Dodynet Montpellier Meeting 21/10/2021

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Double Dynamic Networks Based on Dynamic Covalent Bonds

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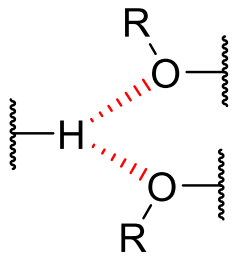
Polymers

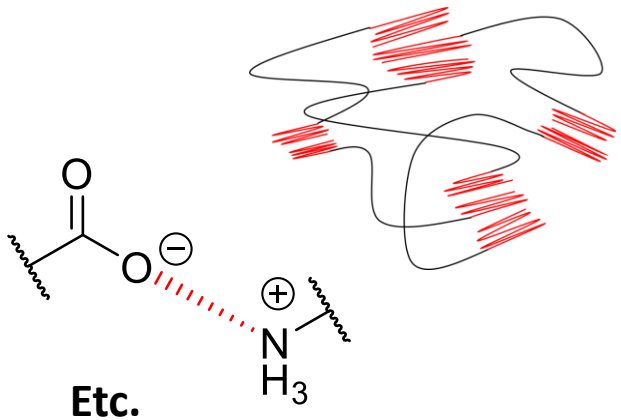
Thermoplastics

Dynamic Networks

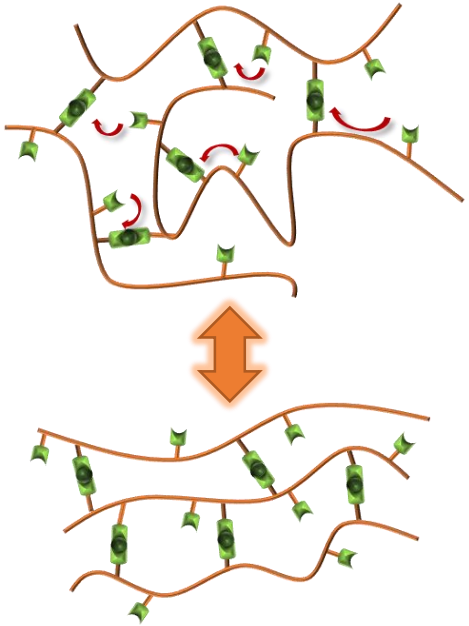
Thermosets

Physical Crosslinks

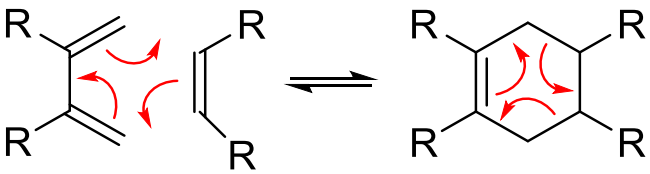


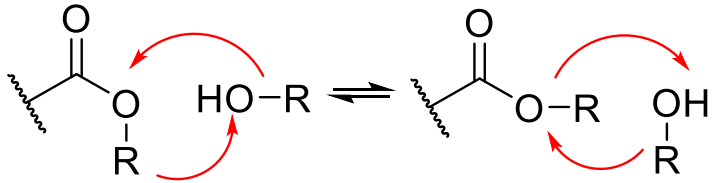


Etc.



Dynamic Covalent Crosslinks





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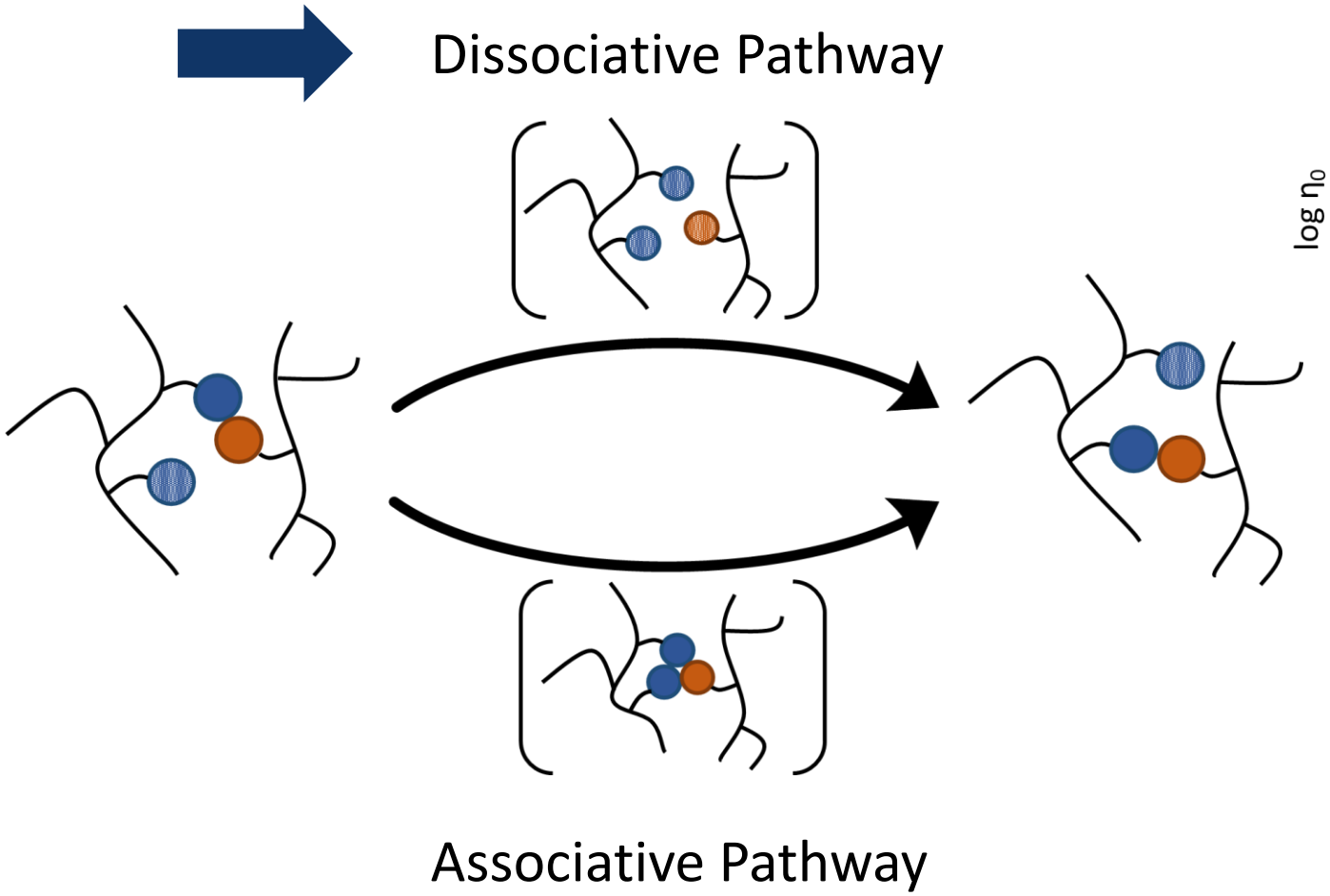
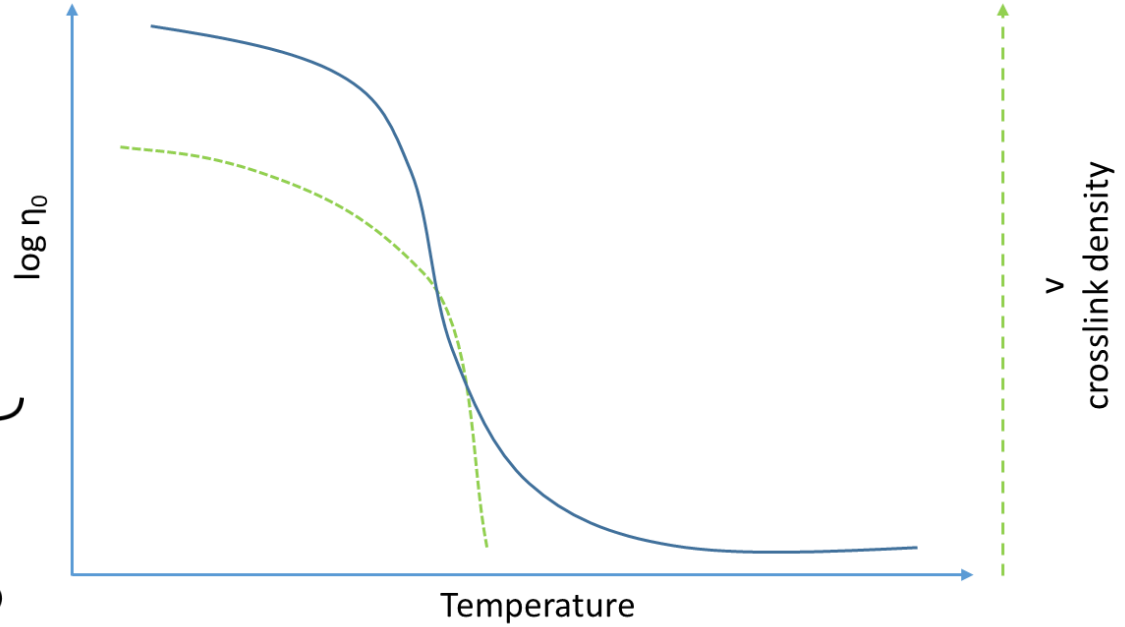
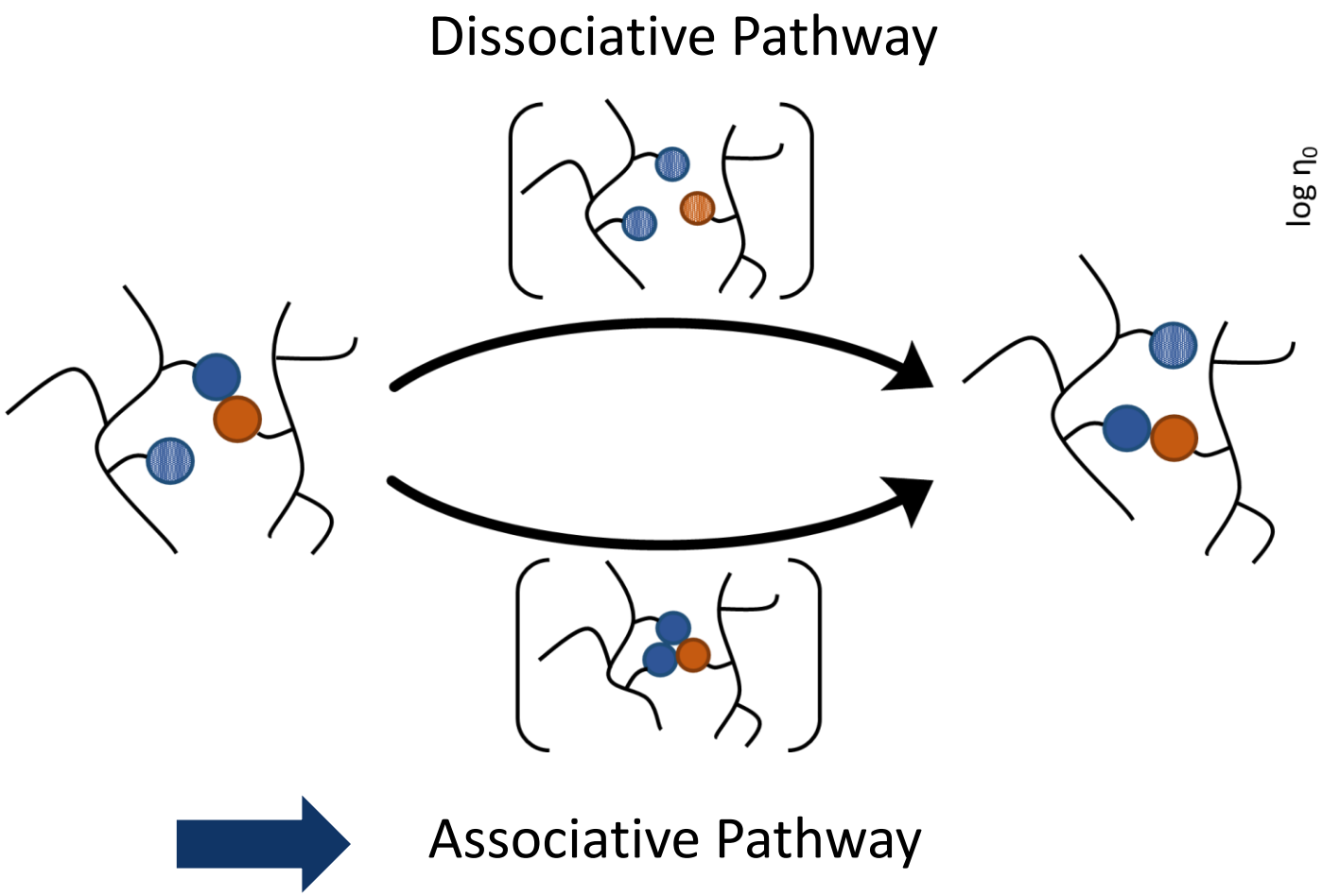
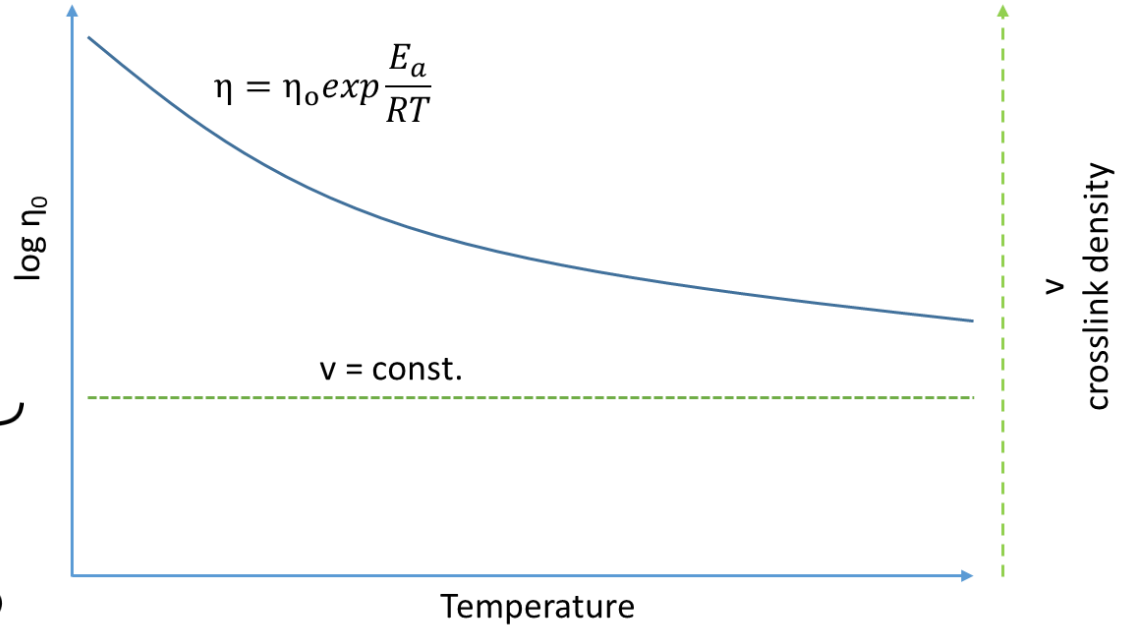




