Samples 11/2019

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Design and Characterization of Double Dynamic Networks Based on Dynamic Covalent Bonds

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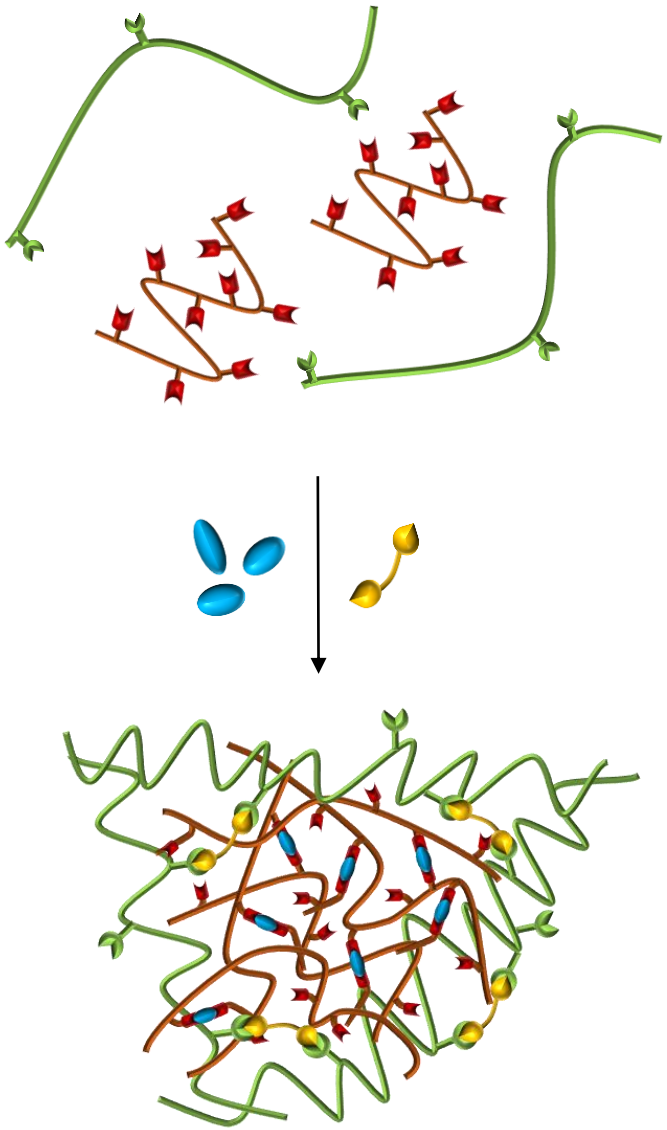
Project Goal

- Double Network elastomer based on dynamic covalent bonds
- Creating two interpenetrating subnetwork structures
  - Creating thermoplastics with functional groups
  - Orthogonal cross-linking with small molecule cross-linker
- Two independent modes

