DoDyNet Samples

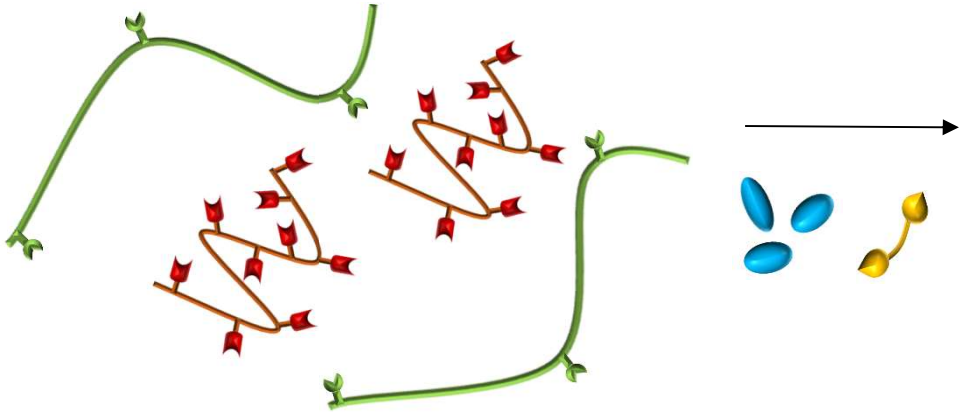
July 8th, 2020

Outline

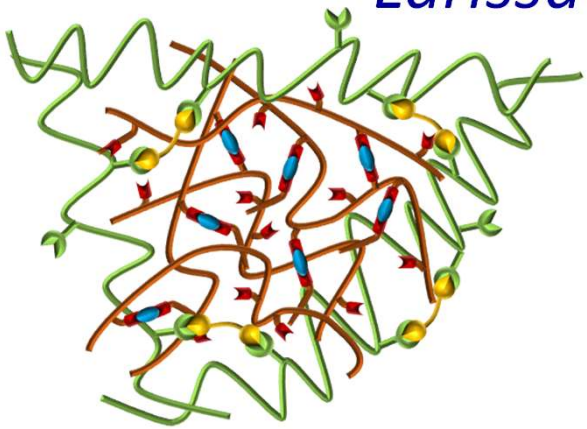
- DDN based on dynamic covalent bonds (Larissa)
- Sticky Unentangled Linear PnBA (Rowanne)
- Sticky entangled Linear PnBA (Clément)
- DDN based on star polymers (Paola)
- Telechelic star polymers (Consiglia)
- Network with pendant groups at x-linking points (Emmanouela)
- Network ABA triblocks (Clément)
- Tesa dual Networks (Bastian and Consiglia)
- Model TPE-E systems (Simone)

DDN based on Dynamic Covalent Bonds

Samples:



Larissa

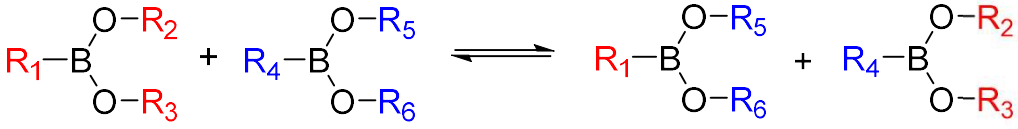


Orthogonal cross-linking with small molecule cross-linker:

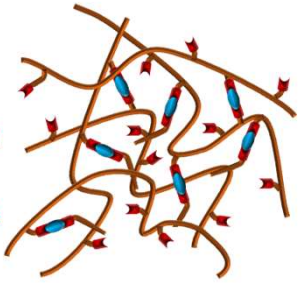
Sacrificial Network:

Boronic ester exchange:

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



Mn=90 kg/mol; 13 groups per chain

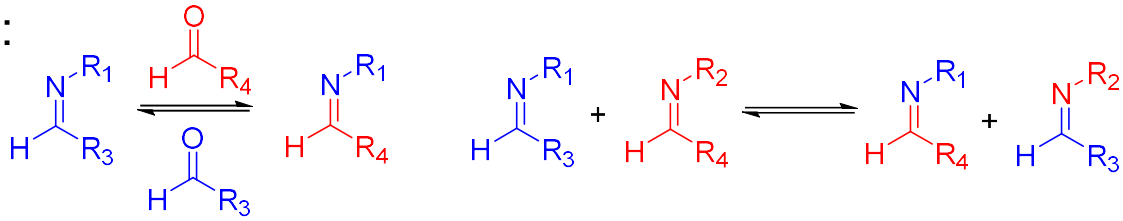


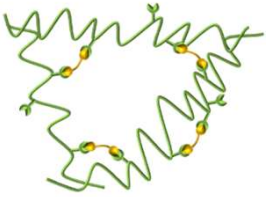
Structural Network:

Imine/ Aldehyde and
Imine/imine exchange:

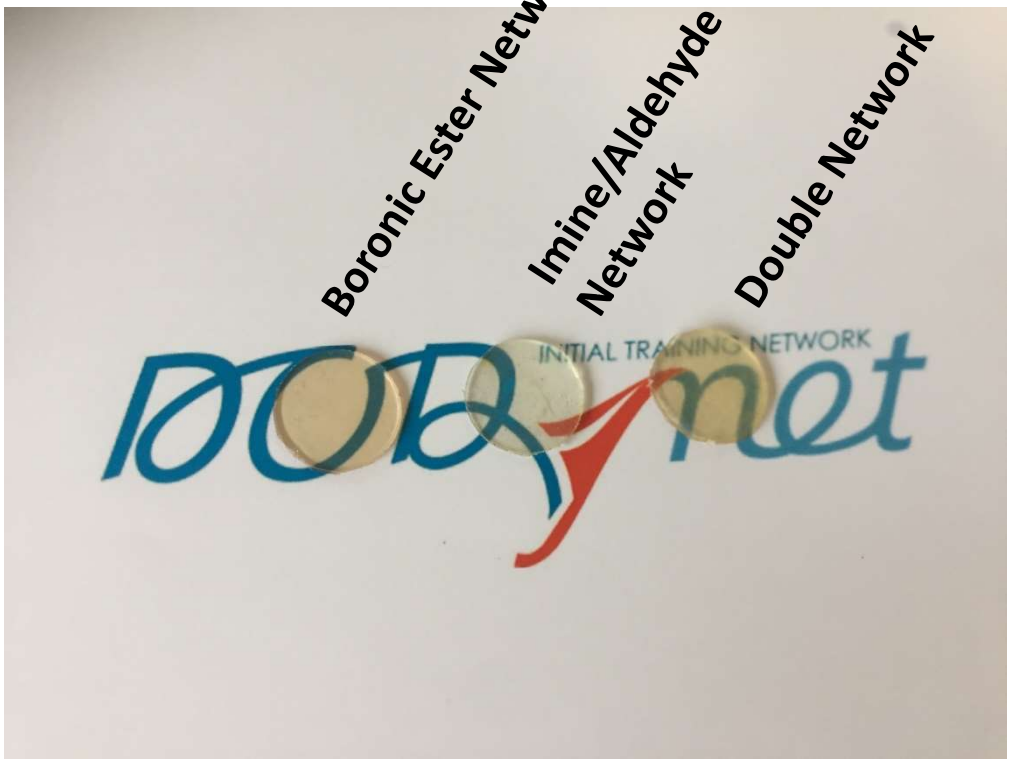
$E_a \approx 30$ kJ mol^{-1}

Mn=500 kg/mol; 10 groups per chain





DDN based on Dynamic Covalent Bonds



Larissa

Batch size: ~10g

Stability:

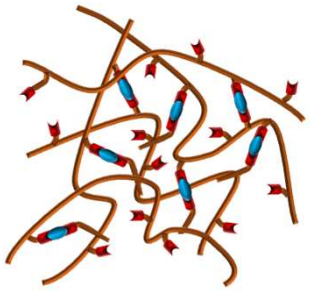
- Boronic ester moiety susceptible to water
- Networks short term stable up to 250ºC (O_2 atm)
- slow degradation over time at >150ºC (O_2 atm)

