

Synthesis and dynamics of model supramolecular polymer networks

Clément Coutouly

Supervisors:

Prof. Charles-André Fustin
Prof. Evelyne Van Ruymbeke

- Born in **Albi** (South of France, near Toulouse), October 27th 1992



- 2 years in **Classes Préparatoires** aux Grandes Ecoles in Lycée Lapérouse, Albi

- 1 year in Engineering School at **ENSCBP** in Bordeaux

- Chemistry License at Bordeaux University in 2015

- Internship (2 months) at **IECB** (European Institute of Chemistry and Biology)
Peptidomimetic Chemistry Lab (Pr. Gilles Guichard)
Supervisor: **Dr. Morgane Paseo**

Synthesis of 1,2-diamines diversely substituted, road to oligureas Foldamers

- Master's degree in Chimie Moléculaire et Macromoléculaire at Bordeaux University (2015-2017):



- Internship (6 months) at **LCPO** (Laboratoire de Chimie des Polymères Organiques)

TEAM: Polymerization Catalysis and Engineering (Pr. Daniel Taton)

Supervisors: **Pr. Daniel Taton and Pr. Stéphane Carlotti**

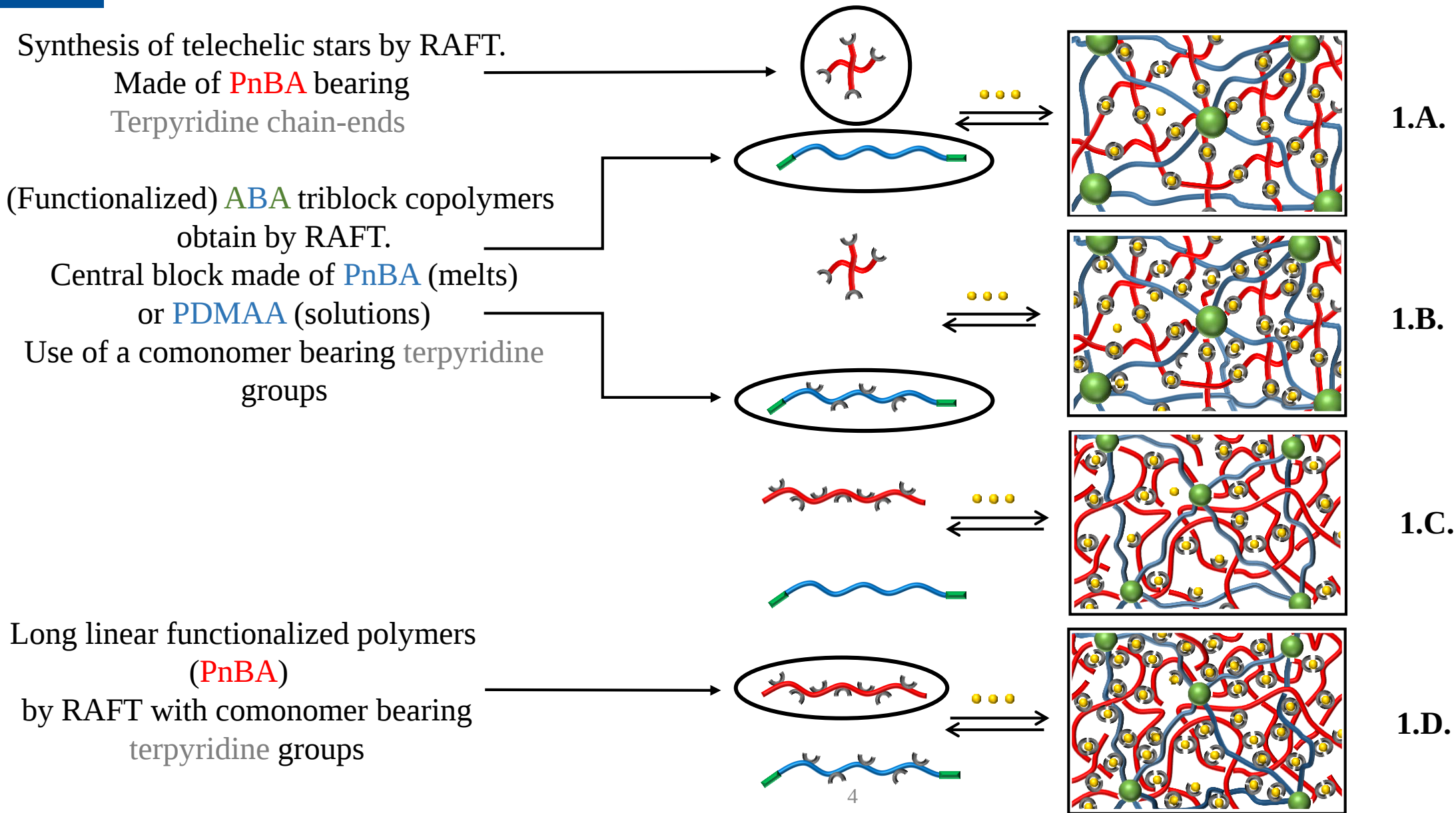
n-Heterocyclic carbene organocatalyzed ring-opening polymerization of activated aziridine

