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Working at DSM Material Science Center, Geleen – The Netherlands – From

May 1st on *"Soft Thermoplastic Elastomer: influence of composition and molecular weight on mechanical properties"*

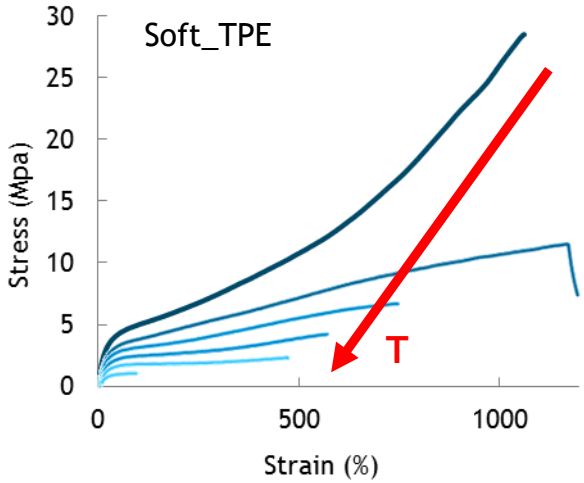
Outline

- Recap
  - -Thermoplastic Elastomers (TPEs):
    - Morphology and Structure
  - -Experimental results:
    - Influence of SB/HB ratio
    - Influence of Mw
- Results interpretation
  - -Connectivity:
    - Chain size and number of blocks/chain
    - Inter and intra-crystals connectivity
- Future directions

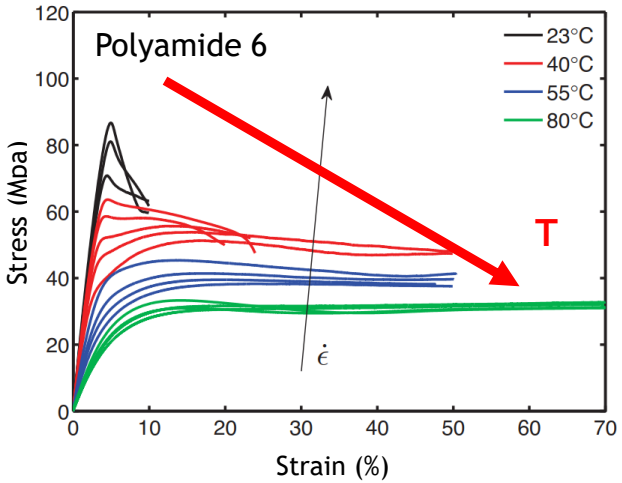
Motivation

Limited information about the high T mechanical behavior of thermoplastic elastomers (TPEs) in the literature

Loss of ductility with temperature



Typically ductility increases with temperature



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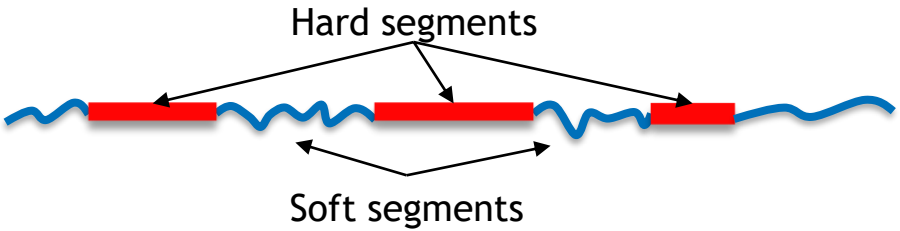
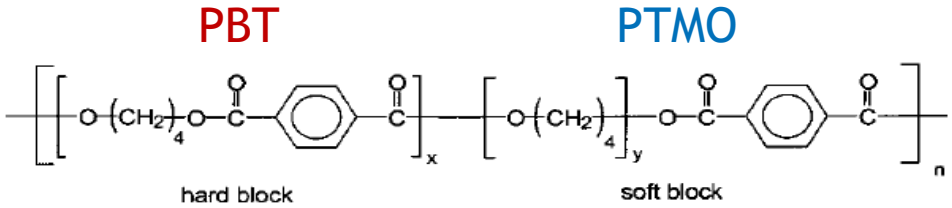
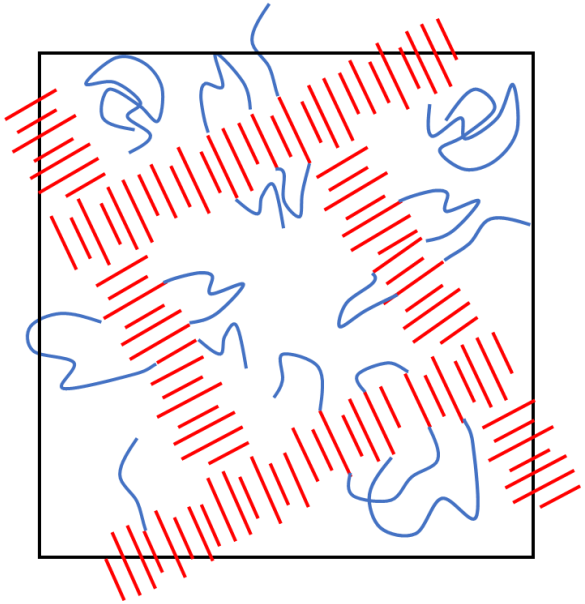
Thermoplastic Elastomers (TPEs)

Segmented block copolymer







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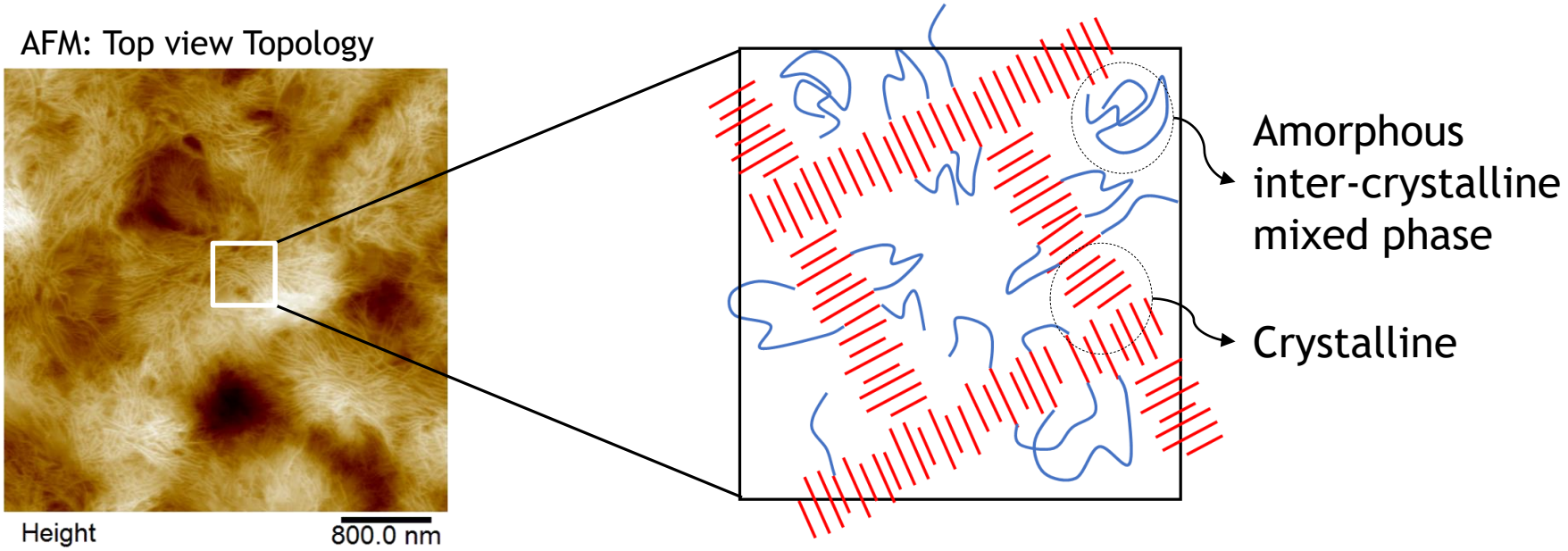
Thermoplastic Elastomers (TPEs)

Lamellar structure – Network of ribbons



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Experiments

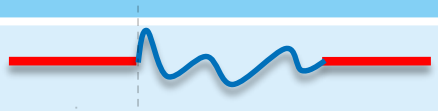
High T mechanical properties investigation

System description

Model System: SB/HB

1st System: different SB/HB ratio

Decreasing amount of PBT

Material	SB [wt%]	HB [wt%]	SB length [KDa]	Block length [PBT units]	
60_PTMO2k_29	60	40	2000	6.5	
70_PTMO2k_33	70	30	2000	4.5	
75_PTMO3k_32	75	25	3000	5	

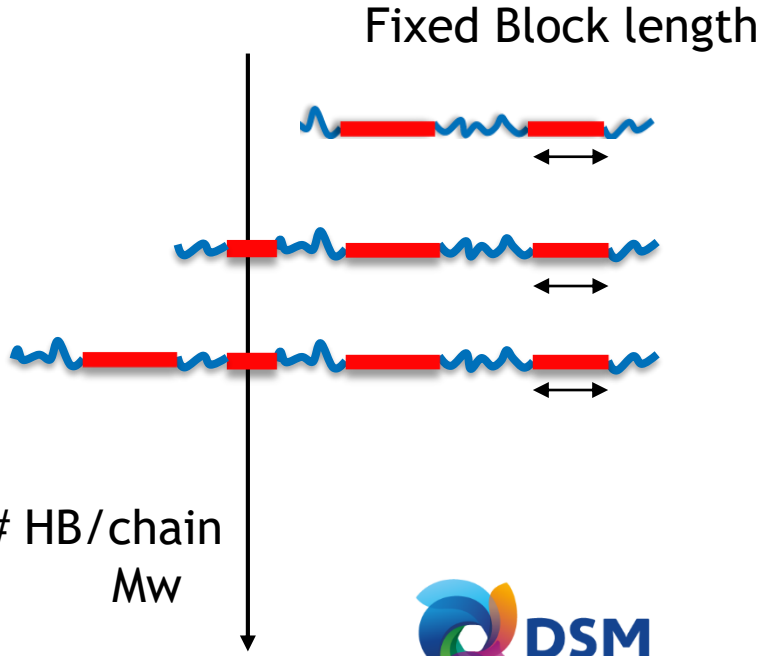
Model System: Mw

2nd System: different Molecular Weights – two different SB/HB ratio investigated - other parameters fixed

