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

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ESR8 Position

FOUNDATION FOR RESEARCH AND TECHNOLOGY - HELLAS

UNIVERSITY OF CRETE

Outline

- Main goals
- Linear viscoelastic properties of entangled polymers based on linear copolymer
- Linear approach for the study of a double dynamic network
- Open questions
- Future targets

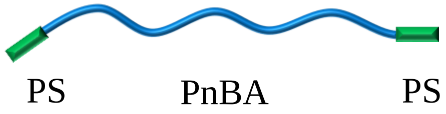
Goals

- Provide a link between molecular structure and rheology

- Provide a link between molecular structure and final properties (mechanical, application)

Samples

➢ UCL



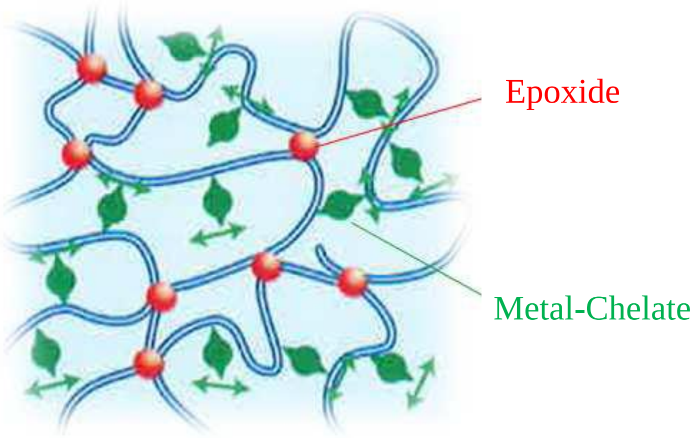
PS (13K)-PnBA

- $M_{n\ total}$ = 121 kg/mol
- PDI = 1.14

PS (6.4K)-PnBA

- Mn = 111 kg/mol
- PDI = 1.19

➢ TESA



Mw ≈ 851.000 g/ mol

PD ≈ 22.51

Tg ≈ - 45 °C

1.
Chemical Crosslink:
0,025% w/w

Physical Crosslink:
0,05% w/w

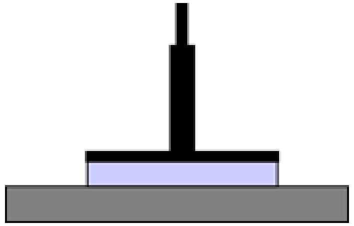
2.
Chemical Crosslink:
0,035% w/w

Physical Crosslink:
0,075% w/w

Experimental Protocol

Linear Measurements:

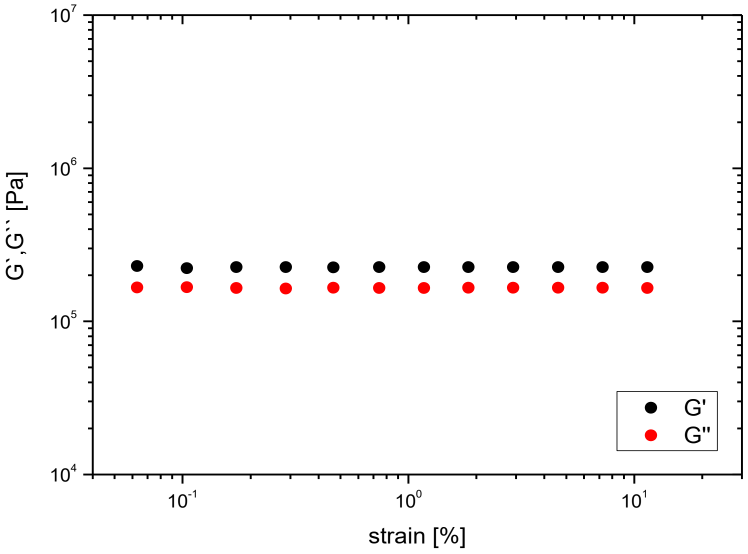
- Stainless steel Plate-Plate geometry (D=8mm)
- Heating system: Air/Nitrogen convection oven



