Combining two supramolecular dynamics to develop transient double polymer networks with multiscale viscoelastic response

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Prof. Evelyne Van Ruymbeke

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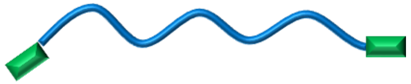
State of the Art

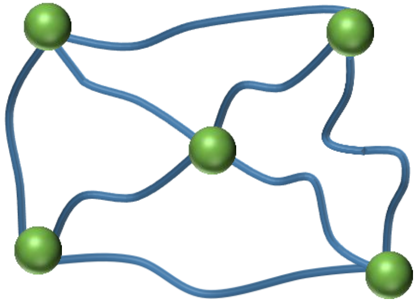
Objectives

Synthesis

Understand the dynamics of the simple networks

Double Networks

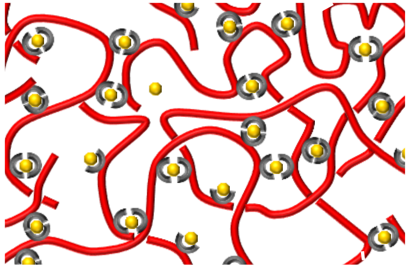




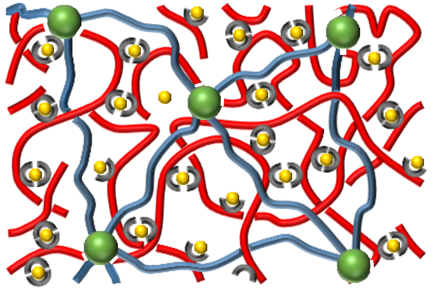
Define a procedure for the blends
Linear Rheology in Bulk

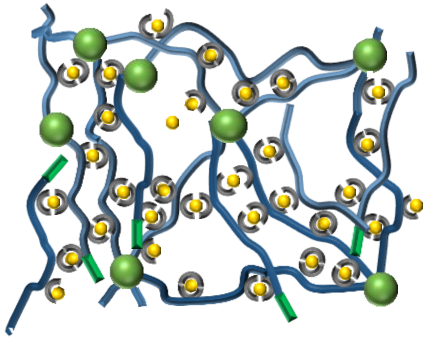
Metal ion

ZnCl2, CuCl2



Blends





Structure-properties relationship
Mechanical properties

Outline

I

Reference triblock:
SAXS and linear rheology

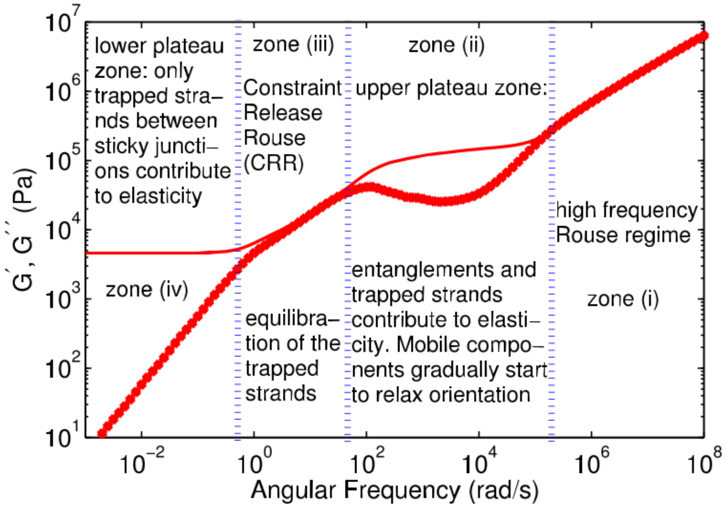
II

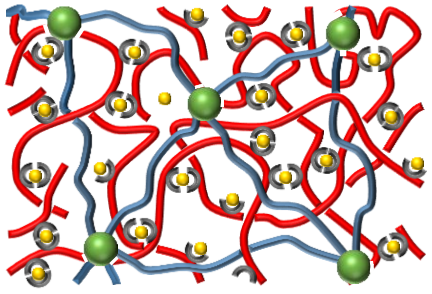
Formation of stable network

III

Double Networks

PS-*b*-*PnBA*-*b*-*PS*





Hawke LGD, Ahmadi M, Goldansaz H, van Ruymbeke E.. *J Rheol*. 2016;60(2):297-310.

PS-b-PnBA-b-PS triblock

Network PS-PnBA-PS

PS**25k**-co-PnBA**120k**-co-PS**25k**

PS12,5k-co-PnBA62k-co-PS12,5k

PS**12,5k**-co-PnBA**35k**-co-PS**12,5k**

Sample	Components			PS content (%)	Đ	T_{g1} / T_{g2} (°C)[c]
	Mn_{PnBA} (g/mol)[a,b]	Mn_{PS} (g/mol)[a,b]	$Mn_{triblock}$ (g/mol)[a,b]			
PS12k-*b*-PnBA35k-*b*-PS12k	35 000	25 000	60 000	42	1,45	-48/20
PS12k-*b*-PnBA62k-*b*-PS12k	62 000	25 000	87 000	29	1,45	20
PS10k-*b*-PnBA100k-*b*-PS10k	97 000	19 000	116 000	16	1.51	-47
PS25k-*b*-PnBA120k-*b*-PS25k	120 000	49 000	169 000	29	1,5	-45/90
PnBA	95 000	/	/	0	1,18	-53

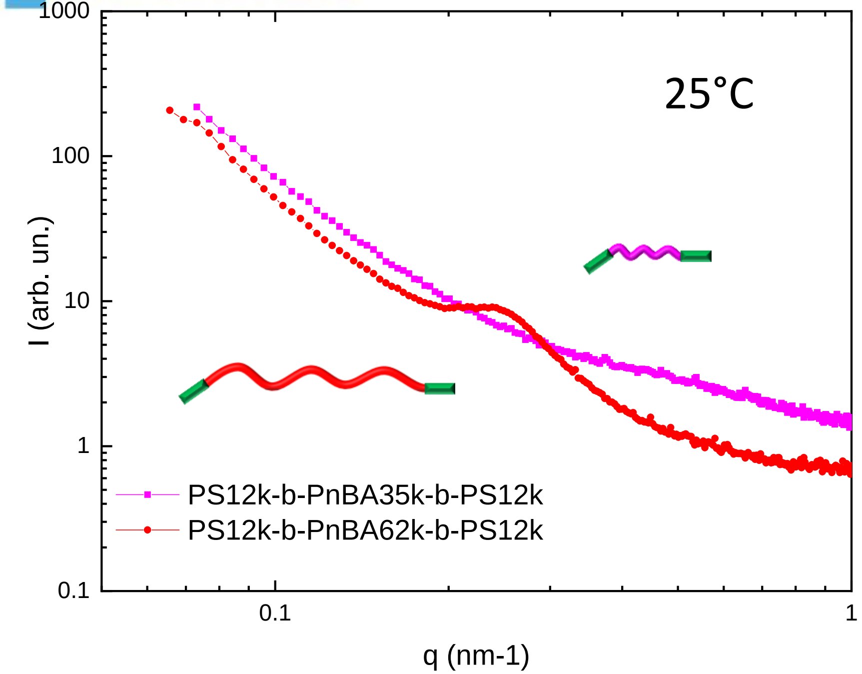
PS**10k**-*b*-PnBA**100k**-*b*-PS**10k**

