Synthesis and dynamics of model supramolecular polymer networks

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Outline

Network ABA triblock

RAFT agent synthesis

Melt

Gels

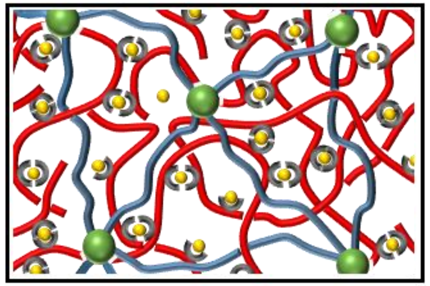
Two steps RAFT polymerization
Linear Rheology

Network
Linear PnBA-co-Ptpy
Star PnBA with Tpy chain-end

Synthesis of the co-monomer
One steps RAFT polymerization
Linear Rheology with metals ions

or

RAFT agent synthesis
RAFT polymerization
Linear Rheology with metals ions



Double Dynamics Networks

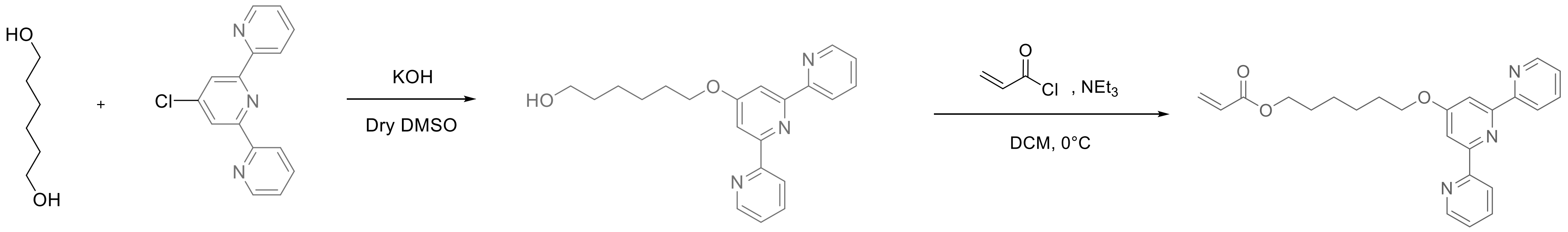
Network linear PnBA-co-Ptpy

UCLouvain

Network linear PnBA-co-Ptpy

Co-Monomer synthesis and RAFT polymerisation

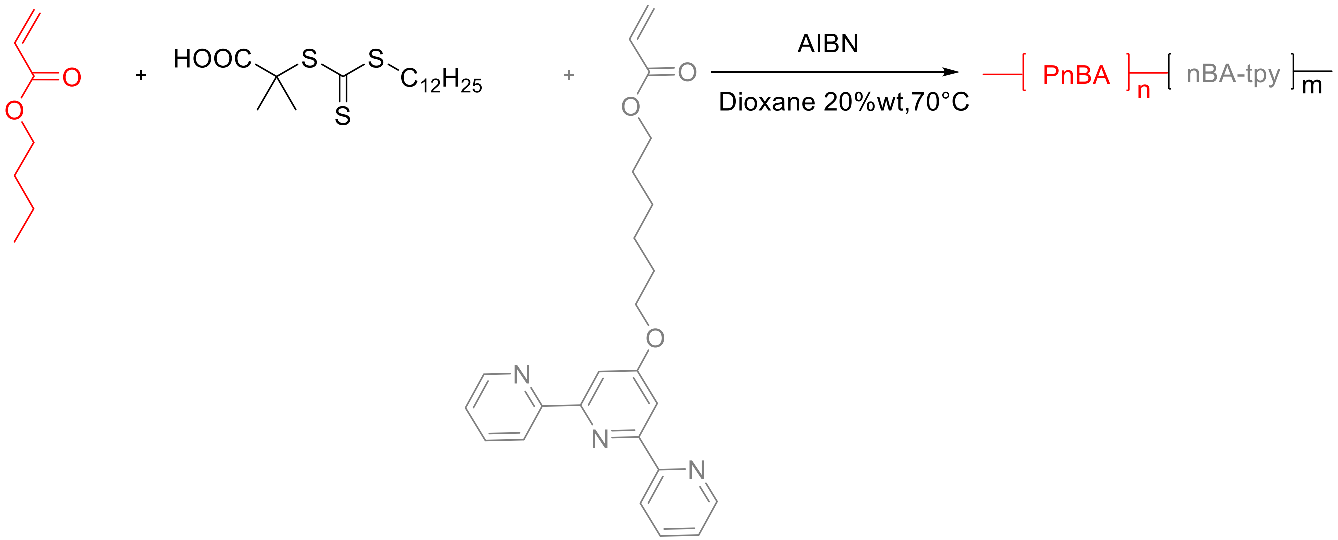
Step 1:



- ✓ Yield = 80%
- ✓ Precursor to nBA-tpy

- ✓ Yield = 65 %
- ✓ White powder

Step 2:



- ✓ Conversion ~70 % [a]
- ✓ Mn ~ 100 $kg.mol^{-1}$ [b]
- ✓ 4 or 14 terpyridine per chains
- ✓ Random linear copolymer

a: determined by ^{1}H NMR in $CDCl_3$
b: determined by GPC in DMF with PS-calibration

Network linear PnBA-co-Ptpy

Name	Mn (kg/mol)	D	m (g)	Tg (°C)	Nb of Terpy	Shear Rheology (linear regime)
(1)PnBA-*co*-PTpy14	102	1,29	~1,1g	-46	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	-46	4	• Reference sample • **0,5 eq : $ZnCl_2$, $CuCl_2$**, $CoCl_2$ • 1 eq : $ZnCl_2$, $CuCl_2$

0,5 eq is considered as the stoichiometric amount

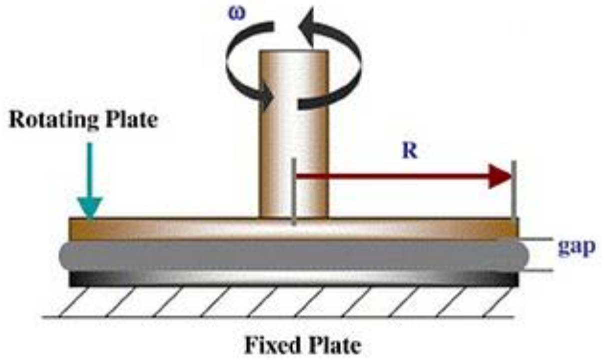
Network linear PnBA-co-Ptpy

Rheometer procedure

Rheometer: ARES-G2
Linear regime

Dynamic Time Sweep at 130°C :

- Remove sample memory shape (due to solvent evaporation)
- Sample equilibration



Start measurement at 100°C until -20°C :

- Dynamic time sweep (~10min)
- Dynamic strain sweep (0,1 to 20%)
- Dynamic frequency sweep (strain= 3…7%)