Leibler *et al*. *Science.* **2011**, *334* (6058), 965–968.





Vitrimers

Leibler *et al*. *Science.* **2011**, *334* (6058), 965–968.

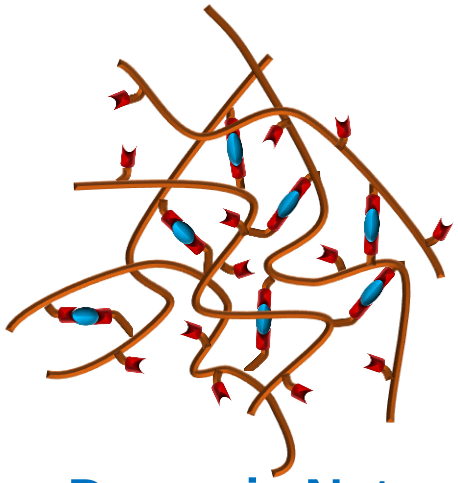
Project Goal

Vitrimer crosslinks A

Double Dynamic Network (DDN)

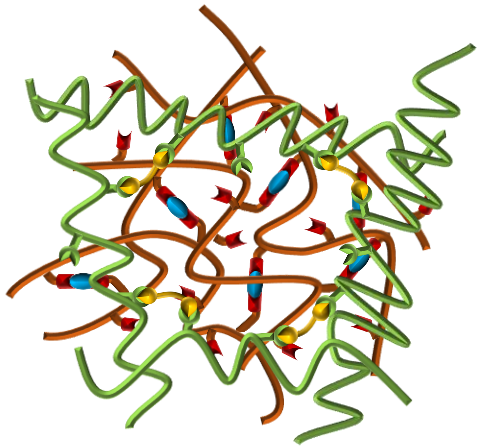
Vitrimer crosslinks B

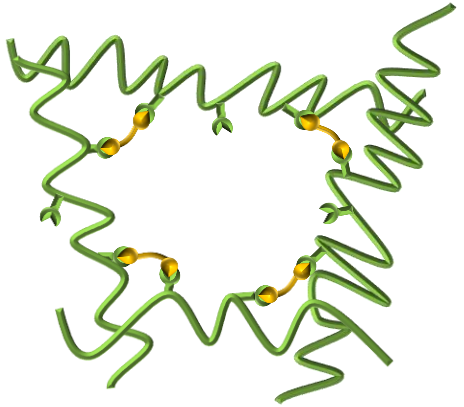
Interpenetrated Network



Dynamic Network

- Fast reshuffeling
- Energy dissipation
- Prevents damage
- Mechanical reinforcement





Structural Network

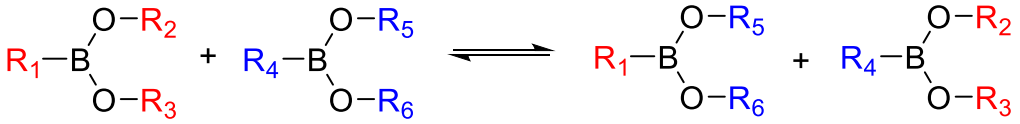
- Dimensional stability
- Elasticity
- Prevents creep
- Slightly dynamic: Maintain processability

Project Goal

Two responsive modes — Associative Mechanisms — Orthogonal

Dynamic Network

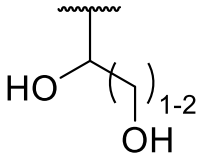
Boronic ester exchange



$E_a \approx 16$ kJ mol^{-1} [1]

- High crosslinking density
- Many functional groups
- Fast exchange

Other reaction partners:

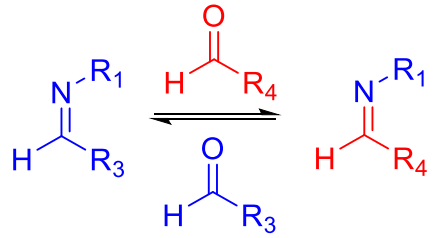


H_2O (neutral, acidic)

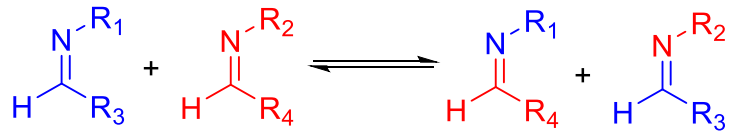
1) Röttger et *al.* ; *Science* **2017**, *356*, 62-65.

Structural Network

Imine/ Aldehyde and Imine/imine exchange



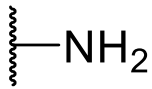
$E_a \approx 30$ kJ mol^{-1} [2]



- Low crosslinking density
- Few functional groups
- Slow Exchange

Other reaction partners:

H_2O (acidic)

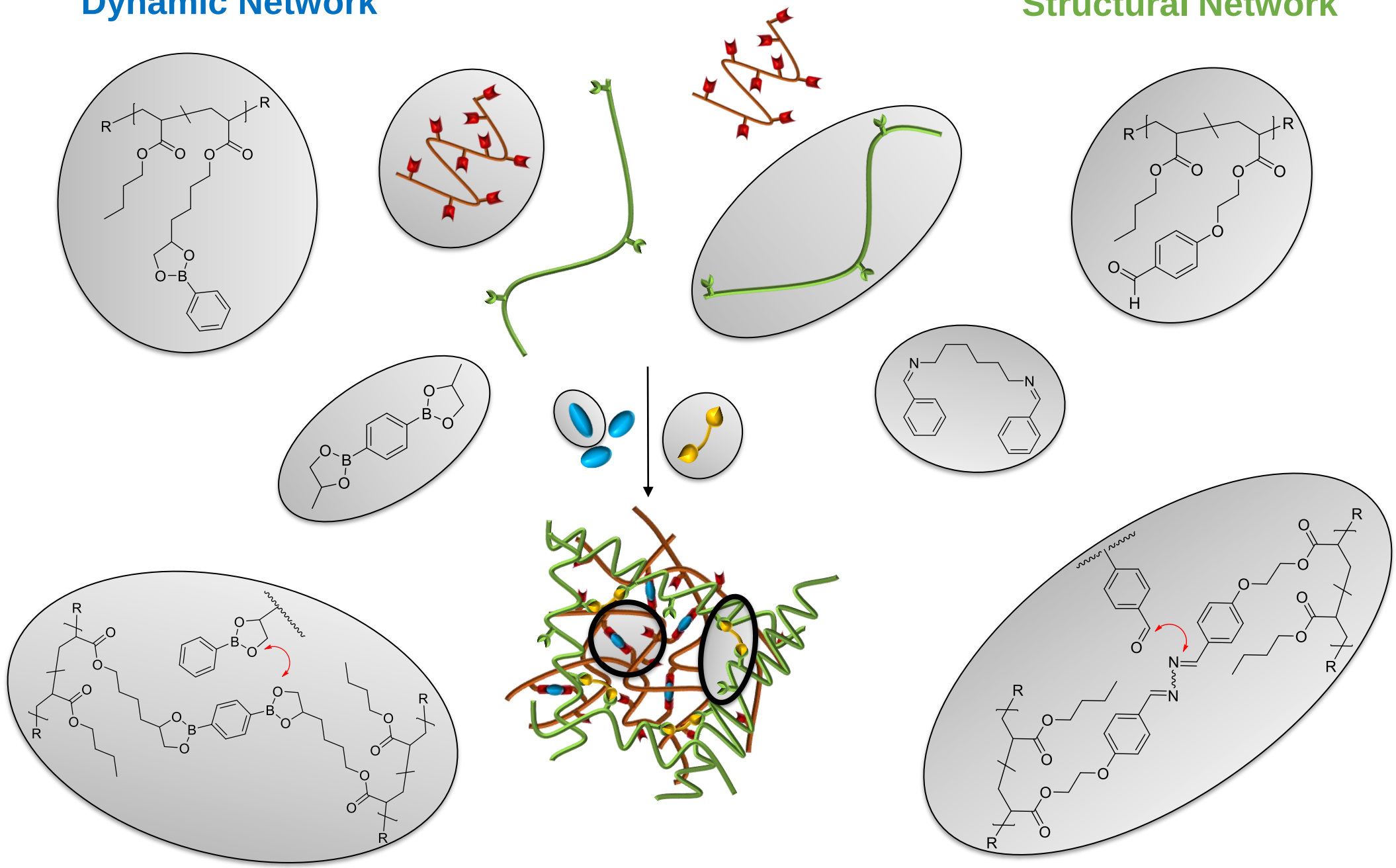


2) Röttger, M., (2016). Associative Exchange Reactions of Boron or Nitrogen Containing Bonds and Design of Vitrimers (Doctoral dissertation).