Parallel Plates

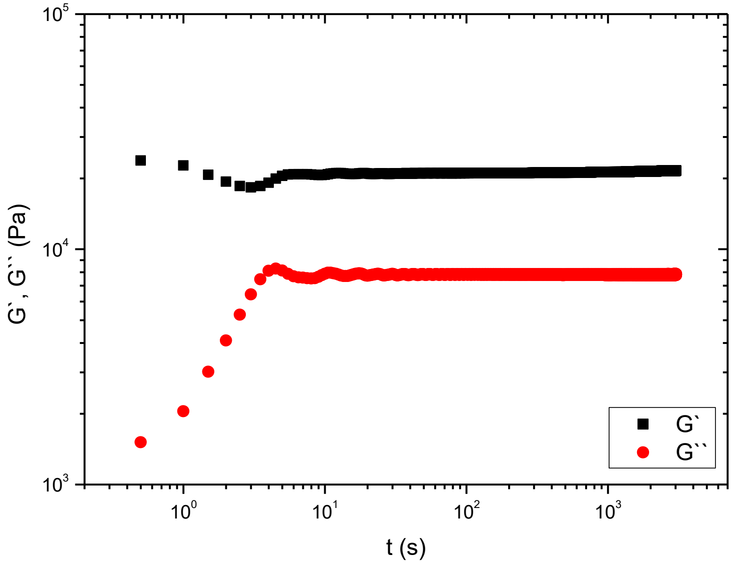
DSST

ω fixed



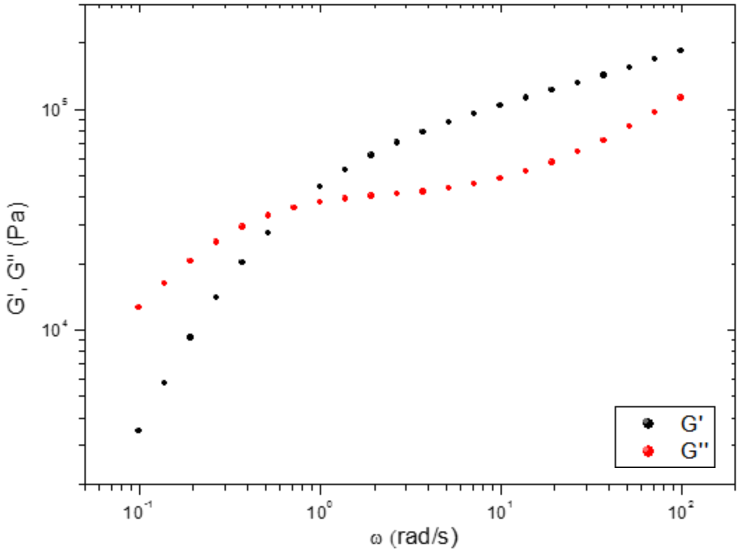
DTST

T, ω and γ fixed

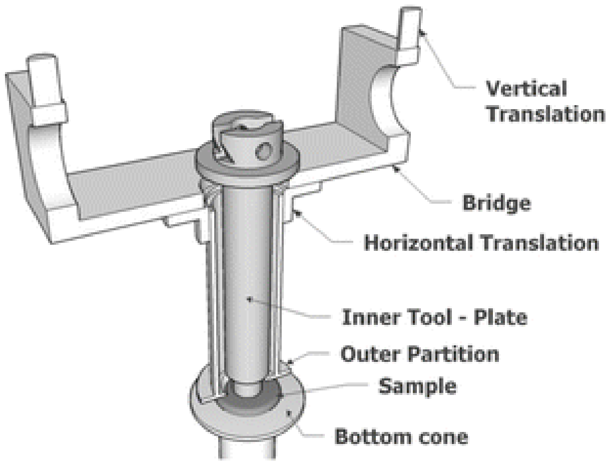


DFST

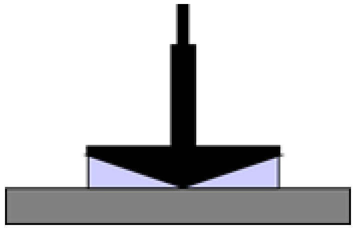
γ and T fixed



Experimental Protocol



S.Costanzo, G.Ianniruberto, G.Marrucci, D.Vlassopoulos, *Rheologica Acta*, (2018), 57:363-376.



Cone and Plate

Non-Linear Measurements:

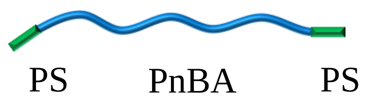
- Step Rates (SR)

Tests performed using Cone-Partitioned Plate geometry of D_{inner}= 8mm.

Fixed Temperature

Shear rate applied in the range : [0.1,100] 1/s

Waiting time: 20min



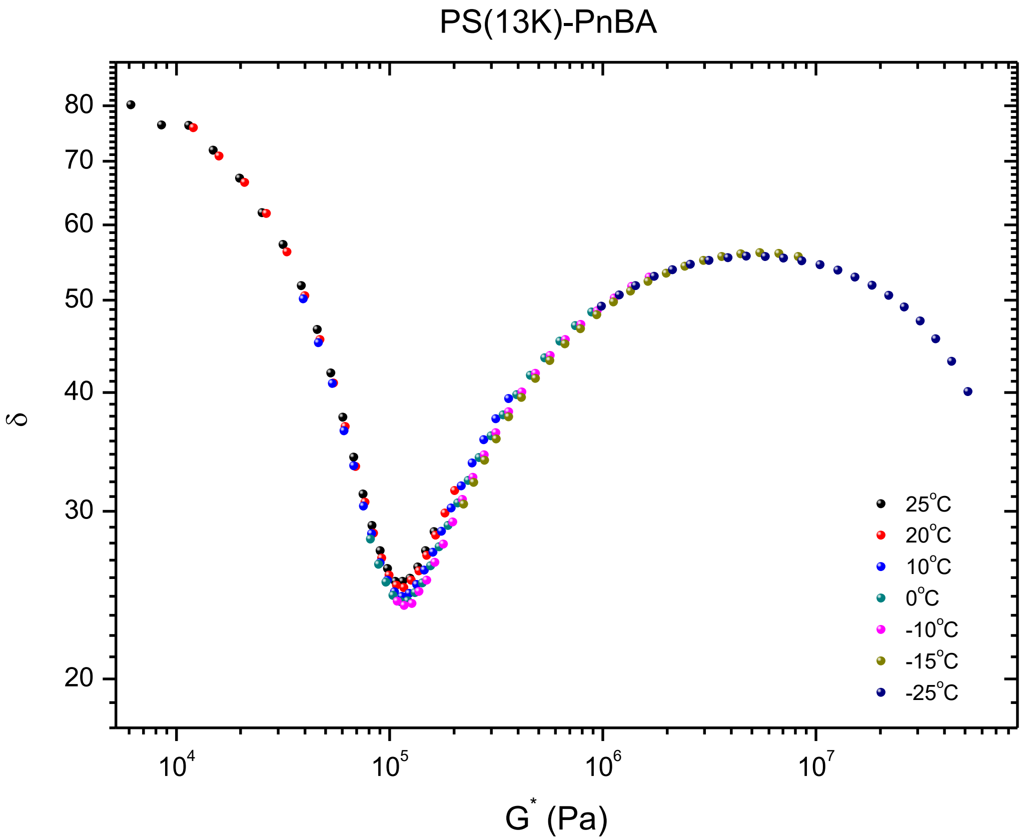
Samples UCL - Results

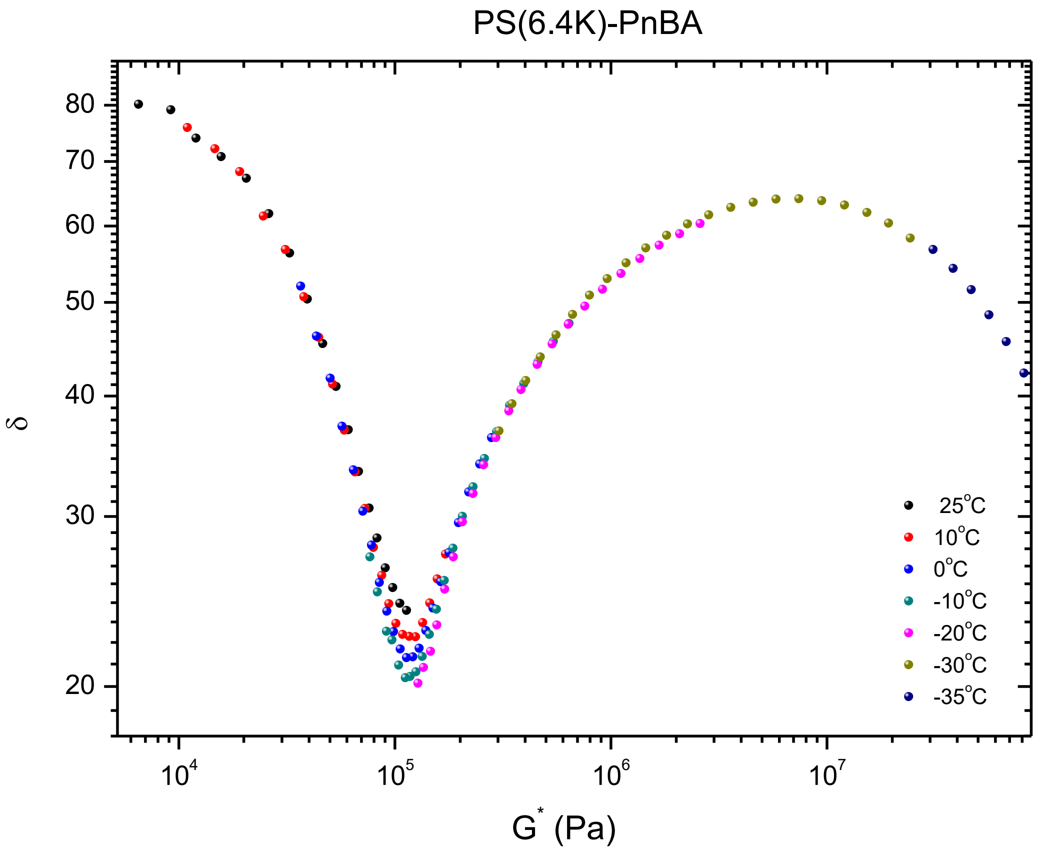
The Range of temperature investigated are:

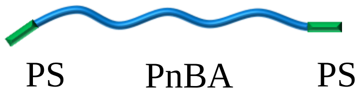
- [-25°C, 25°C] for PS(6.4K)-PnBA
- [-35°C, 25°C] for PS(13K)-PnBA

Time-Temperature Superposition ?

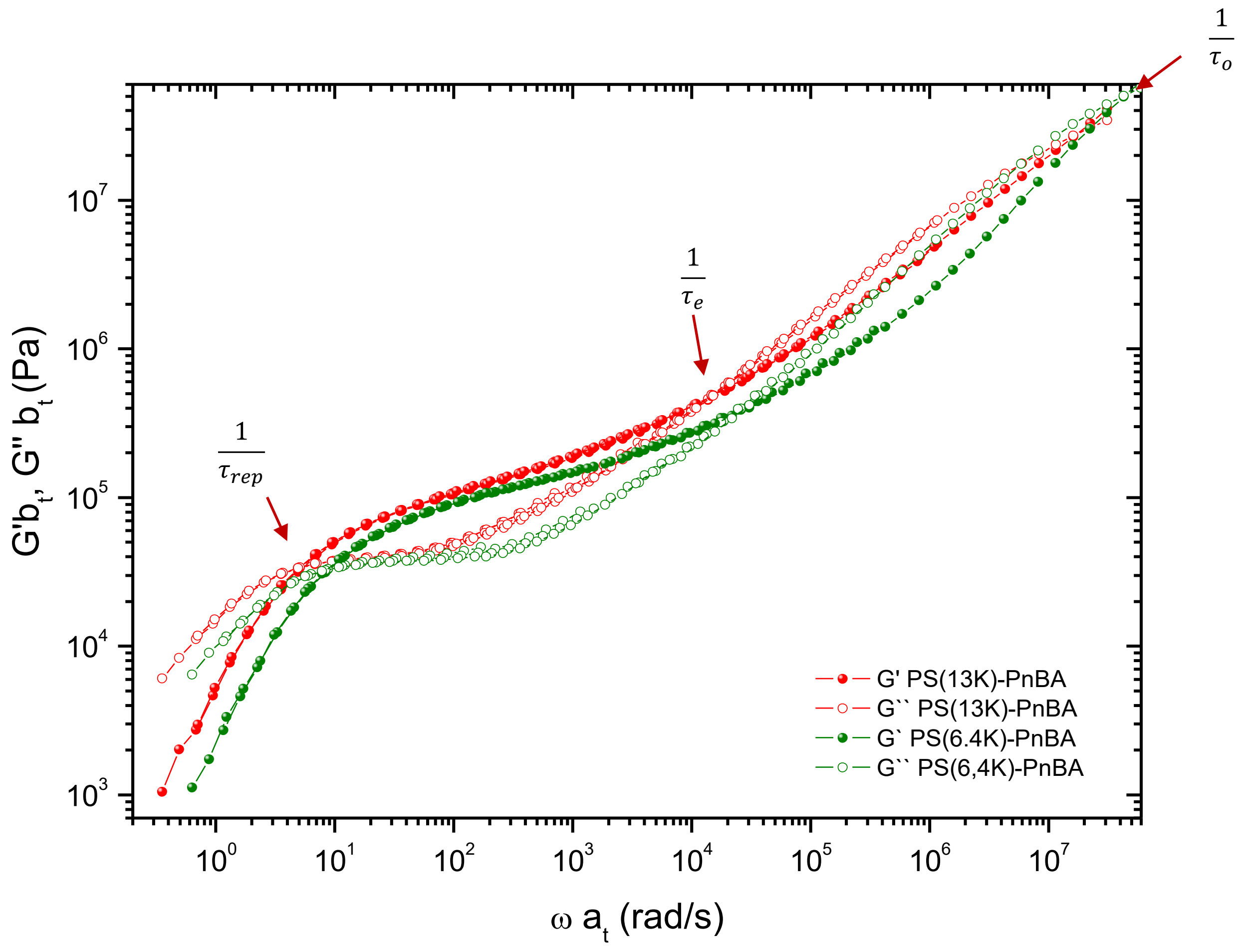
Van Gurp Palmen Plot







Samples UCL - Results



G'$\propto$ $\omega^{1.7}$
G''$\propto$ ω^{1}

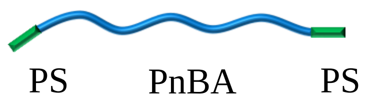
Wait for DSC to confirm!