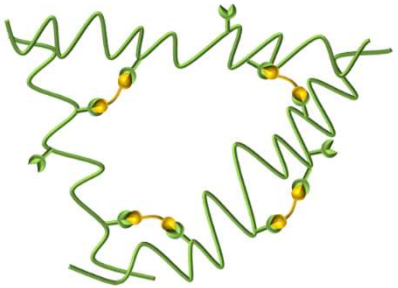
Form: the samples can be compression molded in any form needed

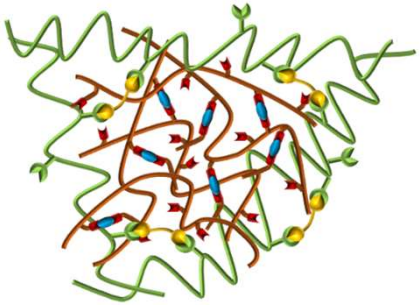
- **Thermoplastic precursors:** Very viscous liquid, well soluble in THF
- **Cross-linking:**
  - BE Network: in solution at rt
  - Imine Network: at rt in batch over long time or by compression molding
- **Networks:** Slightly sticky transparent elastomer (picture)

DDN based on Dynamic Covalent Bonds

Larissa



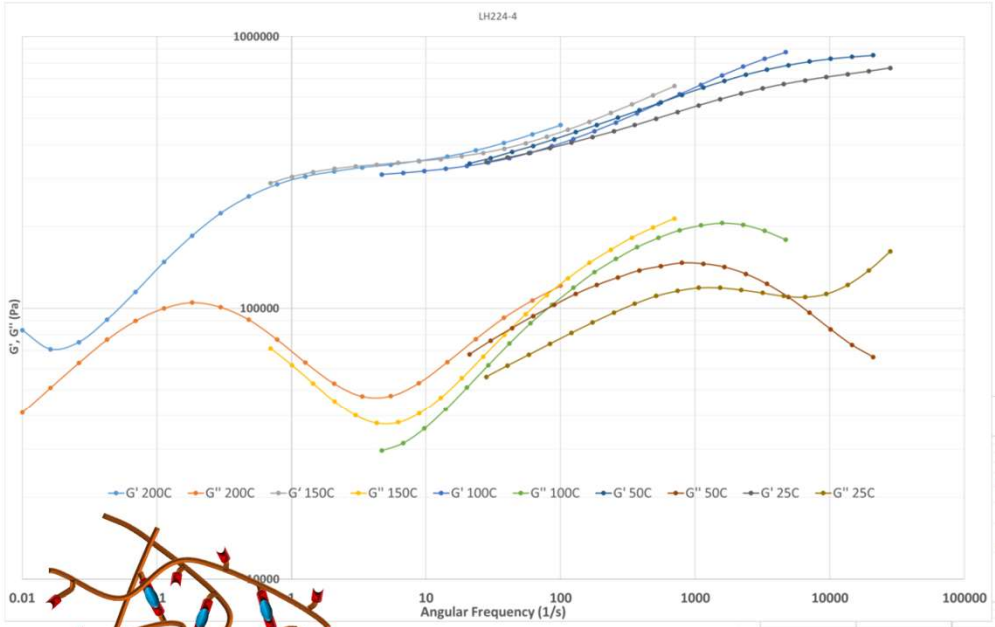


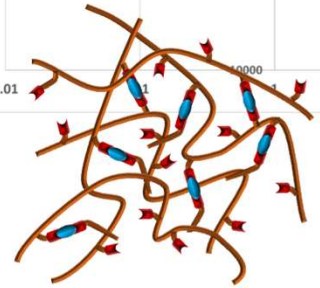


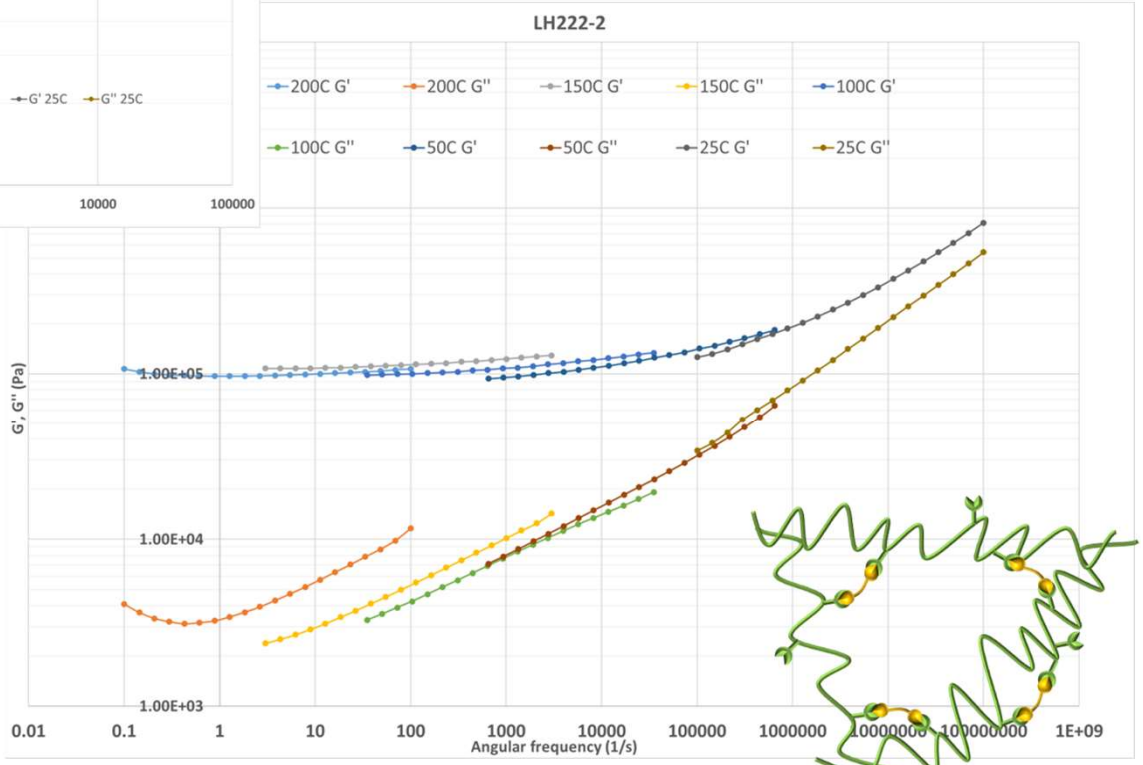
Test	Boronic Ester Subnetwork	Imine/ Aldehyde Subnetwork	Double Network
Synthesis	done	Done/ Adapting	In progress
Swelling test	done	done	planned
Soluble Fraction	done	done	planned
TGA	done	done	planned
DSC	done	done	planned
DMA (T vs E', E'')	done	done	planned
Stress Relaxation (Rheo)	In progress	done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

