Reversible Crosslinking
a potent paradigm for designer materials

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Department of Applied Physics
&
Institute for Complex Molecular Systems

Project
Harnessing Reversible Crosslinks for Toughness of Gels

→

Research Line
Reversible Crosslinks as a powerful motif in high tech materials

TU/e Technische Universiteit Eindhoven University of Technology

3TU.Federatie

Who are we?

Wouter Ellenbroek

Kees Storm

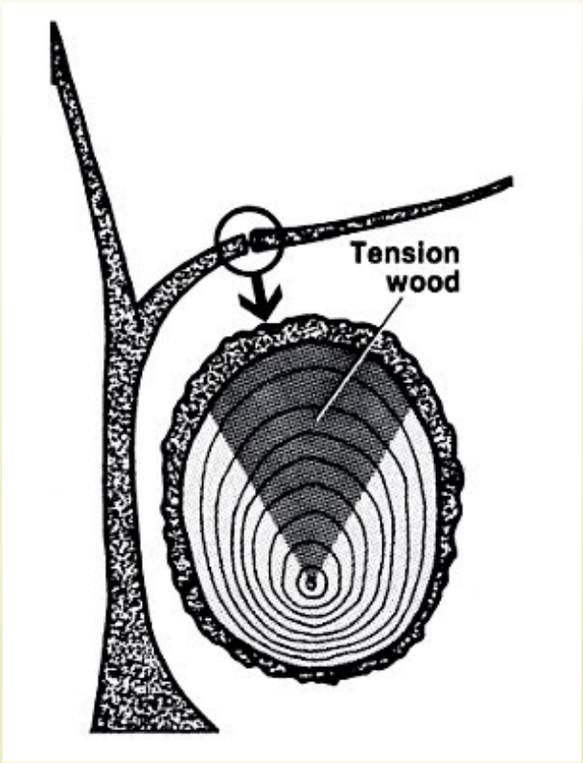
Costantino Creton (ESPCI)

Other members of group TPS
Theory of Polymers and Soft Matter

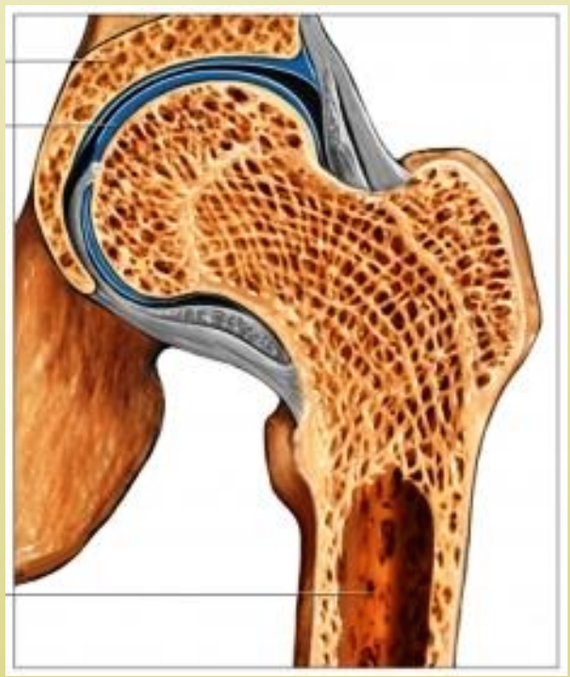
Paul van der Schoot

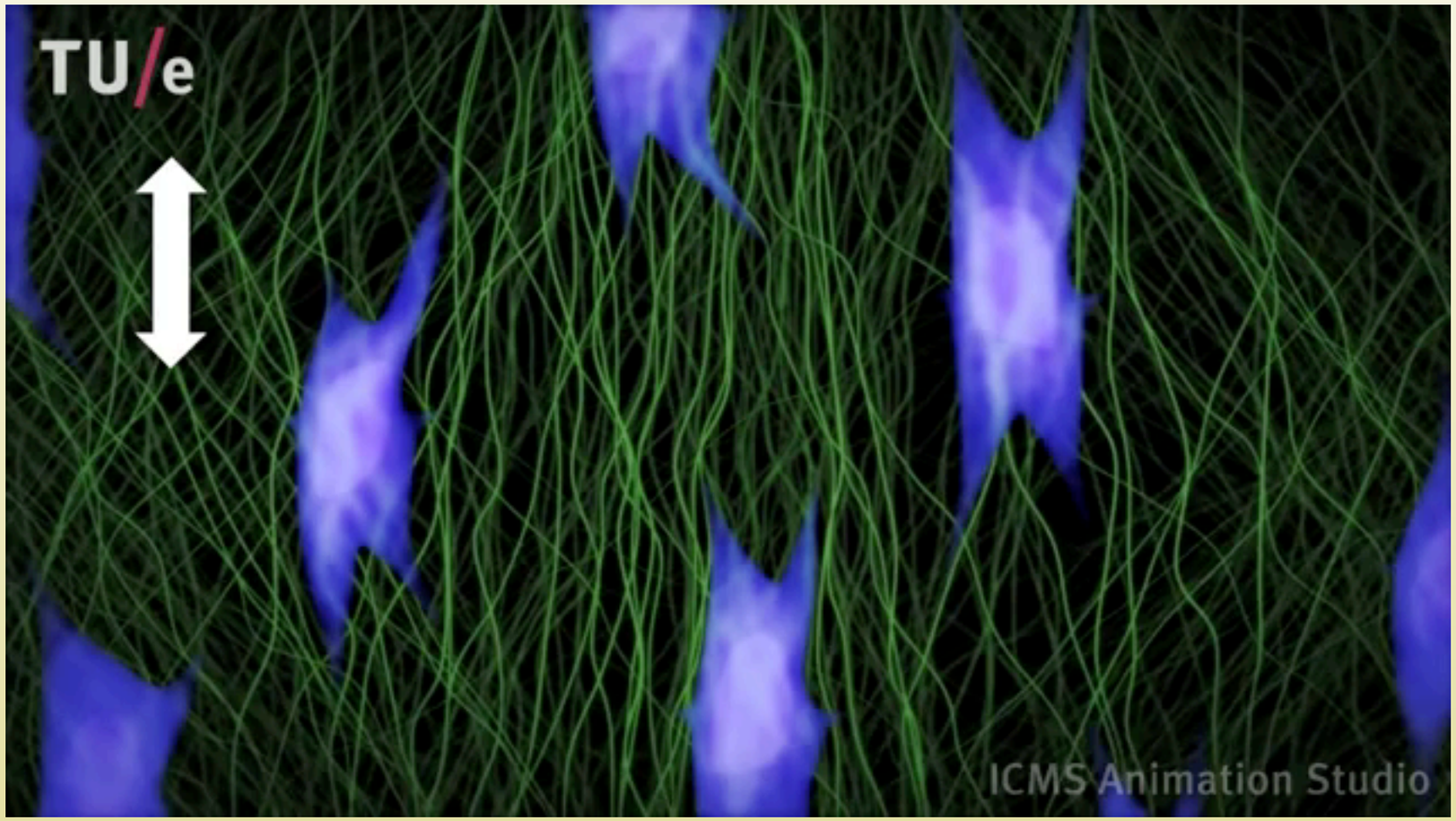
Alexey Lyulin

Dynamic structures in nature: remodeling



http://treewright.blogspot.nl/2010/04/reaction-wood.html





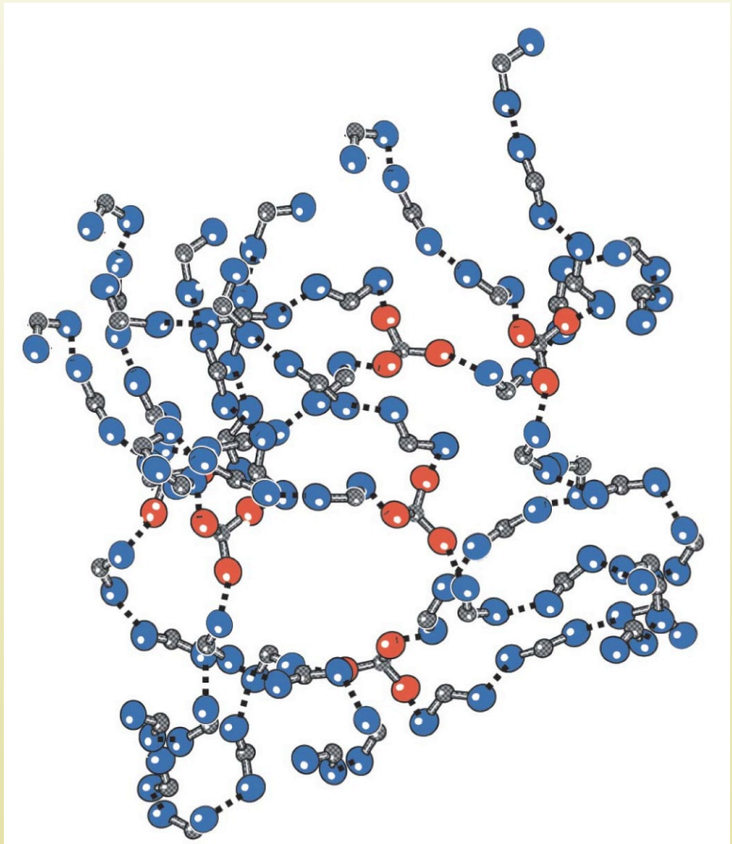
https://www.youtube.com/watch?v=atalSIZSuf8

