Rheological investigations of model linear triblock copolymers and industrial dual crosslinked networks

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ESR8 Position

ITN Marie Curie project
DoDyNet:
Double dynamics for designing new responsive polymer networks and gels

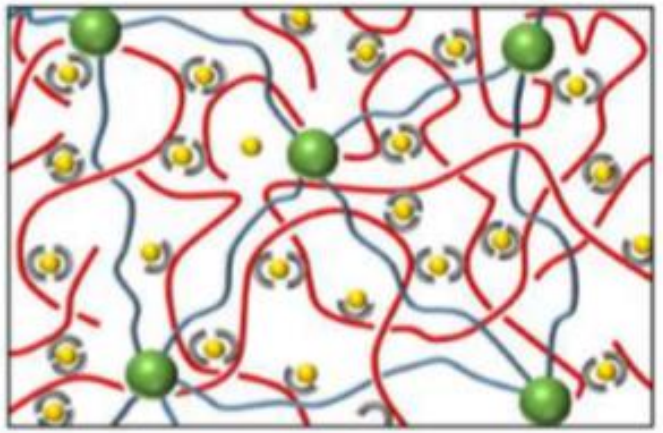
Outline

- Objectives
- Phase separation phenomena and rheological detection
- Effects of corsslinking on the rheological behavior

Objectives

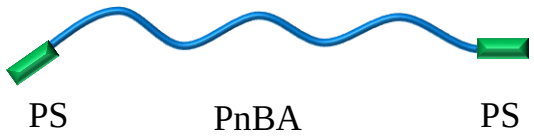
- Study the rheological properties of double networks linking them to the molecular structure

- Establish the influence of the molecular structure on the final material properties



Systems

Triblock copolymer



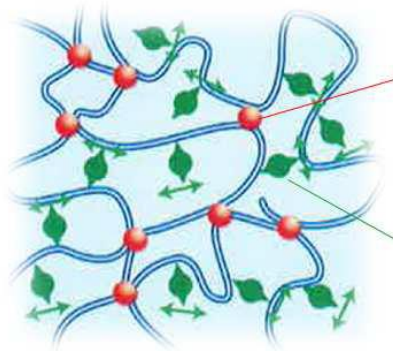
PS (13K)-PnBA

- Mn $_{total}$ = 121 kg/mol
- PDI = 1.14

PS (6.4K)-PnBA

- Mn $_{total}$ = 111 kg/mol
- PDI = 1.19

TESA Sample



Epoxide (0,035% w/w)

Metal-Chelate (0,075% w/w)

- **Single network with dual crosslinks**
- **Network with only physical crosslinks**
- **Network with only chemical crosslinks**
- Main component (linear acrylate without crosslinks)

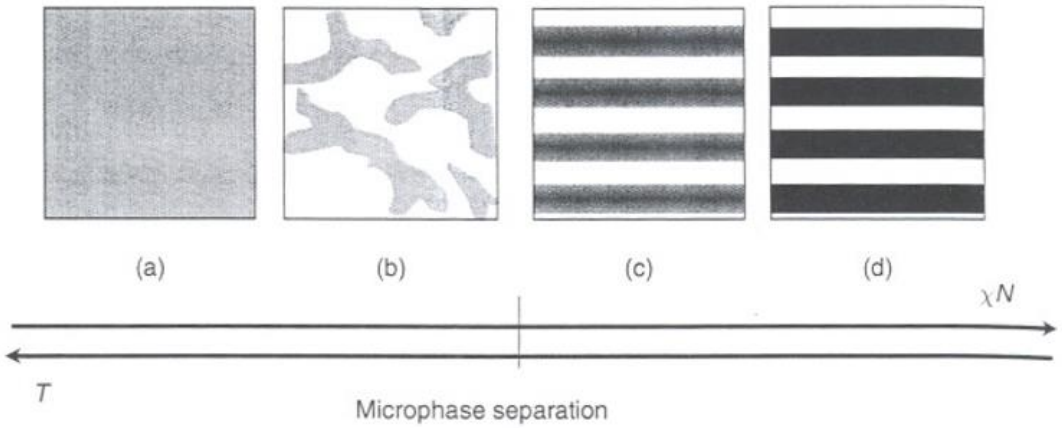
Triblock copolymer

PS PnBA PS

Triblock copolymer - Phase separation

Incompatibilities between different blocks can lead to phase separation. Order structure can be formed.

The architecture of the blocks is connected to mechanical properties and their processing.



ODT (Order disorder Transition)

M. Cloitre, D. Vlassopoulos. *Block copolymers in external fields: rheology, flow-induced phenomena, and applications.* Applied Polymer Rheology: Polymeric Fluids with Industrial Application edited by M. Kontopoulou, John Wiley & Sons, 2012

