Synthesis and dynamics of model supramolecular polymer networks

Clément Coutouly

Supervisors:

Prof. Charles-André Fustin

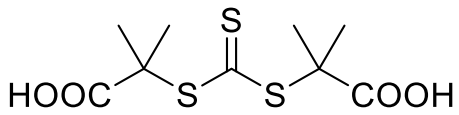
Prof. Evelyne Van Ruymbeke

Vaalsbroek

31 January 2019

RAFT AGENT

- Bifunctional CTA to insure a polymer growth from both sides:



S,S'-Bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate
(**DMAT**)

- ✓ Very efficient chain-transfer RAFT agent
- ✓ Initiation by a small amount of AIBN
- ✓ Easy for block copolymers
- ✓ Good control of polymerization (Bulk and solvent)

- Synthesis route

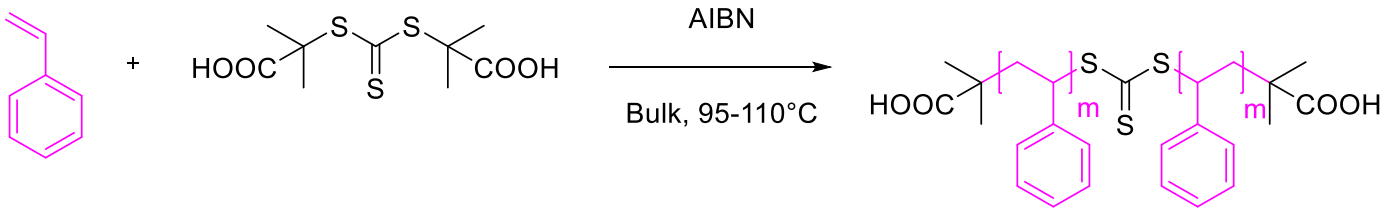
- ✓ Good yield after purification
- ✓ Easy purification

TBAHS: Tetrabutylammonium hydroxide

Macromolecules **2002,** *35,* 6754-6756

RAFT POLYMERIZATION of ABA Triblocks

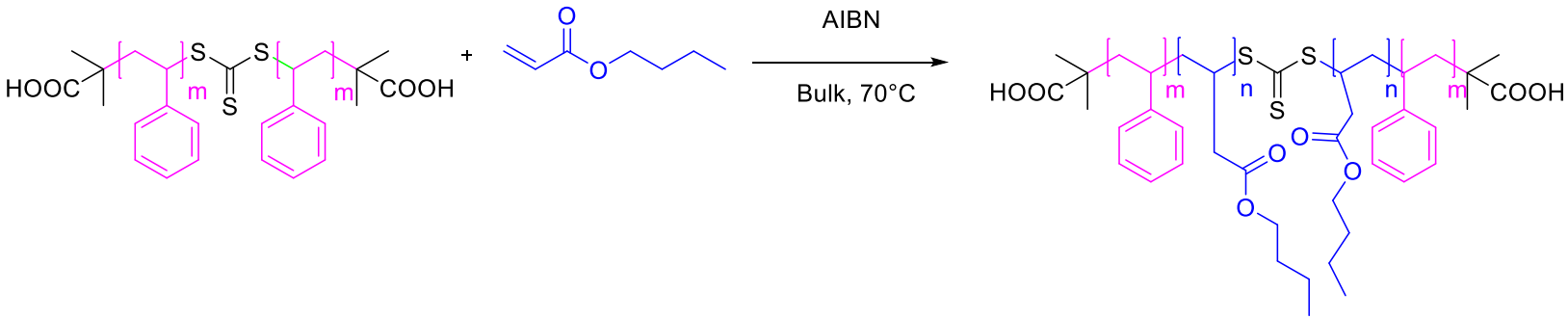
- Synthesis route to PS-*b*-PS (Hard outer blocks)



- ✓ Conversion 35-45 % [a] (depend on the length wanted)
- ✓ Fast kinetics (~ 3-4 h)
- ✓ Mn = 2400-3600-6200-13700 g.mol^{-1} [b]

⟹ Formation of a Macro RAFT Agent

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



- ✓ Conversion ~70 % [a]
- ✓ Mn = ~110 000 g.mol^{-1} [b]

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

PS-2400-PnBA

- Mn_{total} = 112 kg/mol
- Mn_{PS} = 2400 g/mol
- ~ 2,1 % in PS

PS-3700-PnBA

- Mn_{total} = 117 kg/mol
- Mn_{PS} = 3700 g/mol
- ~ 3 % in PS

PS-6100-PnBA

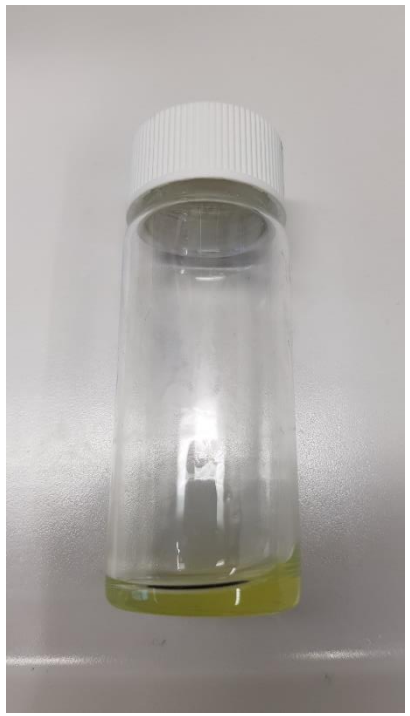
- Mn_{total} = 110 kg/mol
- Mn_{PS} = 6100 g/mol
- ~ 5,4 % in PS