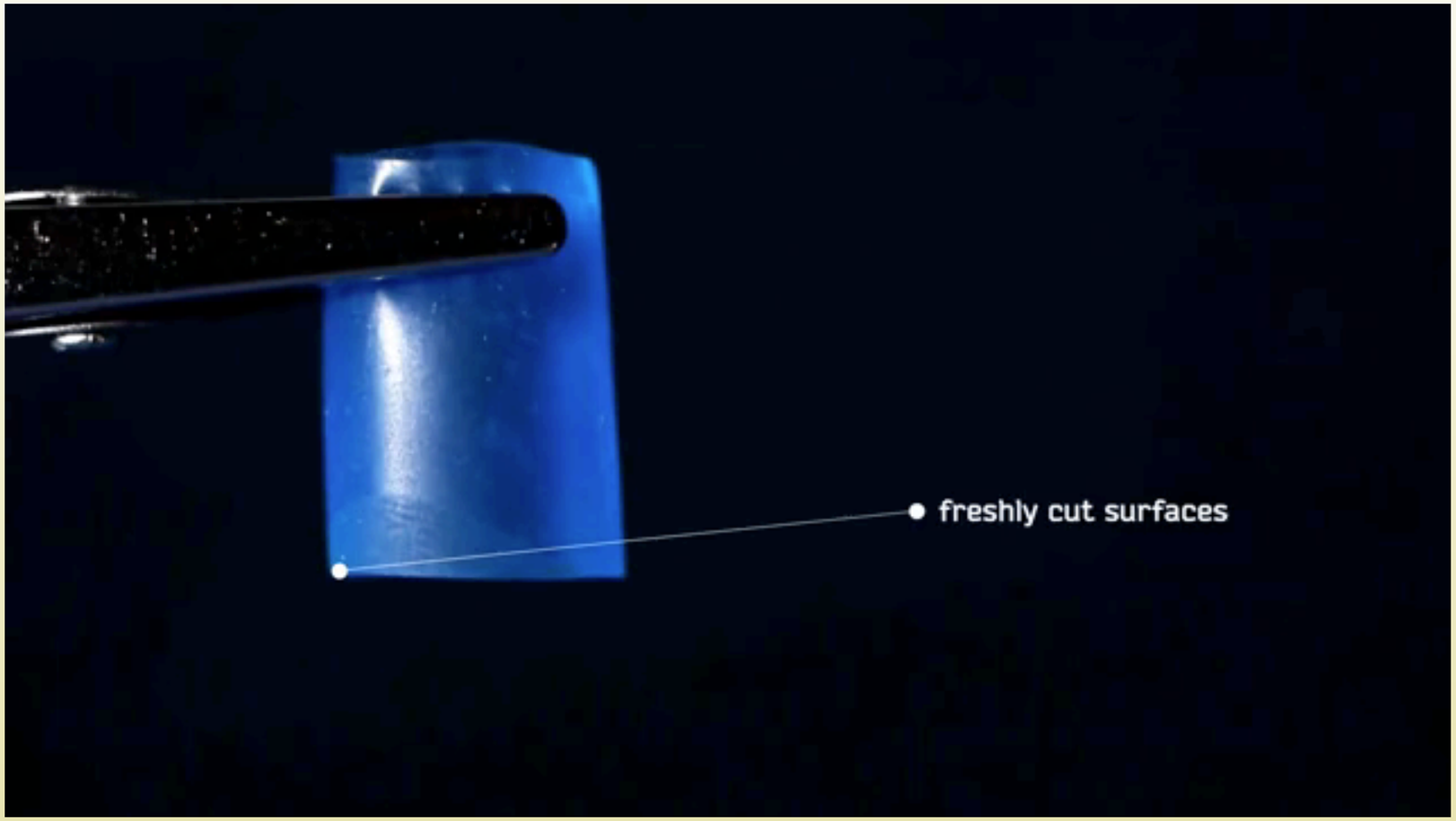
Dynamic structures in synthetics: vitrimers

Vitrimers
As stable as thermosets
As malleable as thermoplasts

http://www.univ-psl.fr/default/EN/all/psl_en/the_vitrimer.htm

Dynamic structures in synthetics: self-healing





https://youtu.be/F0ItKCH24ck?t=27s

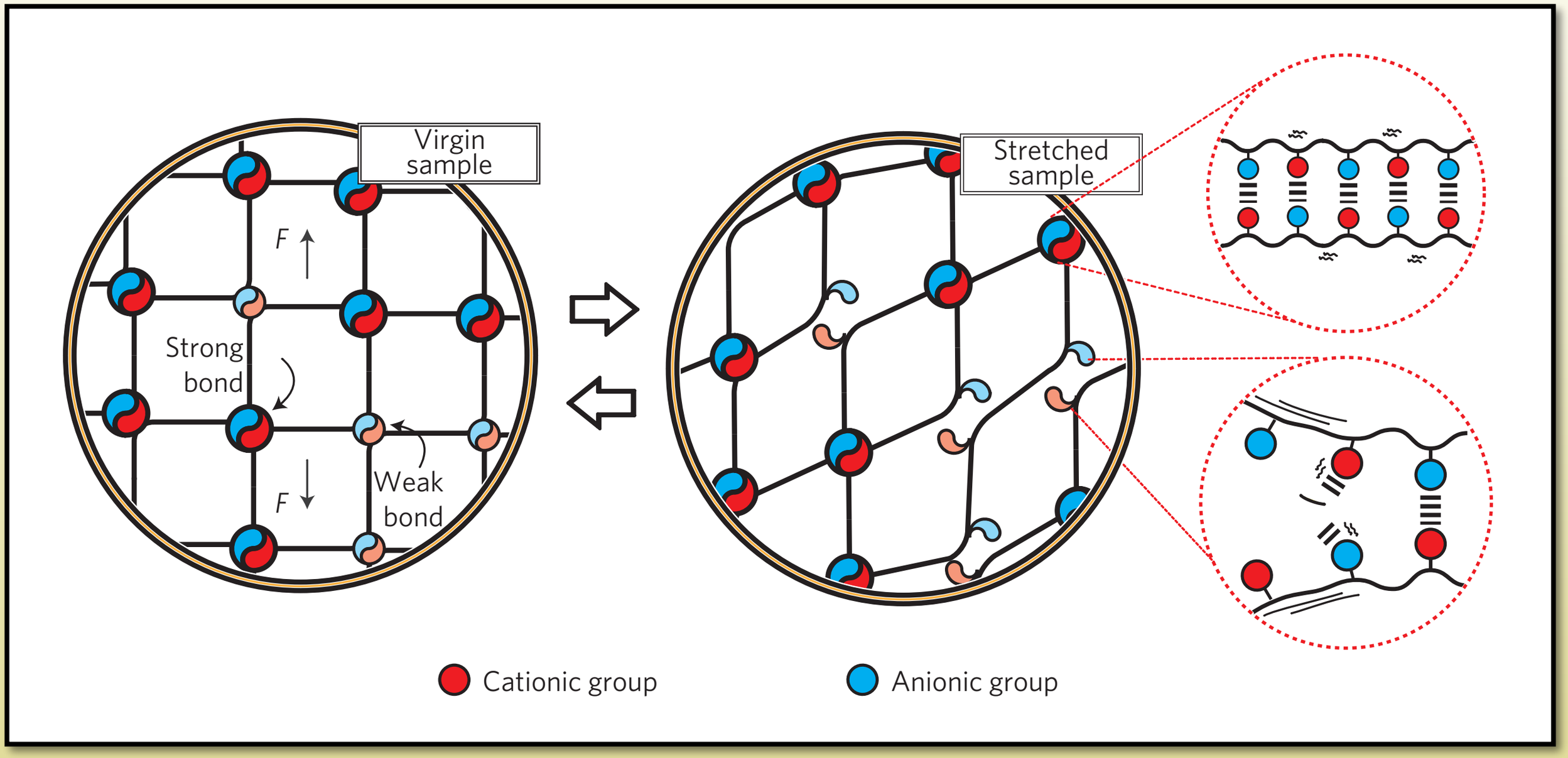
Cordier et al., Nature **451**, 977–980 (2008).