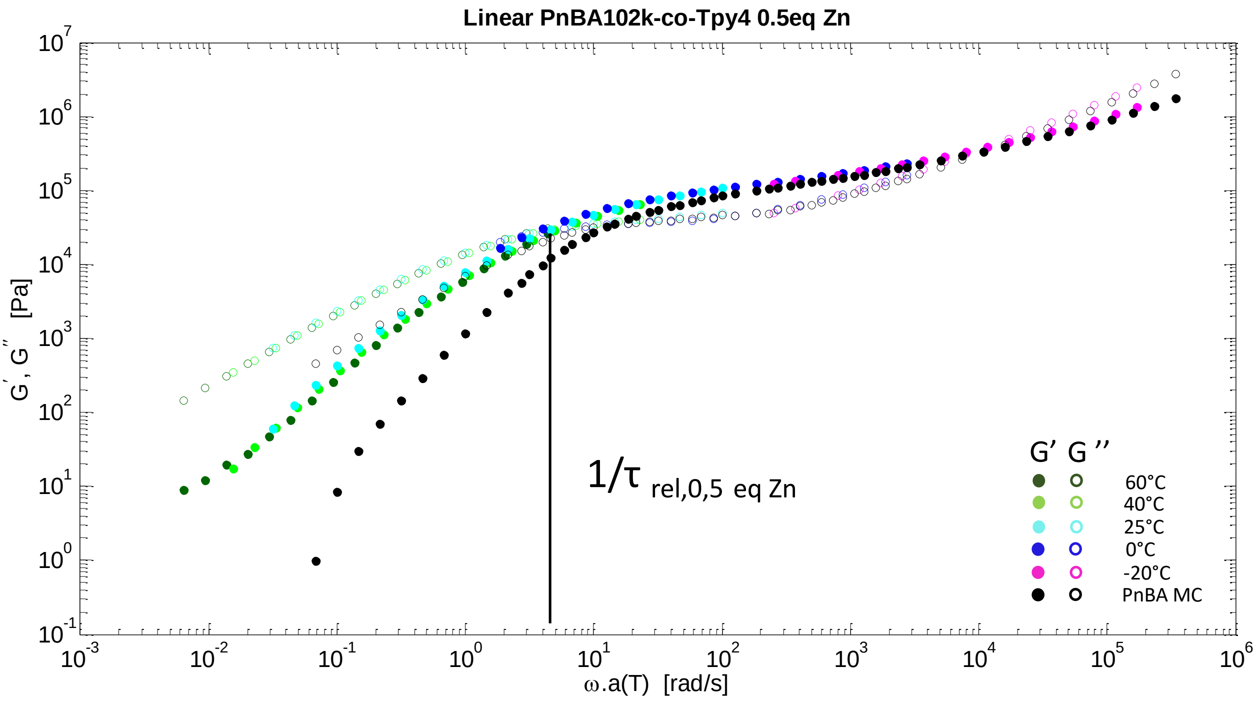
All the Master Curves are built with **the shift factors** used for PnBA-94k Master curve

UCLouvain

Network linear PnBA100k-co-4Ptpy

Linear Rheology with metal ion

4 terpyridine



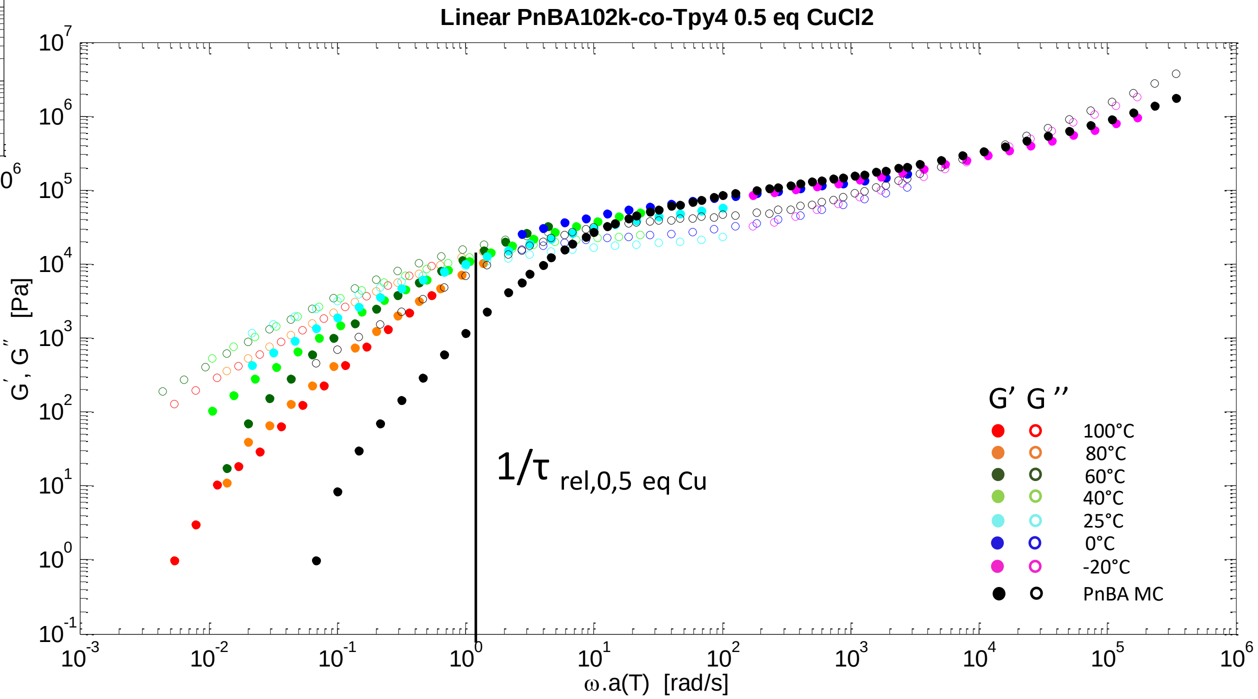
1 terpyridine per entanglement

⇨ Effect on the relaxation time ($\tau_{rel,0,5\ eq\ Zn} > \tau_{rel,PnBA}$) at 25°C

Slight effect of the temperature on the sample dynamics

Effect on the relaxation time ($\tau_{rel,0,5\ eq\ Cu} > \tau_{rel,0,5\ eq\ Zn}$) ⇦
At 25°C

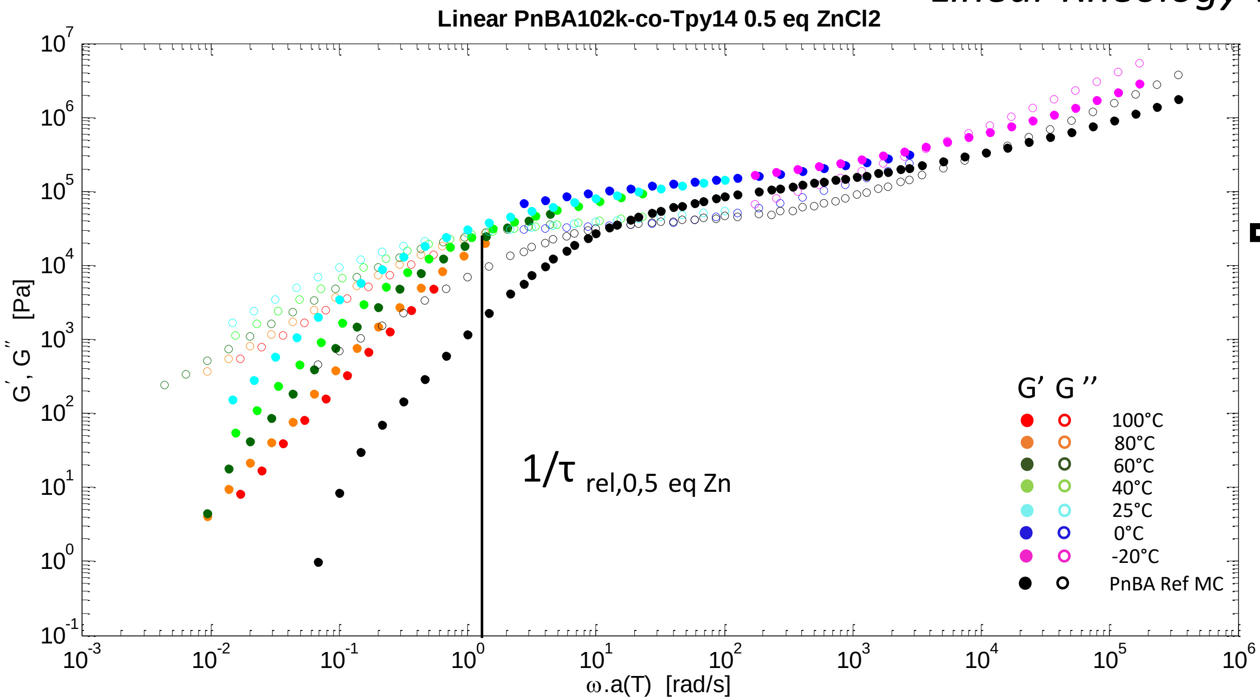
Temperature has a large influence on the sample dynamics