Rheological studies

PS PnBA PS

PS13K-PnBA110K

- Mn $_{total}$ = 122 kg/mol
- Mn $_{PS}$ = 13000 g/mol
- ~ 10,7 % in PS



PS13K-PnBA60K

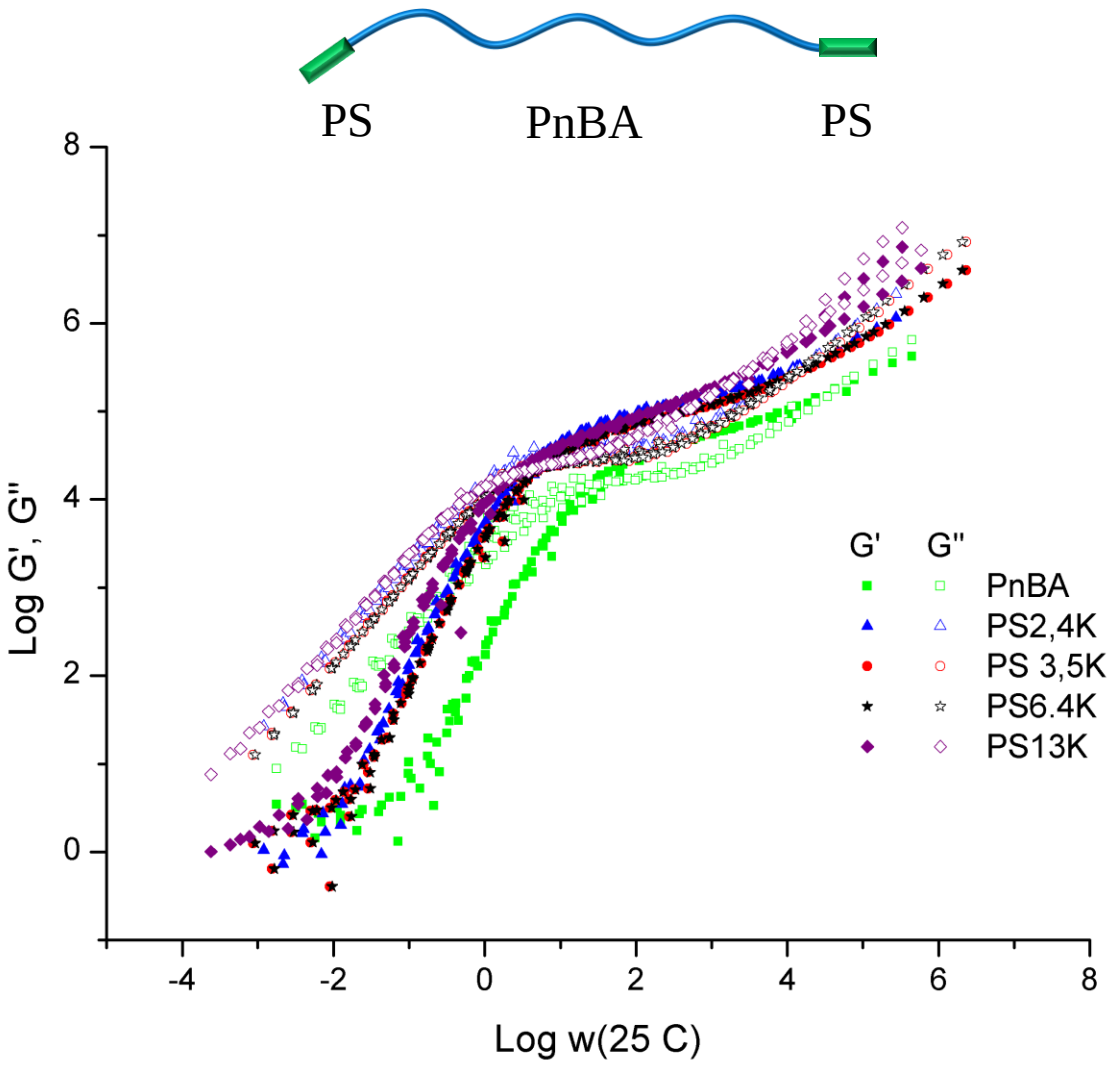
- Mn $_{total}$ = 73 kg/mol
- Mn $_{PS}$ = 13000 g/mol
- ~ 17,8 % in PS