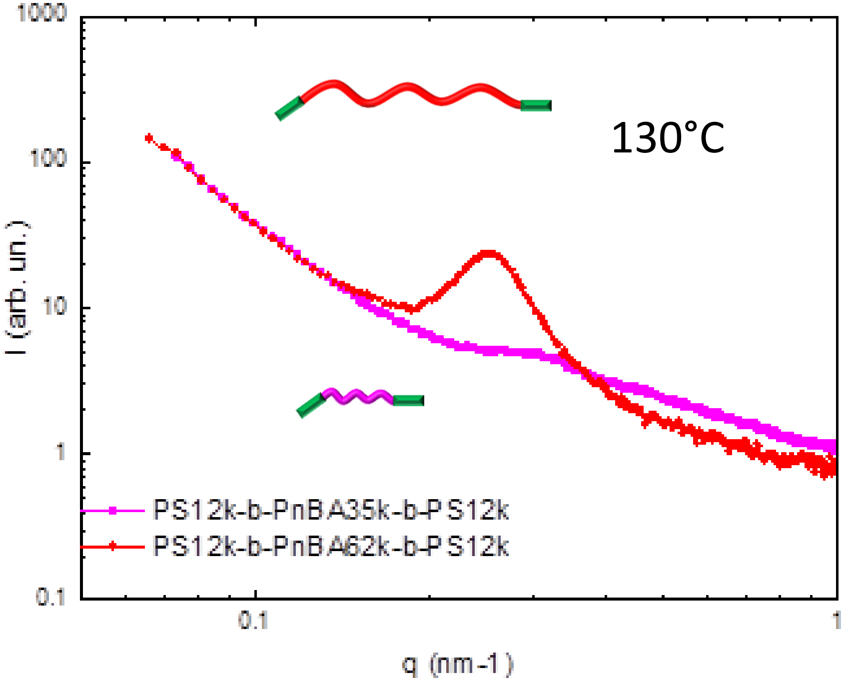
Tg_{PS} = 95°C
Tg_{PnBA} = -52°C

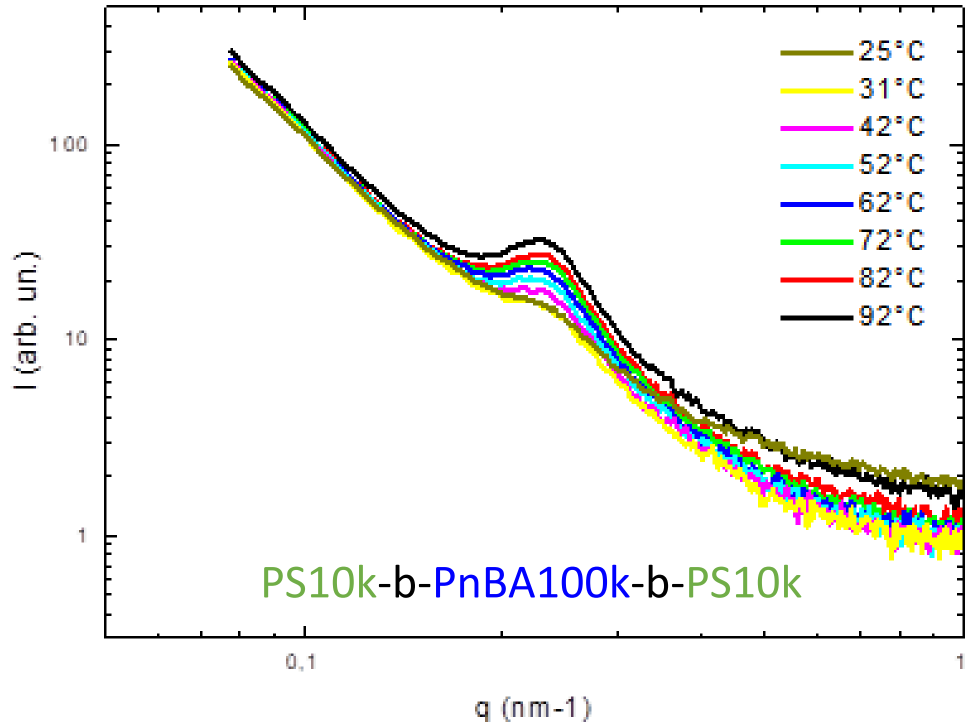
a: determined by ^{1}H NMR in $CDCl_3$
b: determined by GPC in DMF with PS-calibration
c: determined by DSC and/or DMA

Network PS-PnBA-PS

*SAXS**







- The phase separated structure evolves with the temperature
- It is a reversible process
- With concentration of PS domains increase, the structuration of the system increases

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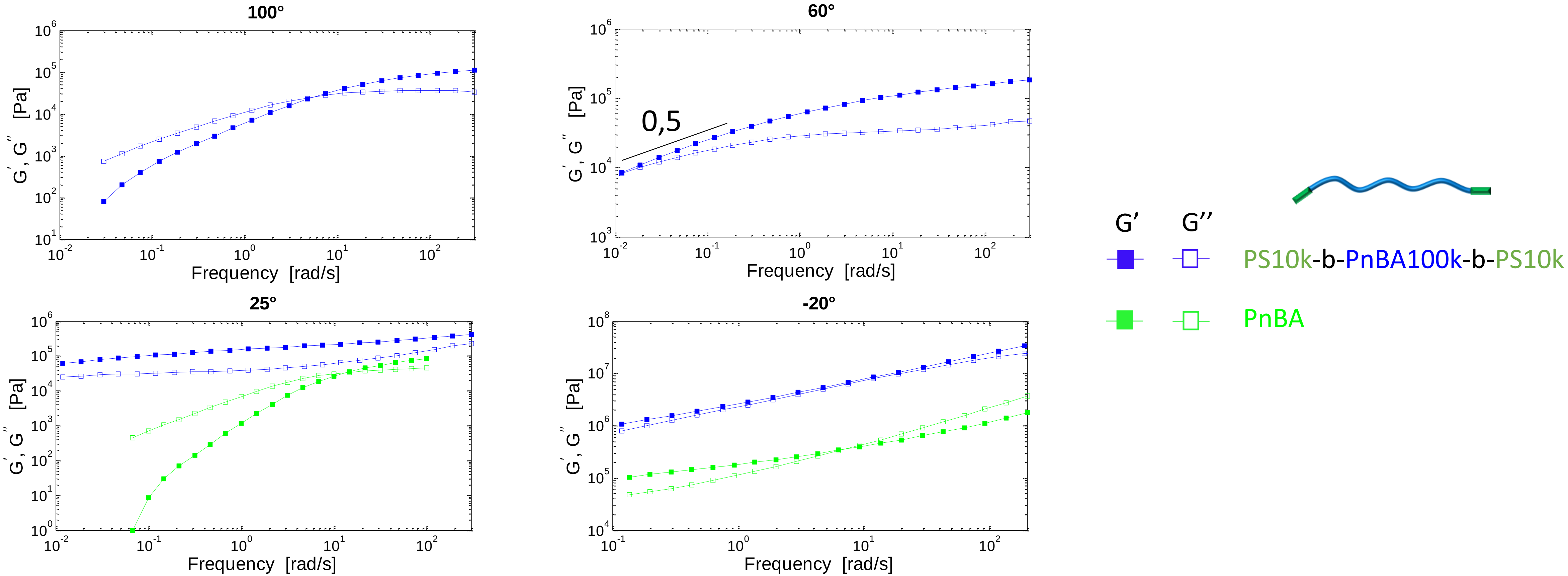
Network PS-PnBA-PS: Linear Rheology