Outline

- Crosslink dynamics ⟺ mechanical properties
- Recent experimental advances
- Our research questions
- Our modeling approach
- 3TU perspective

Strong and weak crosslinks

Reversible Crosslink: Any crosslink that can reform by itself after damage



Sun et al., *Nat. Mater.* **12** 932 (2013)

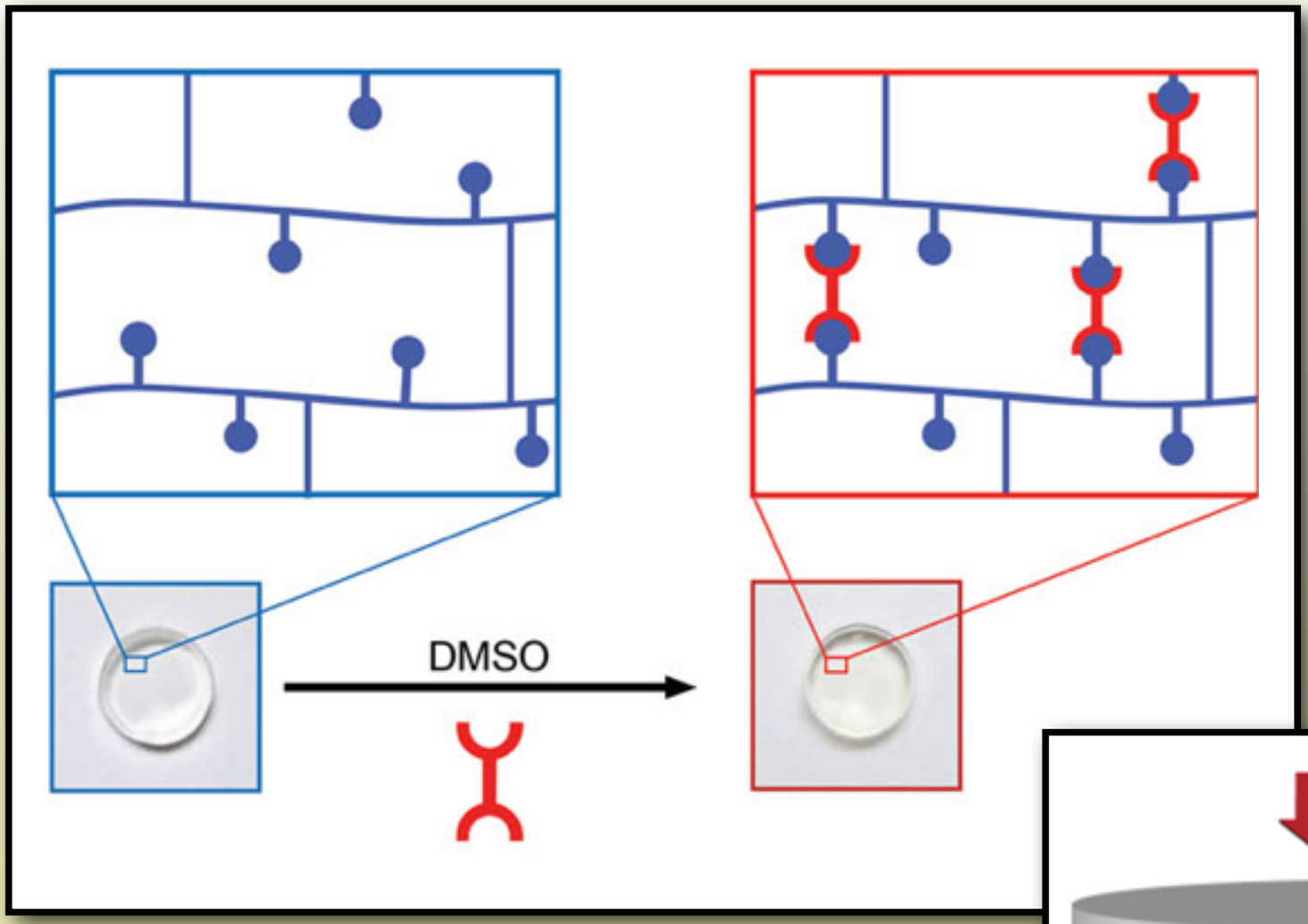
Lifetime vs. Strength of Crosslinks

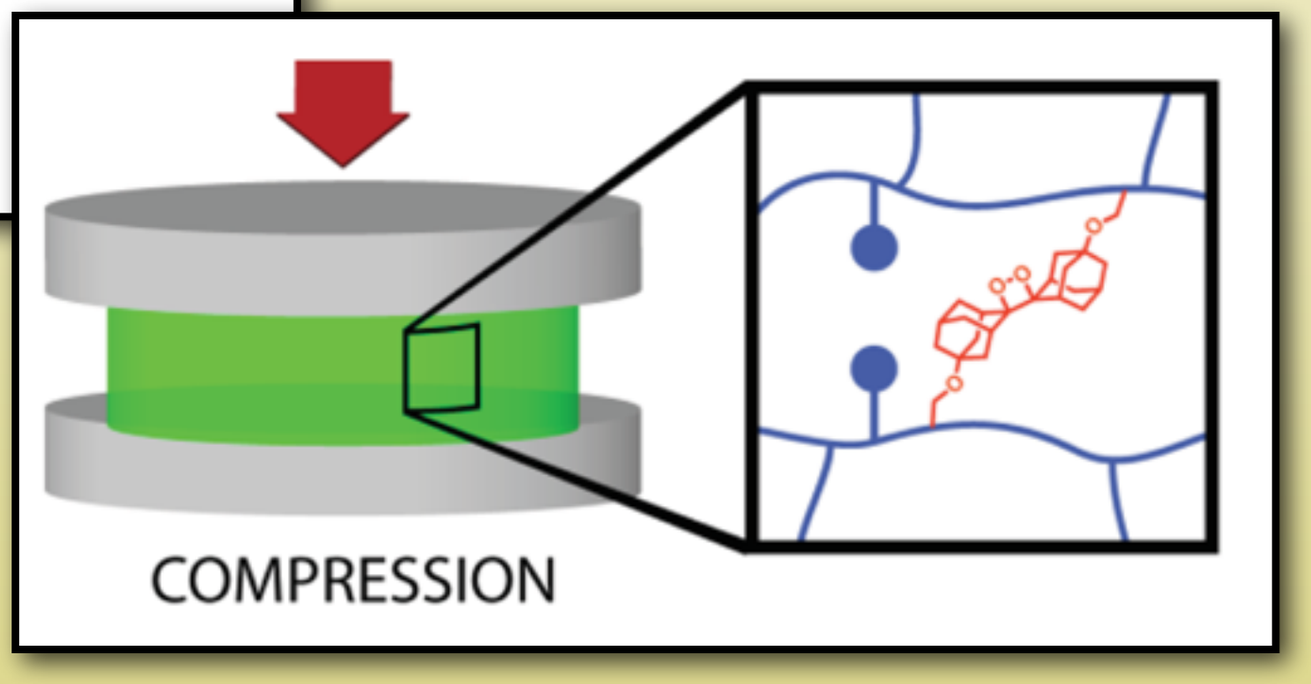
	weak	intermediate	strong
binding energy	*<< thermal energy*	*~ thermal energy*	*>> thermal energy*
lifetime	*very short*	***relevant to timescale of deformations***	*"infinite"*
mechanics	*weak*	***interesting***	*as a permanent bond*

Lifetime vs. Strength of Crosslinks

intermediate-strength reversible crosslinks are most interesting for the mechanics

Gels with added reversible linkers





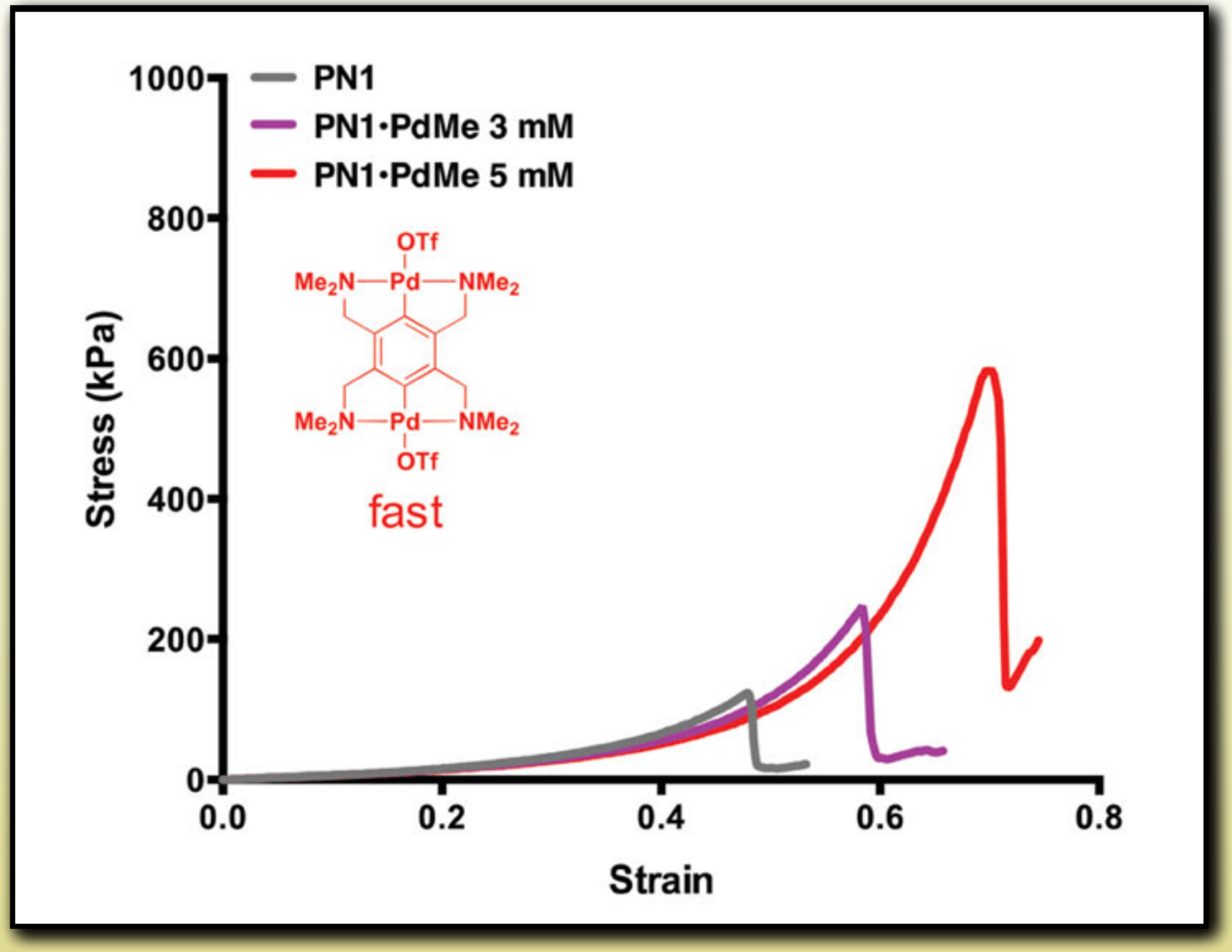
Z.S. Kean *et al.*, *Adv. Mater.* **26** 6013 (2014)

