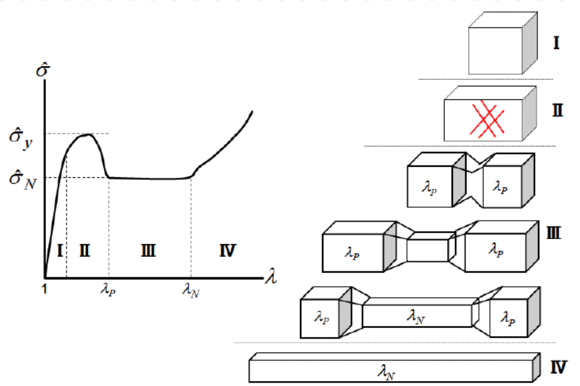
- Net result: The rubber stress relaxation time will strongly decrease with increasing stress.

YIELD STRESS

Yield stress





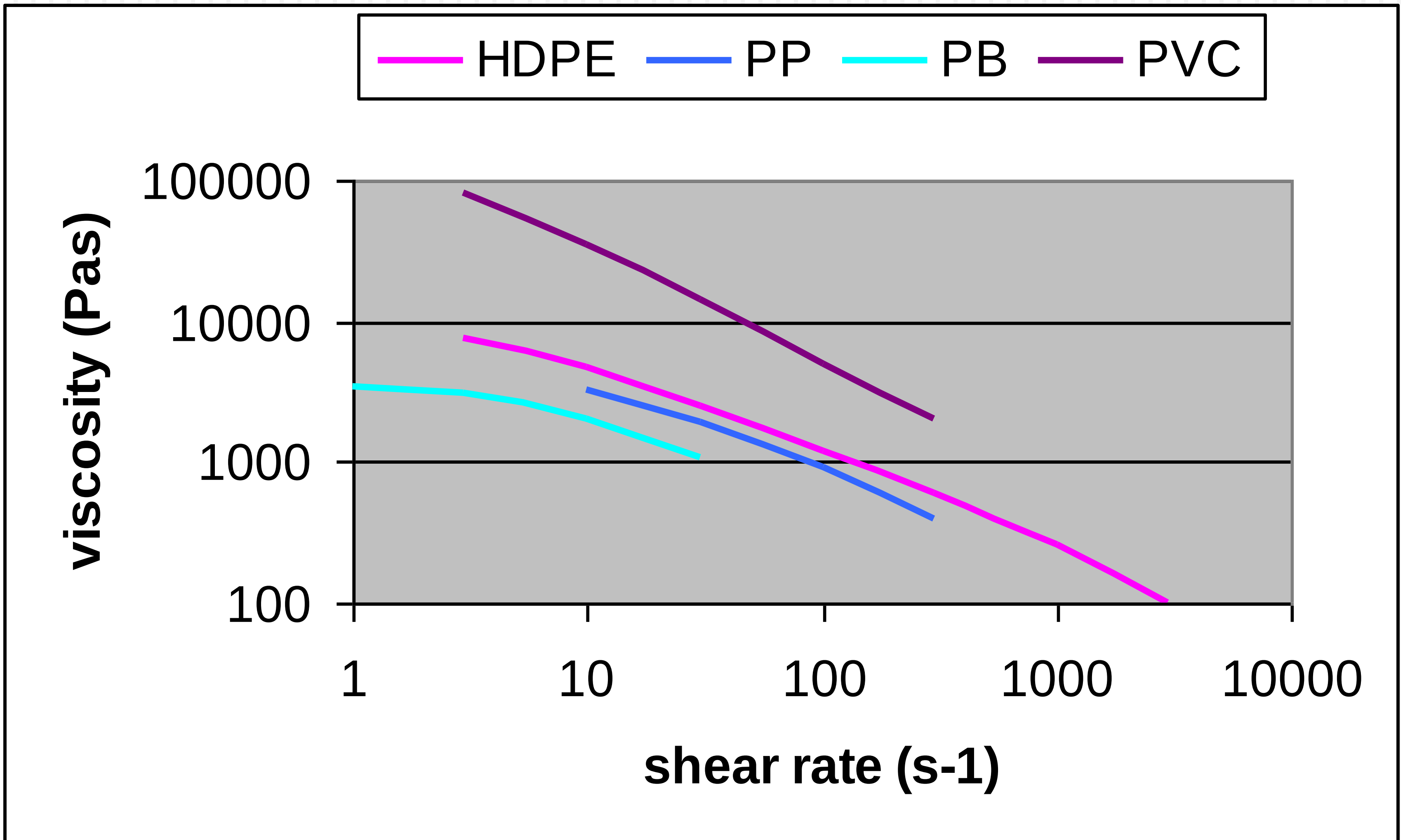


Yield stress

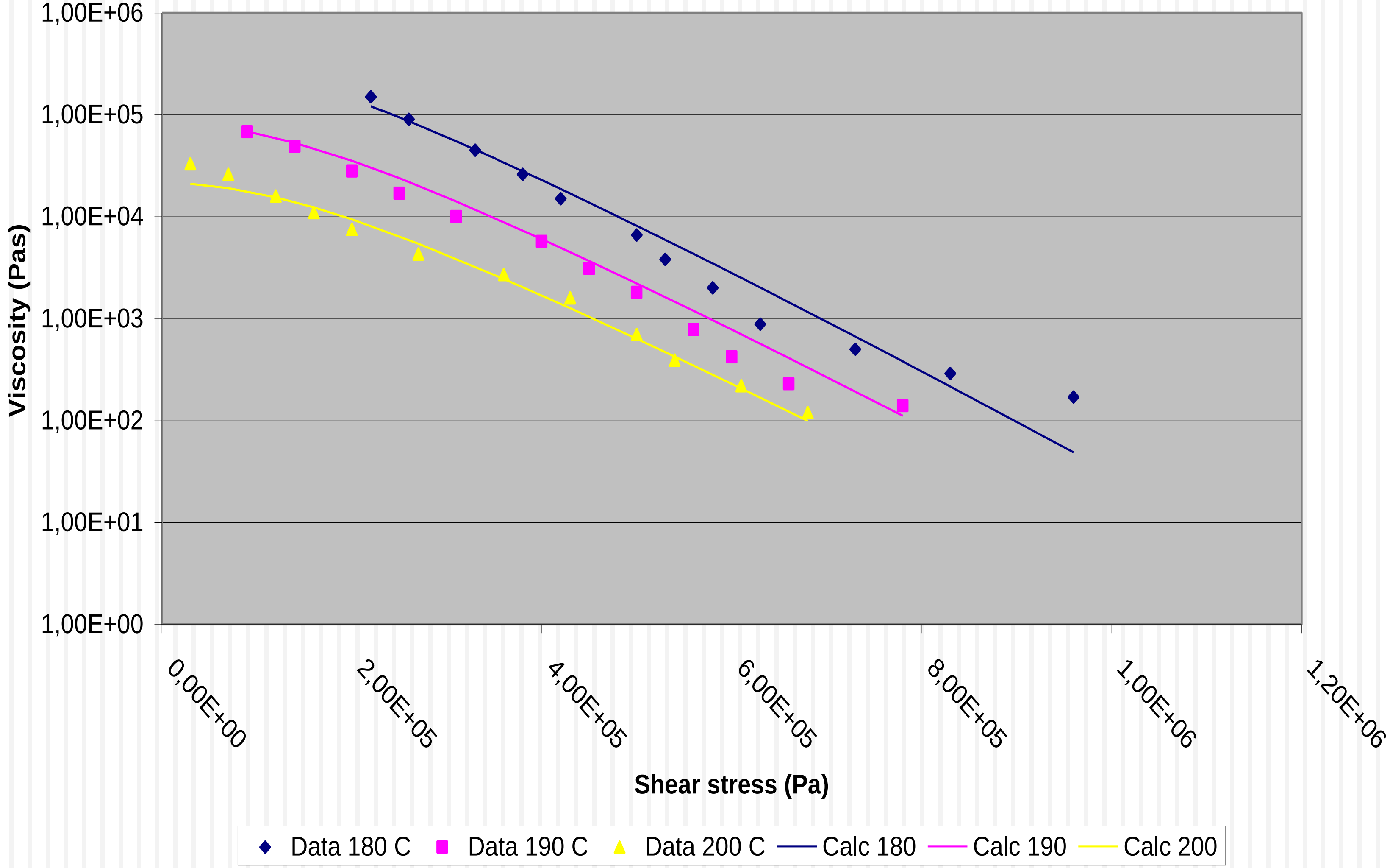
- In the glass phase the rotation time of the Kuhn segments is very long.
- The rotation time strongly reduces with stress.
- At a certain stress the rotation time has reduced to a few seconds.
  - The polymer starts to deform quickly.
  - The yield stress has been reached.

