

Synthesis and dynamics of model supramolecular polymer networks

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I. ABA Triblocks (Melt and Solution)

- a. Polystyrene-Poly(n-butylacrylate)-Polystyrene (PS-PnBA-PS)
- b. Poly(n-butylacrylate)-Poly(N,N-dimethylacrylamide)-Poly(n-butylacrylate) (PnBA-PDMA-PnBA)

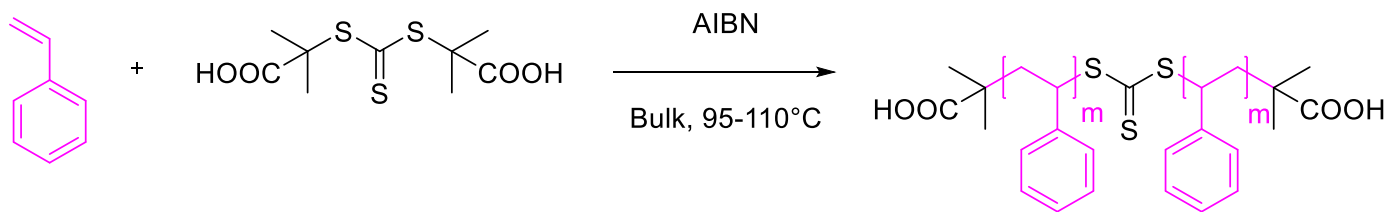
II. Linear Poly(n-butylacrylate)-co-Terpyridine (PnBA-co-tpy)

- a. Synthesis route
- b. Rheology measurement in melt

III. Conclusion and Outlooks

RAFT POLYMERIZATION of ABA Triblocks

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

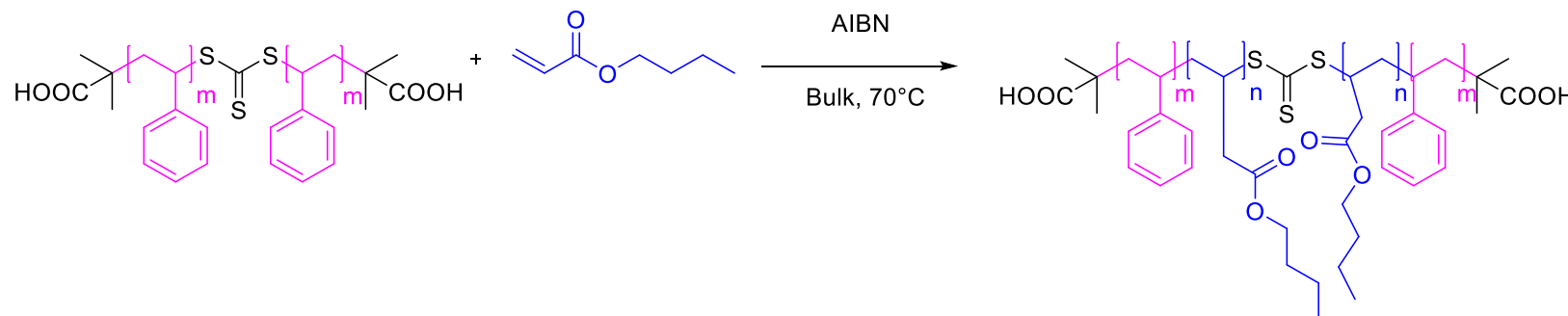


- ✓ Conversion 25-35 %^a (depend on the length wanted)
- ✓ Fast kinetics (~ 3-4 h)
- ✓ $2,4 \text{ kg.mol}^{-1 \text{ b}} < \text{Mn} < 24 \text{ g.mol}^{-1 \text{ b}}$



Formation of a Macro RAFT Agent

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



- ✓ Conversion ~70 %^a
- ✓ $65 \text{ kg.mol}^{-1 \text{ b}} < \text{Mn} < 110 \text{ kg.mol}^{-1 \text{ b}}$

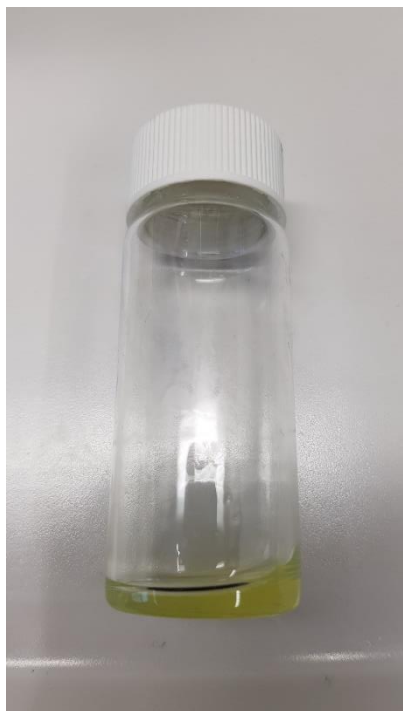
a: determined by ¹H NMR in CDCl₃

b: determined by GPC in DMF with PS-calibration



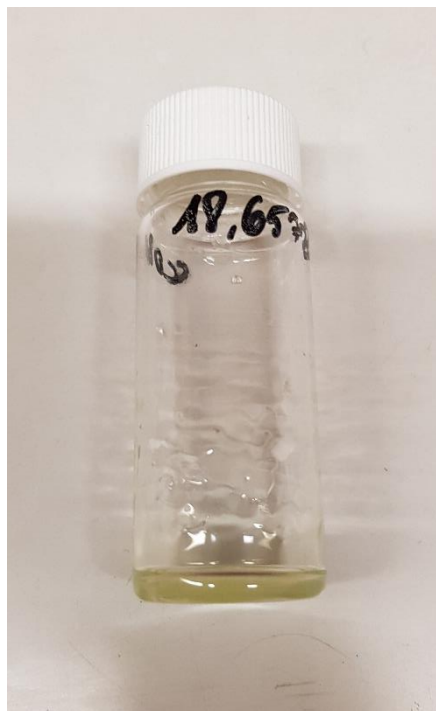
PS13k-PnBA110k

- $Mn_{total} = 122 \text{ kg/mol}$
- $Mn_{PS} = 13000 \text{ g/mol}$
- $\sim 10 \%$ in PS



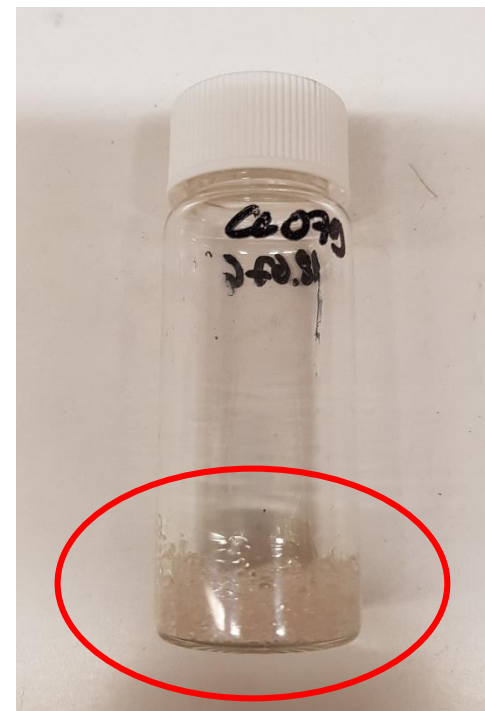
PS12k-PnBA65k

- $Mn_{total} = 78 \text{ kg/mol}$
- $Mn_{PS} = 12300 \text{ g/mol}$
- $\sim 16 \%$ in PS



PS24k-PnBA100k

- $Mn_{total} = 125 \text{ kg/mol}$
- $Mn_{PS} = 23800 \text{ g/mol}$
- $\sim 19 \%$ in PS