PS13K-PnBA45K

- Mn $_{total}$ = 58 kg/mol
- Mn $_{PS}$ = 13000 g/mol
- ~ 22,5 % in PS

→ Soon

Rheology tests

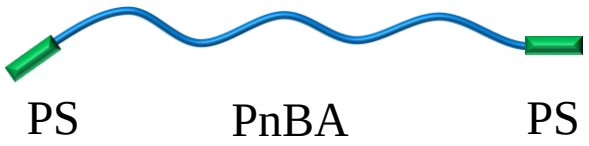


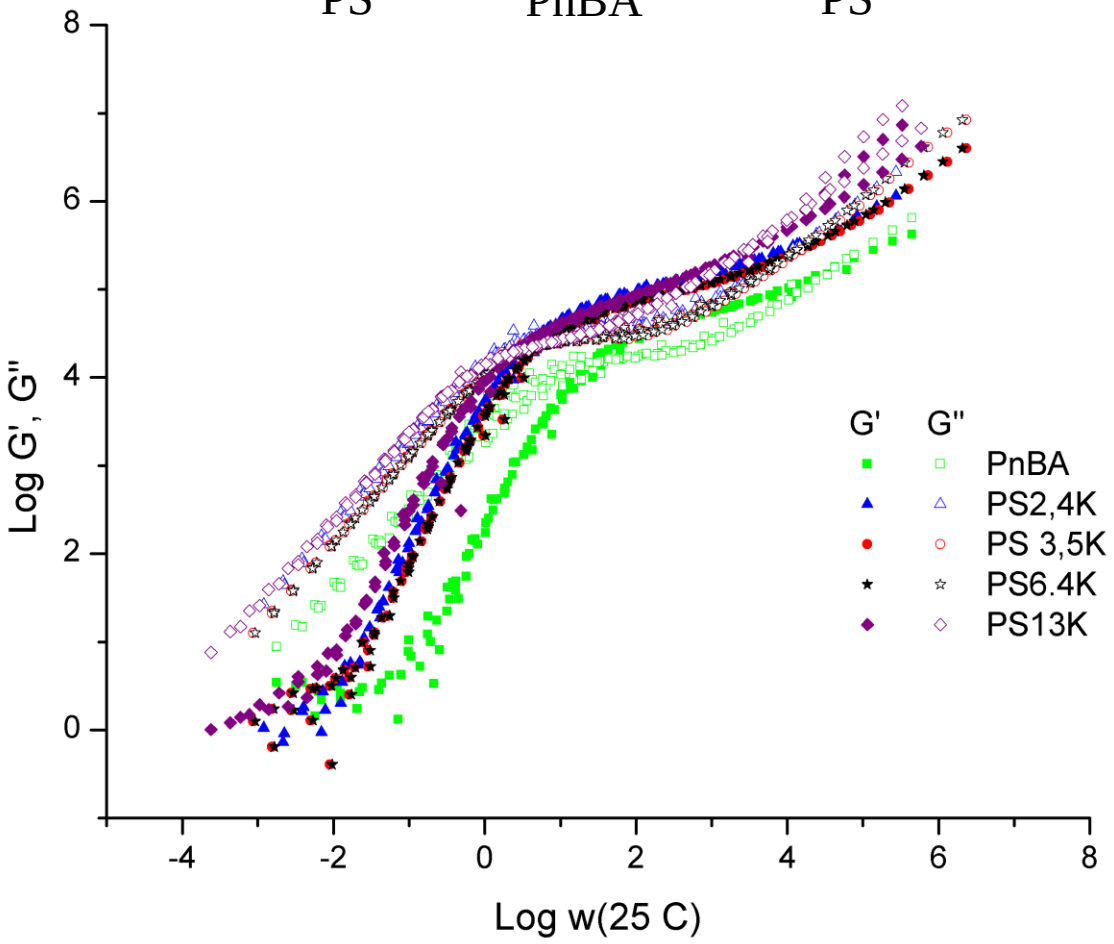
- Rotational shear rheology on the samples
  - ➢ Compare the data with linear PnBA Homopolymer

Procedure:

- High temperature (110°C), low strain, low frequency
  - ➢ Time sweep (10 minutes)
- Frequency sweep (Strain 10%, 200 rad/s…0,1 rad/s) from 85°C to -20°C