Flory–Fox equation

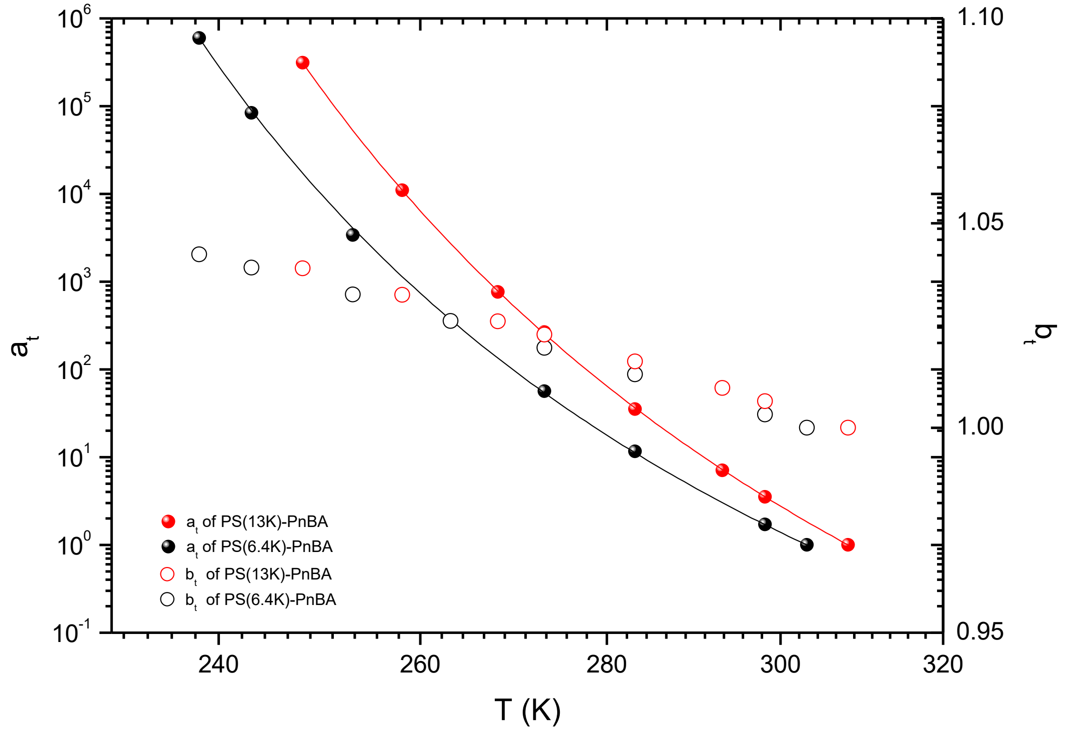
$$\frac{1}{T_g} = \frac{w_{PS}}{T_{PS}} + \frac{w_{PnBA}}{T_{PnBA}}$$

$$G_0 = \frac{\rho RT}{M_e}$$

	T_g (°C)	T_{ref} (°C)	$G_0(Pa)$	M_e (kg/mol)	Z
PS(6.4K)-PnBA	-50	30	$1.16 * 10^5$	22	**5**
PS(13K)-PnBA	-45	35	$1.059 * 10^5$	24	**5**



Samples UCL - Results



a_T → Horizontal shift factor

b_T → Vertical shift factor

WLF (Williams, Landel and Ferry)

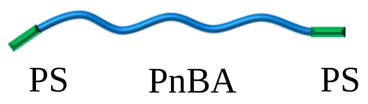
$$\log a_t = \frac{-C_1 * (T - T_{ref})}{C_2 + T - T_{ref}}$$