Rheology tests



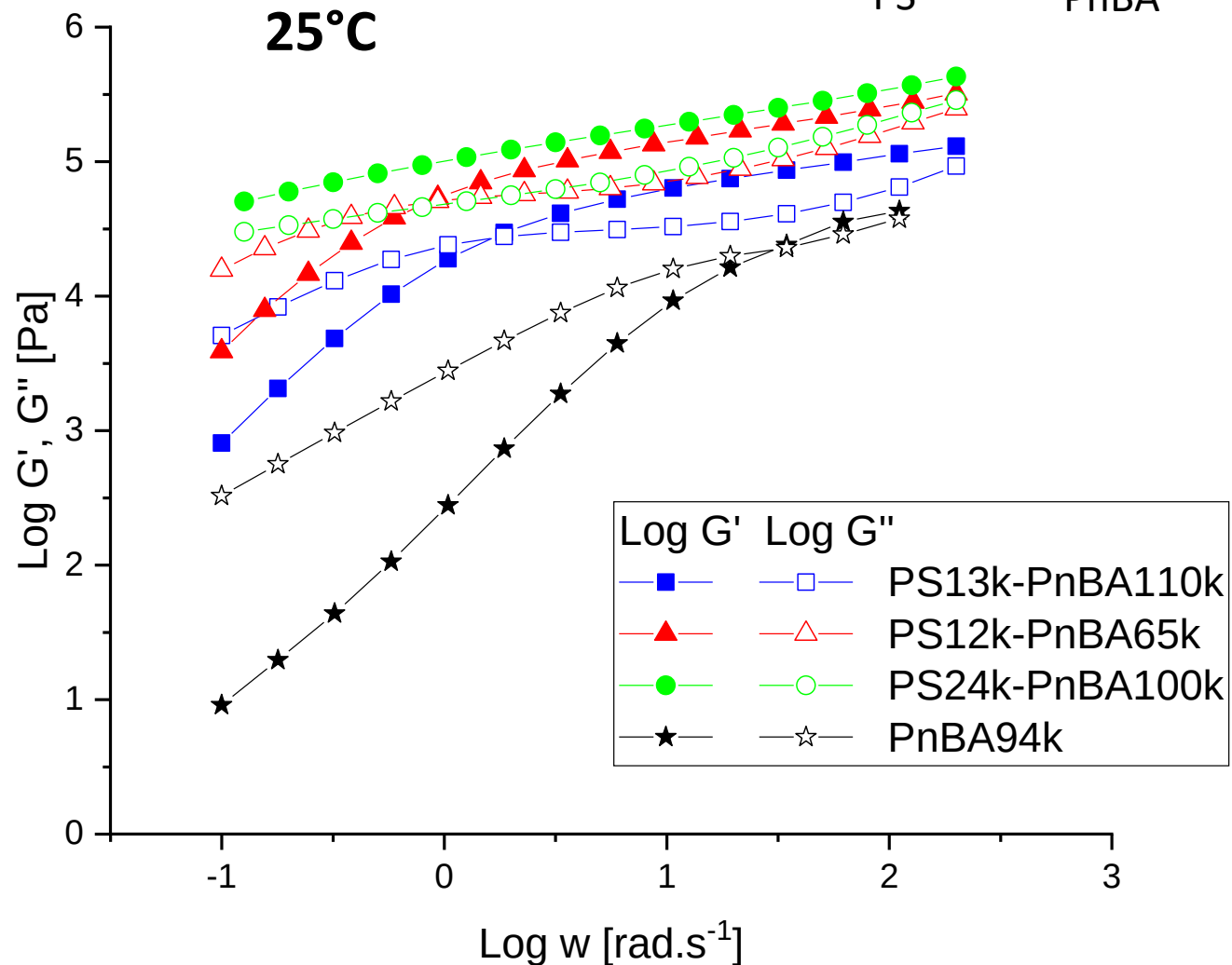
- Rotational shear rheology in melt
 - Compare the effect of PS outer block
In the ABA triblock

Procedure:

- High temperature (110°C), low strain, low frequency
 - time sweep (10 minutes)
- Frequency sweep (Strain 1%, 200 rad/s...0,1 rad/s)
from 80°C to 25°C



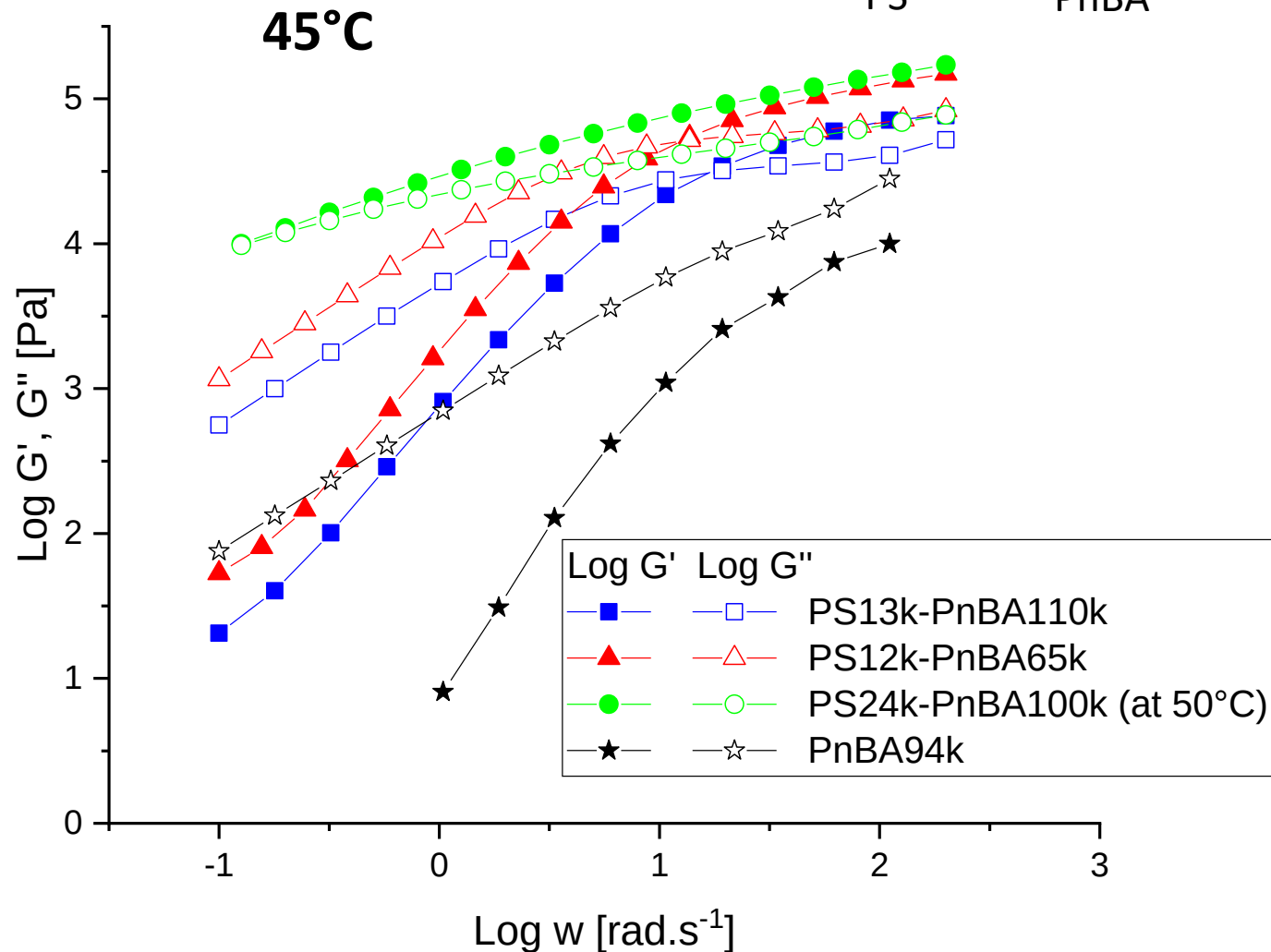
Rheology tests on PS-PnBA-PS



Frequency Sweep at 25°C:

