Soft Thermoplastic Elastomers (TPEs):

Understanding temperature and time dependence of their mechanical properties

Simone Sbrescia - M. Seitz, T. Engels (DSM) – E. Van Ruymbeke (UCLouvain)

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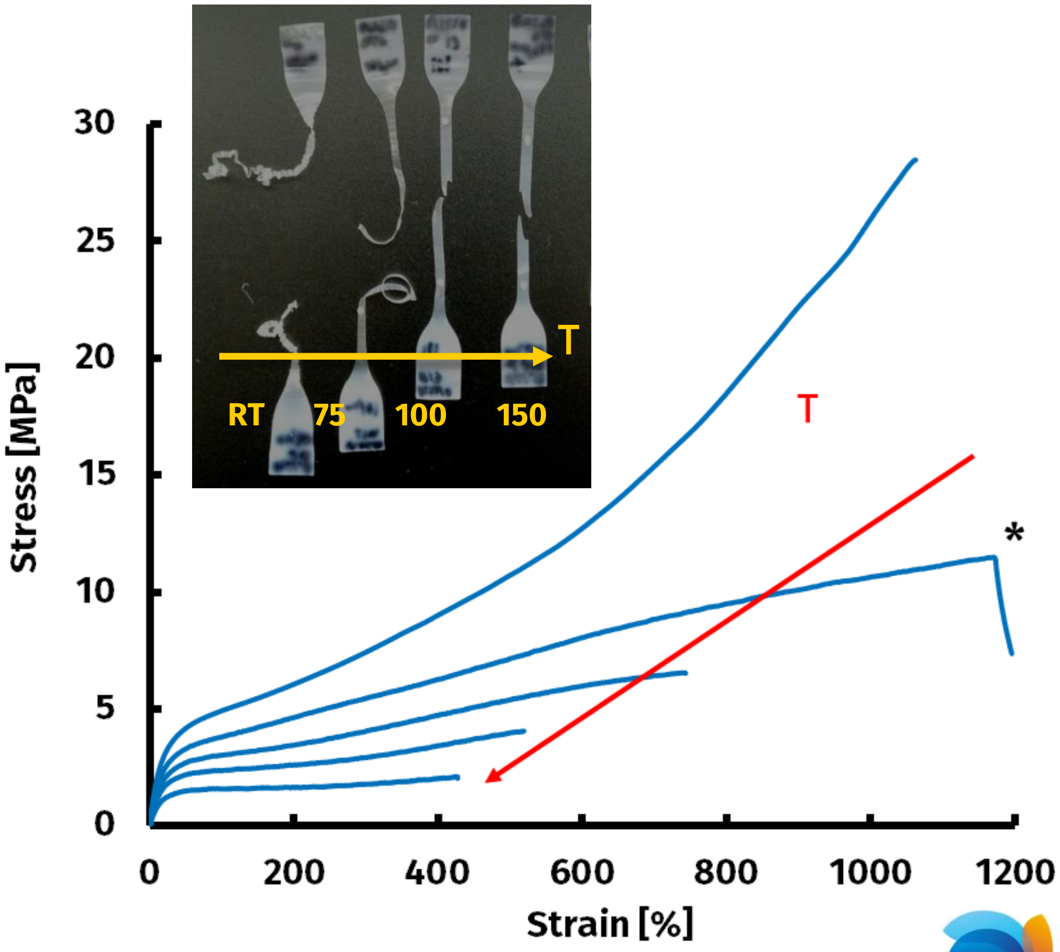
Strain at break dramatically decreases for soft-TPEs

General phenomenon occurring across a range of different chemistries and type of associations.

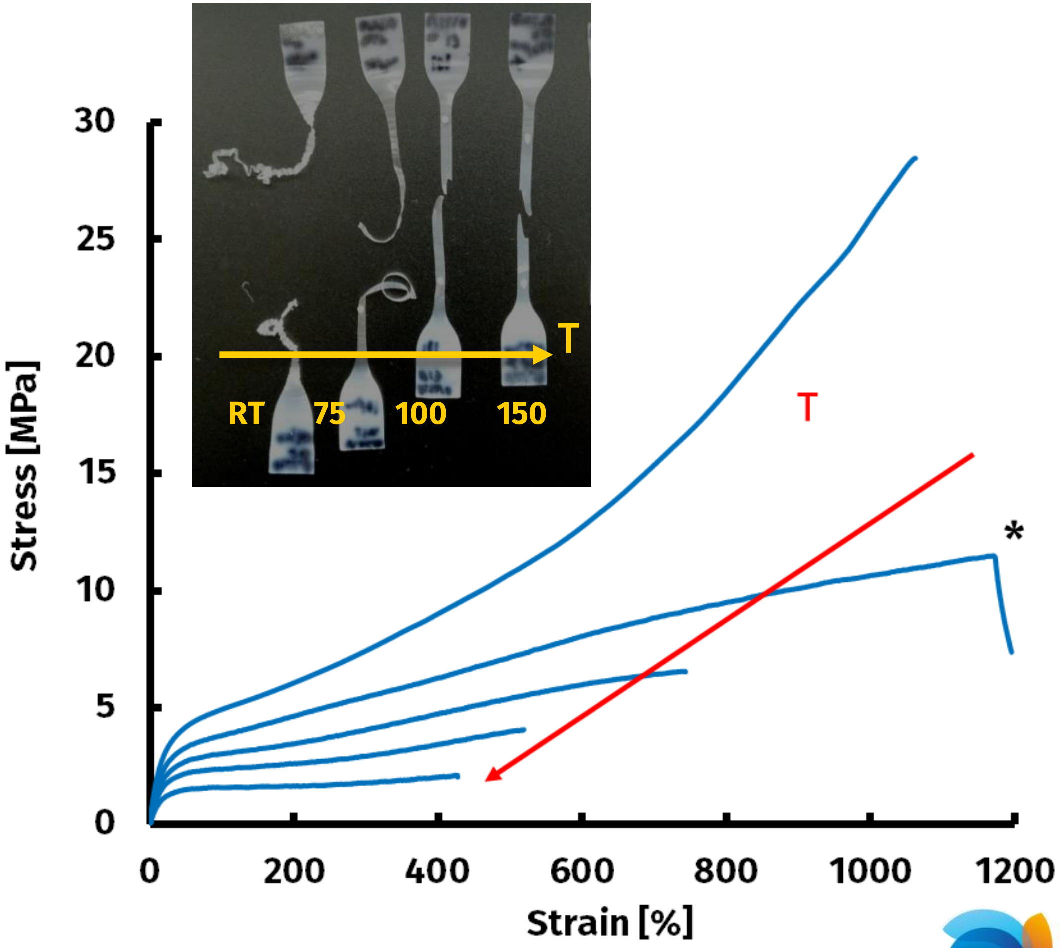
- A problem that can limit the temperature range accessible for some applications and place limitations on processing conditions



Understanding the high-T deformation behavior of soft-TPEs

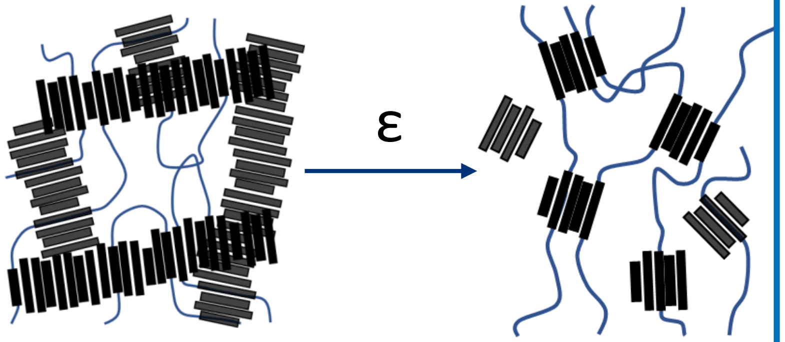
Aim to fill the gap in literature with a systematic description of the effect of M_w and composition on the T resistance and strain hardening

- What controls the level of stress and strain?
- What is the failure mechanism?
- What influences this behavior?



Approach

Materials description:
morphology and its evolution



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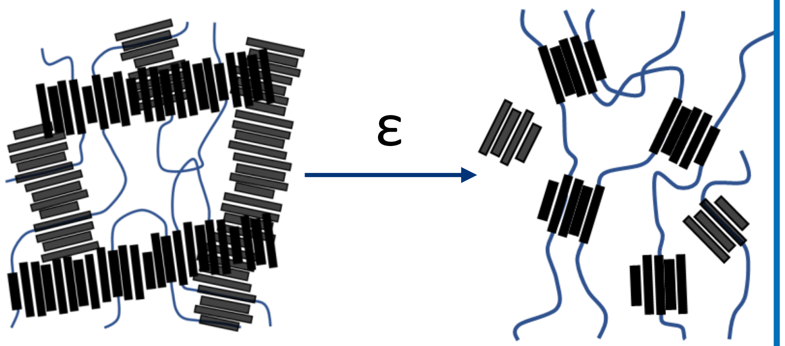
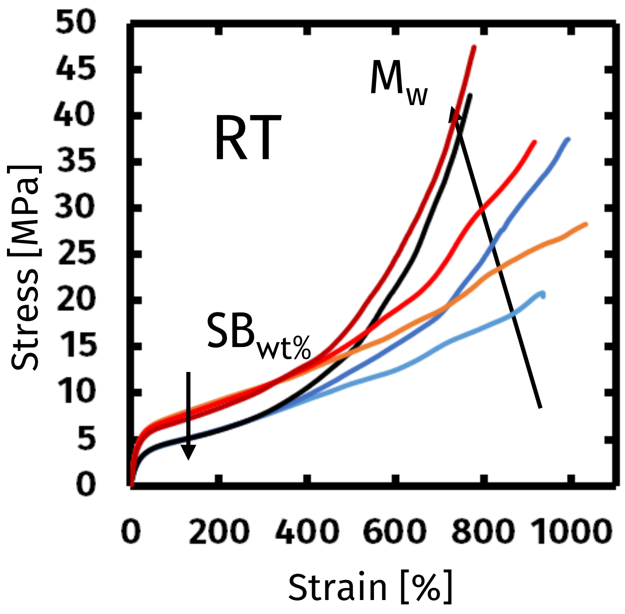


Varying composition and M_w:
linear and nonlinear properties



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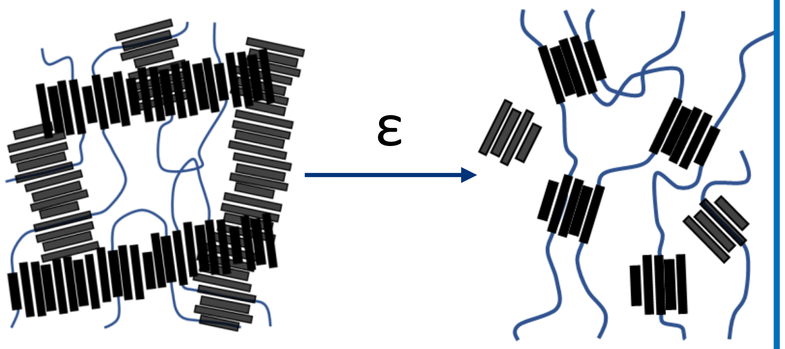
Materials description: morphology and its evolution



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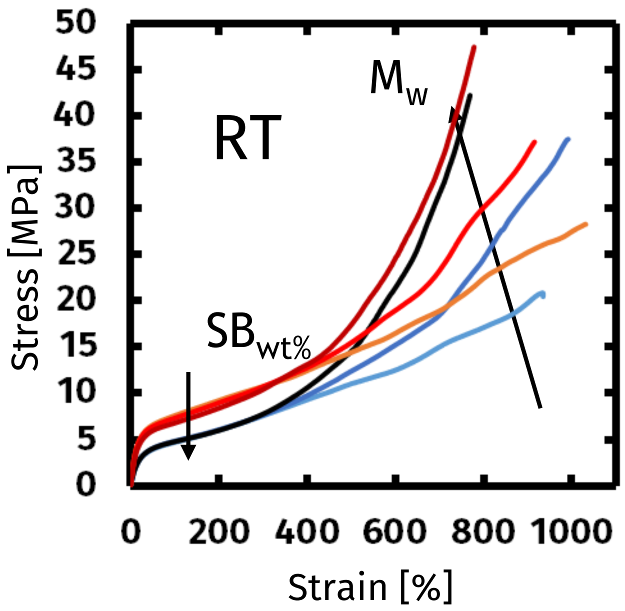
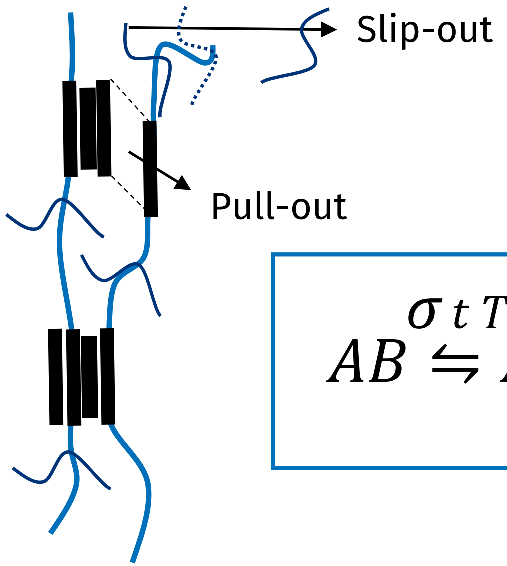


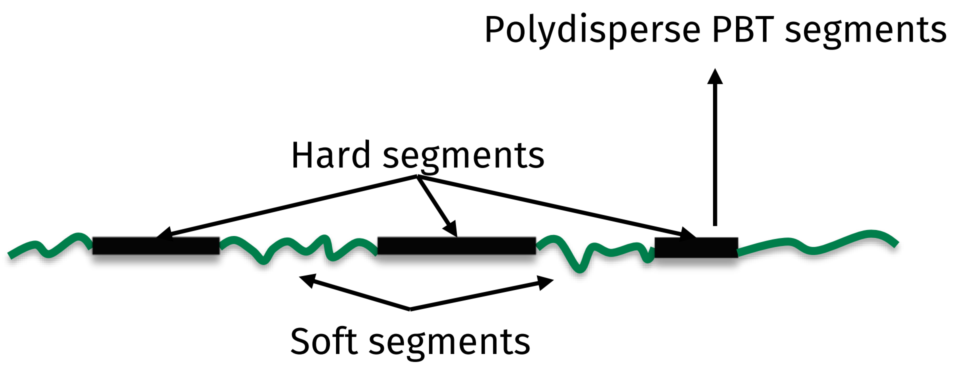
Results interpretation: network connectivity

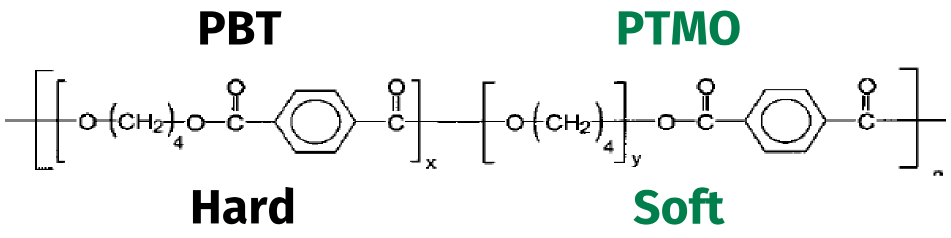


$$AB \overset{\sigma\, t\, T}{\leftrightharpoons} A + B$$

Materials

Soft-Thermoplastic elastomers (TPEs) – Segmented block-copolymers





Materials

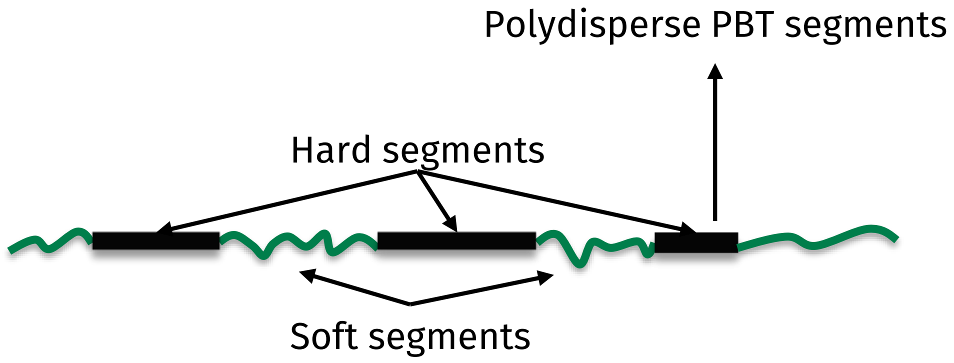
Soft-Thermoplastic elastomers (TPEs) – Segmented block-copolymers

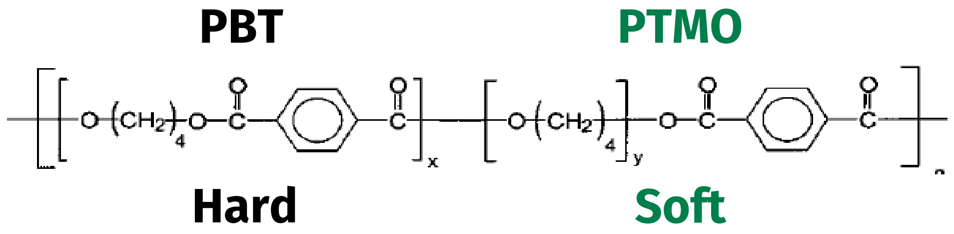
Materials	SB [wt%]	HB [wt%]	Mn_SB [kg/mol]	Tm peak [°C]	X_c [%]	<N> [#]	M_n* [kg/mol]
60_ PTMO2k	60	40	2	200	17	6.9 … 14.1	24.6 … 50.2
70_ PTMO2k	70	30	2	175	9	8.6 … 24.1	27.2 … 67.0

$SB_{wt\%}$

SB_{length}

$^{*}\ PDI \cong 2$





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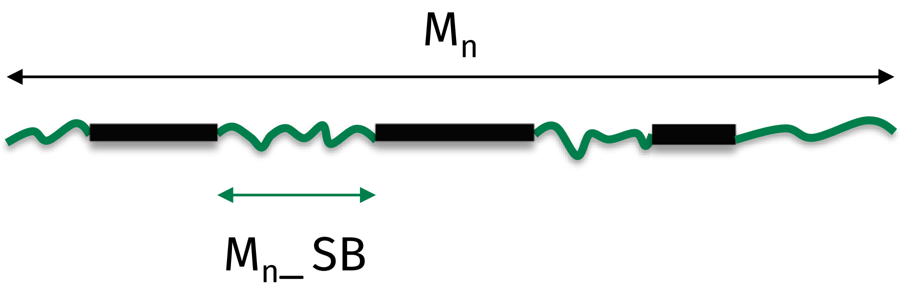

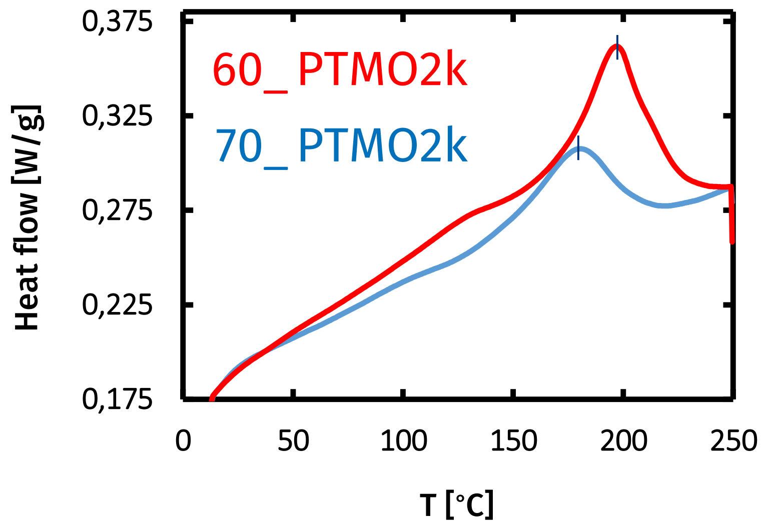

Materials

Soft-Thermoplastic elastomers (TPEs) – Segmented block-copolymers

Linked to network connectivity,
Proportional to M_n

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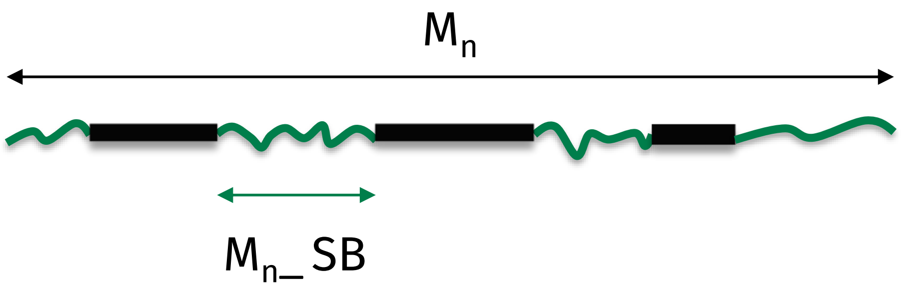
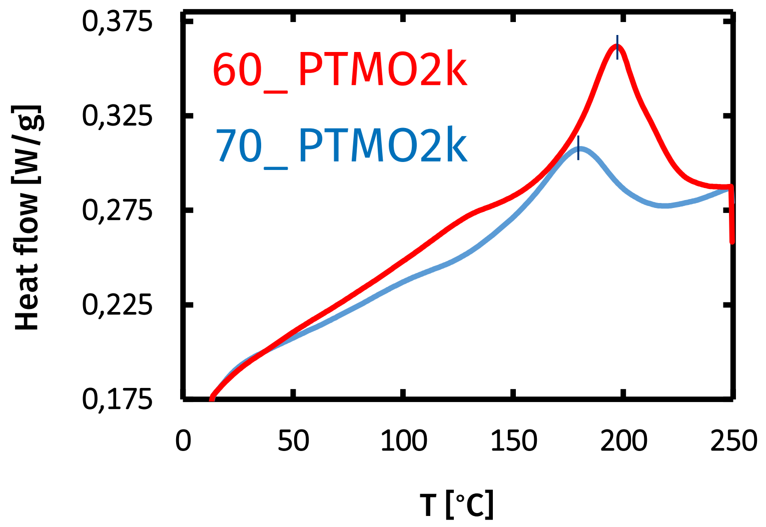