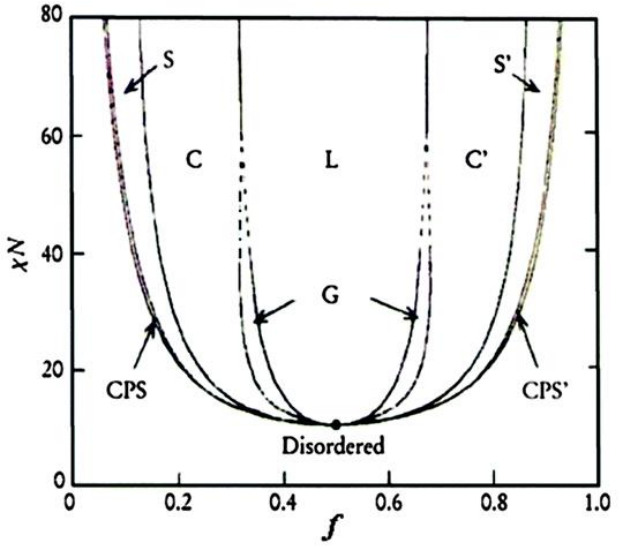
Triblock copolymer - Phase separation

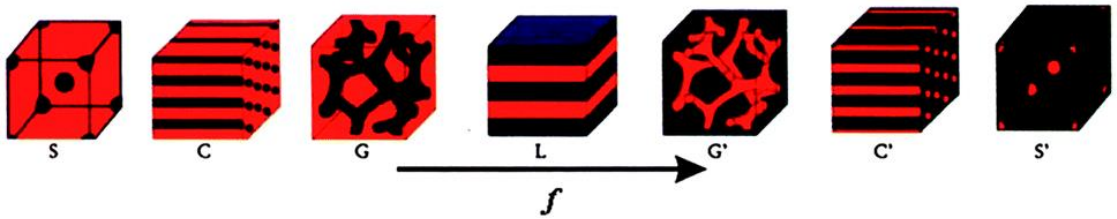
N: total degree of polymerization

χ: Flory-Huggins interaction parameter

f: volume fraction of the components

χ= 0.0064 PS-PnBA



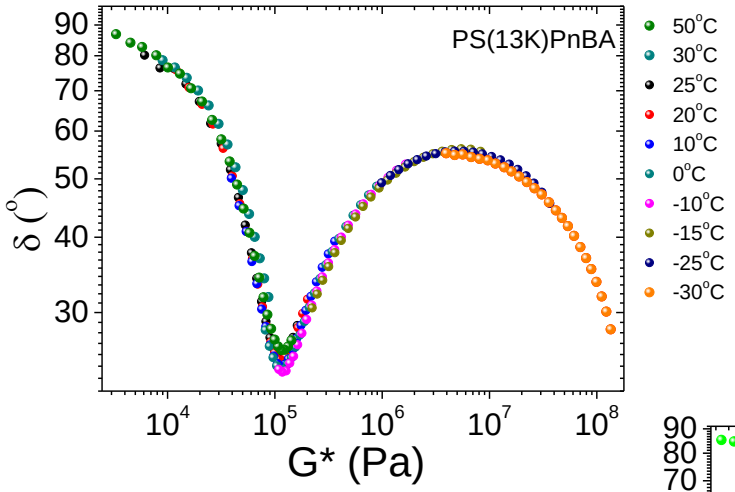


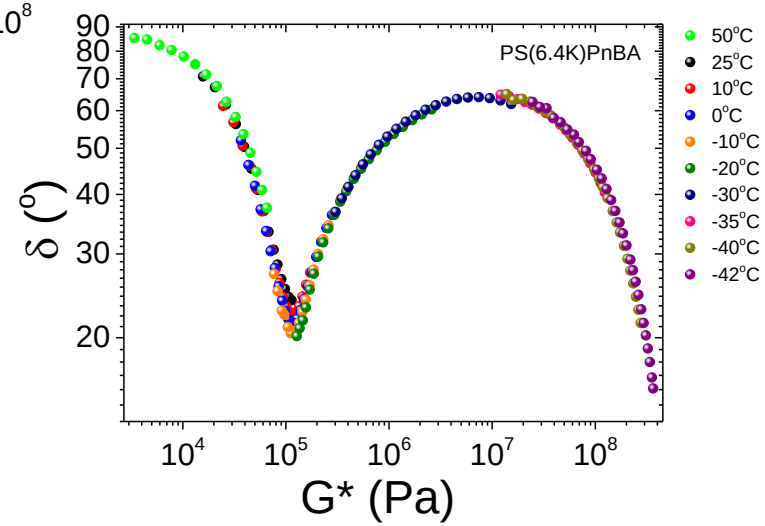
F. S. Bates and G. H. Fredrickson, *Block copolymers- Designer soft materials,* Physics Today, 1999

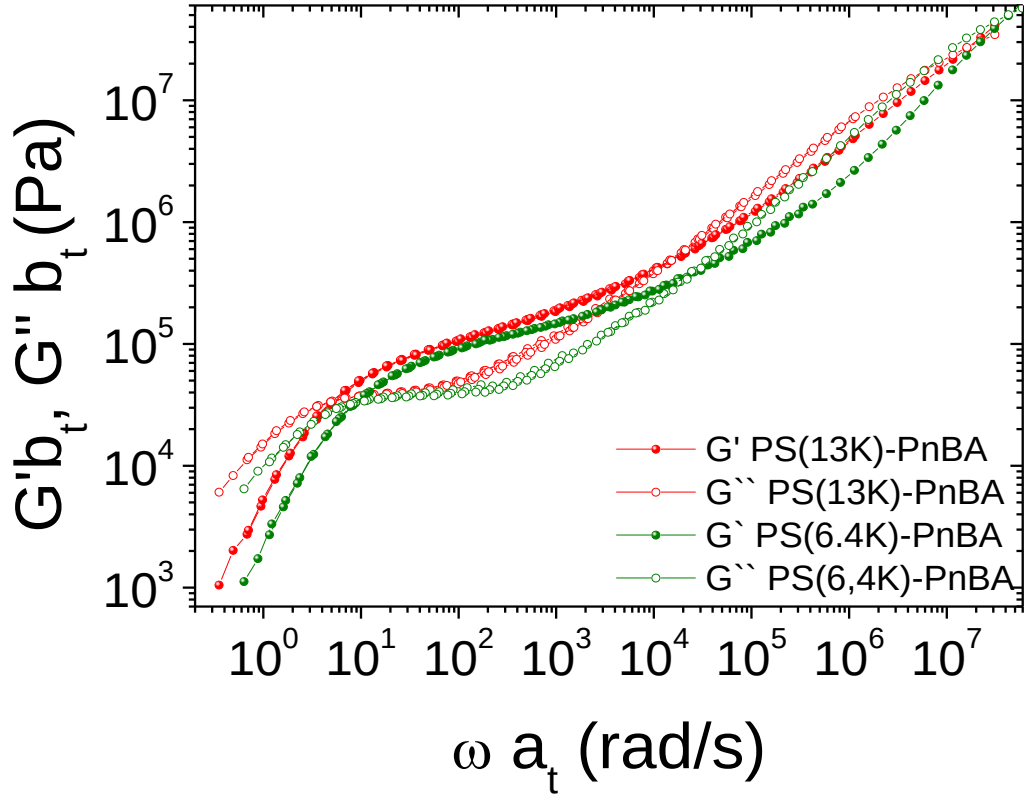
A-V. Ruzette,et. al.., *Molecular Disorder and Mesoscopic Order in Polydisperse Acrylic Block Copolymers Prepared by Controlled Radical Polymerization*, Macromolecules, 2006.

