Viscoelasticity of Supramolecular Center-functionalized Polymer

Effect of the strength of Hydrogen Bonding Stickers

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Costantino Creton, Guylaine Ducouret

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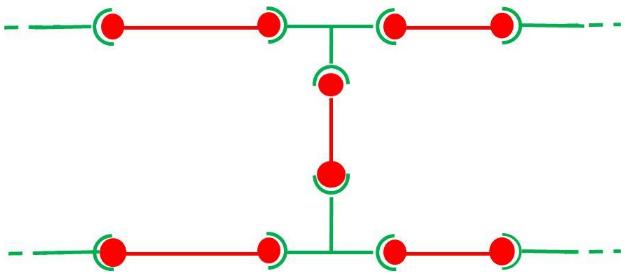
ESPCI ParisTech SIMM cnrs

Supramolecular Polymers ?

Supramolecular Chemistry

Self-assembly of small molecules by **non covalent** bonds (H-bonds, ionic…) in solution



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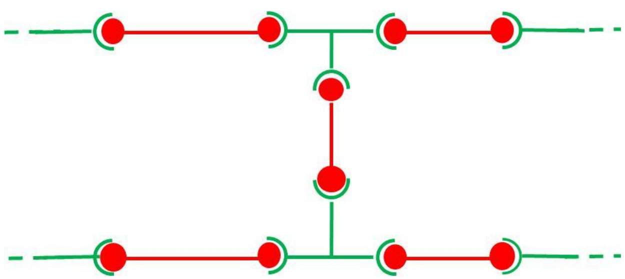

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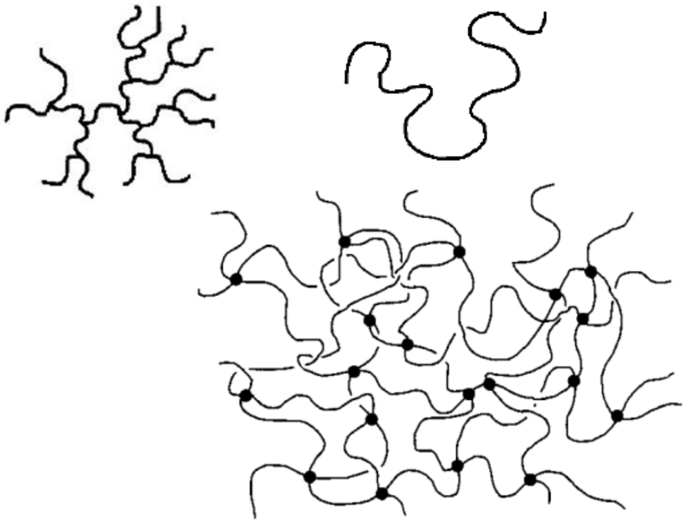
Association by **covalent** bonds of monomers



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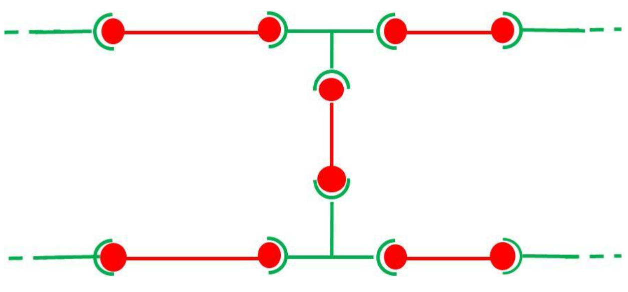

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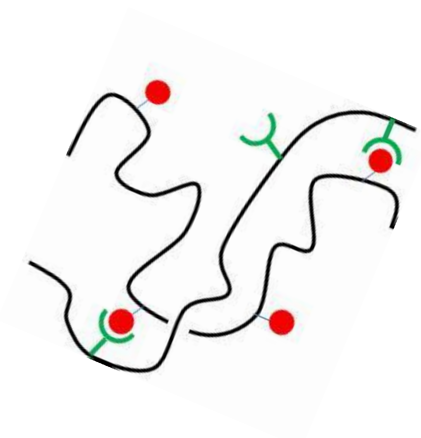


Interest of Supramolecular Polymers ?

Interactions between Stickers

- **Specific** → Clusters, Aggregates, Networks or Nanostructures
- **Reversible** → Strong dependency with their environment

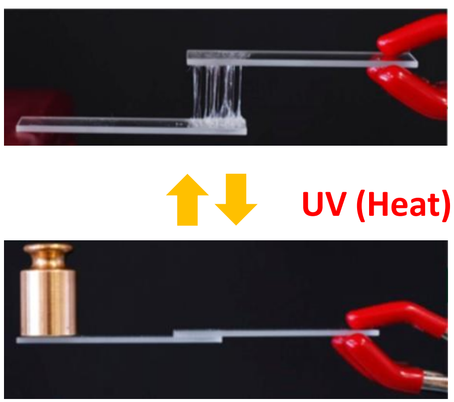
Interest of Supramolecular Polymers ?

Interactions between Stickers

- **Specific** → Clusters, Aggregates, Networks or Nanostructures
- **Reversible** → Strong dependency with their environment

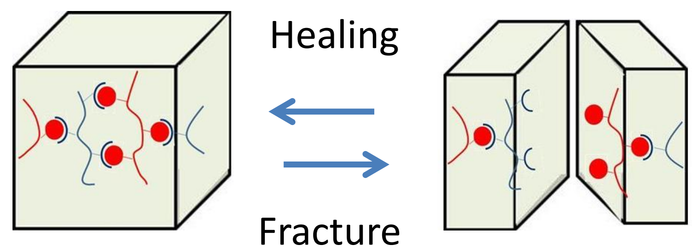
→ *A wide diversity of applications*

Stimuli-responsive Materials



Heinzmann, C. et al, *ACS Appl. Mater. Inter.* **2014**, *6*,4713–4719.

Self-healing by simple contact at RT



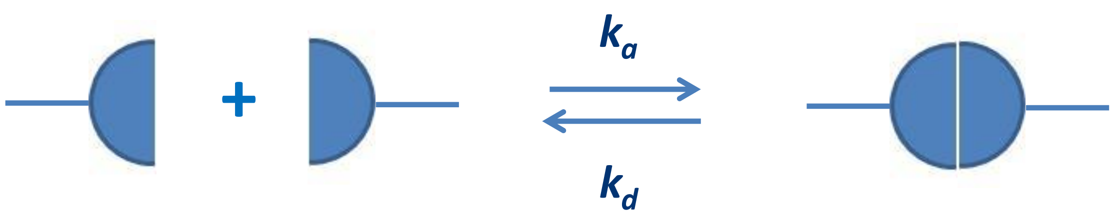
Cordier, P. et al, *Nature* **2008**, *451*, 977–980.

Challenge for all applications

How to link the rheological properties and the chemical structure of the polymer chain ?

→ What is the effect of the strength of stickers on the rheological behavior ?

$$K = k_a / k_d$$



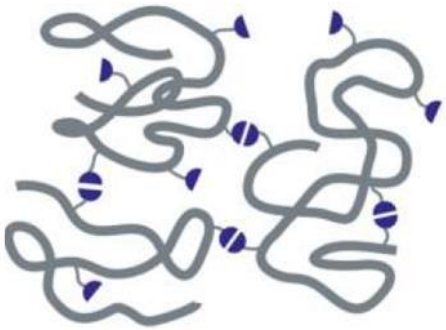
ΔH

Strength of Stickers

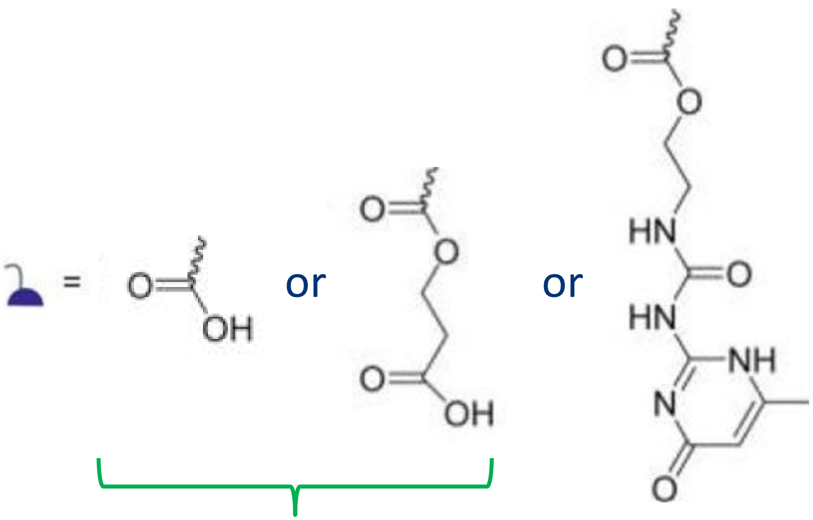
- Chemistry of stickers
- Polarity of Polymer Matrix

Background

Lewis et al, *Macromolecules*, **2014,** *47*, 729–740.