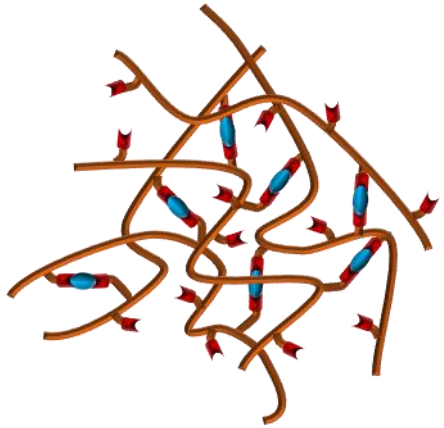
Project Goal

Dynamic Network

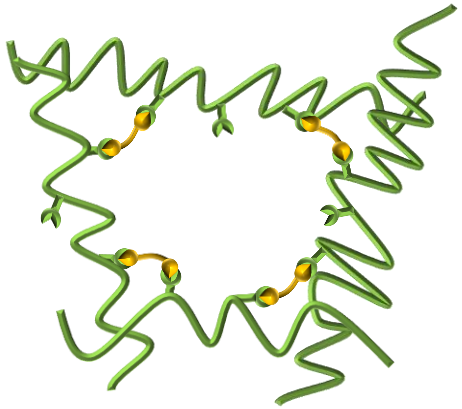
Structural Network



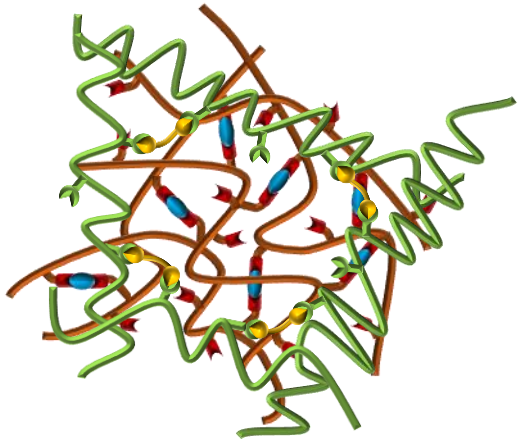
Comparative Study



vs.



vs.



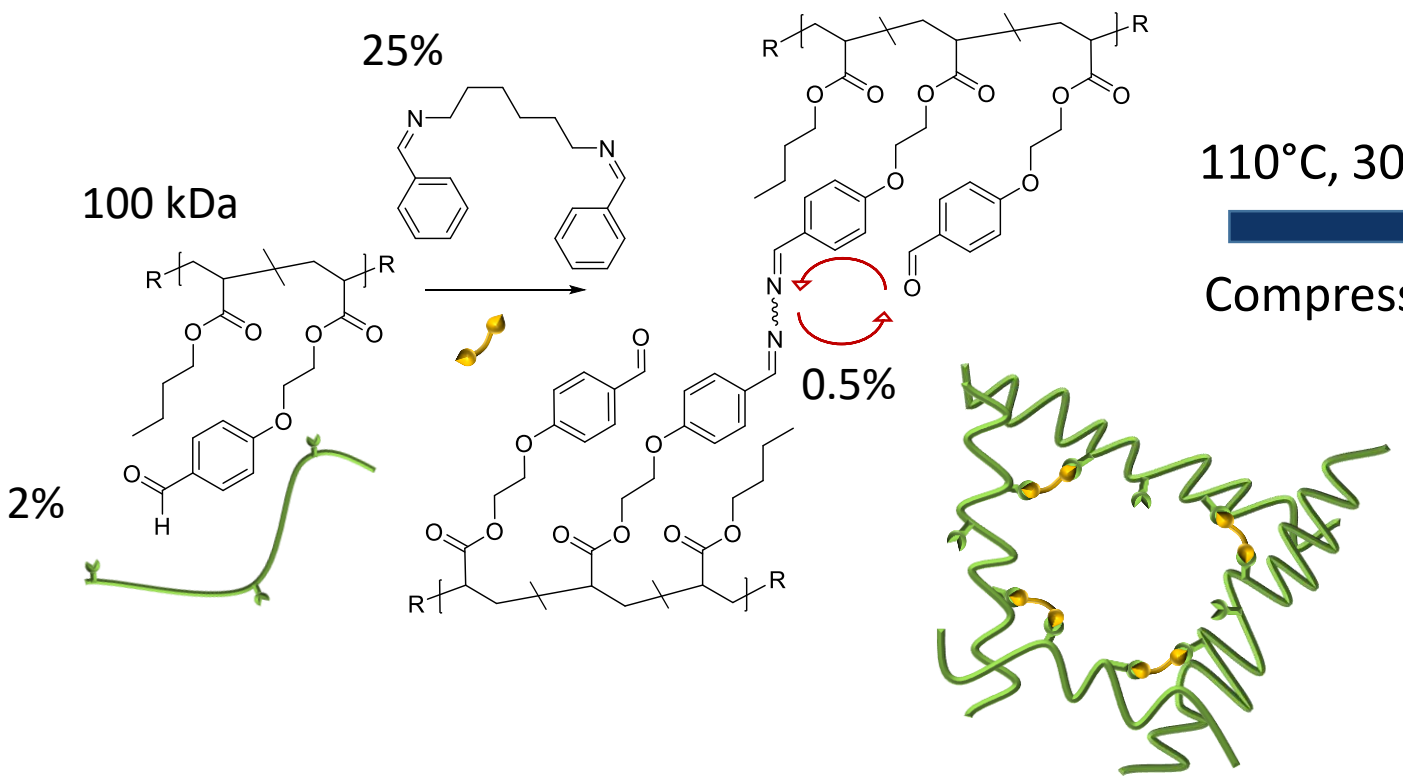
Dynamic

Dimensional stable, but processable

Properties to be determined

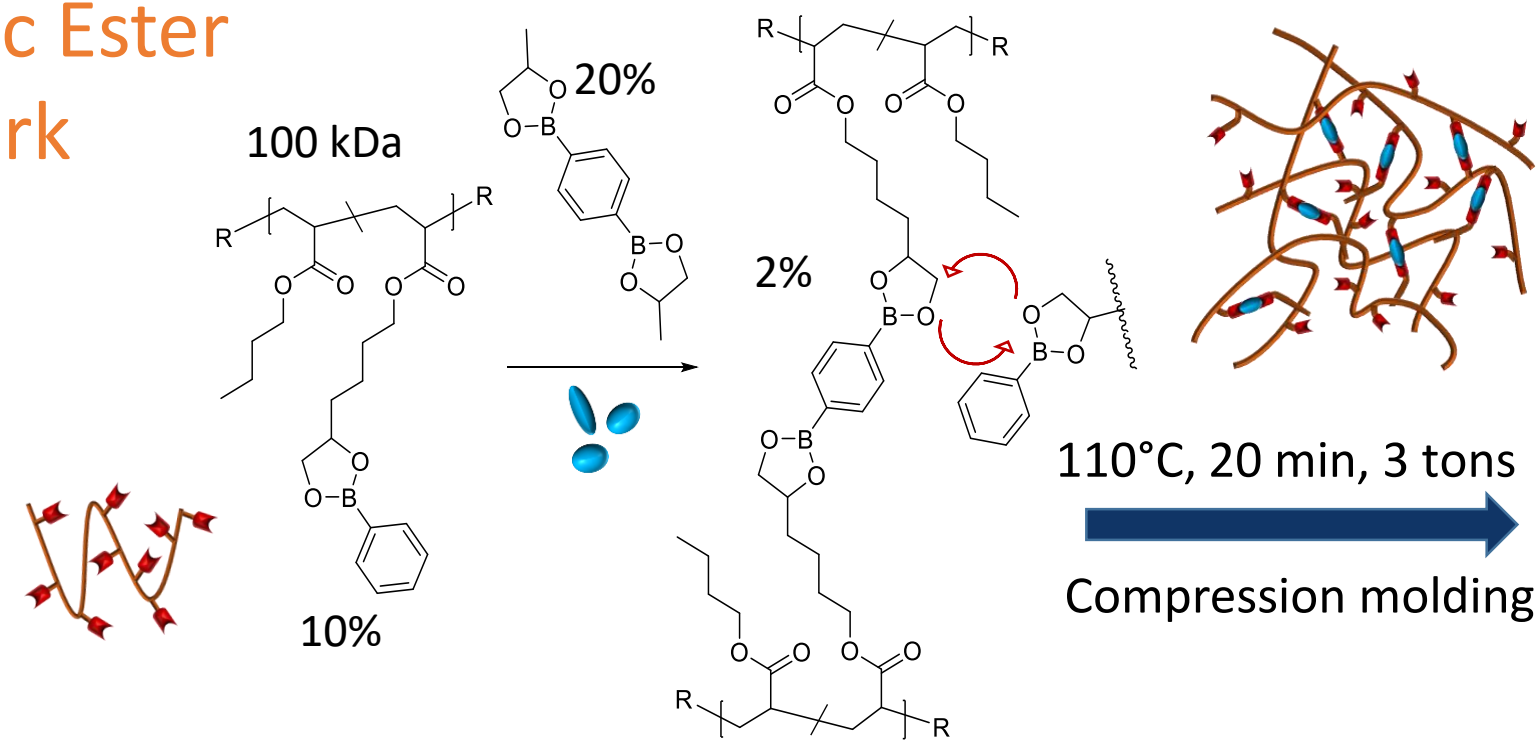
- Prepare single networks
- Adapt to fulfill requirements
- Combine them to double network
- Comparative study

Imine-Aldehyde Network



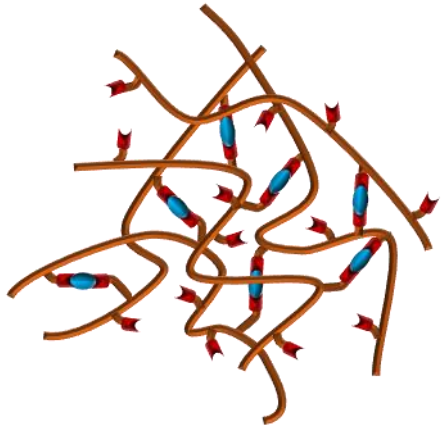
- Shows sufficient dimensional stability at ambient conditions
- Well processable at elevated temperatures

Boronic Ester Network



- Shows complete stress relaxation
- Well processable at elevated temperatures

Comparative Study



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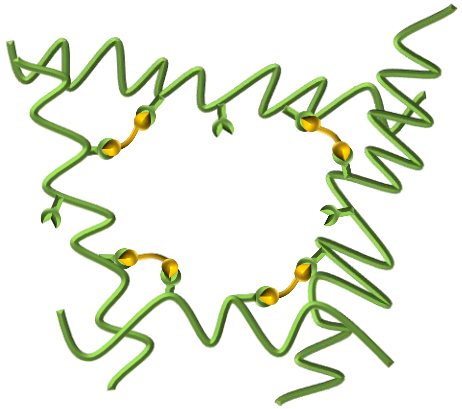
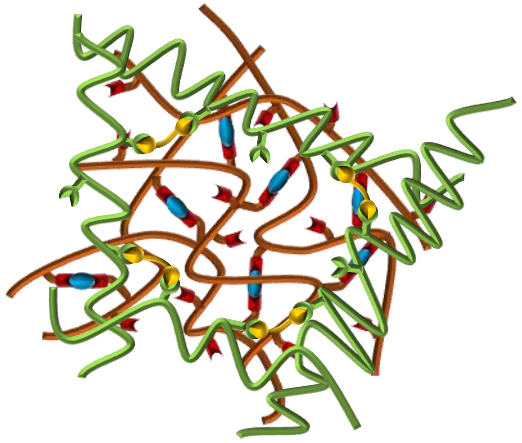


vs.