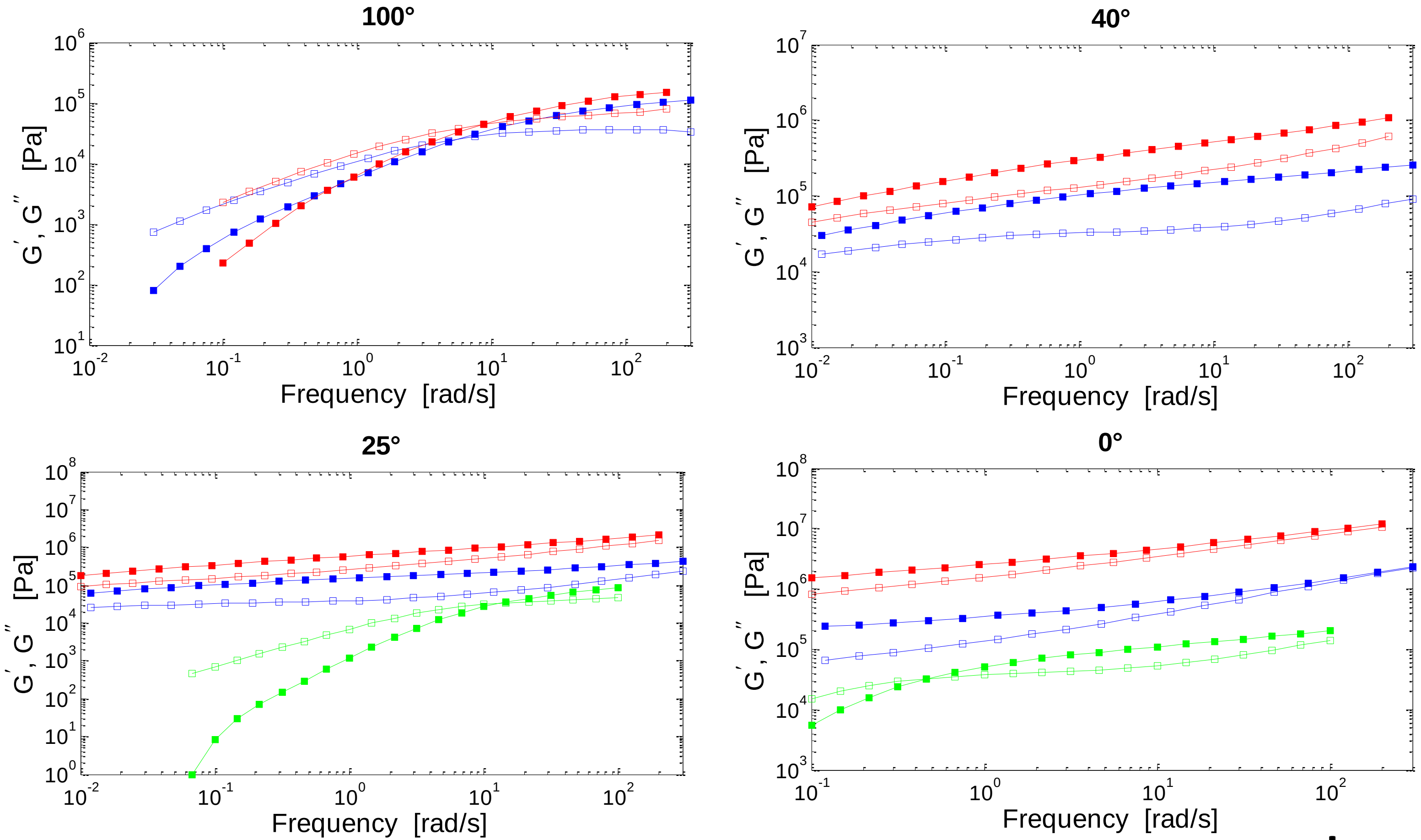
High temperature (100°C and 60°C)

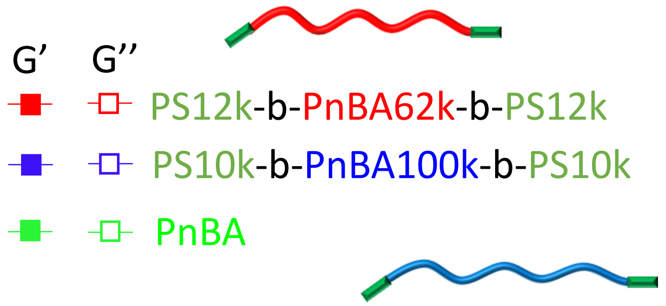
- The sample is fully relaxing at low frequency
- At 60°C, the relaxation mechanism is dominated by a Rouse process at low frequency

Low temperature (25°C and 40°C)

- The lifetime of the phase separated domains is long enough to lead to the formation of a network
- The level of the elastic modulus increases because of hard segments in the triblock.

Network PS-PnBA-PS: Linear Rheology





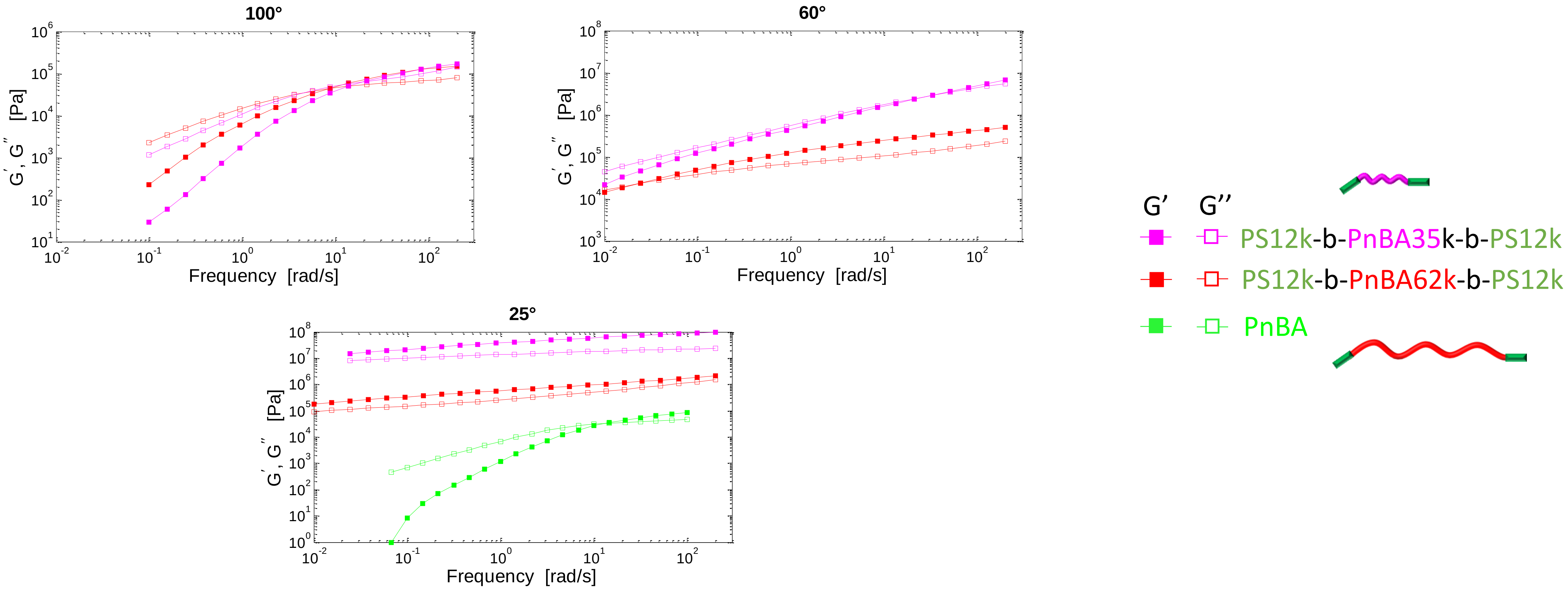
High temperature (130°C)

- Weakly entangled samples relax faster
- the sample do not fully relax

Low temperature (25°C and 40°C)

- The lifetime of the phase separated domains is long enough to lead to the formation of a network
- The level of the elastic modulus strongly increases with the proportion of hard segments.

Network PS-PnBA-PS: Linear Rheology



High temperature (100°C)

- Weakly entangled samples relax faster
- the sample do not fully relax
- Same relaxation process

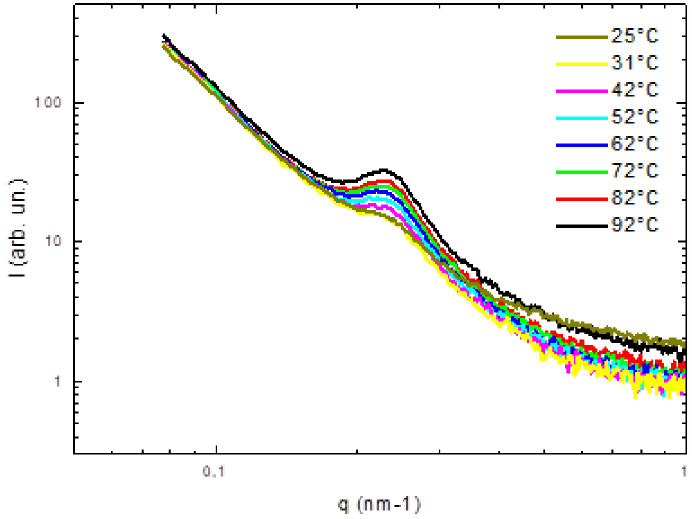
Low temperature (25°C and 60°C)

- The lifetime of the phase separated domains is long enough to lead to the formation of a network
- The level of the elastic modulus strongly increases with the proportion of hard segments.