Network linear PnBA100k-co-14Ptpy

Linear Rheology with metal ion

14 terpyridine



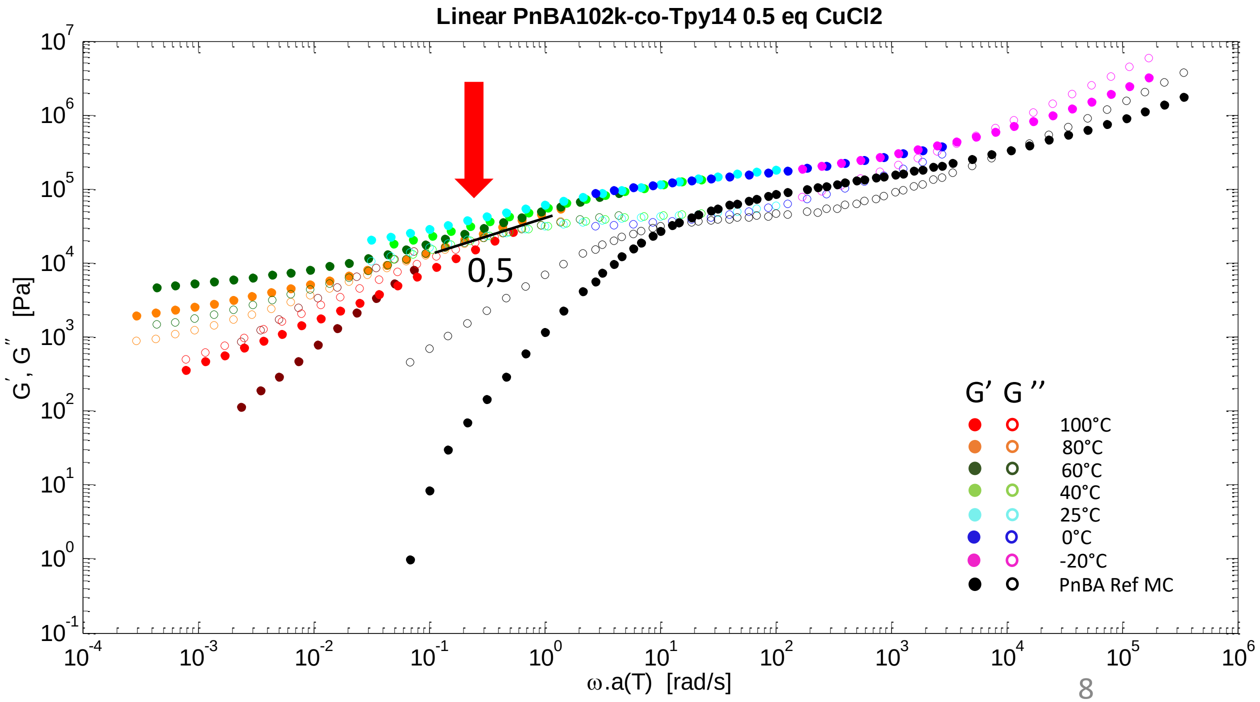
3 terpyridine per entanglement

⇨ Effect on the relaxation time ($\tau_{rel,0,5\ eq\ Zn} > \tau_{rel,PnBA}$) at 25°C

Effect of the temperature on the sample dynamics

Effect on the relaxation time ($\tau_{rel,0,5\ eq\ Cu} > \tau_{rel,0,5\ eq\ Zn}$) ⇦
Sample is not relaxing at 25°C, reaching a second plateau?
Second rouse process: Sticky Reptation

Temperature has a large influence on the sample dynamics



UCLouvain

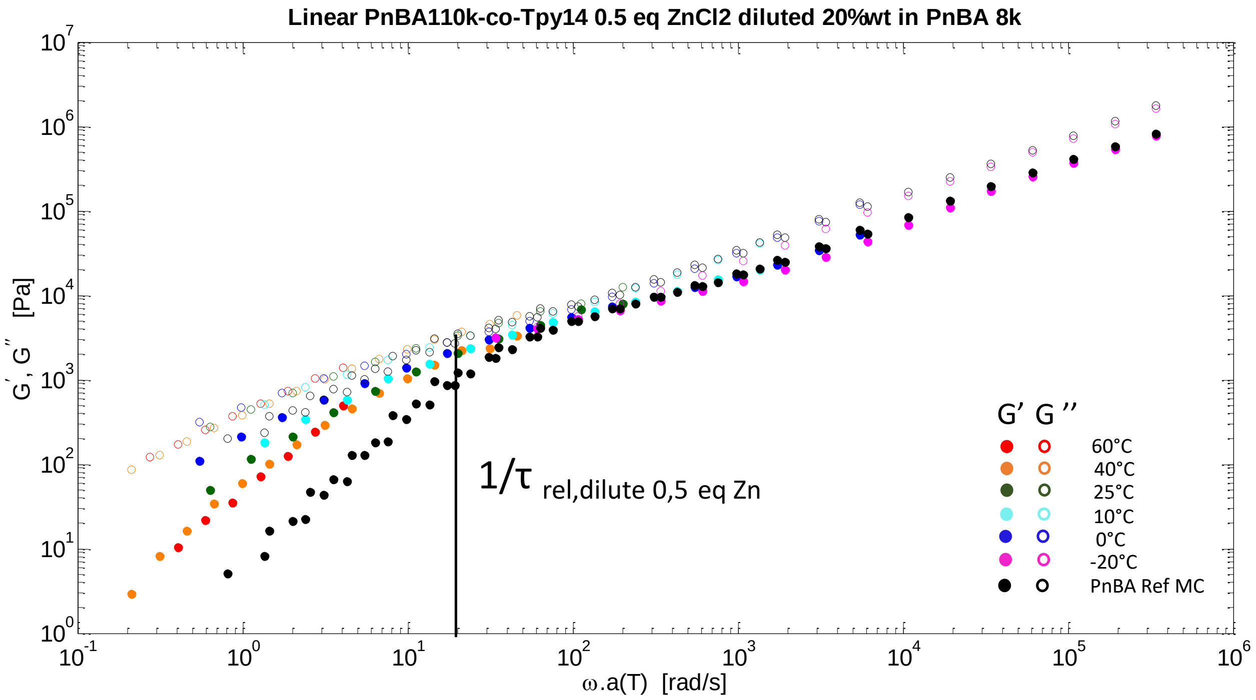
Network linear PnBA100k-co-14Ptpy

Linear Rheology with metal ion

in PnBA-8k

(20%wt)

14 terpyridine



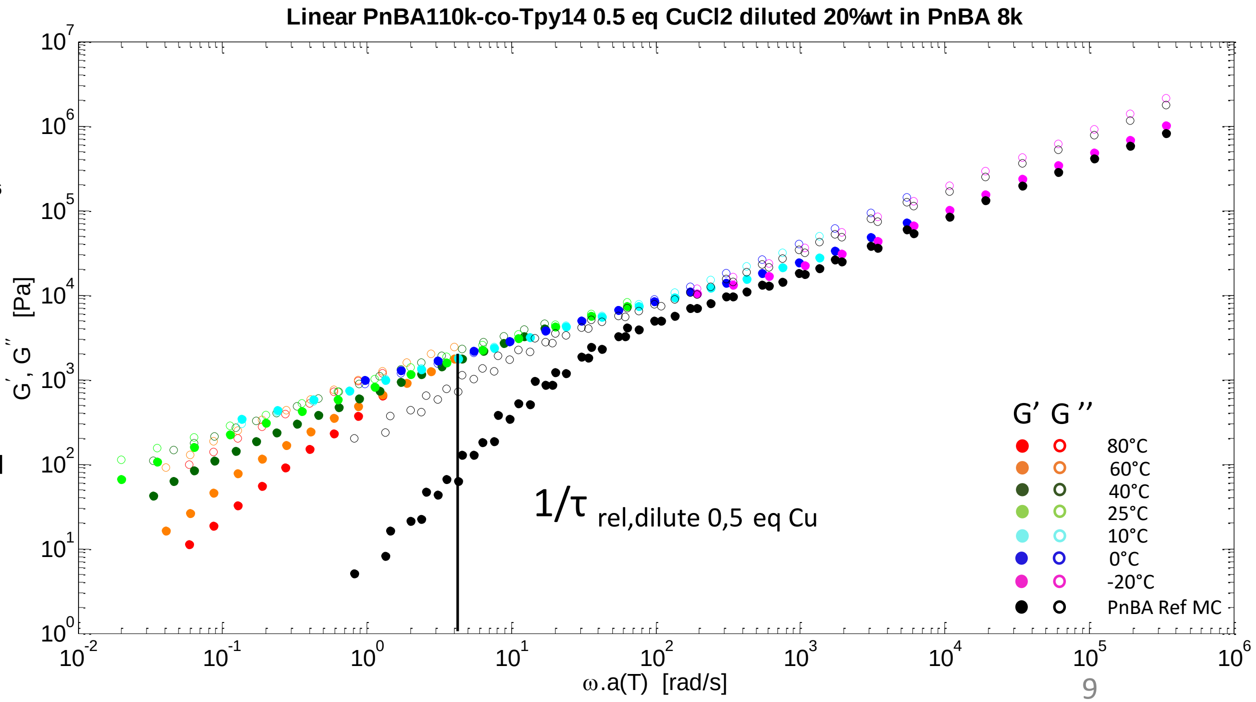
Dilution in short PnBA to remove entanglements effect on the sample