SSPC time (hrs)	Mn (kDa)	Mw/Mn
0	24.6	2.0
4	31.9	2.0
6	34.2	2.0
9	43.9	2.0
12	50.2	2.0
0	27.2	2.0
4	37.6	2.0
6	38.5	2.0
9	50.6	2.0
12	67.0	1.9

Hard grade
60_PTMO2k

Soft grade
70_PTMO2k



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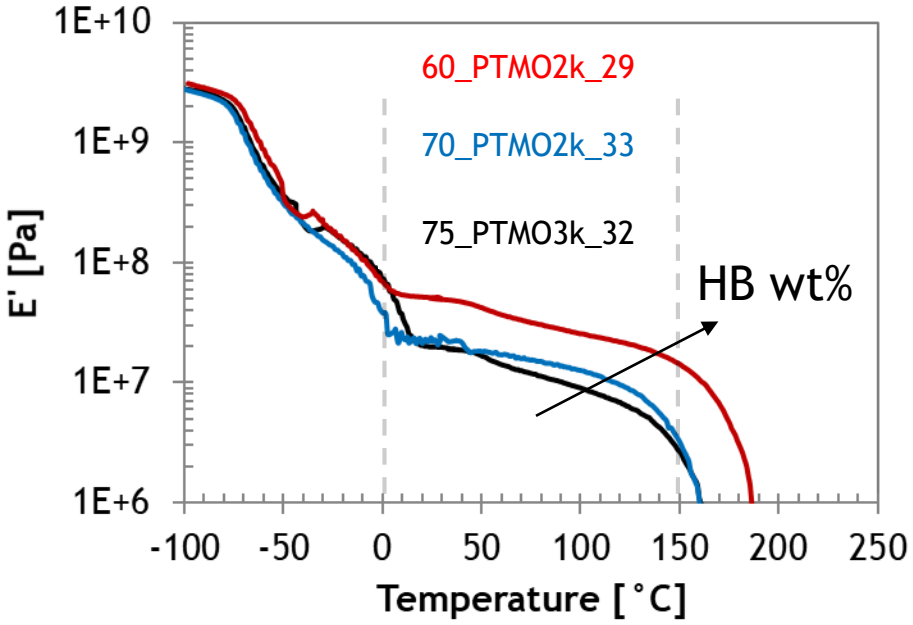
Experiments

High T mechanical properties investigation

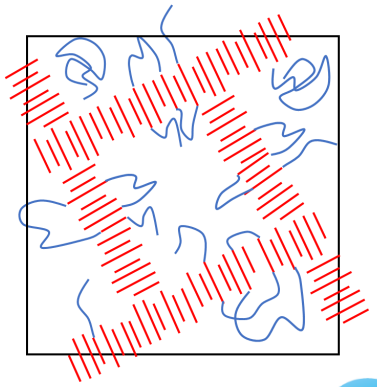
Results

The modulus and the plateau-end scale with the HB content.

Linear properties: DMTA



Rubbery plateau slightly decreasing with Temperature. The modulus is governed by the network of ribbons



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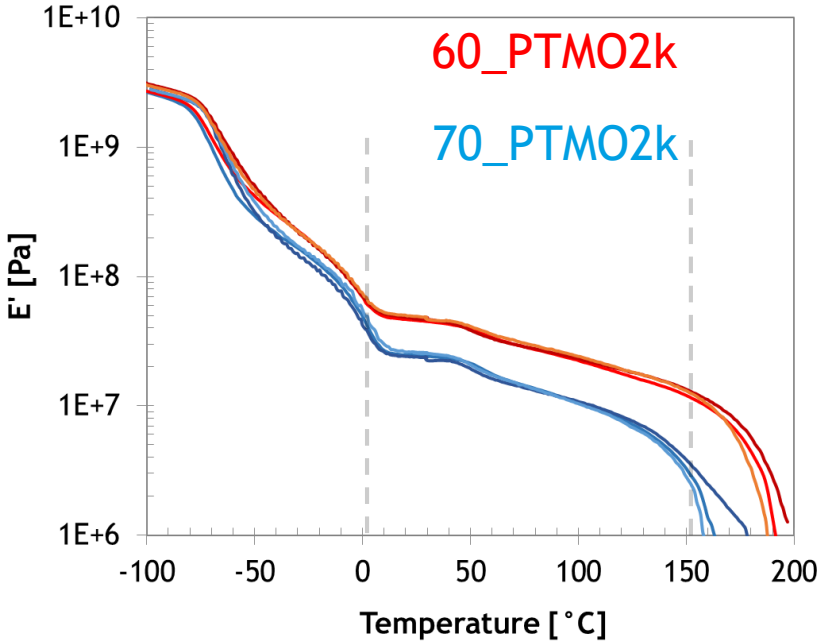
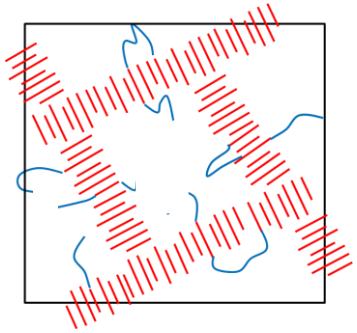
Molecular weight does not affect the linear properties

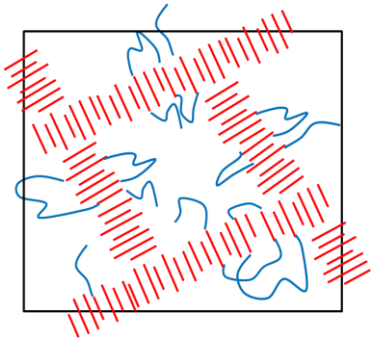
Linear properties: DMTA



The initial network of ribbons is not influenced by the chain length.



Low Mn



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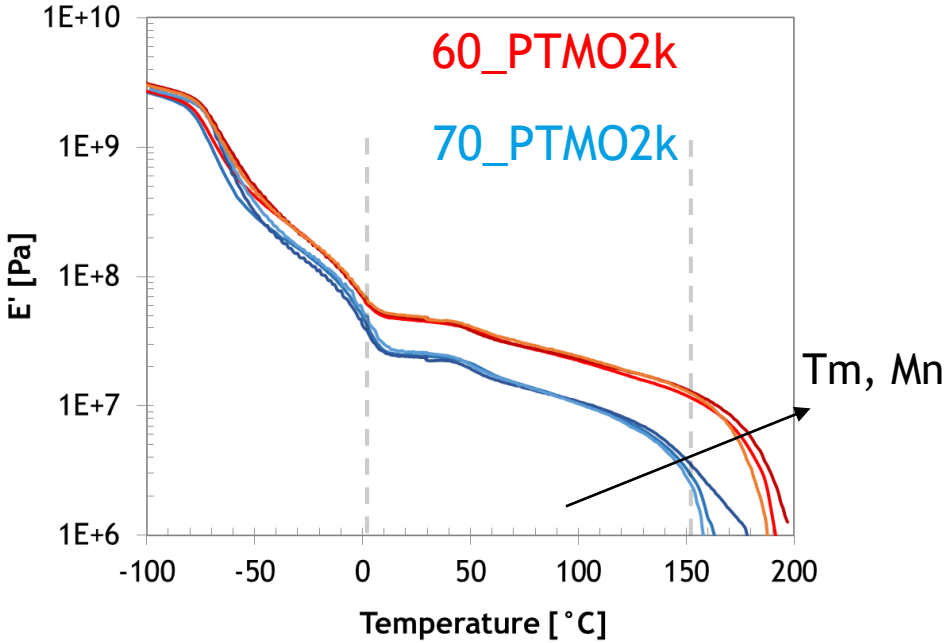
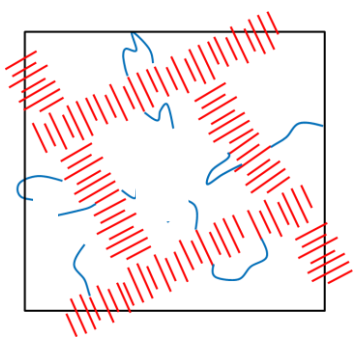
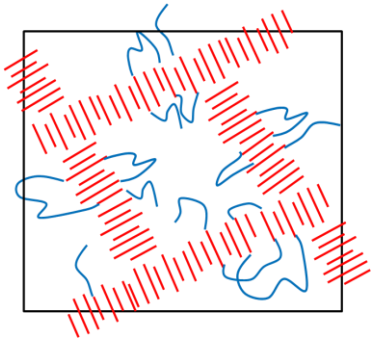
Linear properties: DMTA



The plateau end increases due to the way we increase the Mw (SSPC), which indirectly increases the Tm.



Low Mn



High Mn

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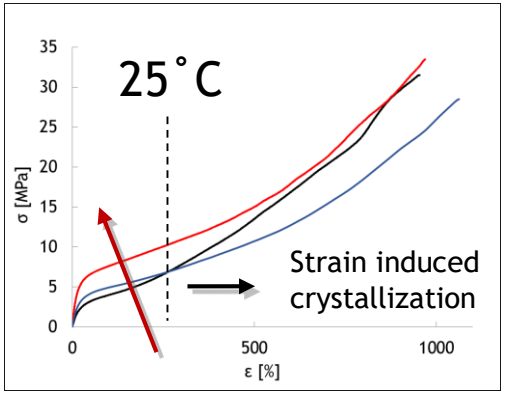
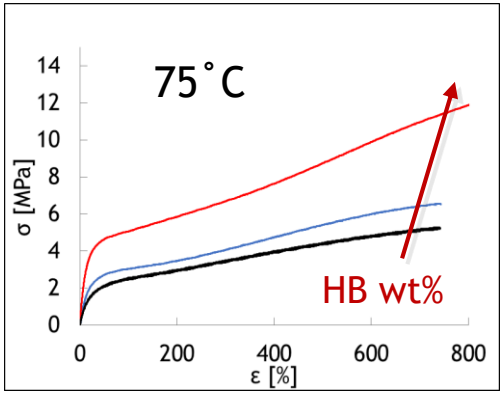
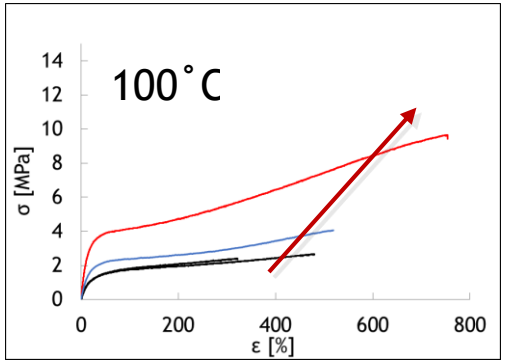
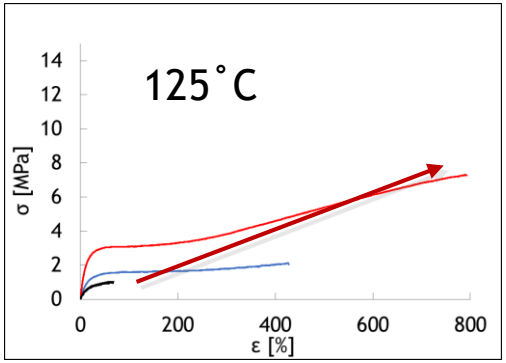
Temperature resistance increases with HB content