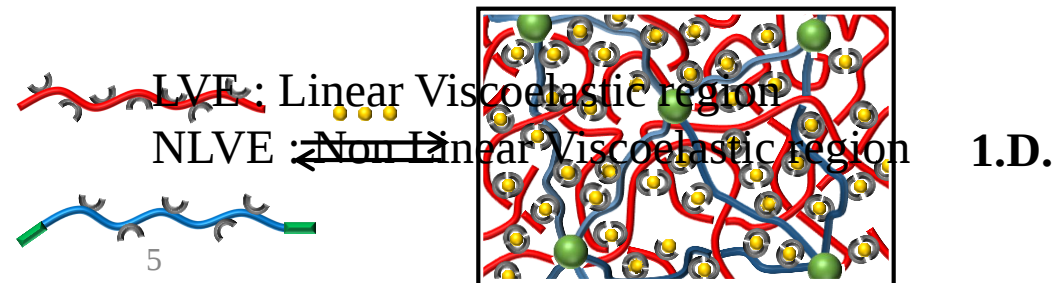
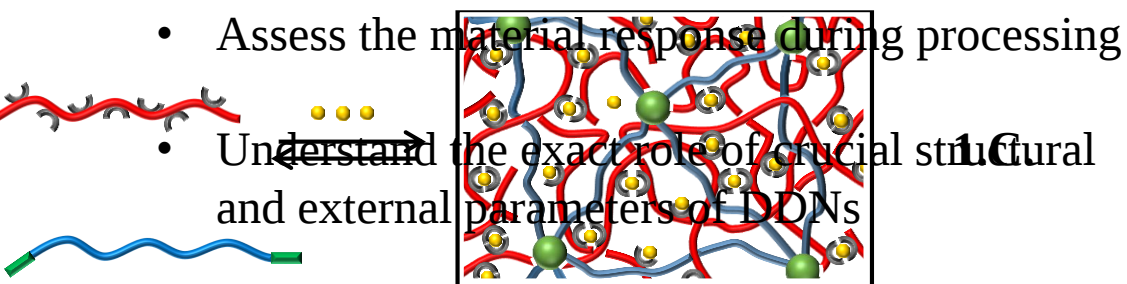
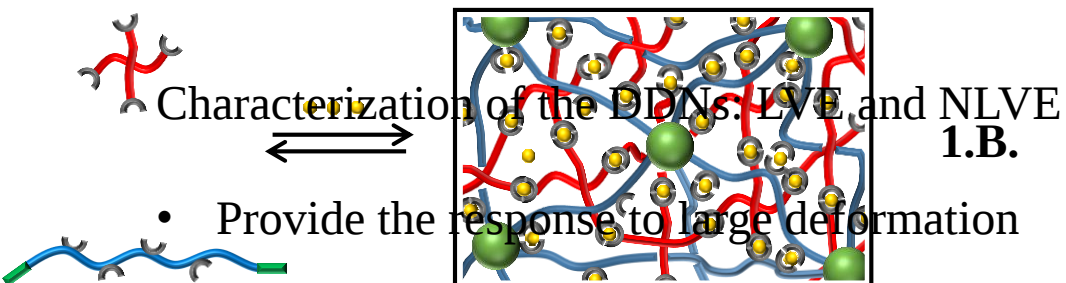
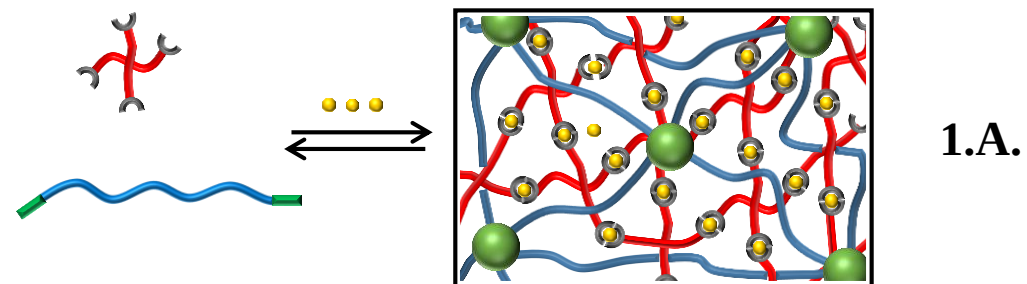