DDN based on Dynamic Covalent Bonds

Larissa



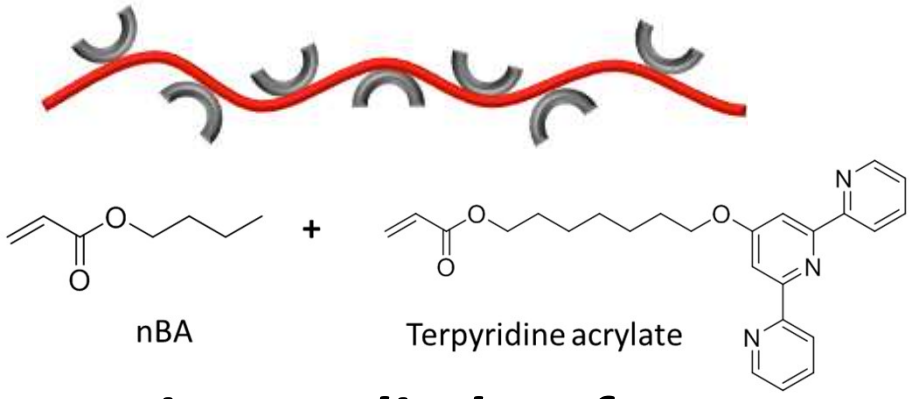




Sticky unentangled linear PnBA

Rowanne

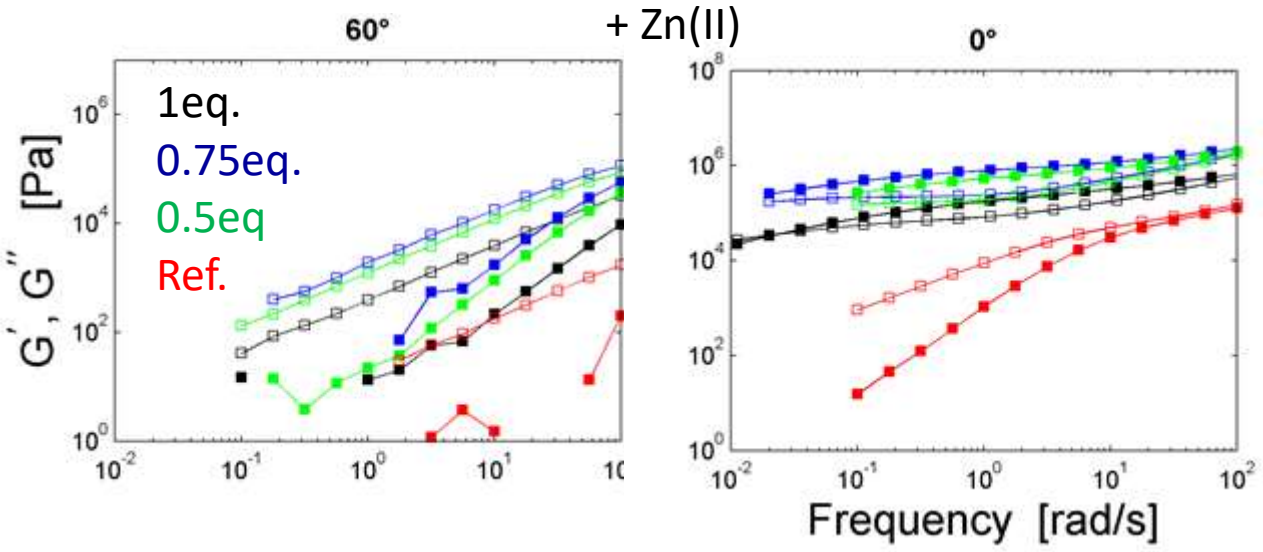
Samples:



M_n: 25 – 30 kg/mol
(M_e: 17 kg/mol)
PDI: 1.2

Around 6 stickers per chain

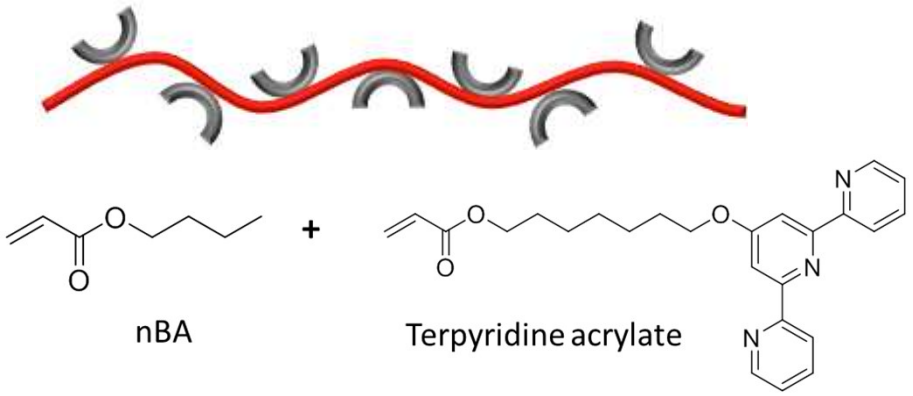
Properties studied so far:



- Sticky Rouse model
- Role of mono-complexes

Sticky unentangled linear PnBA

Rowanne

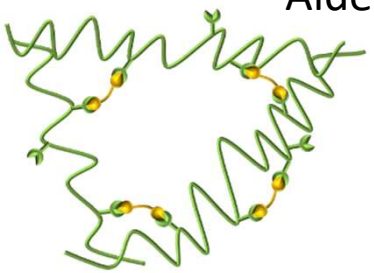


M_n: 25 – 30 kg/mol
(M_e: 17 kg/mol)
PDI: 1.2

Around 6 stickers per chain

Next step: Linear rheology of the DDNs:

+



Aldehyde thermoplastic

From Larissa

Interesting to do:

Mechanical tests: role of the two networks

Sticky entangled linear PnBA

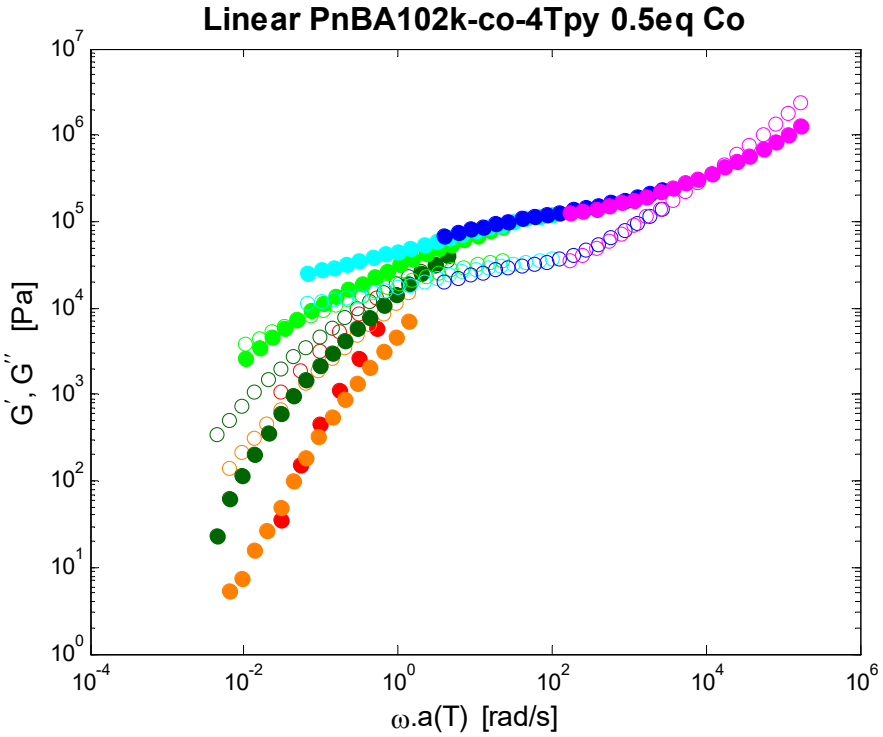
Clément

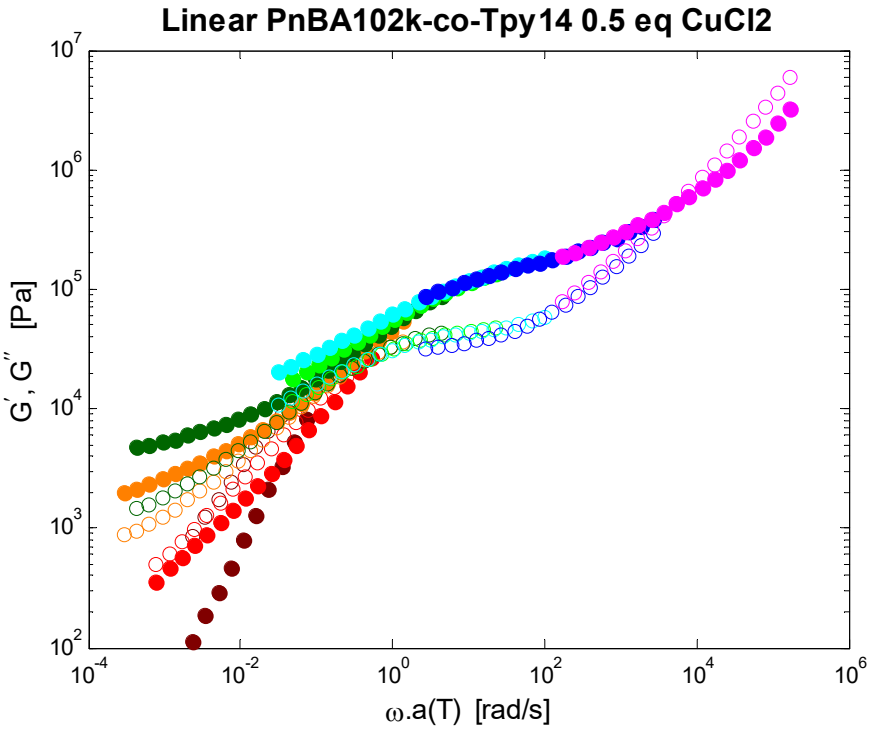
Samples:

Name	Mn (kg/mol)	D	m (g)	Nb of Terpy	Shear Rheology (linear regime)
(1)PnBA-*co*-PTpy14	102	1,29	~1,1g	14	• Reference sample • 0,5 eq : $ZnCl_2$, $CuCl_2$ (+ Dilution in PnBA-8k) • 1 eq : $ZnCl_2$, $CuCl_2$ ((+ Dilution in PnBA-8k)