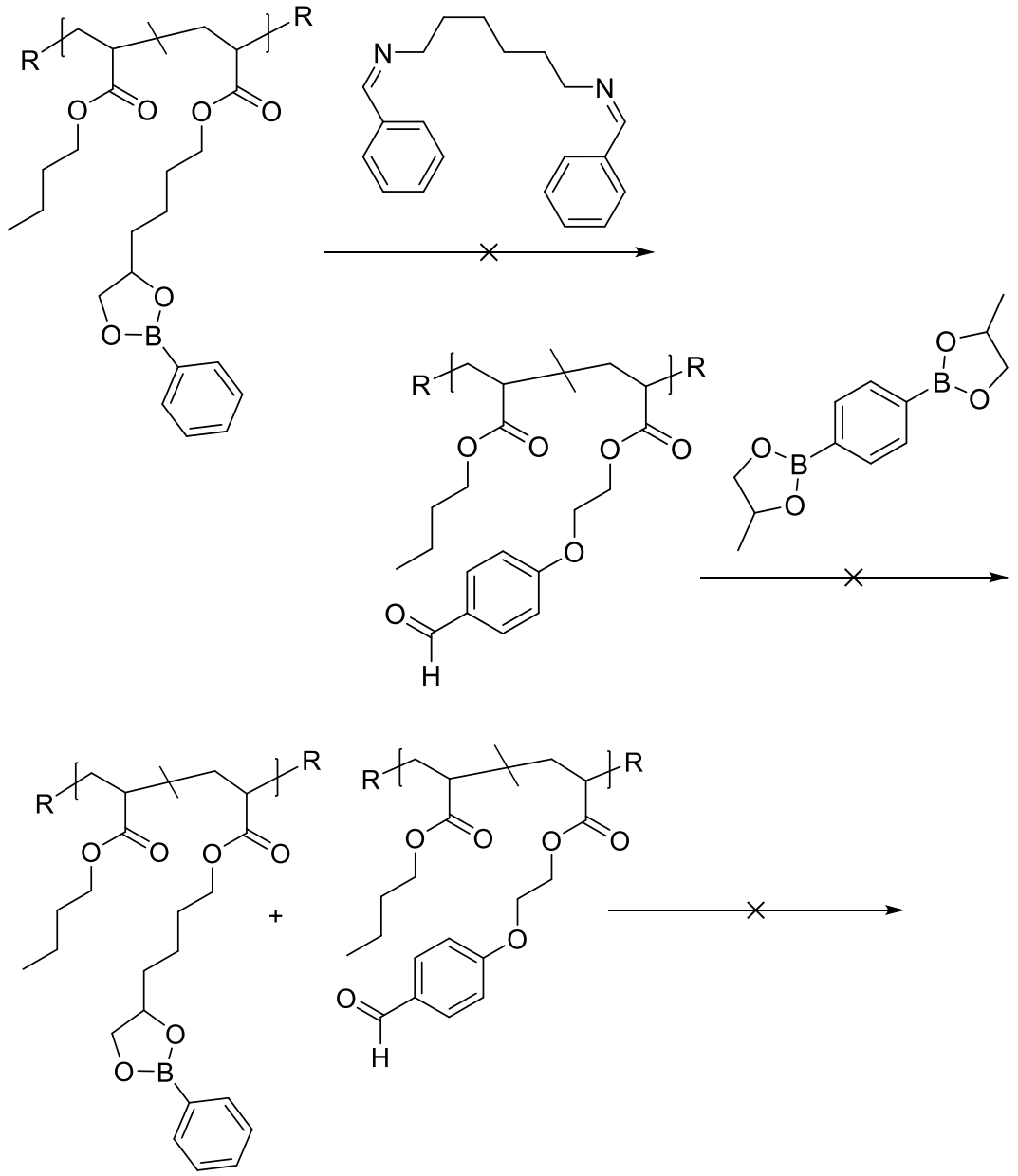
Dynamic ✓

Dimensional stable, but processable ✓

Properties to be determined

- Processability
- Mechanical behavior
- Dynamics
  - Stress relaxation
  - Creep resistance
- Swelling behavior
- Solubility
- Recyclability
  - Mechanically
  - Chemically

Orthogonality Test

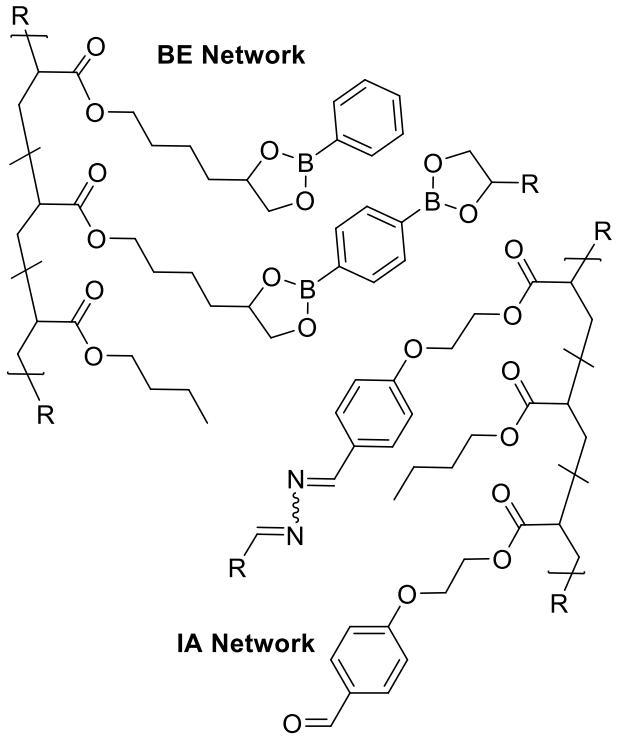


- Mixed and processed like DN
  - Curing at 80°C
  - Compression Molded
  - Analysis: NMR + SEC

- Well soluble
- No change in chemical composition, M_n or $Đ$

Comparative Study

Network	Exchange	Mn [kDa]	DPn	Đ	m (g)	f [%]	N_f(chain)	f(CL) [%]	CL/chain	ρ(CL) [%]
BE	Boronic Ester Metathesis	100	721	1.22	4.87	9.7	70.3	20	14.1	2.0
IA	Imine/Aldehyde Exchange	92	713	1.33	4.87	1.95	13.9	25	3.5	0.5



20-30 min
110°C

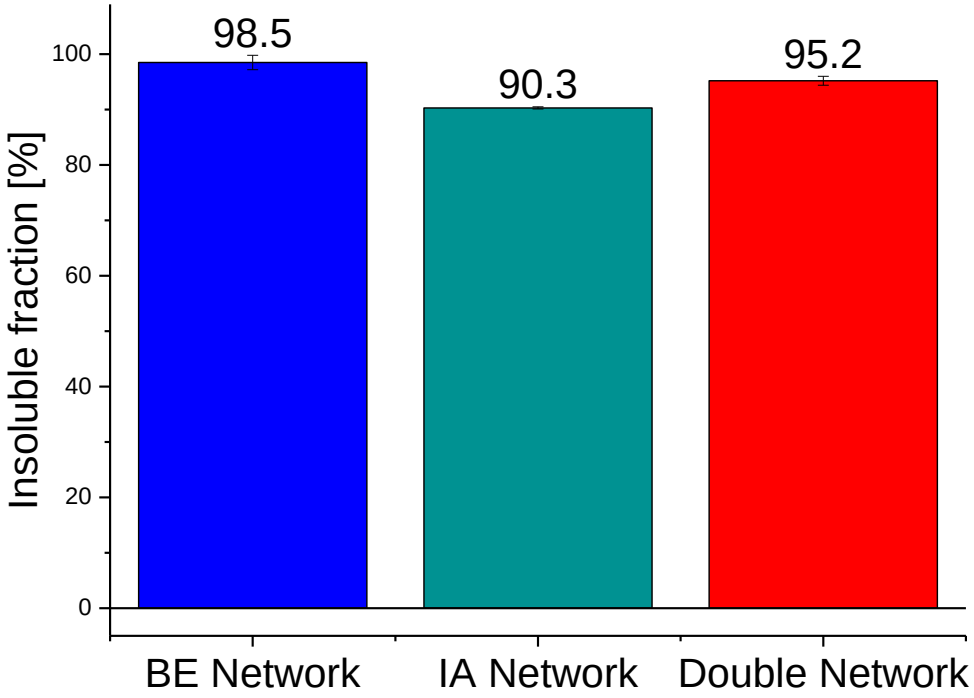
DN

IA Network

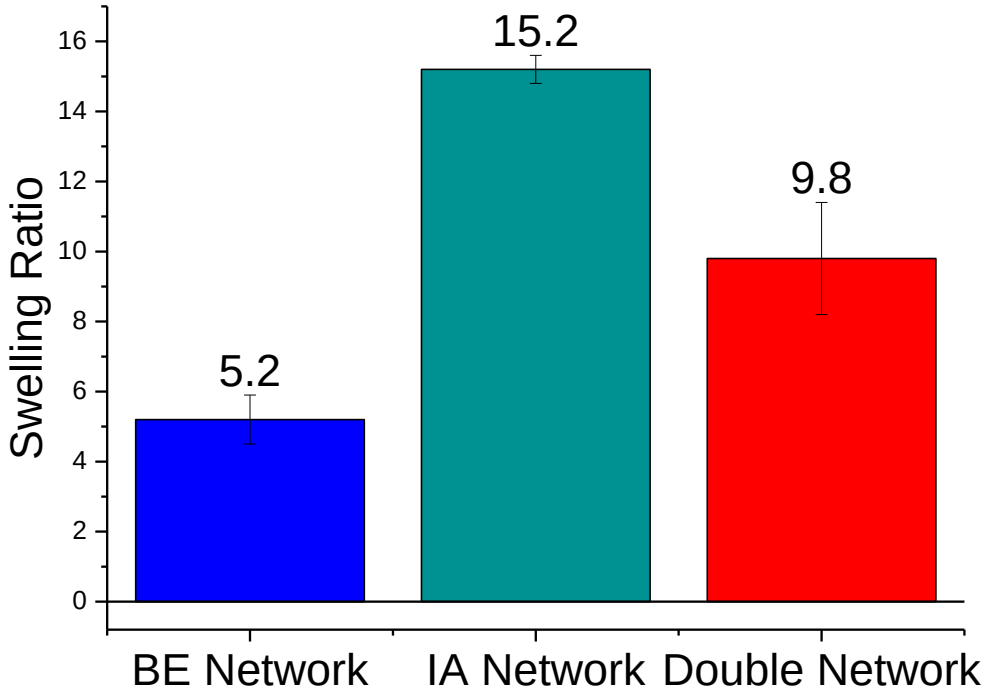
BE Network

Swelling/Solubility Behavior

- In THF for 24 h
- BE network showed to dissolve on longer time scales (72 h) /higher T (formation and diffusion of soluble species)
- IA network remained stable