Research Objective:

Design new soft functional materials with improved properties based on the central concept of double dynamics

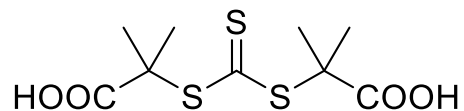
- **Easy to process:** Avoid permanent bond
- **Resist flow and creep:** Phase separation will be studied promoting reversible chain association under specific conditions
- **Dissipate energy to resist fracture:** Presence of supramolecular junctions like metal-ligand bond
Variation of the molecular structure of the building blocks
- **Large equilibrium:** Dense supramolecular network needed (large bond concentration)
➡ Phase separation for example
- **Double network properties in melt and in solution:** Select different systems by changing their concentration





RAFT AGENT

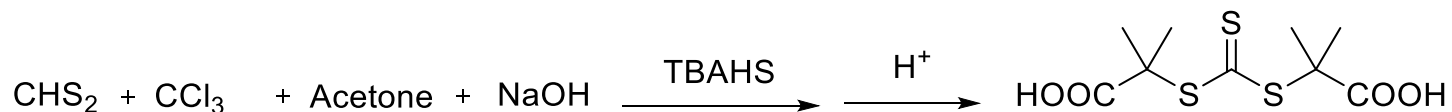
- Bifunctional CTA to insure a polymer growth from both sides:



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



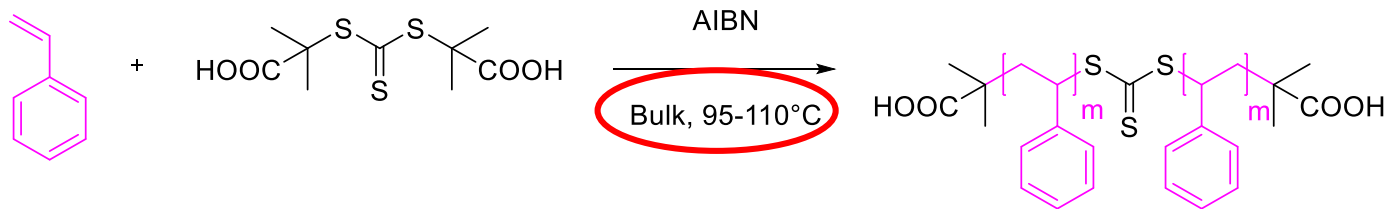
- ✓ Good yield after purification
- ✓ Easy purification