Network PS-PnBA-PS: Conclusion

PS10k-*b*-PnBA100k-*b*-PS10k

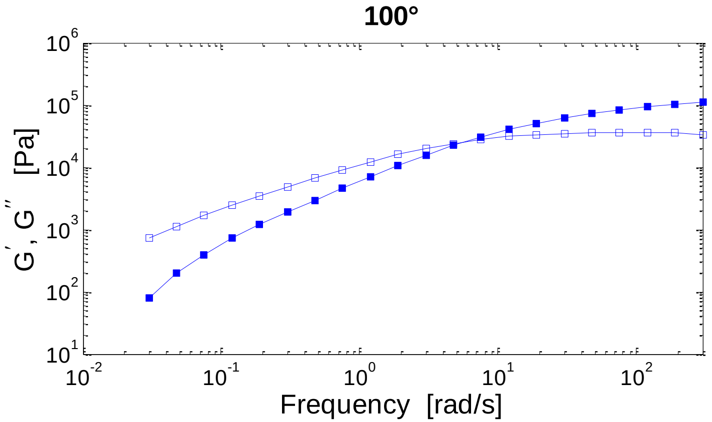
SAXS and viscoelastic properties for the reference samples:

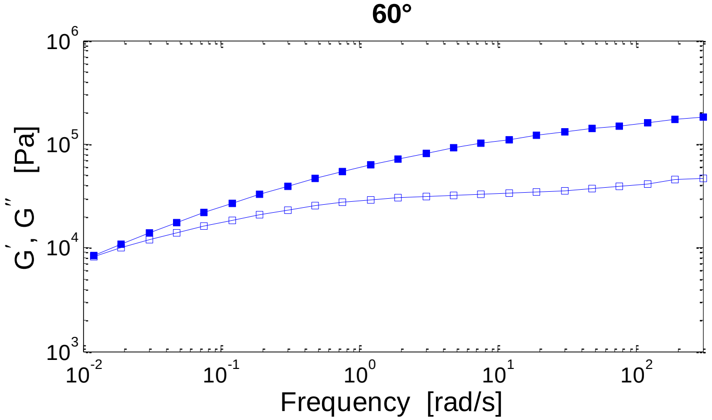


Increase of intensity

Longer relaxation time with a CRR mechanism

The sample is relaxation at low frequency





Network PS-PnBA-PS

PS25k-co-PnBA120k-co-PS25k

PS12,5k-co-PnBA62k-co-PS12,5k

PS12,5k-co-PnBA35k-co-PS12,5k

Sample	Components			PS content (%)	Đ	T_{g1} / T_{g2} (°C)[c]
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a: determined by ^{1}H NMR in $CDCl_3$

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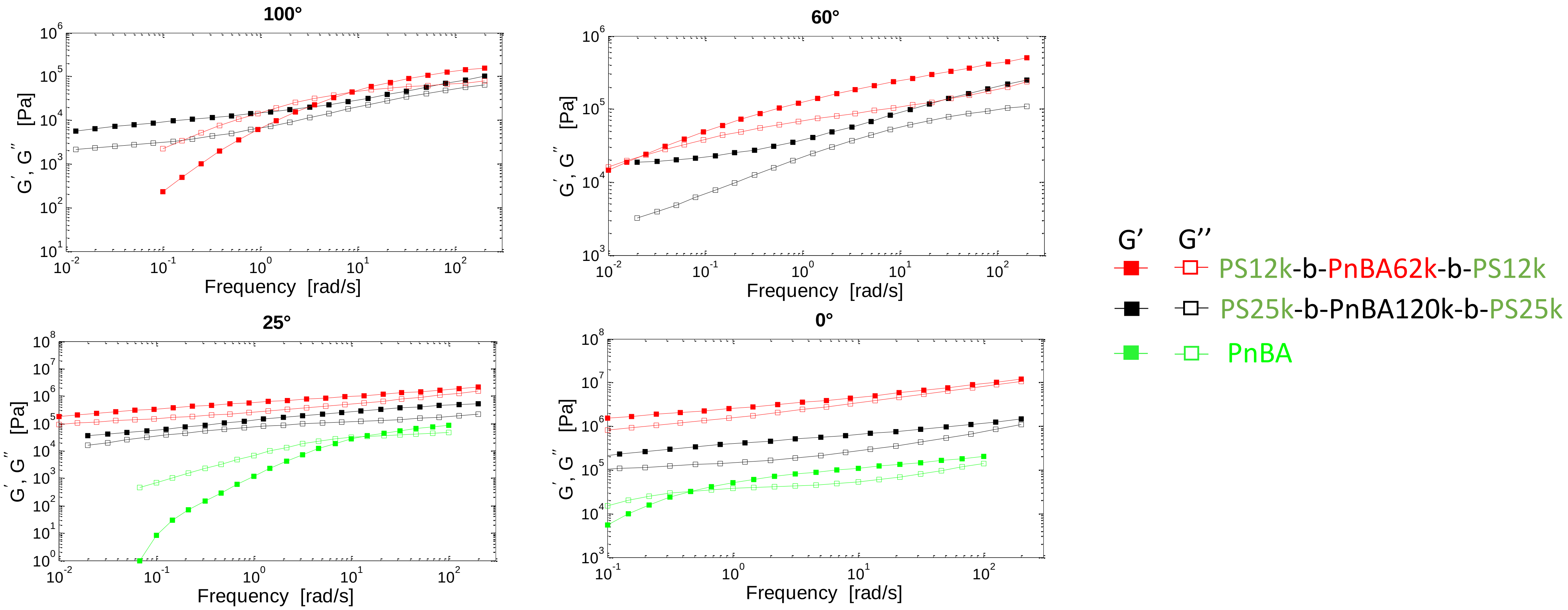
Network PS-PnBA-PS: Linear Rheology



High temperature (100°C)