(2)PnBA-*co*-PTpy4	100	1,25	~3,3 g	4	• Reference sample • 0,5 eq : $ZnCl_2$, $CuCl_2$, $CoCl_2$ • 1 eq : $ZnCl_2$, $CuCl_2$

Sticky entangled linear PnBA

Clément





Properties studied so far:

LVE →

- Tube model: cumulative effect of the stickers
- Influence of the density of stickers (lower or larger than the entanglement density)

Sticky entangled linear PnBA

Clément

Next step: Linear rheology of the DDNs:

Interesting to do:

- Nonlinear rheology

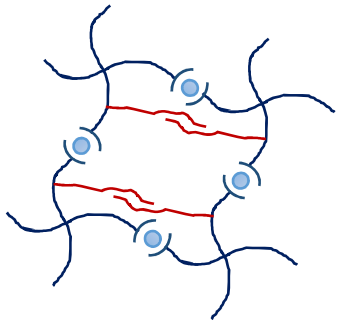
- Tensile tests: role of the two networks

DDN based on star polymers

Paola

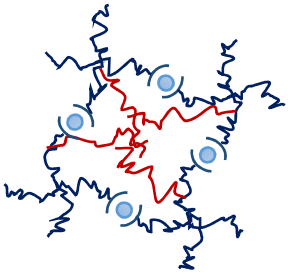
Samples:

Tetra-Polyethylene glycol functionalized with therpyridine and Pnipam.