TBAHS: Tetrabutylammonium hydroxide

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

RAFT POLYMERIZATION of ABA Triblocks

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

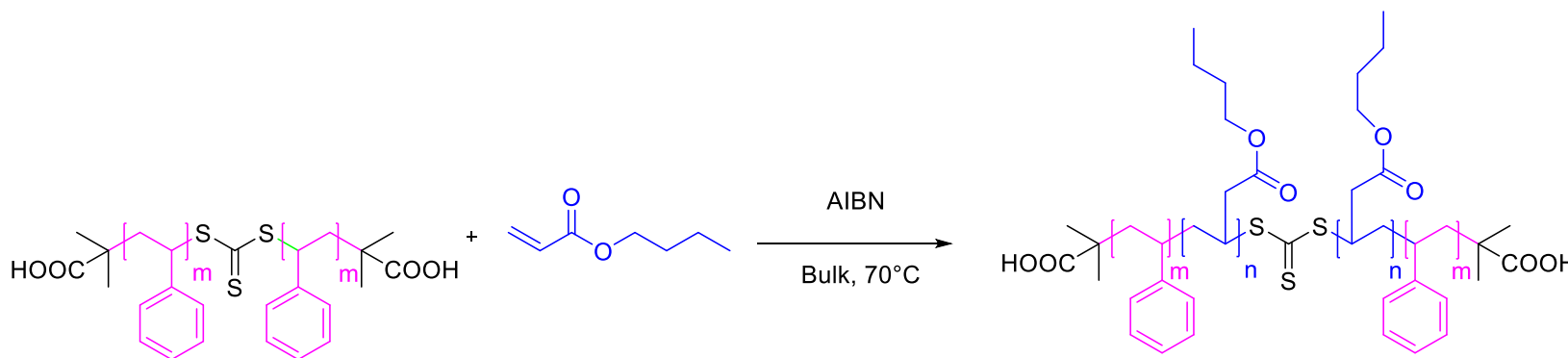


- ✓ Conversion 35-45 % ^a (depend on the length wanted)
- ✓ Fast kinetics (~ 3-4 h)
- ✓ $M_n = 2400-3600-6200 \text{ g.mol}^{-1}$ ^b



Formation of a Macro RAFT Agent

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



- ✓ Conversion ~70 % ^a
- ✓ $M_n = \sim 110\,000 \text{ g.mol}^{-1}$ ^b

a: determined by ^1H NMR in CDCl_3

b: determined by GPC in DMF with PS-calibration



PS-2400-PnBA

- $Mn_{total} = 112 \text{ kg/mol}$
- $Mn_{PS} = 2400 \text{ g/mol}$
- $\sim 2,1 \%$ in PS

PS-3700-PnBA

- $Mn_{total} = 117 \text{ kg/mol}$
- $Mn_{PS} = 3700 \text{ g/mol}$
- $\sim 3 \%$ in PS

PS-6100-PnBA

- $Mn_{total} = 110 \text{ kg/mol}$
- $Mn_{PS} = 6100 \text{ g/mol}$
- $\sim 5,4 \%$ in PS