Rheological test for phase separation

- Time-temperature superposition principle: VanGurp – Palmen plots



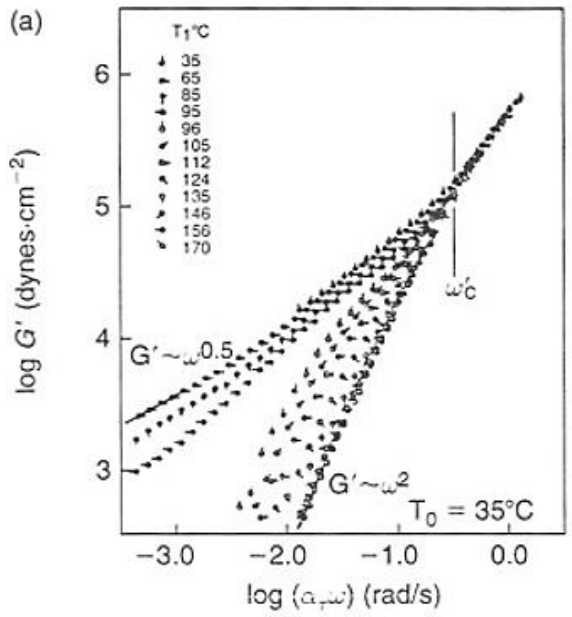


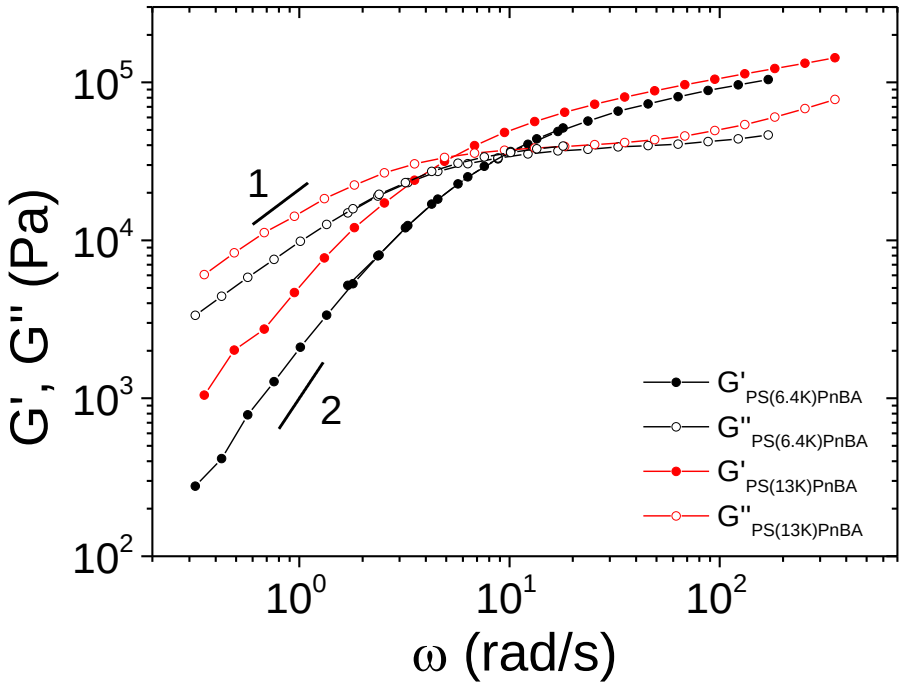


S. Trinkle, C. Friedrich. *Van Gurp-Palmen-plot: A way to characterize polydispersity of linear polymer,* Rheologica Acta 2001

Rheological test for phase separation

- Time-temperature superposition principle
- Low-frequency scaling of the storage modulus