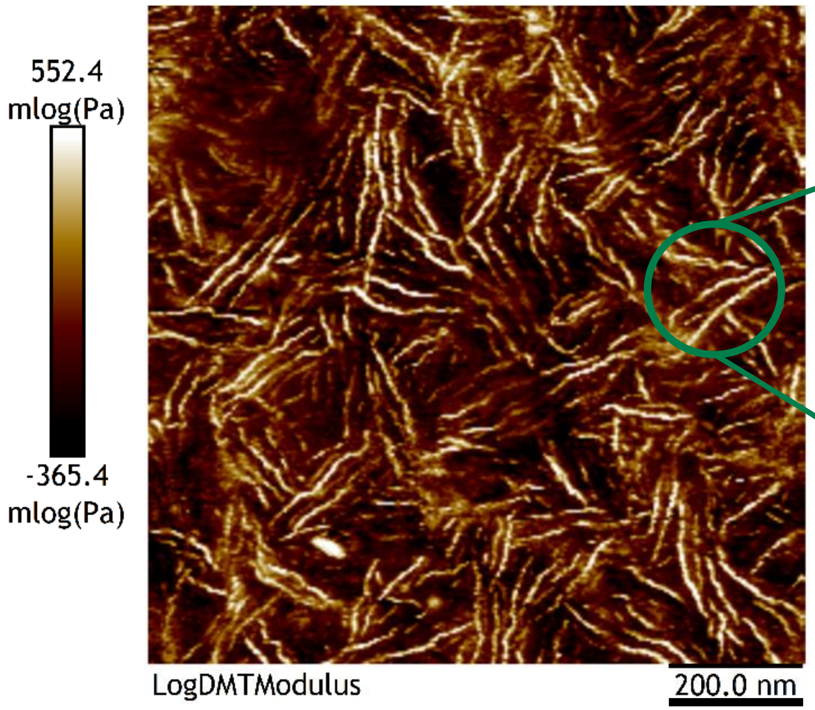


Morphology and its evolution

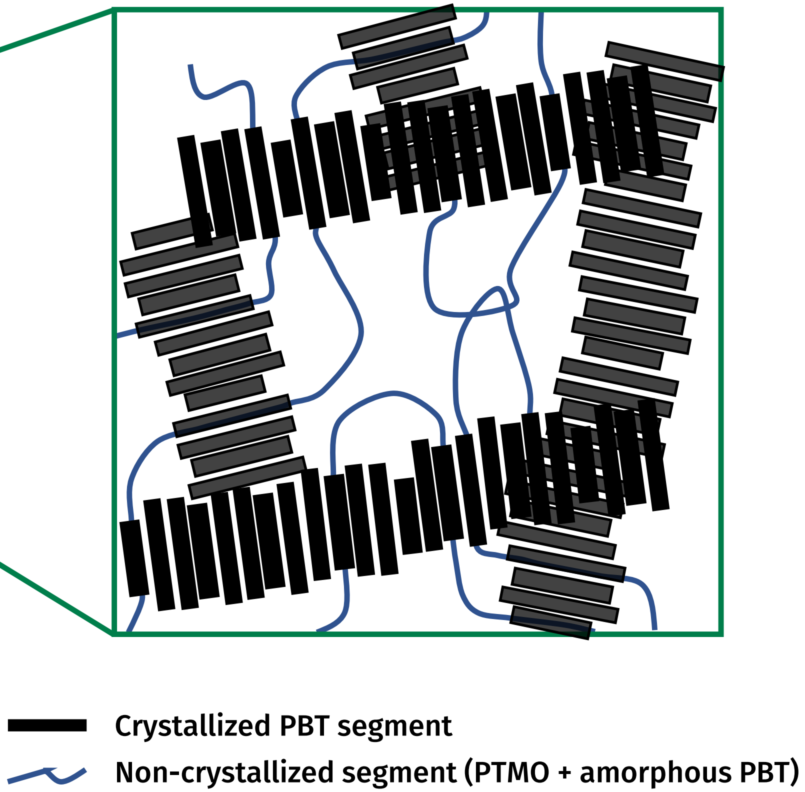
Morphology: network of ribbon-like PBT crystals

- The crystal skeleton of PBT crystals is the stress-bearing structure in the linear regime.
- PBT crystals are interconnected with each other via non-crystallized segments.

Hardness mapping



AFM QNM mode



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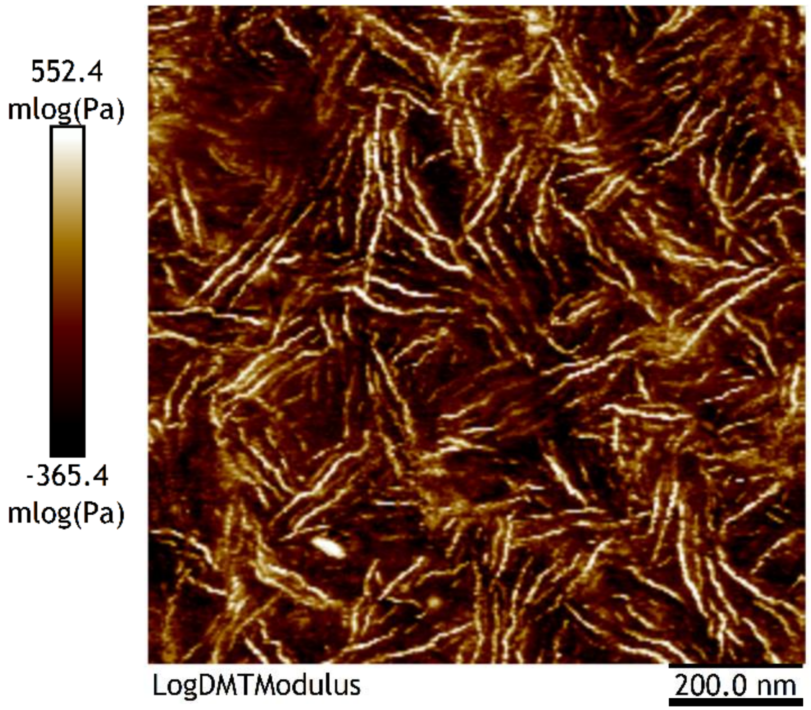

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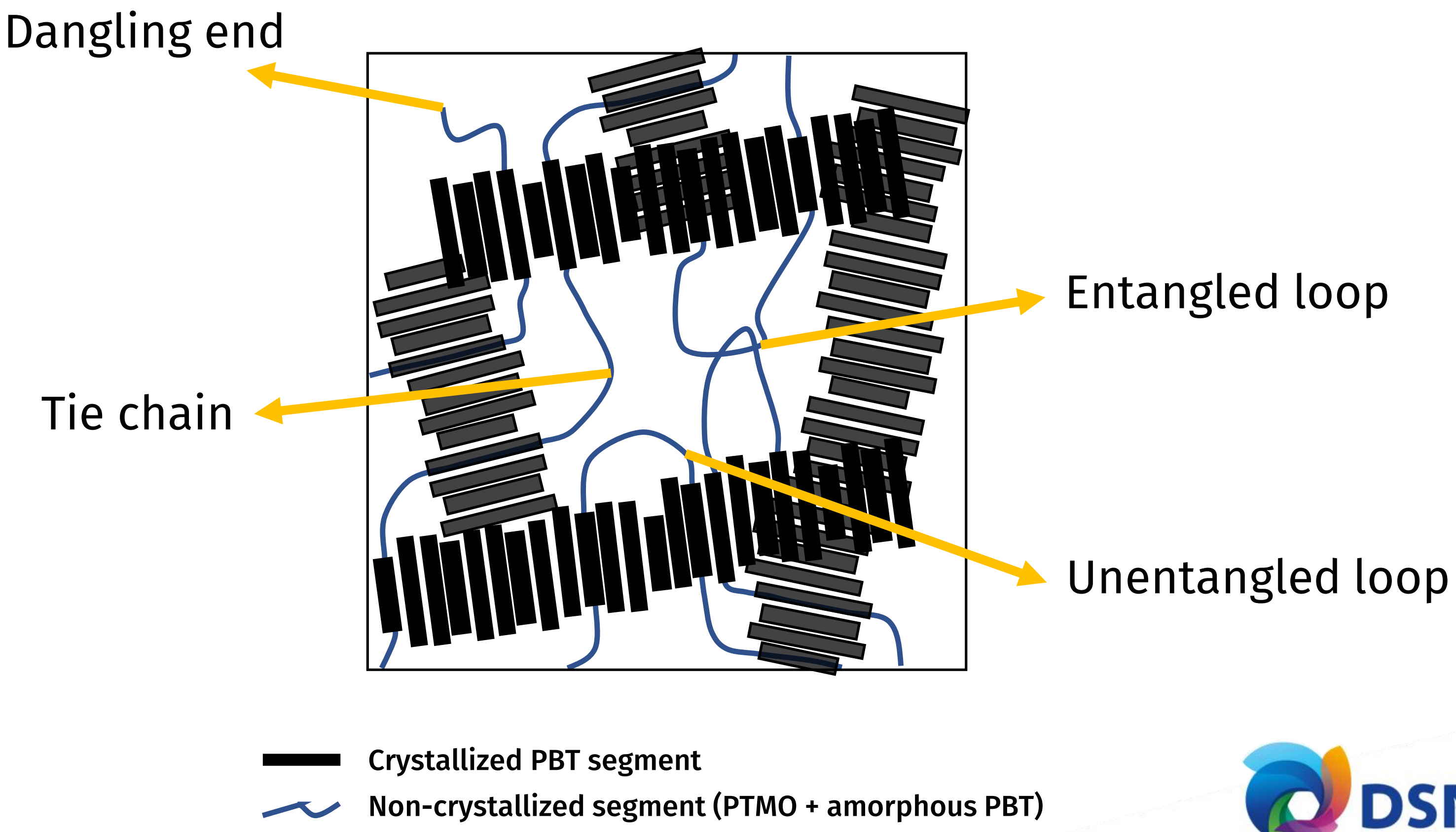

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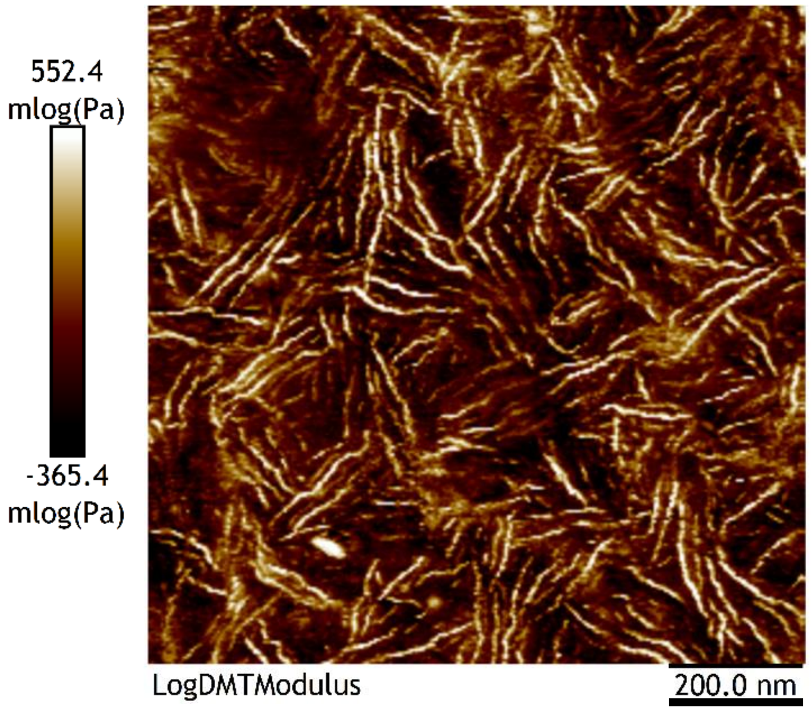

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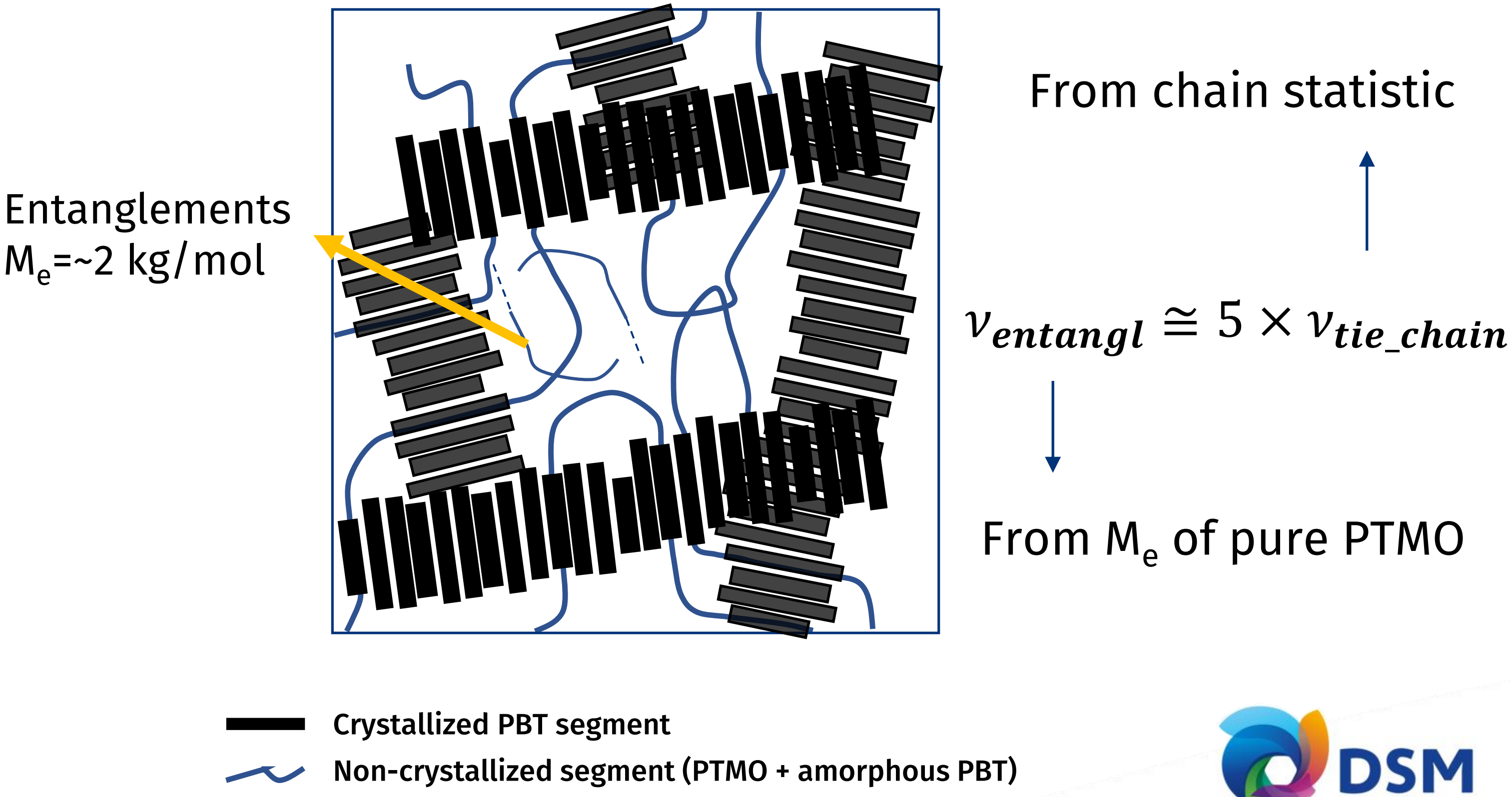
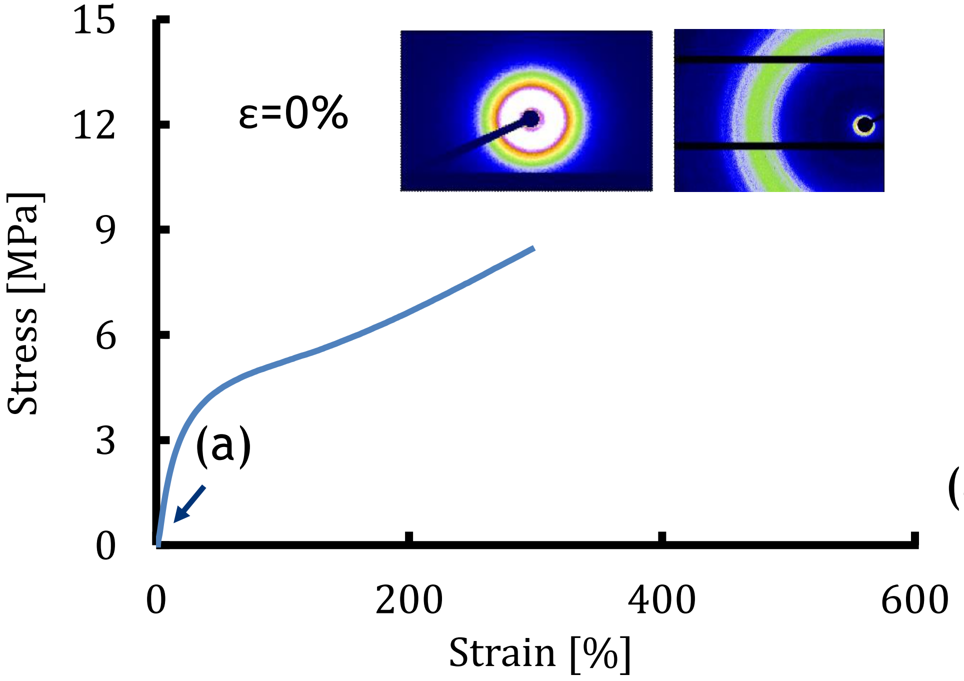
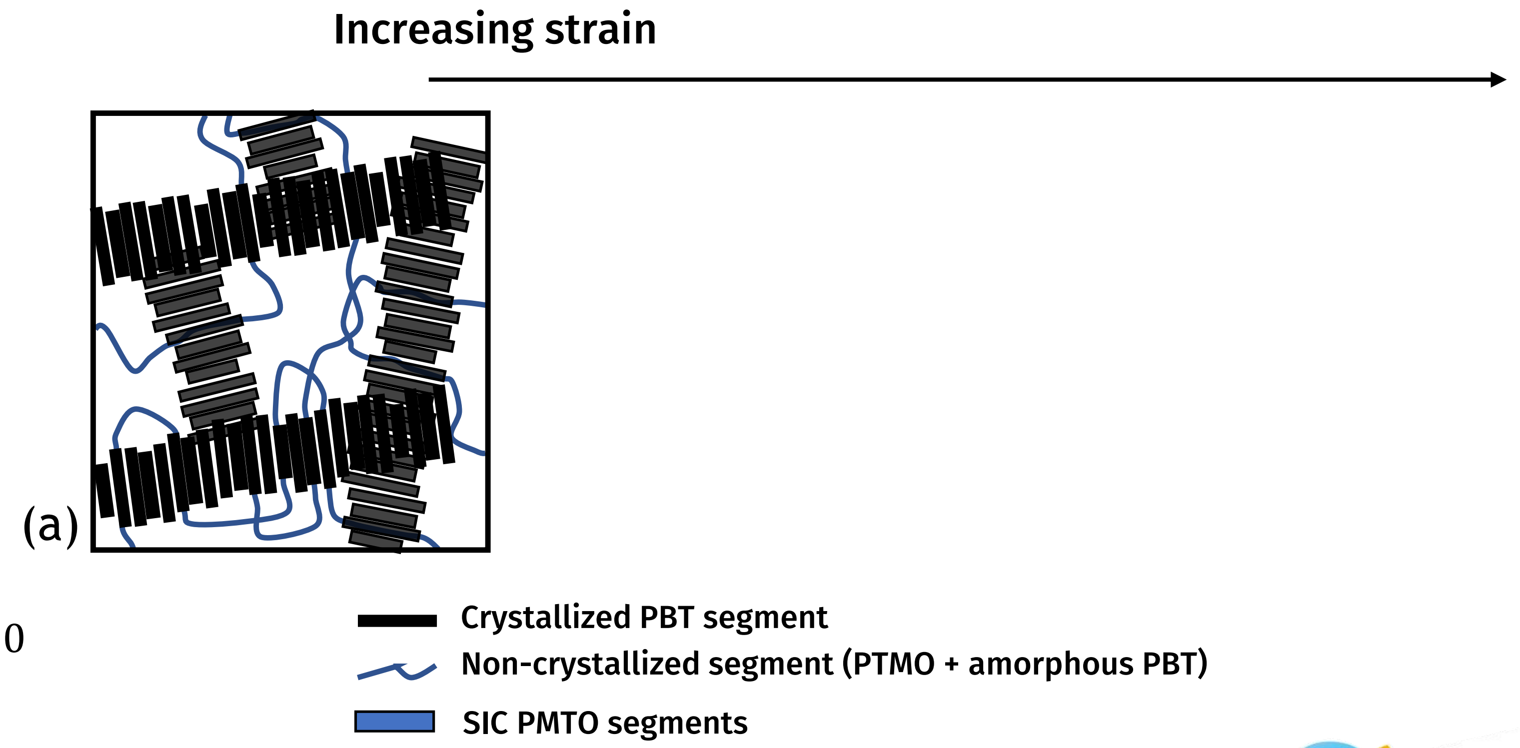


Morphology evolves during deformation

Transition from a percolated network of crystals (a) to an elastomeric-like network (b).