Non-linear properties: Tensile tests – 1st system









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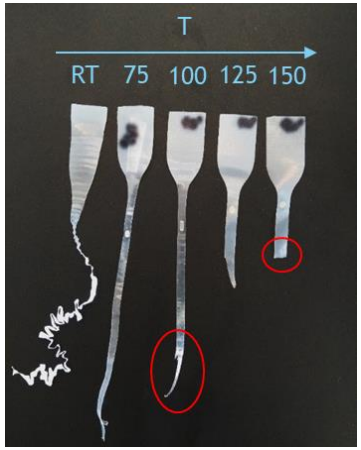

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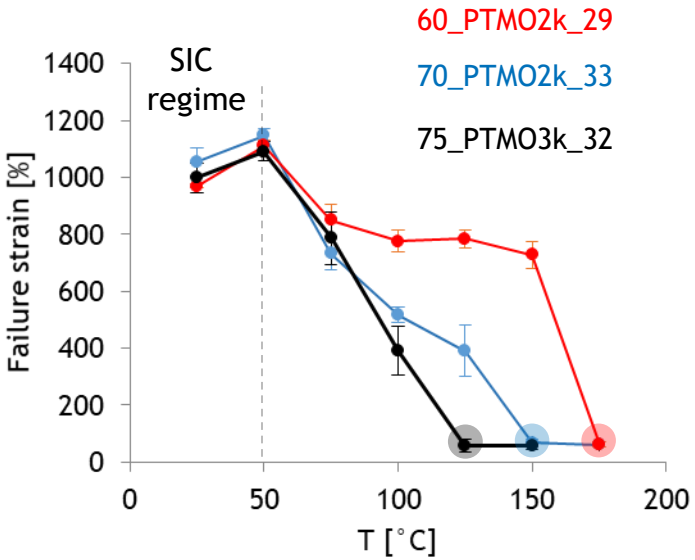
Temperature resistance not related to the melting peak position

DSC - DMA - Failure strain Vs T

- Temperatures where the failure strain is <100%



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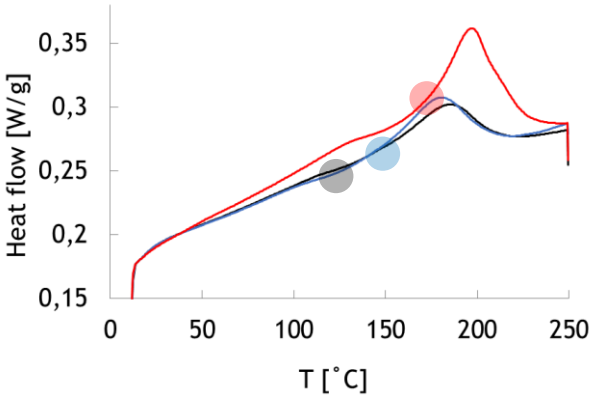

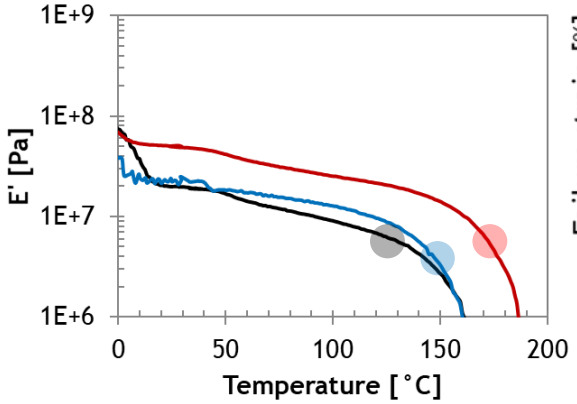

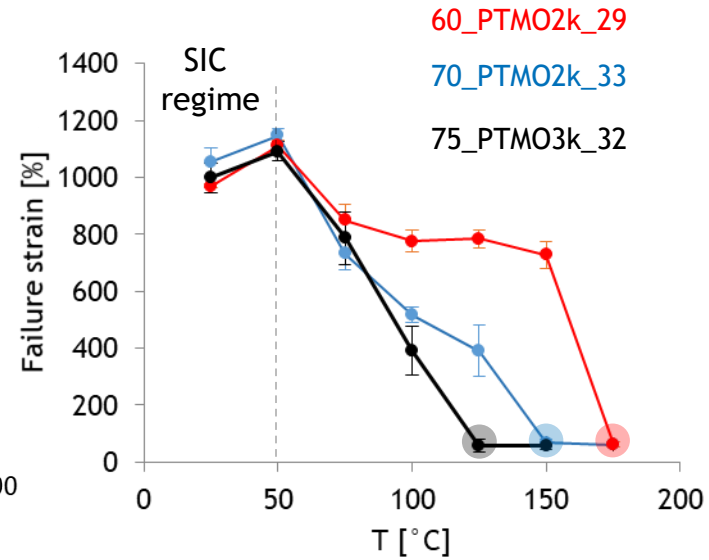

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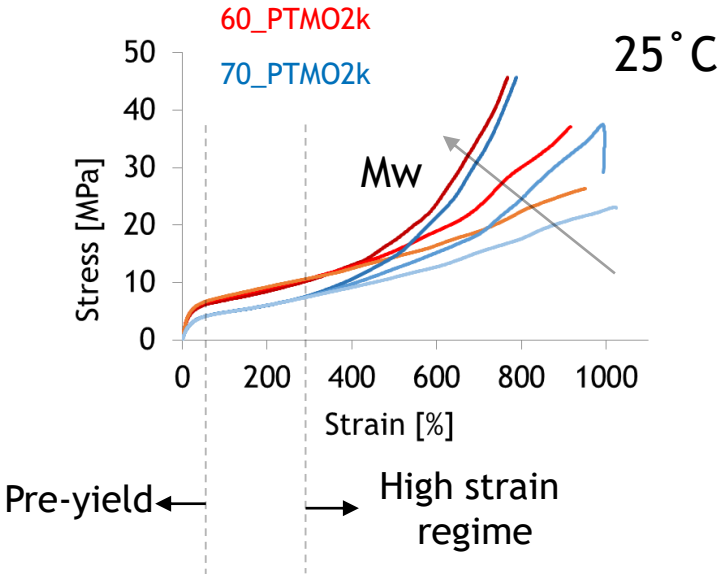
Three identifiable regions: low strain, intermediate and high strain regimes

Non-linear properties: Tensile tests – 2nd system



Mw affects the mechanical properties only in the high strain regime, i.e. after ~250% of strain, increasing stresses and failure strain

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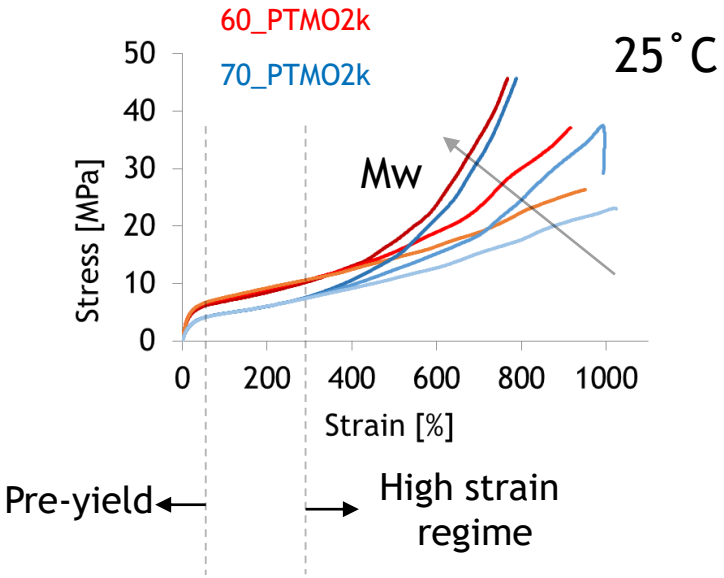

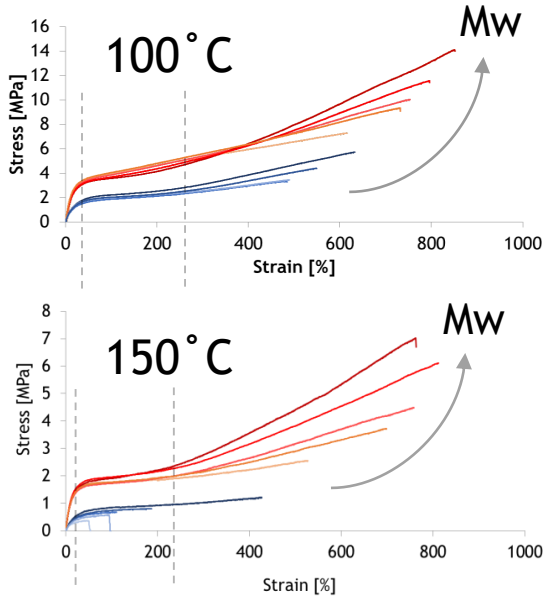

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Experimental results – Summary

- Increasing HB wt%:

  - Higher stresses and moduli at all T
  - Higher strain and stresses at break at high T and delayed effect of T on strain at break

- Increasing Mw:

  - Same stresses in the pre-yield and intermediate regimes (ε<~250%)
  - Boosted hardening in the high strain regime and even at T where there is no strain induced crystallization of the SB
  - Higher strain at break and stresses at higher temperatures

Results interpretation

Samples with higher Mw or # of blocks/chain produce better connected network

- **A model for failure in thermoplastic elastomers based on Eyring kinetics and network Connectivity -** *S. Aime, N. D. Eisenmenger, and T. A. P. Engels*
- **Structure and Mechanical Properties of Ethylene/1-Octene Multiblock Copolymers from Chain Shuttling Technology -** *Finizia Auriemma, Claudio De Rosa, Miriam Scoti, Rocco Di Girolamo, Anna Malafronte, Massimo Christian D'Alterio, Laura Boggioni, Simona Losio, Antonella Caterina Boccia, and Incoronata Tritto.*
- **Deformation Behavior of PET, PBT and PBT-Based Thermoplastic Elastomers as Revealed by SAXS from Synchrotron -** *Norbert Stribeck Stoyko Fakirov Anton A. Apostolov Zlatan Denchev Rainer Gehrke*