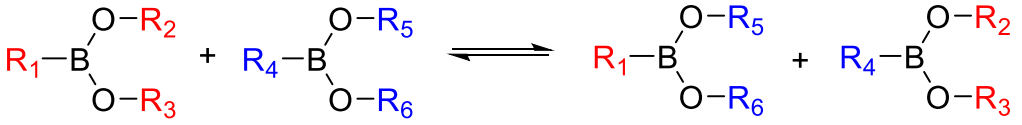


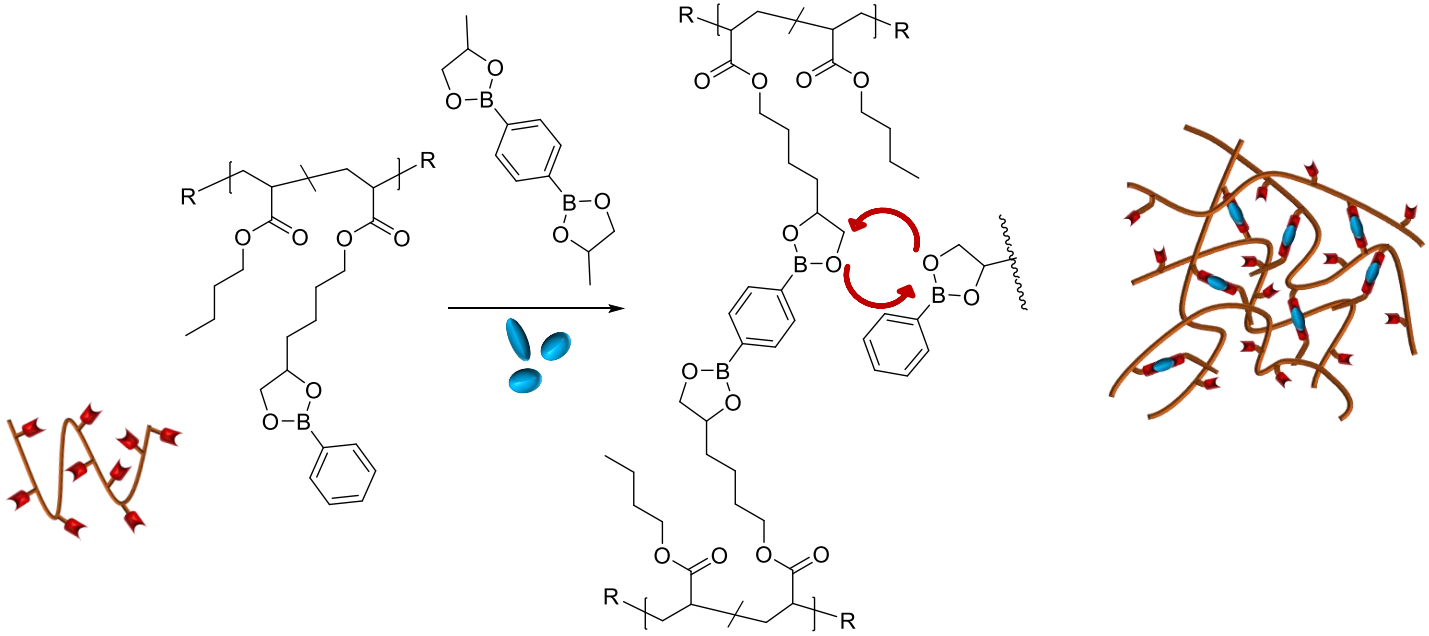
System Network 1

Sacrificial network → Dissipates energy

Boronic ester exchange:

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





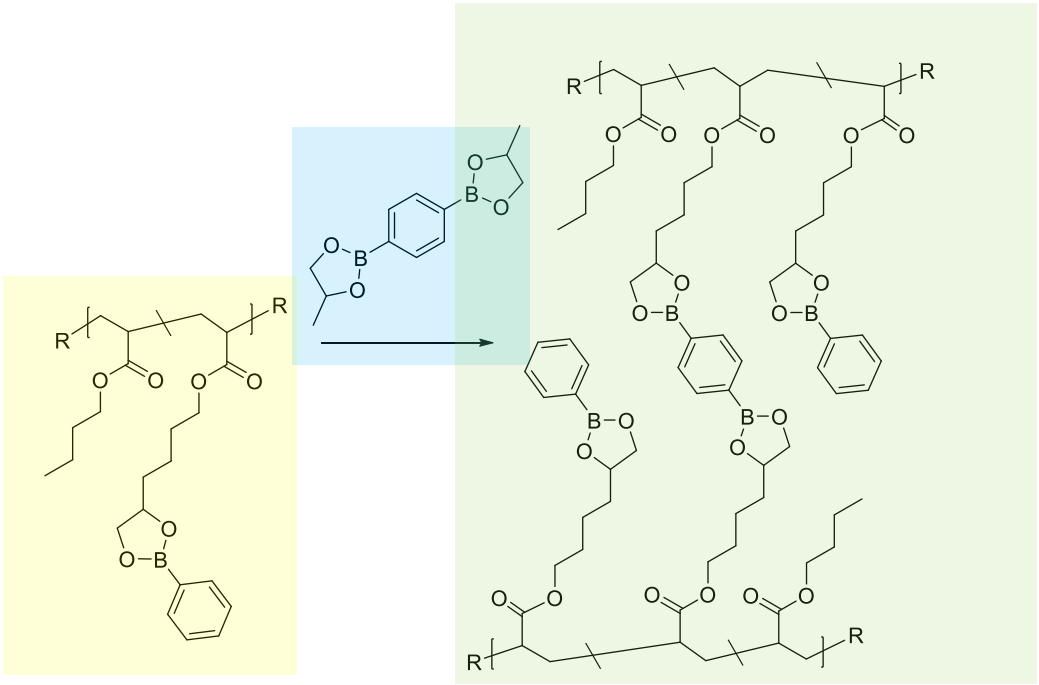
High density of functional groups, high density of cross-links → Fast Exchange

1) Röttger, M.; Domenech ,T.; van der Weegen, R.; Breuillac, A.; Nicolaÿ, R.; Leibler, L.; *Science* **2017**, *356*, 62-65.