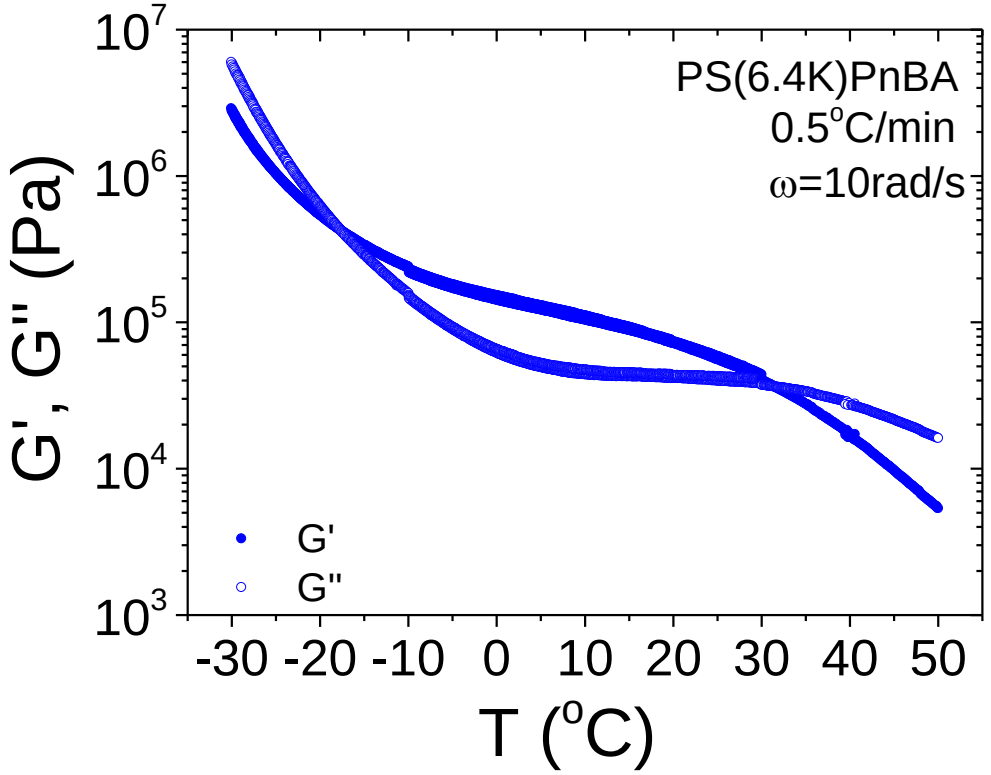


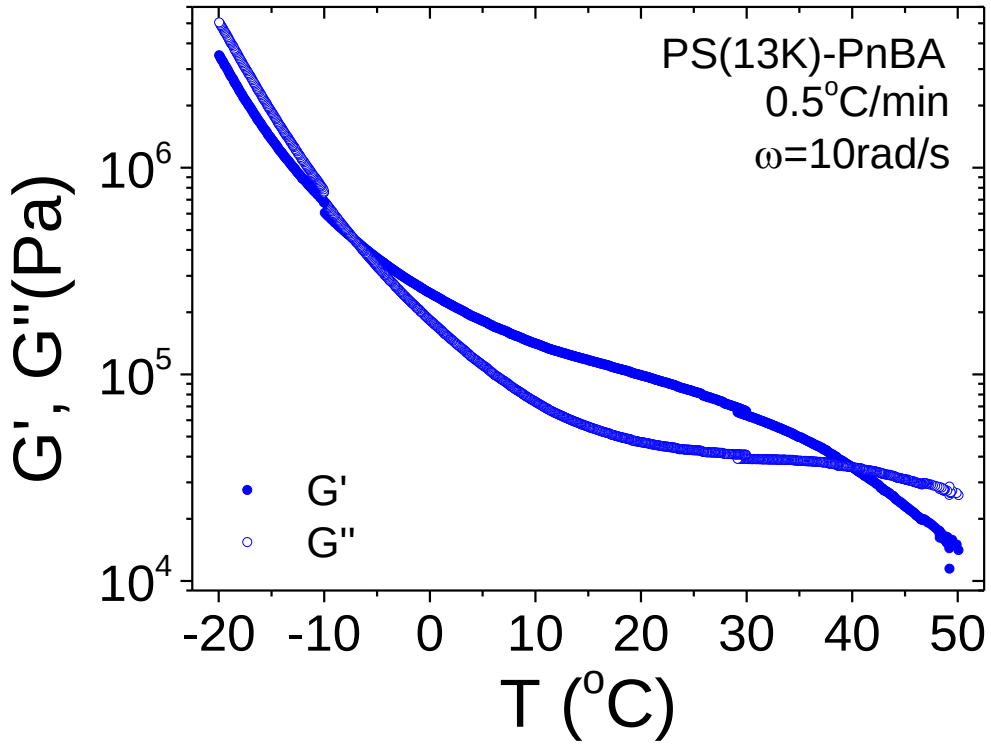


M. Cloitre, D. Vlassopoulos. *Block copolymers in external fields: rheology, flow-induced phenomena, and applications.* Applied Polymer Rheology: Polymeric Fluids with Industrial Application edited by M. Kontopoulou, John Wiley & Sons, 2012

Rheological test for phase separation

- Time-temperature superposition principle
- Low-frequency scaling of the storage modulus
- Temperature ramp