Stress and strain for various linkers

Fast linkers
no linear effect
some toughening

Slow linkers
no linear effect
large toughening

Very slow linkers
higher modulus
more brittle



Z.S. Kean *et al.*, *Adv. Mater.* **26** 6013 (2014)

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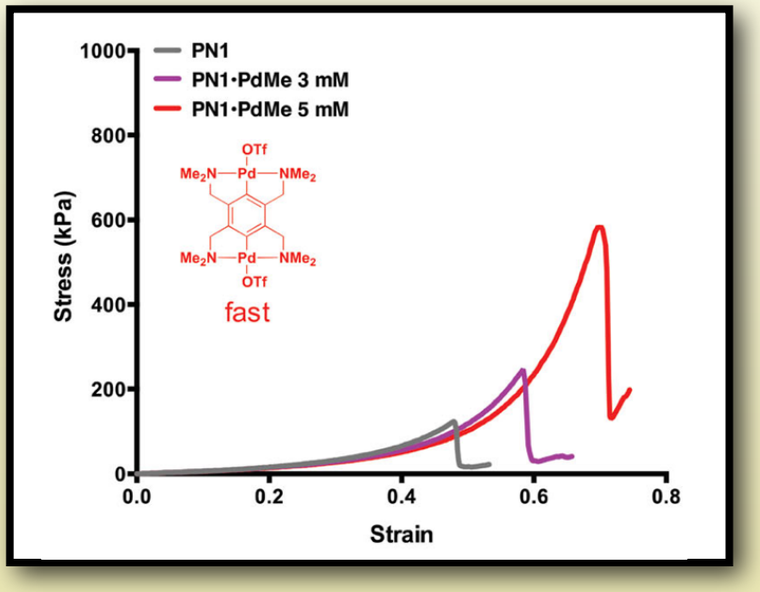

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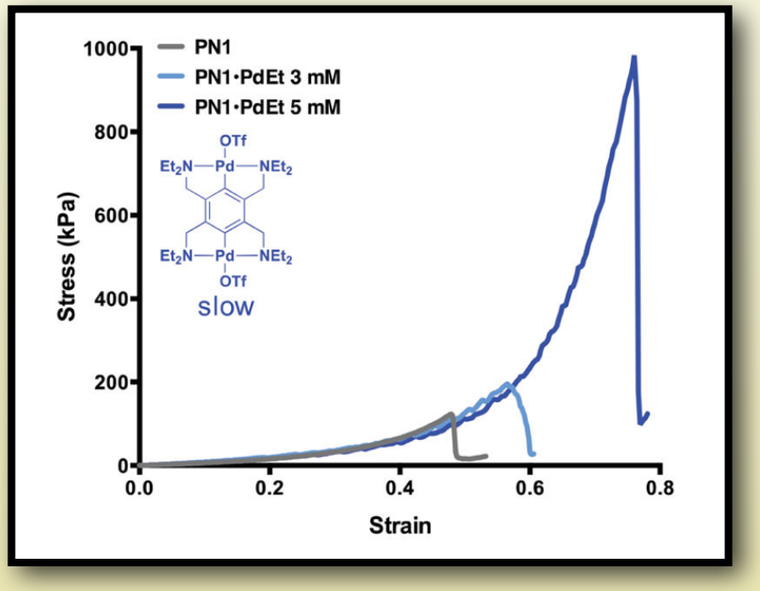

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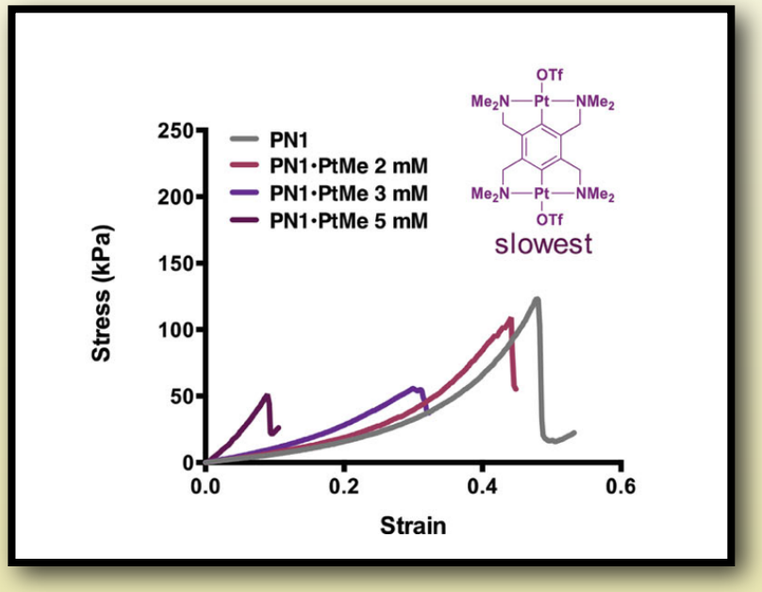


The "slow" (intermediate) linkers increase the strain-at-break and the toughness

Z.S. Kean *et al.*, *Adv. Mater.* **26** 6013 (2014)

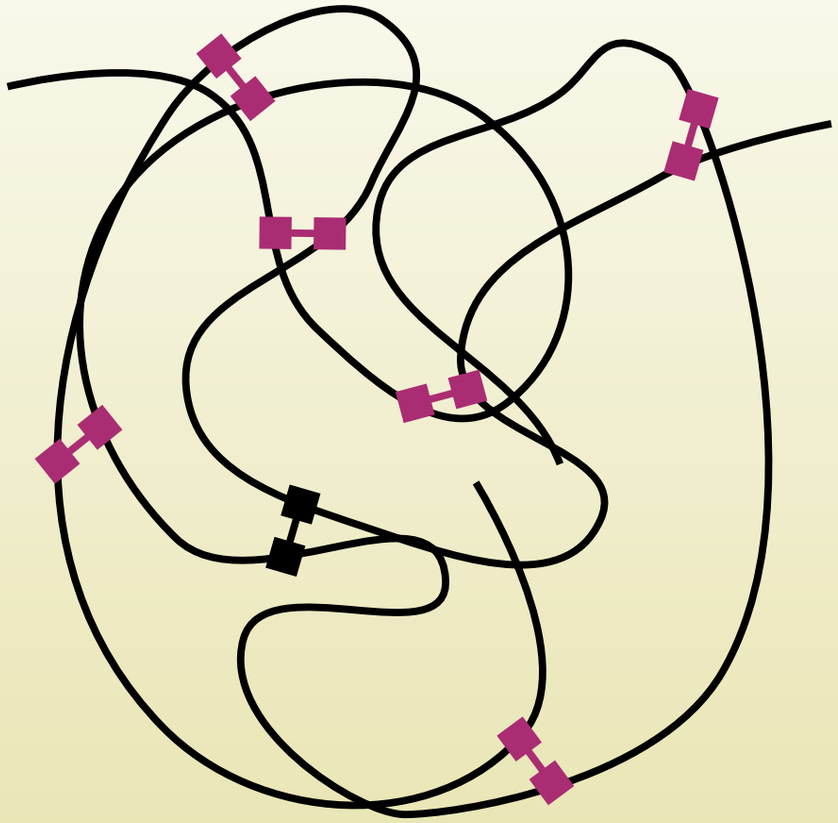
Questions

1. How does the toughening work?

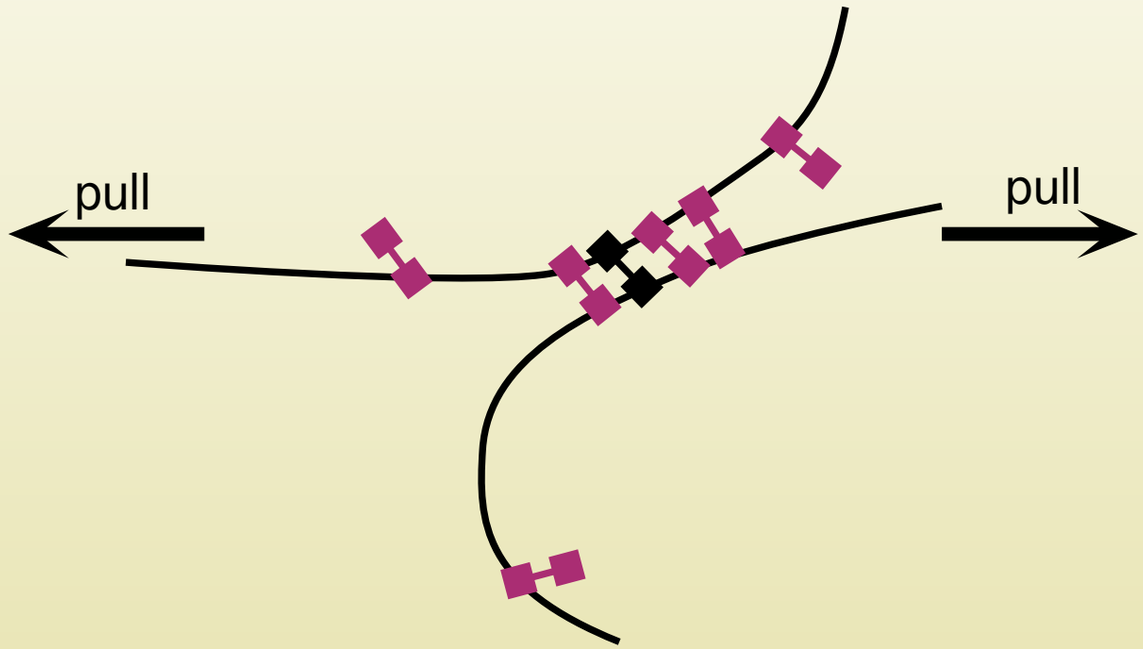
2. Why is the linear modulus unaffected while toughening is induced at larger strains?