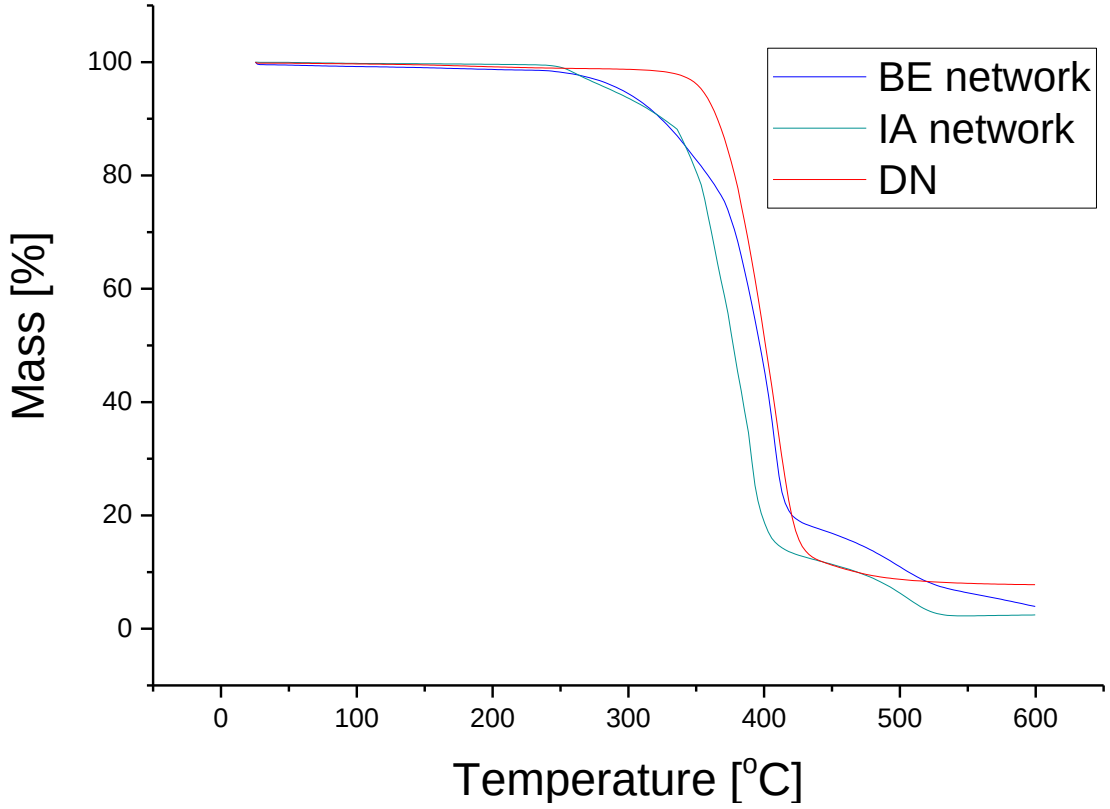


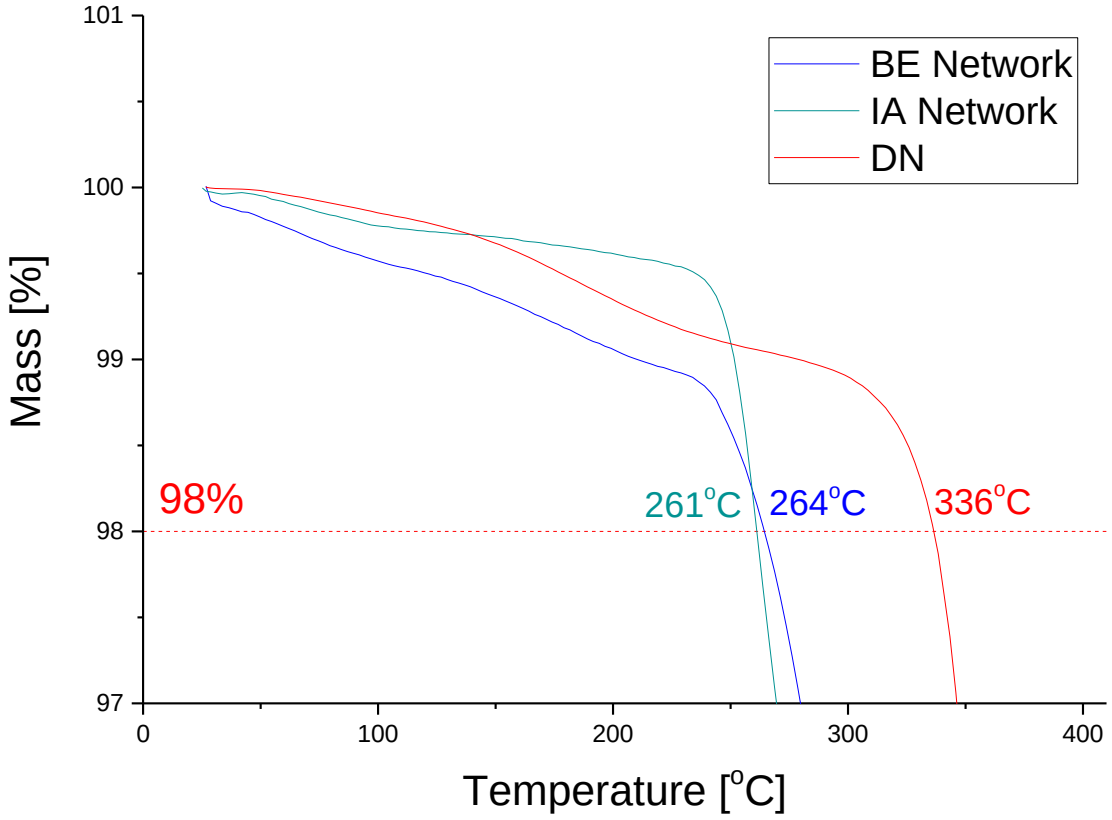
- Solubility fraction in the expected range
- Similar connectivity than as SN



- BE network is not restricting the more loose IA network from swelling
- Maybe BE network reshuffels fast and adapts to the swelling pressure of the IA network