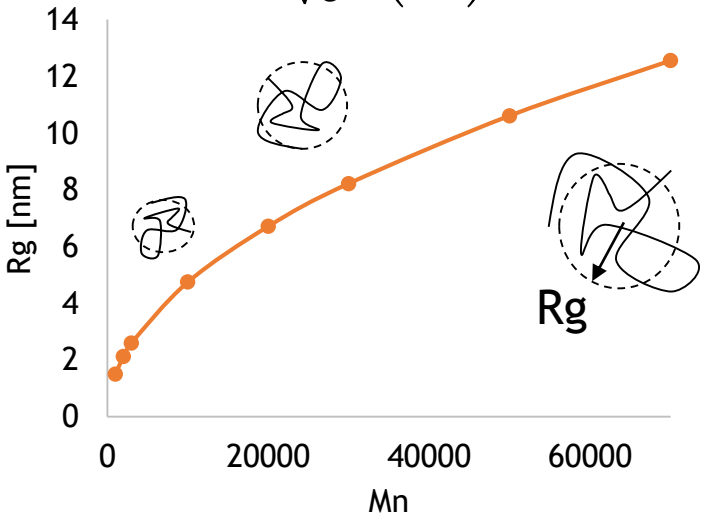
We also start from this idea and try to understand what connectivity means in our system:

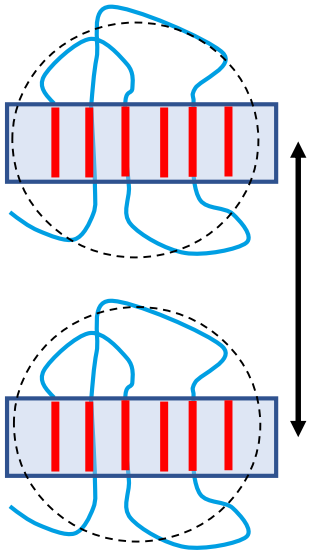
- Compare polymer size with distance between crystals
- Calculate the number of HBs per chain when Mw increases

Rg is lower than the average distance between crystals (d*)

d* obtained from SAXS – Rg of a pure PTMO ideal chain

$$Rg = \frac{1}{\sqrt{6}} b \left(\frac{Mn}{Mo}\right)^{0.5}$$





d* = 38 nm

d* value from
Baeza et al. (2018)

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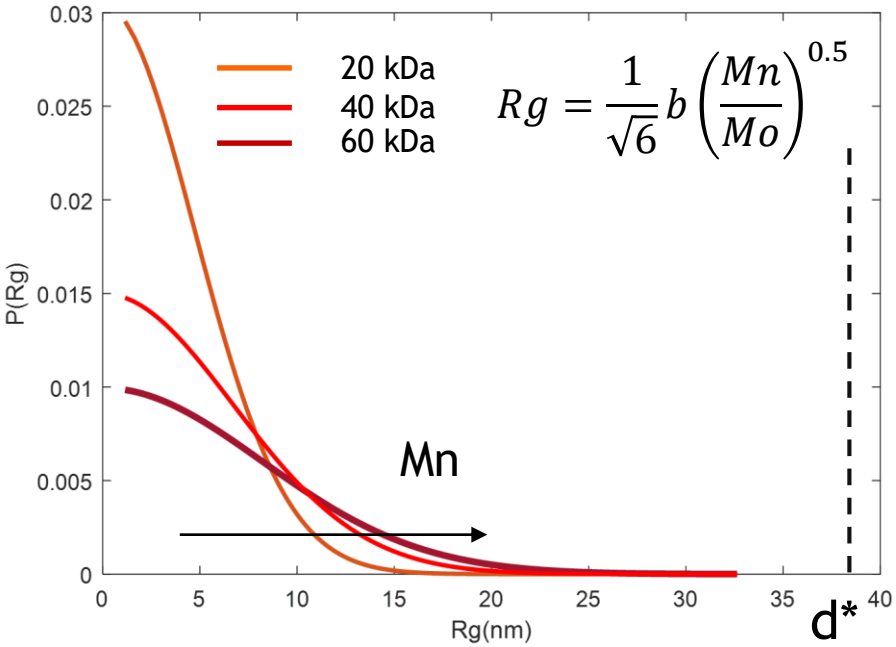
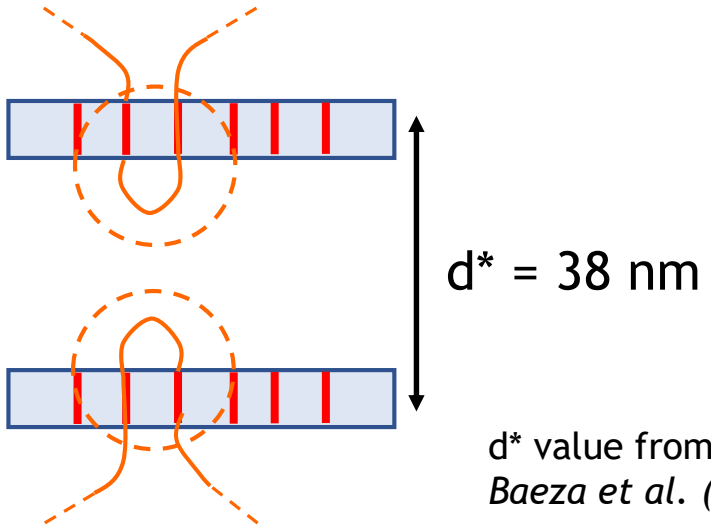
Rg distribution not reaching the average distance between crystals (d*)

Very low probability of inter-crystal connectivity





d* value from
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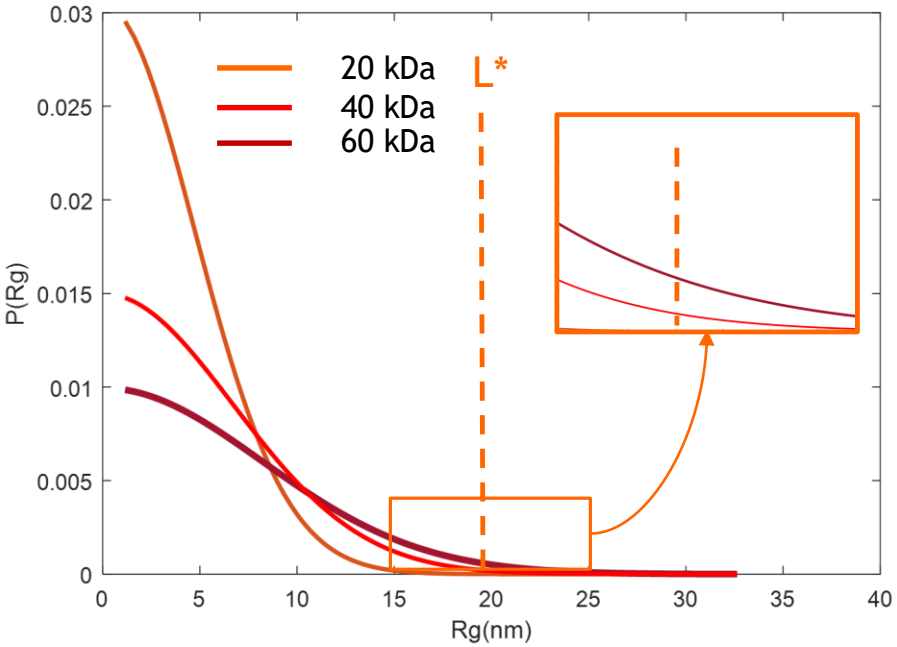
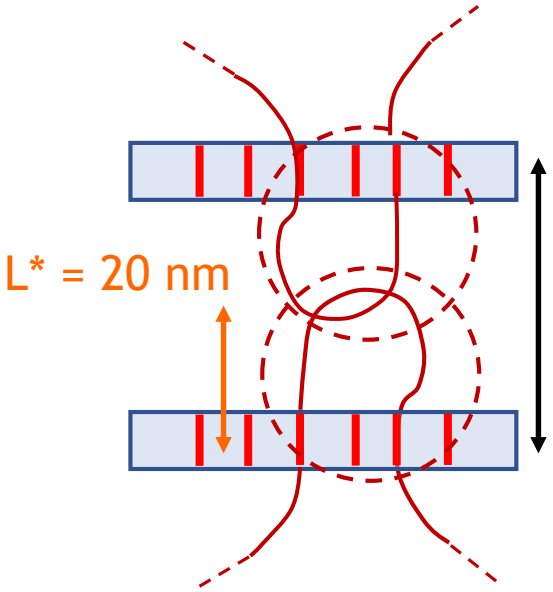
Fraction of chains from adjacent crystals joined together in a strong entanglement (trapped entanglement) increases with Mn