⇩

Dilution affects the relaxation time ($\tau_{rel,0,5\ eq\ Cu} > \tau_{rel,dilute\ 0,5\ eq\ Cu}$)
Dynamics of the system influenced by the entanglements

⇦

Temperature has a large influence on the sample dynamics

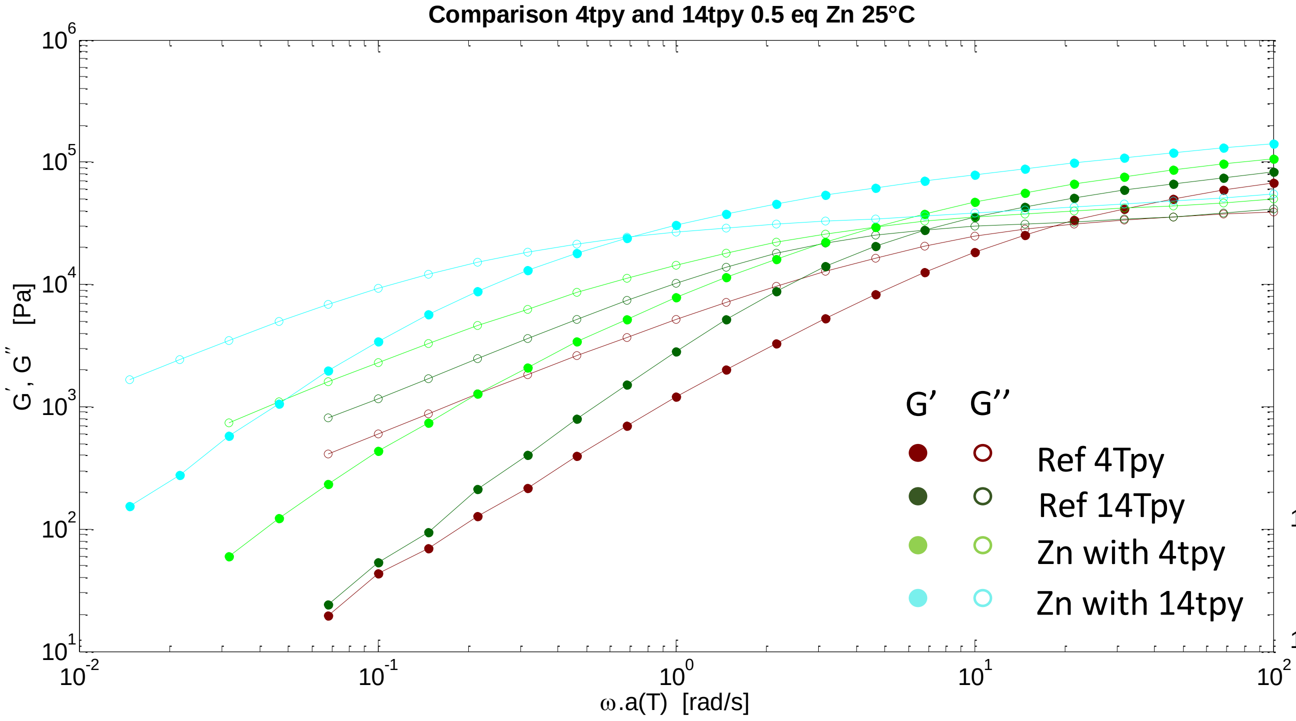


UCLouvain

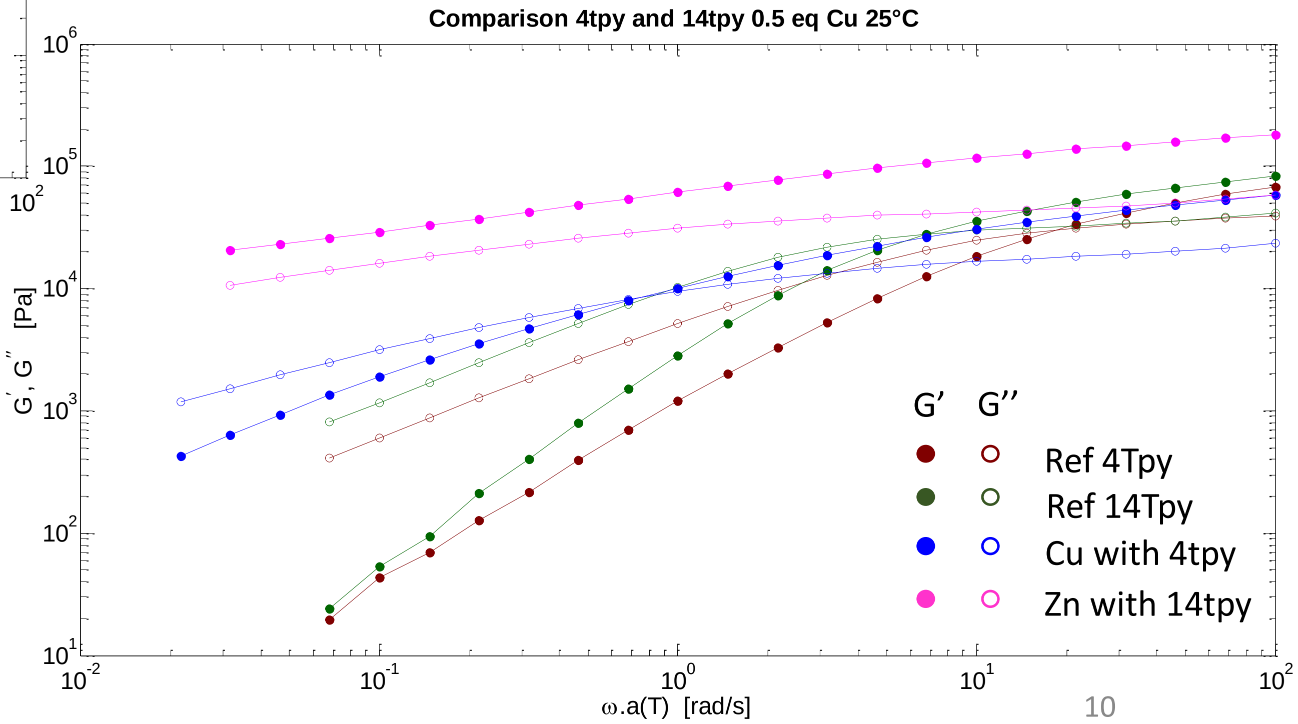
Network linear PnBA100k-co-Ptpy

Linear Rheology with metal ion

14 Tpy vs 4 Tpy



$\tau_{rel,14\ Tpy} > \tau_{rel,\ 4Tpy}$ at 25°C



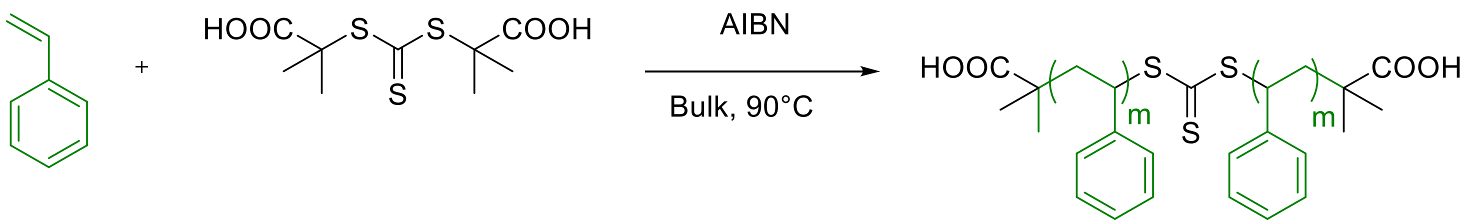
We are able to tailor systems with various number of terpyridine compared to the number of entanglements