Thermal Properties: TGA

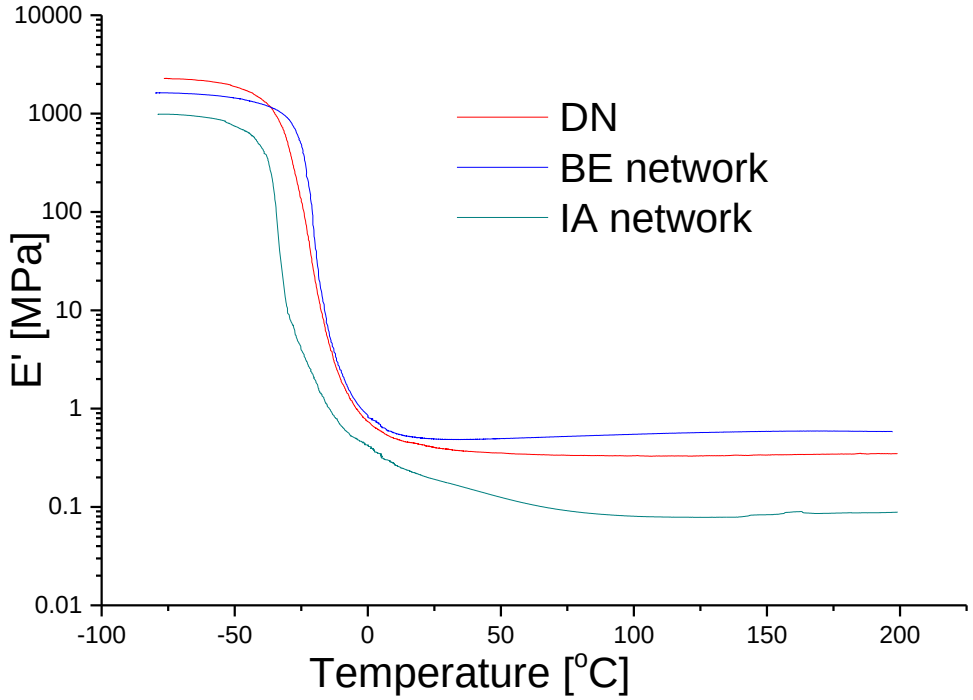


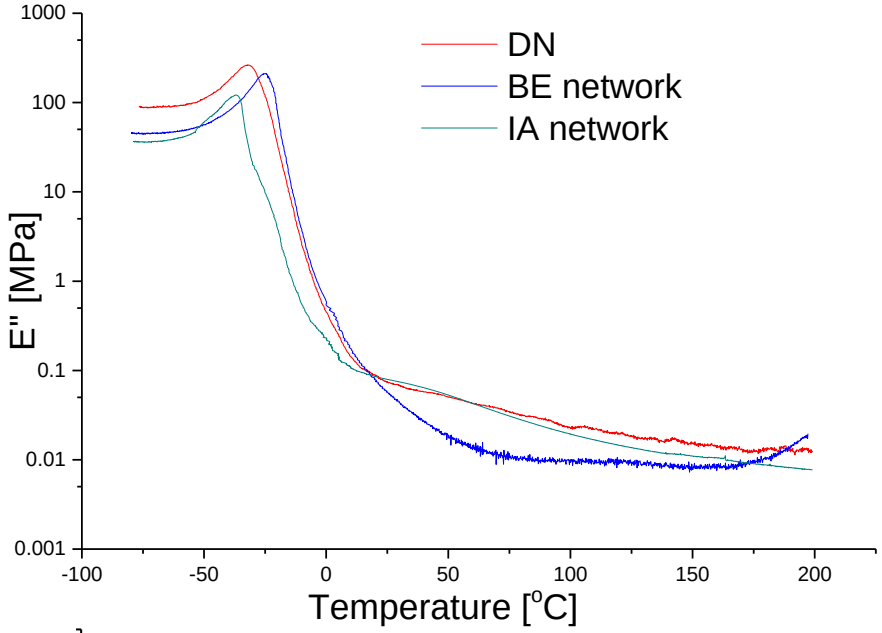


- DN shows a higher thermal stability than the individual networks

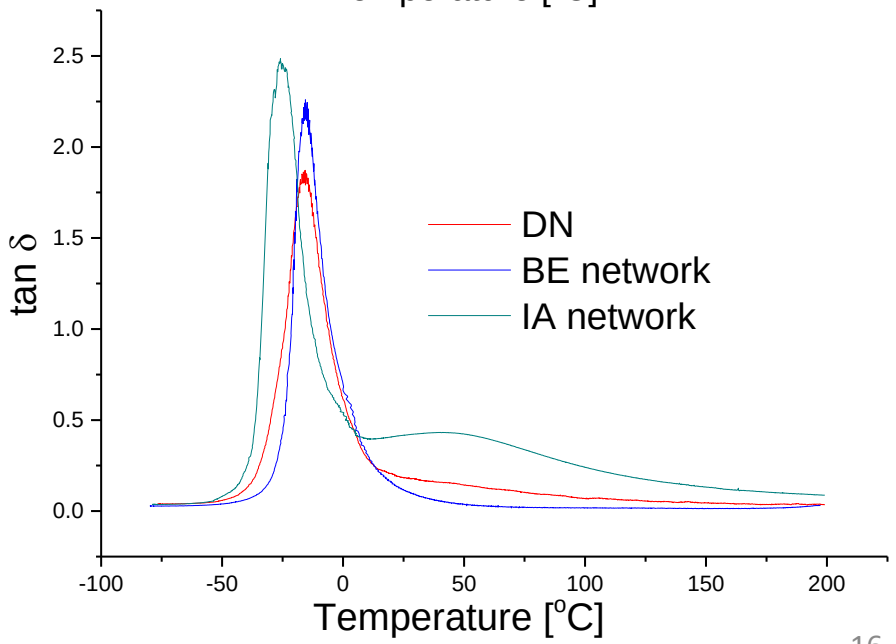
TGA: ramp: 10°C/min

Thermal/Mechanical Properties: DMA





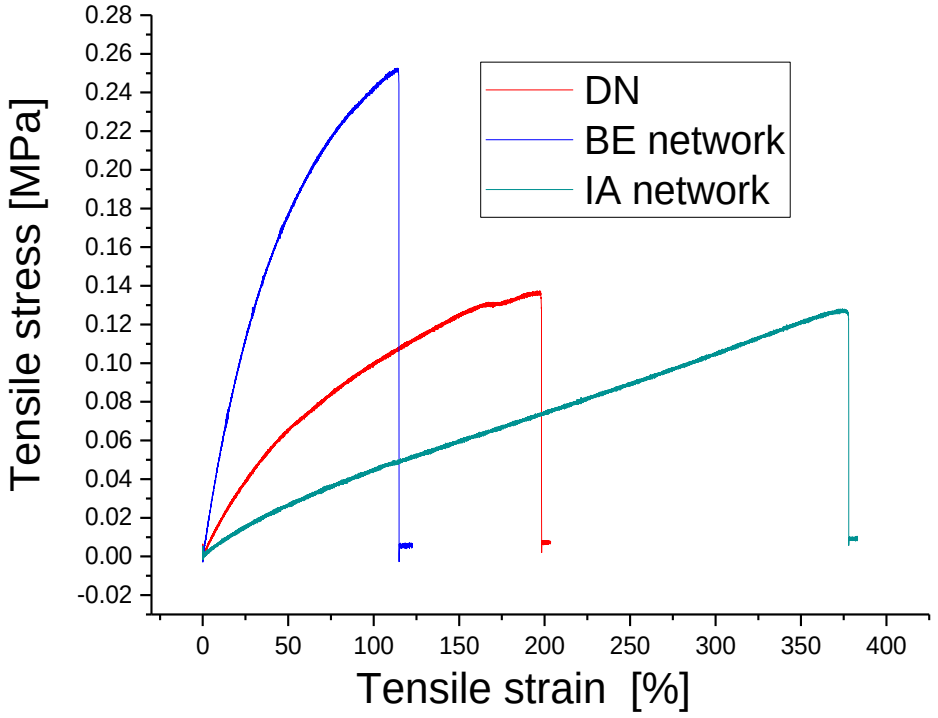
	DN	BE network	IA network
T_g [°C]	-31.9	-25.0	-37.0
E’ [kpa] (25°C)	403	491	191
E’ [kpa] (150°C)	337	587	83

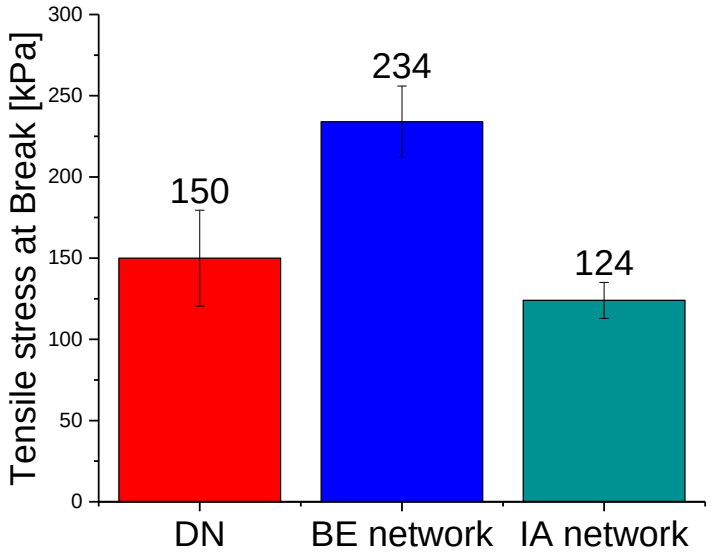


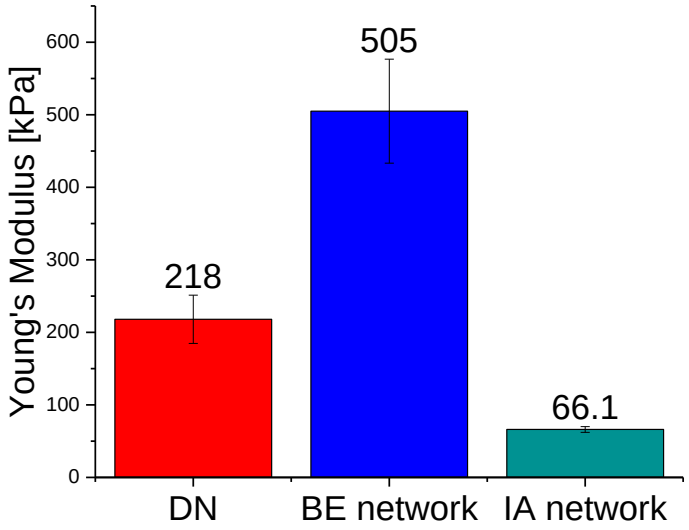
- Behaves below 25°C more like the BE network
- Deviates at higher temperatures
- Loss modulus closer to IA network from 25°C

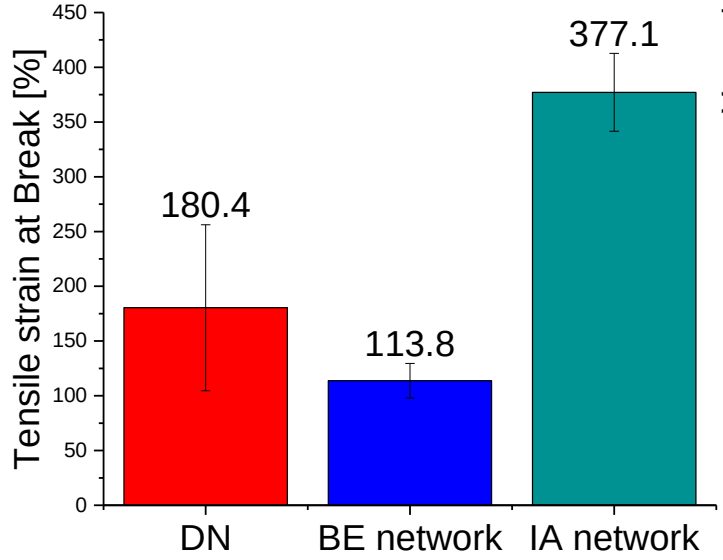
DMA: 1 Hz, 1 % strain, ramp: 3°C/min

Mechanical Properties: Tensile Tests





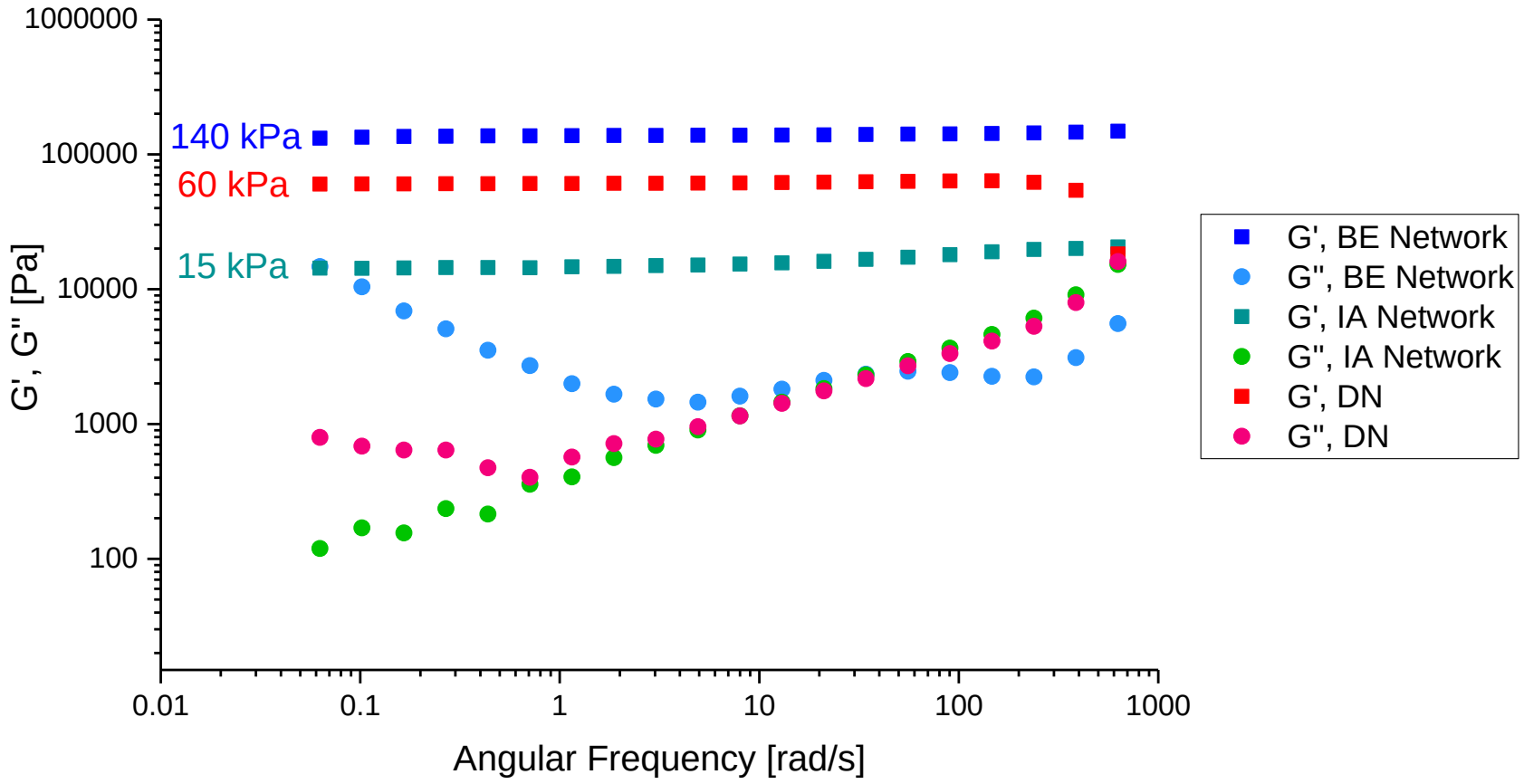




- No strain hardening could be detected
- Uniaxial tensile tests showed no synergistic effects
- Change in properties can be explained by the change in crosslinking density