- Viscous
- limpid



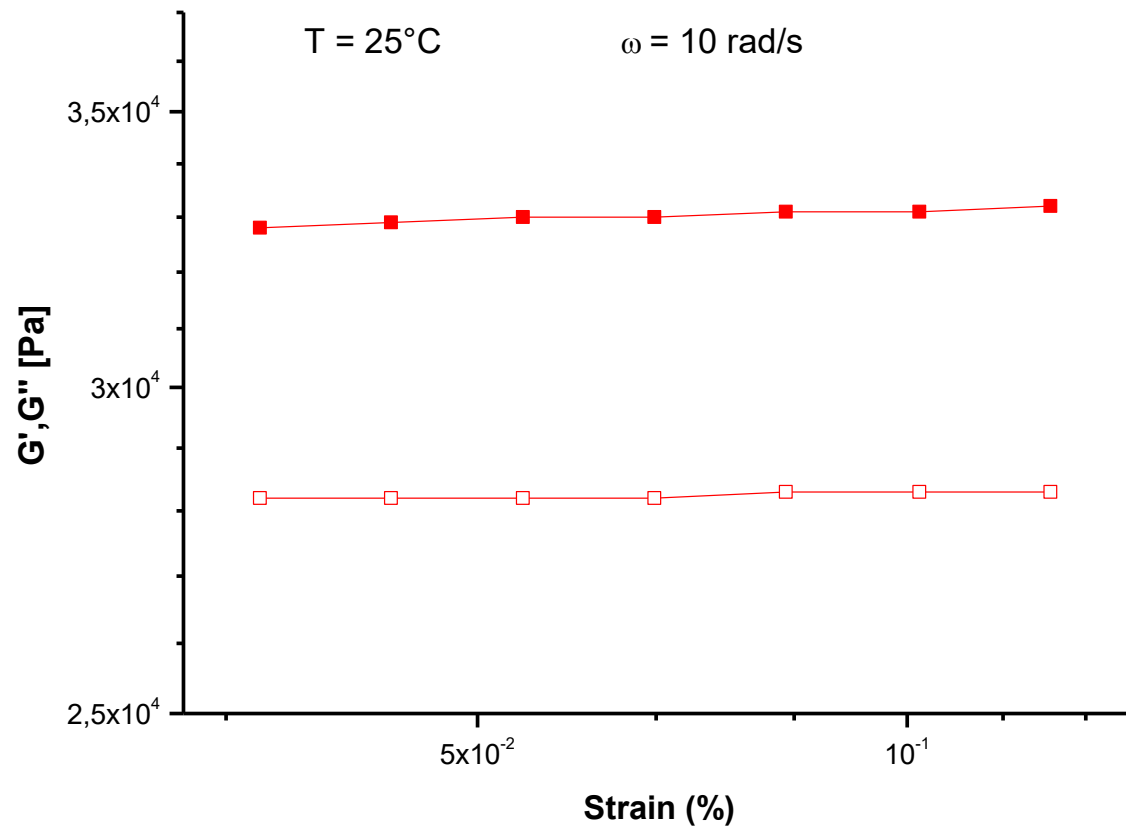
- Viscous
- Turbid
- Phase separation ?