Systems can be tune by the choice of the metal ion

Network ABA triblock

Network ABA triblock 1

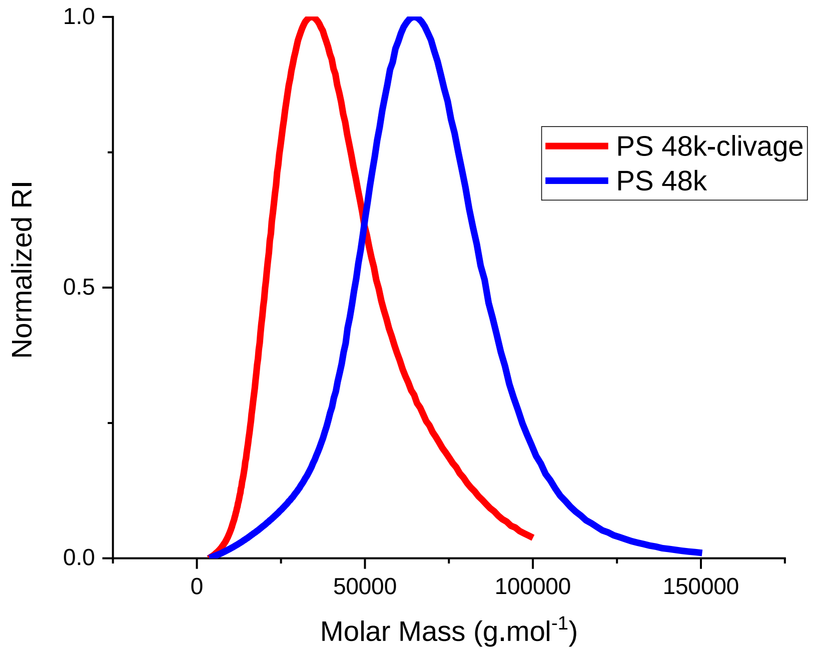
Step 1:



Synthesis route to PS-b-PS (Hard outer blocks)

- ✓ Conversion ~50 % [a]
- ✓ slow kinetics (~ 40 h) but controlled
- ✓ M_n = 25 000-50 000 $g.mol^{-1}$ [b]

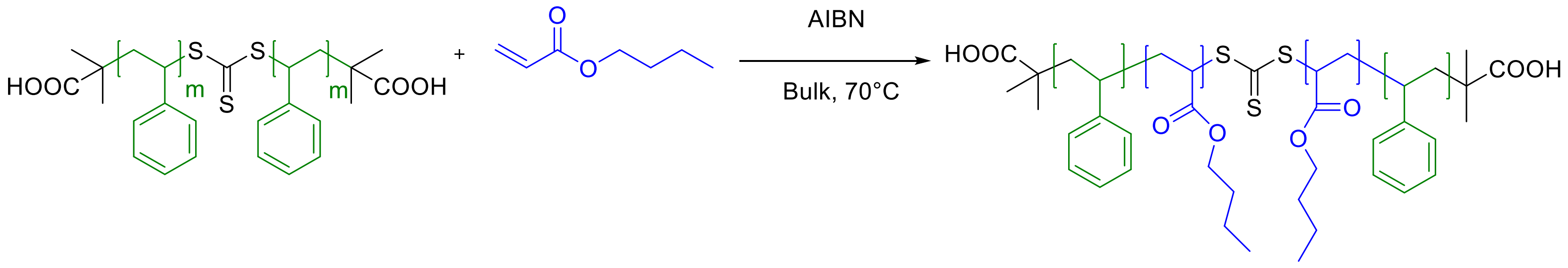
Procedure:
The polymer is dissolved in THF.
A small amount of DDT was added (reducing agent).
Subsequently, 10 eq BuNH2 was added and the mixture is stirred for 4h. Then 10eq of BuNH2 with 20 eq of Butyl Acrylate are added and the mixture is stirred for 24h .
Finally the mixture is precipated in MeOH and filtrated.



UCLouvain

Network ABA triblock 1

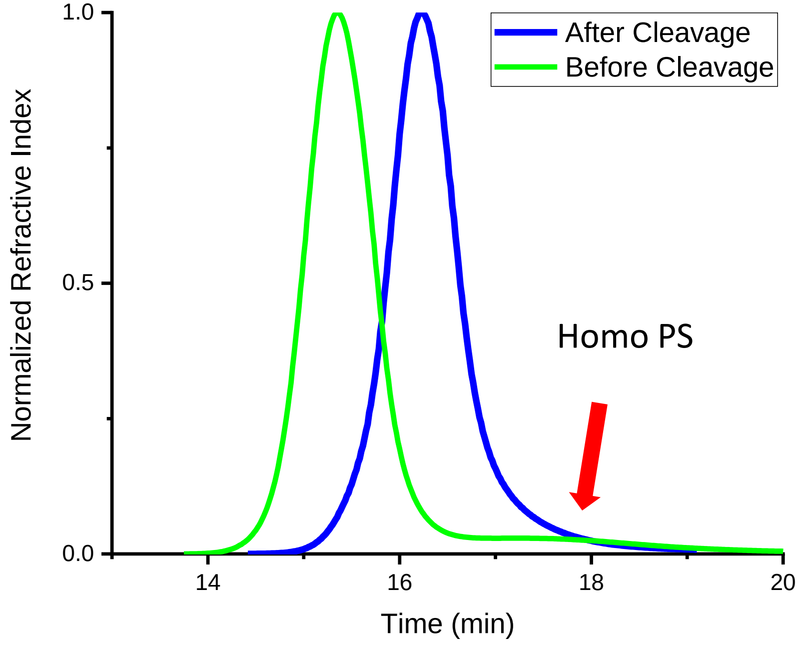
Step 2:



- ✓ Conversion ~50 % [a]
- ✓ M_n = 30 000-100 000 g.mol^{-1} [b]

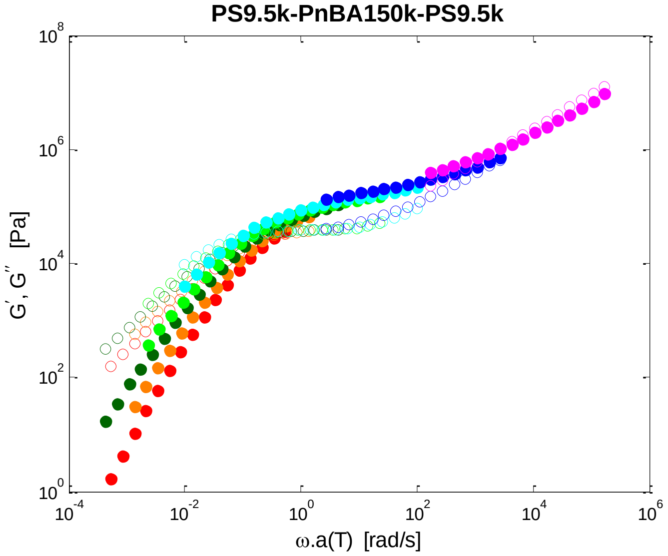
Block copolymer PS-b-PnBA-b-PS (With PnBA as soft central block)

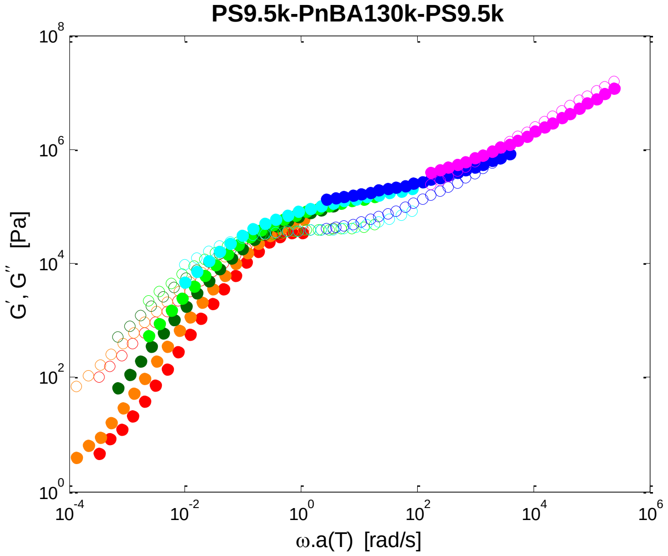
Procedure:
The polymer is dissolved in THF and an excess of nBa is added.
A small amount of DDT was added (reducing agent).
Subsequently, 10 eq BuNH2 was added and same amount 16h after.
Finally the mixture is precipated in MeOH/water and dried.