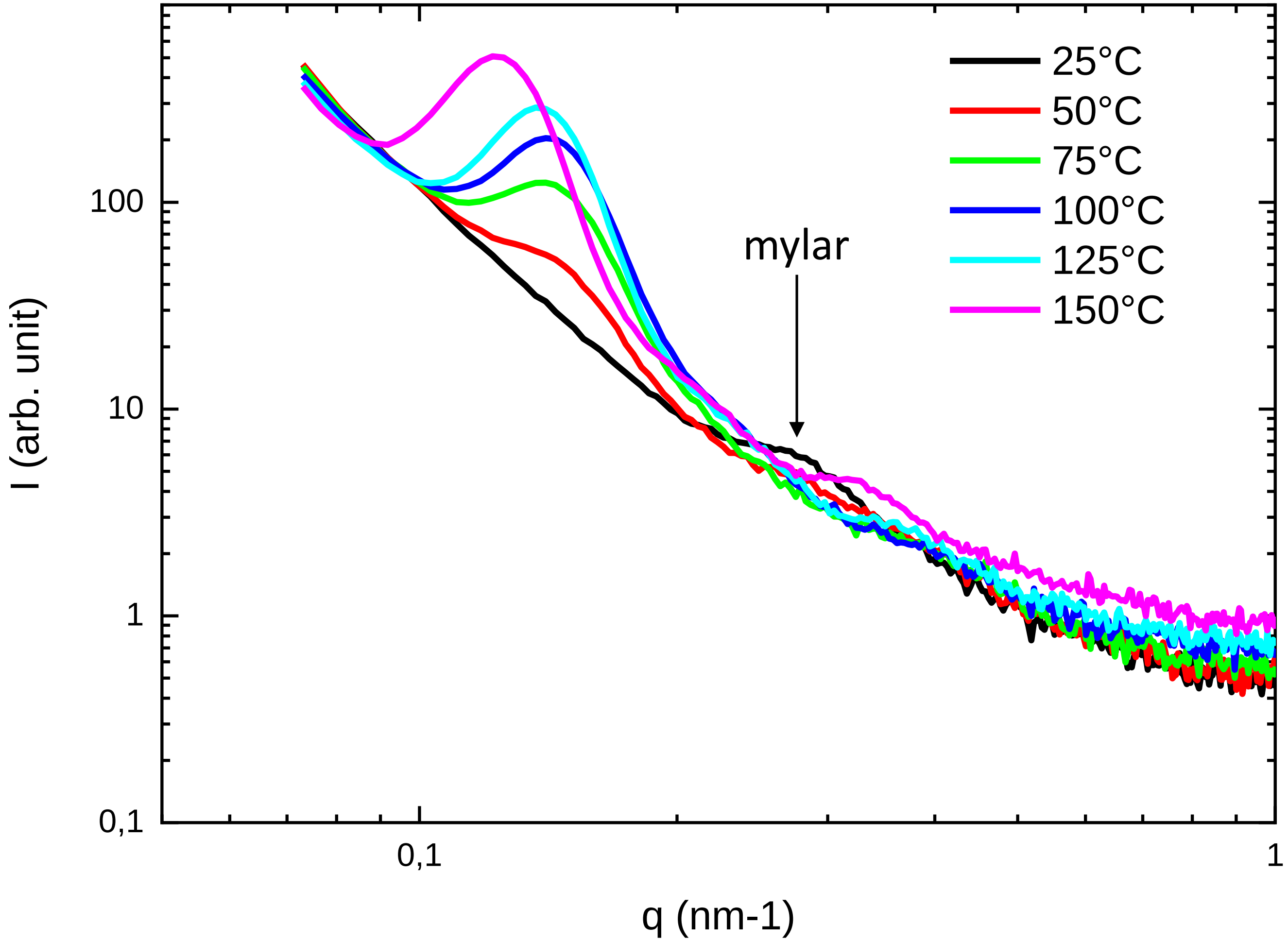
- Weakly entangled samples relax faster
- the sample do not fully relax
- Same relaxation process

Low temperature (25°C and 0°C)

- The lifetime of the phase separated domains is long enough to lead to the formation of a network
- The level of the elastic modulus strongly increases with the proportion of hard segments depending on the central block length.

Network PS-PnBA-PS

SAXS*



- The phase separated structure evolves with the temperature
- It is a reversible process
- With concentration of PS domains increase, the structuration of the system increases
- Above 125°C, the pic shift to lower q: evolution of the structuration

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Network PS-PnBA-PS

*SAXS**

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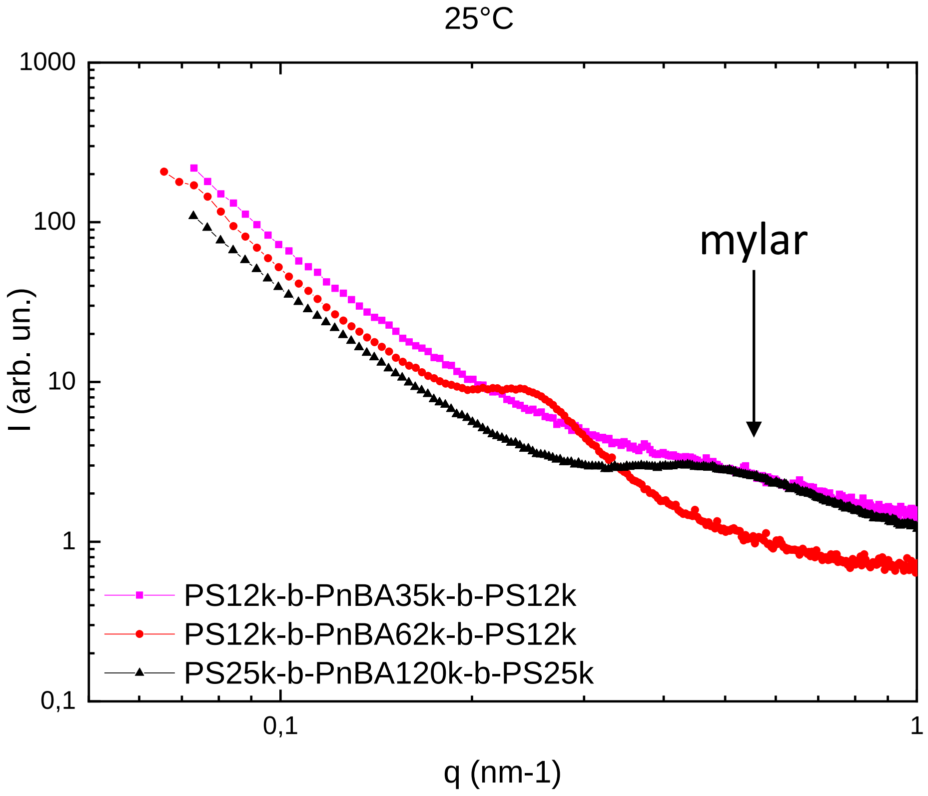