VISCOSITY

Viscosity of several polymers



Viscosity of PVC

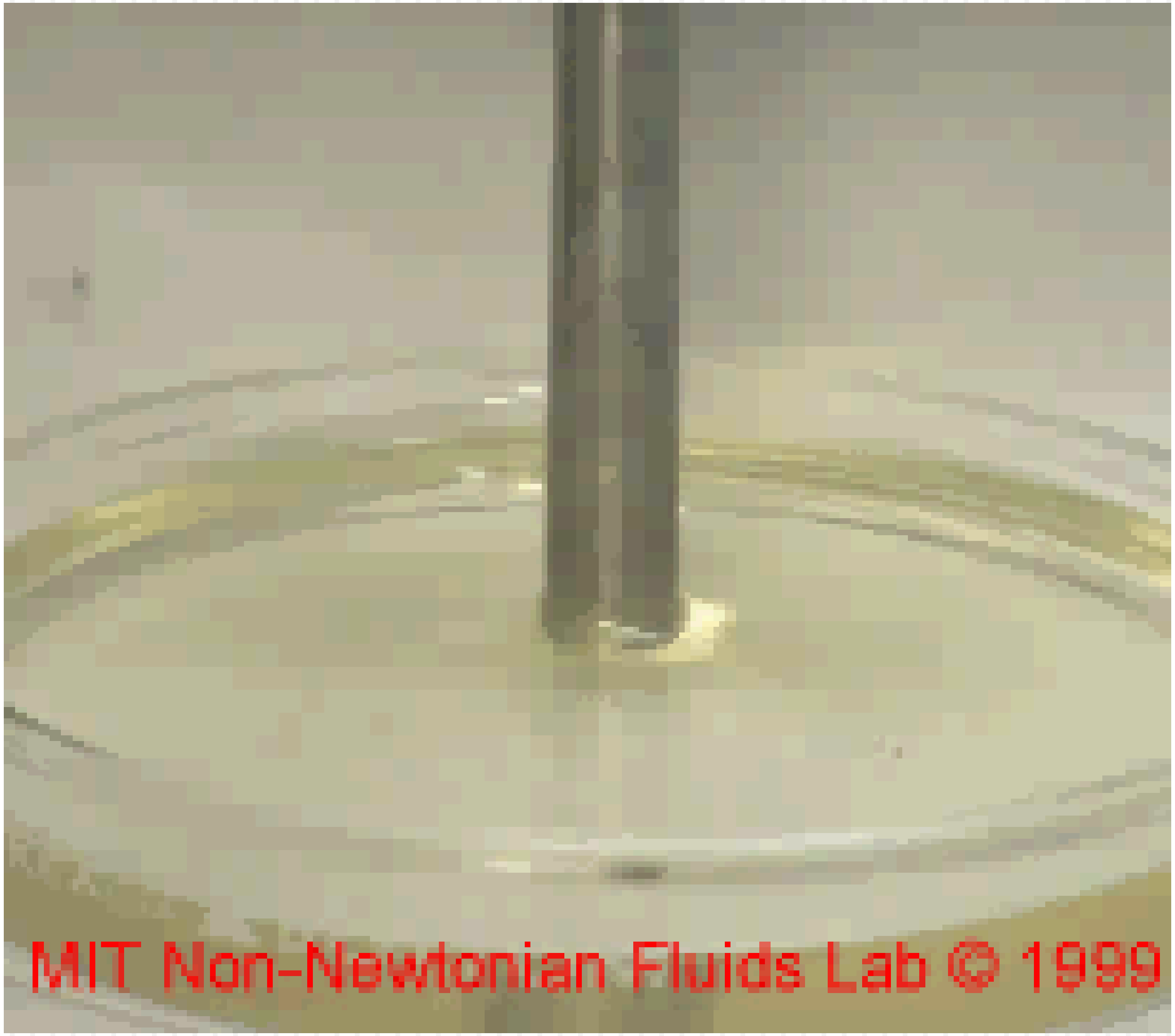


Reduction of viscosity

- With increasing stress the reptation time of the polymer molecules reduces.
- The viscosity is the product of rubber shear modulus and reptation time: $\eta = G_{rub}\theta_{rep}$
- The viscosity will reduce with stress because the reptation time reduces with stress.
- High stress = high shear rate:
- The viscosity will reduce with shear rate.