Data Sample Network 1

M_n [1)] [kDa]	PDI	DP_n	f [%]	N_f	Eq (CL)	N_{CL}	f_{CL} [%]	m [g]	T_g [2)] [°C]
90	1.3	650	10	65	6.5	13	20	10	-42

Typical characteristics of the thermoplastic precursor, the respective cross-linking conditions and the subnetwork. f: functionality, N_f : number of functional groups per chain, CL: cross-linker, N_{CL} : number of cross-links per chain, 1) determined via size exclusion chromatography (SEC) with a standard polystyrene (PS) calibration, 2) determined via DSC.

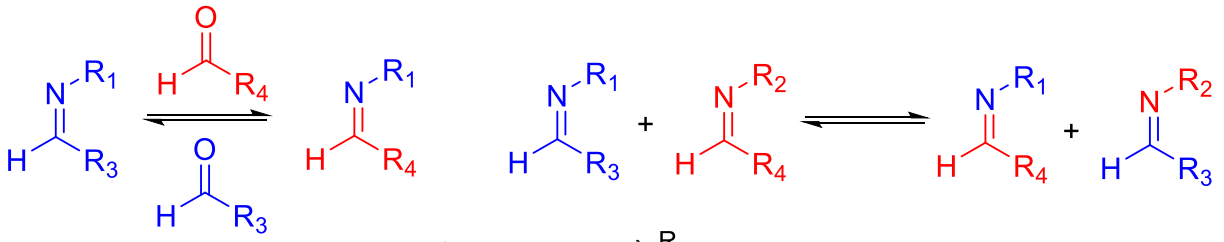


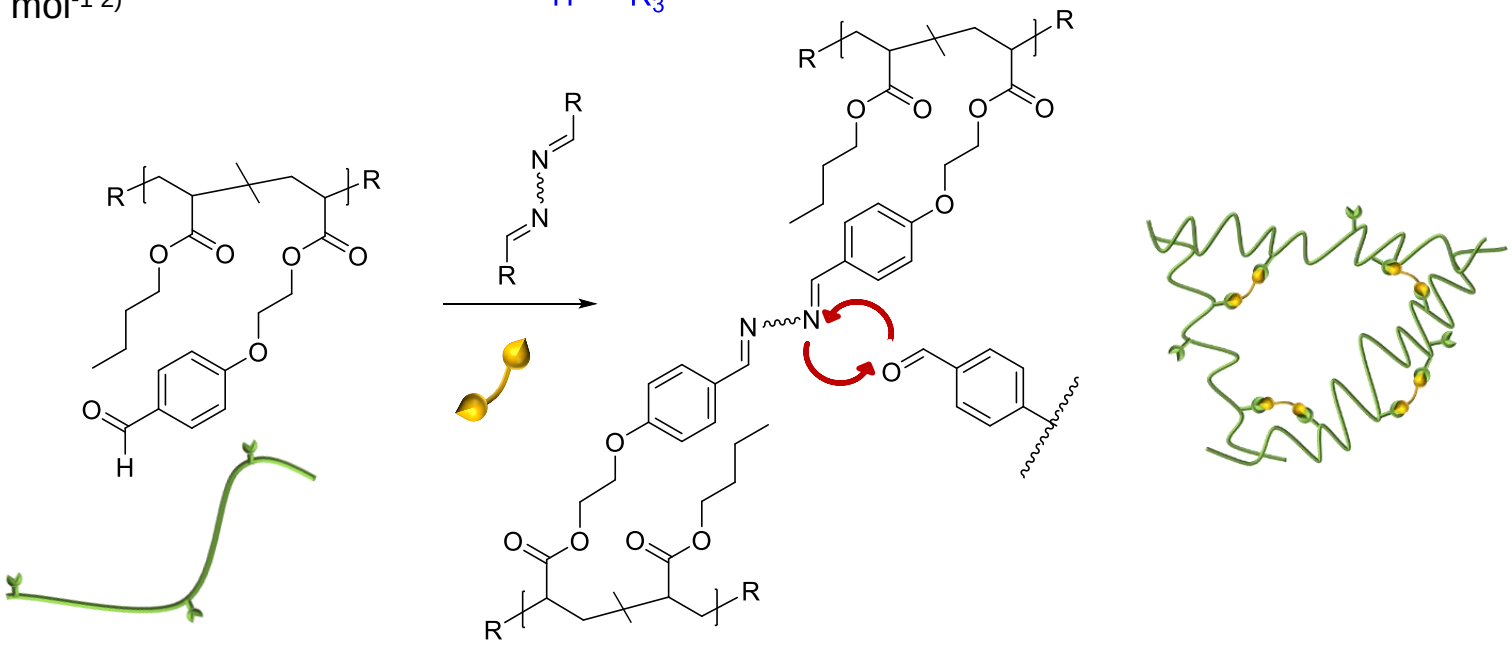