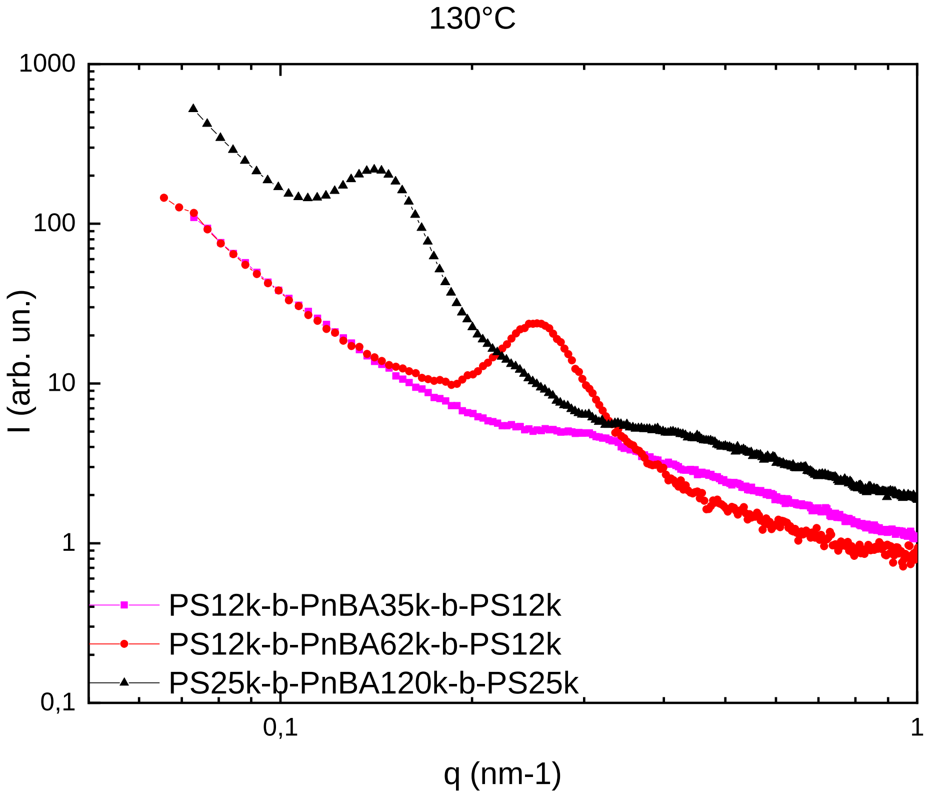

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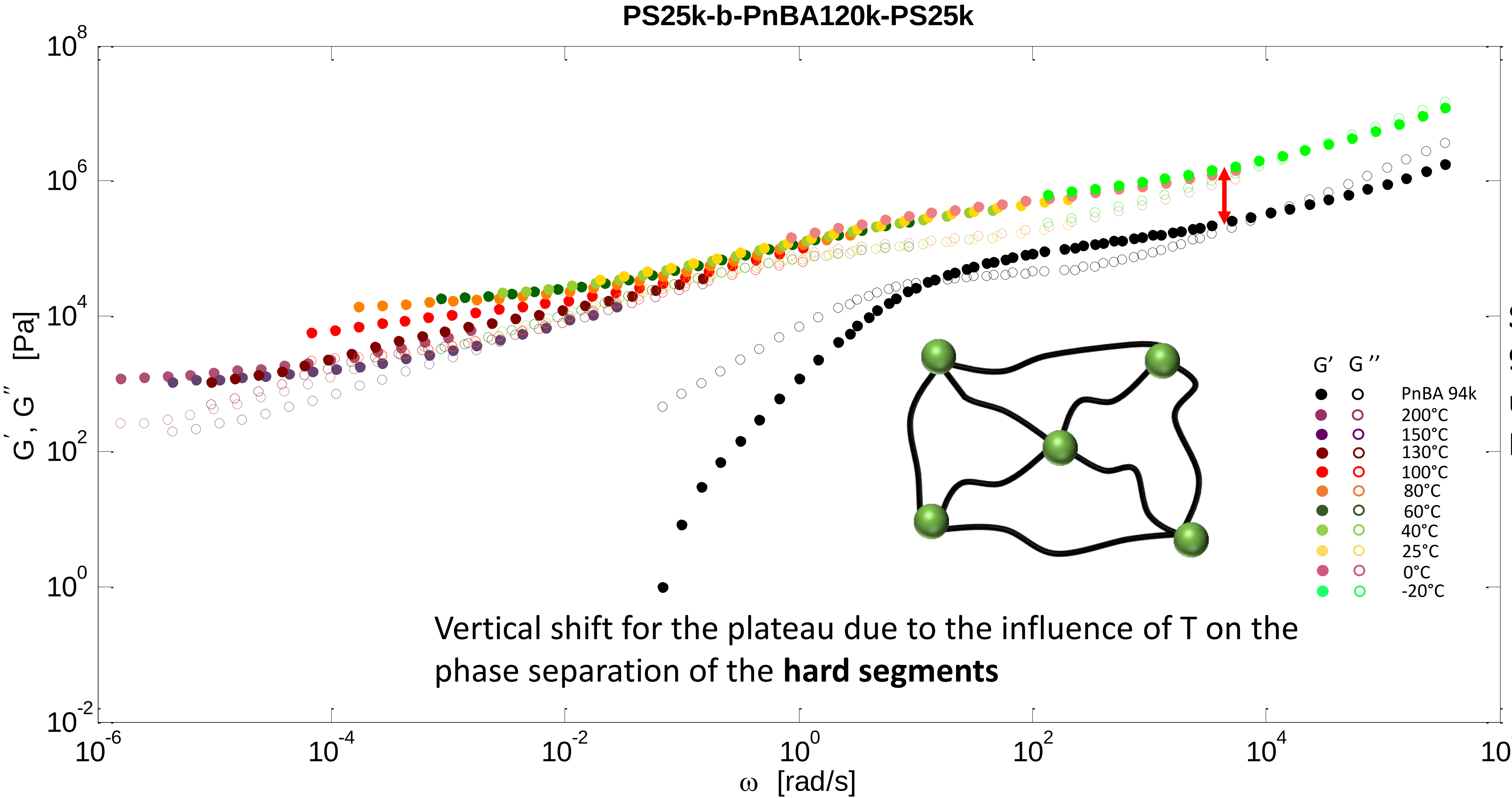
Network PS-PnBA-PS: Linear Rheology