- Cyclic / Hysteresis tests



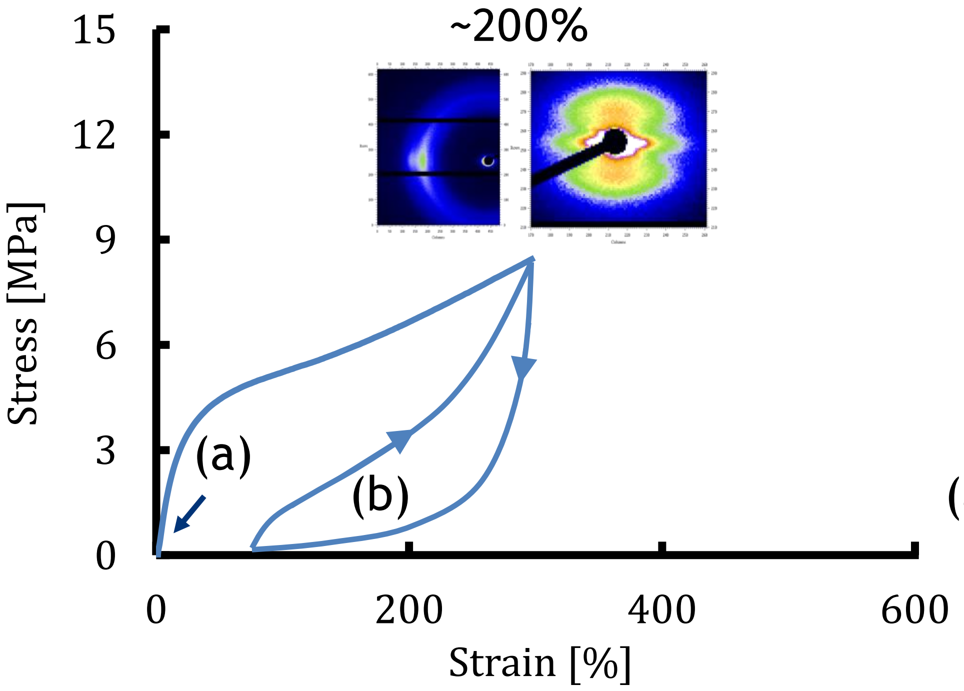


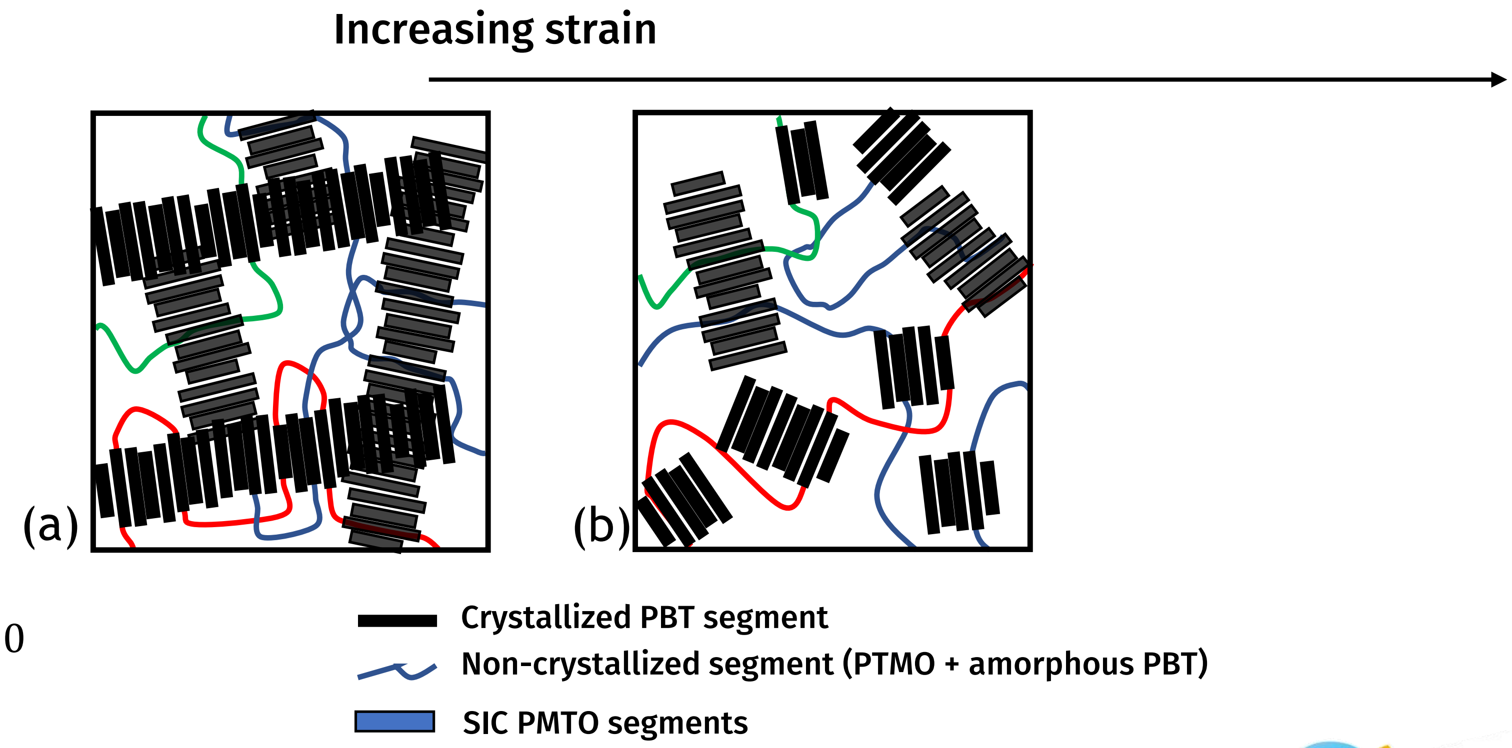
A big thanks to Jianzhu for the help with X-ray!

Morphology evolves during deformation

Transition from a percolated network of crystals (a) to an elastomeric-like network (b).

- Cyclic / Hysteresis tests: breaking and reorientation of PBT crystals + extension of a molecular network. Previous loops count as tie molecules.





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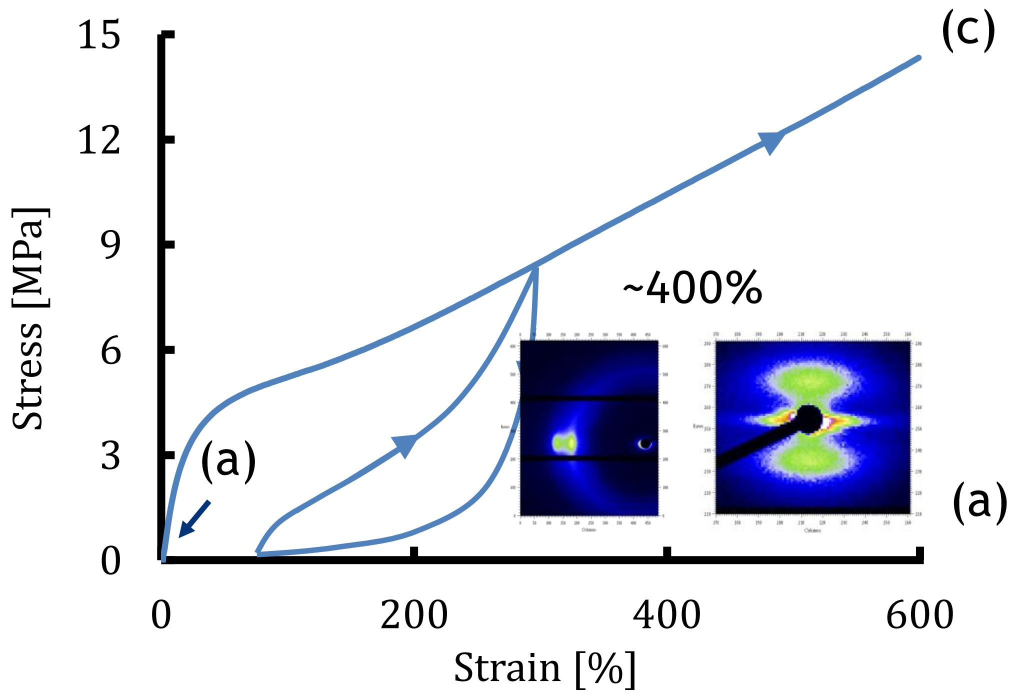
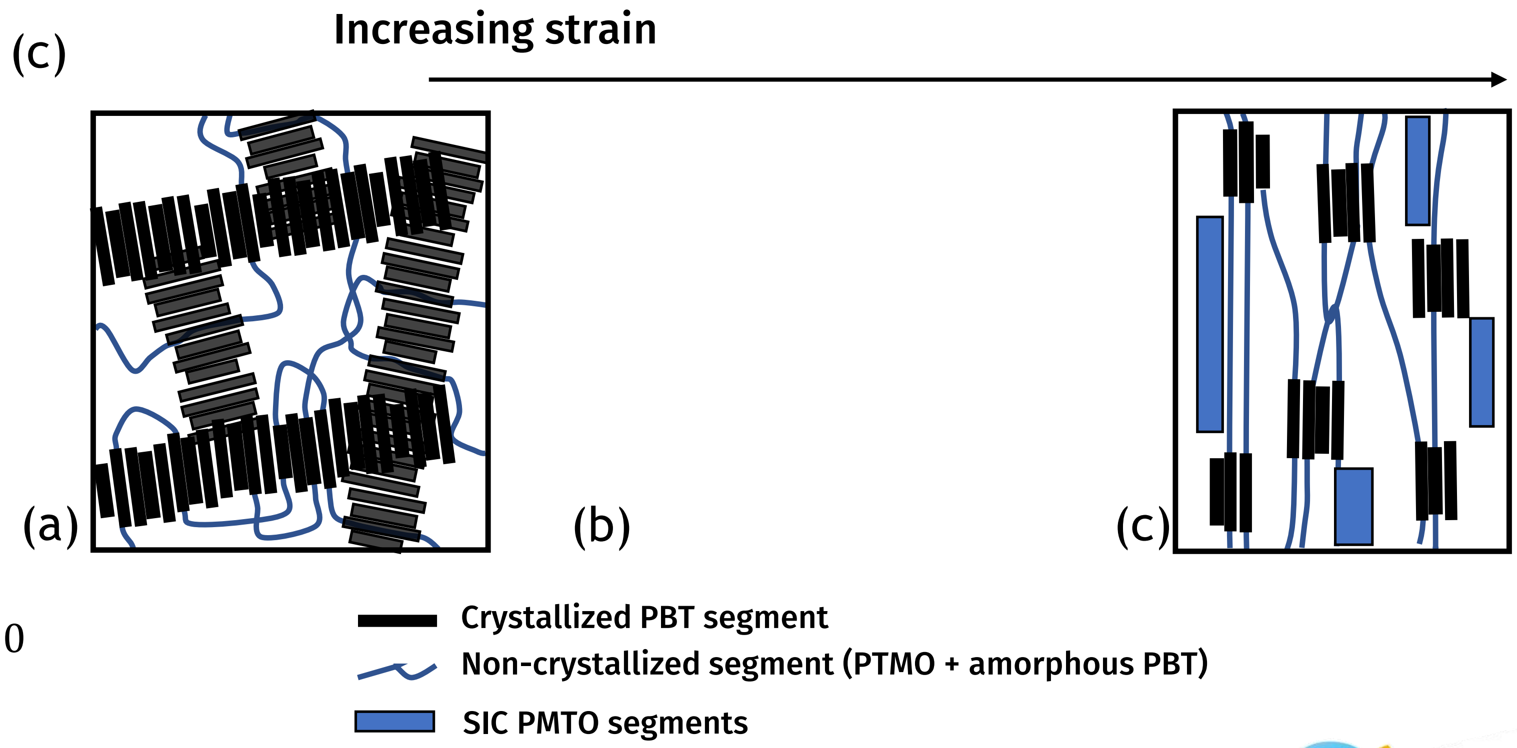
Morphology evolves during deformation

Transition from a percolated network of crystals (a) to an elastomeric-like network (b).

- Further stretching leads to more crystal breakage and to a highly oriented conformation (c)





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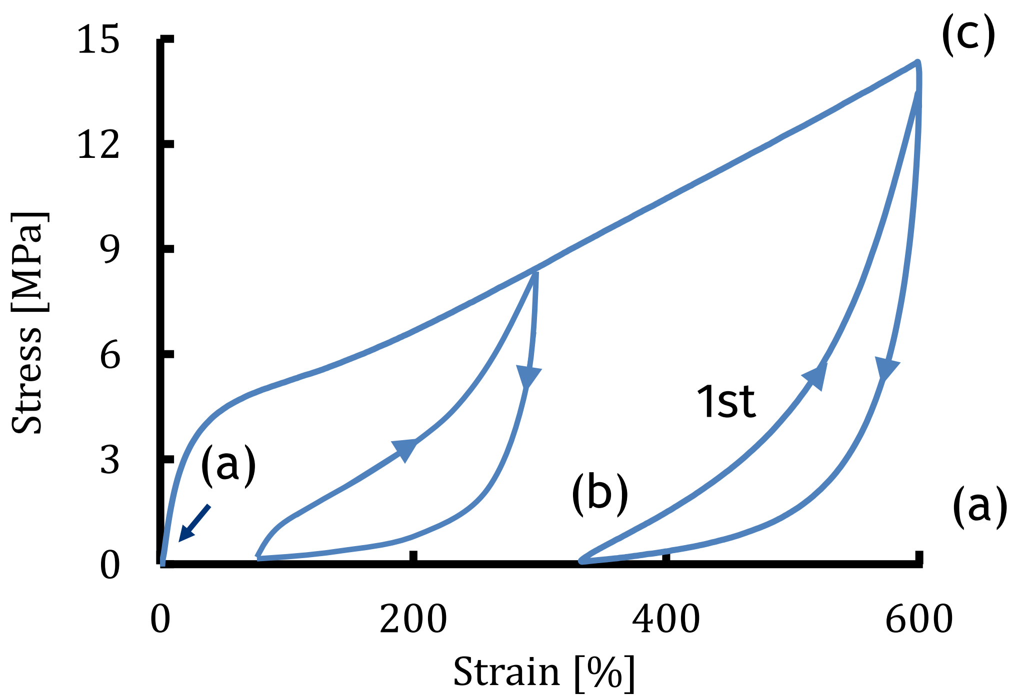

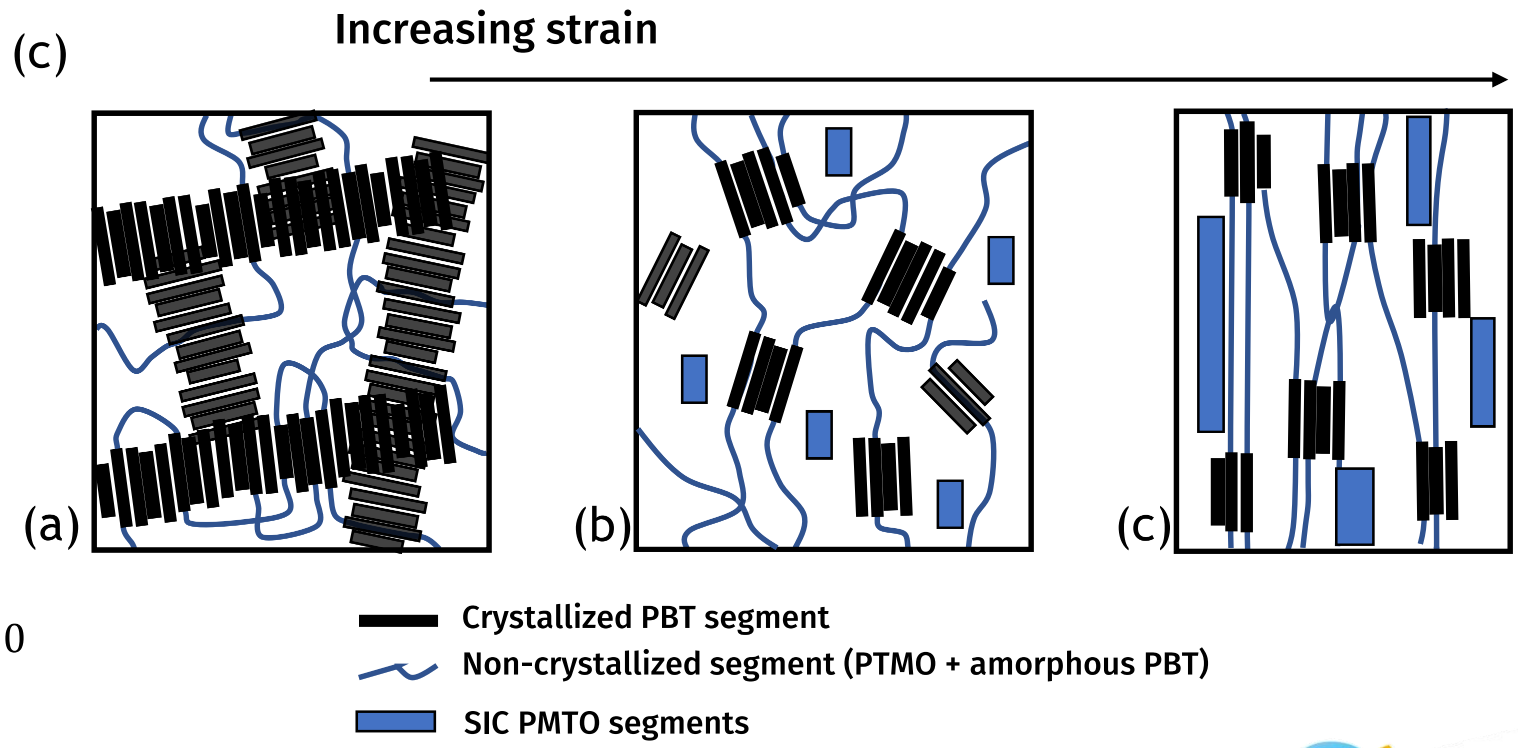

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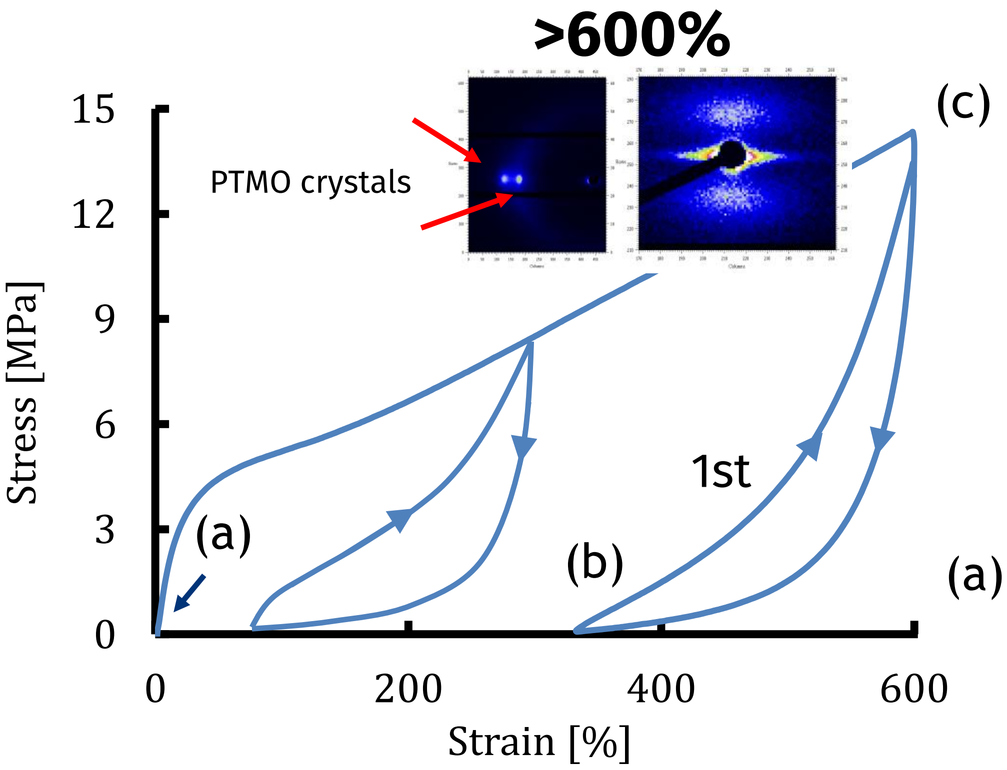