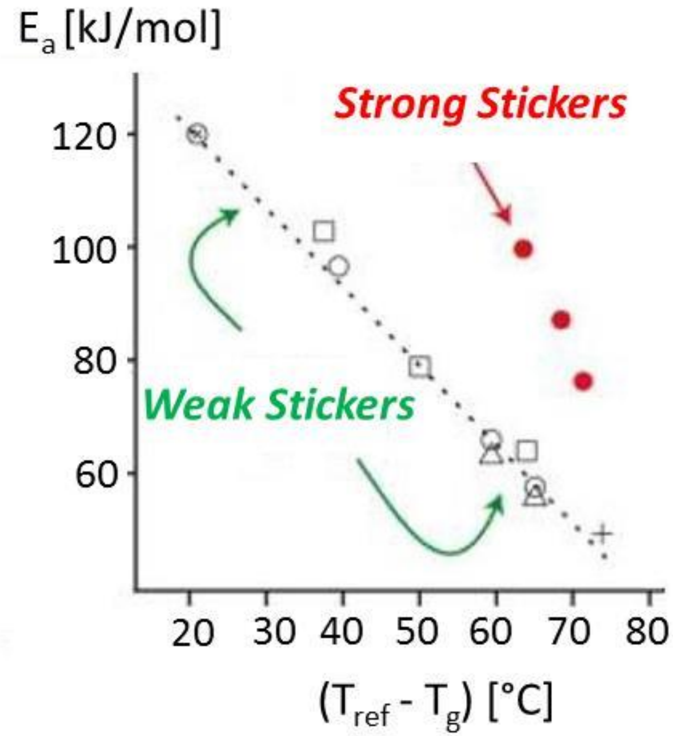


Poly(butylacrylate) Copolymers



Weak
Stickers

Strong
Stickers



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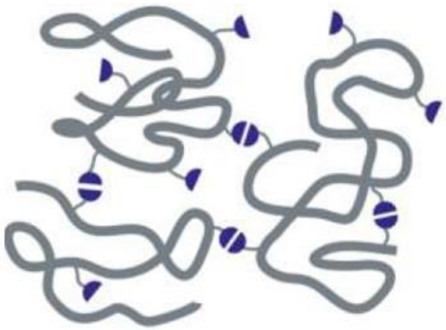

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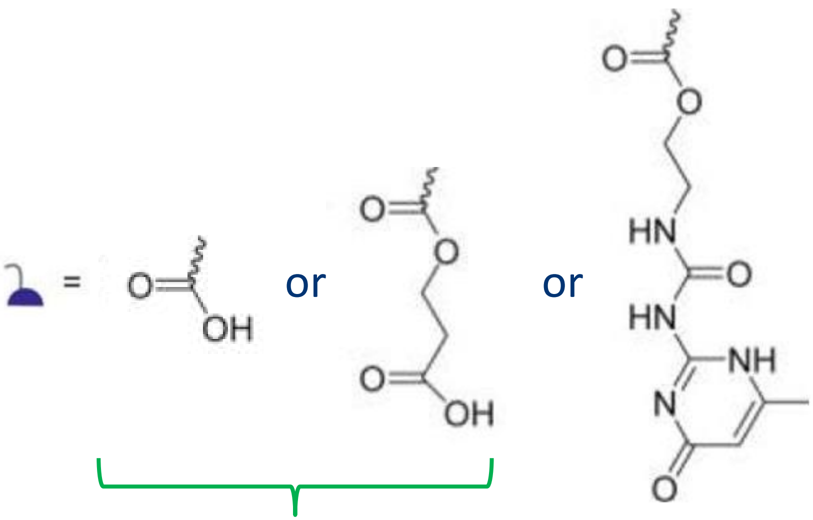

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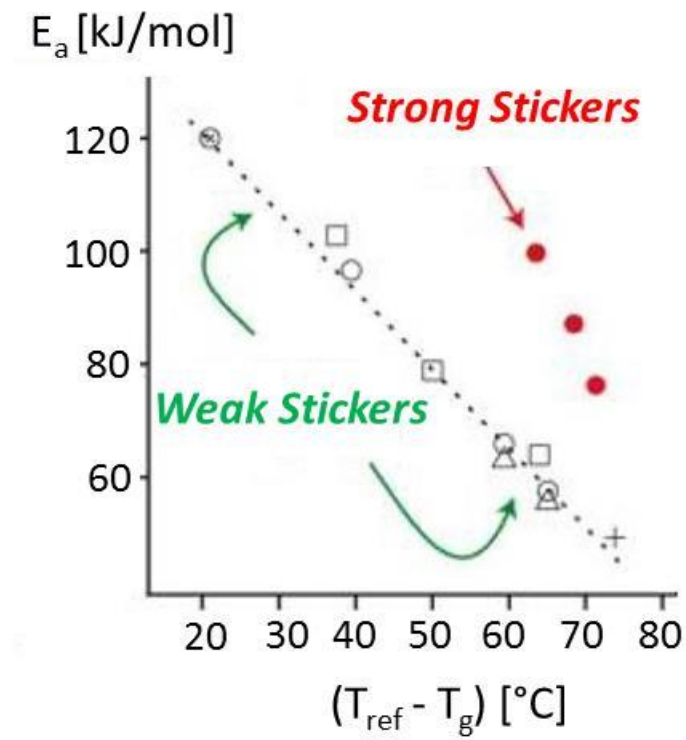
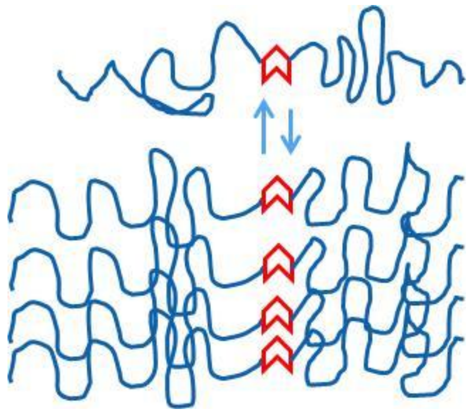


Weak Stickers → ”T_g effect”

Strong Stickers → ”T_g effect” + supramolecular **network**

Center-functionalized Polymers ?



Self-assembly of stickers

into **filaments is favored**

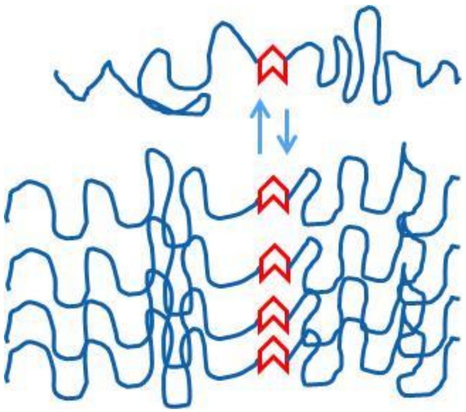
Bouteiller, L. *et al.*. *Adv. Funct. Mater.* 20**,** 1803–1811 (2010).

Frauenrath, H. et al. *Chem. Sci.* 3, 1512-1521 (2012)

→ **Predictable shape** of the aggregates

→ Link the rheology and the supramolecular Chemistry

Center-functionalized Polymers ?



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→ **Predictable shape** of the aggregates

→ Link the rheology and the supramolecular Chemistry

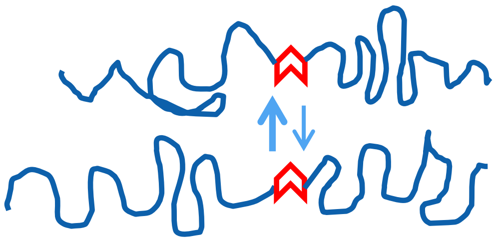
Strategy of our Project

→ Synthesis of monodisperse and linear center-functionalized polymers

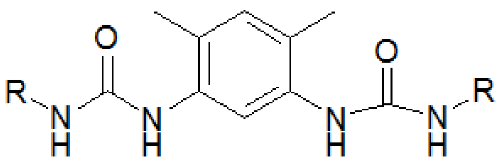
→ Change the molecular parameters in a highly controlled way

→ Systematic characterization of the nanostructure and linear rheology.

Key-molecular parameters

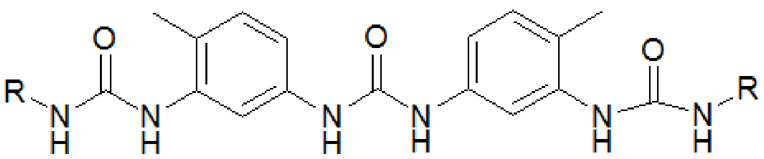


1. **Level of interactions** : Two **hydrogen bonding** stickers.