Heating

Cooling



T < LCST

T > LCST

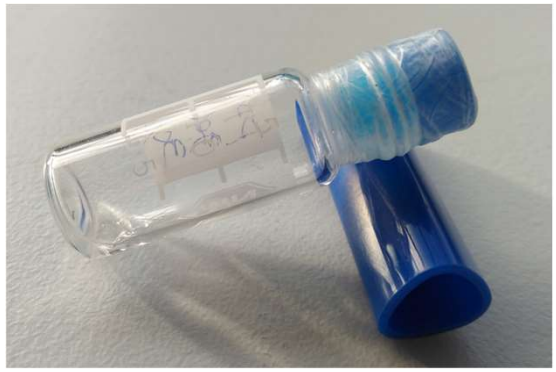
Peg

Pnipam

Terpyridine metal ion complex

Iron

Zinc



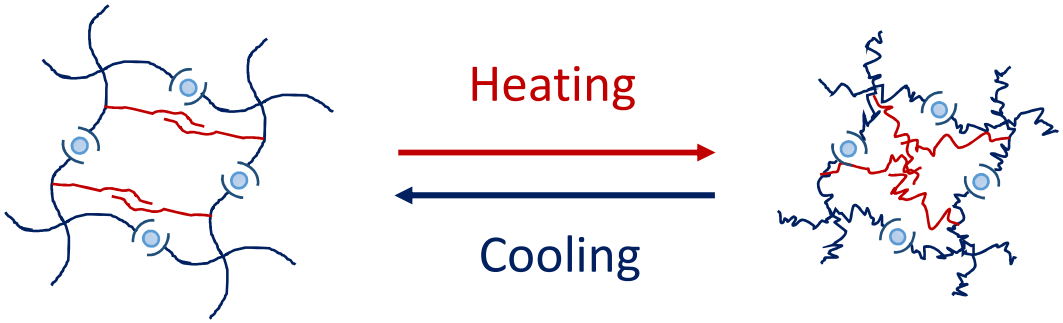
Zinc above LCST

DDN based on star polymers

Paola

Properties studied so far:

- Light scattering (solution)
- FCS/FRAP (planned)



Interesting to do:

- Rheological characterization (FORTH)

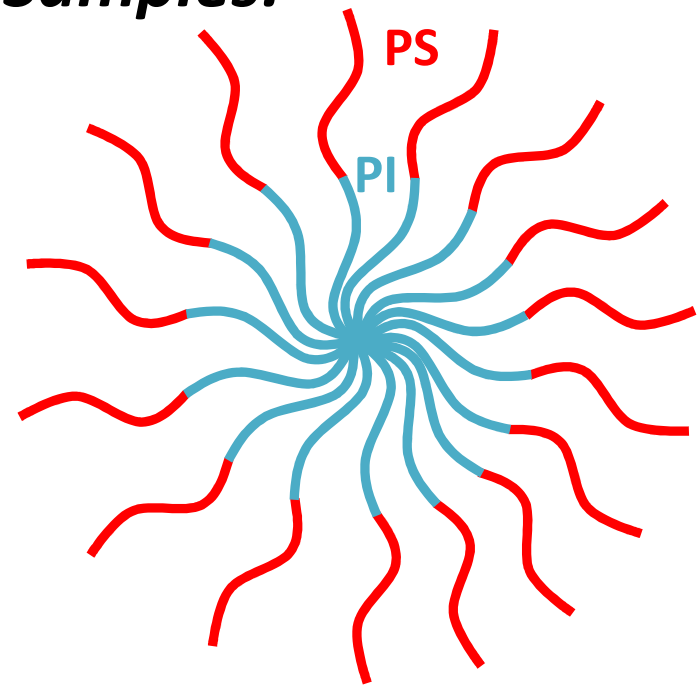
Possibility to change:

- Peg Mw (10 K, 20 K)
- Pnipam Mw (2.5 K and 5.5 K)
- The metal ion (Fe, Ni, Co, Zn,…)

Telechelic star polymers

Consiglia

Samples:



Synthesis: N. Hadjichristidis

Functionality: f =16 arms

Arms are block copolymers of PS and PI

Inner part: Polyisoprene (PI)

Outer part: Polystyrene (PS)

Solvent: 1-Phenyldodecane

Good for inner block for PI (at T>22^{0}C)
Theta for outer block PS (at T=53^{0}C) .
High boiling point (330^{0}C)

	Mw tot [kg/mol]	Mw arm [kg/mol]	Fraction of PS	Polydispersity	Quantity
$PS_{26k}PI_{27k}$	835.2	53	0.49	1.12	$< 1g$
$PS_{16k}PI_{47k}$	996.4	63	0.25	1.10	$< 1g$