Rheology tests



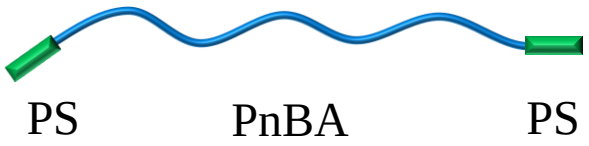


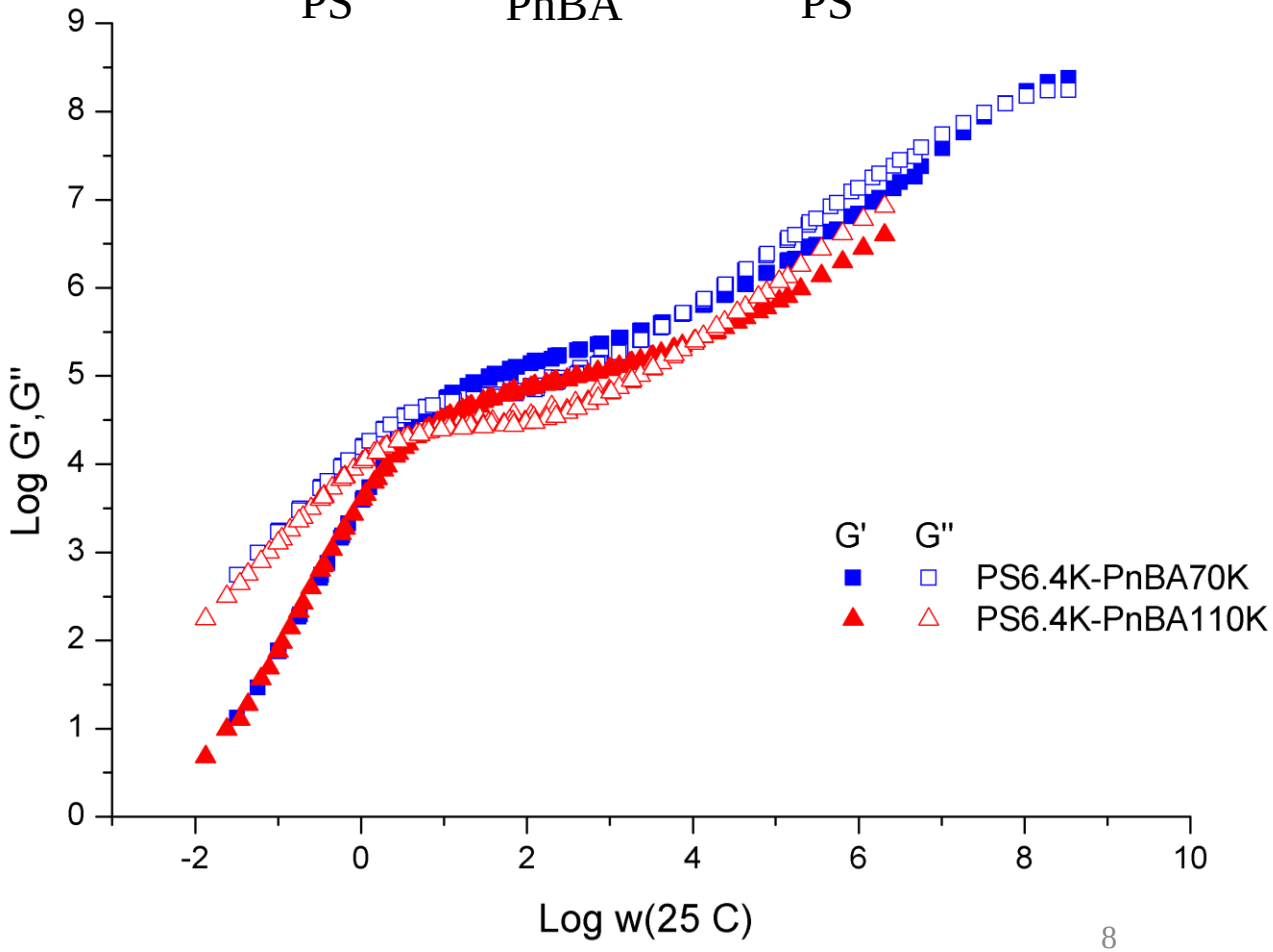
Masters Curves PS-PnBA110K:

- Similar curve shape
- Increase of the modulus (G', G'')
- Slope of 1 (G') and 2 (G'')

- Ratio PS/PnBA enough ?
- Change of strain needed?

Rheology tests





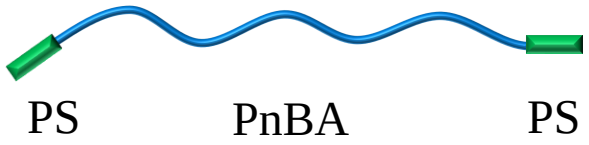
Master Curves PS6,4K-PnBA110K/70K

- Increase of the plateau modulus (G', G'') for PS6,4K-PnBA70K
- Longer plateau modulus for PS6,4K-PnBA70K
- Slope of 1 (G') and 2 (G'') for both

Increase the ratio PS/PnBA

- Decrease the Molecular Mass of PnBA
- Increase the Molecular Mass Outer Blocks of PS

⇒ Lack of mobility ?



Selected procedure for Gels preparation in solvent :

- Dissolve a given amount of polymer in DCM (Dichloromethane)
  - (for ex : 120 mg in 120 µL of DCM)

  5 min in the Vortex, 15 min in the Ultrasonic Bath
- Add the given volume of **solvent** according to the concentration by small amout
  - 5 min Vortex each time
- Let evaporate DCM under agitation for few hours and reach stable state for the gel

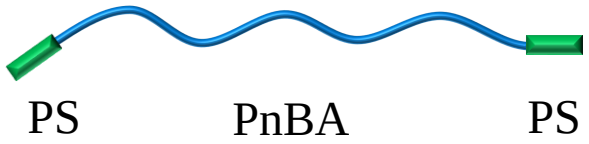
Selected procedure for Gels preparation in solvent :