d* value from
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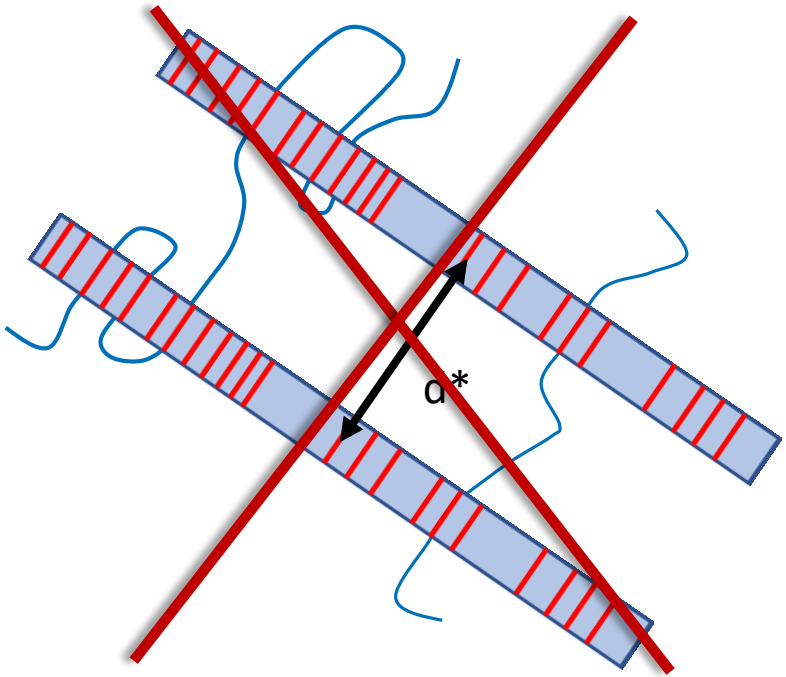
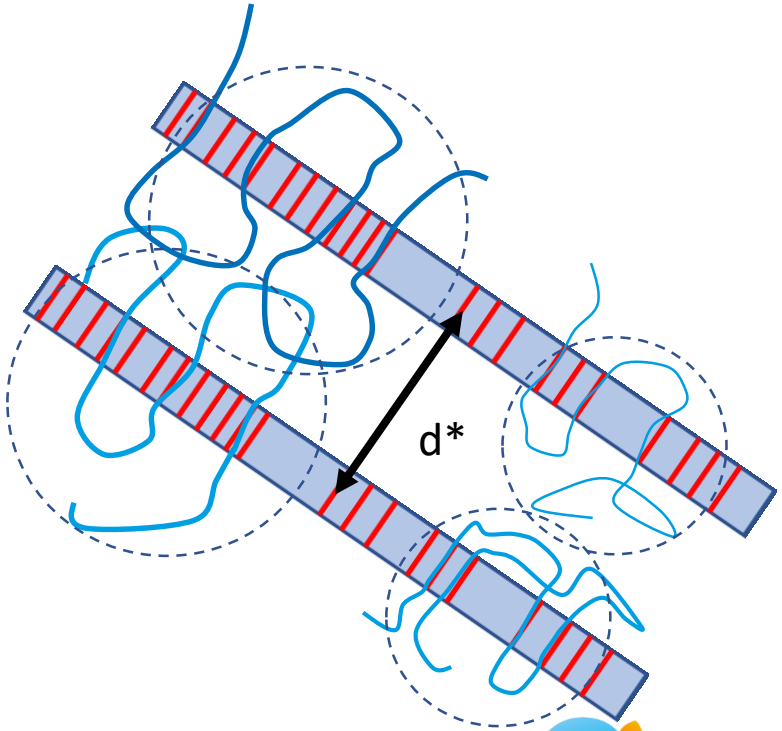
The number of trapped entanglements increases with Mn





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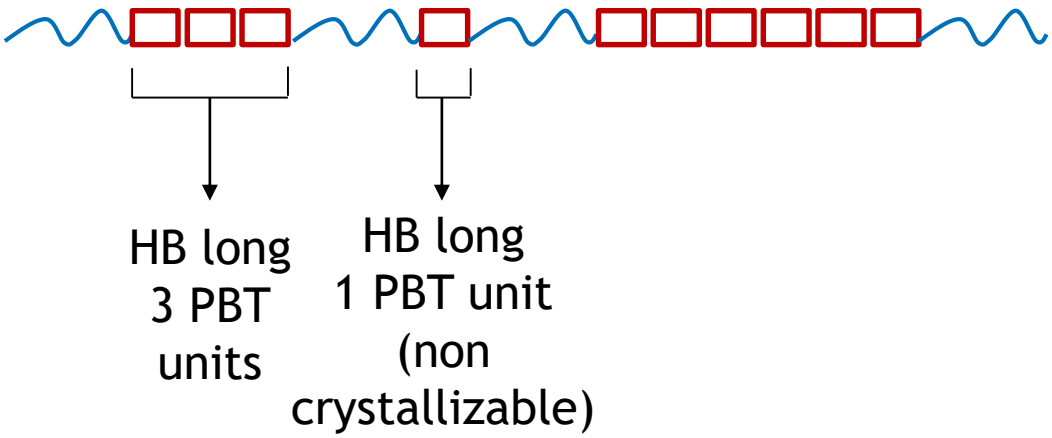
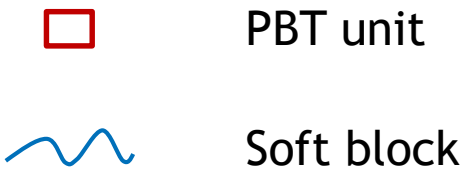
Statistical tool to assess the number of HB/chain

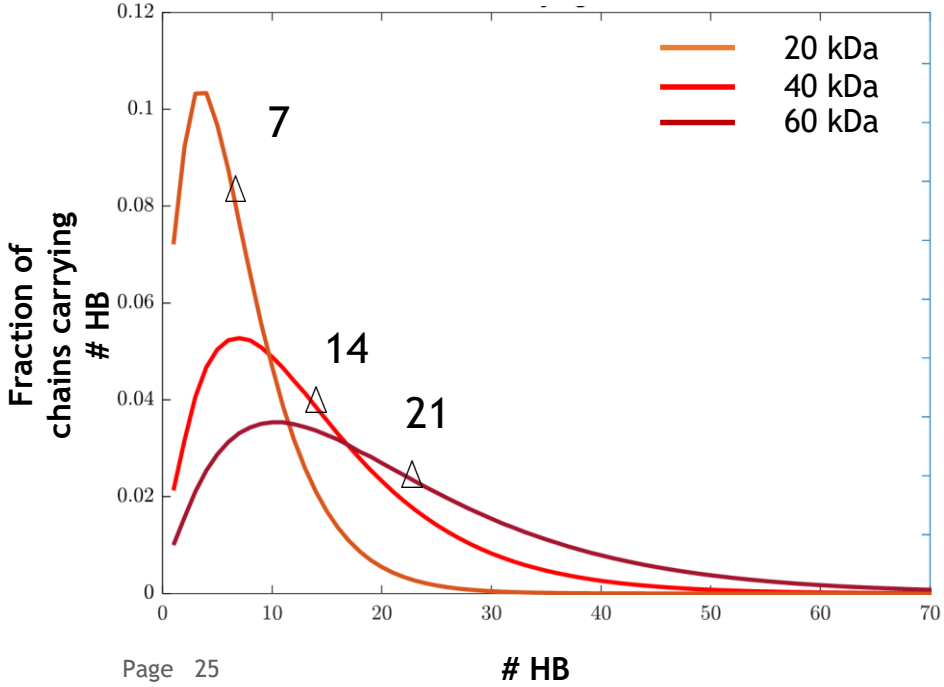
Building up chains with a Flory-Schulz distribution.
Monomers will be either Soft block or a PBT unit with a probability dependent only on the respective amounts





The number of blocks/chain is highly influenced by the Mw

Fraction of chains carrying # HBs Vs #HBs



△ Average # HBs/chain linearly increases with Mn

Here we're counting only the HBs longer than 3 PBT units, assumes shorter units can't crystallize

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Rg ($\propto \sqrt{Mn}$) always lower than d*
#HBs/chain $\propto$ Mn

Assuming that:

- Crystallinity and d* are Mn independent
- Initial morphology doesn't change with Mn
- Rg always lower than d*

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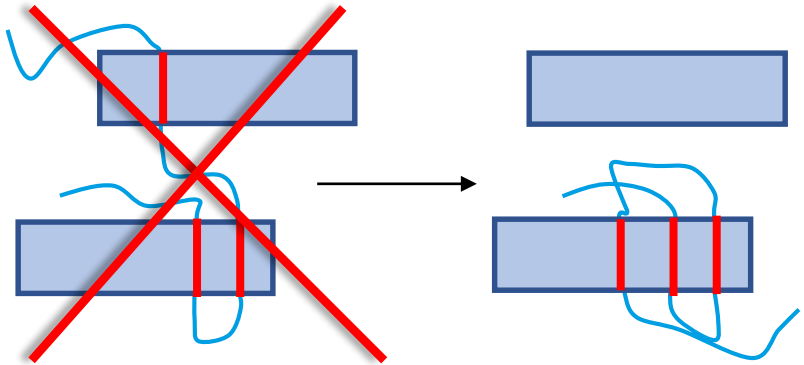
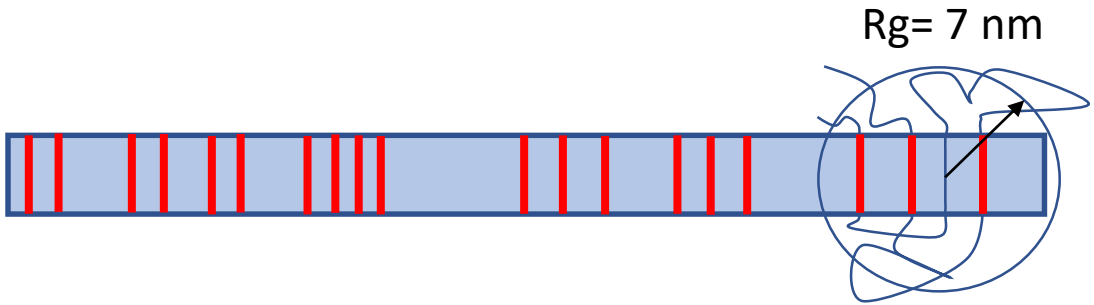


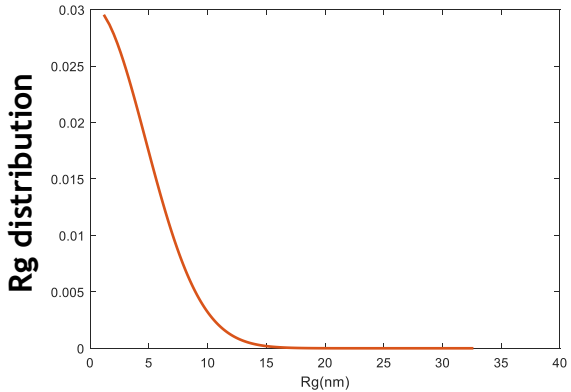
Consequence:

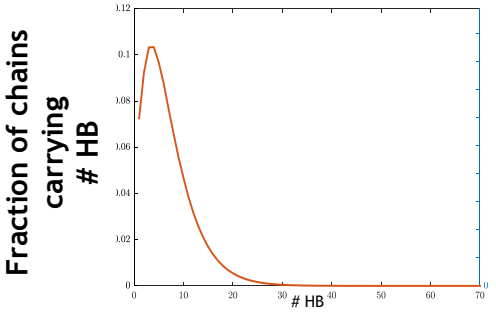
Each chain is forced to be connected multiple times within the same ribbon