System Network 2

Structural network → Highly extendable

Imine/ Aldehyde and
Imine/imine exchange:

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





Low density of functional groups,
low density of cross-links

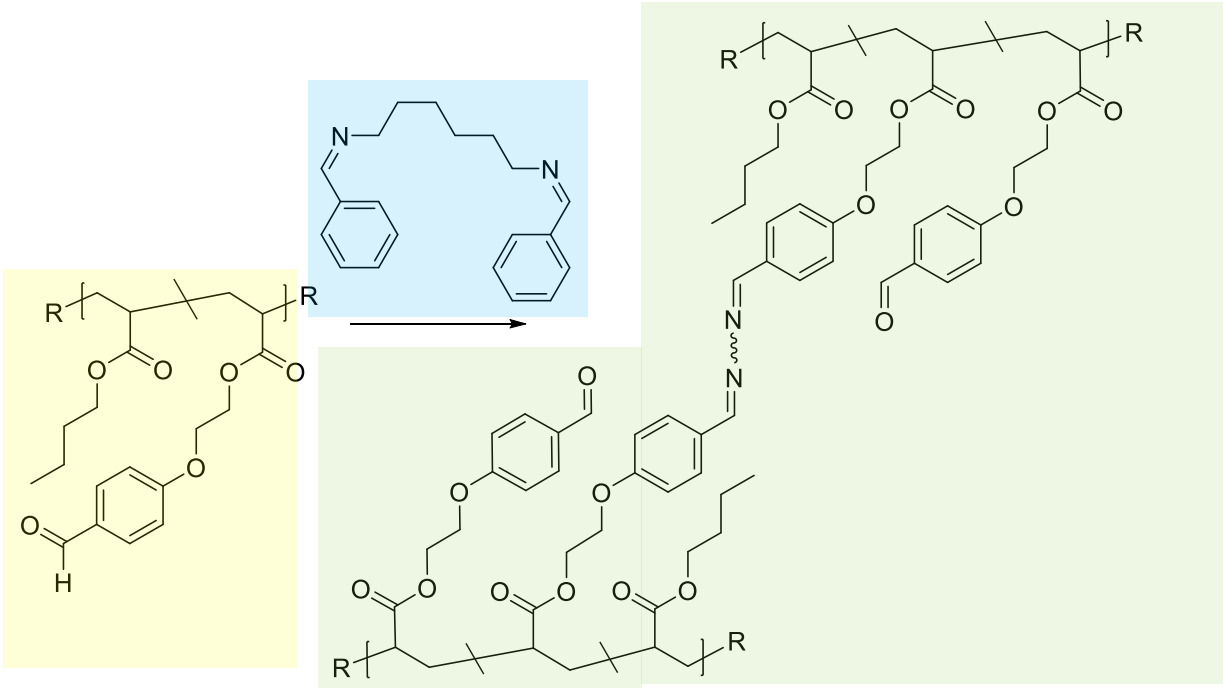
→ Exchange only at
elevated temperatures

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

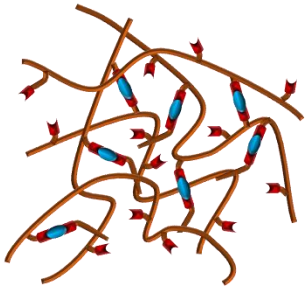
Data Sample Network 2

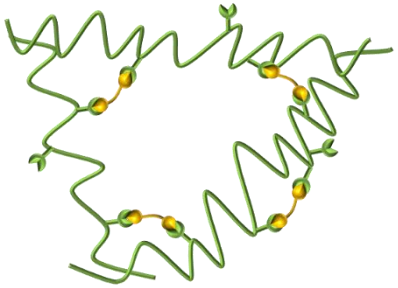
M_n [1)] [kDa]	PDI	DP_n	f [%]	N_f	Eq (CL)	N_{CL}	f_{CL} [%]	m [g]	T_g [2)] [°C]
500	2.2	4000	0.5	20	5	10	50	5	-47