- Reference: PnBA-94k
- Shift of the modulus (G' , G'')
- PnBA is flowing with curve of 1 (G') and 2 (G'')
- $\tau_{rel,PS12k-PnBA-65k} > \tau_{rel,PS13K-PnBA110k} > \tau_{rel,PnBA-94K}$

Rheology tests on PS-PnBA-PS



Frequency Sweep at 45°C:

- Reference: PnBA-94k
- Shift of the modulus (G' , G'')
- PS13k and PS12k are flowing with curve of 1 (G') and 2 (G'')
- Huge shift of τ_{rel} , PS24k-PnBA100k

Rheology tests on PnBA-PDMA-PnBA



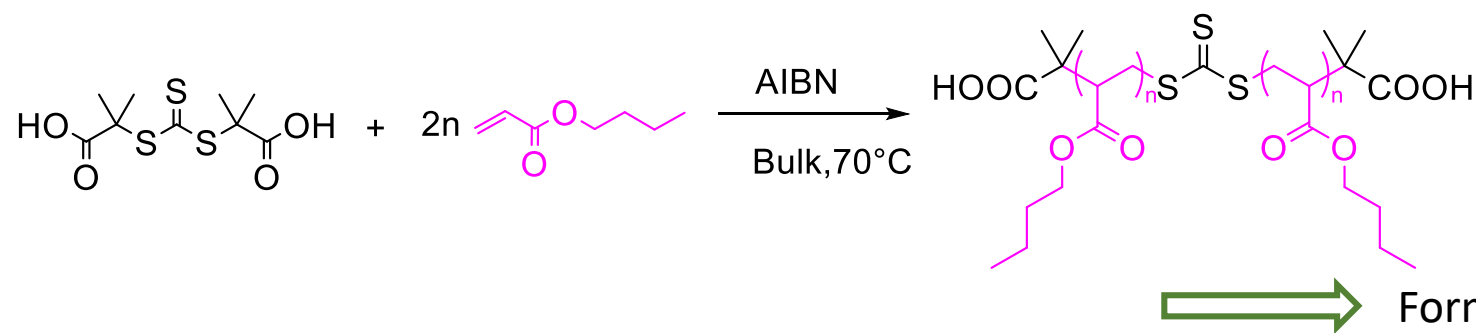
- Rotational shear rheology in aqueous solution
 - Study gel behavior

Procedure:

- Room temperature (20°C), low strain, low frequency
 - time sweep (10 minutes)
- Frequency sweep (Strain 1%, 100 rad/s...0,1 rad/s)

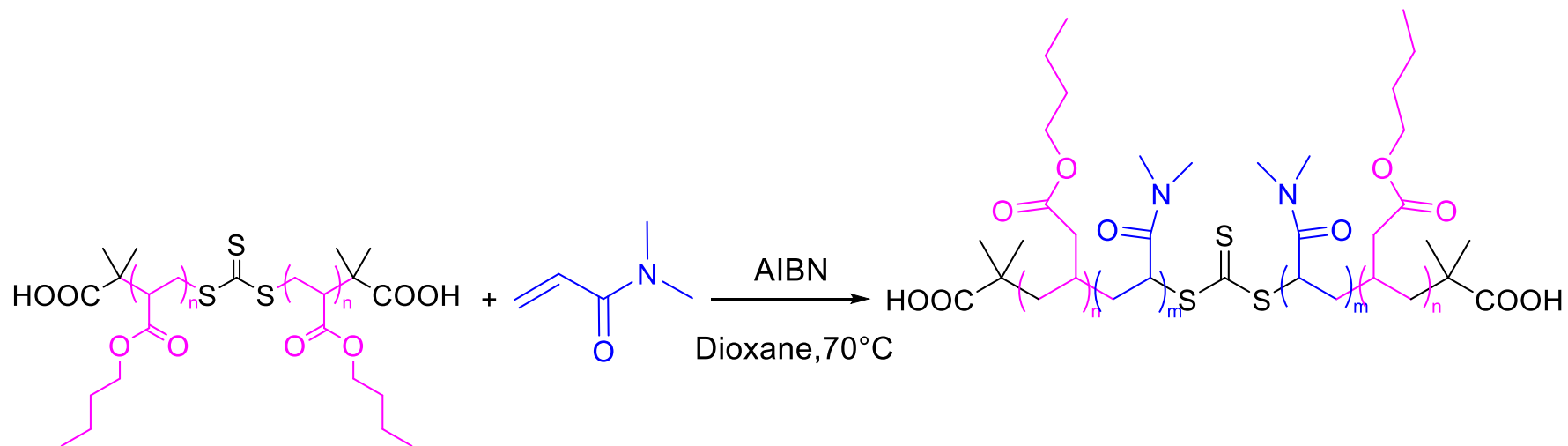


- Synthesis route to PnBA-*b*-PnBA (Hydrophobic outer blocks)



- ✓ Conversion 45-60%^a (difficult to control)
- ✓ Ratio 10:1 [CTA:AIBN]
- ✓ $M_n = 6000-47000 \text{ g.mol}^{-1}$ ^b

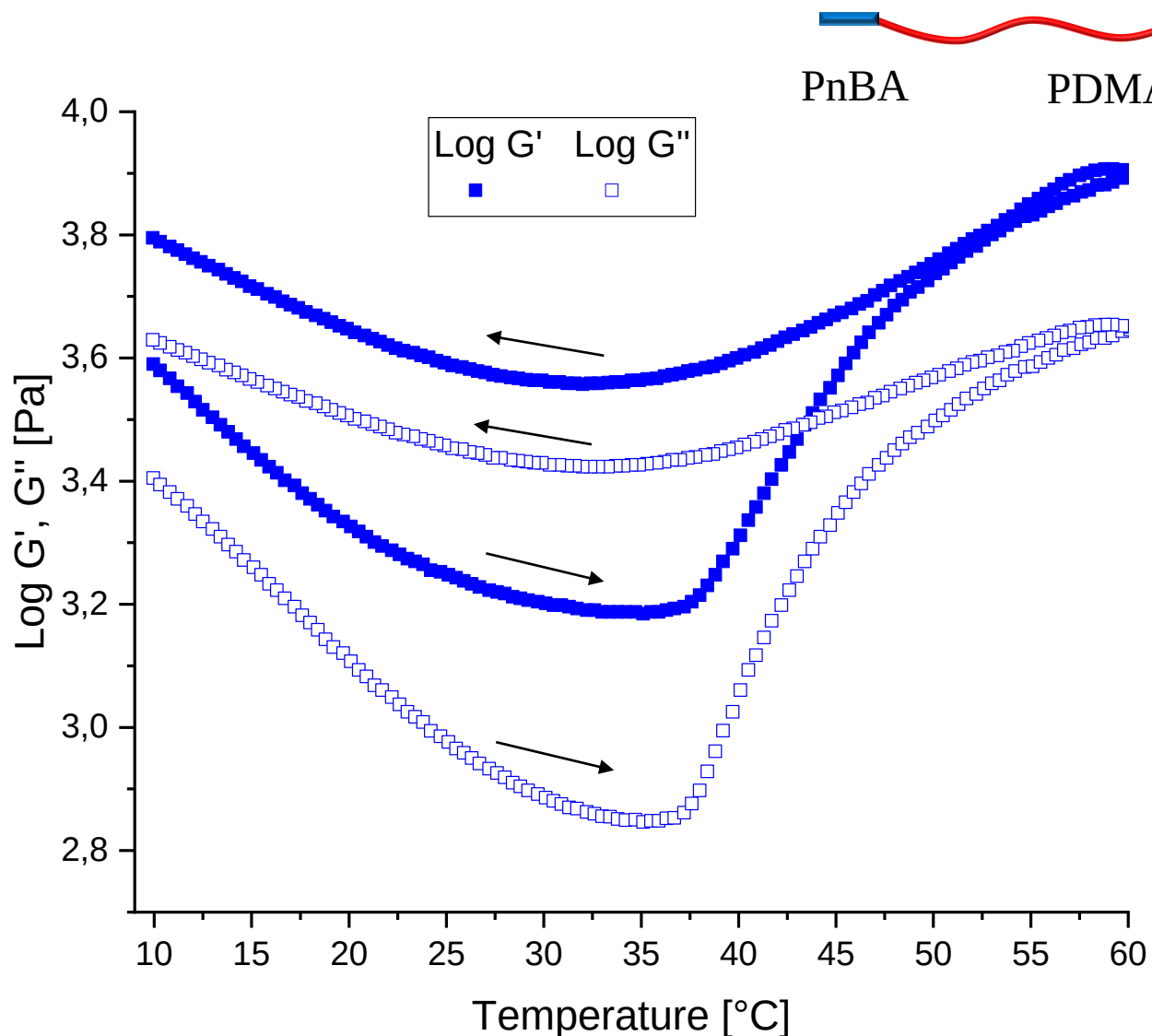
- Block copolymer PnBA-*b*-PDMAA-*b*-PnBA (With PDMAA as hydrophilic central block)