Bis-urea Xylene

"**Weak** Sticker"



Tri-Urea Toluene

"**Strong** Sticker"

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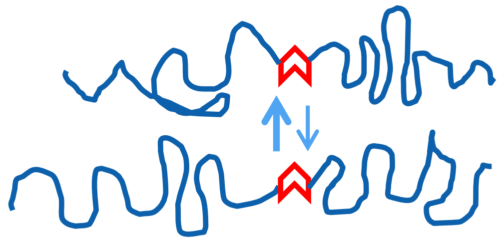

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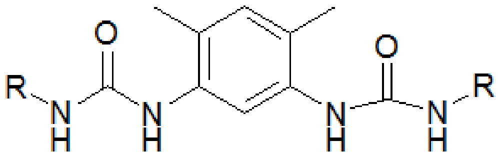

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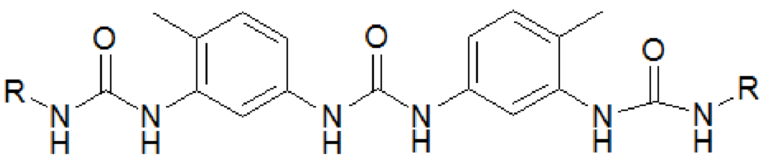
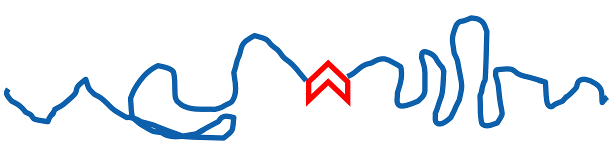


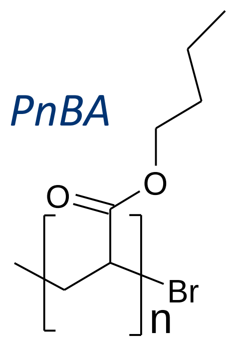
Tri-Urea Toluene

"**Strong** Sticker"

2. **the interacting moieties density** : the **size** of the linear non polar chains



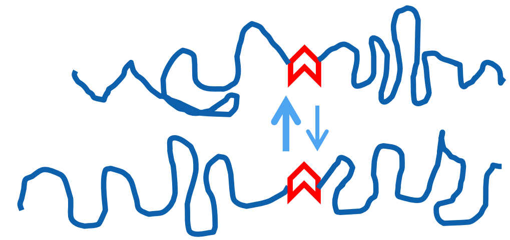
PnBA



$I_p \leq 1,4$

5 kg/mol ≤ M_w ≤ 100 kg/mol ⟷ 4% ≥ Sticker (w%) ≥ 0,2%

Key-molecular parameters



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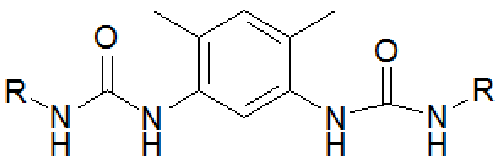
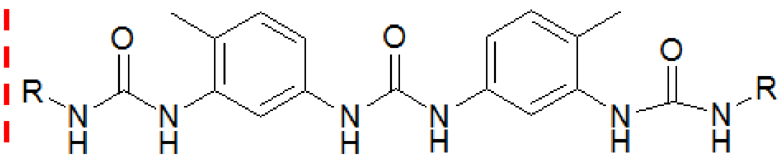


Bis-urea Xylene

"**Weak** Sticker"

2nd Part



Tri-Urea Toluene

"**Strong** Sticker"

1srt Part

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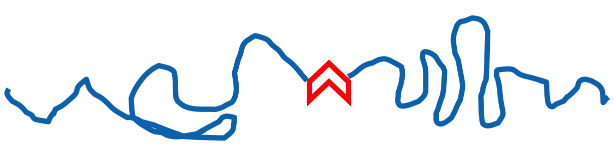

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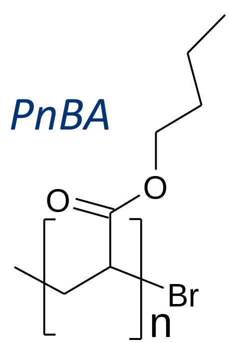

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T_g and Nanostructure for **Strong** Stickers

- No variation of $\mathbf{T_g}$ with M_n (between 5 and 100kg/mol): $\mathbf{T_g = -49 \pm 1°C}$ (DSC)

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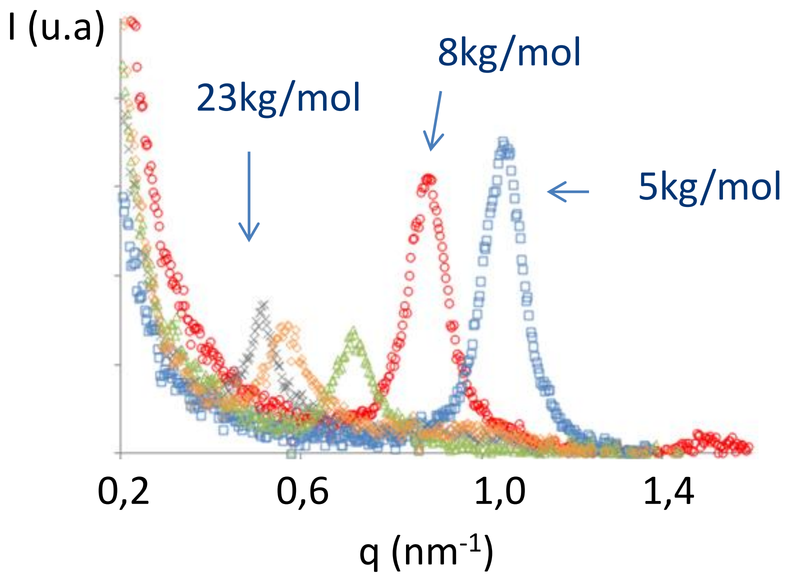
SAXS Investigation



No peak for $M_n \geq 40$ kg/mol

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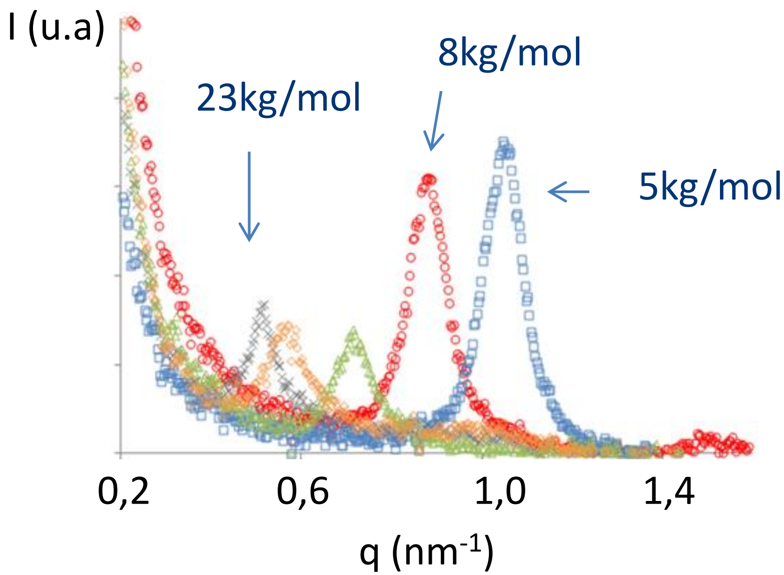