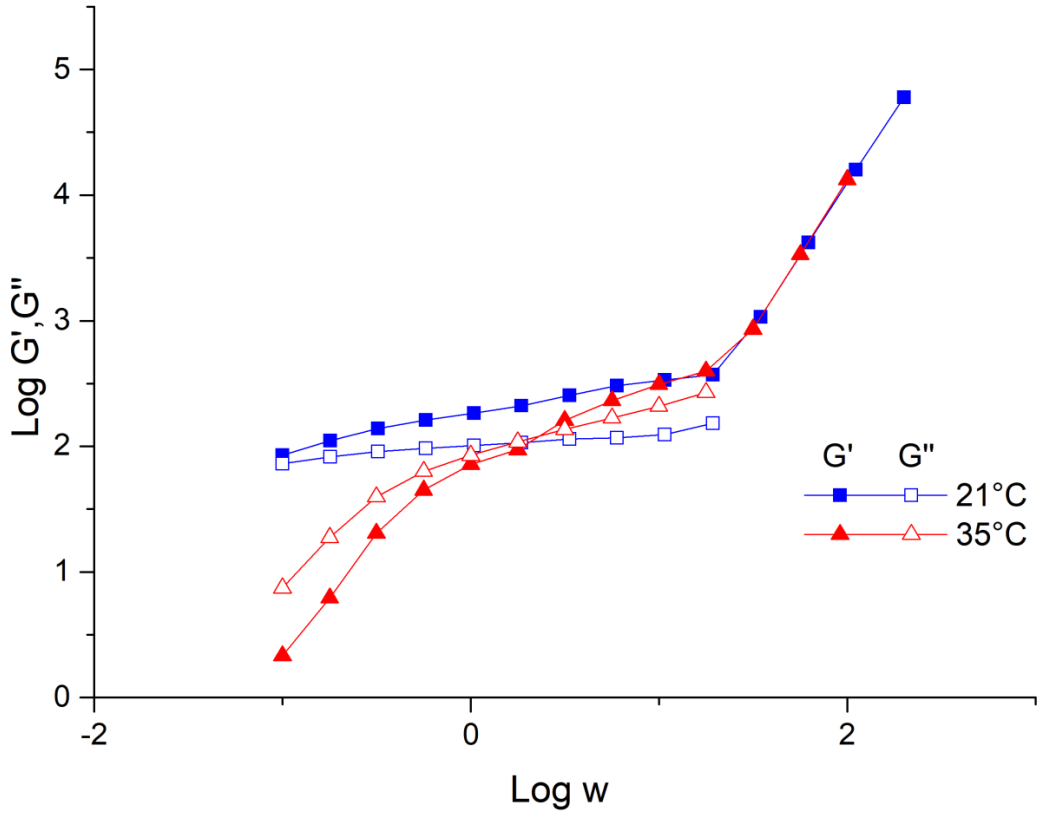
- Amount of polymer weighed in vial
- The precised amount of deionized **water** added in order to have the wanted wt%
  - And to solubilize, 5 min Vortex
- Let the gel rest for some hours in order to reach stable state

PS PnBA PS

	Boiling Point (°C)	Solubility Parameter δ ($MPA^{1/2}$)	Pol. Concentration (%)	PS2,4K-PnBA110K	PS3,5K-PnBA110K	PS6,4K-PnBA110K	PS13K-PnBA110K
2-Propanol	82	23,57	50	liquid	liquid	liquid	Visco-elastic
			35	liquid	liquid	liquid	Visco-elastic
			20	liquid	liquid	liquid	Visco-elastic
1-Propanol	97	24,6	50	liquid	liquid	liquid	liquid
			40	liquid	liquid	liquid	liquid
Ethanol	79	26,5	50	liquid	liquid	liquid	liquid
				liquid	liquid	liquid	liquid
1,4 Butanediol	230	31,3	50	liquid	liquid	liquid	liquid
				liquid	liquid	liquid	liquid
2-Methoxyethanol	124	23,4	50	liquid	liquid	liquid	liquid
				liquid	liquid	liquid	liquid
2-Ethyl-1-Hexanol	184	20,2	50	liquid	liquid	liquid	liquid