Intra-crystal connectivity increases with Molecular weight

A chain goes through the same ribbon multiple times







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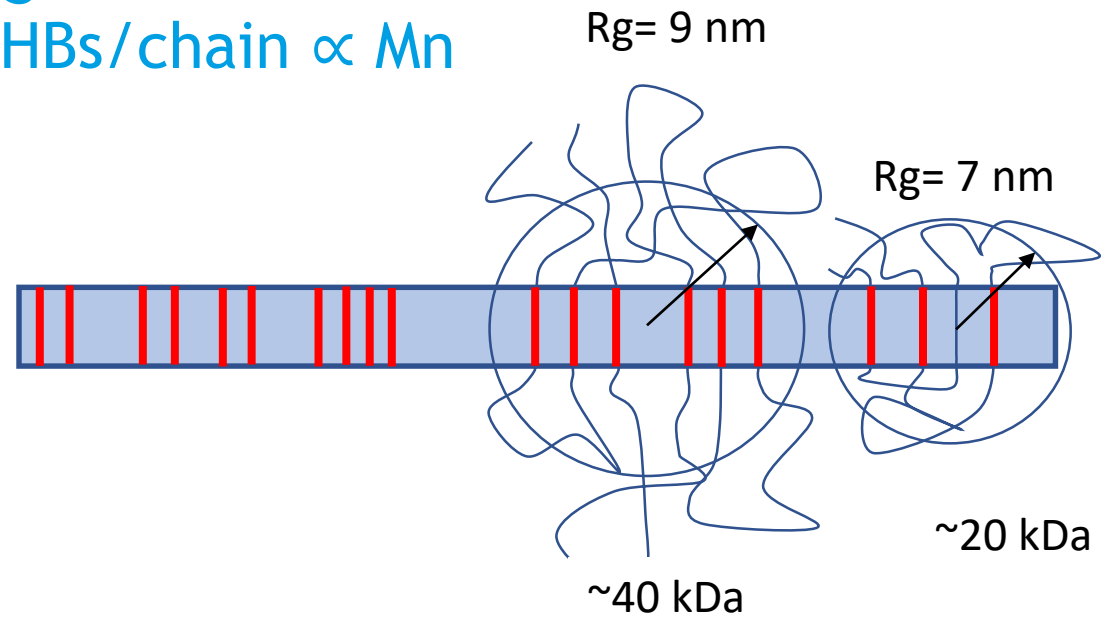
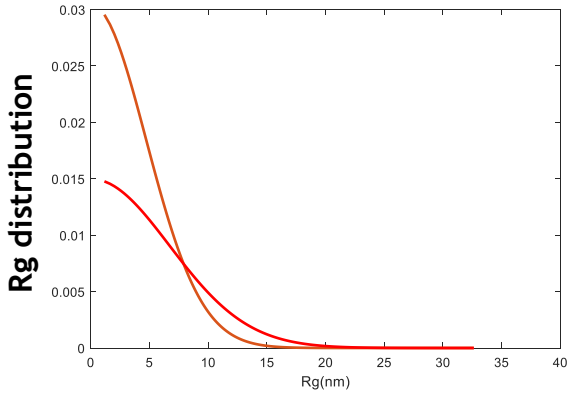
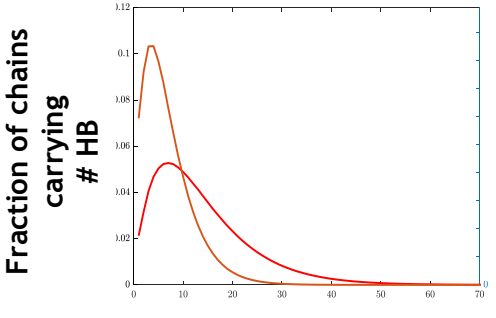
The number of intra-connections increases with #HB/chain

Rg ∝ √Mn

#HBs/chain ∝ Mn







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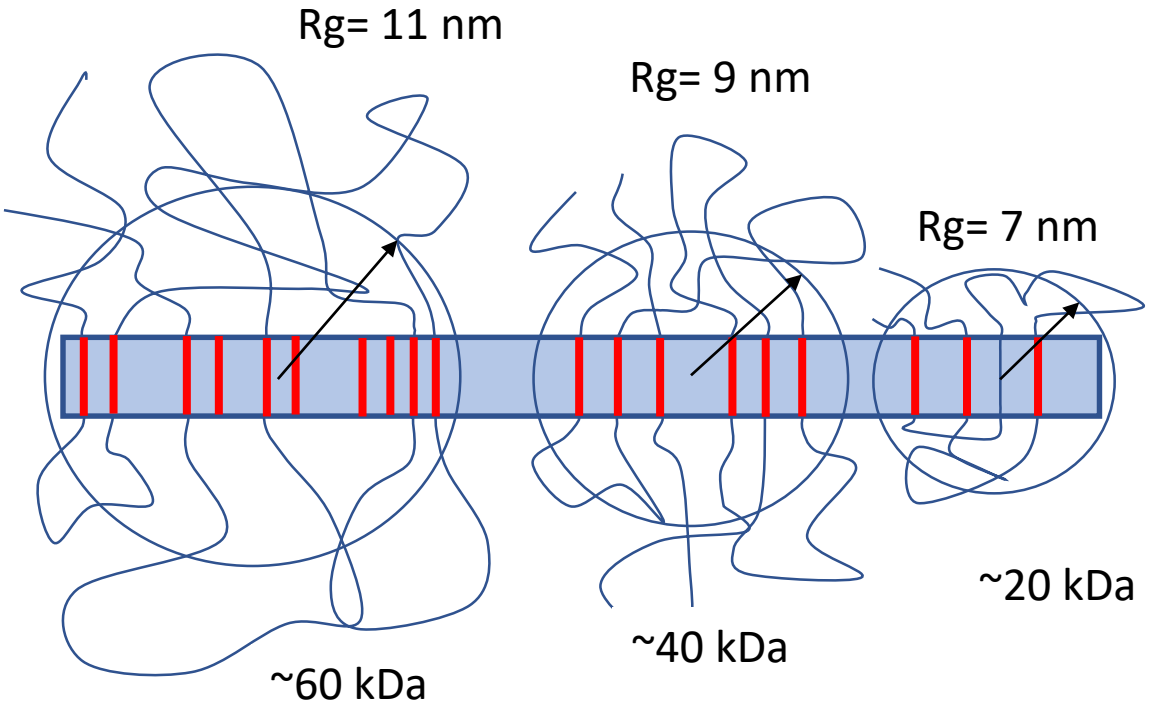
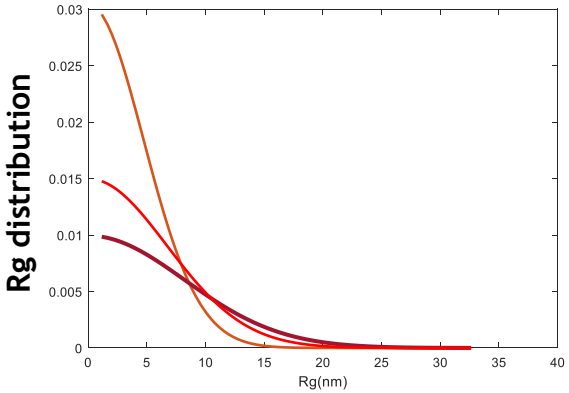
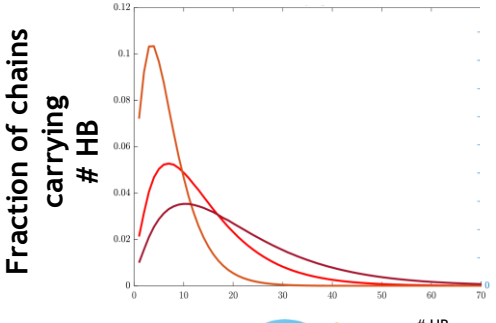
Intra-crystal connectivity increases with Molecular weight







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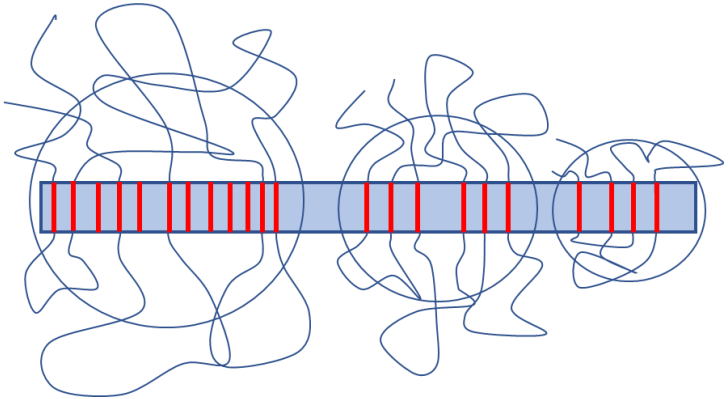
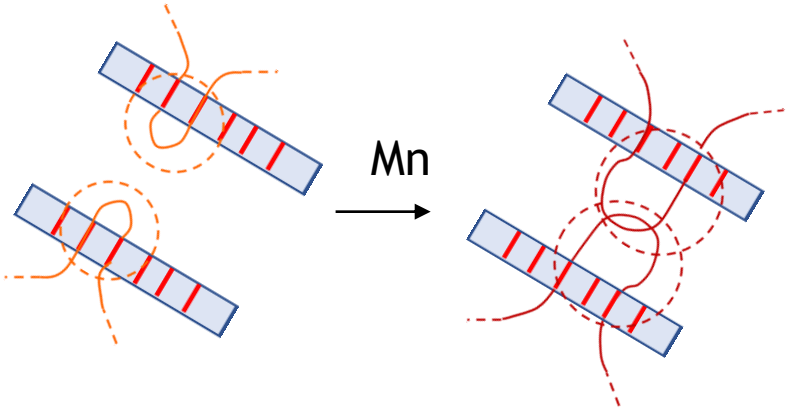
Mn influences the initial (undeformed state) connectivity in the system by increasing:

- The intra-crystal connectivity of the chains
- The fraction of trapped entanglements in the inter-crystalline amorphous phase