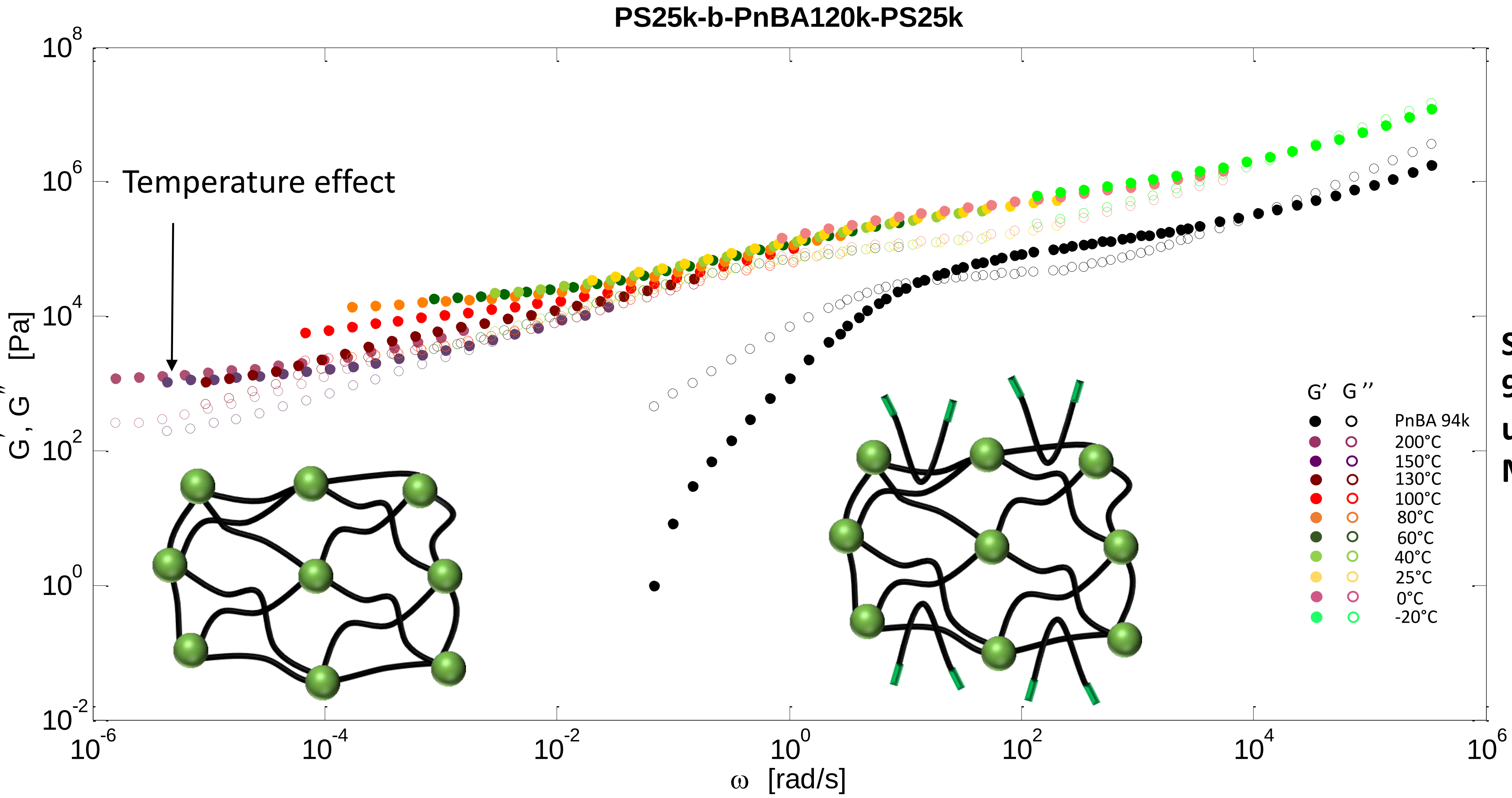
PS**25k**-co-PnBA**120k**-co-PS**25k**



Shift factors from PnBA 94k master curve are used to built all the Master curves

Network PS-PnBA-PS: Linear Rheology

PS**25k**-co-PnBA**120k**-co-PS**25k**



Shift factors from PnBA 94k master curve are used to built all the Master curves

Double Network

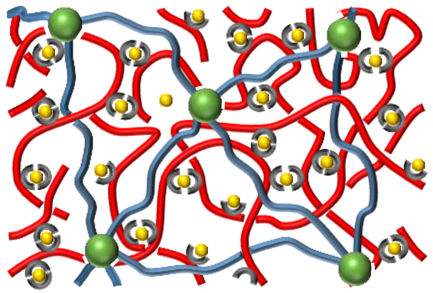
Outlook for tensile tests

50%w

+

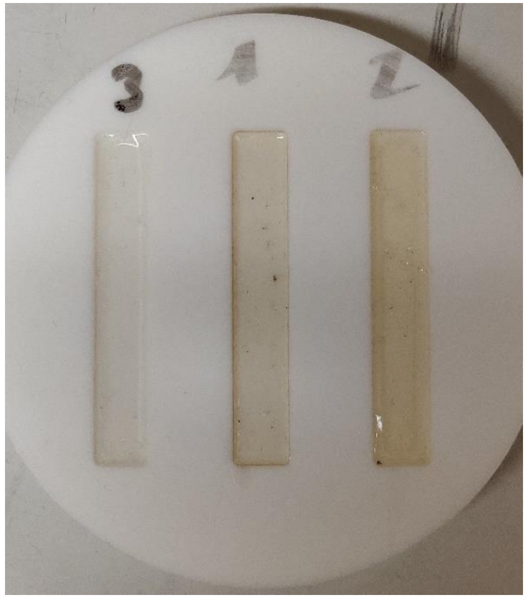
50%w 0,5 eq Zn

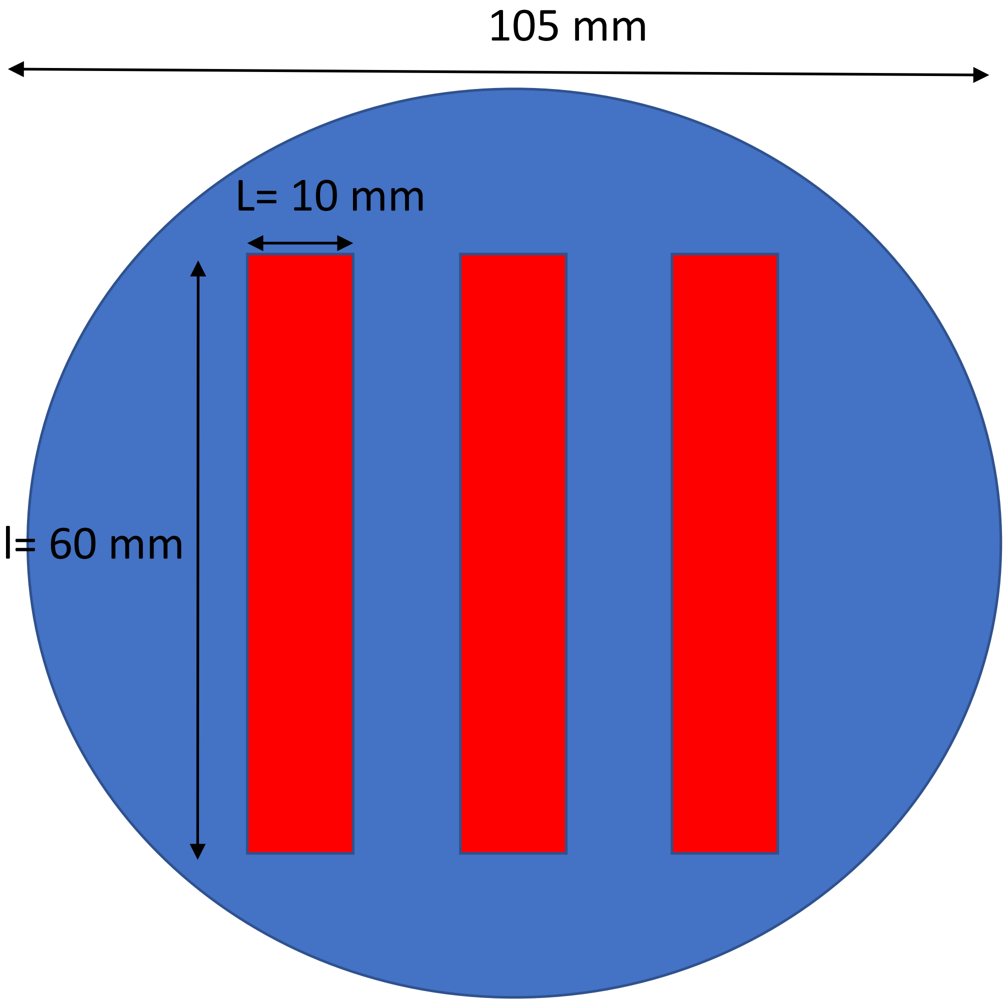
→



<u>Procedure</u>:

- Weight the desire amount of polymer in a vial (~150 mg)
- Dissolve the polymer in acetone to reach a C_m between 250-400 g/mL
- The mixture is stirred few hours until the mixture is homogeneous
- Transfer the mixture to the mold
- Slow evaporation via air-drying for few days
- Final evaporation under vacuum at 130°C for 24h