PS(6.4K)-PnBA

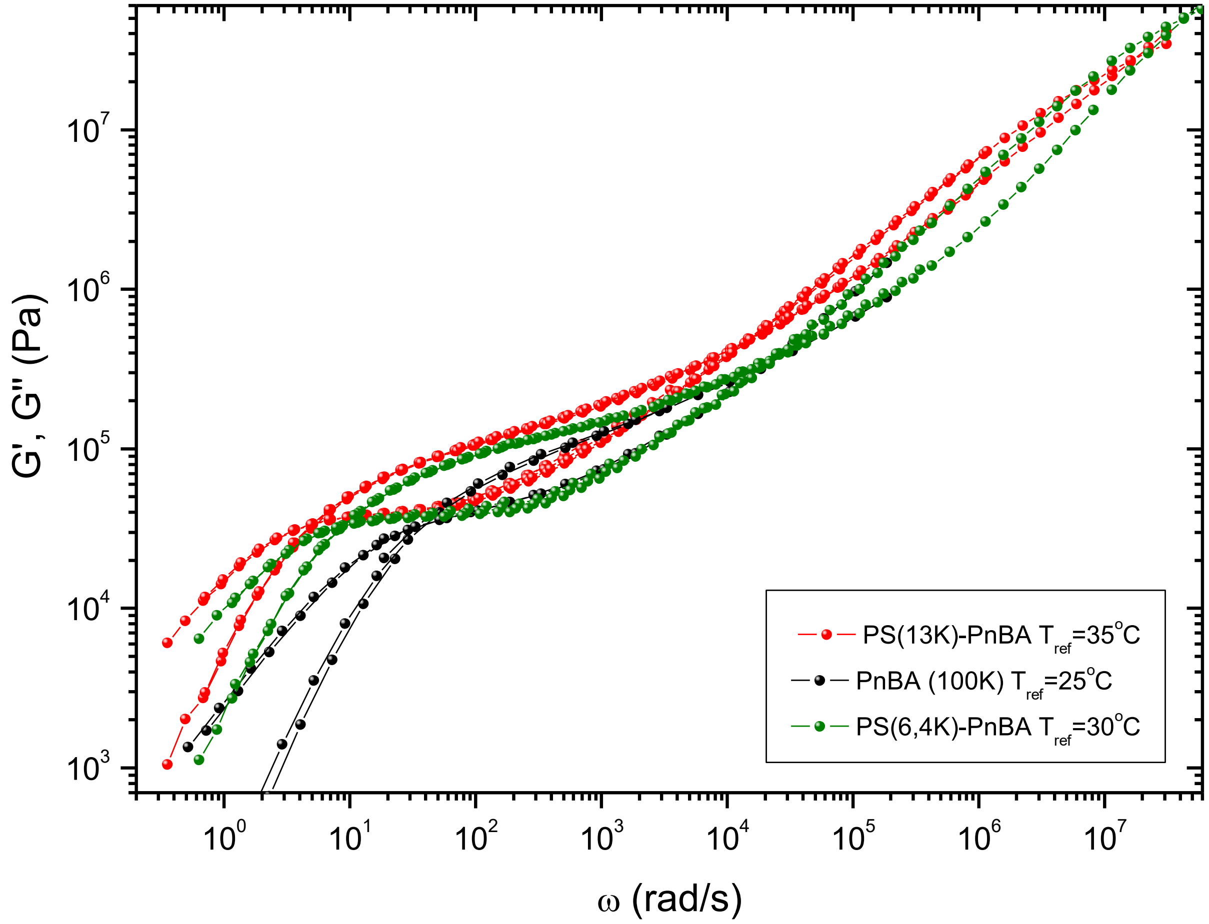
$C_1 = 5.77$
$C_2 = 130\ K$

PS(13K)-PnBA

$C_1 = 6.78$
$C_2 = 135\ \mathrm{K}$

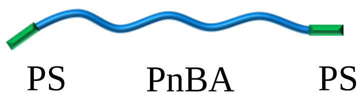


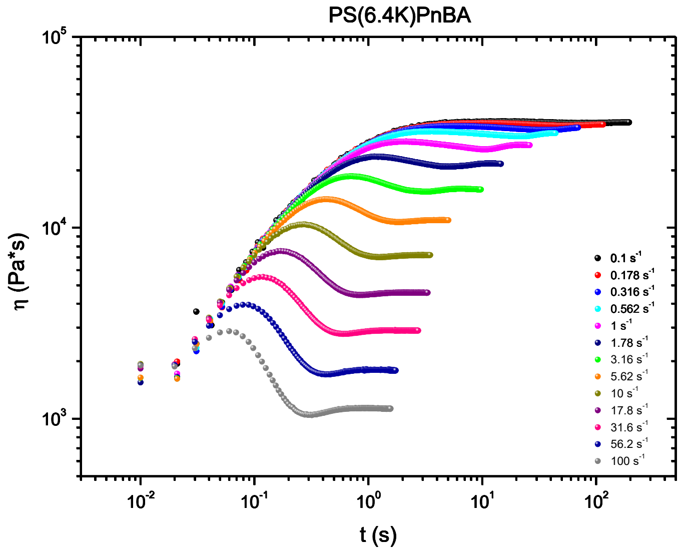
Samples UCL - Results

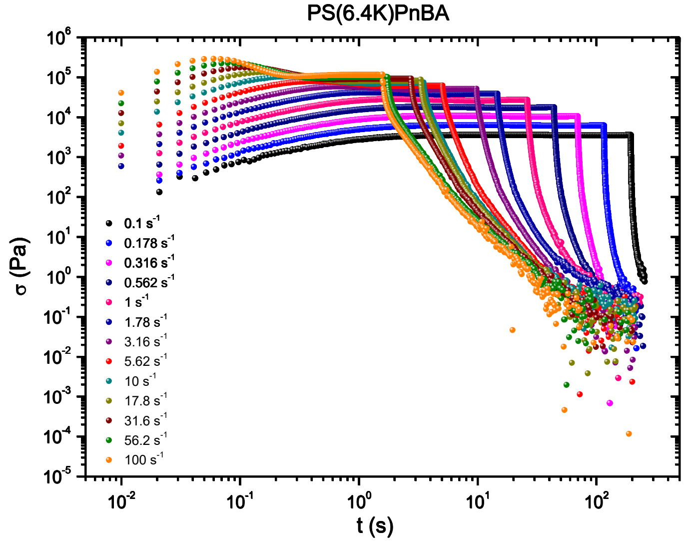


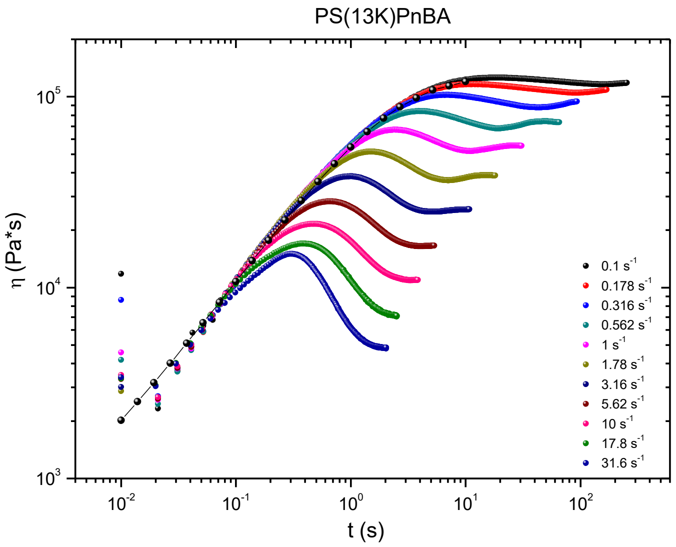
- T_{ref} effect?
- Length of the chain?
- Stickers effect?