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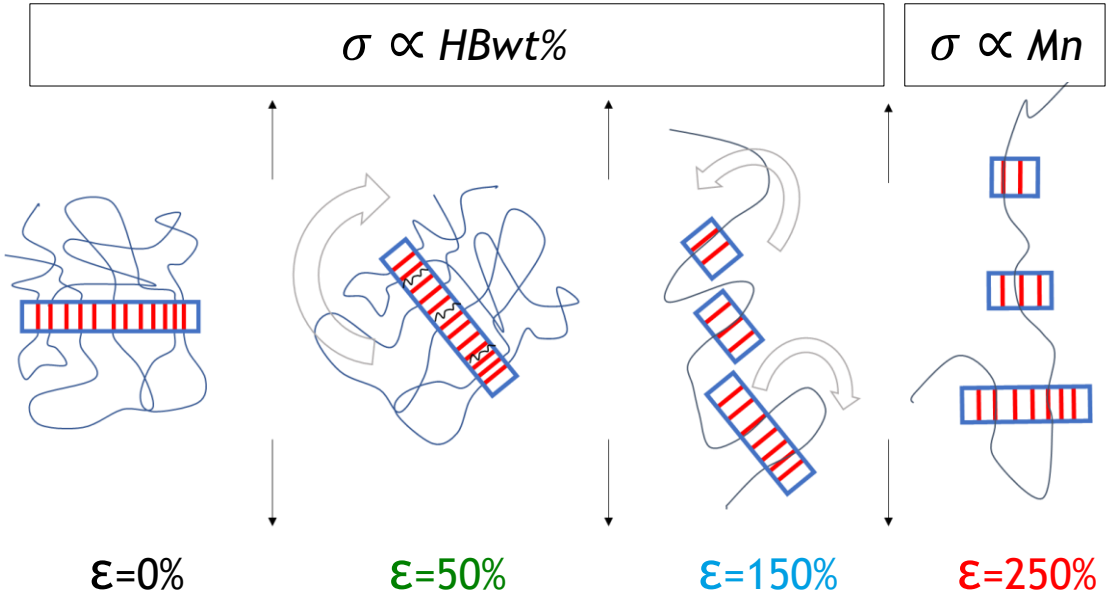
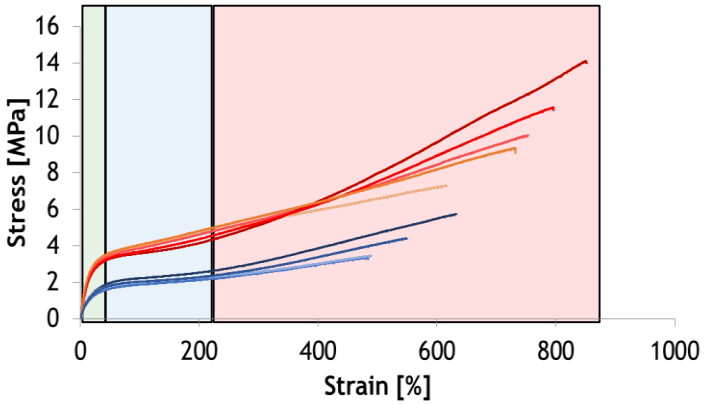
Crystalline regions from the same and adjacent ribbons interconnected with each others

Microstructural evolution upon deformation



Soft segments progressively stretched -> hardening



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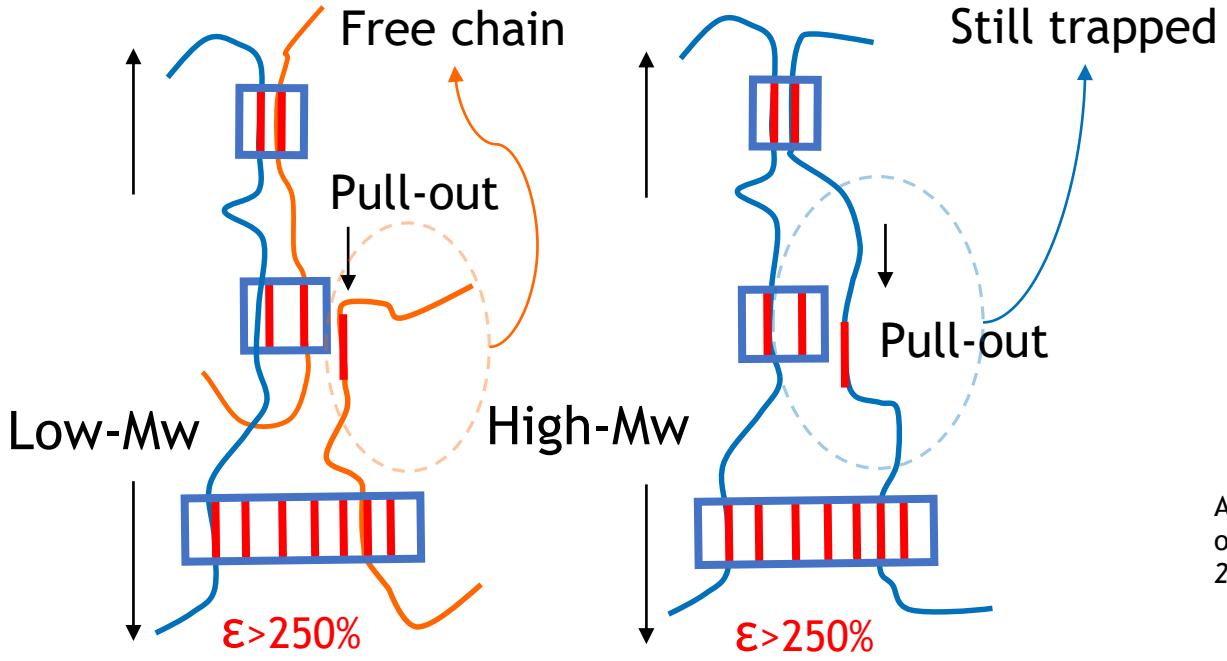
Pull-out of HBs causes disconnection to occur earlier for shorter chains - Mw effect



Kinetics matters at high stresses. Pull-out events activation

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

A model for failure in thermoplastic elastomers based on Eyring kinetics and network Connectivity - *S. Aime, 2017*

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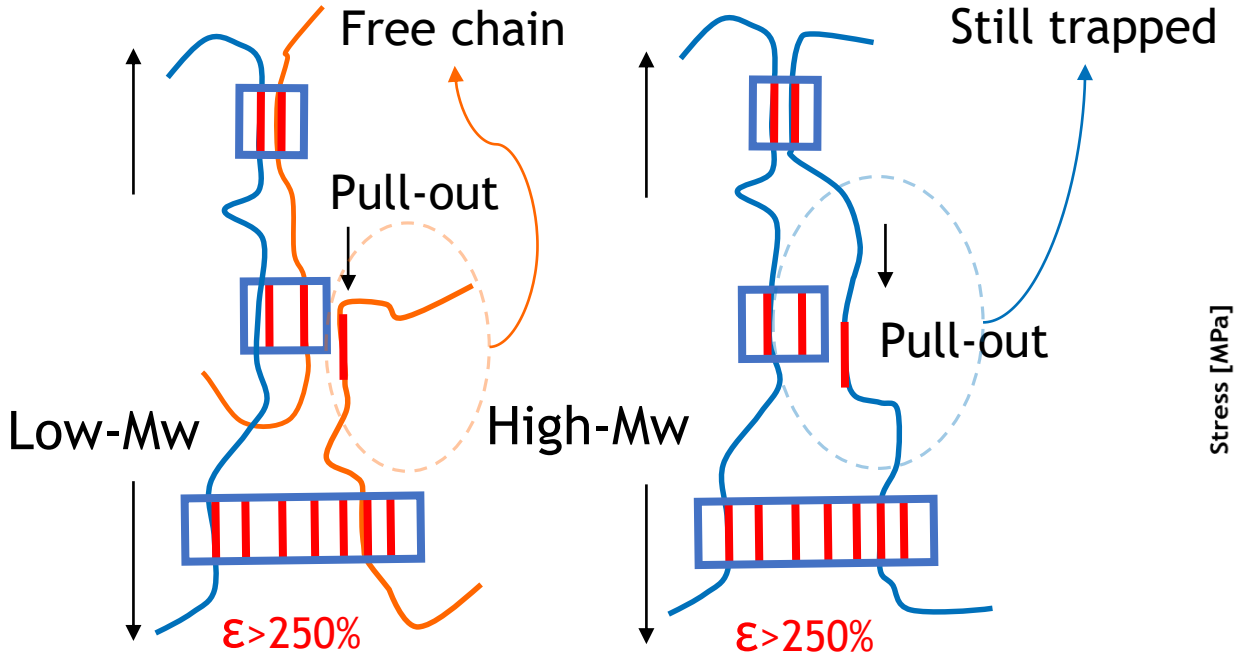
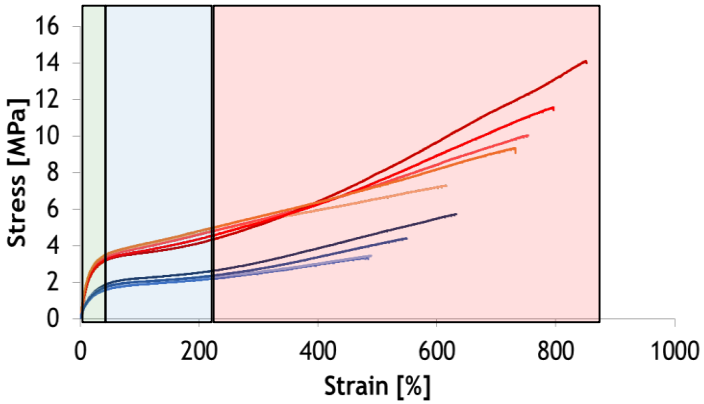
Pull-out of HBs causes disconnection to occur earlier for shorter chains - Mw effect



Connectivity remains even at a lower level of association between HBs



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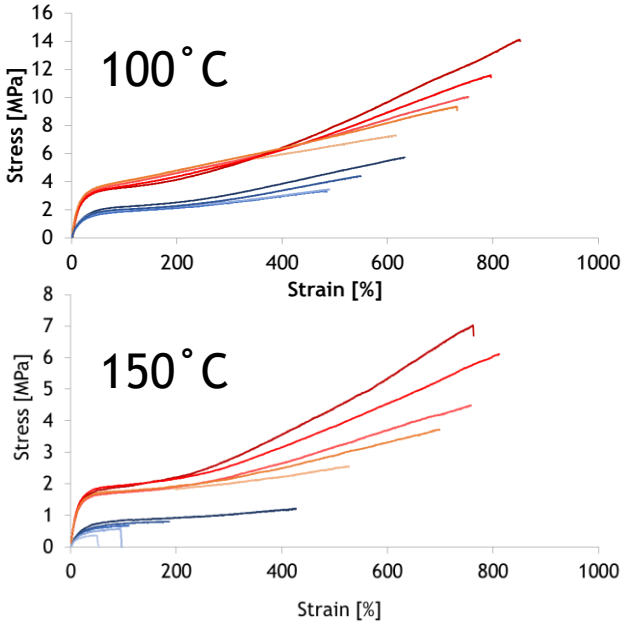
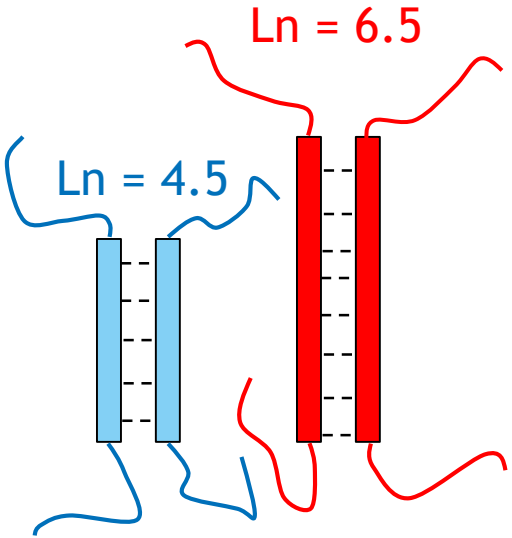
Does average block length (Ln) determine temperature resistance?