Rheology tests



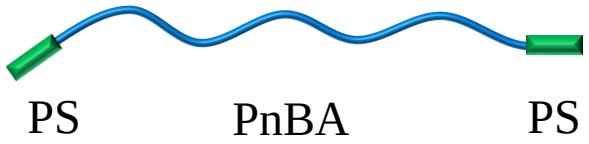


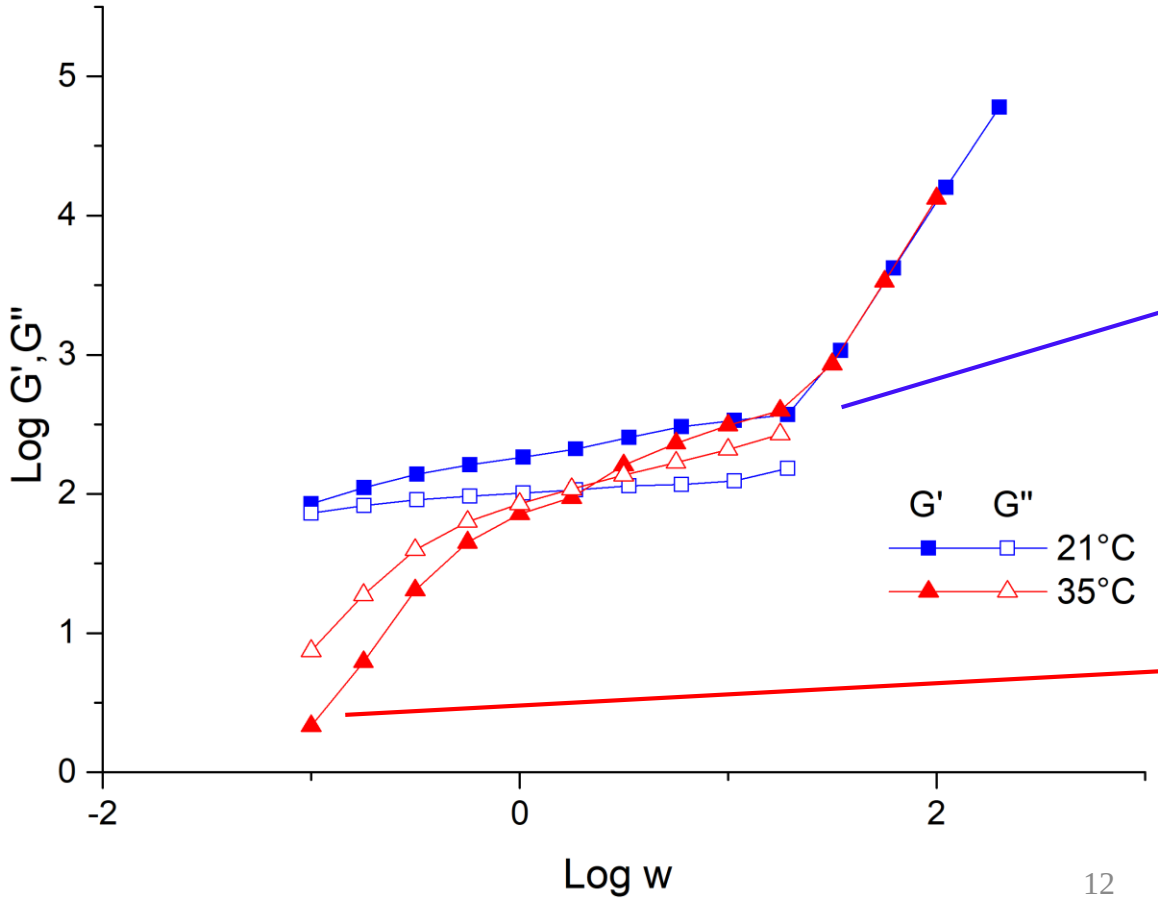
Frequency Sweep for

PS13K-PnBA110K 25%wt in Isopropanol:

- Strain 1%
- 100 rad/s…0,1 rad/s

Rheology tests





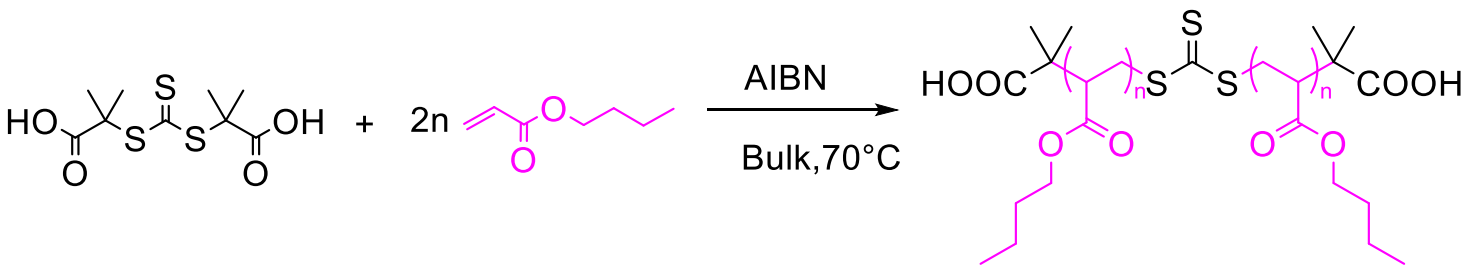
Plateau at 21°C :

Typical for Gel formation

Flow at 35°C:

- Slope 1 for G' and G"

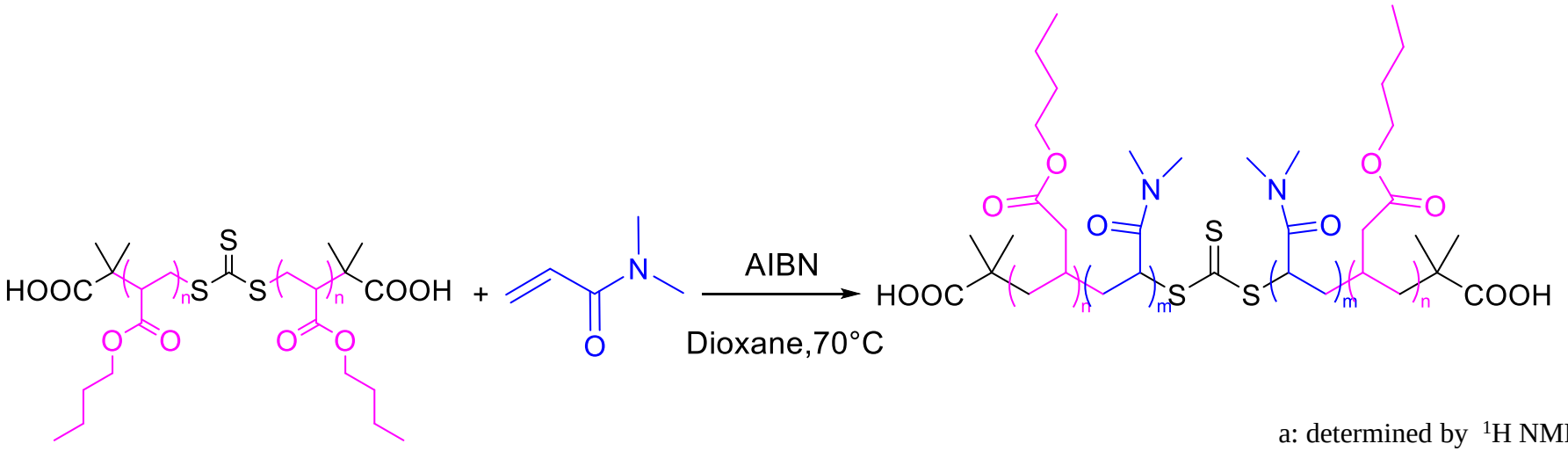
- Synthesis route to PnBA-*b*-PnBA (Hydrophobic outer blocks)