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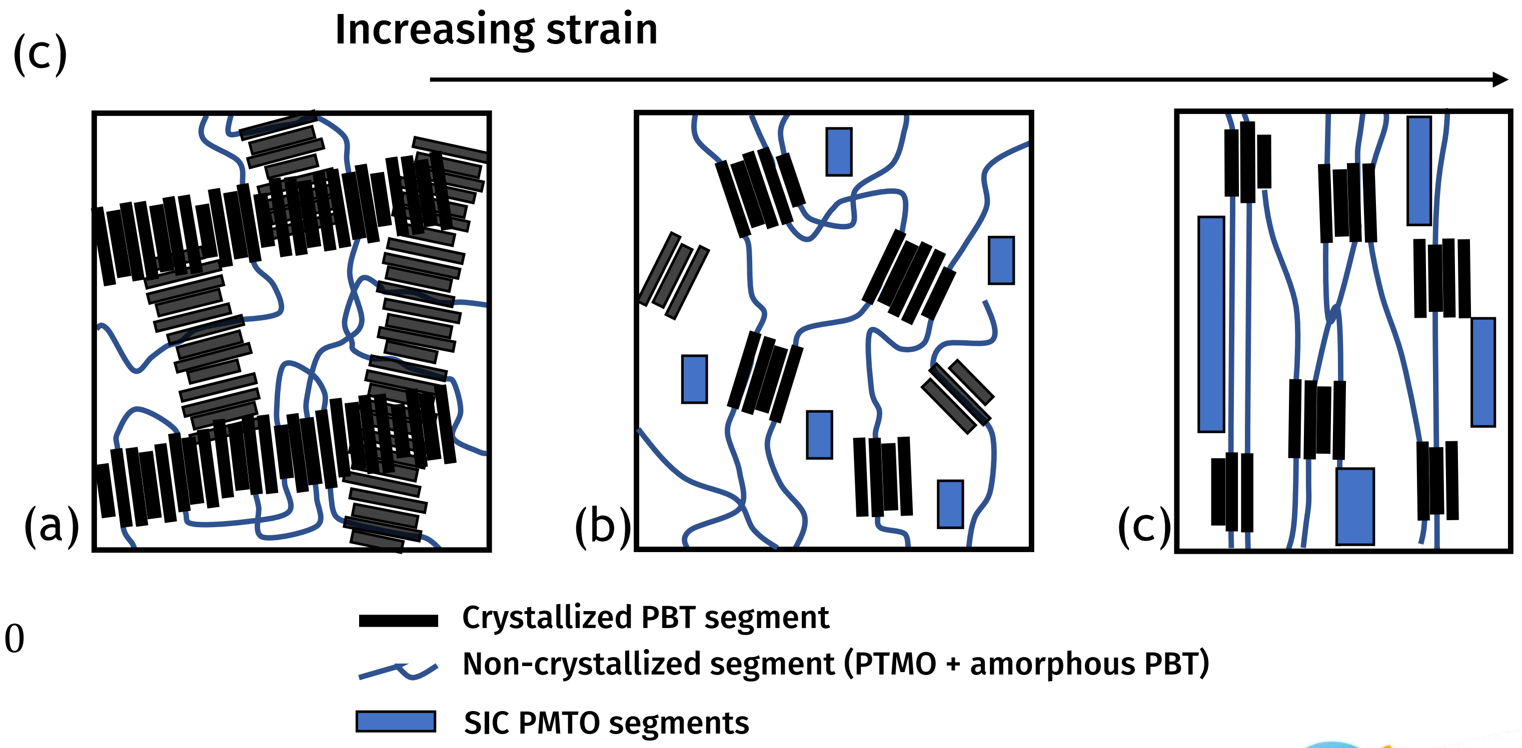
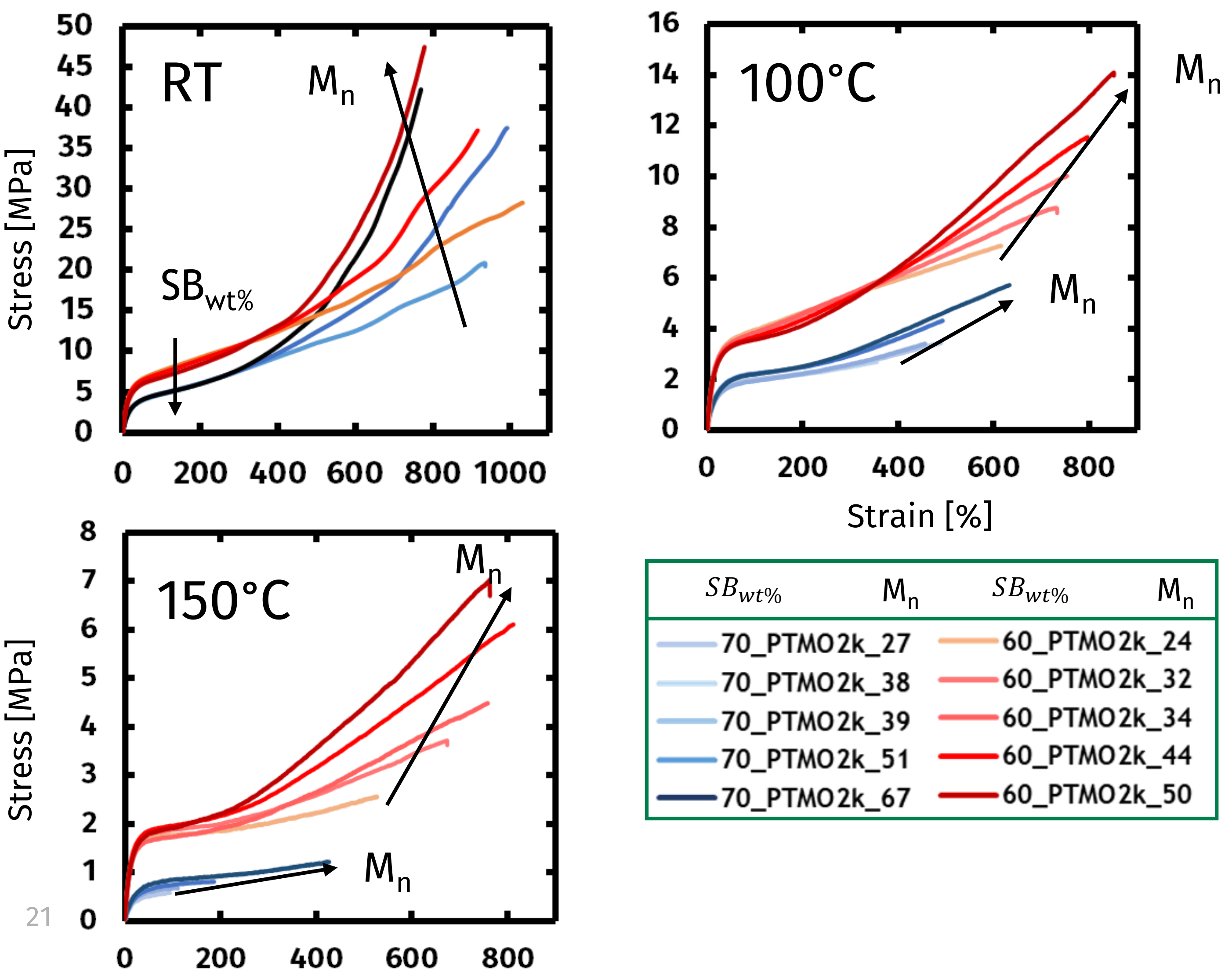


Tensile tests:

Varying Mw – fixed SB/HB

Tensile tests:

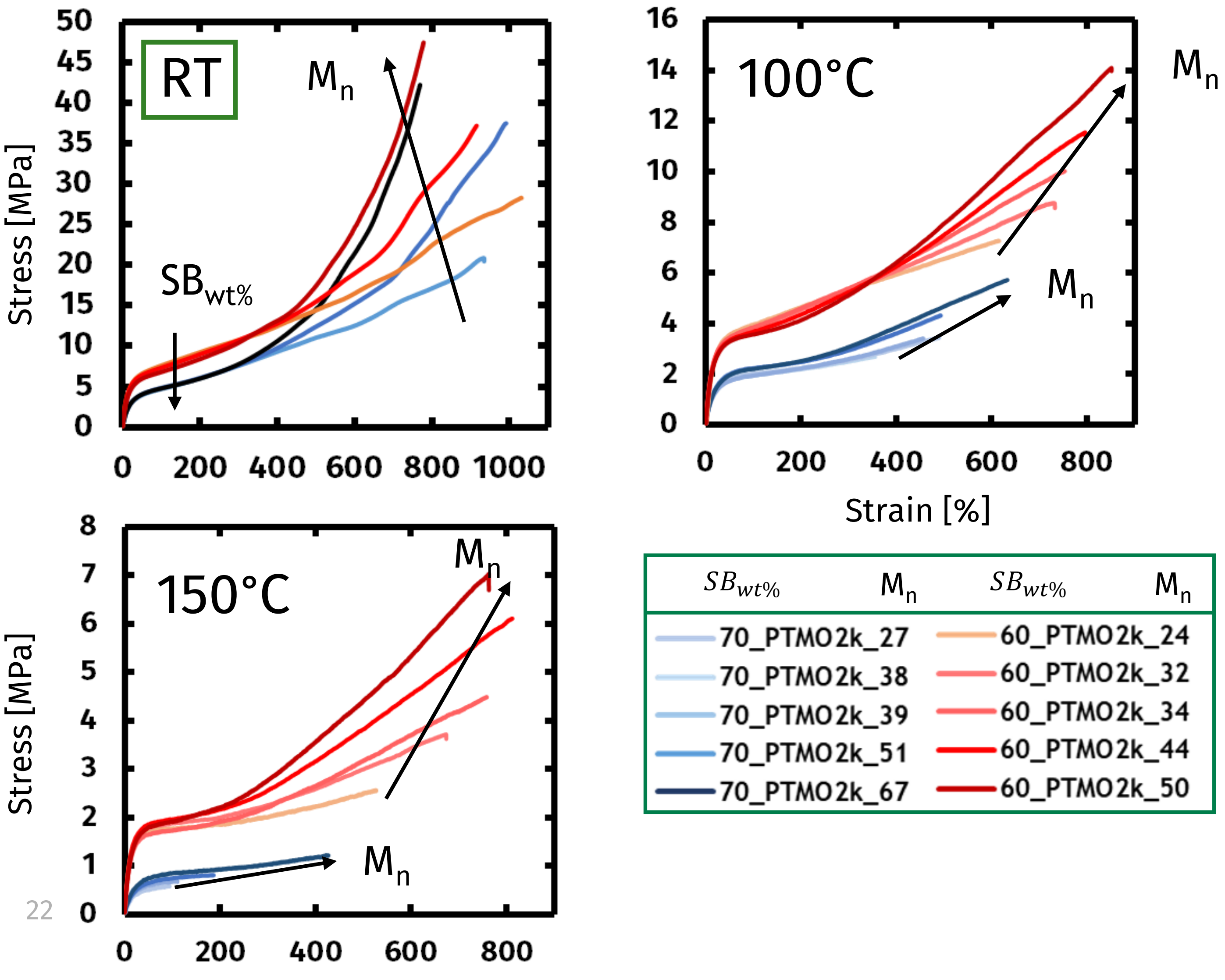
Varying M_n – fixed SB/HB



- Increasing the M_n shows little effects at low/moderate strains, while boosts the strain hardening in the high strain regime.

Tensile tests:

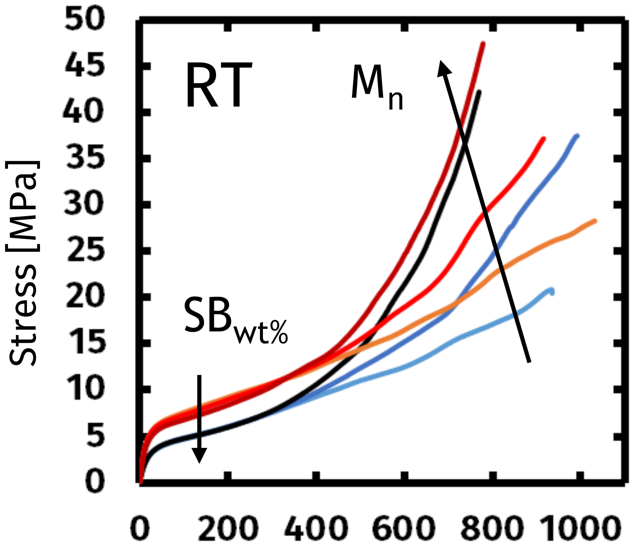
Varying M_n – fixed SB/HB

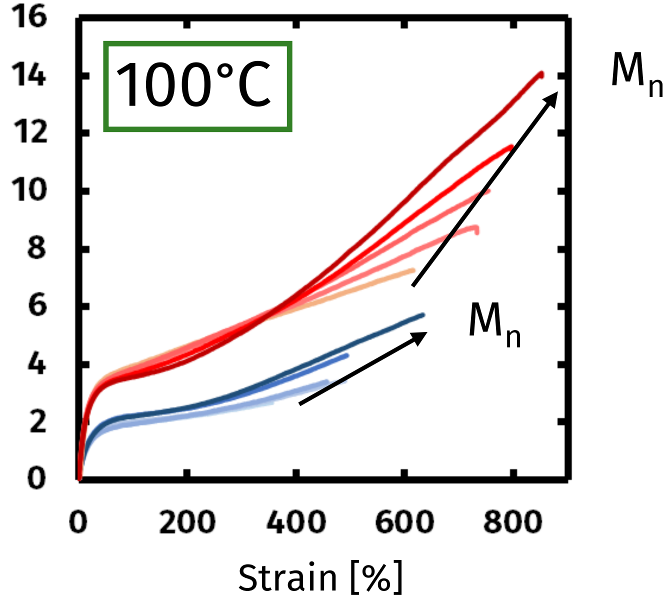


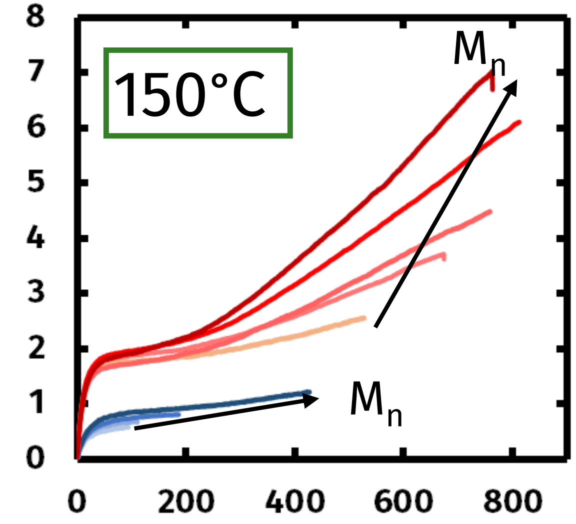
- Increasing the M_n shows little effects at low/moderate strains, while boosts the strain hardening in the high strain regime.
- Strong influence of SIC_{PTMO} on the nonlinear behavior at T < ~50°C

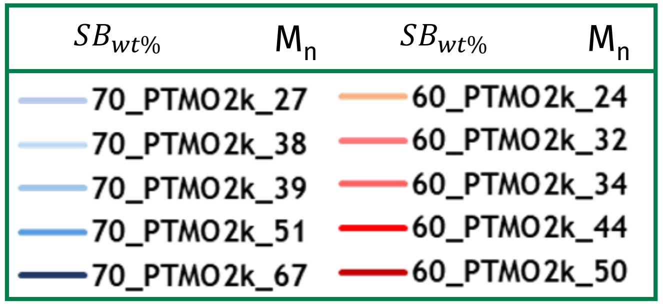
Higher M_n leads to better connected samples – + T resistant

Varying M_n – fixed SB/HB









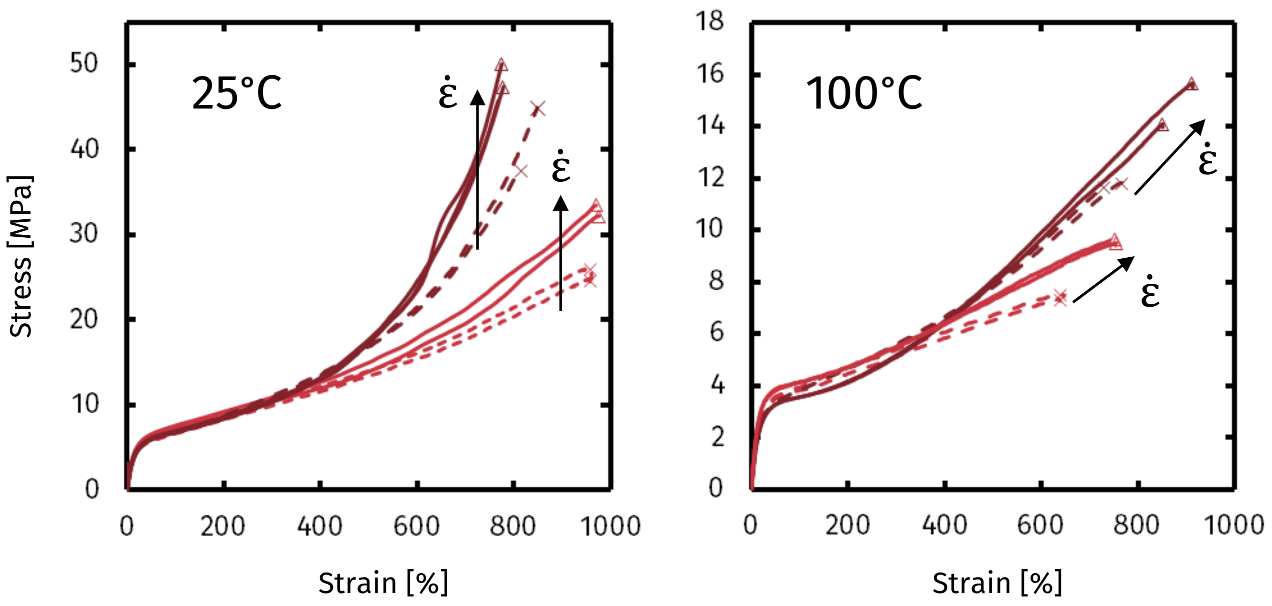
- Increasing the M_n shows little effects at low/moderate strains, while boosts the strain hardening in the high strain regime.
- Strong influence of SIC_{PTMO} on the nonlinear behavior at T < ~50°C
- Strain hardening increases with M_n even at $T > T_{m,\ SIC\_PTMO}$ (~50°C)
- Final extensibility increases with M_n at $T > T_{m,\ SIC\_PTMO}$ (~50°C)

Tensile tests:

Effect of strain rate

Tensile tests

Effect of strain rate (ε̇) on the strain hardening - Different Mn



- At 25°C, there is no strain-rate dependence up to ~400% , later on at higher strain rates correspond higher stresses.