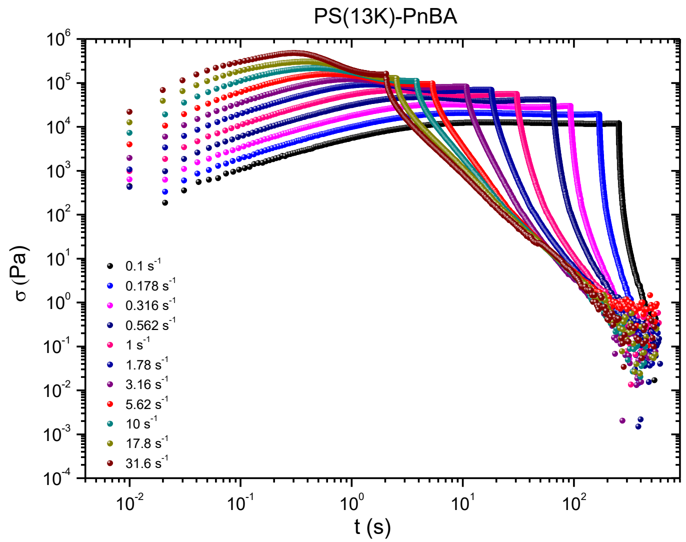
Samples UCL – Non Linear Results

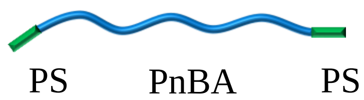




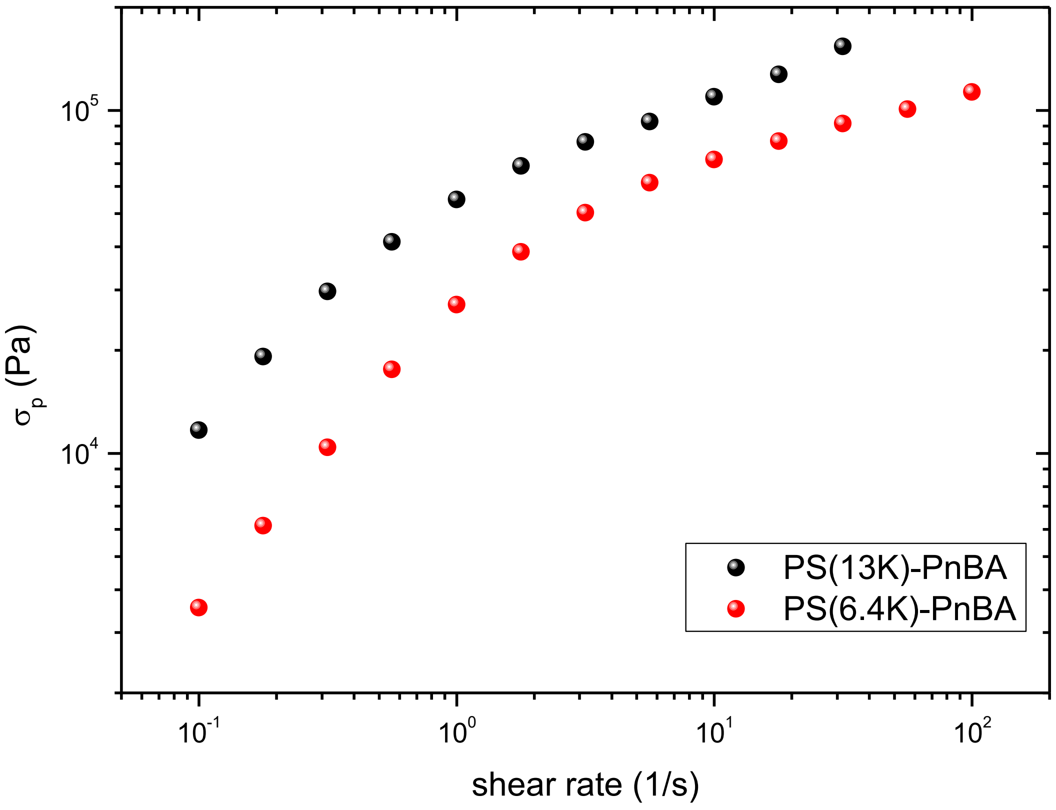






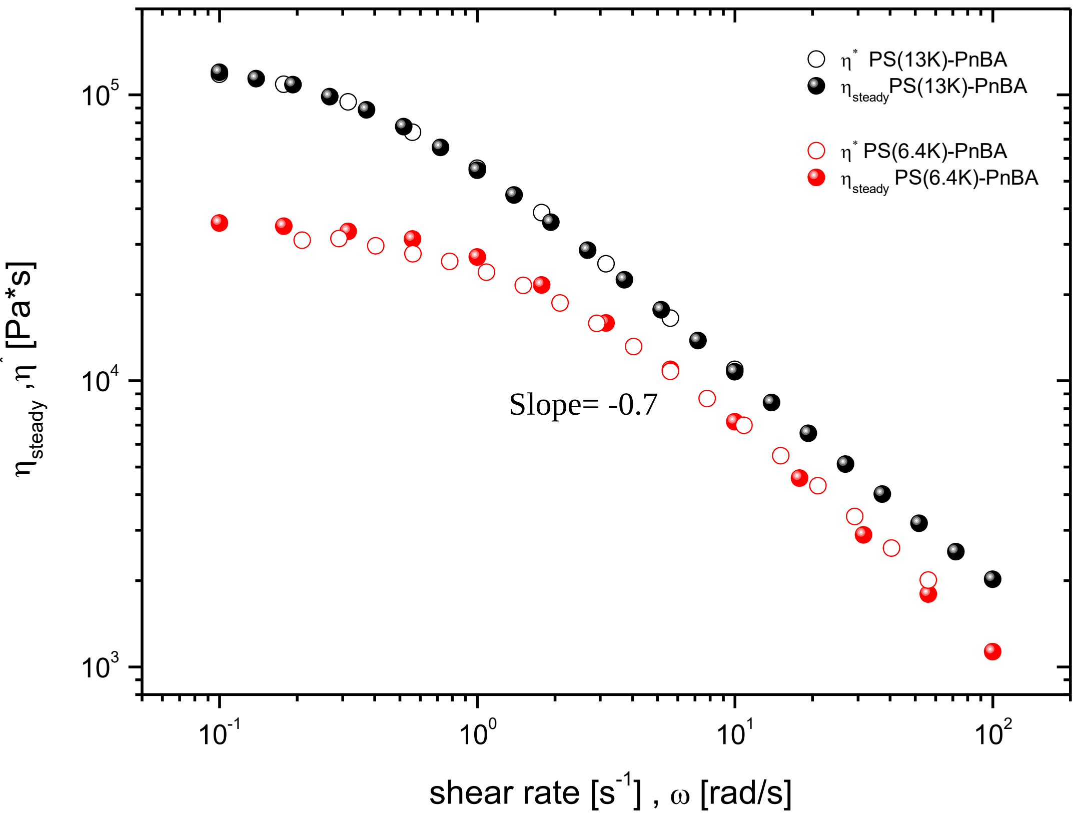


Samples UCL – Non Linear Results

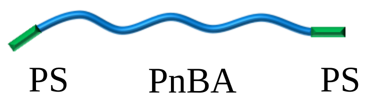


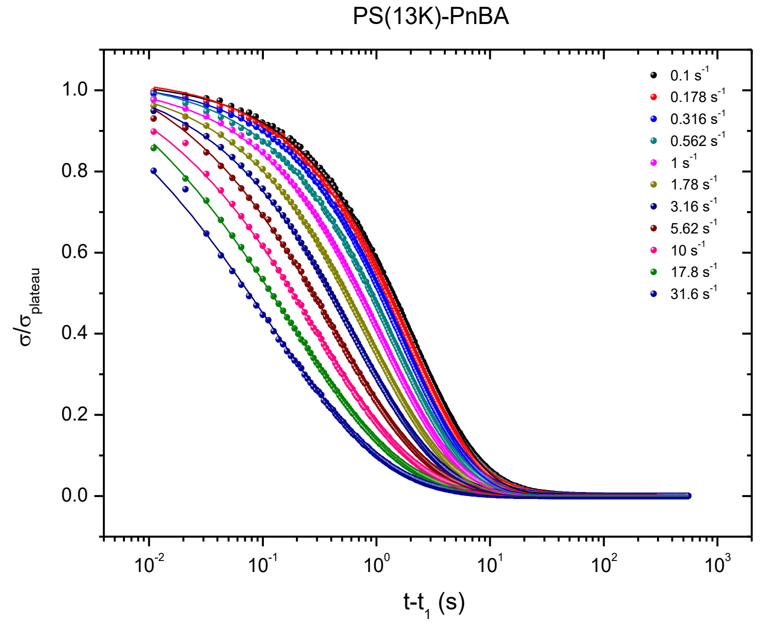
Cox-Merz Rule

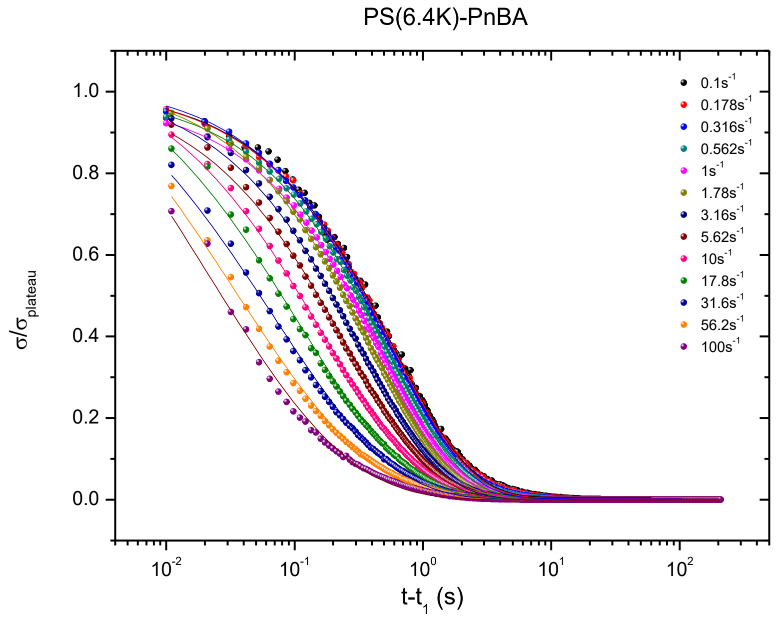
$$\boxed{\eta^*_{\omega\to 0} = \eta(\dot{\gamma})_{\gamma\to 0}}$$