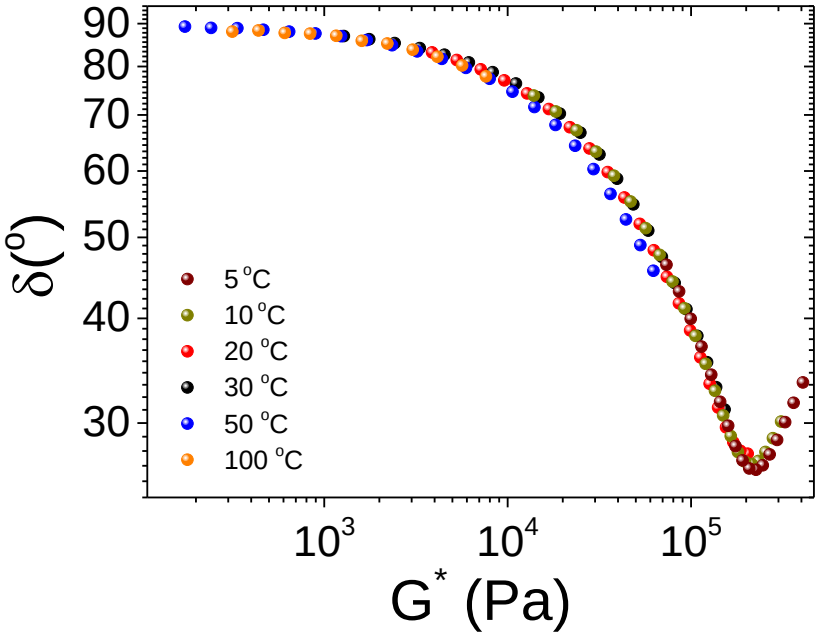


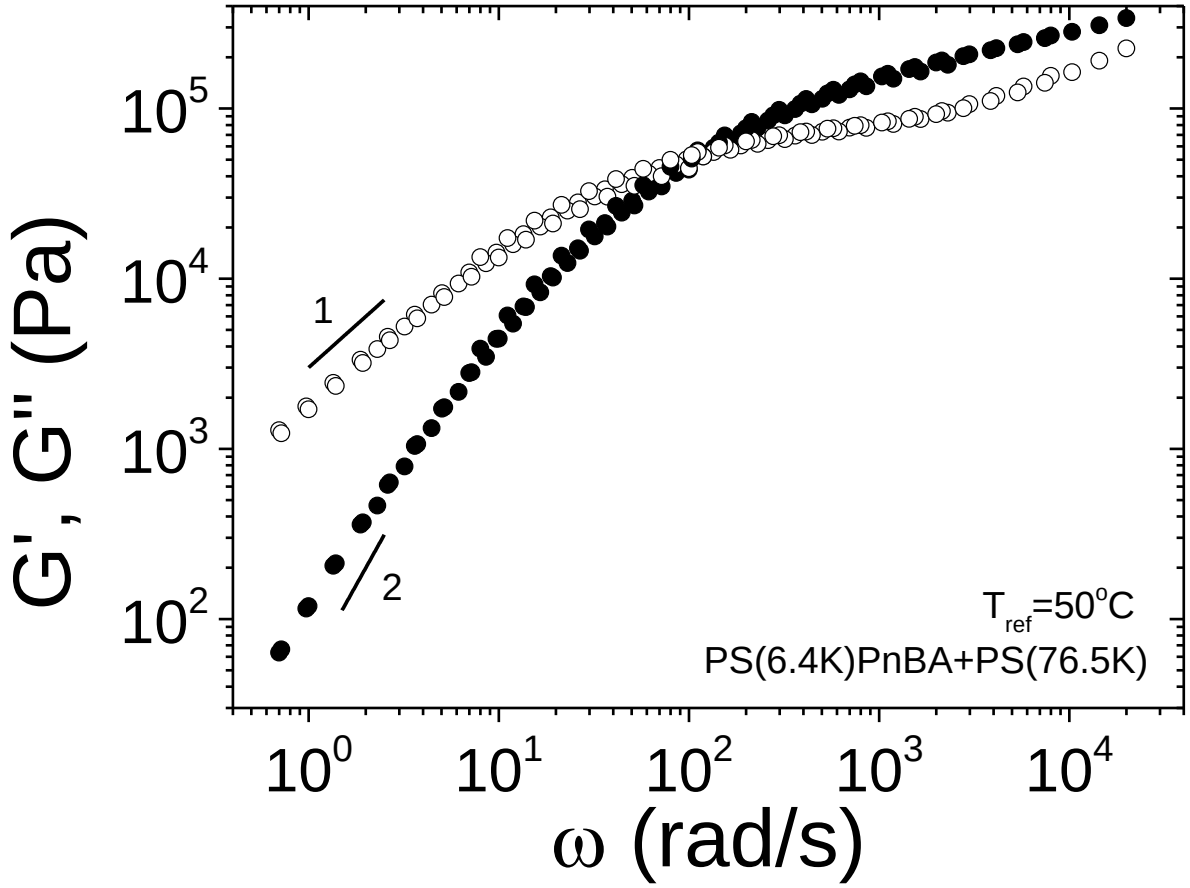


Effects of adding polystyrene to the copolymer

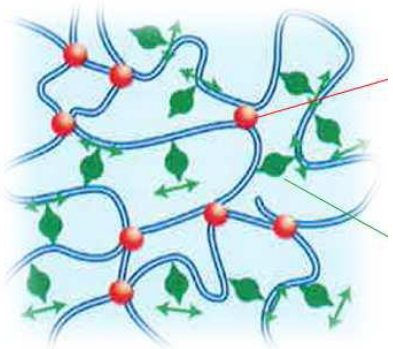
PS (6.4K)-PnBA

PS (76.5K)