Kinetics matters at high T (thermally activated bond-breakage)

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

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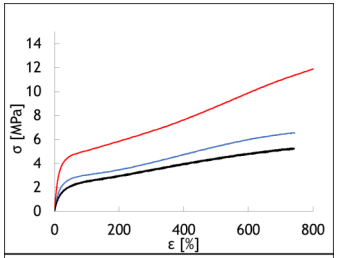
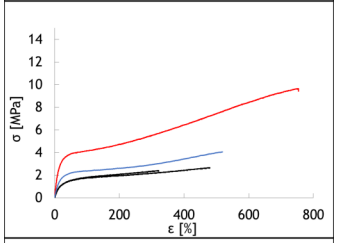
Temperature resistance cannot be explained by average block length alone

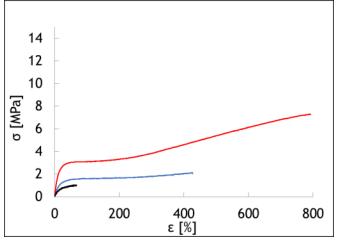
75˚C



100˚C



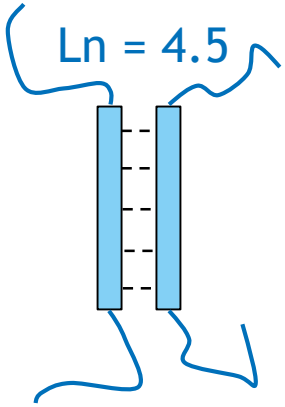
125˚C

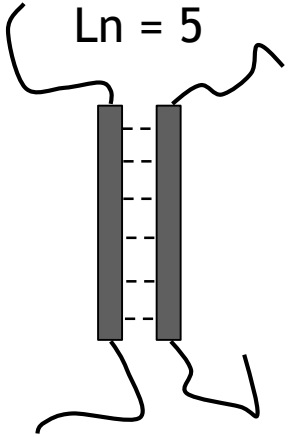


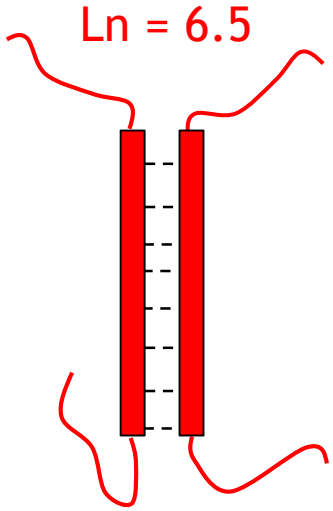
60_PTMO2k_29

70_PTMO2k_33

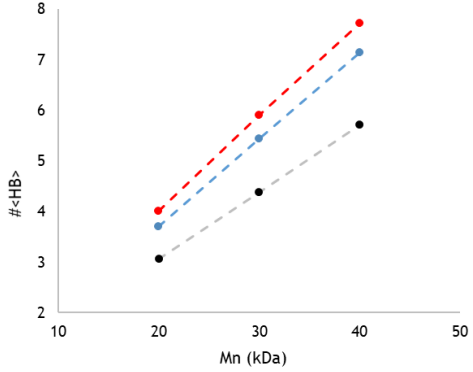
75_PTMO3k_32







Change in SB length leads also to a significant change in the average #HB/chain



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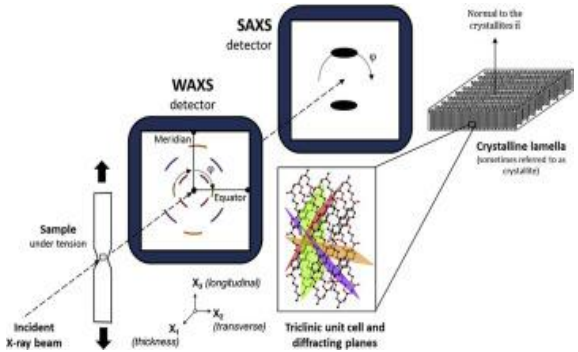
Results interpretation – Summary

- Undeformed state:
  Intra-crystals connectivity and number of trapped entanglements between crystals increased with Mn
- Low strain regime:
  Stress governed by the network made up by the ribbons
- Intermediate regime:
  Reorientation and breakage of crystal domains, creation of a new microstructures made up by the inter-connected small crystal domains.
- High strain regime:
  Chains alignment along the stress direction with consequent pull-out and loss of connectivity depending on Mn – effect of kinetics

Future directions

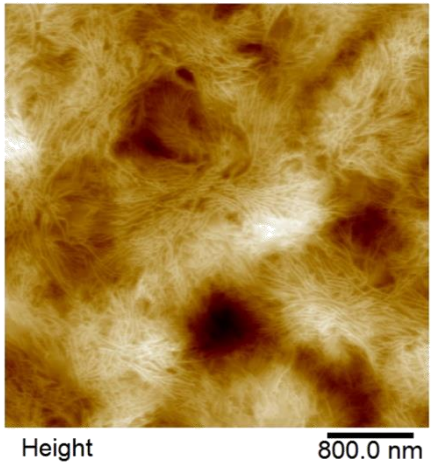
Assessing quantitatively morphological parameters (e.g. d*) of our samples, both in the undeformed and deformed state, at room and higher T

In-situ X-ray



Donnay et al.,2016

AFM topology



How much the initial and the under-deformation morphology change at higher T?

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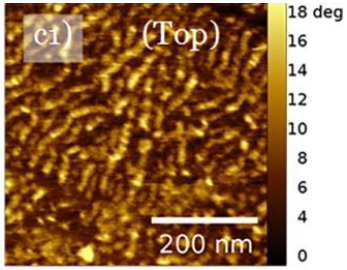
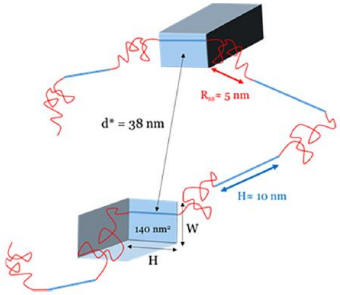
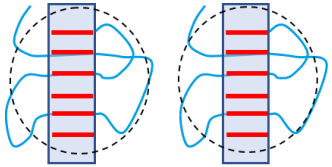
Different initial morphology should lead to a different kind of connectivity – tests on SC samples

HP samples

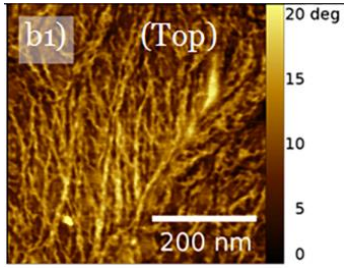


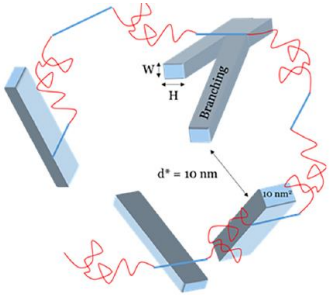


d*=38 nm

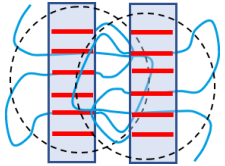


SC samples





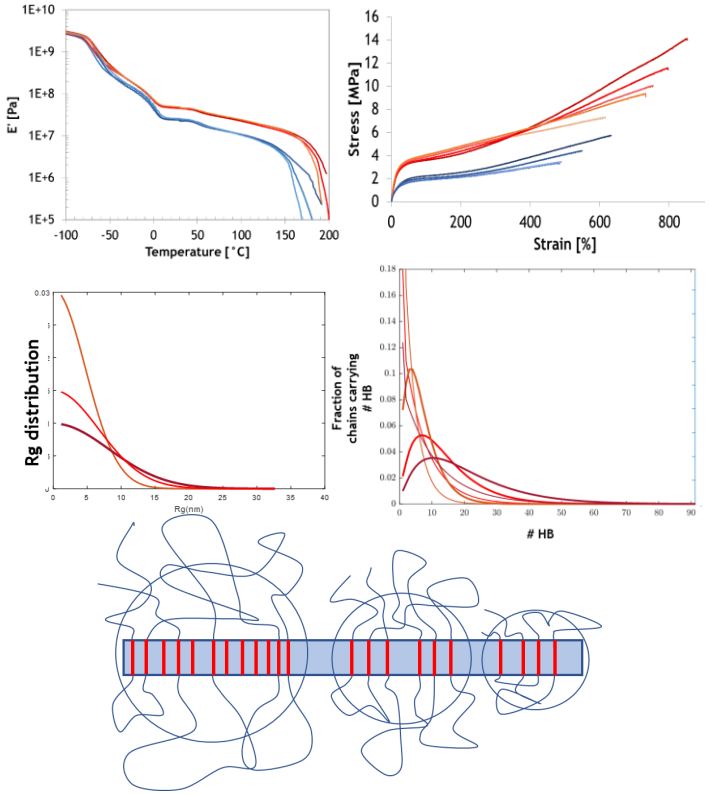
d*=10 nm



"Process-Oriented Structure Tuning of PBT/PTHF Thermoplastic Elastomers"
[Matthias Nébouy, André de Almeida, Solène Brottet, and Guilhem P. Baeza]

Wrap-up

- We investigated the linear and non-linear high-temperature mechanical properties by systematically varying SB/HB and Mw
- With the help of a statistical tool and data from literature we compared the size of our chains with the distances between crystals and assessed the number of HBs/chain: intra and inter-crystal connectivity
- We proposed a picture regarding the evolution during deformation of the microstructural rearrangement of the chains taking into account the effects of Mw and SB/HB content



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