60_PTMO2k_29 @ 500 mm/min
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60_PTMO2k_29 @ 5 mm/min
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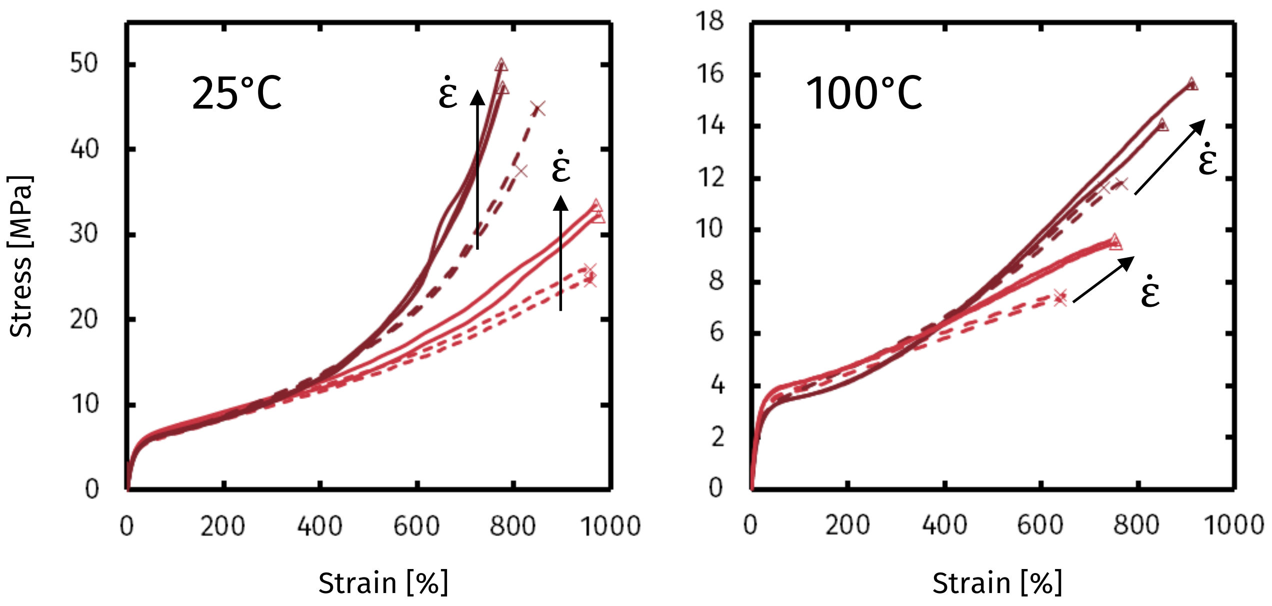
Tensile tests

Effect of strain rate (ε̇) on the strain hardening - Different Mn

Time-Temperature-Mw dependent relaxation mechanism



- At 25°C, there is no strain-rate dependence up to ~400% , later on at higher strain rates correspond higher stresses.
- At 100°C :
  - Failure strain increases with strain rate.
  - Strain hardening of the high Mn is less affected by strain rate.

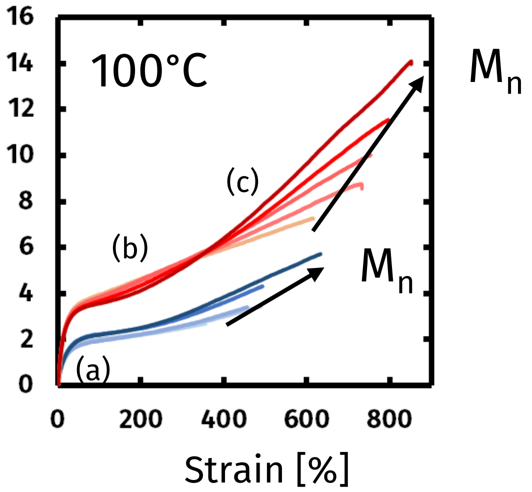
60_PTMO2k_29 @ 500 mm/min
60_PTMO2k_50 @ 500 mm/min
60_PTMO2k_29 @ 5 mm/min
60_PTMO2k_50 @ 5 mm/min

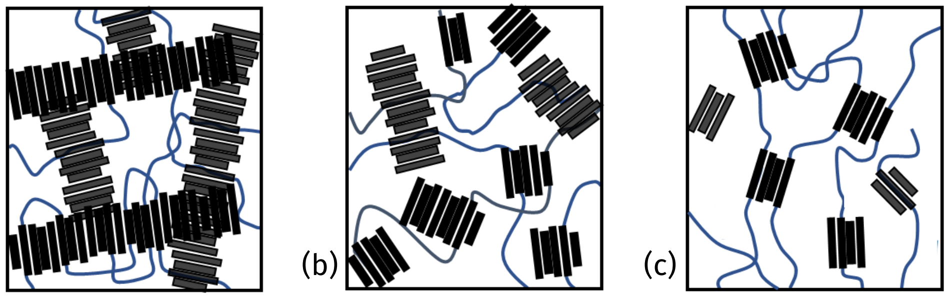
Results explanation: setting the basis for modelling

Summary of the molecular interpretation of the mechanical results

- Amount of stress bearing units at each stage of deformation: entanglements and HBs.

- Loss of network connectivity



(a)
(b)
(c)


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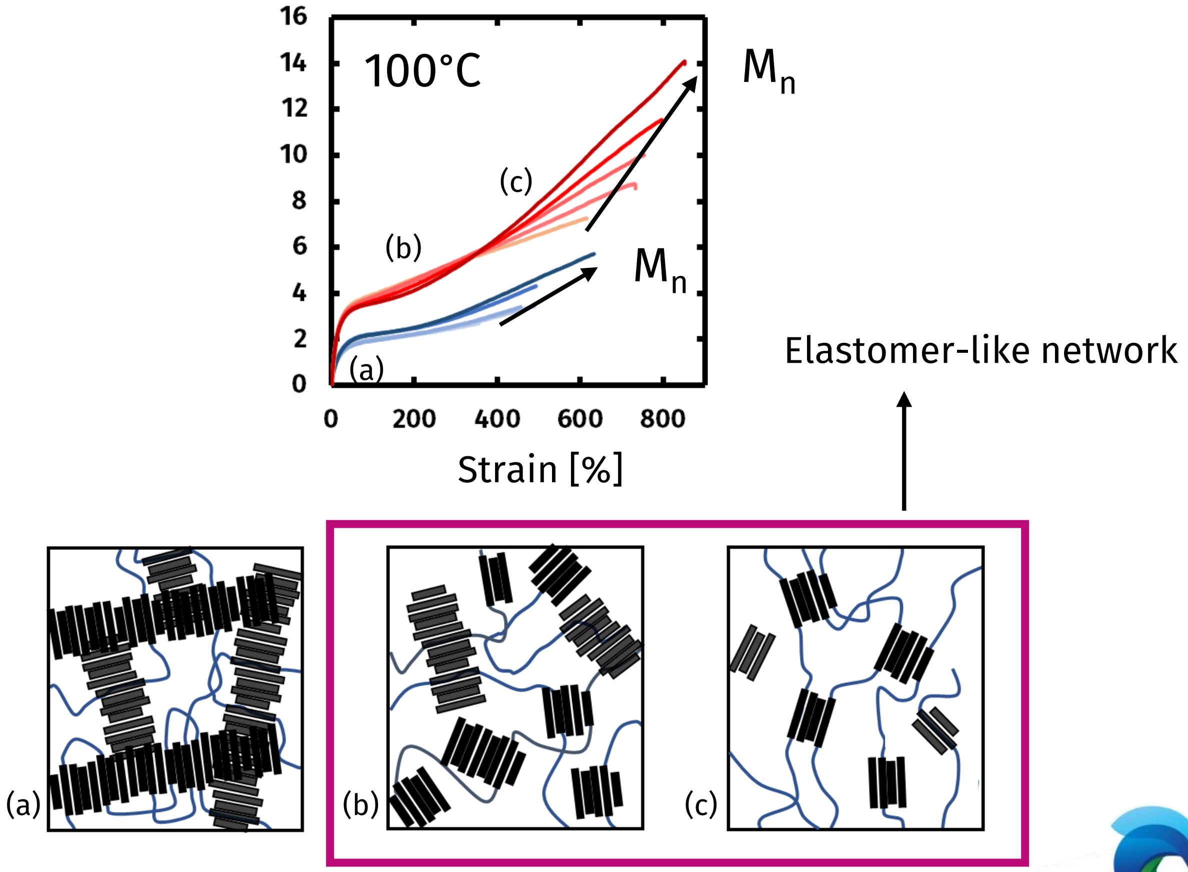
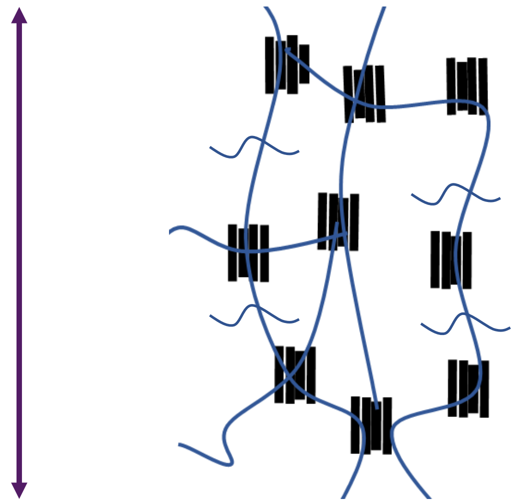


Higher M_n : more HB/chain -> more stress bearing units at each stage of deformation

Up to ~300% of strain no differences in mechanical response with M_n

Low M_n = high M_n
(besides the initial # of dangling ends)



$\varepsilon \cong 300\%$

Crystallized PBT segment

Non-crystallized segment (PTMO + amorphous PBT)

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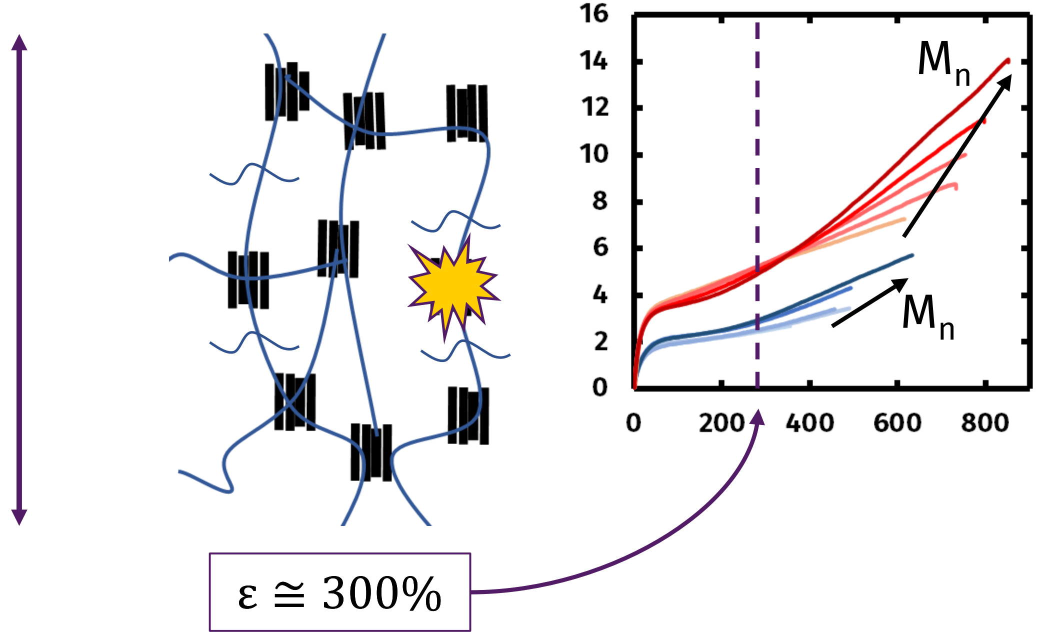

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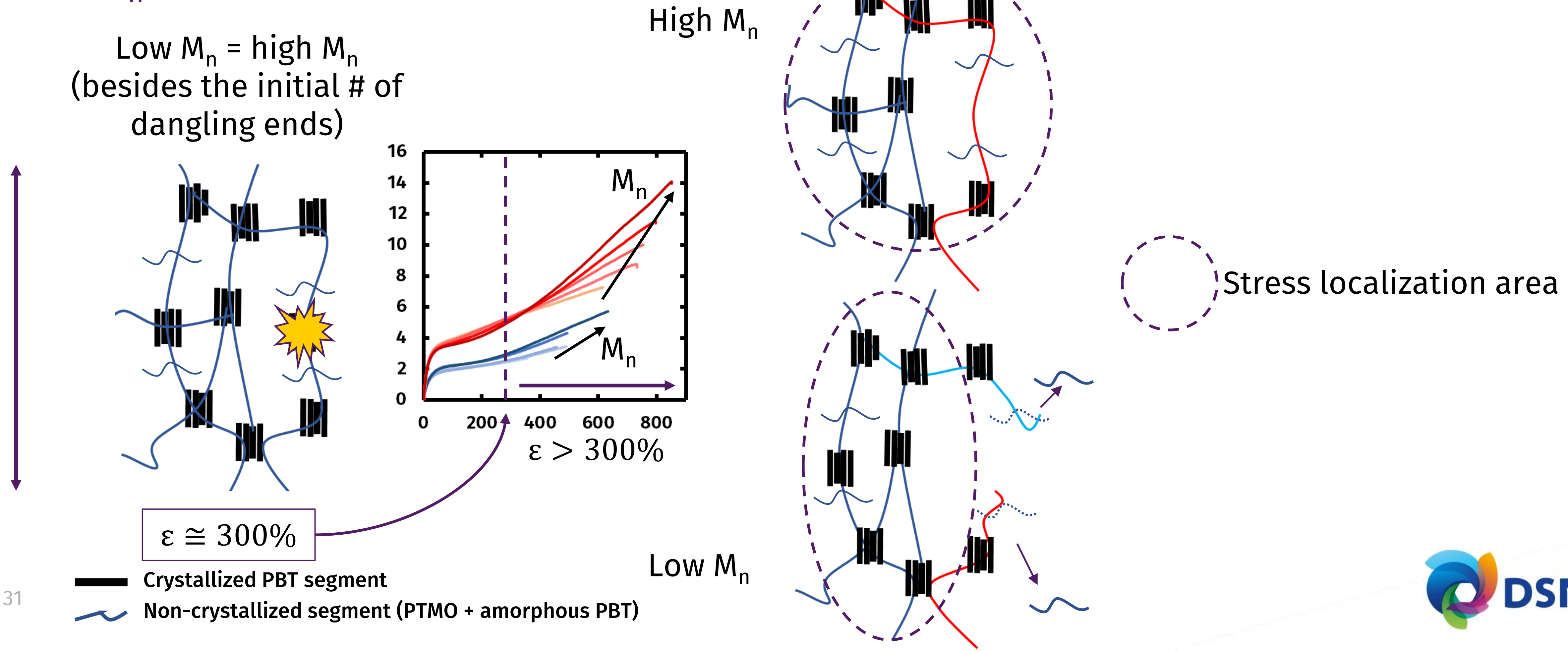

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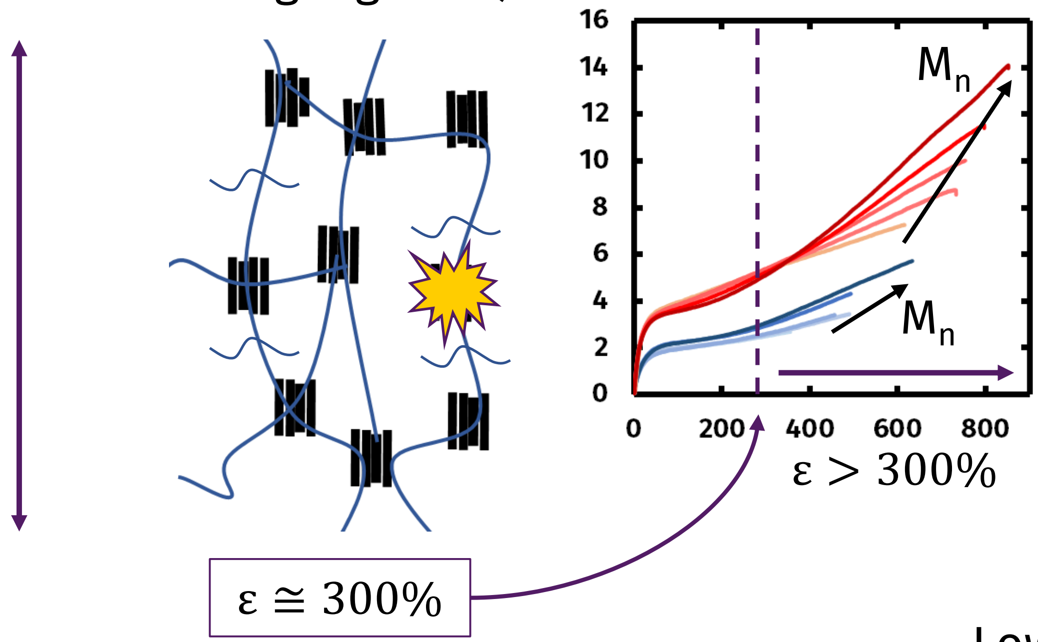

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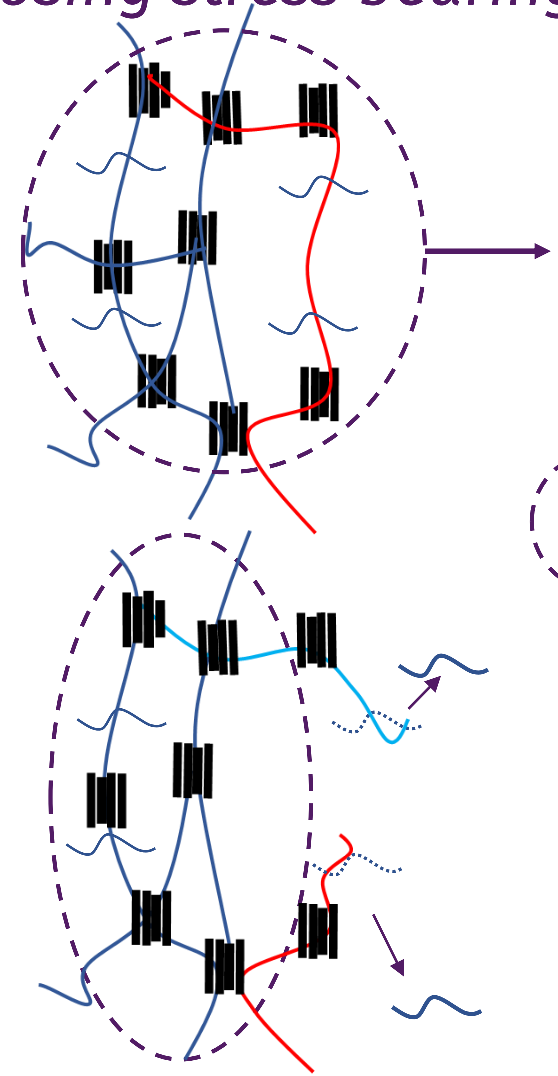

Low M_n

- ~Same amount of stress bearing units.
- Better stress homogenization.

Stress localization area

Crystallized PBT segment

Non-crystallized segment (PTMO + amorphous PBT)

DSM

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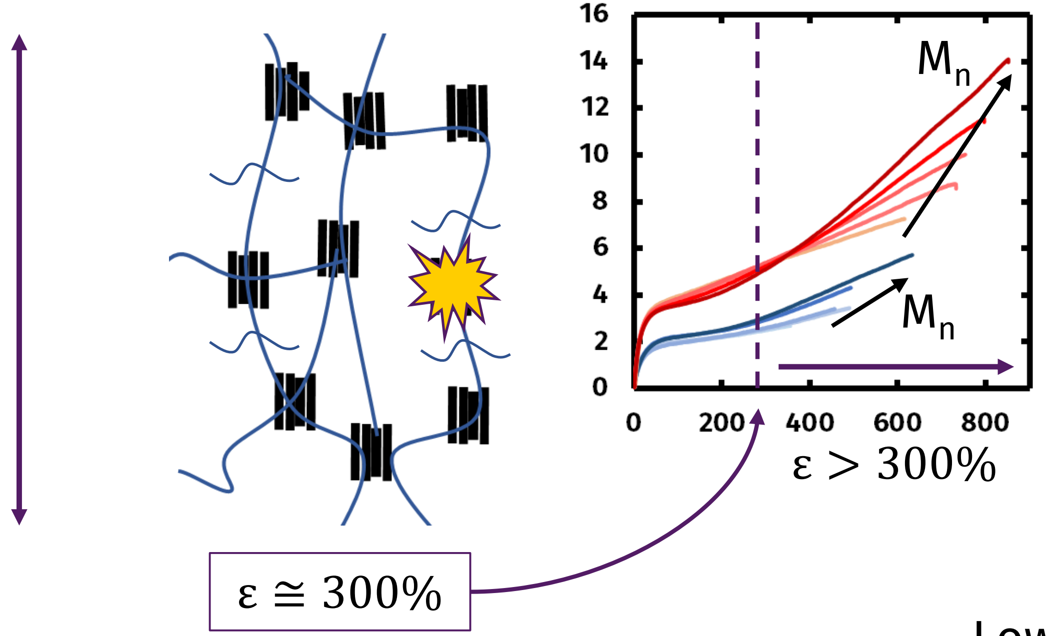
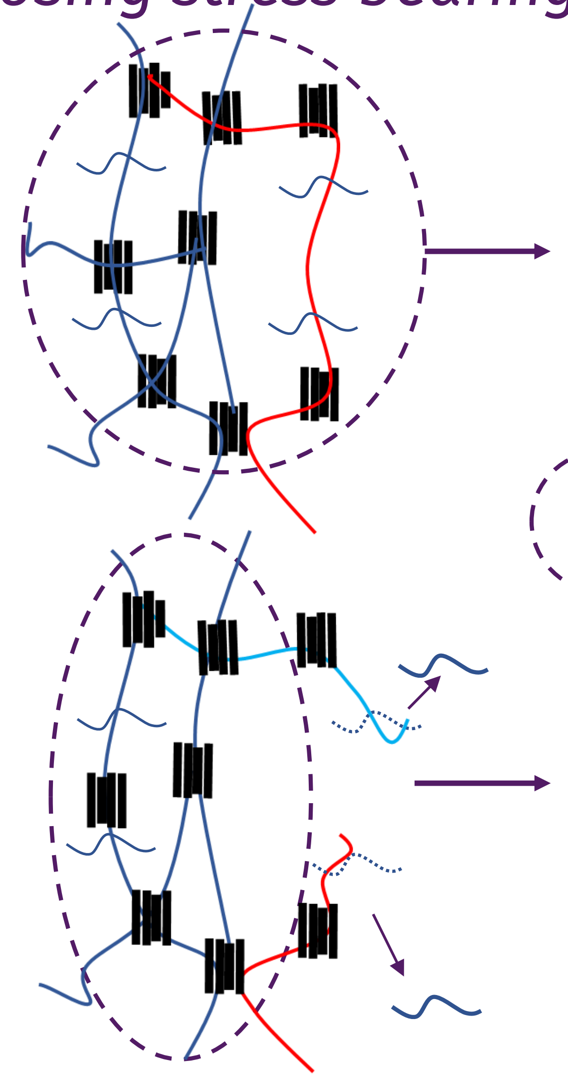


High M_n

Low M_n



- ~Same amount of stress bearing units.
- Better stress homogenization.