TESA Sample

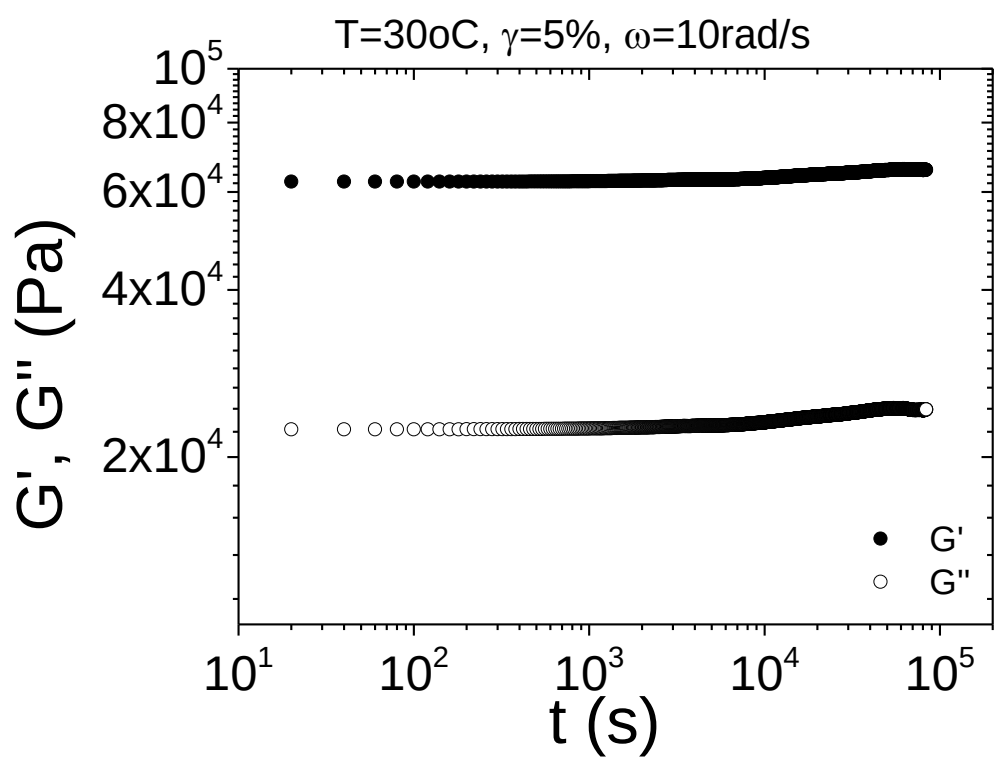


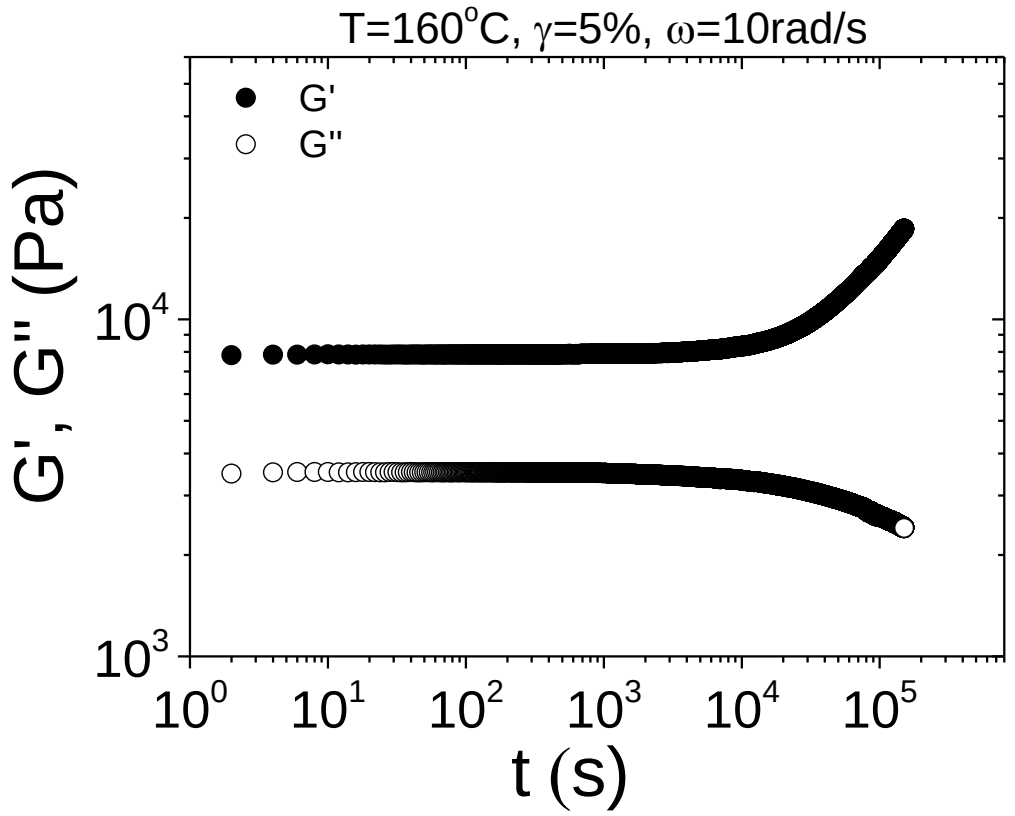
Epoxide (0,035% w/w)

Metal-Chelate (0,075% w/w)