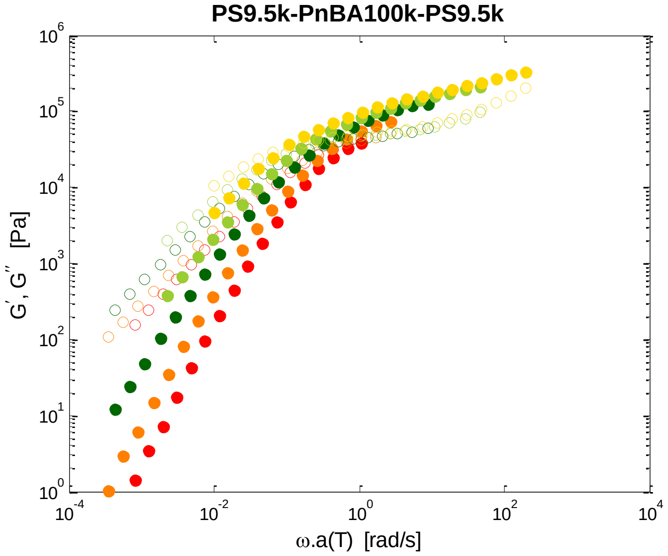


Network ABA triblock 1

Name	Mn (kg/mol)	D	m (g)	Tg (°C)	PS total length (kg/mol)	PS content (%)	Shear Rheology (linear regime)
(3) PS9,5k-co-PnBA82k-co-PS9,5k	100	1,48	2,5g	-45	19	16	G_N^0= 2.10^5
(4) PS9,5k-co-PnBA130k-co-PS9,5k	145	1,53	5,6g	-45	19	13	G_N^0= 2.10^5
(5)PS9,5k-co-PnBA150k-co-PS9,5k	165	1,56	3,9g	-45	19	11	G_N^0= 2.10^5







UCLouvain

Network ABA triblock 1

Name	Mn (kg/mol)	D	m (g)	Tg (°C)	PS total length (kg/mol)	PS content (%)	Shear Rheology (linear regime)
(6) PS12,5k-co-PnBA62k-co-PS12,5k	87	1,45	~1,6	~20	25	29	G_N^0= 1,5.10^6
(7) PS12,5k-co-PnBA35k-co-PS12,5k	60	1,45	1,5	1:-45 2:80	25	42	G_N^0= 2.10^7
(8) PS25k-co-PnBA120k-co-PS25k	170	1,5	2	1: -45 2: 100	50	30	

Plan:

- Blend sample (6) with different chain length of PS to enhance phase separation
- Blend sample (7) with short (8 kg/mol) and long (94 kg/mol) PnBA to swell the PnBA matrix

} Shear Rheology In the linear regime

Network ABA triblock

Rheometer procedure

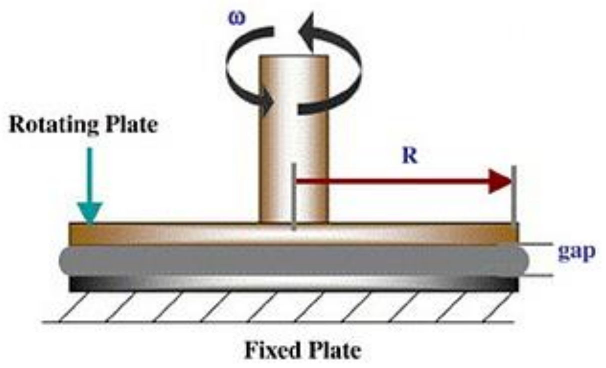
Rheometer: ARES-G2
Linear regime

Dynamic Time Sweep at 130°C :

- Remove sample memory shape (due to solvent evaporation)
- Sample equilibration

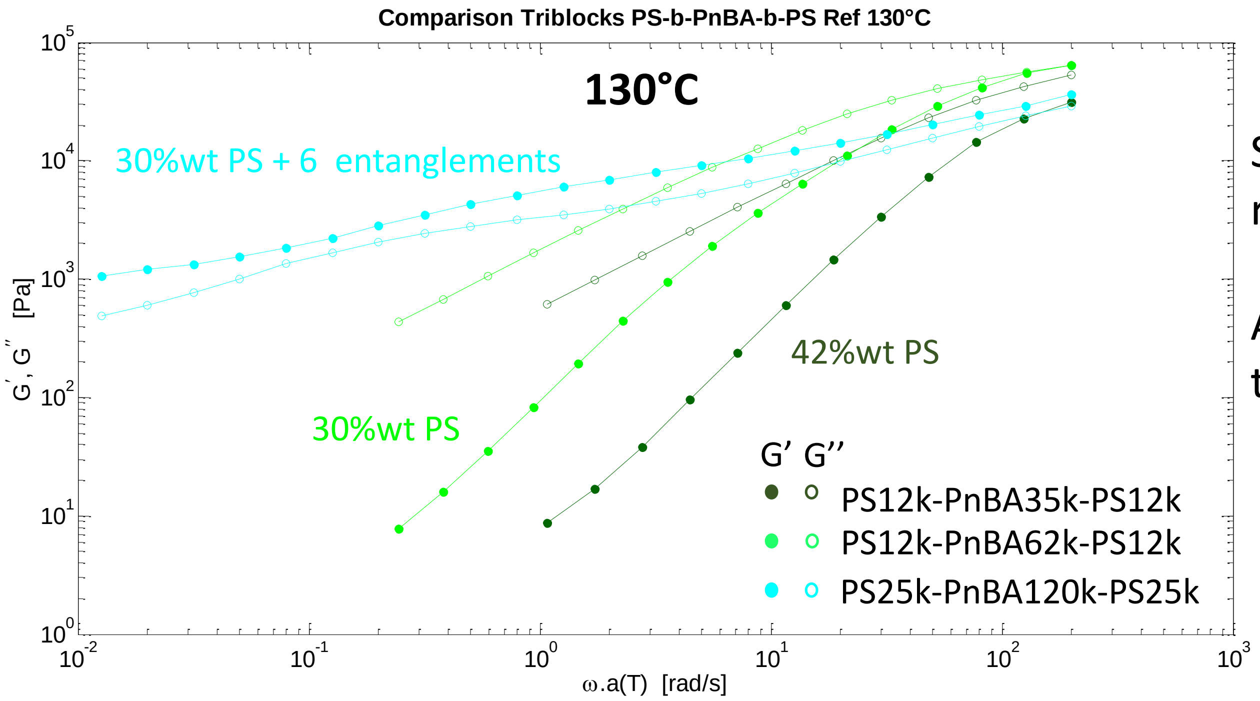
Start measurement at 100°C until -20°C :

- Dynamic time sweep (~10min)
- Dynamic strain sweep (0,1 to 20%)
- Dynamic frequency sweep (strain= 3…7%)