- ✓ Conversion 60-90% [a] (depend on the length wanted)
- ✓ Ratio 10:2 [CTA:AIBN]
- ✓ Mn = 6000-47000 g.mol^{-1} [b]

⇒ Formation of a Macro RAFT Agent

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

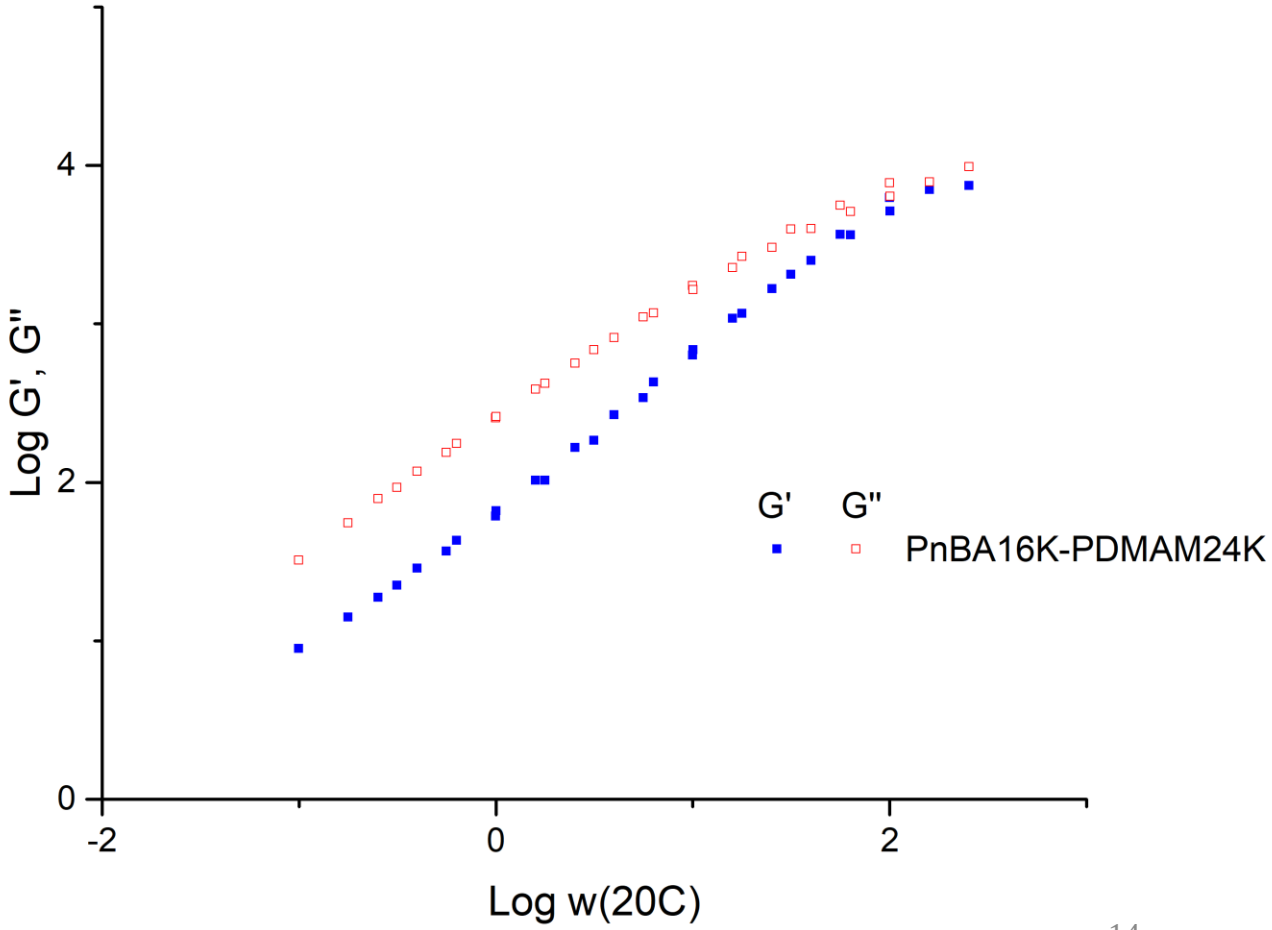


- ✓ Conversion ~95 % [a]
- ✓ Range of Mn ~30000 g.mol^{-1} [b]