- ✓ Conversion ~ 95 %^a
- ✓ Ratio 10:2 [CTA:AIBN]
- ✓ $M_{n_{tot}} \sim 79 \text{ kg.mol}^{-1}$ ^b
(with $M_{n_{PnBA}} = 56 \text{ kg.mol}^{-1}$)

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

Rheology tests on PnBA-PDMA-PnBA



Temperature Sweep from 10°C to 60°C:

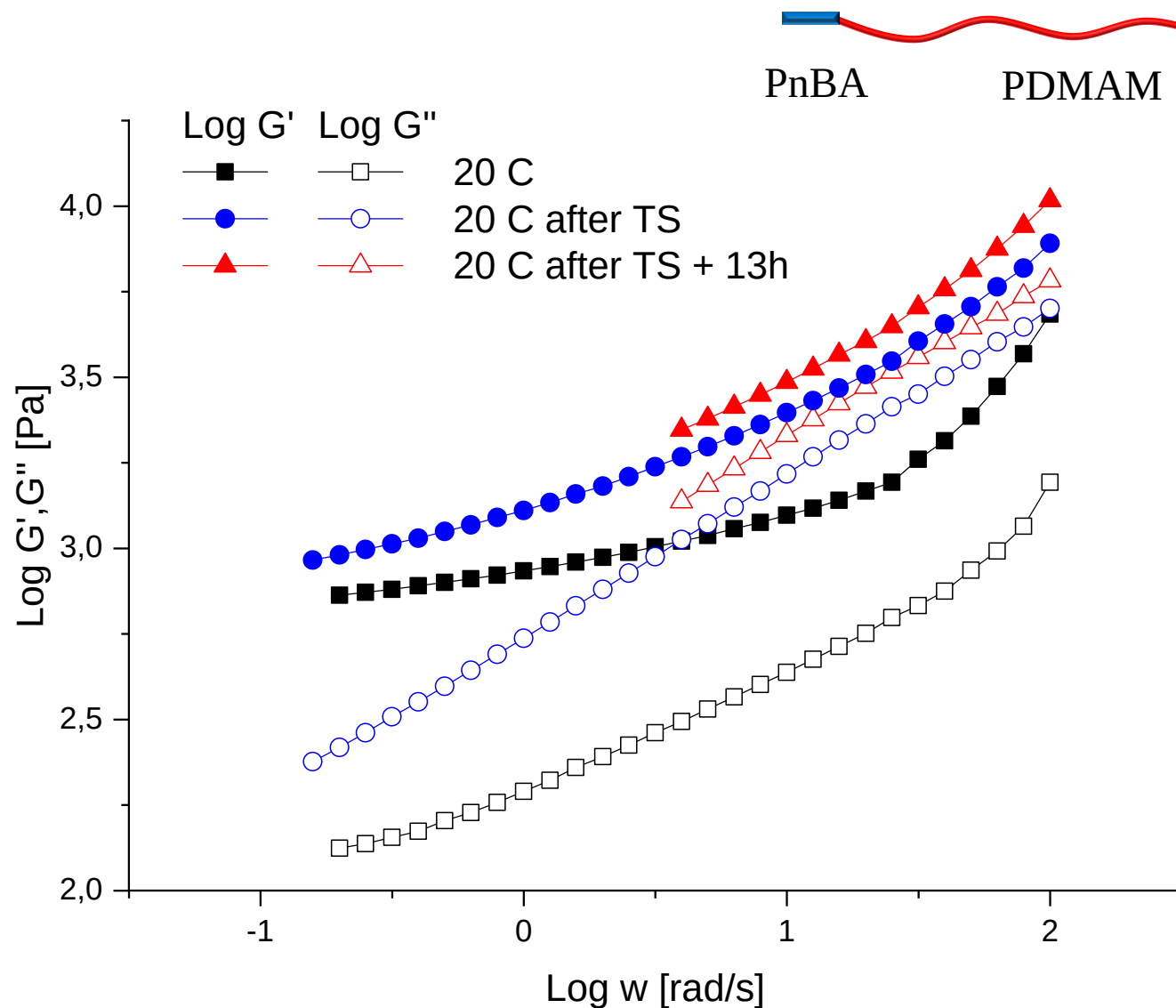
Go:

- Decrease of G' , G'' with temperature raise
- Inflexion point at 35,4°C
- Increase of G' , G'' → Structure change

Back

- Higher modulus (G' and G'')
- Lower inflexion
- Structure changed compare to the beginning or maybe evaporation of water