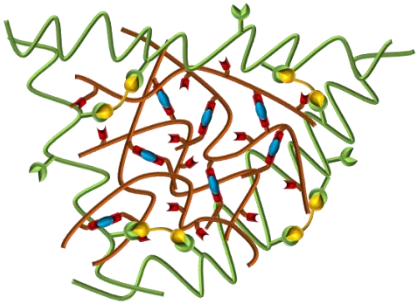
Typical characteristics of the thermoplastic precursor, the respective cross-linking conditions and the subnetwork. f: functionality, N_f : number of functional groups per chain, CL: cross-linker, N_{CL} : number of cross-links per chain, 1) determined via size exclusion chromatography (SEC) with a standard polystyrene (PS) calibration, 2) determined via DSC.



Conducted and planned testing at ESPCI

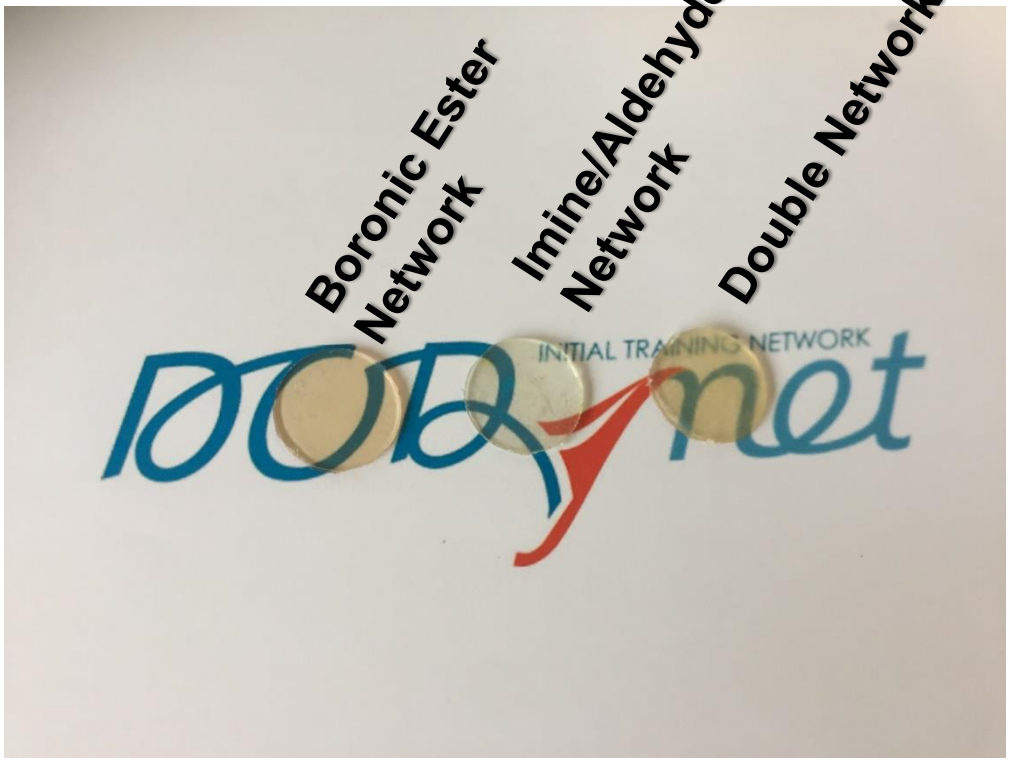






Test	Boronic Ester Subnetwork	Imine/ Aldehyde Subnetwork	Double Network
Synthesis	done	done	In progress
Swelling test	done	planned	planned
Soluble Fraction	done	planned	planned
TGA	done	done	planned
DSC	done	done	planned
DMA (T vs E', E'')	done	done	planned
Stress Relaxation (Rheo)	In progress	planned	planned
Creep (Rheo)	planned	planned	planned
Uniaxial Tensile Tests	planned	planned	planned

Samples Practical Information



Batch size: ~10g

Stability:

- Boronic ester moiety susceptible to water
- Networks short term stable up to 250ºC (O_2 atm)
- slow degradation over time at ~200ºC (O_2 atm)

Form: the samples can be compression molded in any form needed

- Thermoplastic precursors: Very viscous liquid, well soluble in THF
- Networks: Transparent elastomer (picture)