Tensile test: 100 N transducer, 10 mm/min

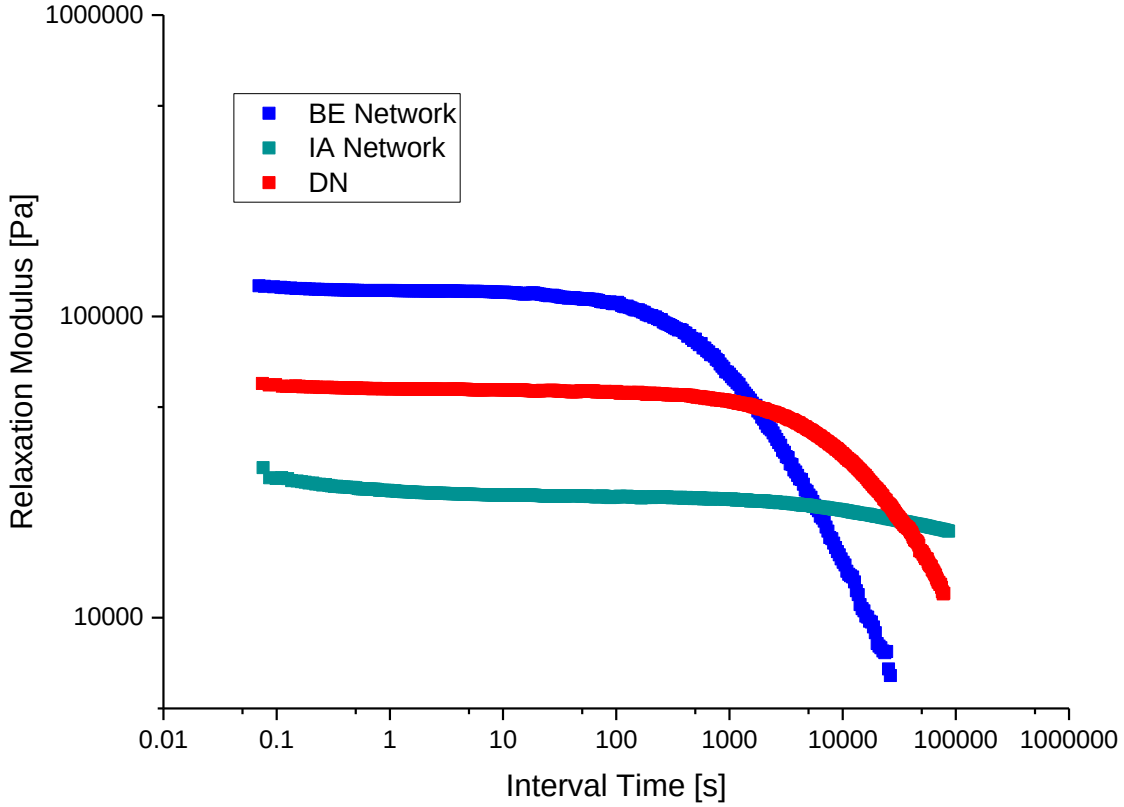
Rheometry: Frequency Sweeps

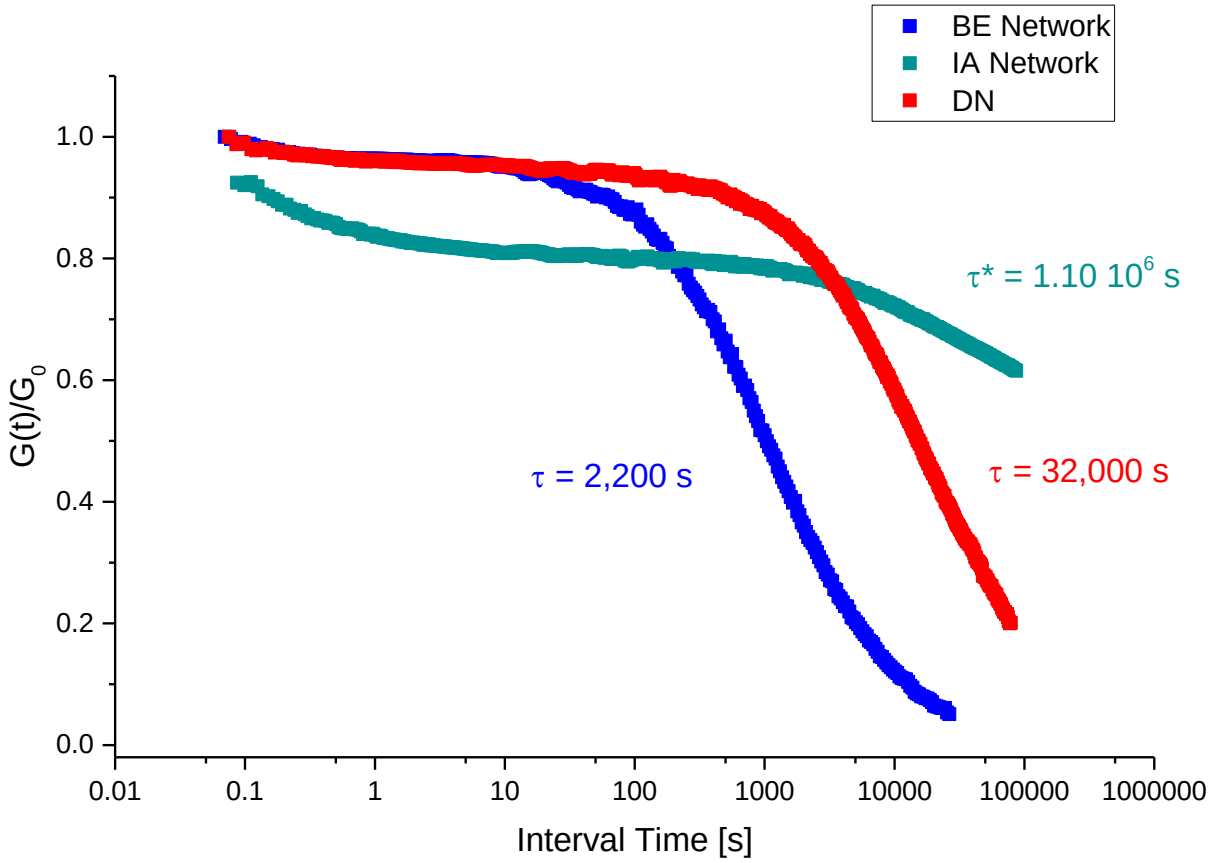


- Storage modulus in between the individual networks
- Explained by crosslinking density

Anton Paar MCR 501, 25 mm PP, N_2, F_N= 0.4 N; FS: γ = 1%, f = 0.01-100 Hz log, 110°C

Rheometry: Stress relaxation

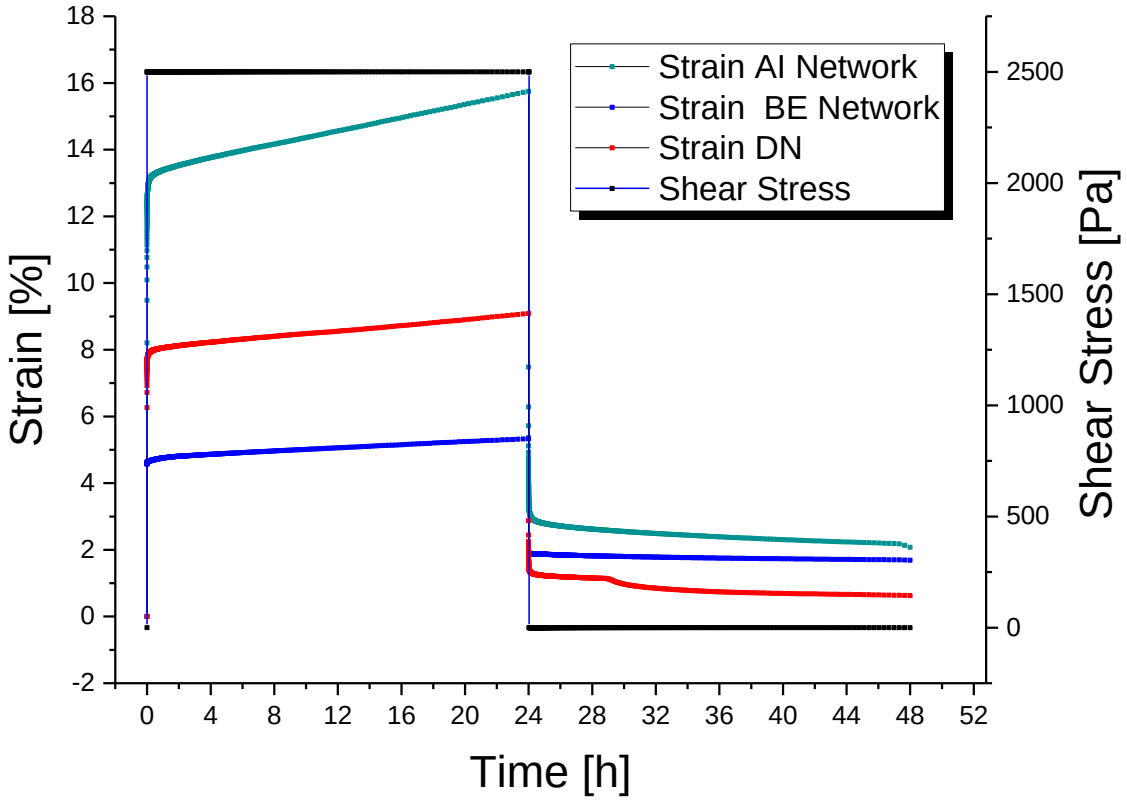


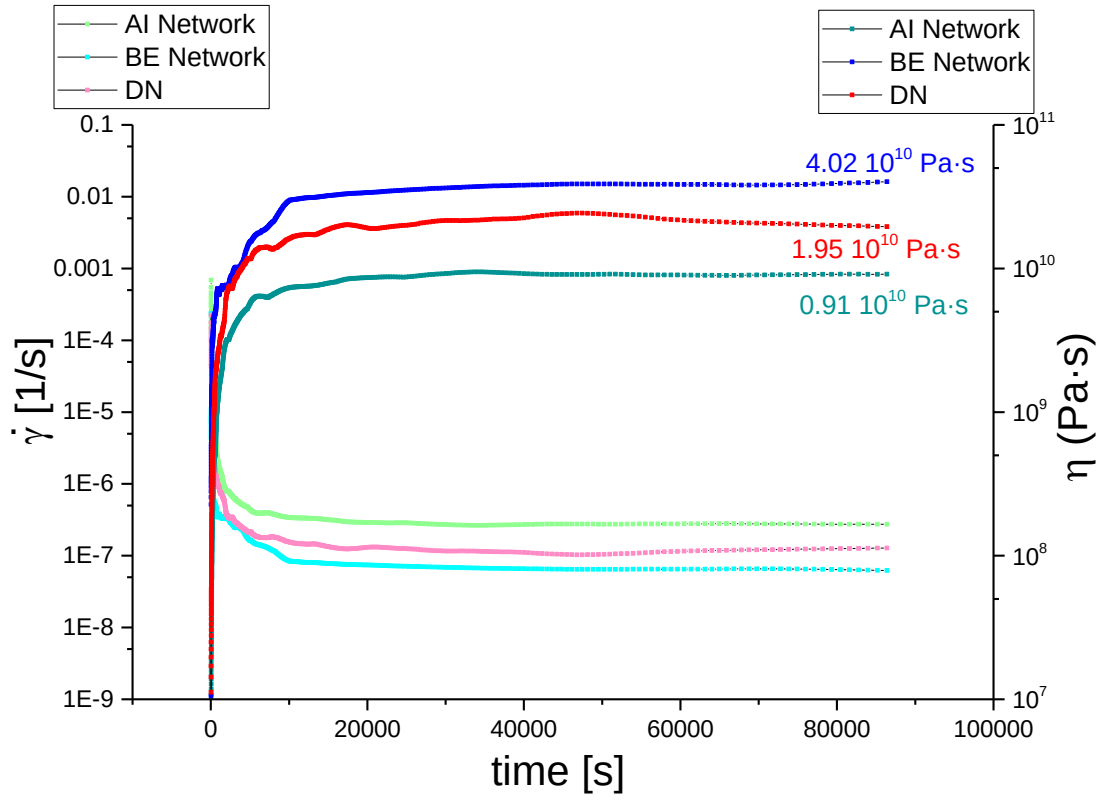


- Initial modulus in between the individual networks
- No short term relaxation as with the IA network (dangling ends)
- Incorporation in DN prevents these species to relax
- Relaxation postponed (in respect to the BE network)