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

Rheology tests

PnBA PDMAM PnBA



Masters Curves PnBA16K-PDMAM24K

in water 50%wt:

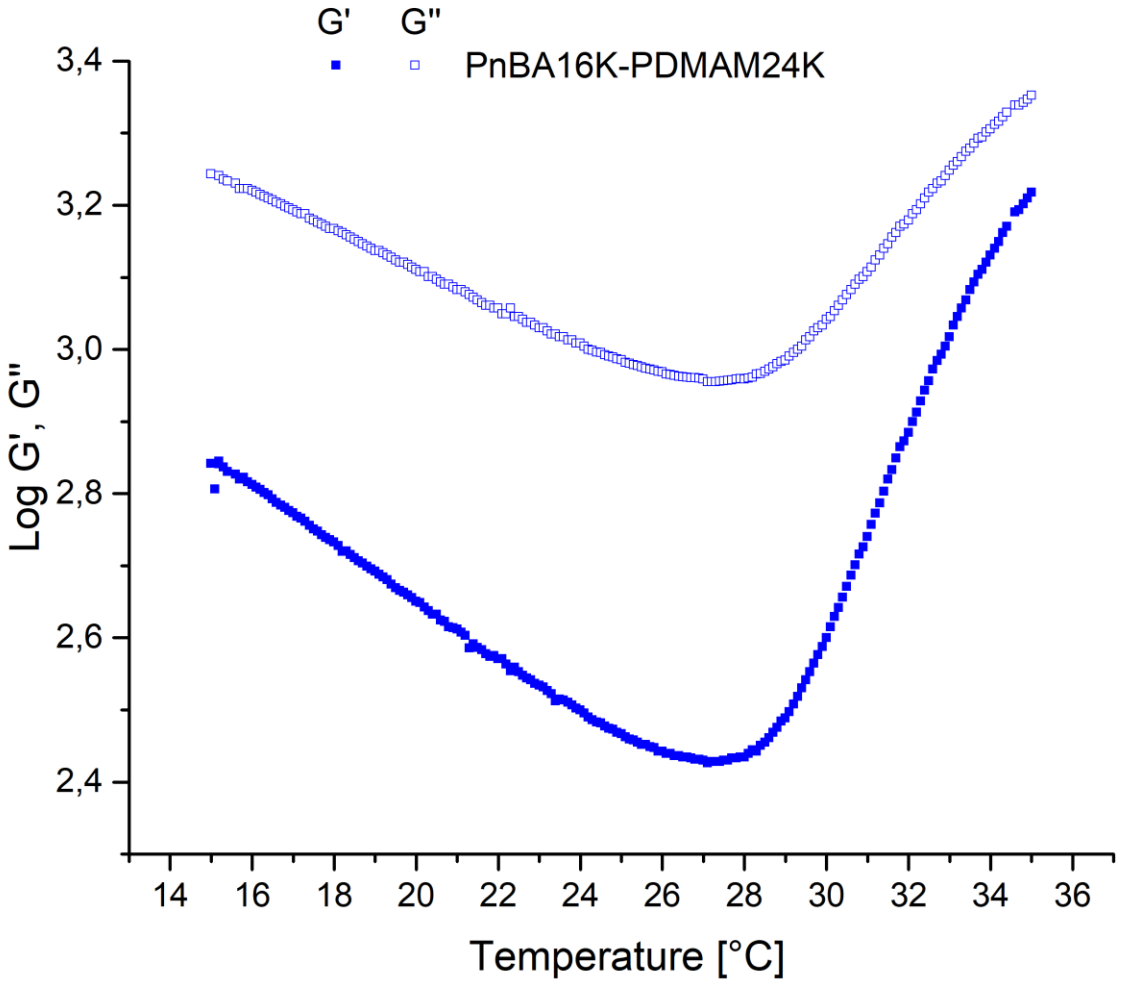
- Decrease of Modulus G' and G'', flowing
- Slope of 1 (G') and 1 (G'')
  - ➢ Aggregation ?

- At 25°C, the gel is not at the equilibrium

⇒ Temperature sweep

Rheology tests

PnBA PDMAM PnBA



Temperature sweep PnBA16K-PDMAM24K:

- Inflection point around 28°C
- Hysteresis when recovery
- Micelles due to gel preparation

- At 20°C, time needed to stabilize

⇒ Frequency sweep at 34°C

Outlooks on available samples:

- Develop gels with PS13K-PnBA110K
- Range of rheology test on these gels and polymer melt
- Study gels of PnBA-PDMAM in water
- Improve synthesis route of PnBA-PDMAM

Outlooks on future samples:

- Rheology tests on triblocks with terpyridine links
- Ions gels formation
- Synthesis of PS-PnBA With an increase of PS ratio: 2 kinds of systems

Thank you for your attention

UCL Université catholique de Louvain

MARIE CURIE ACTIONS

IMCN