ROD CLIMBING EFFECT

Rod climbing effect



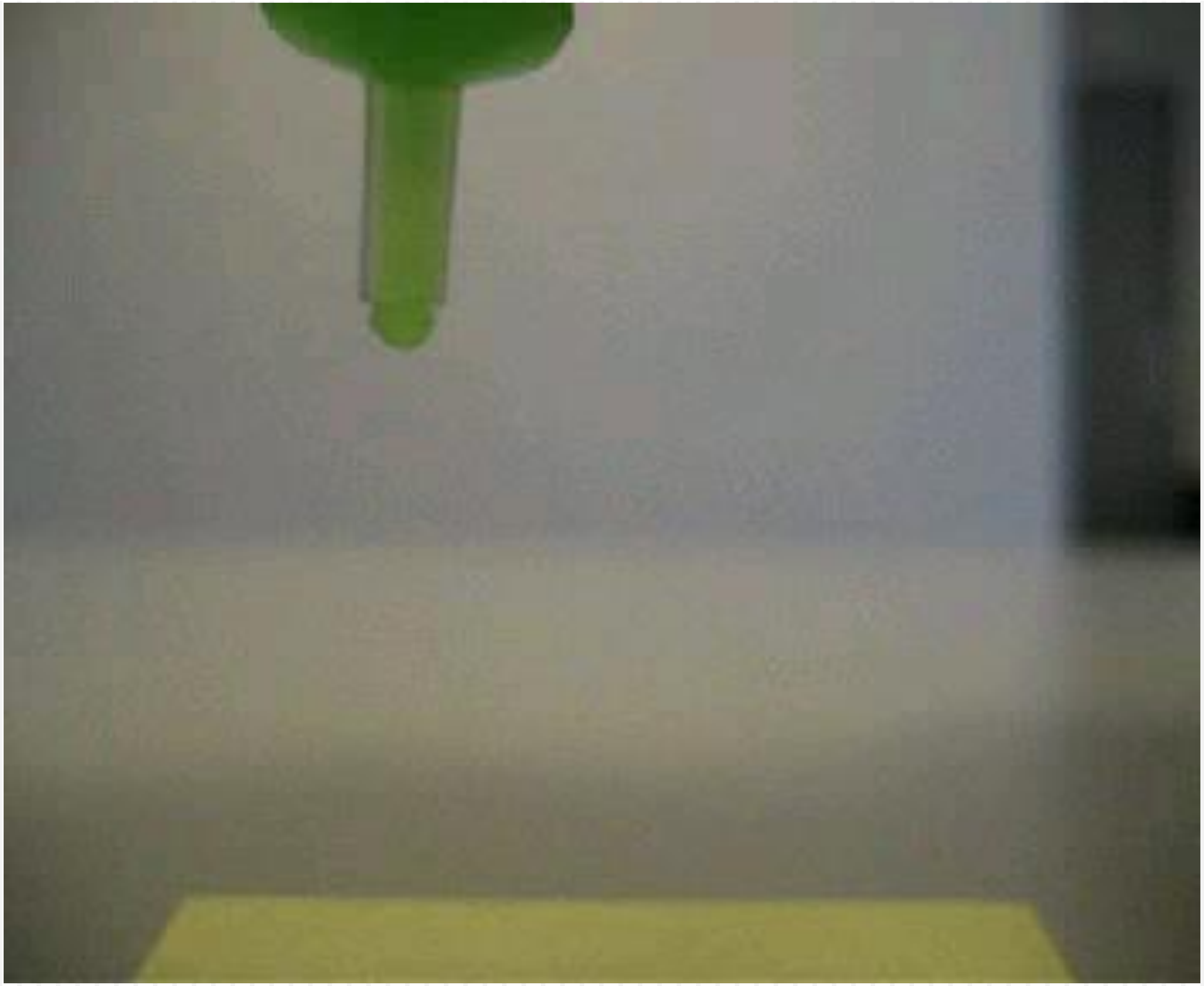
Rod climbing effect

Rod climbing effect

- The rotating rod pulls at the entangled molecules.
- The molecules move towards the rod.
- The molecules near the rod are pushed upwards.

DIE SWELL

Die swell



Die swell

- The reduction of the cross-section creates a stress in the polymer.
- At the exit the stress is released; the thickness increases.