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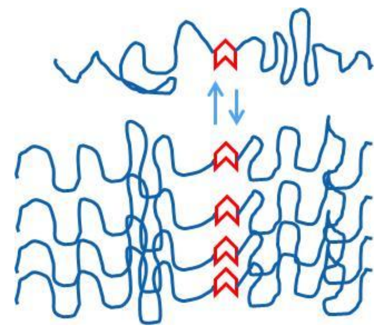
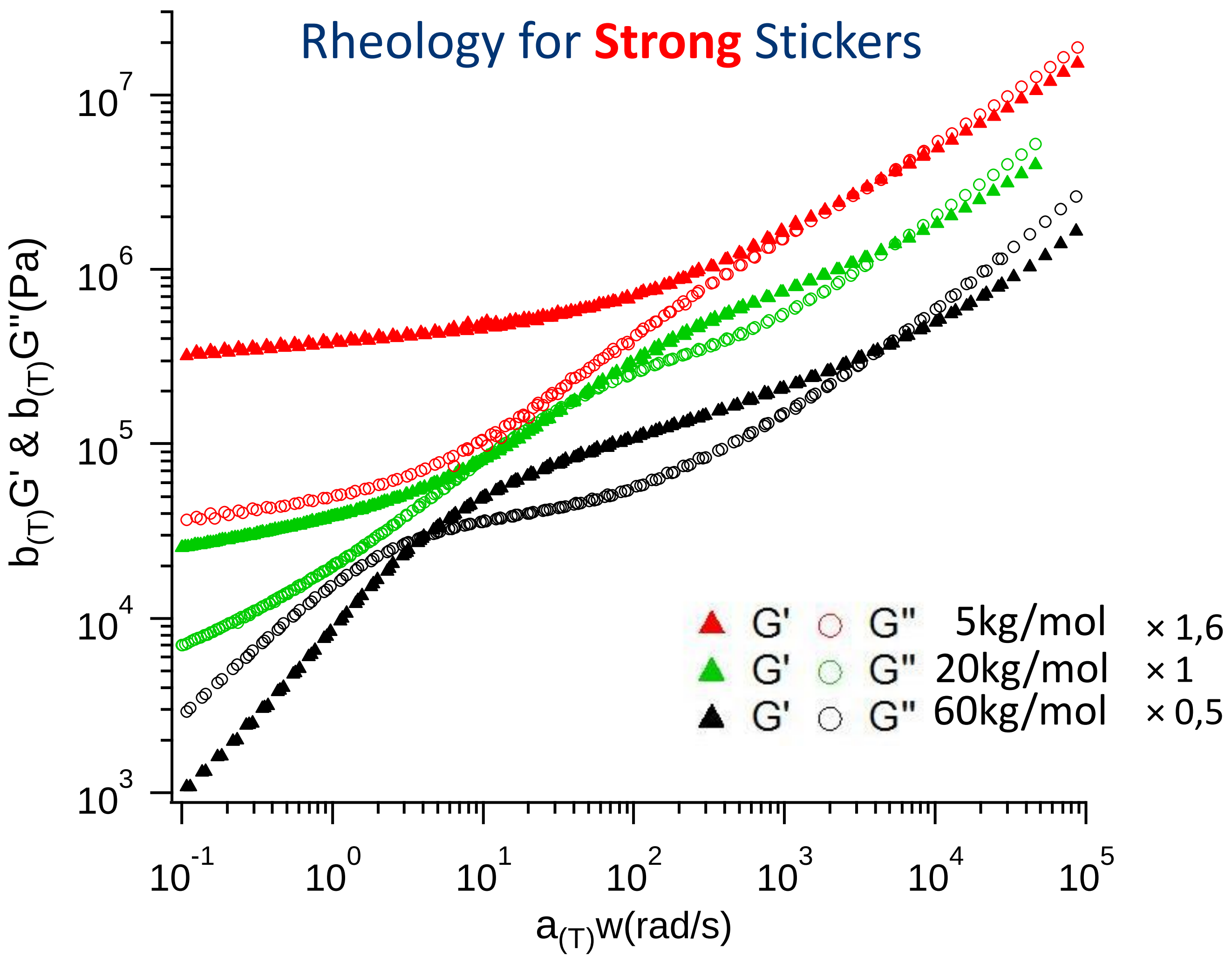
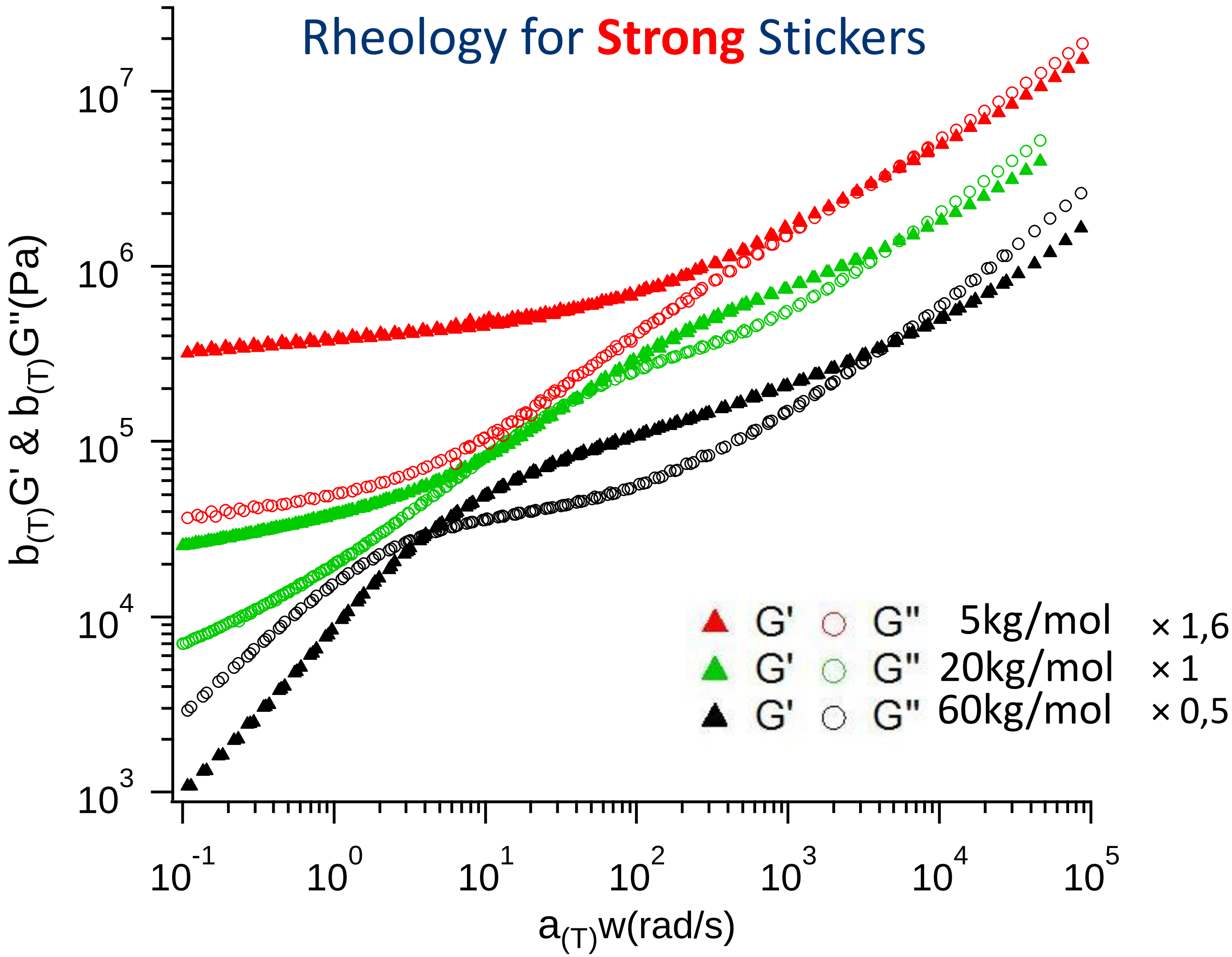


Self-assembly of stickers into filaments

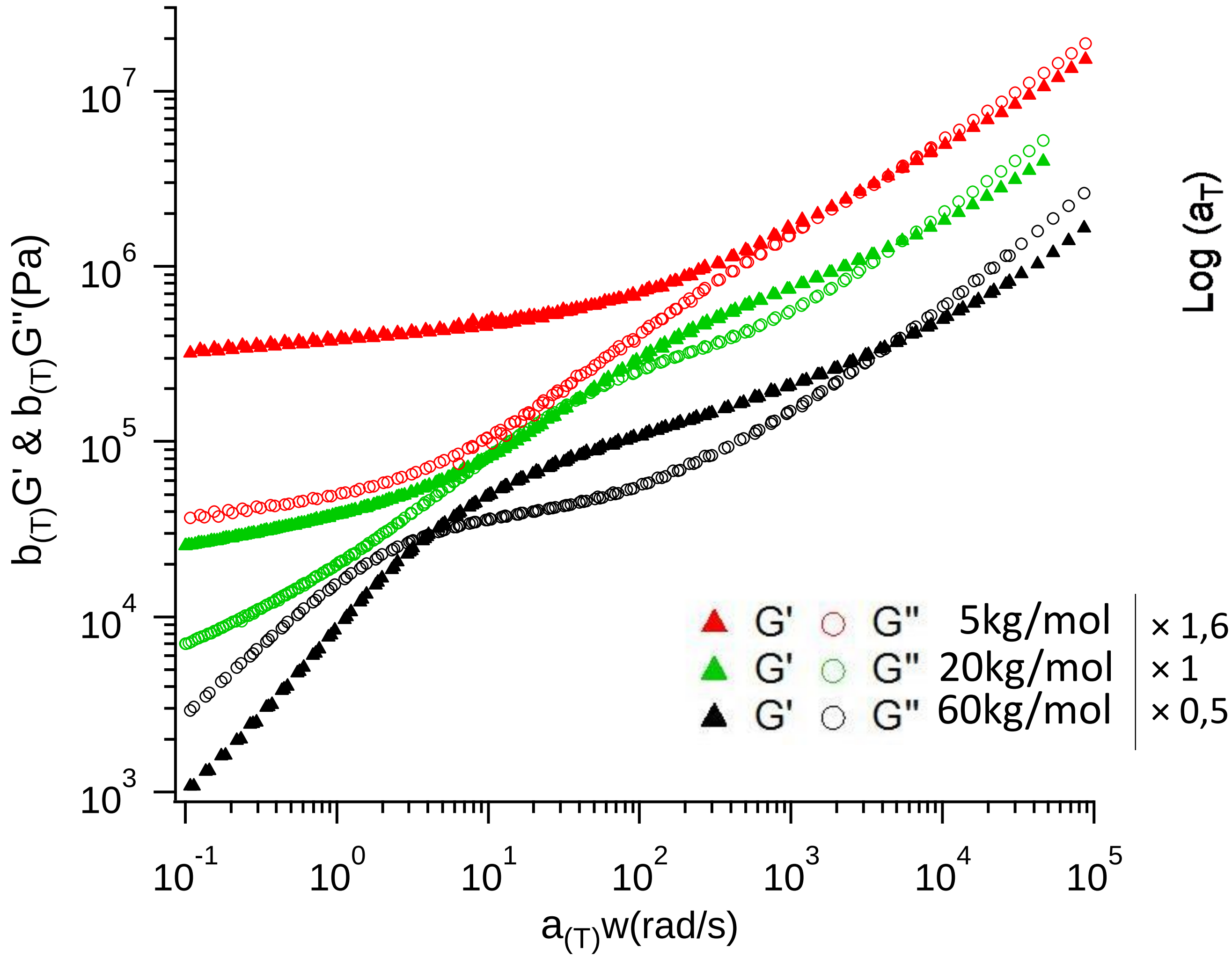
Oriented Filaments → Randomly Oriented Rods