Samples UCL – Non Linear Results

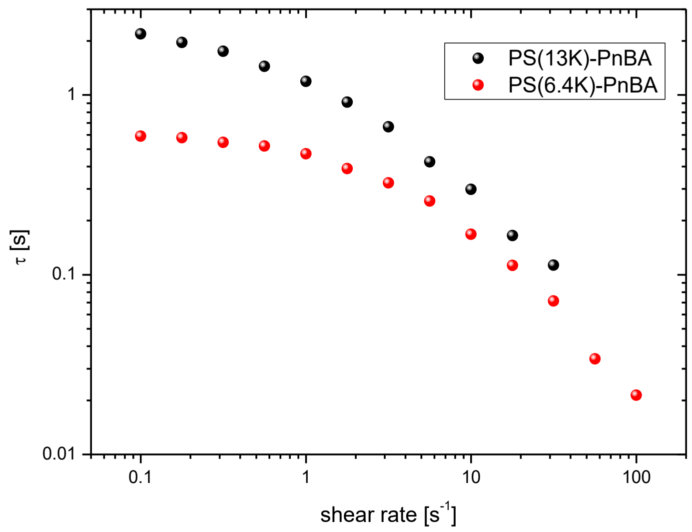


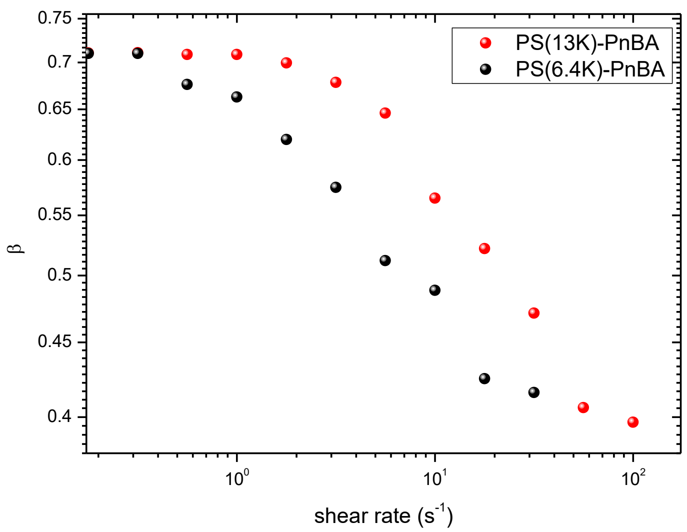




$$f(t) = A + B * \exp[-(\frac{t}{\tau})^{\beta}]$$

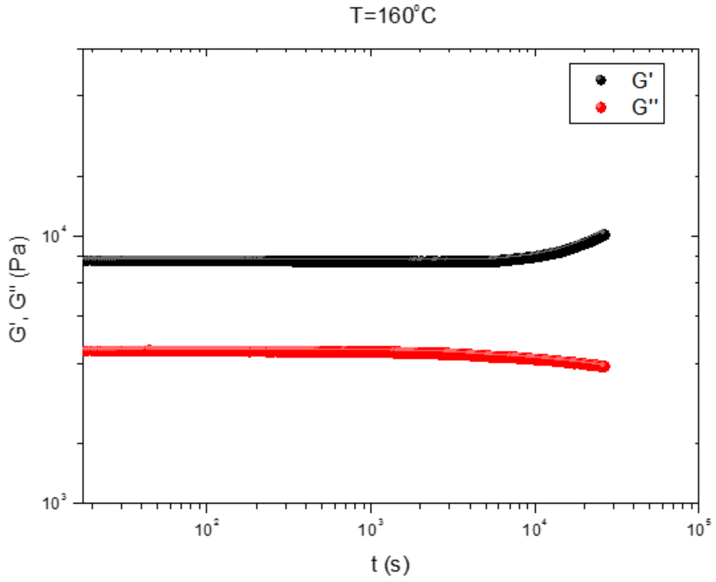
τ_d =1.39s τ_d=0.343s

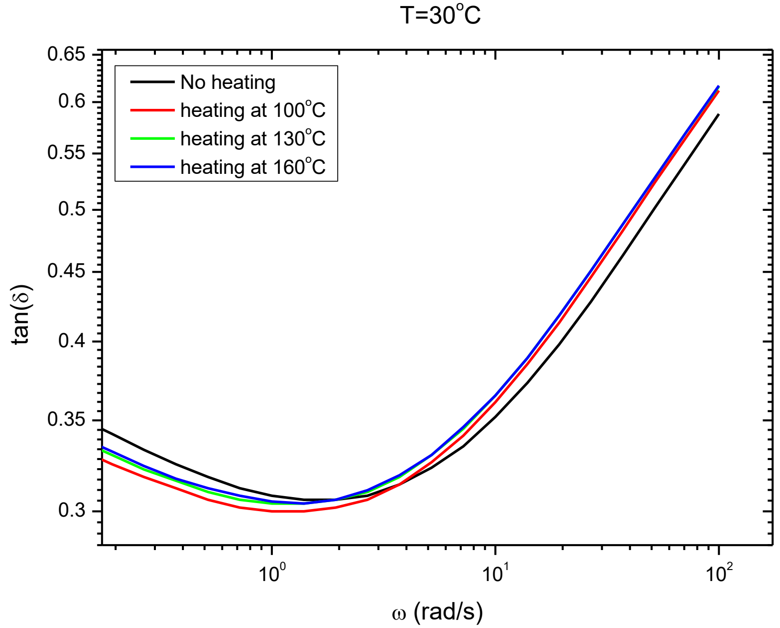




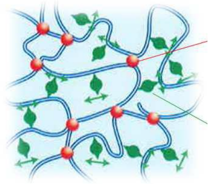
Tesa Samples – Protocol

- Heat the sample at different temperature (until 160 °C)
- DTST (60min)
- Cooling the sample at 30°C
- DTST (60min)
- DSST
- DFST