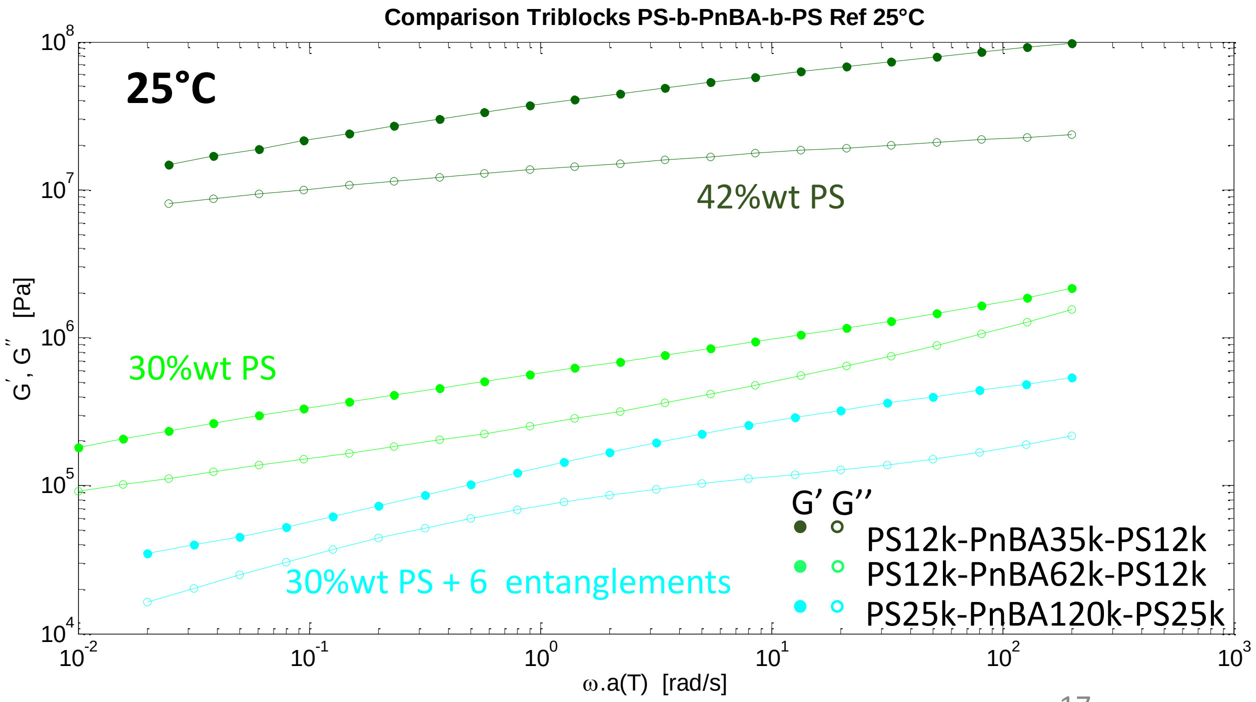
Network ABA triblock 1

Linear Rheology



Samples with low entanglements (green and dark green) at 130°C relaxes at low frequency

A strong network is built when more entanglements are added to high PS content (blue curve)

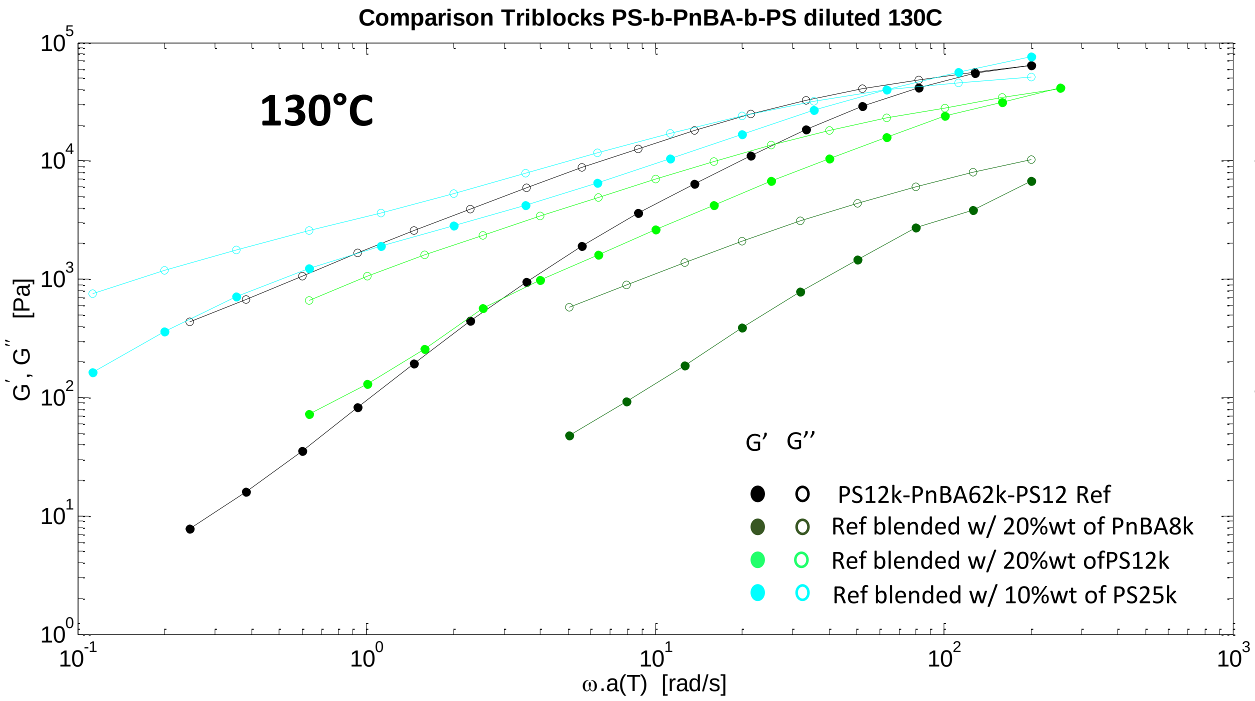


Modulus are higher with PS content increase in the samples
It could be related to the structure formed by Phase Separation

UCLouvain

Network ABA triblock 1

Linear Rheology



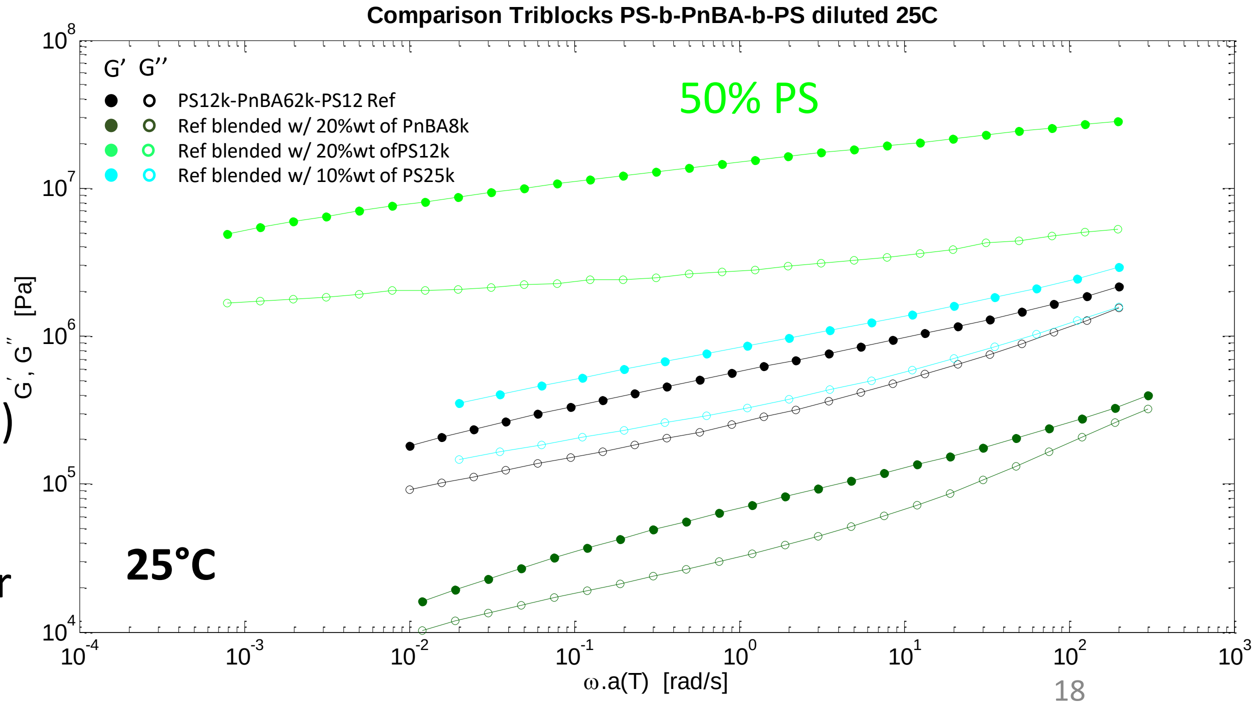
⇩

Increase of the modulus in the case of short PS
But not similar to PS12k-PnBA35k-PS12k (lower plateau modulus)