3. How can we maximize the toughening effect?

Ideas: Rebinding and cooperativity



Relaxed



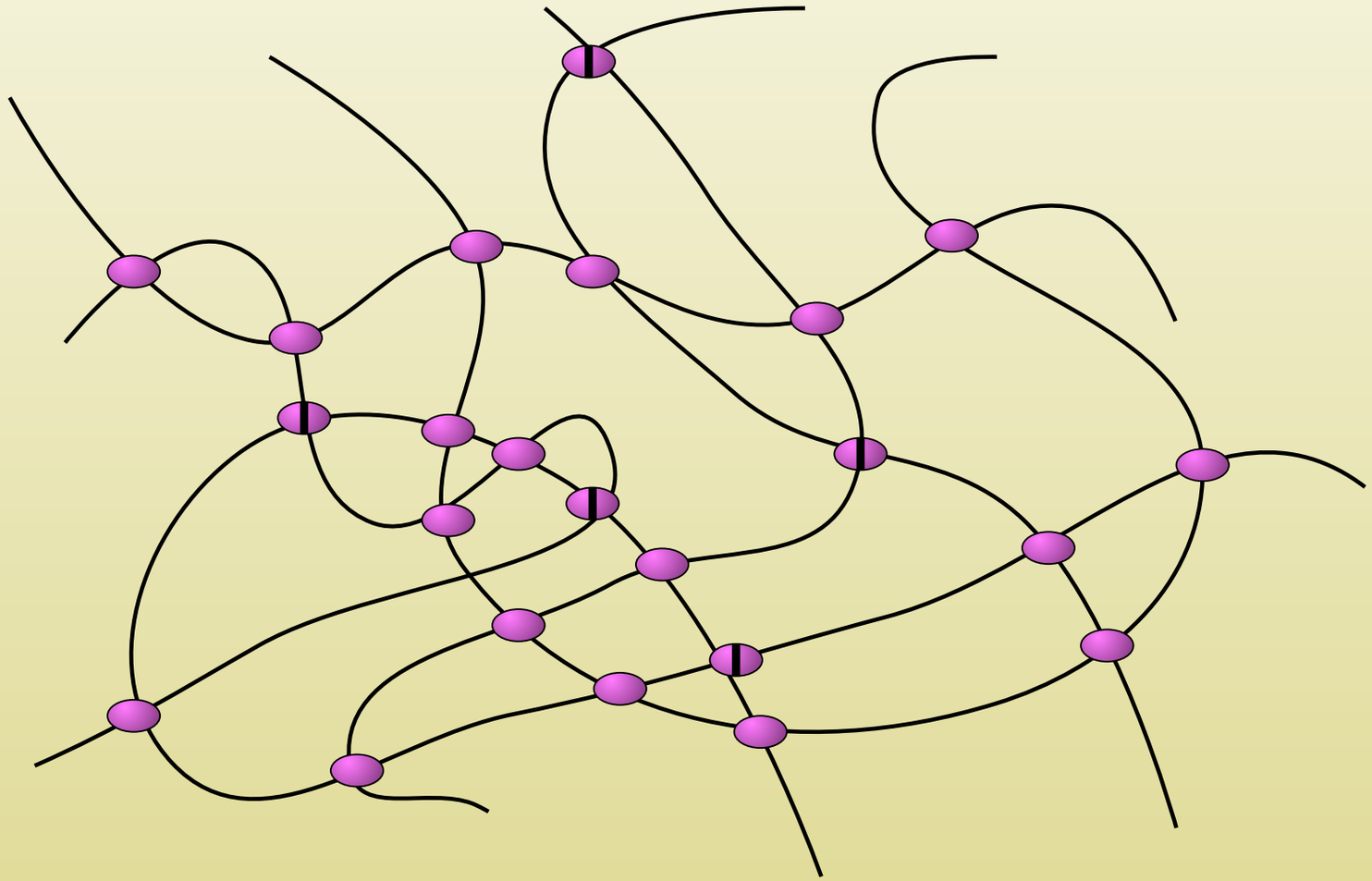
Under tension

reversible crosslinker

permanent crosslinker

Ideas: Clusters of Linkers

- cluster of reversible linkers
- cluster of reversible linkers around permanent linker



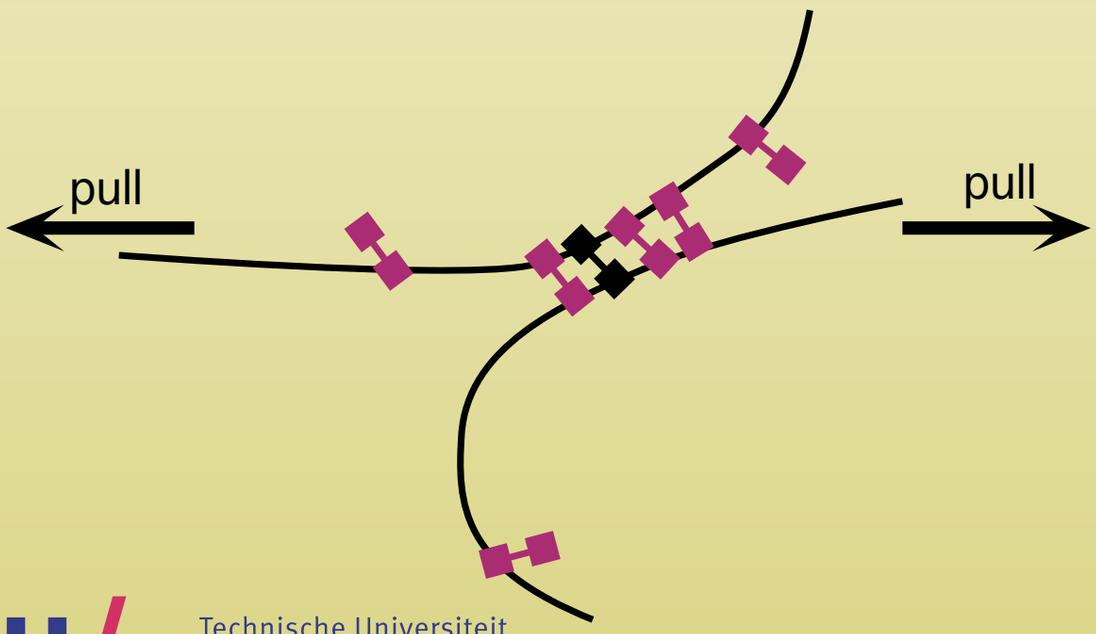
Multiscale approach

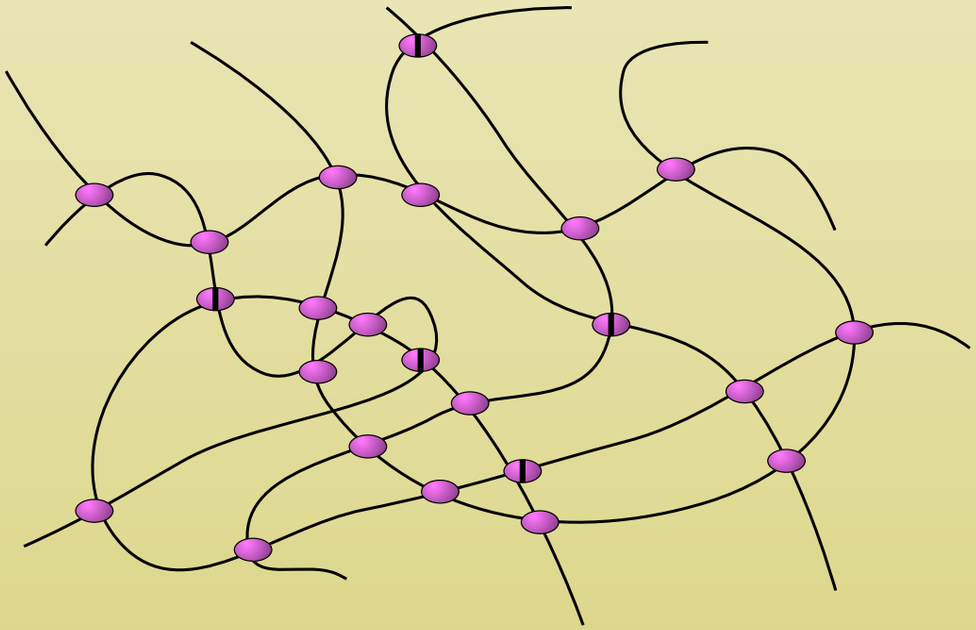
Step 1
understand dynamics of clusters of linkers