$M_n \leq 40$ kg/mol → *$M_n \geq 40$ kg/mol*

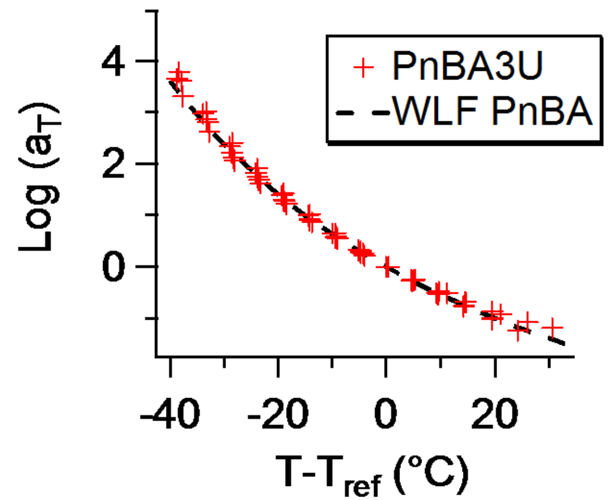

Rheology for Strong Stickers
b(T)G' & b(T)G"(Pa)
a(T)w(rad/s)
G' G" 5kg/mol × 1,6
G' G" 20kg/mol × 1
G' G" 60kg/mol × 0,5



$M_n \leq 40kg/mol$			$M_n \geq 40kg/mol$
Oriented Filaments →	Dissipative **Gel**	**Randomly Oriented Rods** →	Viscoelastic **Fluid**