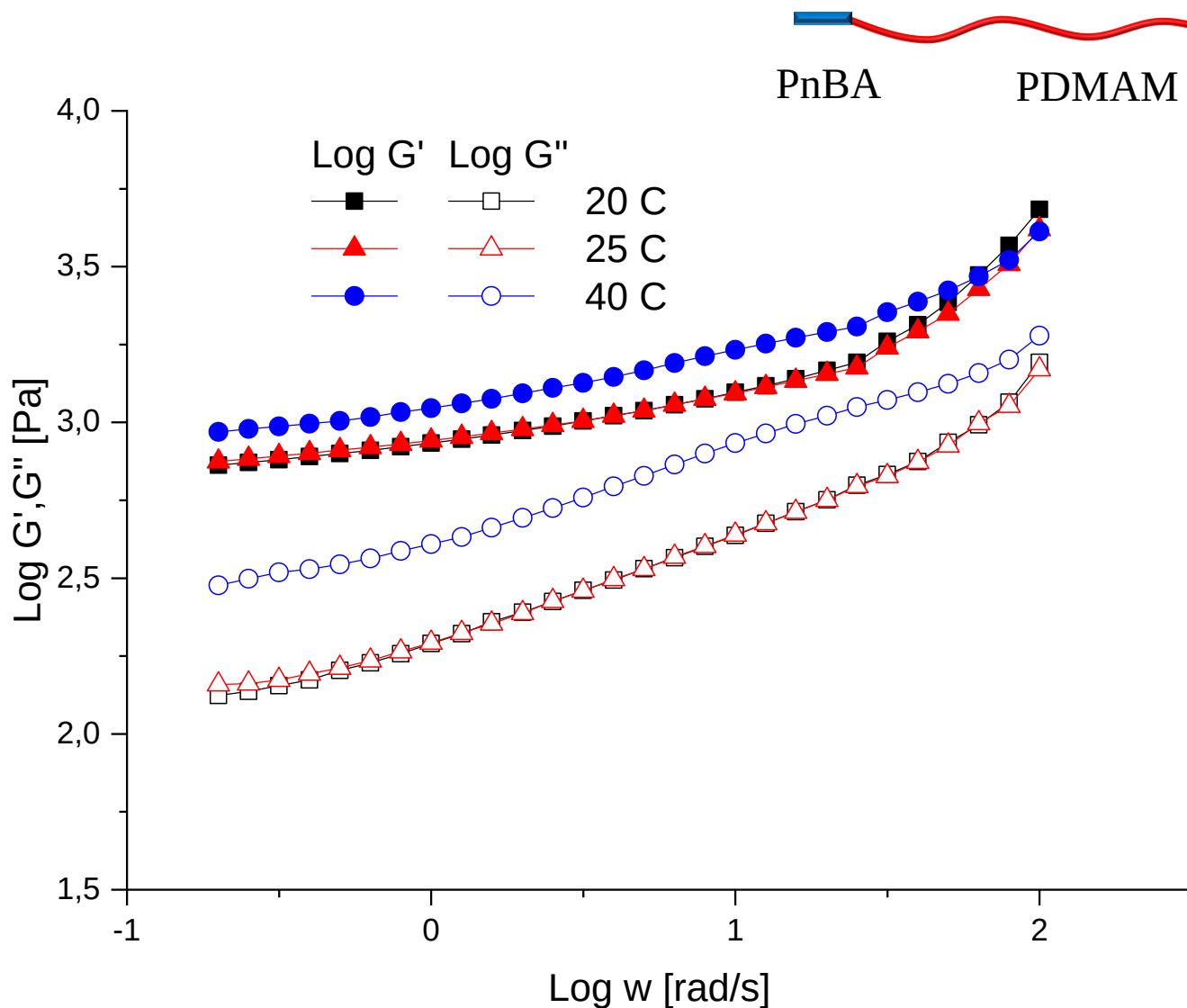
Rheology tests on PnBA-PDMA-PnBA



Frequency Sweep at 20°C:

- Increase of modulus after time sweep (no recovery) and after time (13h)
- Slope of 1 for G''
- G' reaches a plateau

Rheology tests on PnBA-PDMA-PnBA



Frequency Sweep at several temperatures:

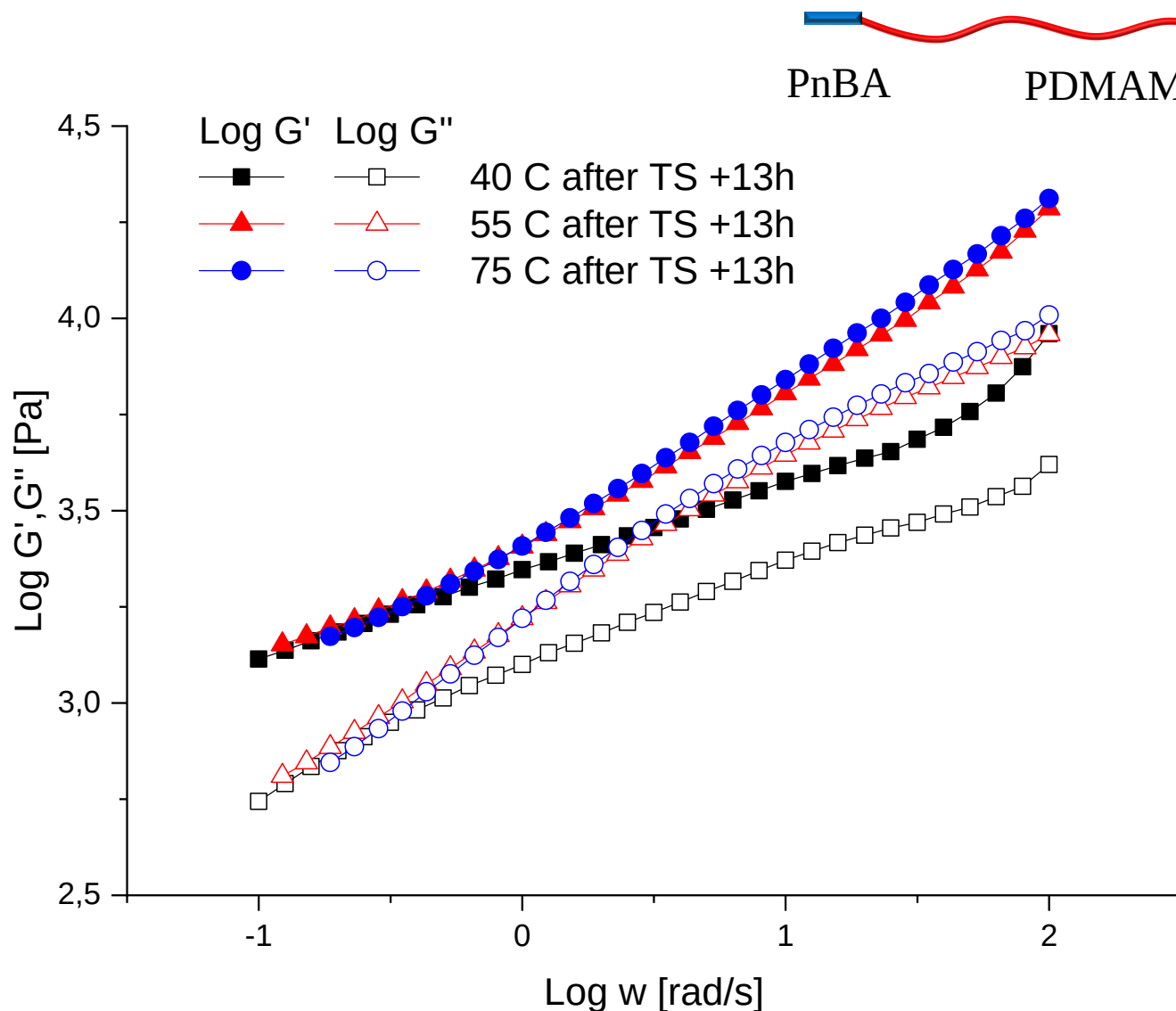
□ 20°C and 25°C:

- Small difference at high frequency in G'
- Small difference at low frequency in G''
- G', G'' seem to reach a plateau

□ 40°C:

- Same G' behavior in high frequency as black and red curve
- Higher G' when frequency decreases
- Slope of 1 for G''

Rheology tests on PnBA-PDMA-PnBA



Frequency sweep at several temperature:

□ 55°C and 75°C:

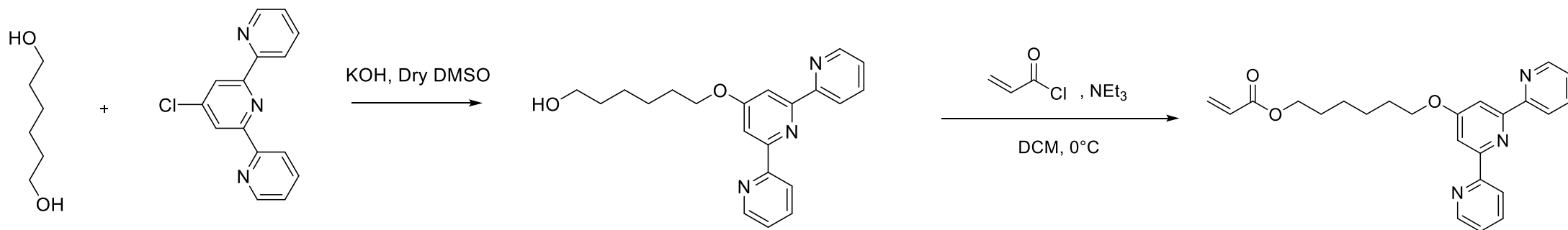
- Small difference at high frequency in G' and G''
- Same Behavior at low frequency
- Solvent evaporation ?