Rheological
studies

Rheology tests

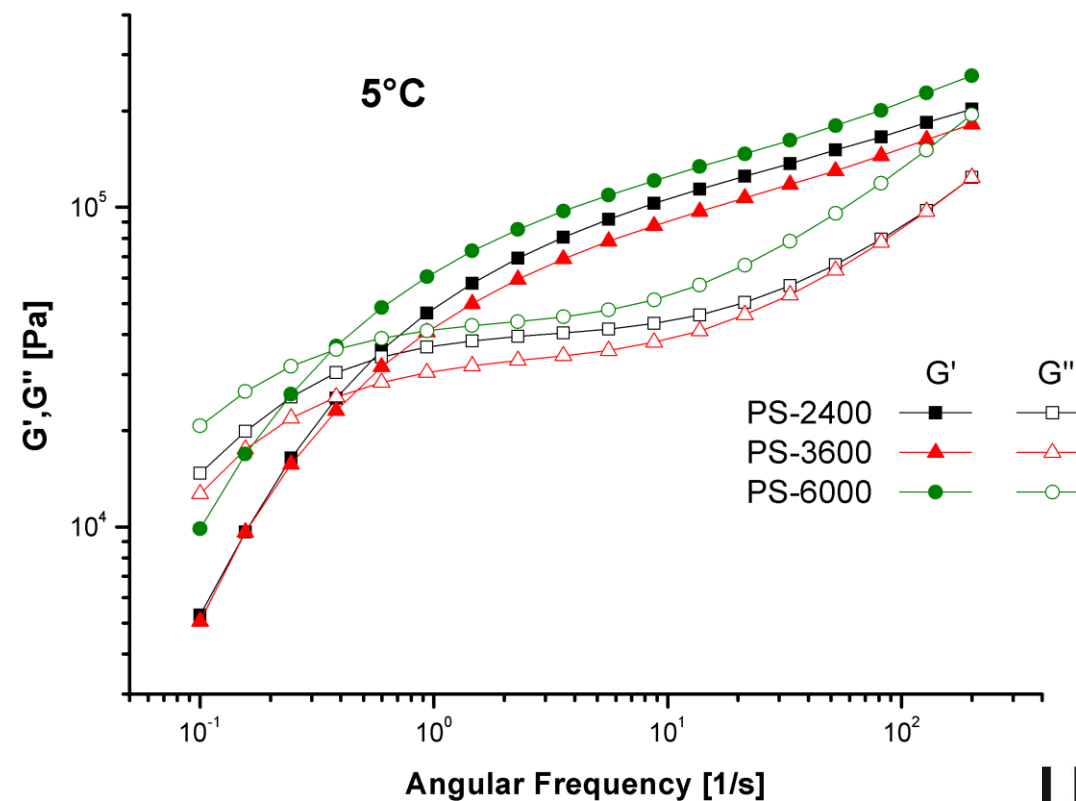
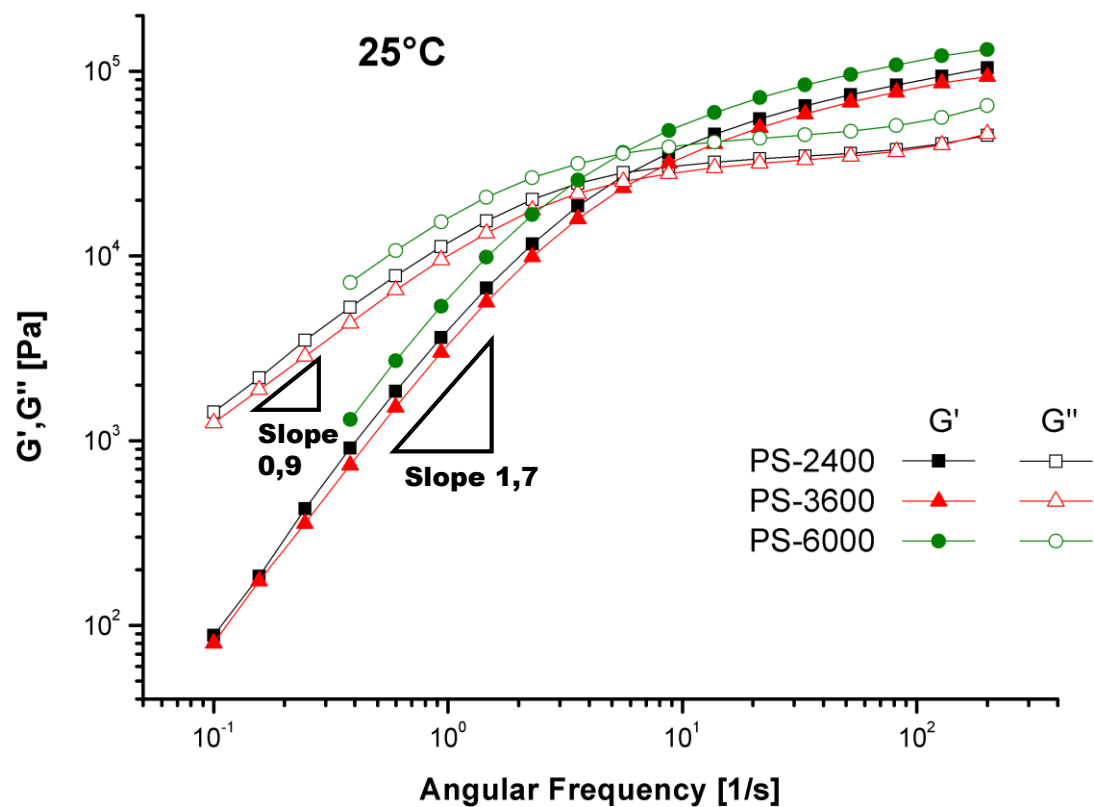
- Strain sweep ($0,01 \text{ s}^{-1} - 0,2 \text{ s}^{-1}$)
- Determine the linear regim



Strain fixed at 0,1 %

Rheology tests

- Frequency sweep study ($200 \text{ s}^{-1} - 0,01 \text{ s}^{-1}$)
- Range of temperatures (95°C to -25°C)



Outlooks on available samples:

- DSC tests (in progress)
 - Presence of two T_g ? (-55°C for PnBA and around 70°C for PS)
- Check rheology at higher temperatures ($\sim 130^{\circ}\text{C}$)
- Increase the ratio of PS
- Compare to linear PnBA

Outlooks on future samples:

- Rheology tests on triblocks with terpyridine links
- Formation of gels



Thank you for your
attention

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