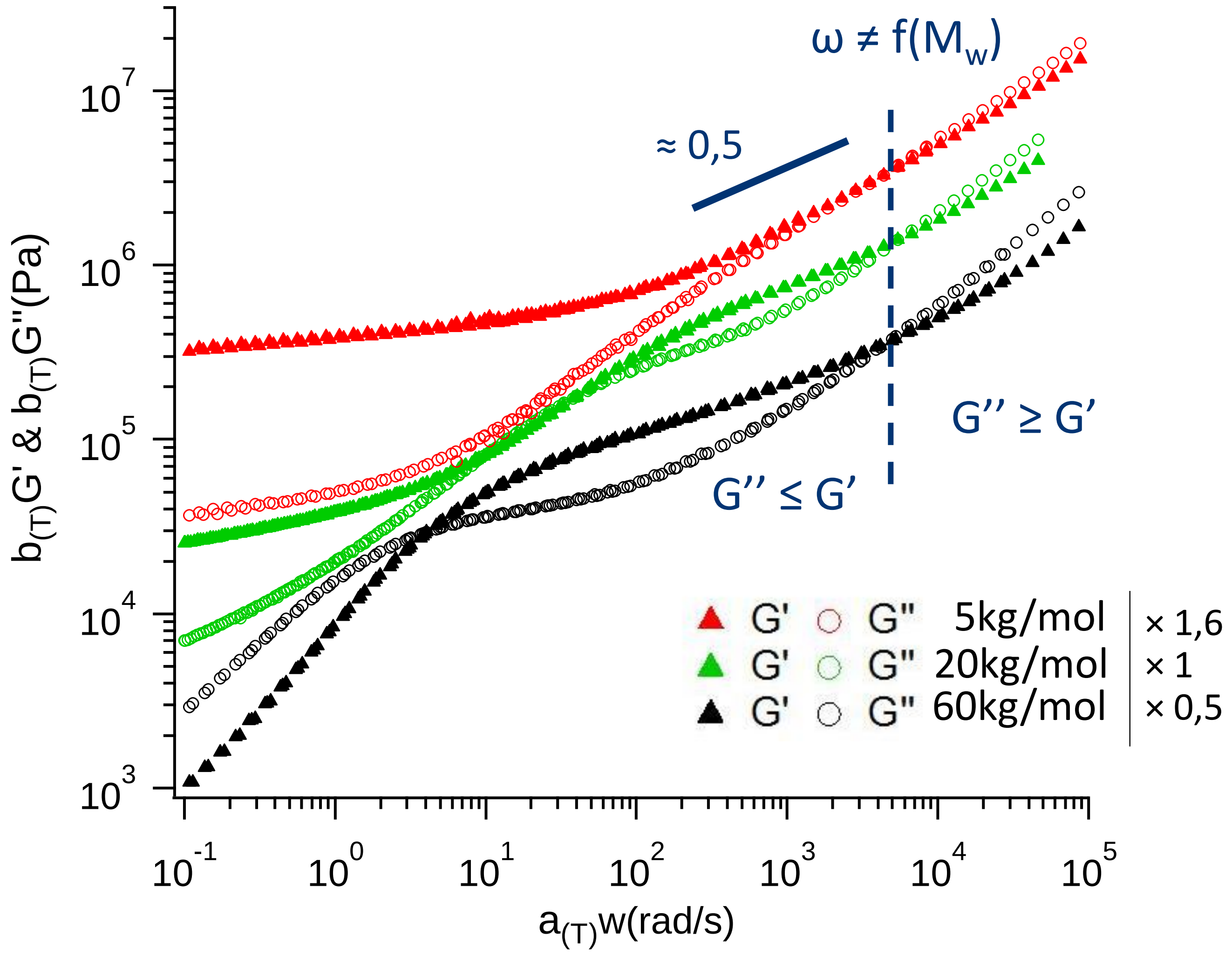


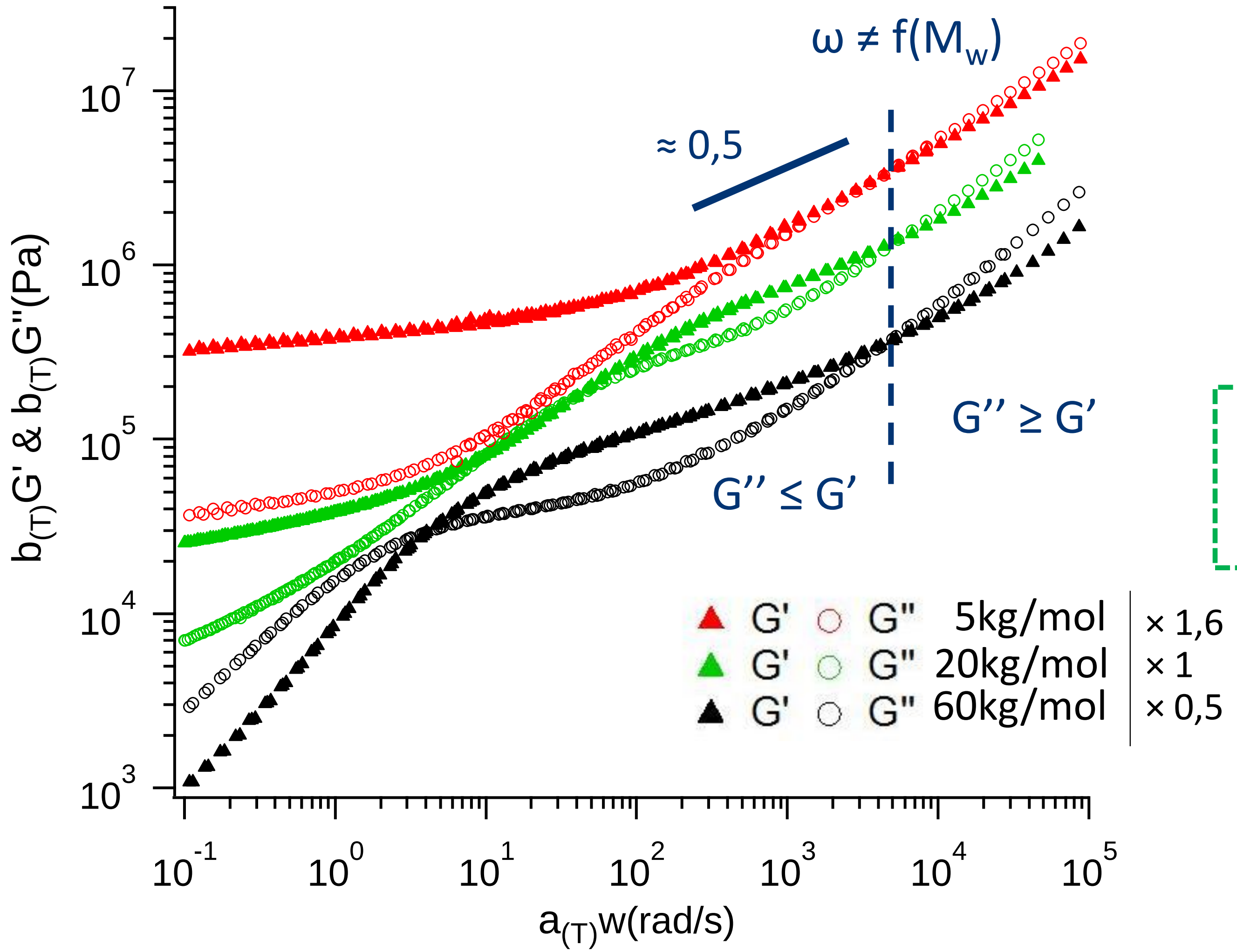
Shifts

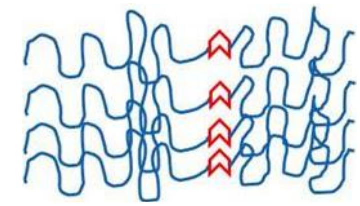


« Frozen » Aggregates

Dissipative Relaxation of the **side chains**


ω ≠ f(Mw)
≈ 0,5
G'' ≥ G'
G'' ≤ G'
G' G'' 5kg/mol × 1,6
G' G'' 20kg/mol × 1
G' G'' 60kg/mol × 0,5
b(T)G' & b(T)G''(Pa)
a(T)w(rad/s)
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
10^3
10^4
10^5
10^6
10^7





Comb-shaped Aggregates

≈

Comb-shaped Polymers

Self-assembly of Stickers ***Polymer Matrix***

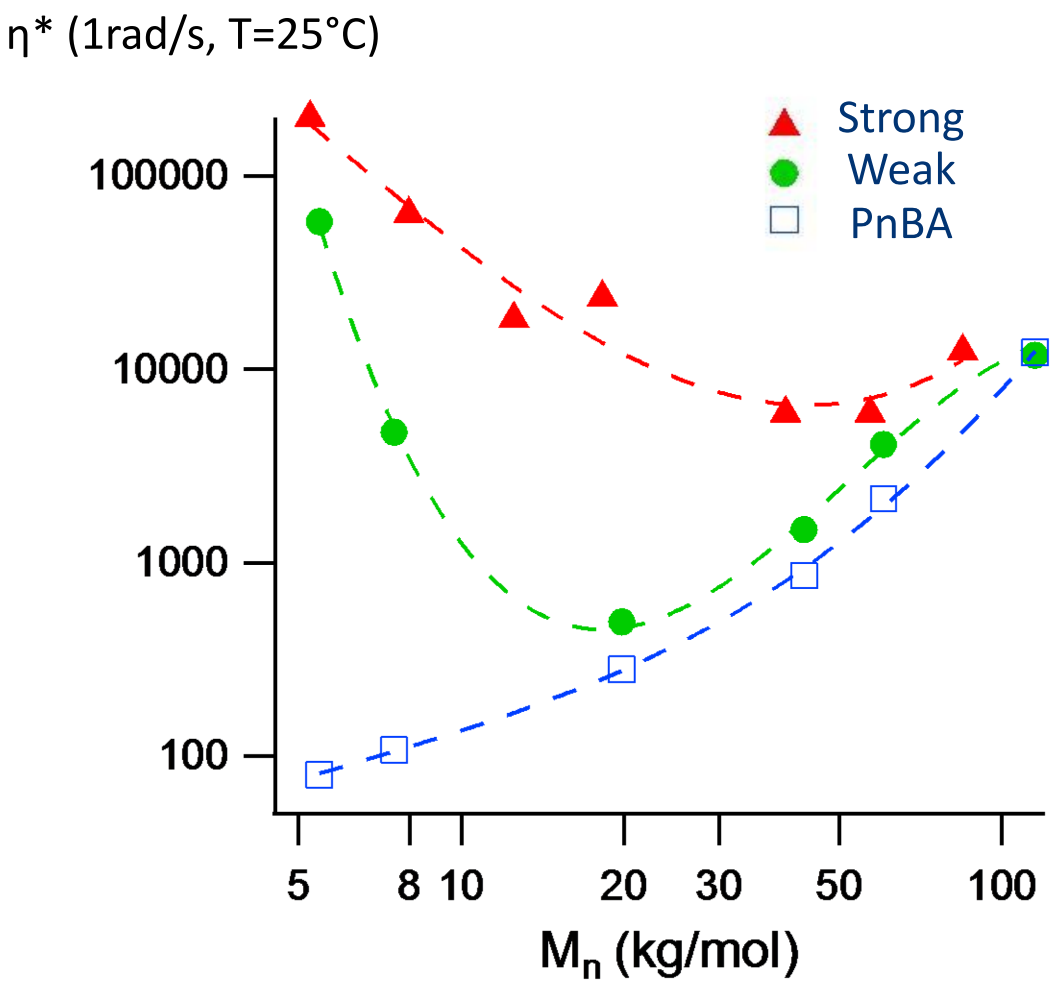
Gel / Fluid *Rouse / Entanglements* *T_g*

Strong Stickers vs **Weak** Stickers ?

Molecular weight dependency ?

Strong Stickers vs Weak Stickers ?

Molecular weight dependency ?



Critical Molecular weight (M_c) ?

Stickers' Regime

$M_n \leq M_c$

Entanglements' Regime

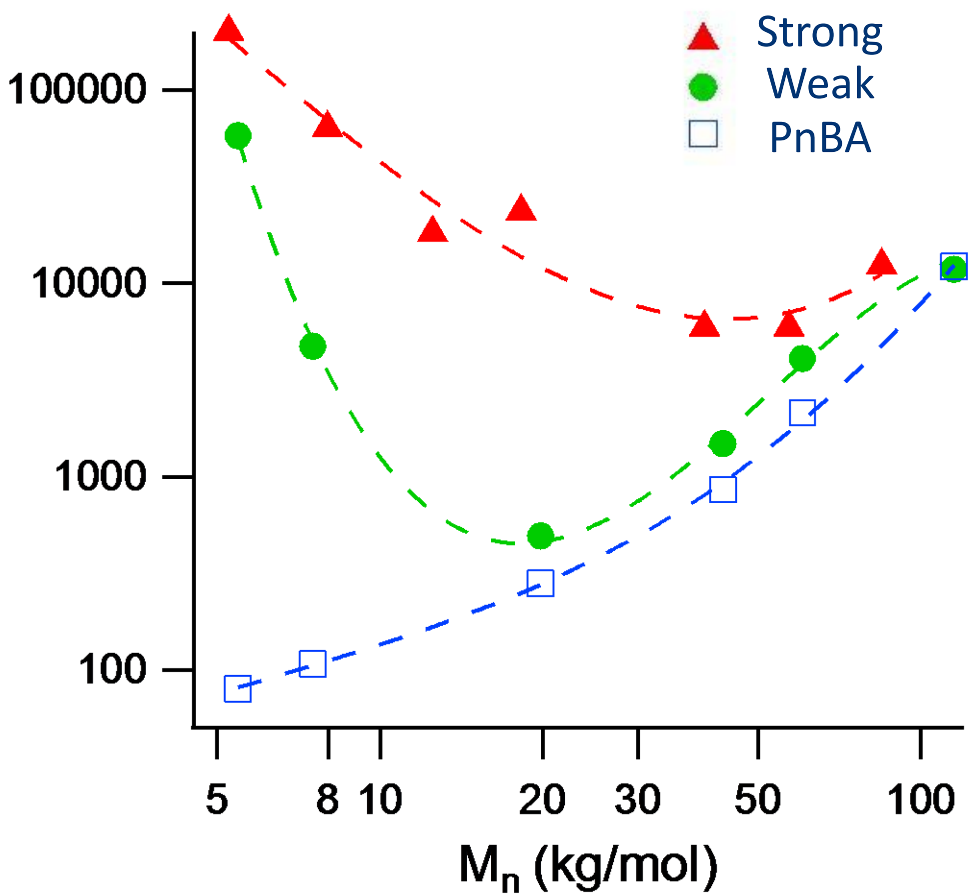
$M_n \geq M_c$

Jullian, N.; Leonardi, F.; Grassl, B.; Peyrelasse, J.; Derail, C. *Appl. Rheol.* **2010**, *20*, 33685.

Strong Stickers vs Weak Stickers ?

Molecular weight dependency ?

η* (1rad/s, T=25°C)



Critical Molecular weight (M_c) ?