□ 40°C:

- Lower G'' and G'
- Same behavior at very low frequency

RAFT POLYMERIZATION of Linear PnBA-co-tpy

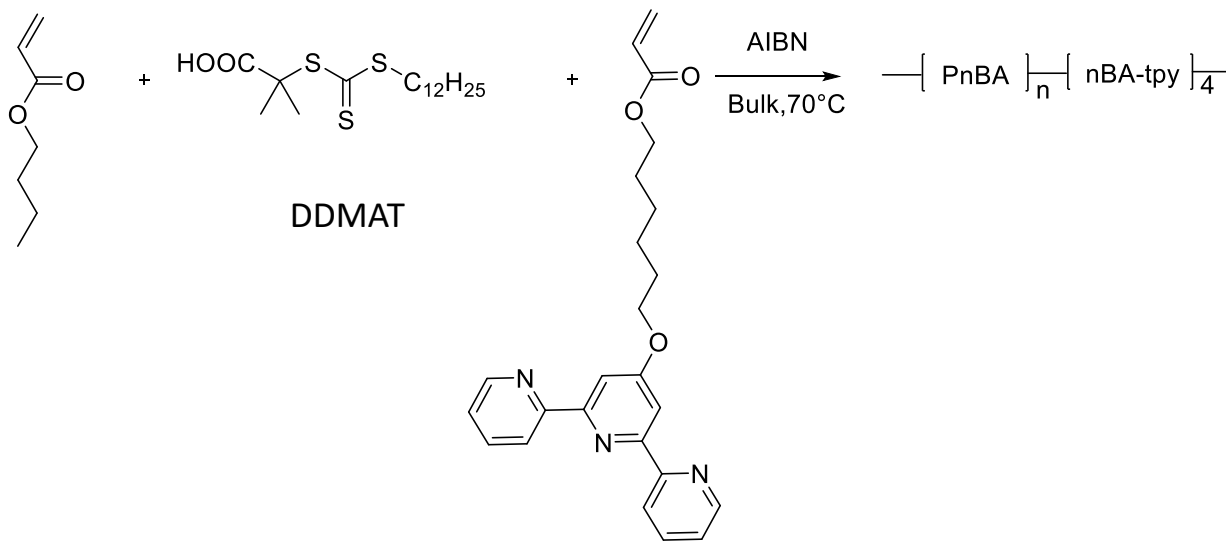
Synthesis of nBA-tpy monomer



- ✓ Yield = 70%
- ✓ Precursor to nBA-tpy

- ✓ Yield = 65 %
- ✓ White powder

Polymerisation of PnBA-co-tpy



- ✓ Conversion ~70 %^a
- ✓ $M_n \sim 100 \text{ kg.mol}^{-1}$ ^b
- ✓ 4 terpyridine per chains
- ✓ Random linear copolymer

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

Rheology tests on PnBA-co-tpy



PnBA-co-tpy

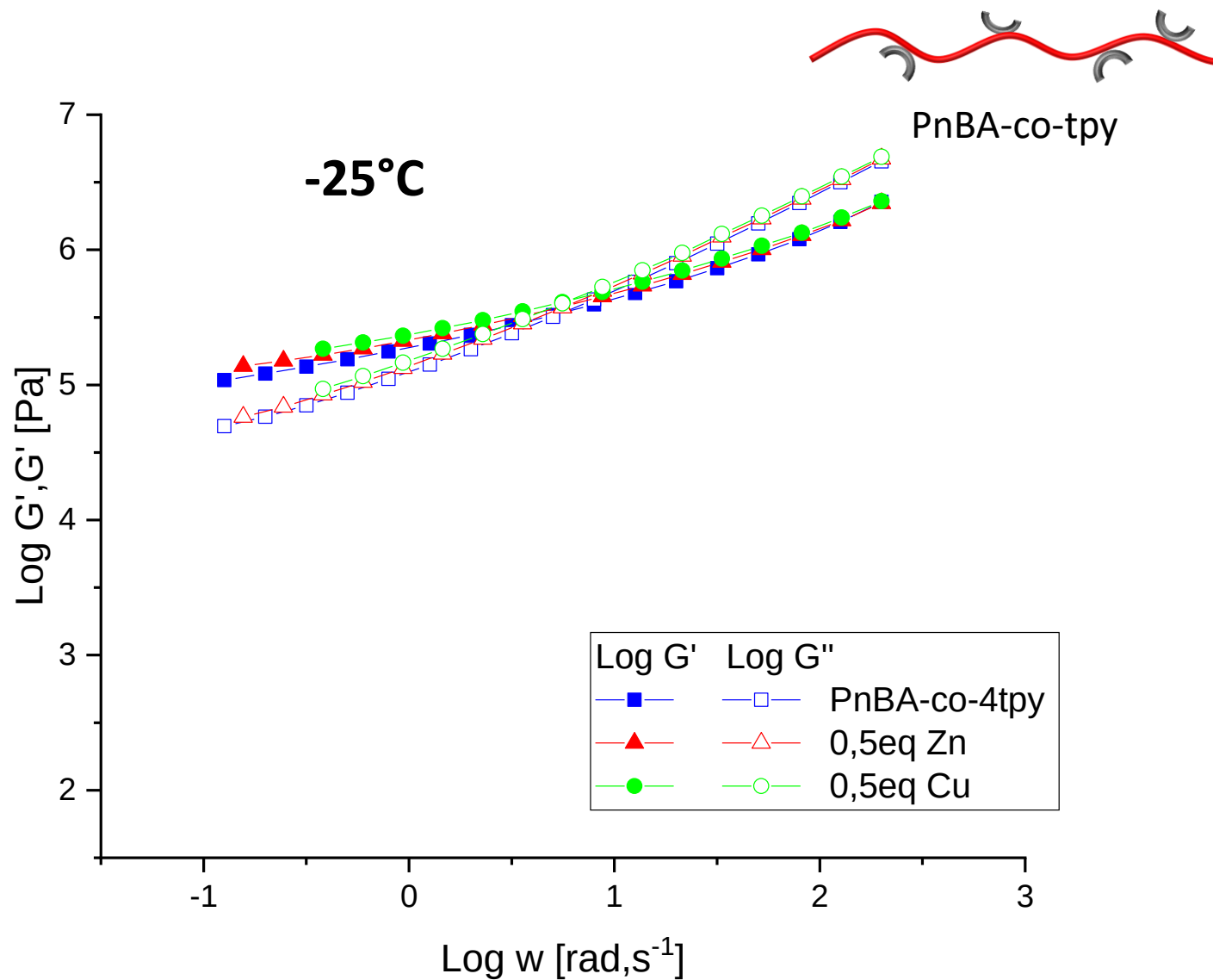
- Rotational shear rheology in melt
 - Compare the effect of stickers with metal ions

Procedure:

- High temperature (130°C), low strain, low frequency
 - Time sweep (15 minutes)
 - Frequency sweep (Strain 1%, 200 rad/s...0,1 rad/s)
- from 80°C to -25°C



Rheology tests on PnBA-co-tpy



Frequency sweep at -25°C:

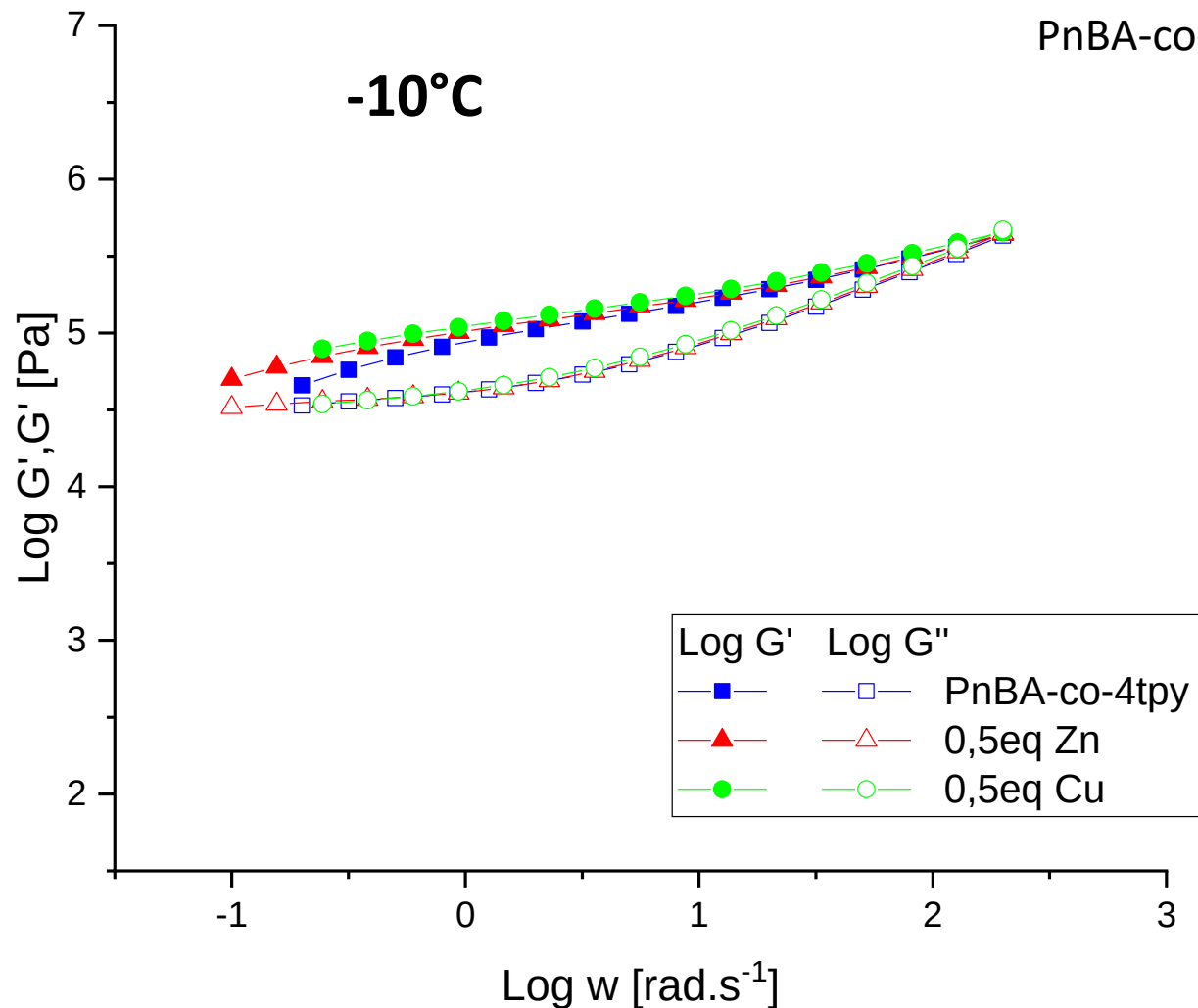
- Same behavior for Rouse relaxation
- At low temperature, metal ion is not active

Rheology tests on PnBA-co-tpy



PnBA-co-tpy

-10°C



Frequency Sweep at -10°C

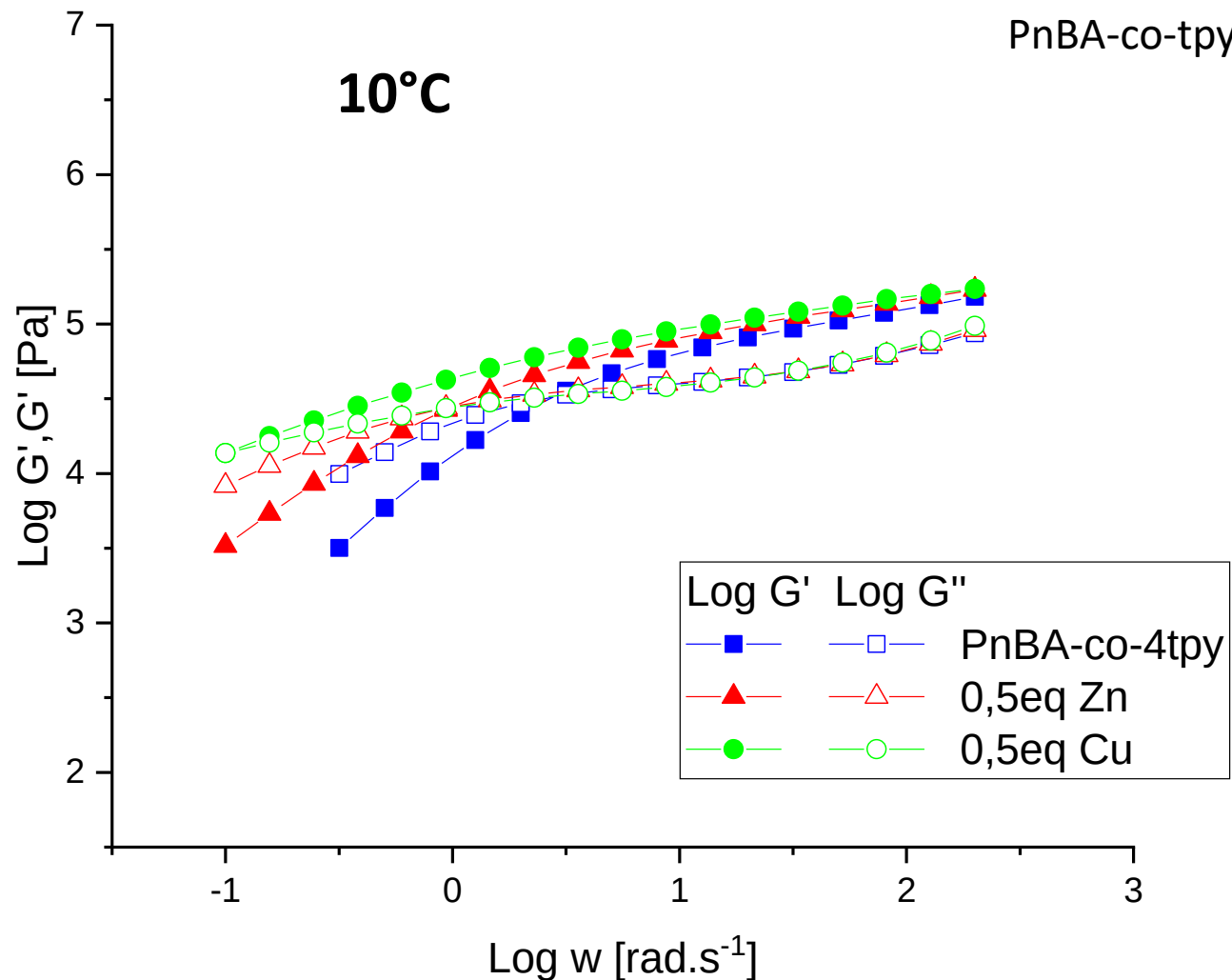
- Same Behavior at high frequency
 - No effect of metal ion in the Rouse regime

Rheology tests on PnBA-co-tpy



PnBA-co-tpy

10°C



Frequency Sweep at 10°C:

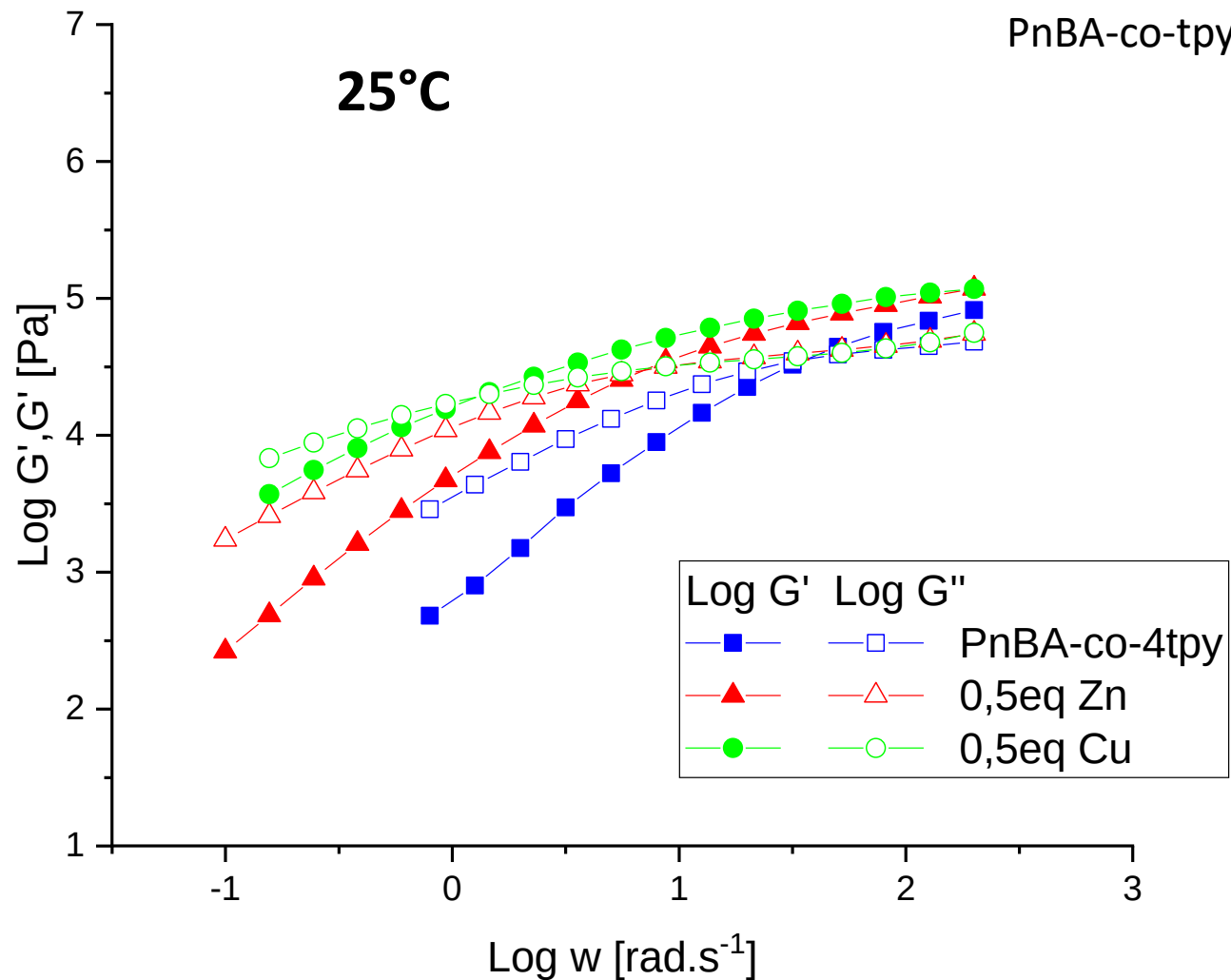
- All G'' overlapping at high frequency
- $\tau_{rel,Cu} > \tau_{rel,Zn} > \tau_{rel}$
- 0,5eq Cu is not flowing

Rheology tests on PnBA-co-tpy



PnBA-co-tpy

25°C



Frequency Sweep at 25°C:

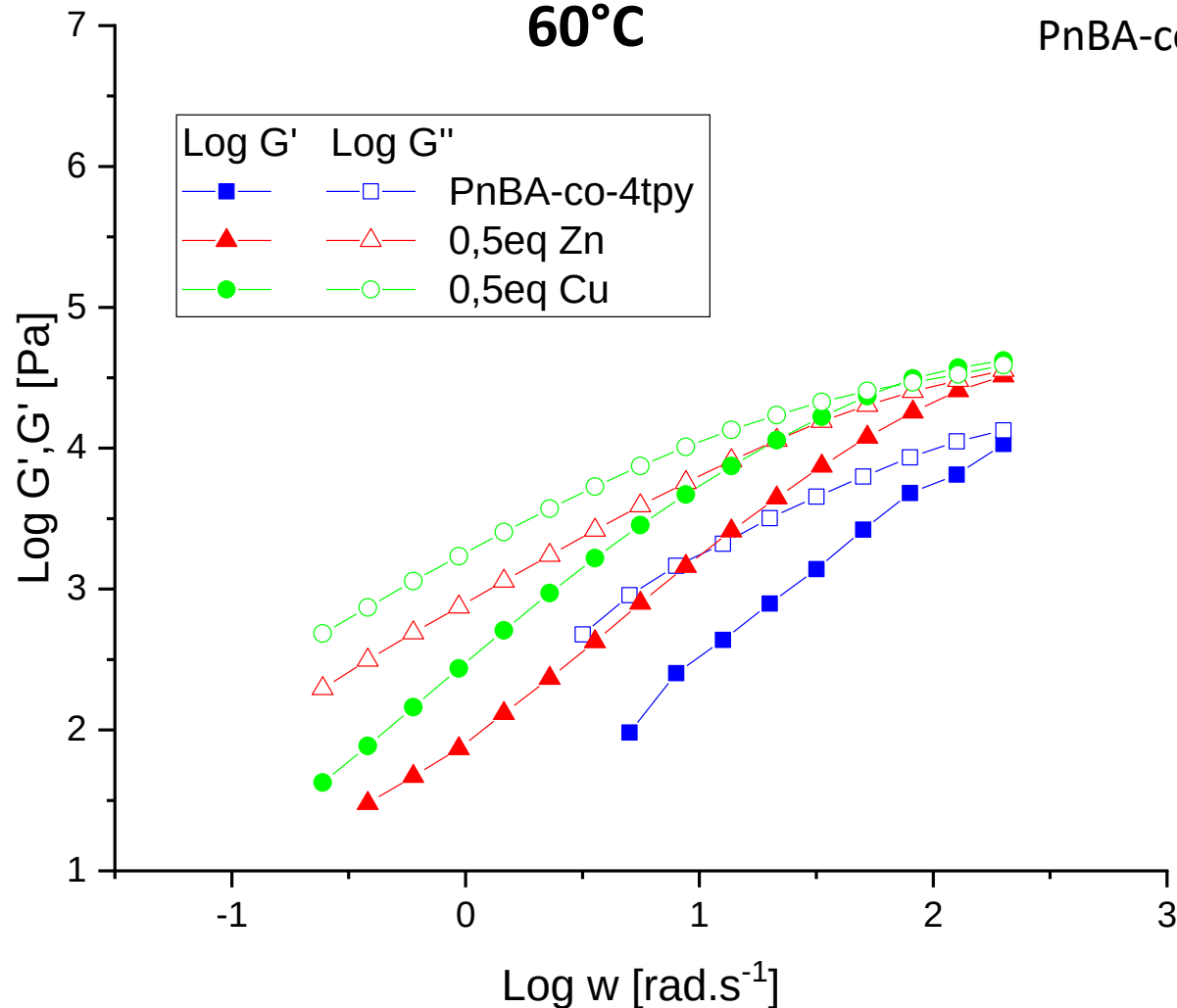
- $\tau_{rel,Cu} > \tau_{rel,Zn} > \tau_{rel}$
- Slope of 1 (G') and 2 (G'') for 0,5eq Zn and PnBA-co-4tpy

Rheology tests on PnBA-co-tpy



PnBA-co-tpy

60°C



Frequency sweep at 60°C :

- Slope of 1 (G') and 2 (G'') all samples

Conclusion

❑ ABA triblocks in melt:

- Phase separation increased when you increase PS ratio
- Loss of flow when PS molar mass reach a certain point

❑ ABA triblocks in solution:

- Change of structure with temperature
- No recovery
- Difficult to have the gel stabilized

❑ Linear PnBA-co-tpy:

- Effect of the stickers on τ_{rel} with 0,5 eq of metal ion

Outlooks

❑ ABA triblocks :

- Test PS12,3K-PnBA65K in isopropanol to form a gel
- Characterize by linear rheology this gel
- Use PS substitute with trifluoromethyl to increase phase separation
- SAXS to check the structure of the samples

❑ ABA triblocks in aqueous solution:

- Adapt the system (PDMA issues)
- Solve polymerization issues

❑ Linear PnBA-co-tpy:

- Characterize deeper with Cu and Zn
- Different equivalent of metal ion
- Synthesize Star Polymer ($M_n = 100K-250K$)

Thank you for your attention