Stress localization area

- Load carried by less stress-bearing units.
- Pull-out rate increases.
- Disentanglement allowed.

Crystallized PBT segment

Non-crystallized segment (PTMO + amorphous PBT)

Counting the # of Stress Bearing Units (SBUs) as HBs gets pulled out

Assumptions and inputs for the model

Assumptions

- Monodisperse chains
- Monodisperse SBs and HBs
- Entanglements between two HBs cannot relax (trapped)
- Arrhenius scaling of relaxation constants

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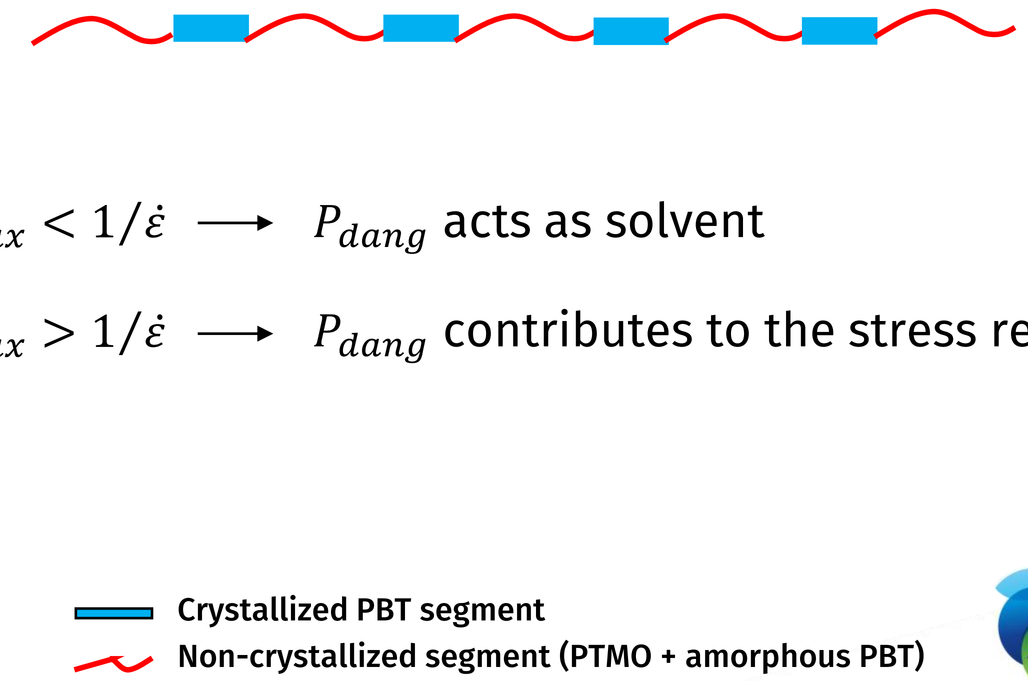
- Arrhenius scaling of relaxation constants

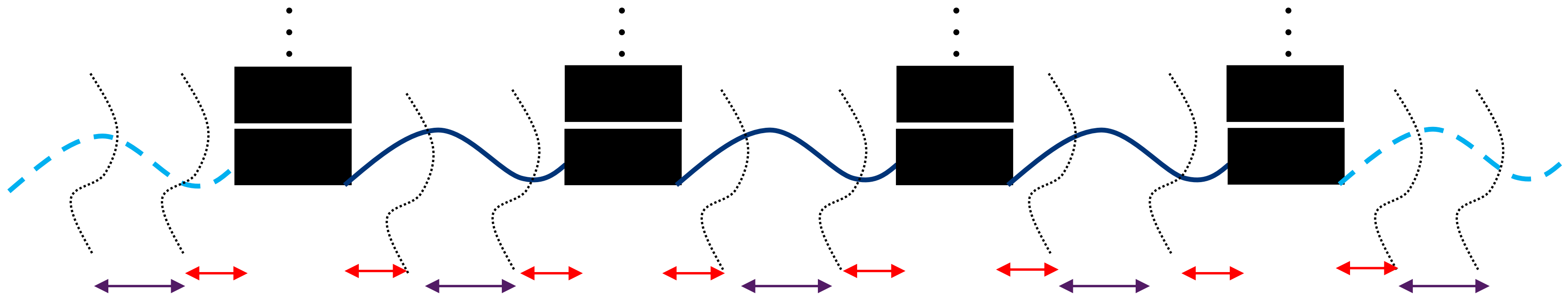
$$\frac{P_{dang}}{2} = \frac{M_{dang}}{M_{chain}} \cong \frac{1 - < \#HB > (t) \times \frac{HB_{length}}{M_{chain}}}{[1 + < \#HB > (t)]}$$



If:
- $\tau_{relax} < 1/\dot{\varepsilon} \longrightarrow P_{dang}$ acts as solvent
- $\tau_{relax} > 1/\dot{\varepsilon} \longrightarrow P_{dang}$ contributes to the stress response

Counting the # of Stress Bearing Units (SBUs) as HBs gets pulled out

What happens when the chains lose associations



#SBUs: # segments btw 2 entanglements + # segments btw entanglements and HB

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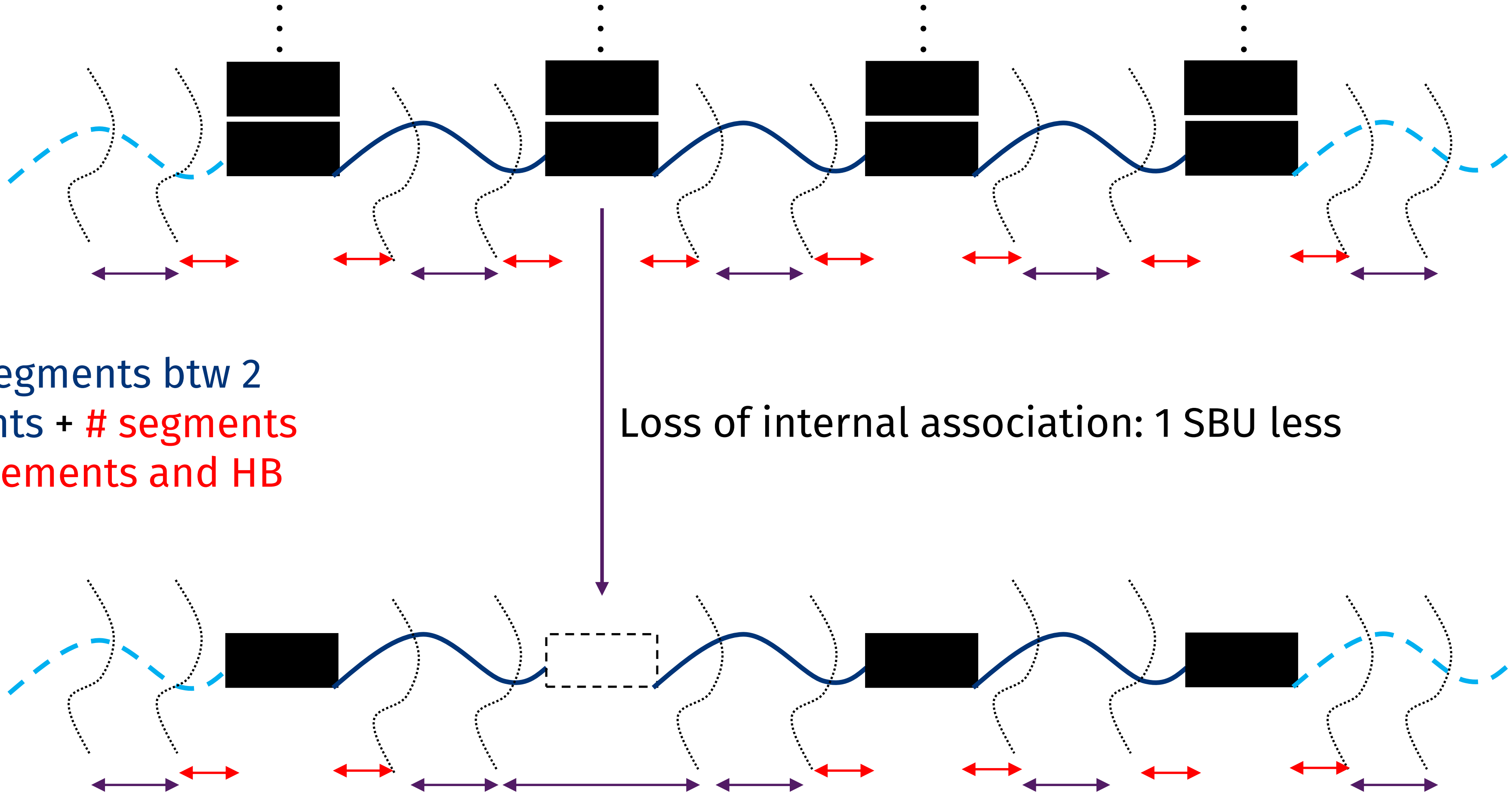

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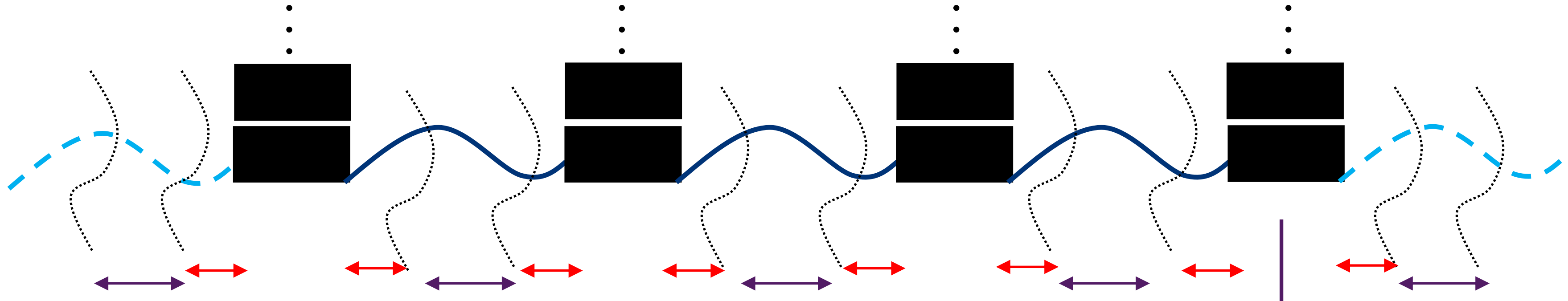
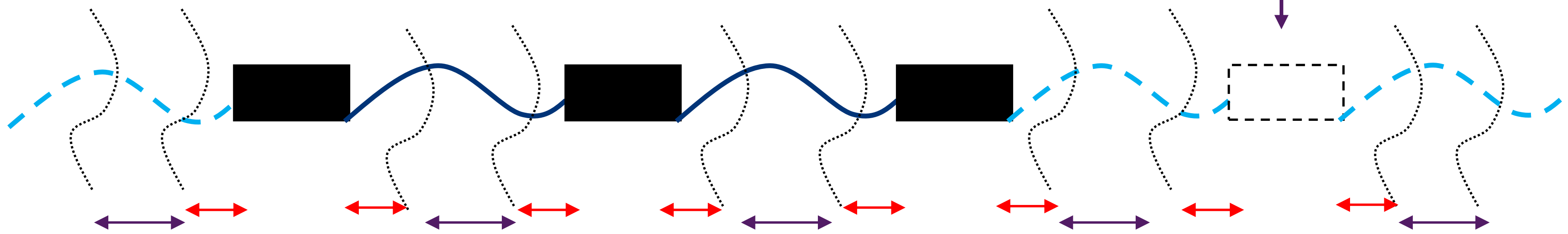


#SBUs: # segments btw 2 entanglements + # segments btw entanglements and HB

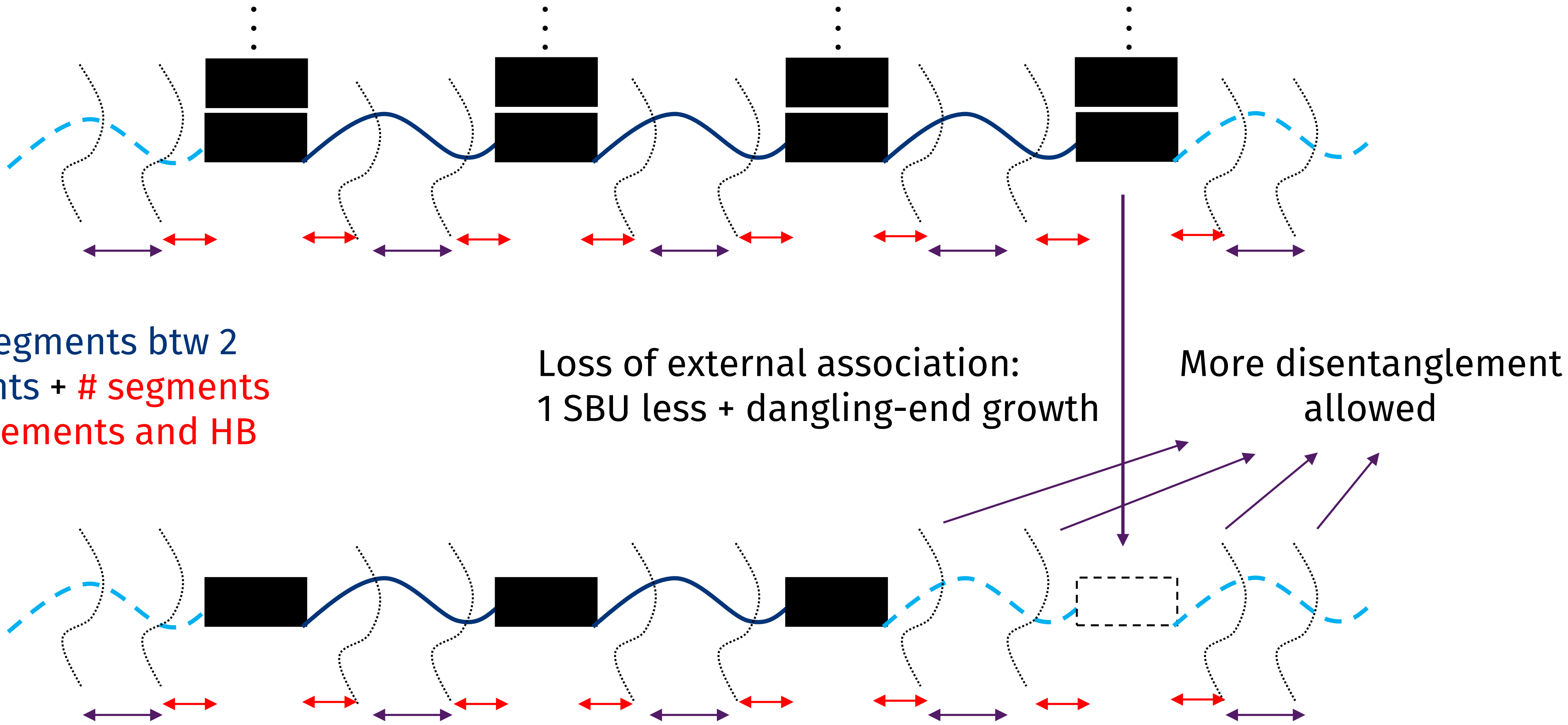
Loss of external association:
1 SBU less + dangling-end growth



Counting the # of Stress Bearing Units (SBUs) as HBs gets pulled out

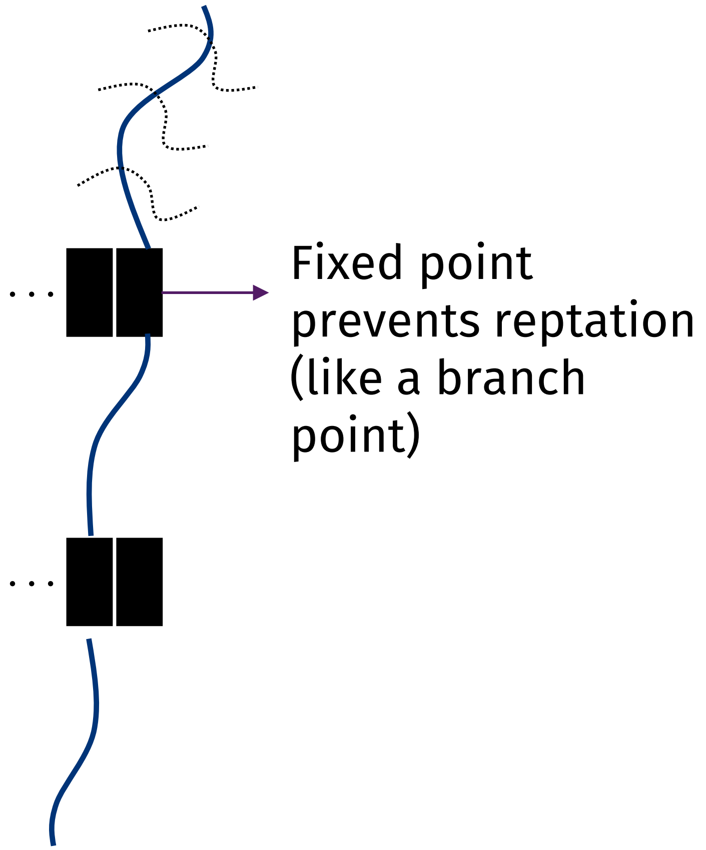
What happens when the chains lose associations

#SBUs: # segments btw 2 entanglements + # segments btw entanglements and HB



Slip-out depends on T, $\dot{\varepsilon}$ and dangling-end length

Dangling-end modelled as an arm of a star polymer



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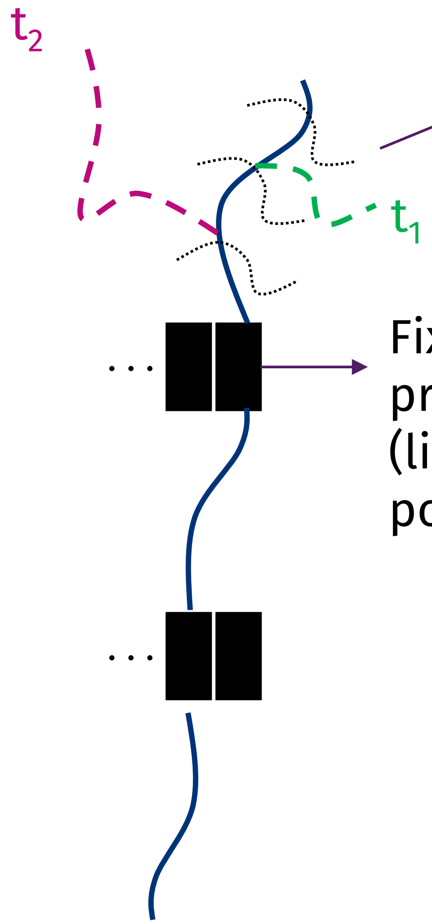
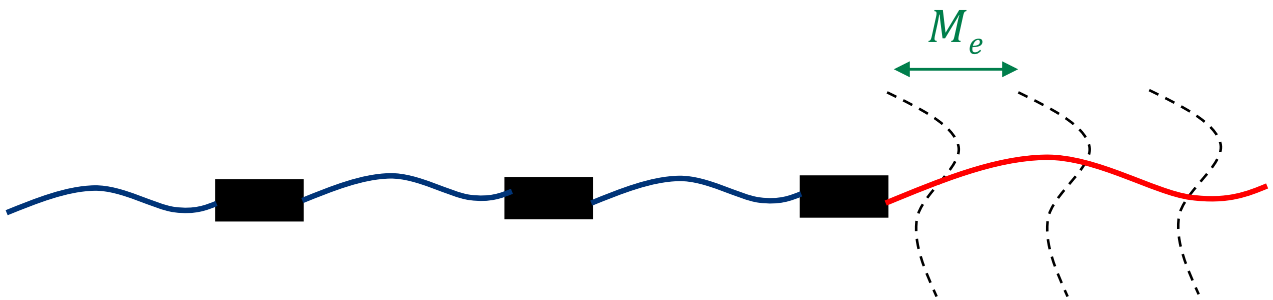