Stickers' Regime

$M_n \leq M_c$

Entanglements' Regime

$M_n \geq M_c$

$M_c \approx$ 40kg/mol

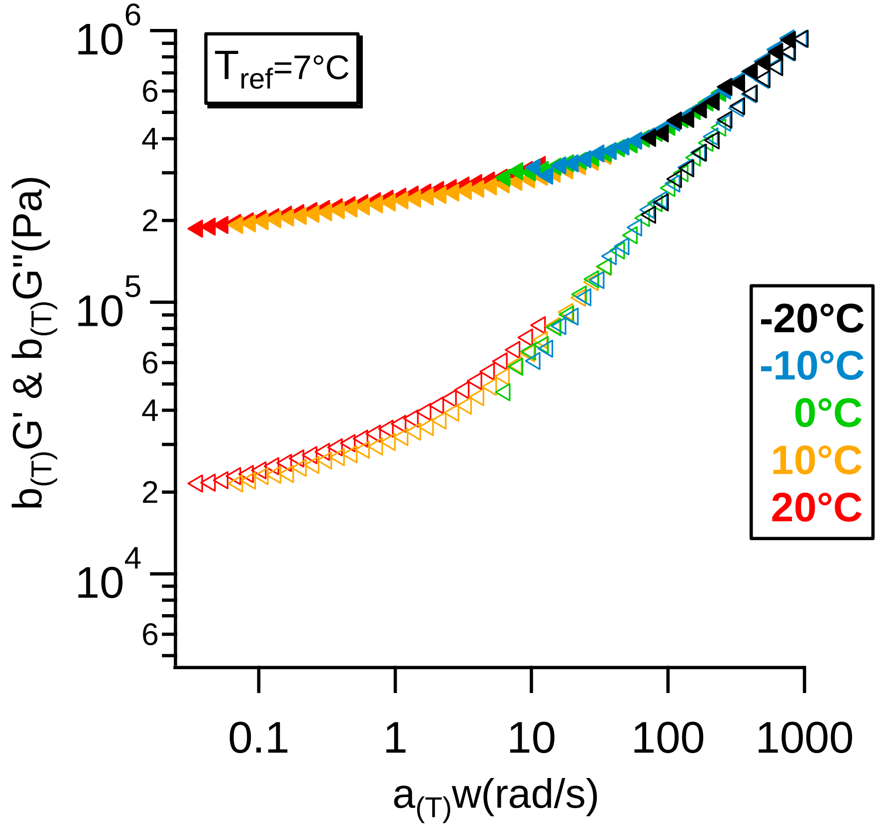
$M_c \approx$ 20kg/mol

Strength ↗, M_c ↗

Jullian, N.; Leonardi, F.; Grassl, B.; Peyrelasse, J.; Derail, C. *Appl. Rheol.* **2010**, *20*, 33685.

Strong Stickers vs Weak Stickers ?

Stability of the nanostructure (below M_c) ?



M_n = 5kg/mol

Strong Sticker

◀ G' ◁ G''

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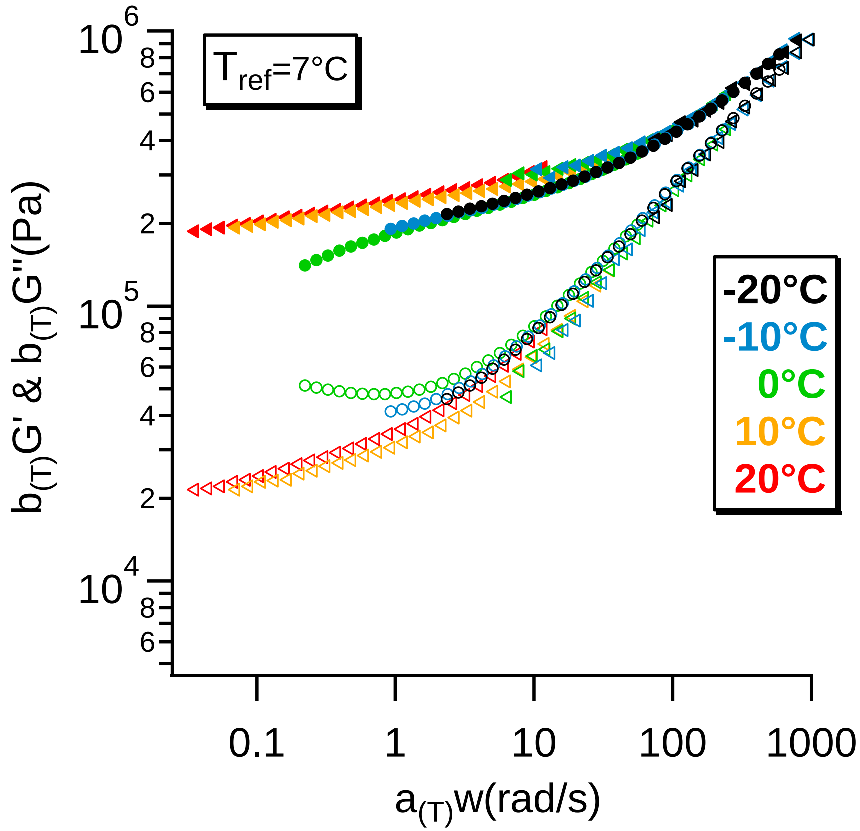

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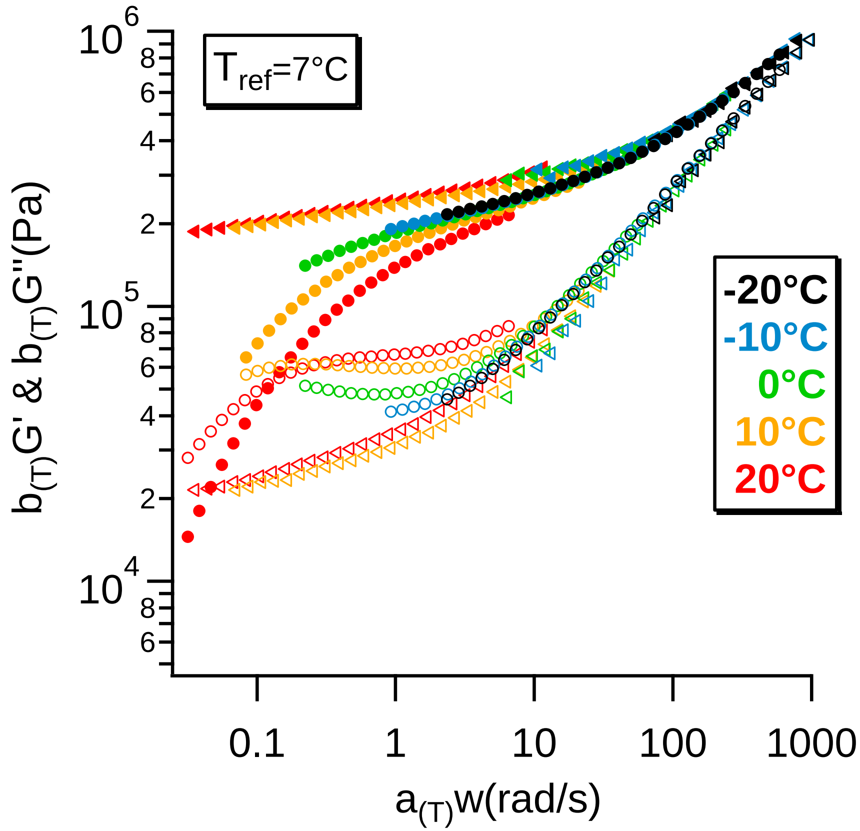

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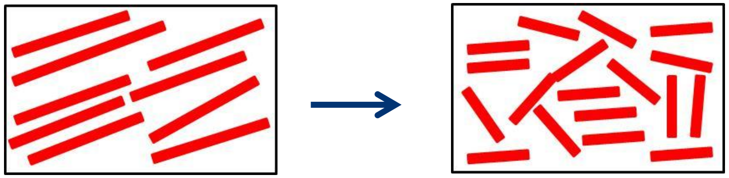
T ≤ T_{ODT}



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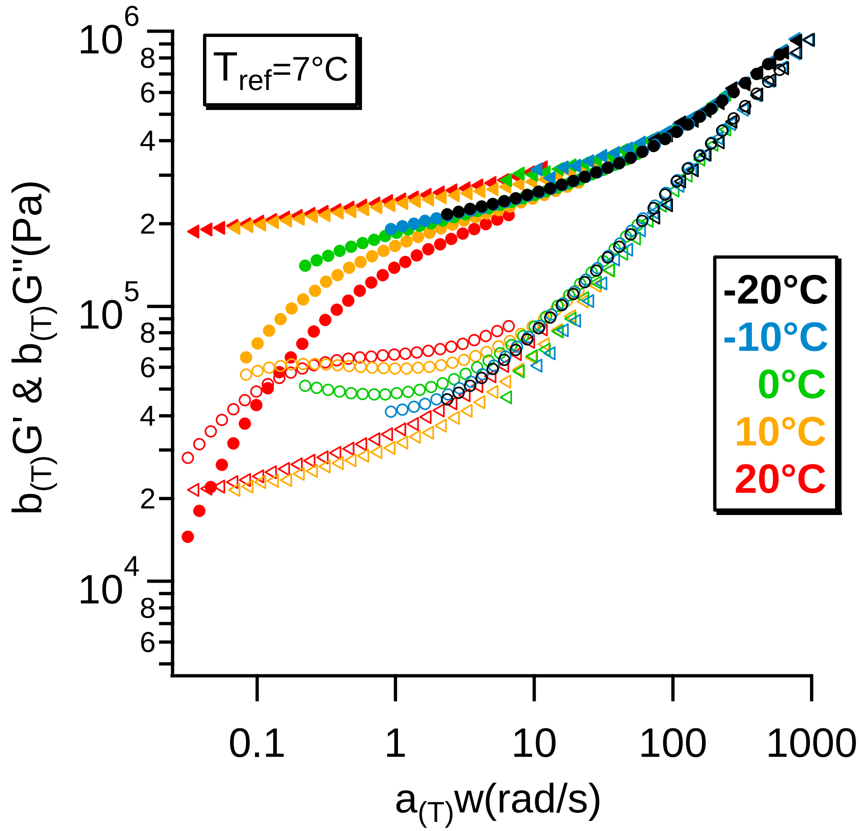