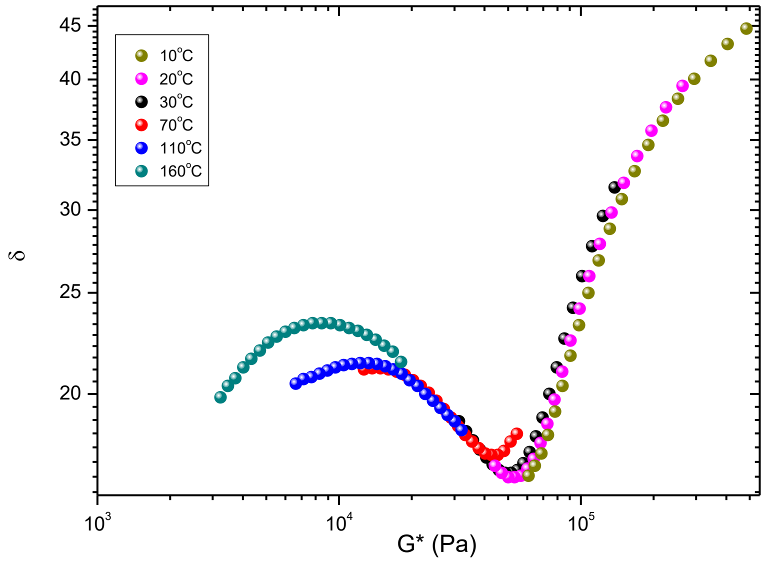




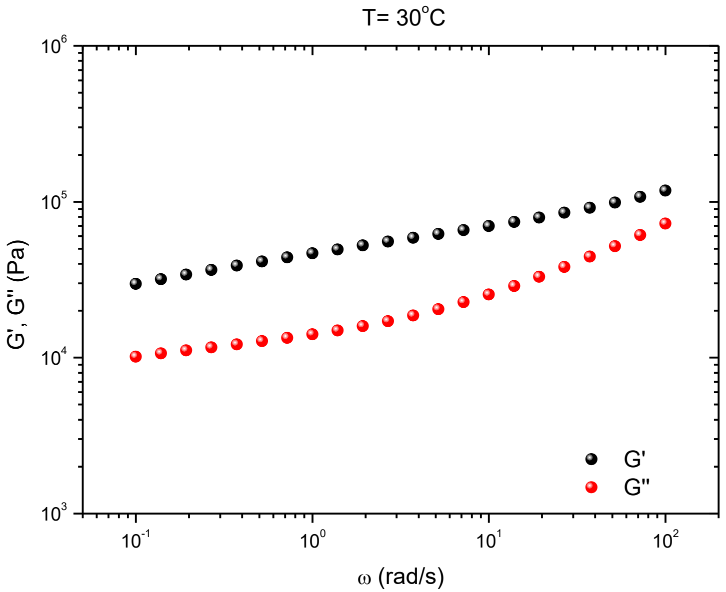
Tesa Samples - Results

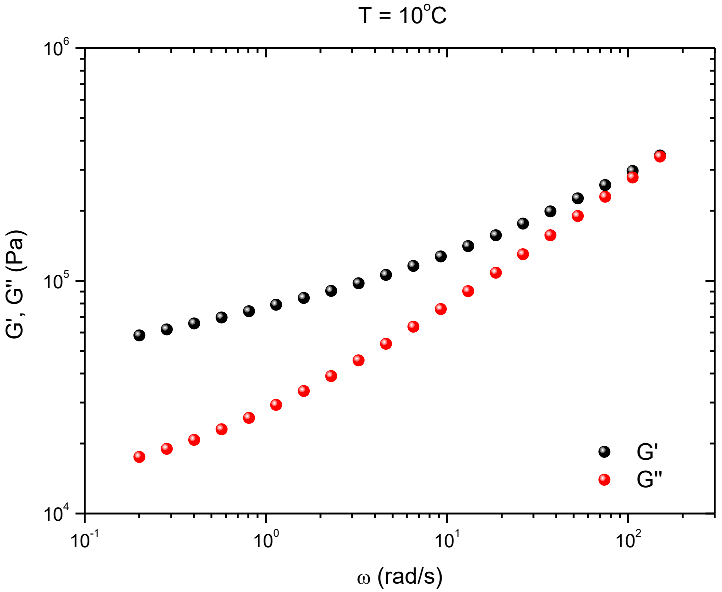


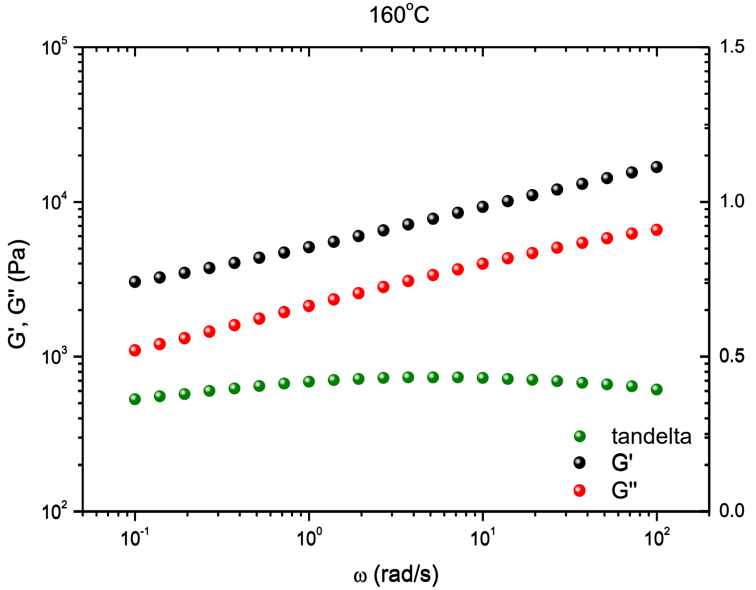
Van Gurp Palmen Plot



~~Time Temperature Superposition~~







Conclusions

We have investigated the linear viscoelastic behavior of double dynamic network and of linear copolymer based on Polybutil-acrylate and Polystyrene.

Based on the experimental data, it is possible to applied the Time Temperature Superposition only for the first system which shows the typical behavior of an entangled polymer.

The second system, as expected, doesn’t show any terminal crossover due to the presence of crosslinked. Furthermore, it’s possible to observe that the sample is not stable for long time at high temperature.

Future Targets

- Probe the influence of adding Polystyrene to the UCL sample.
- Ensure the stability of the Tesa sample with Temperature and time.
- Investigate the behavior of Tesa and UCL samples at high and low frequency (Creep experiment).
- Compare the two different Tesa sample and examine the influence of chemical and physical crosslink to the system.
- Study the local dynamic of the samples.
- Micro-rheology.
- Tack experiment.
- Extensional rheology.

THANKS FOR THE ATTENTION!