Entropically unfavourable → Exponential increase of the relaxation time with the dangling-end length

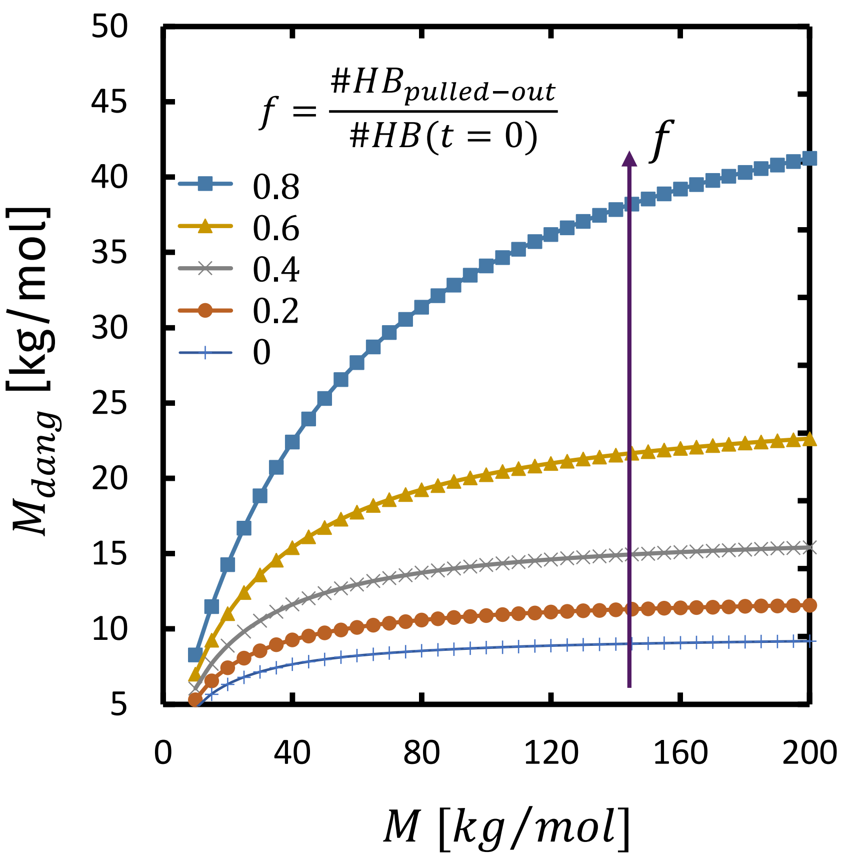
$$Z = {M_{dang}}/{M_e}$$

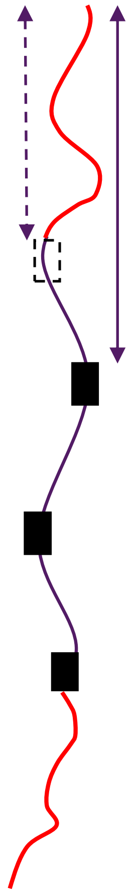
Fixed point prevents reptation (like a branch point) → Disentanglements happens via retraction if $\dot{\varepsilon} > 1/\tau_{retraction}$ → $\tau_{retraction} = \tau_o(T) \times \exp(\frac{15}{8} \times Z)$

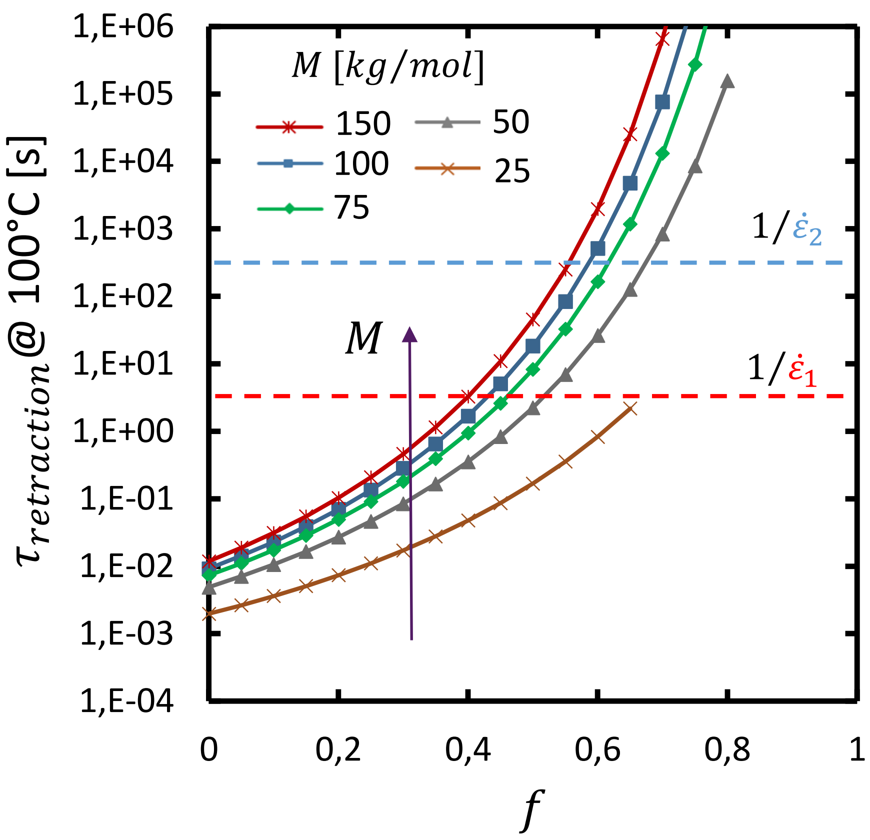


Dangling-end length (M_{dang}) increases as the HB are pulled-out

Relaxation time increases with M_{dang}. Estimated times are very close to experimental time scales ($1/\dot{\varepsilon}_2$).







Tensile speed

5 mm/min

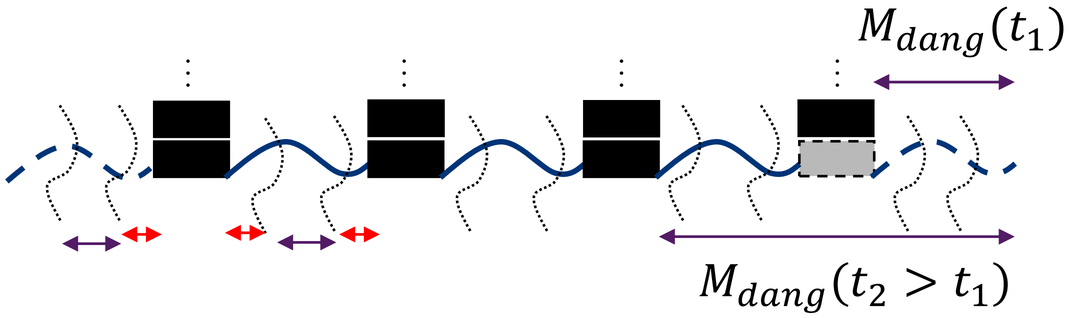
$\dot{\varepsilon}_2 = 0.0017\ s^{-1}$

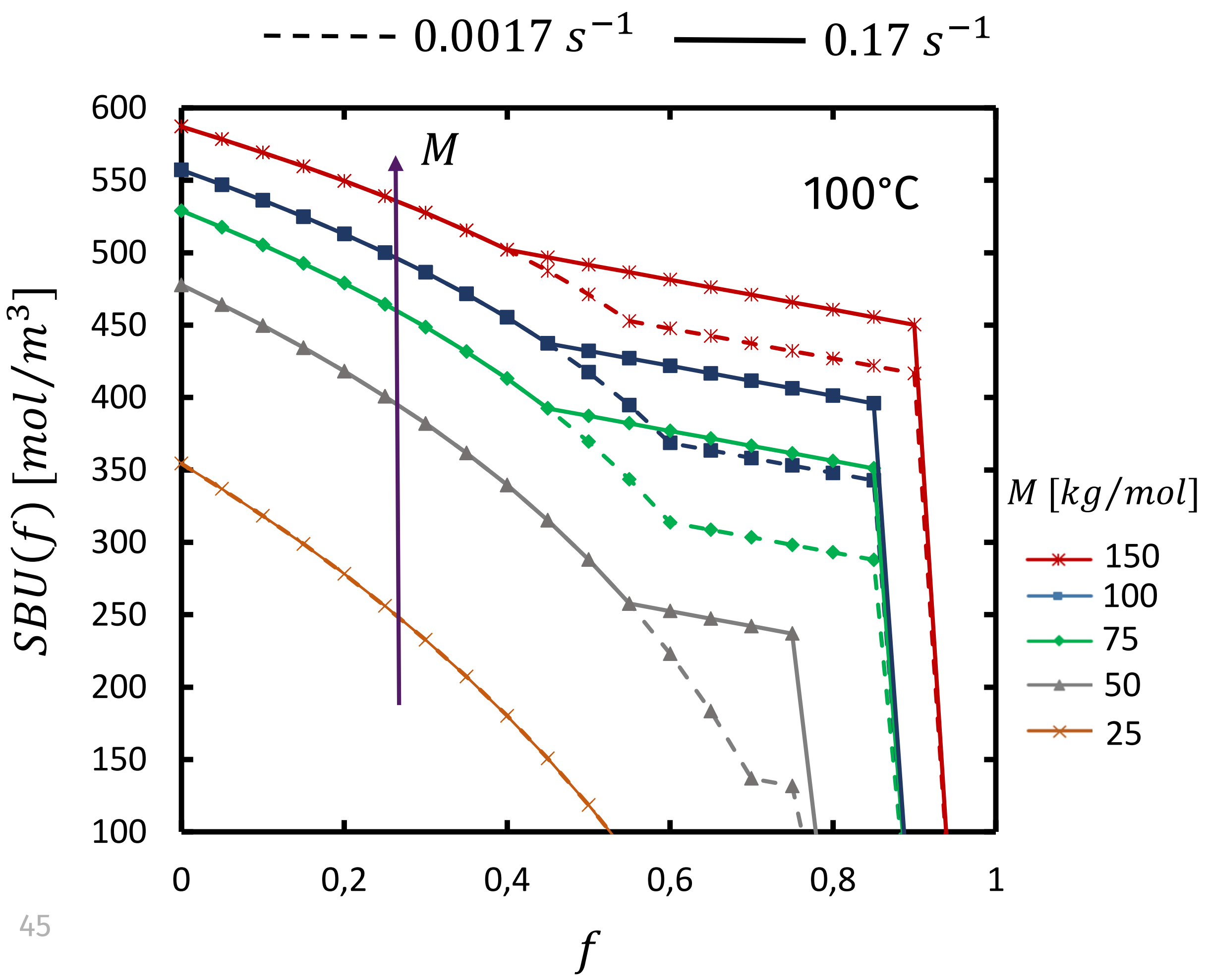
500 mm/min

$\dot{\varepsilon}_1 = 0.17\ s^{-1}$

Counting the # of Stress Bearing Units (SBUs) as HBs are lost

The strain-rate dependency decreases with Mw – by decreasing the rate more segments of chain are allowed to relax





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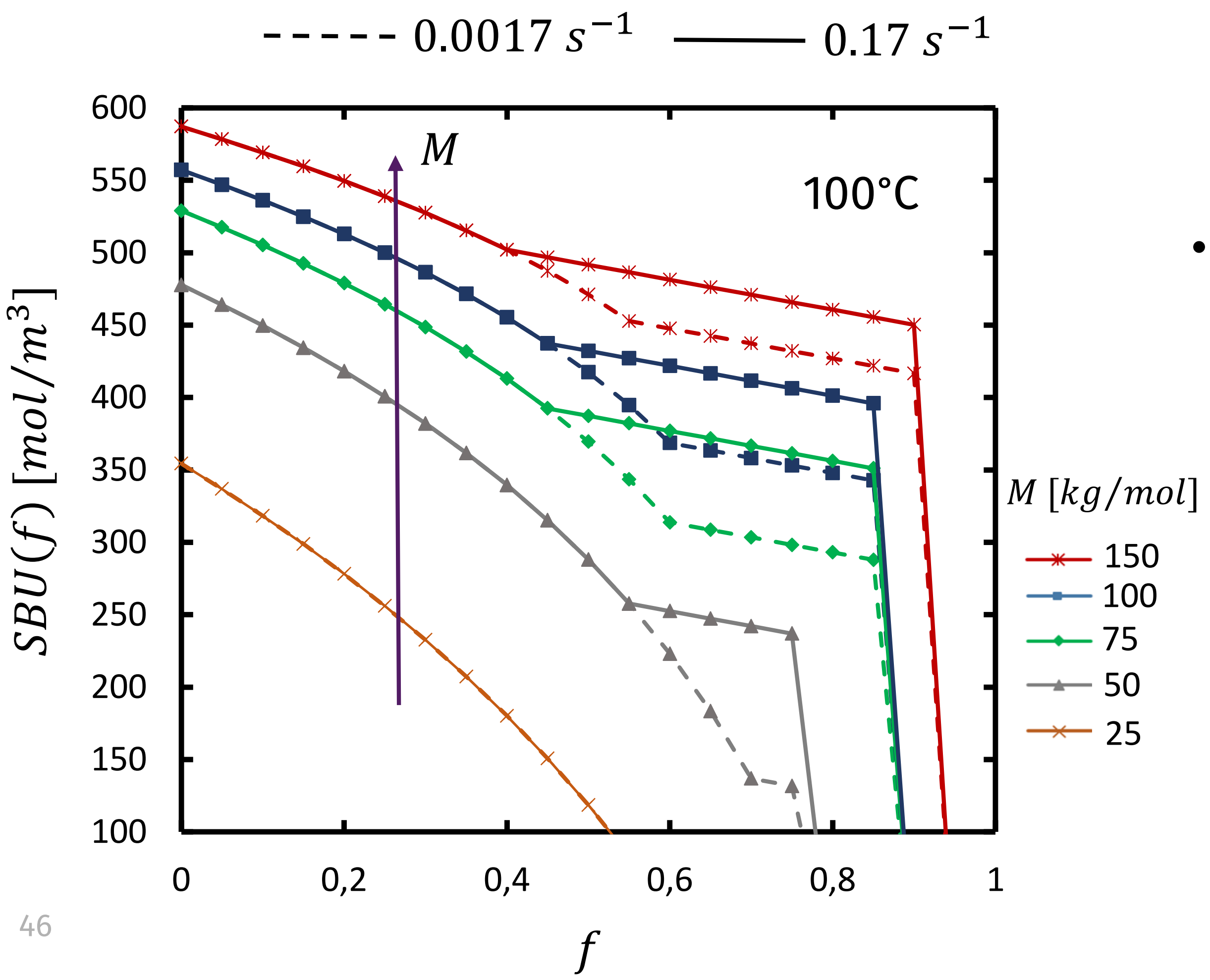