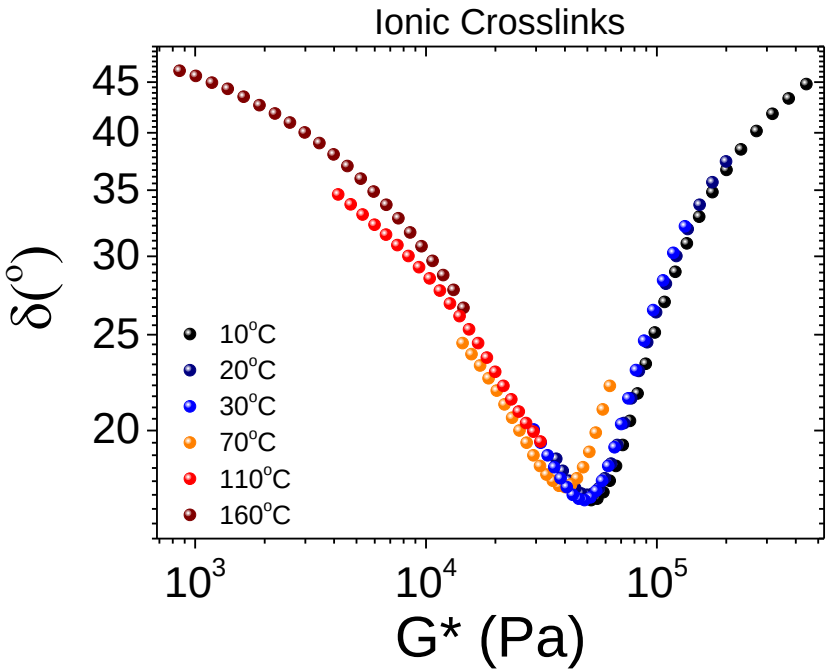
TESA samples - Protocol

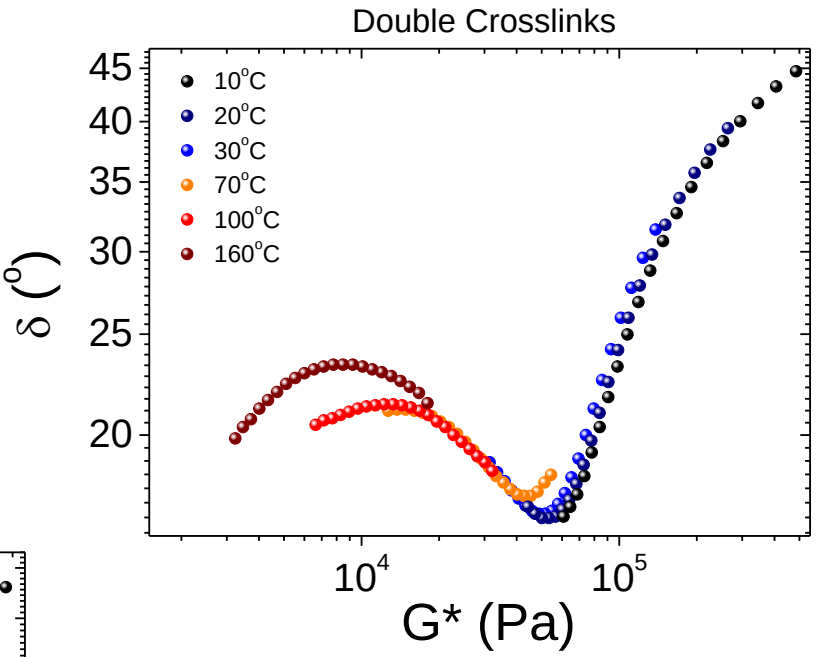
- Investigation of time dependent phenomena and of temperature effects.