Anton Paar MCR 501, 25 mm PP, N_2, F_N= 0.4 N , SR: γ = 1%, 110°C, τ determined with KWW stretched exponential decay fit

Rheometry: Creep

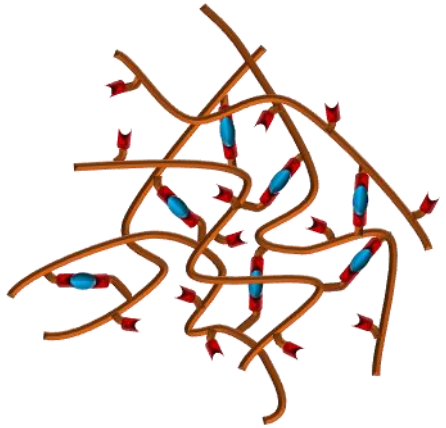




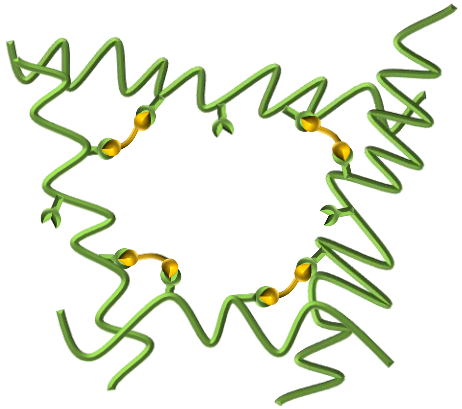
- DN shows elastic response in between the subnetworks
- When stress is released: recovers the most strain, lowest residual strain
- Maybe: Networks keep each other in place, less degrees of freedom
- Experiments done at same shear stress. Repeat with same initial strain

Anton Paar MCR 501, 25 mm PP, N_2, F_N= 0.4 N, creep: σ = 2500 Pa, 24h, 25°C, recovery: σ = 0, 24h, 25°C

Conclusion



vs.



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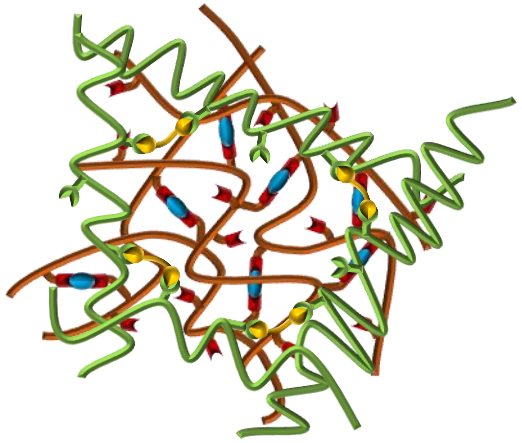


Not dynamic enough

Dimensional stable, processable

Properties of two interwoven structural networks

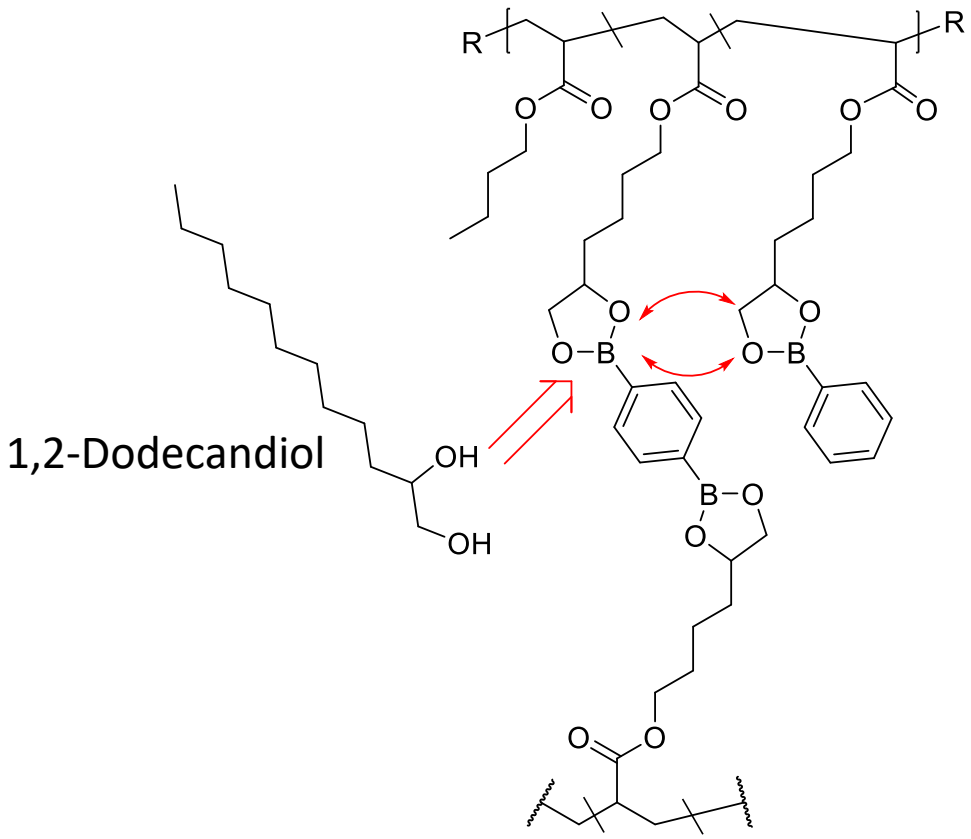
- Possible to create DN with boronic ester and imine-aldehyde system
- DN did not show targeted synergistic effects
- Most properties direct result of a difference in crosslinking density
- IPN showed advantages in regard to structural stability (TGA, short term SR, residual strain)

Outlook:

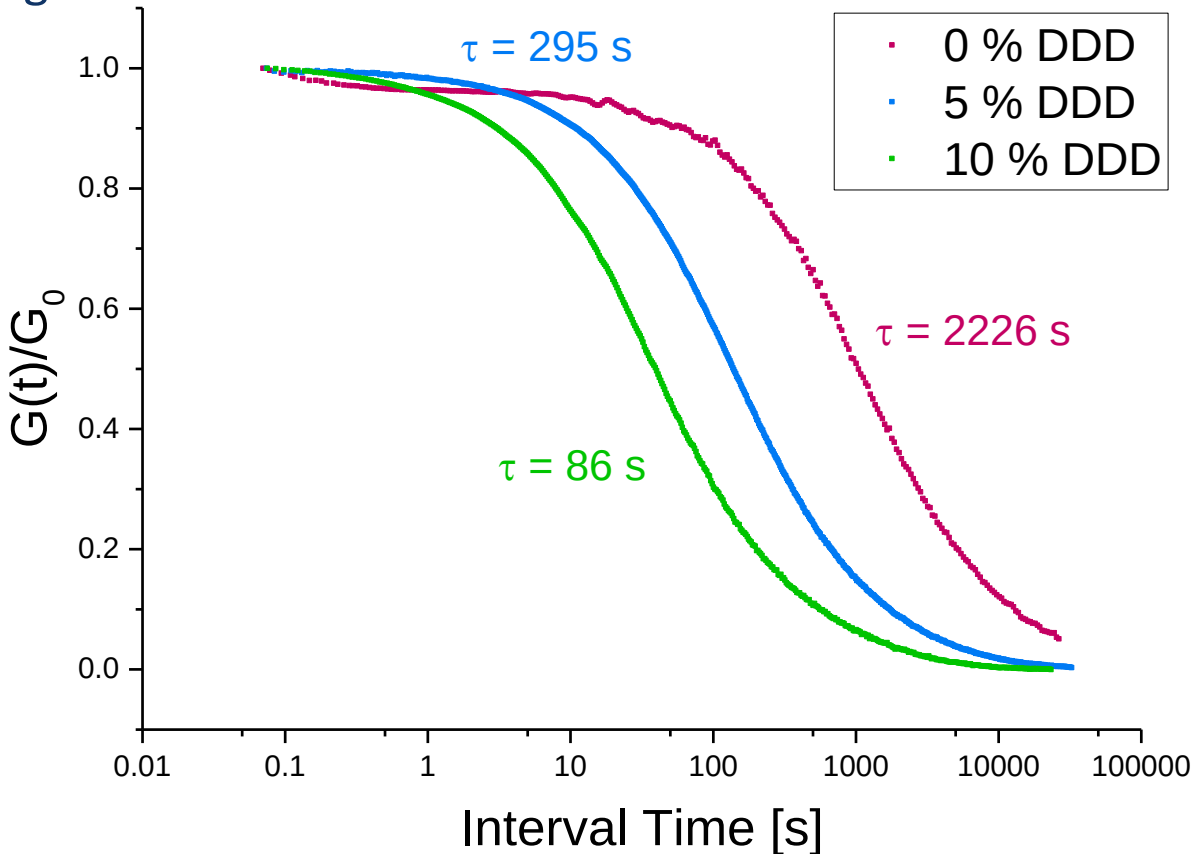
- Different ratio of the subnetworks, 1 : 2 or 1 : 3 BE : IA. Tool to control material properties
- BE network not dynamic enough to dissipate energy at ambient conditions

How to make the BE network more dynamic?

- Literature: diols accelerate boronic ester metathesis[1,2)]
- Add some mol% of free diol after the crosslinking
- Disadvantages: reduced crosslinking density
- Free diols in the chain (transesterification)



Anton Paar MCR 501, 25 mm PP, N_2, F_N= 0.4 N , SR: γ = 1%, 110°C



Will this be fast enough to achieve active energy dissipation at ambient conditions?

1) Cash, J. J.; Kubo, T.; Dobbins, D. J.; Sumerlin, B. S. *Polym. Chem.* **2018**, *9* (15), 2011–2020.
2) Yang, Y.; Du, F.-S.; Li, Z.-C. *Polym. Chem.* **2020**, No. 11, 1860–1870.

Thank you for your attention

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