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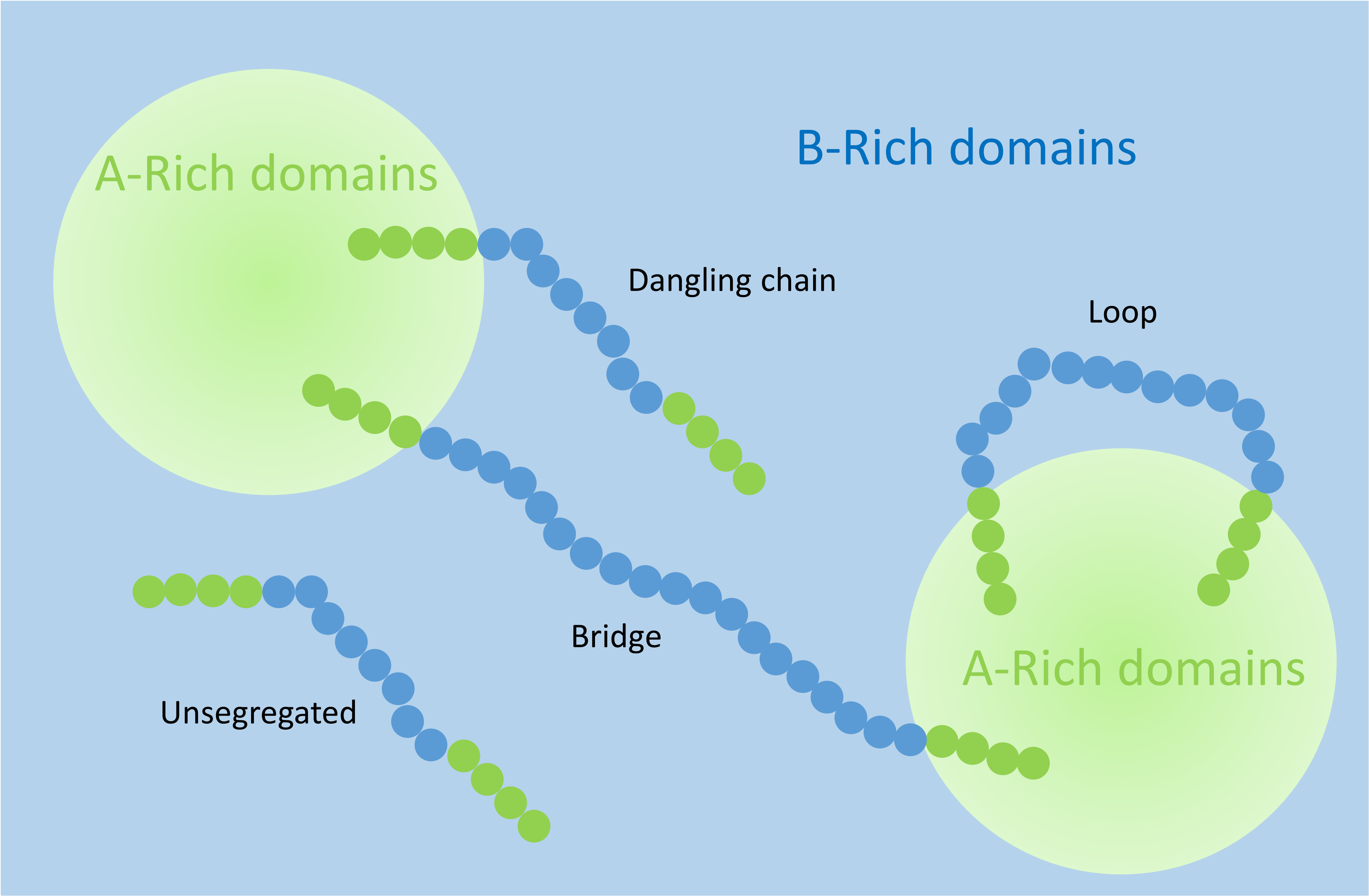
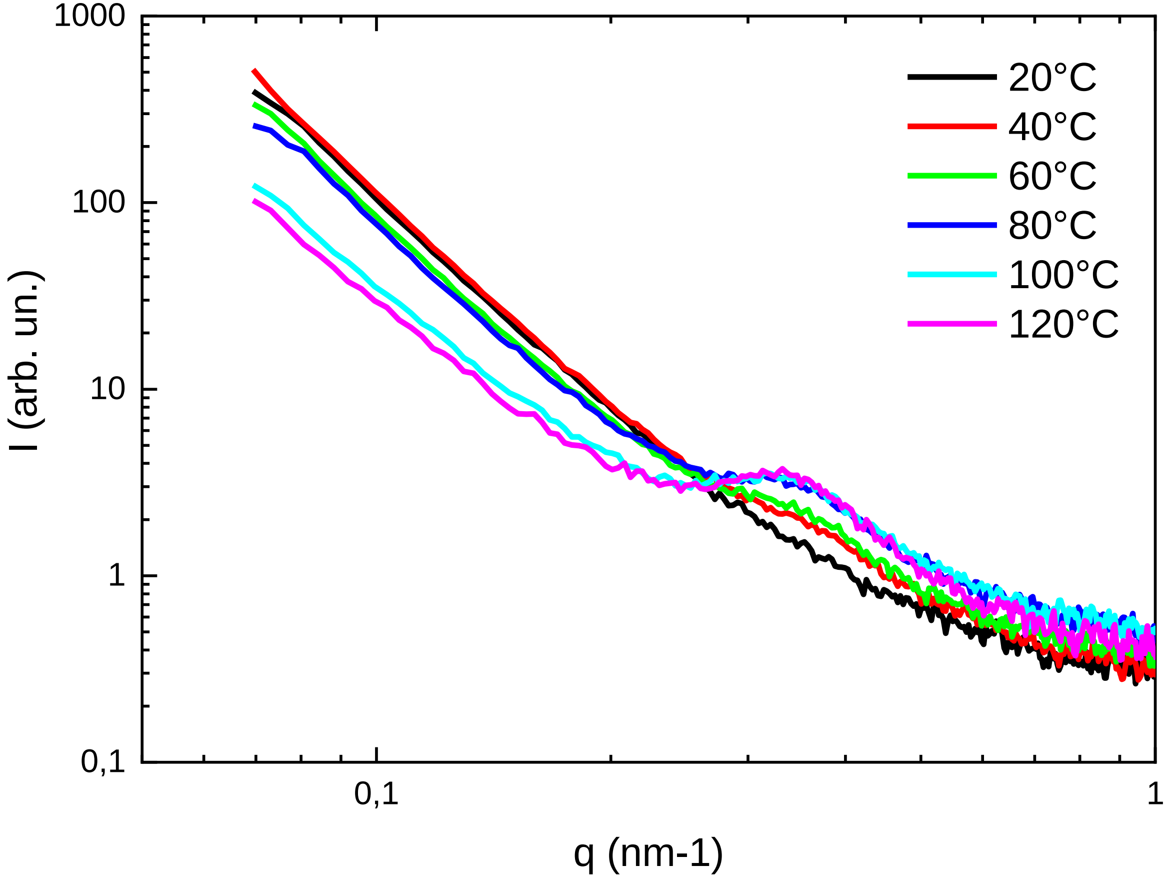
Pr Laurence RAMOS (Laboratoire Charles Coulomb, Université de Montpellier) for the SAXS analysis

DoDyNet Summer School in Capri, July 2019

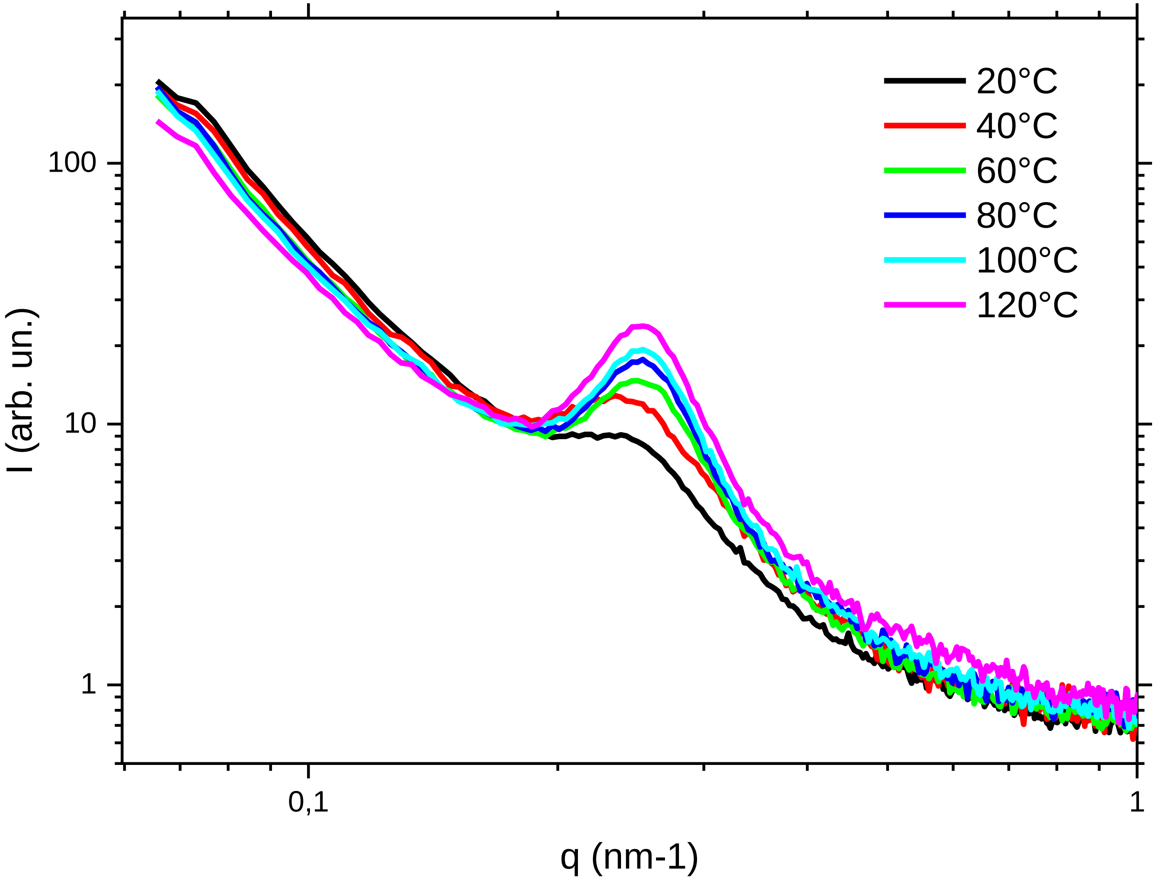
Thank you for your attention


B-Rich domains
A-Rich domains
Dangling chain
Loop
Bridge
Unsegregated
A-Rich domains

PS12k-PnBA35k-PS12k



PS12k-PnBA65k-PS12k



Sample	d_{SAXS} (n.m^{-1})	$d_{radius\ of\ gyration}$ (n.m^{-1})	$d_{stretched\ chain}$ (n.m^{-1})
PS_{115}-$PnBA_{273}$-PS_{115}	18	14,1	157,8
PS_{115}-$PnBA_{484}$-PS_{115}	25	16,8	295,8
PS_{240}-$PnBA_{936}$-PS_{240}	47,2	23,7	435,6
PS_{96}-$PnBA_{780}$-PS_{96}	28,6	19,6	300,8

ABA triblock

Conclusion and Outlook