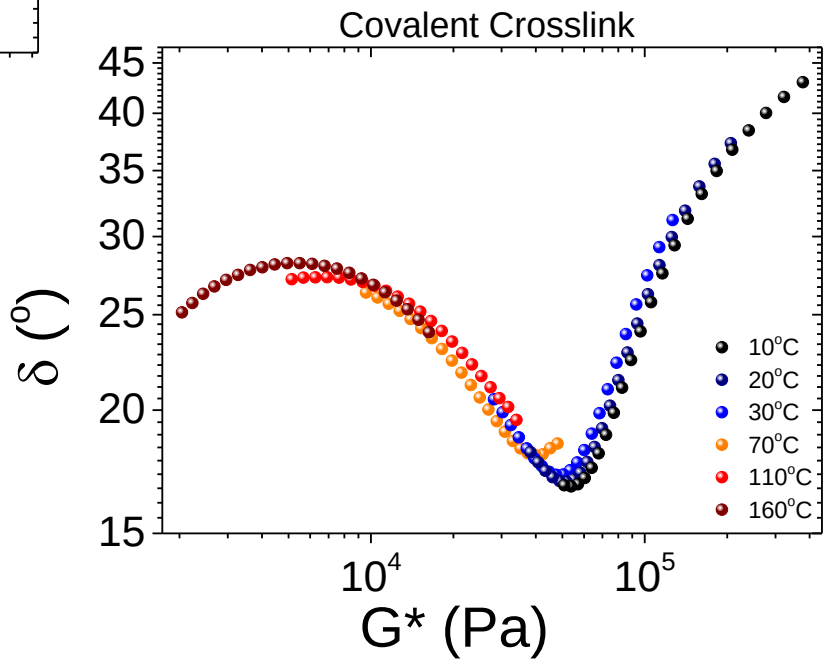




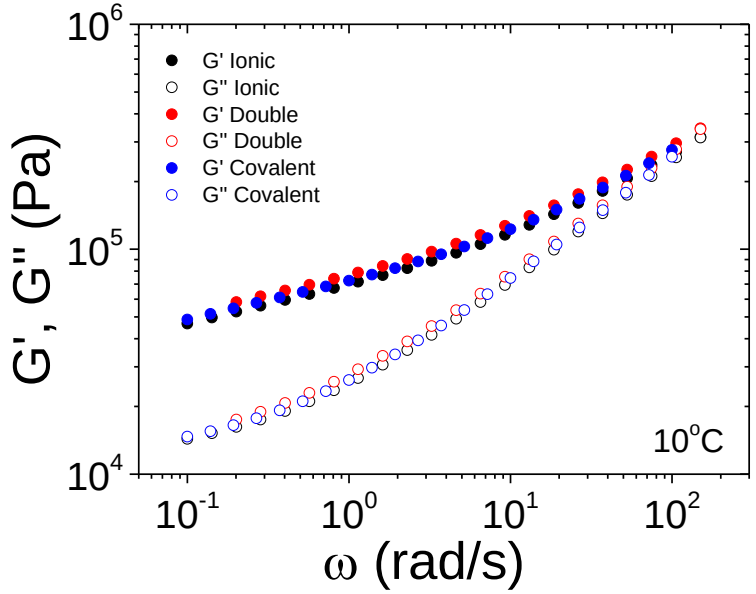
TESA samples - TTS

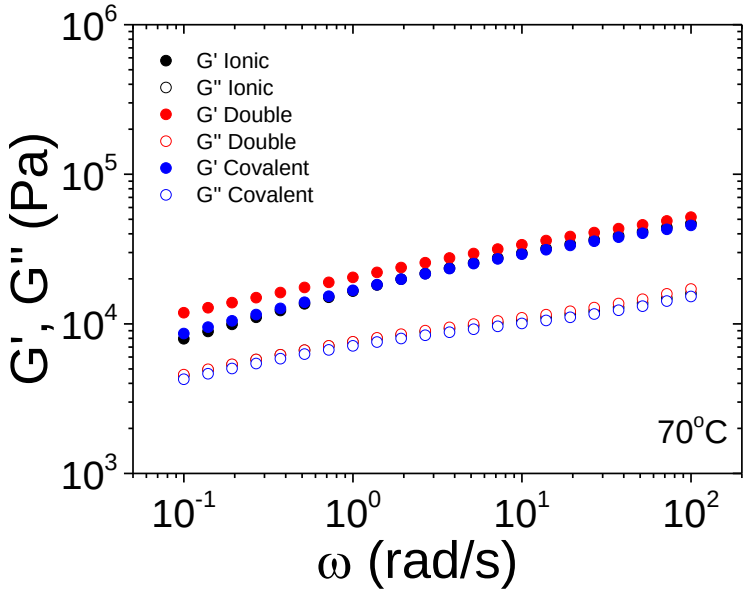


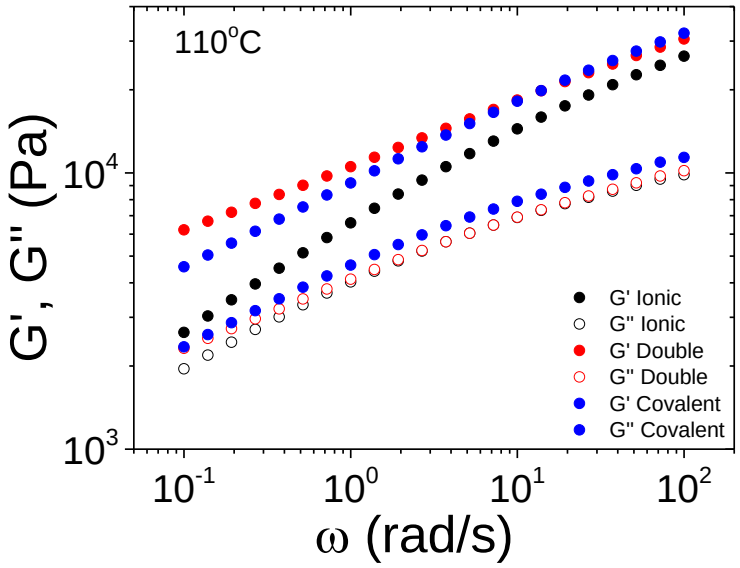


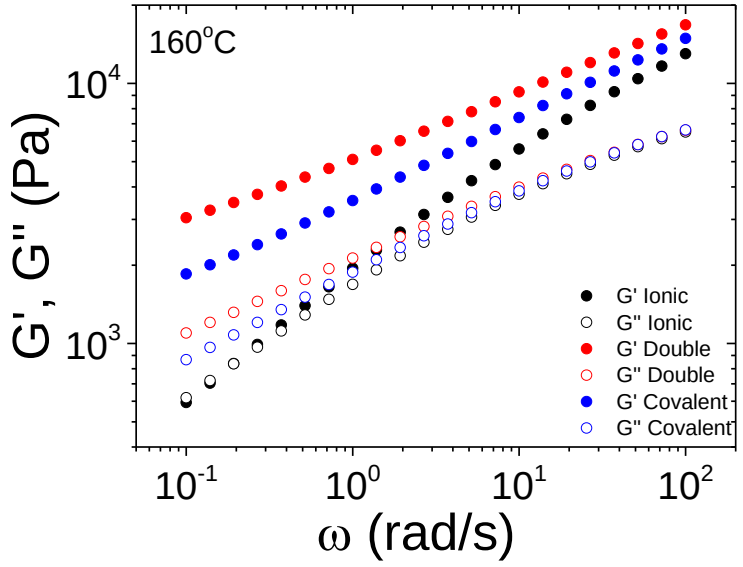


Tesa samples - Comparison









Conclusions

- No rheological signature of microphase separation in the triblock copolymer over the examined temperature range.
- Failure of time temperature superposition principle for the TESA samples.
- In the range of frequencies investigated, crosslinks don’t affect the dynamics of the TESA materials, contrary to what happens at high temperatures (stability issues).

Perspectives

- Rheological characterization of the main component of TESA Samples
- Creep experiment to access slow dynamics of TESA samples
- Investigate the influence of different concentration of crosslinks in TESA samples
- Use of χ for investigation of phase diagram of triblock system
- Understand the influence of adding polystyrene to triblock copolymers
- Nonlinear rheology

THANKS FOR THE ATTENTION!