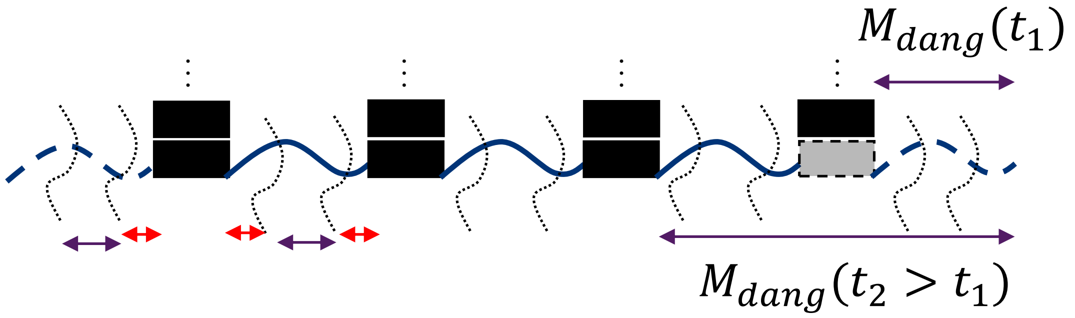

- Dangling-end short enough to relax via retraction

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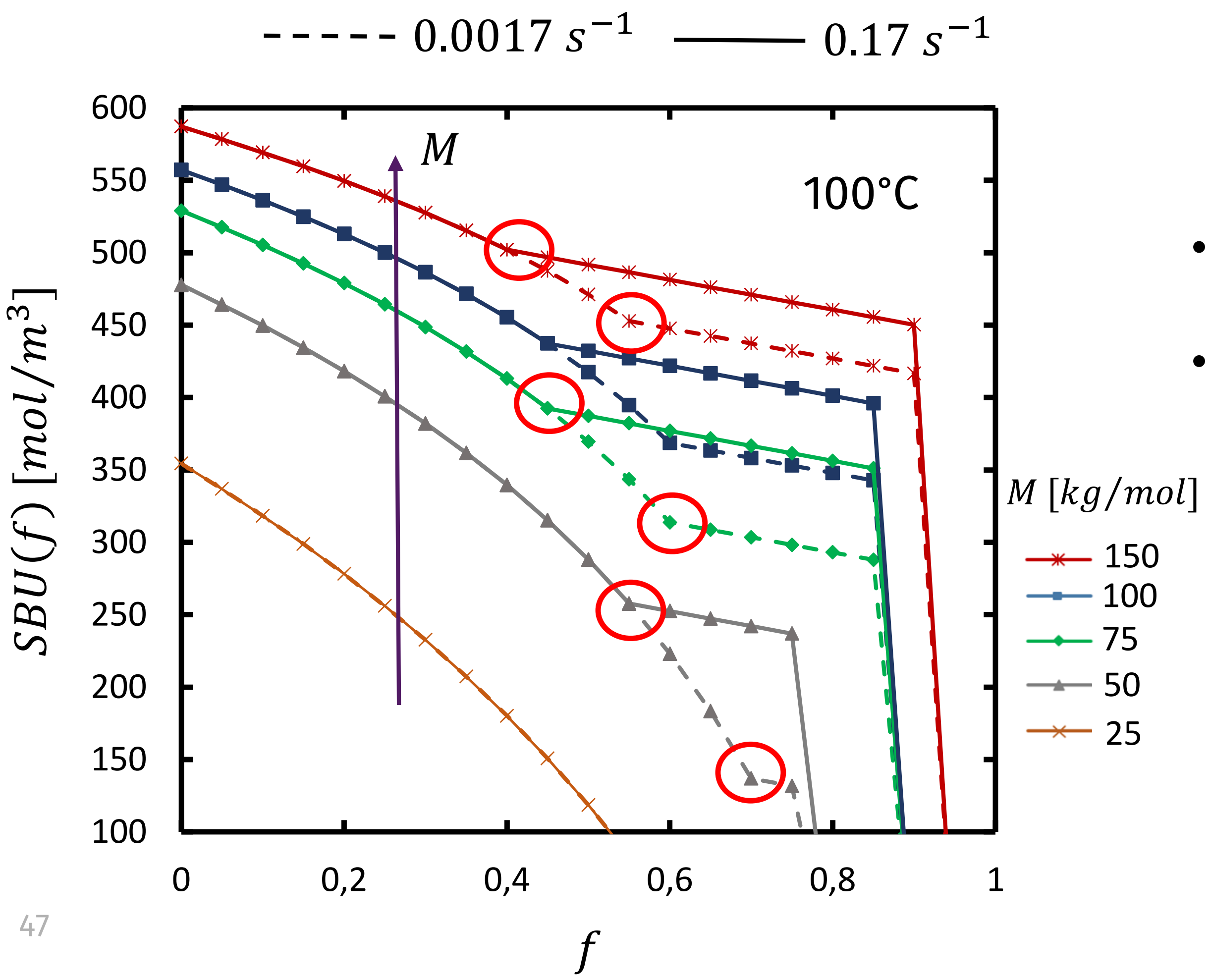
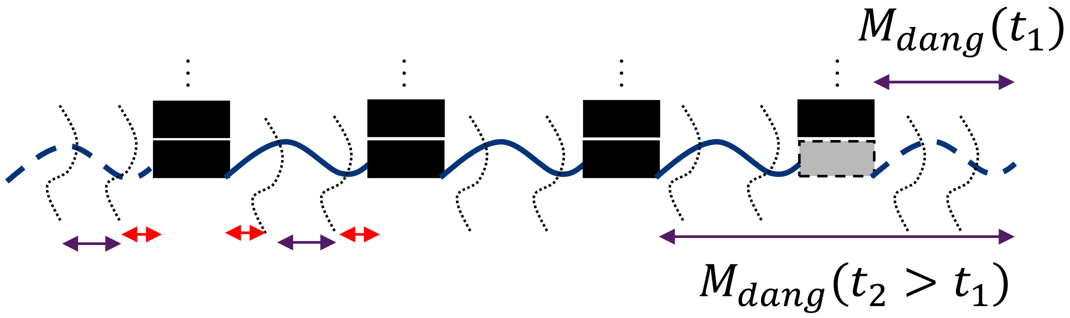
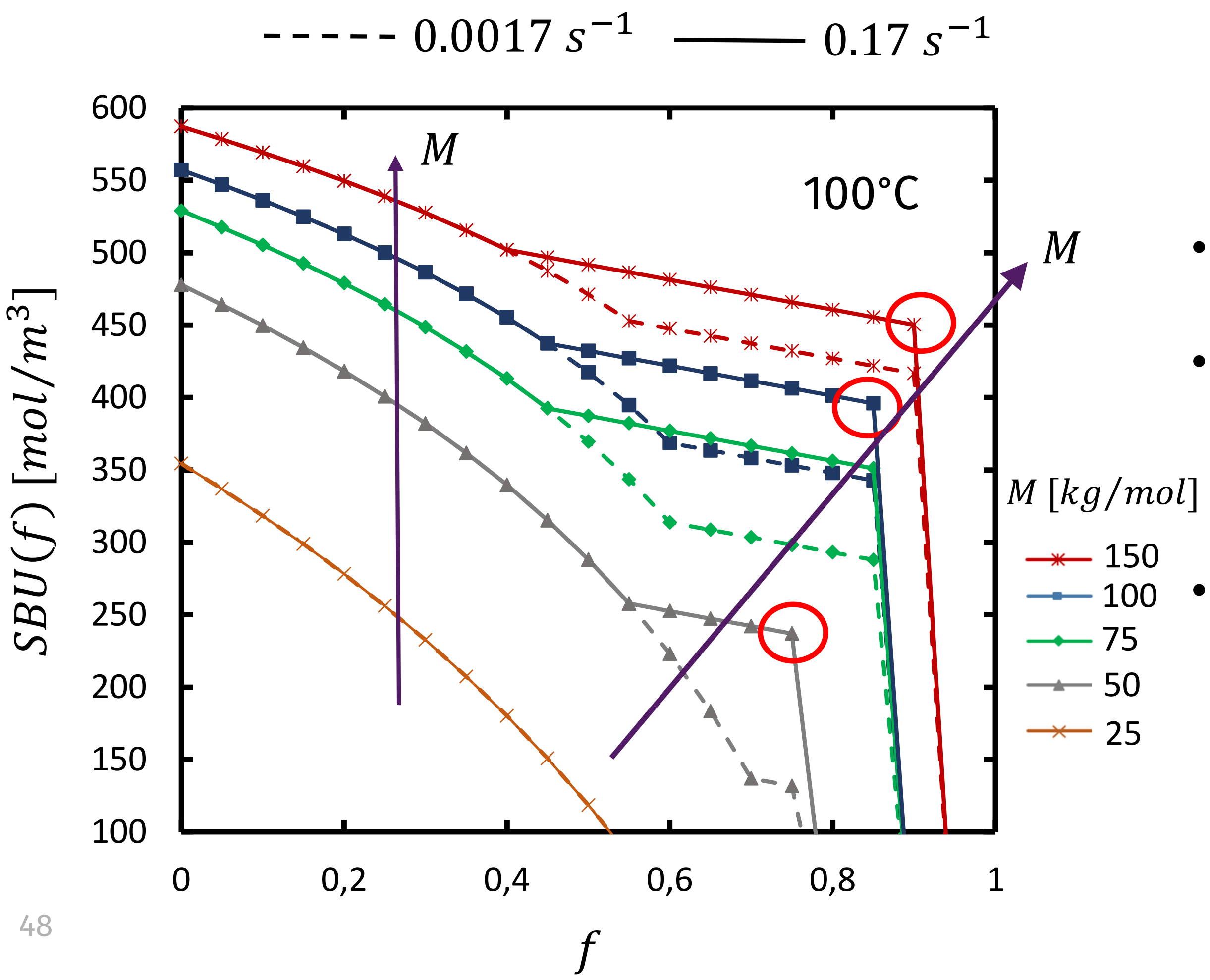


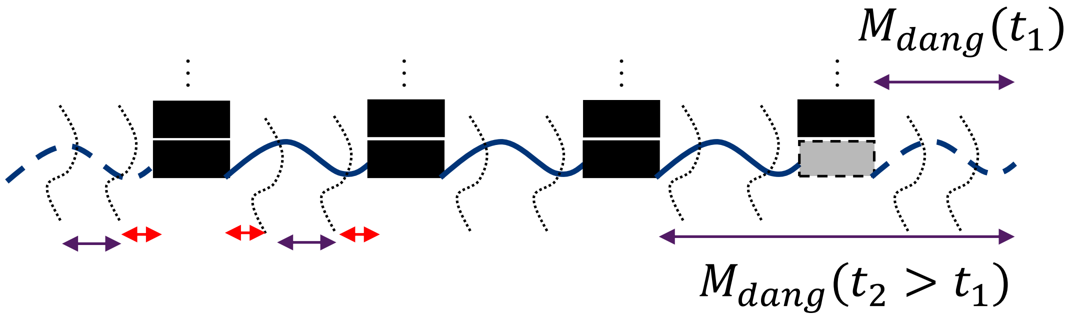


- Dangling-end short enough to relax via retraction
- Dangling-end too long to relax: plateau stress which decrease is determined only by the loss of hard segments

Counting the # of Stress Bearing Units (SBUs) as HBs are lost

The strain-rate dependency decreases with Mw

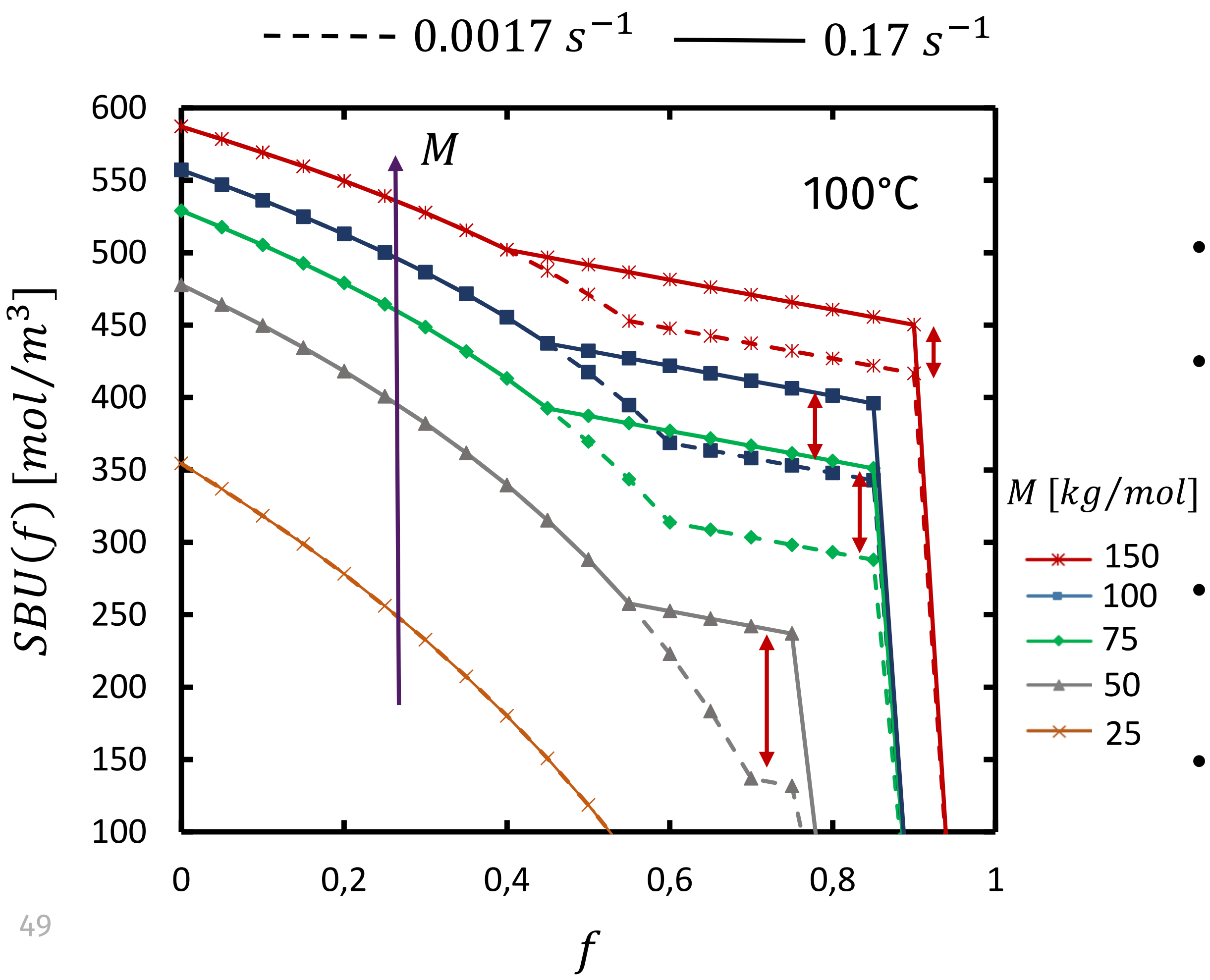


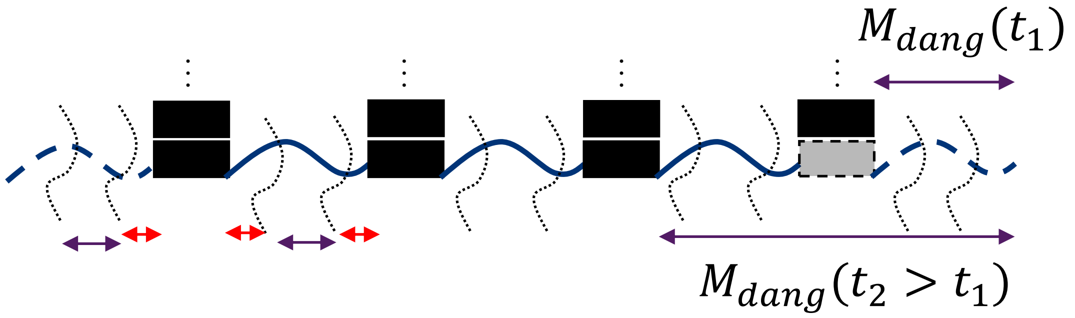


- Dangling-end short enough to relax via retraction
- Dangling-end too long to relax: plateau stress which decrease is determined only by the loss of hard segments
- Higher Mn – higher connectivity: lower chances for chains to be disconnected from the network

Counting the # of Stress Bearing Units (SBUs) as HBs are lost

The strain-rate dependency decreases with Mw





- Dangling-end short enough to relax via retraction
- Dangling-end too long to relax: plateau stress which decrease is determined only by the loss of hard segments
- Higher Mn – higher connectivity: lower chances for chains to be disconnected from the network
- Higher Mn – less strain rate dependency

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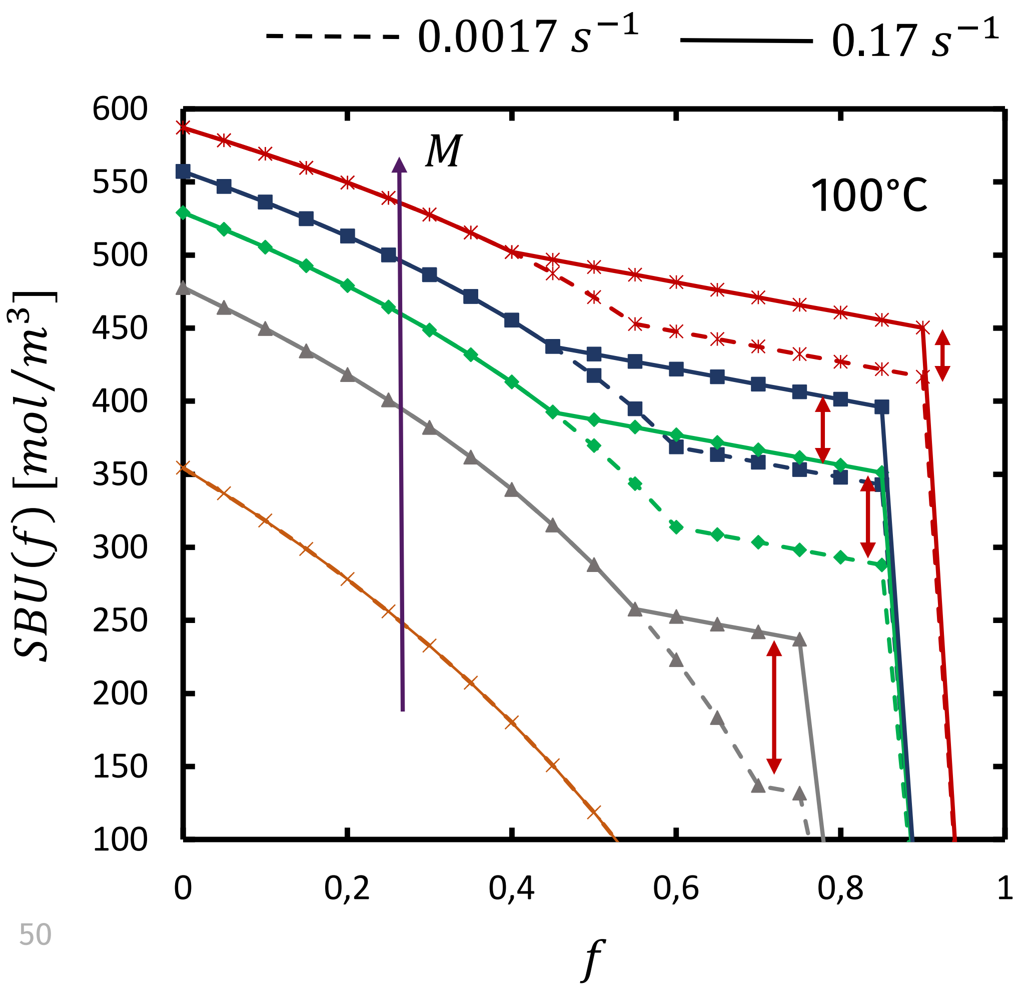
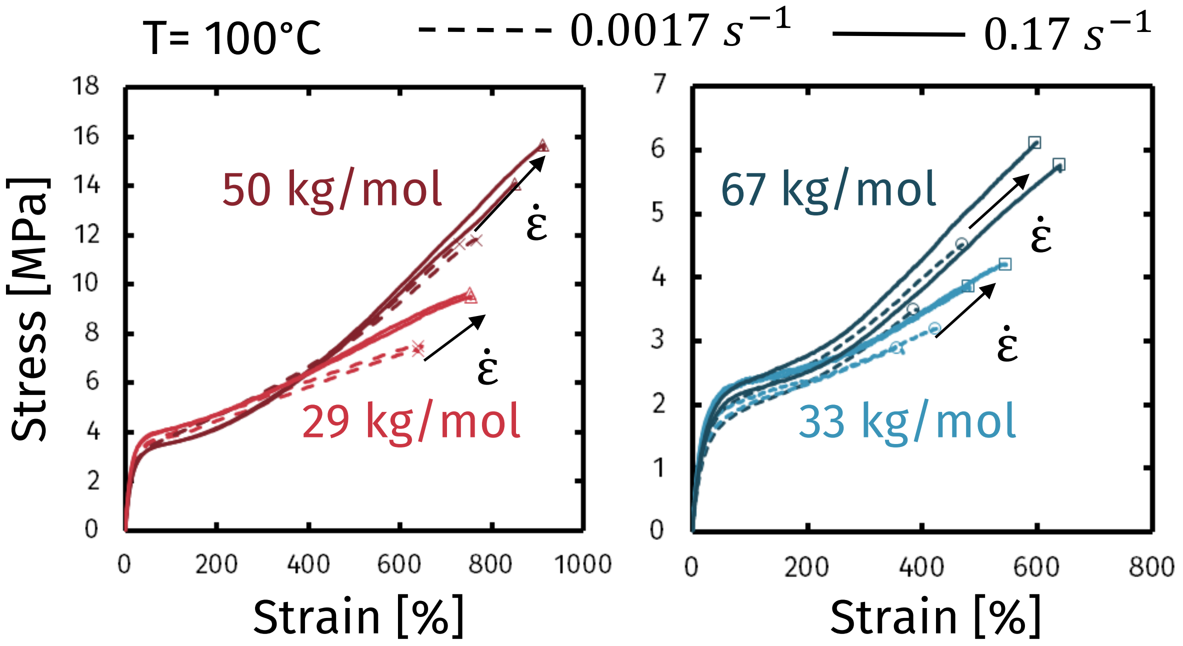
Explanation of the experimental results

Many assumption behind the model, but it gives a possible physical explanation for the different strain-rate dependency with Mw



Mw impacts the dangling-end relaxation, thus the SBUs density: higher stresses and lower strain-rate dependency for high-Mw samples



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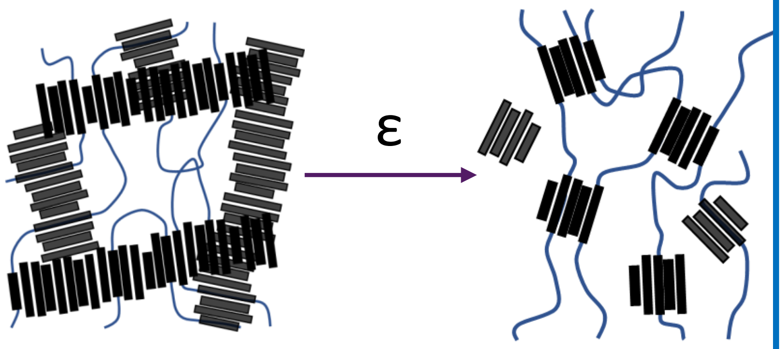
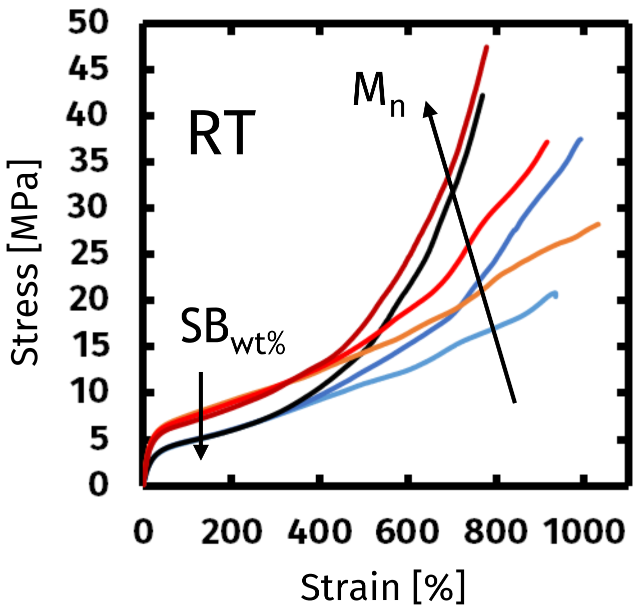
Conclusions

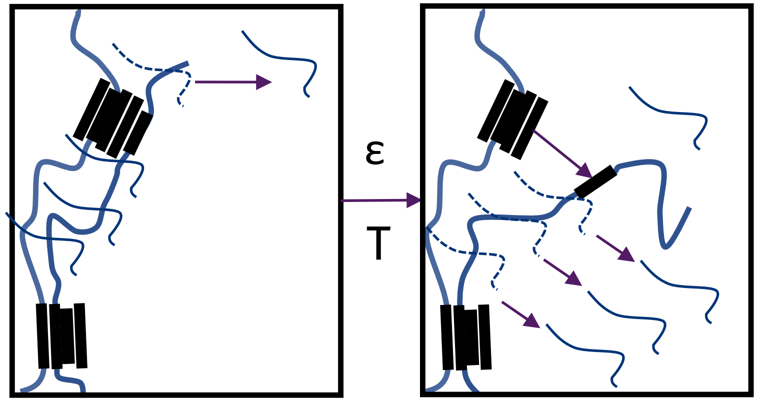
Mechanical properties dependent on the actual morphology at each stage of deformation.



Mechanical tests to investigate the different dynamics influencing the deformation behavior.



Stress response linked to the residual connectivity: HB pull-out and slip-out of non trapped entanglements.



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