Part of the PS12k blended should be soluble in the PnBA polymer matrix

To increase the weigh faction of PS in the sample **PS12k-b-PnBA62k-PS12k** (reference sample) is blended :

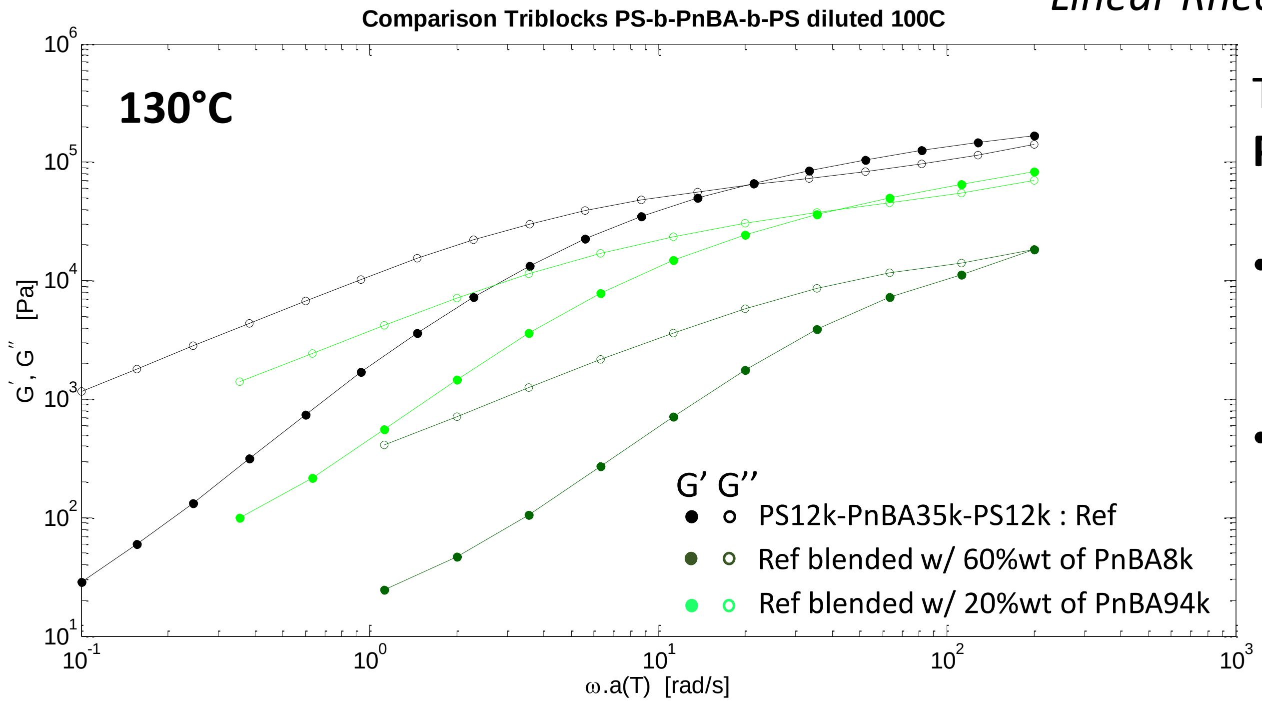
- With PS 25k : corresponding to the total amount of PS (total of the phase A) in the triblock
  -> **Macro Phase Separation**
- With PS 12 k: corresponding to the half of the total amount of PS in the triblock



Network ABA triblock 1

Linear Rheology

Ref : 42% PS content

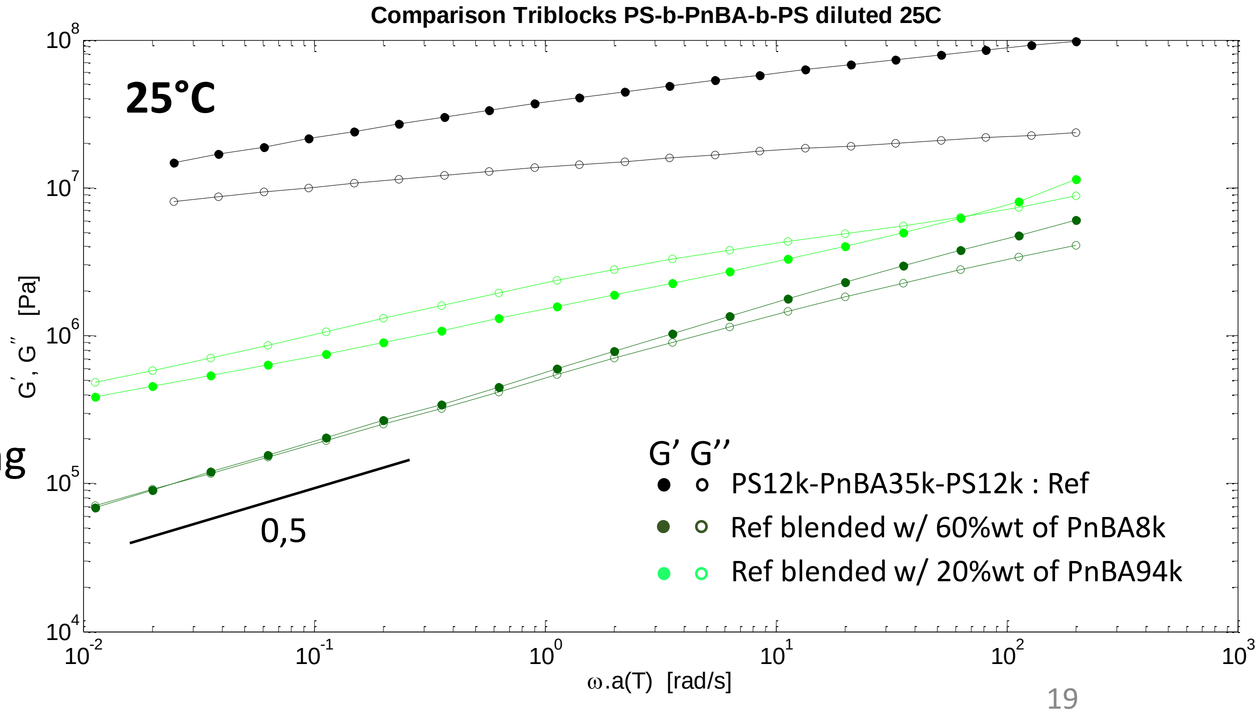


To lower the weigh faction of PS in the sample **PS12k-b-PnBA35k-PS12k** (reference sample) is blended:

- With PnBA 94k : to swell the PnBA matrix

  -> **Macro Phase Separation**

- With PnBA 8 k : to swell the central Block B made of PnBA



Structure information about the sample

Slope of 0,5 characteristic from lamellar structure

The lamellar structure is well-preserved after PnBA matrix swelling

Outlook and future work

Triblock PS-*b*-PnBA-*b*-PS :

- Select the system for double network : Blend with short linear PnBA-co-Ptpy or Star PnBA for non linear study
- Choose a system for dual network based on phase separation and Metal-Ligand association
- Study the effect of PnBA matrix swelling on the PS25k-b-PnBA120k-b-PS25k sample and the structure by SAXS

Metal-Ligand based system:

- Synthesize a linear PnBA-co-Ptpy around 20k for Double Dynamics Network use
- Characterize Star PnBA100k for Double Network use

Thank you for your attention

10/09/2020