Step 2
effective description of linker clusters for network study

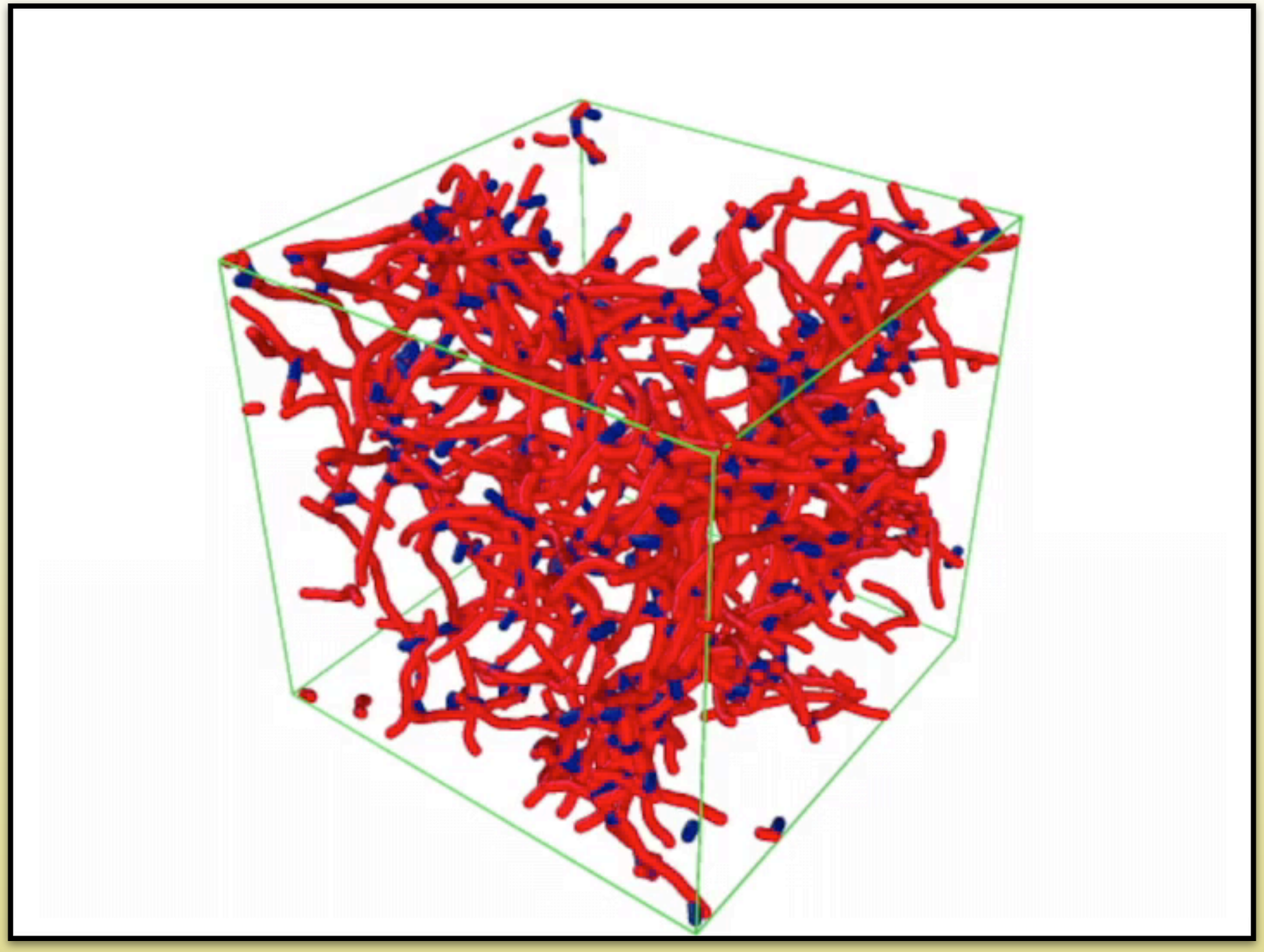
Coarse grained MD
- include permanent and reversible linkers
- vary composition
- vary lifetime of reversible linkers
- find strain-rate dependent stress-strain curves

Hybrid Langevin / MC model
- add linker clusters
- study strain-rate dependent mechanics





Reversible linkers in model collagen



Movie by Cyril Vrusch (Ph.D. student)

Design optimization

Goals
- Identify high-potential material designs
- Other targets than strain-at-break or toughness?

Additional experiments to verify numerically obtained ideas?

Collaborations towards new applications?

Perspective within 3TU

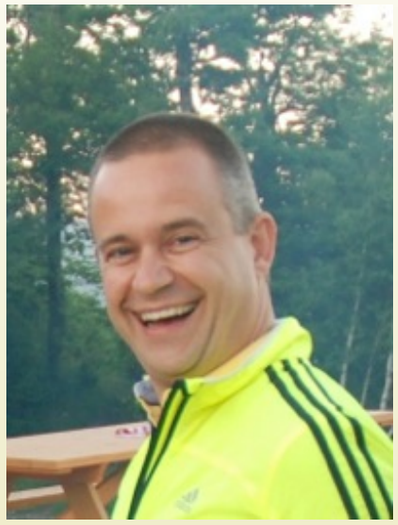
within the context of this project

Eindhoven
Macromolecular and Organic Chemistry
Delft
Advanced Soft Matter Group (Chem.E)
Engineering Thermodynamics Group (3ME)
Twente
Materials science and Technology of Polymers

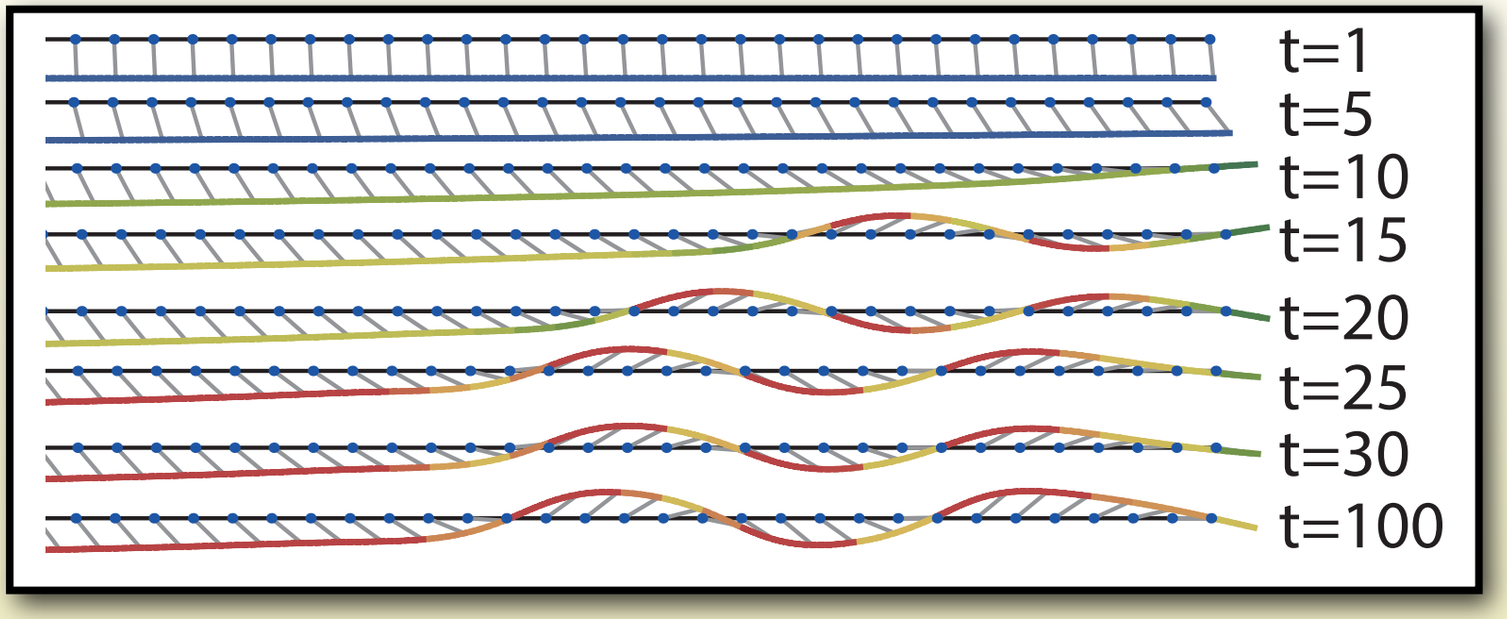
other topics?

???