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Strong Sticker

◄ G' ◁ G''

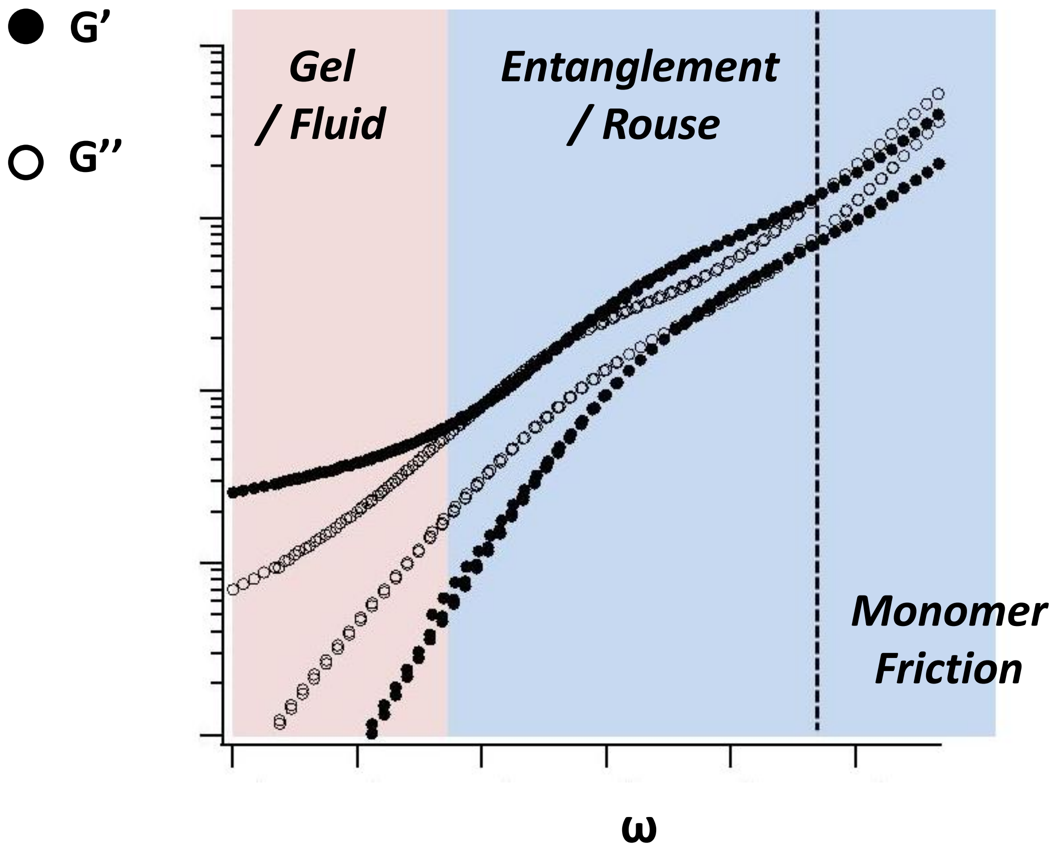
Weak Sticker

● G' ○ G''

$T \leq T_{ODT}$ → Frozen Structure over a long distance range → Gel plateau

$T \geq T_{ODT}$ → Scission / Association of Stickers → Viscoelastic Fluids

Conclusion on linear rheology of center-functionalized Polymers



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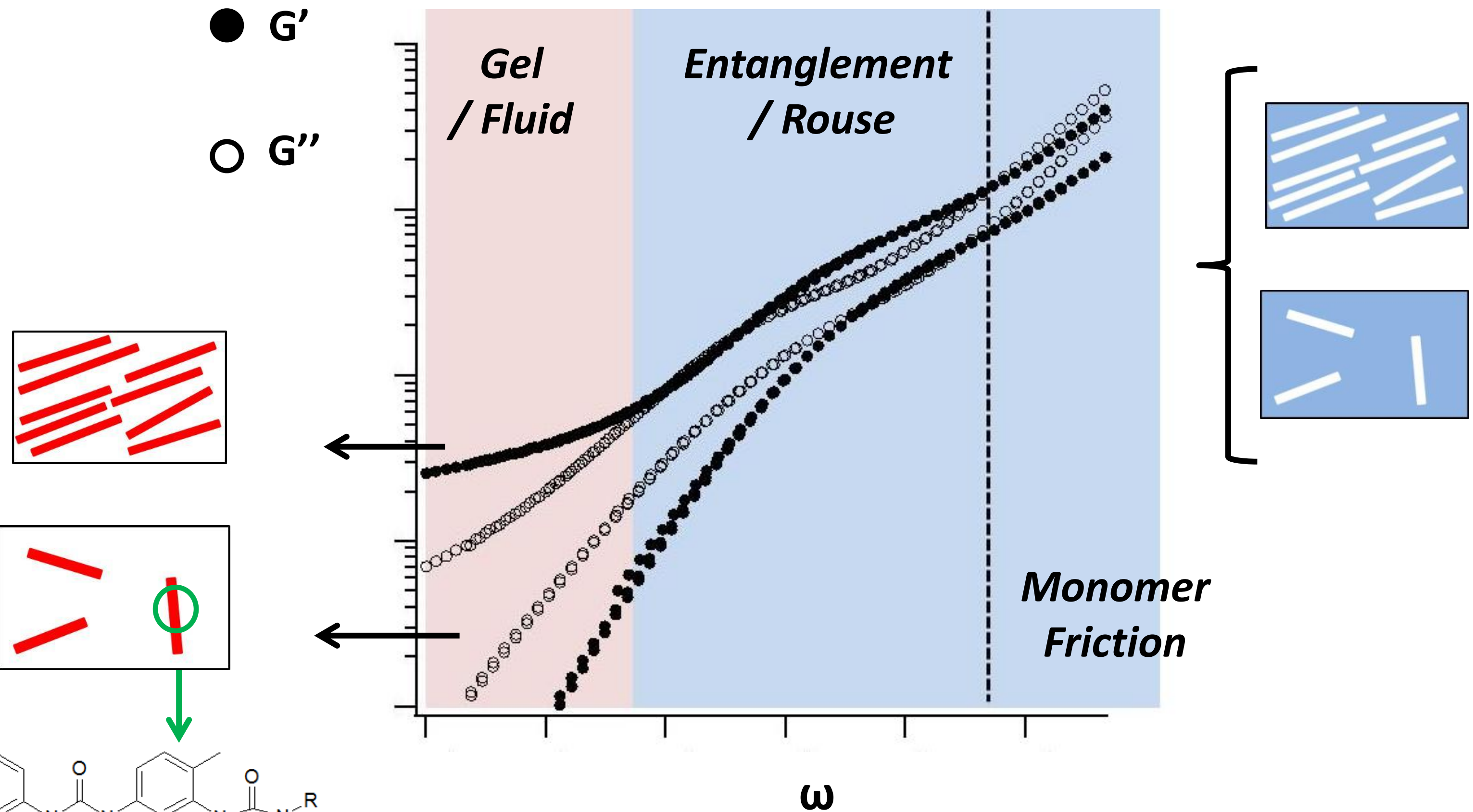

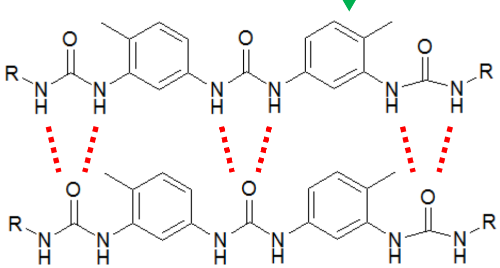

Density and Strength of Stickers ← *T_{ODT} and M_c*

Fine Control of the viscoelasticity via the chemical structure

Thank you for all People
in Project ANR SUPRADHESION

Guylaine Ducouret
Costantino Creton

Cécile Fonteneau
Sandrine Pensec, Laurent Bouteiller

Cyril Véchambre
Jean-Marc Chenal, Laurent Chazeau

Thank you for your attention !