Activities within TPS

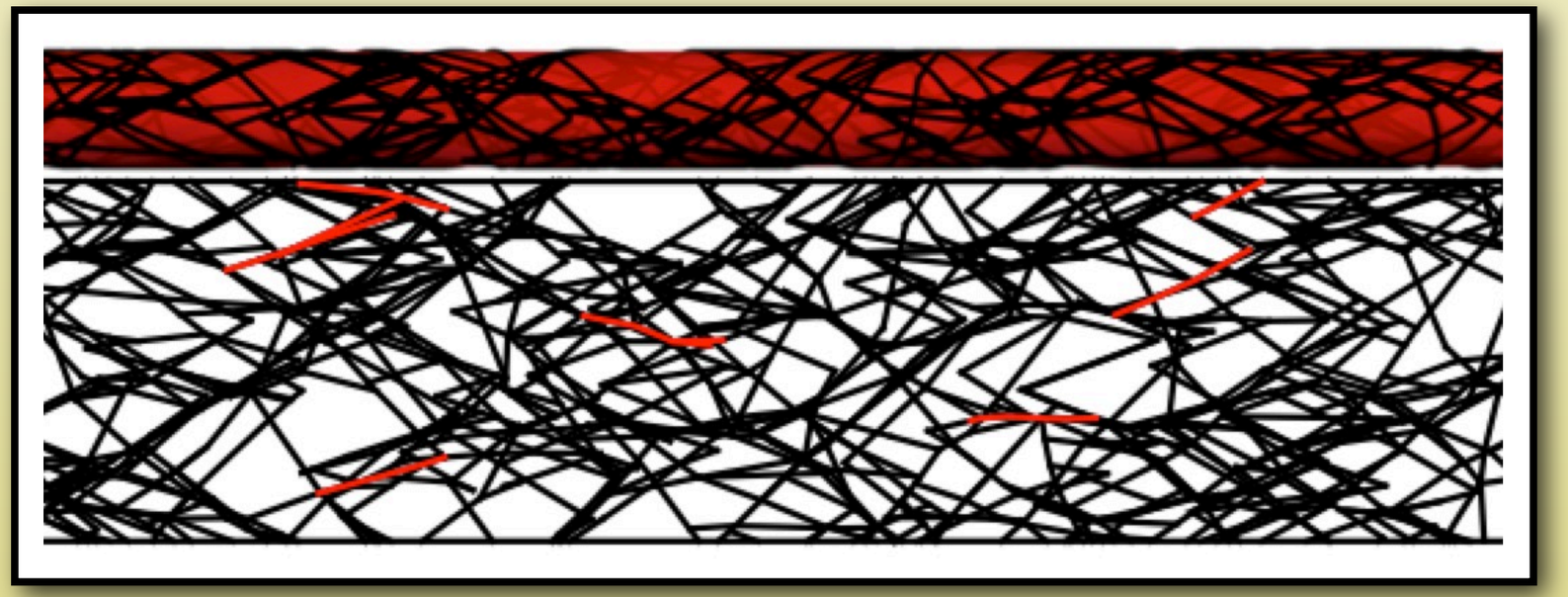


Kees Storm



buckling of growing filaments (with Remy Kusters, L. Mahadevan)

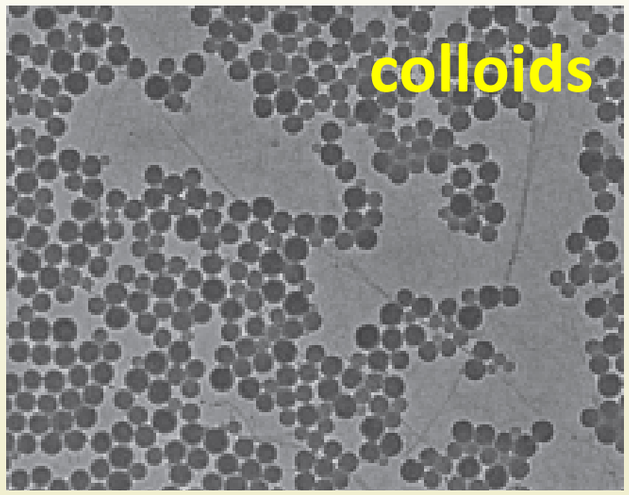
Function and soft mechanics of biomaterials



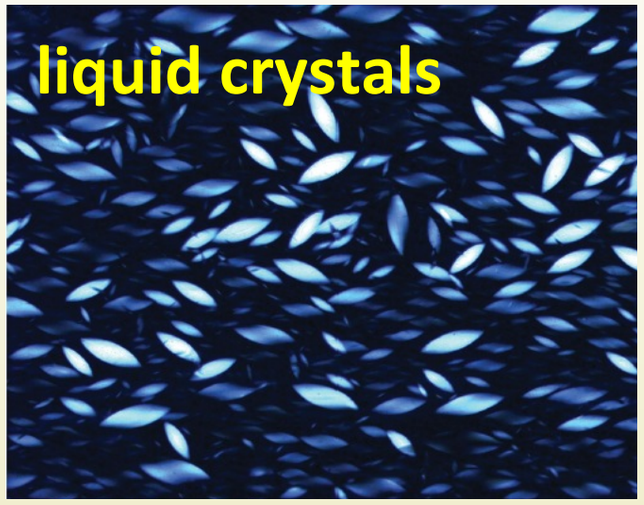
cross-hatched ordering of collagen fibers (with Cyril Vrusch, Carlijn Bouten)

Activities within TPS

Paul van der Schoot

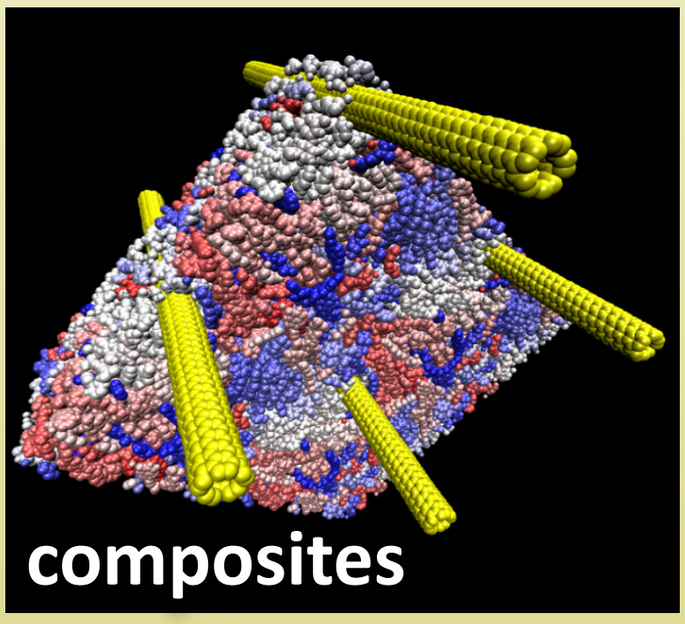


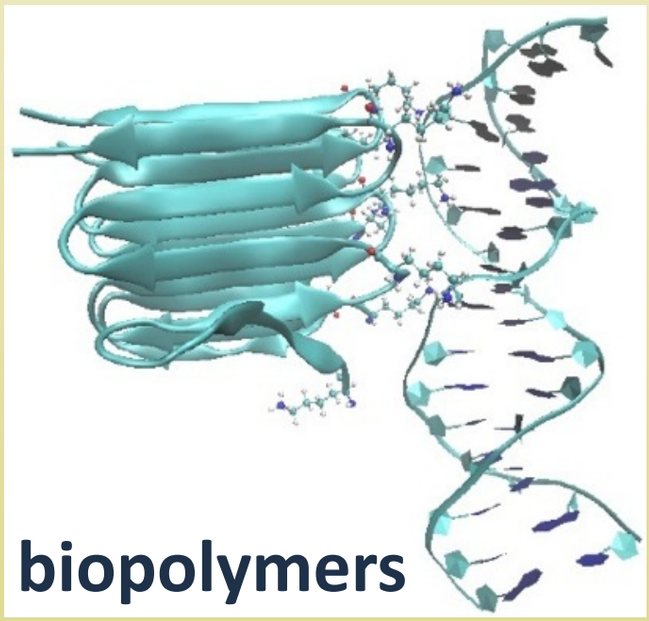
Kyrylyuk et al. *Nature Nano* **6** (2011), 364



Jamali et al. *PRE* **91** (2015), 042507

Self-assemby of soft and biomaterials





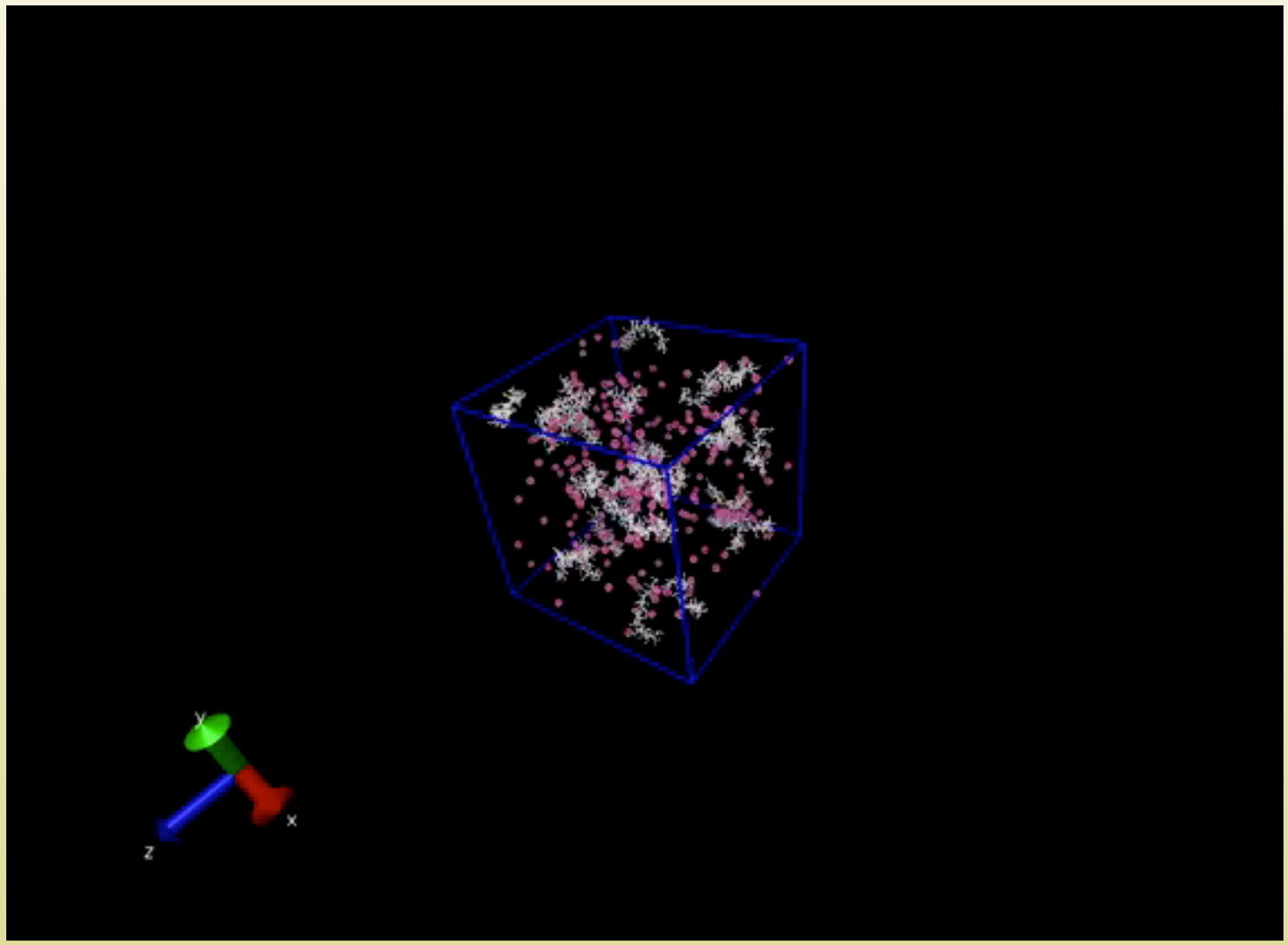
Activities within TPS

Alexey Lyulin

Multiscale simulation of polymer dynamics

Focus on Nanocomposites

CNT, graphene – polyimide
carbon black – rubber
silica – rubber
modified cellulose - PLA
silica - Nafion
fullerene - P3HT
CNT – vitrimer epoxy
….

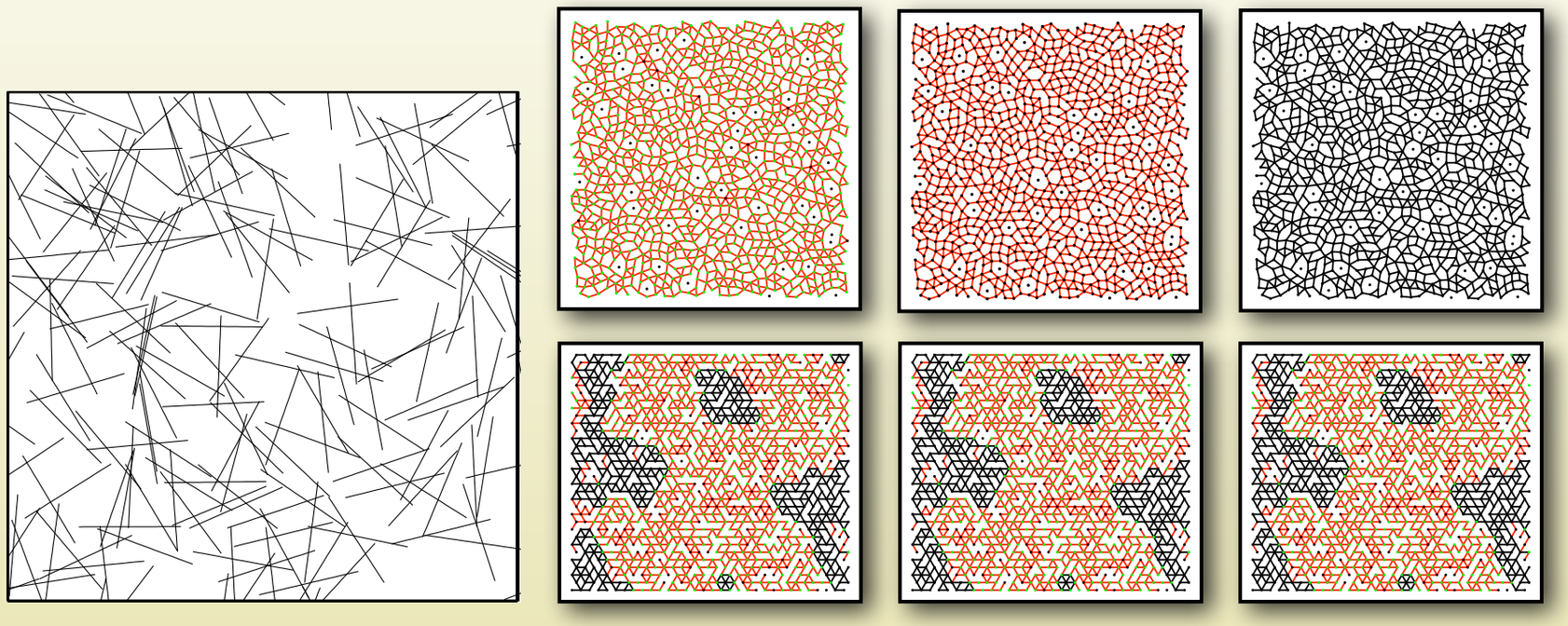


Formation of P3HT/PCBM solar cells

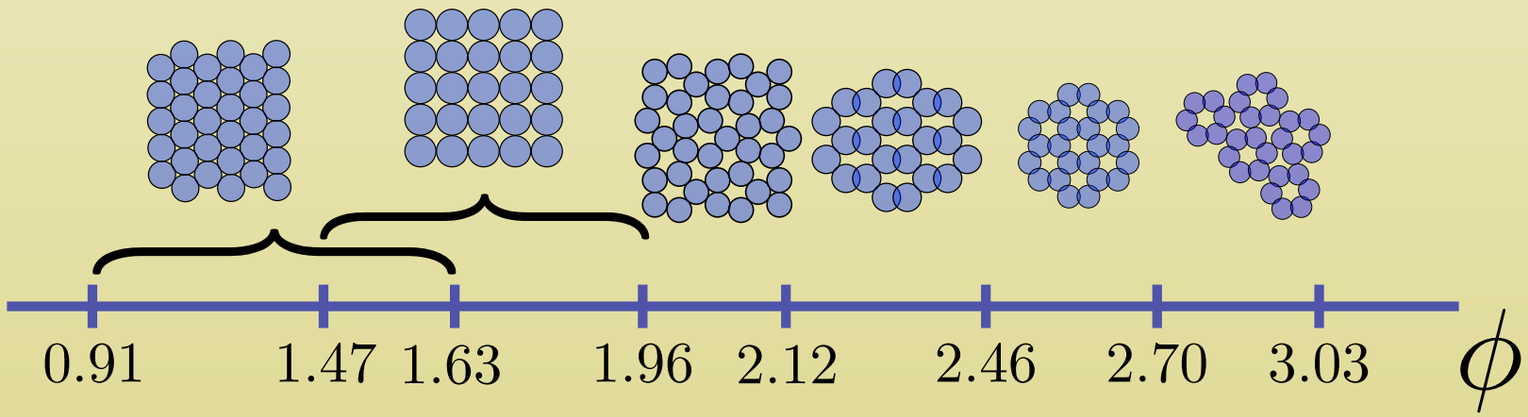
Activities within TPS

Wouter Ellenbroek

Responsive soft matter

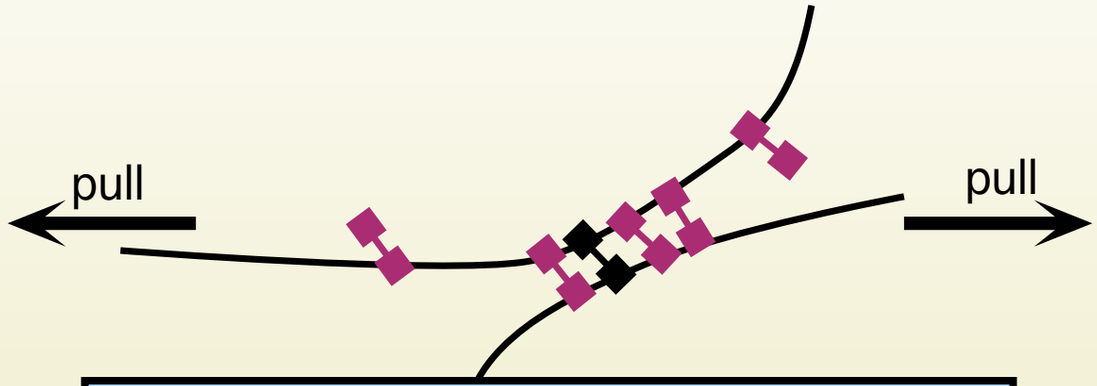


disordered networks and composites on the verge of losing rigidity



Simple building blocks for unusual self-assembling structures

In short...



How and why do intermediate-strength reversible crosslinks toughen gels?

Kees Storm

Cyril Vrusch

Rint Sijbesma

Costantino Creton (ESPCI)

FOM

TU/e Technische Universiteit Eindhoven University of Technology

NWO Netherlands Organisation for Scientific Research

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