Viscoelasticity of Supramolecular Center-functionalized Polymer

Effect of the strength of Hydrogen Bonding Stickers

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Supramolecular Polymers?

Supramolecular Chemistry

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

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Polymer Physics

Association by covalent bonds of monomers


Supramolecular Polymers?

**Supramolecular Chemistry**

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


**Polymer Physics**

Association by **covalent** bonds of monomers

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
- Reversible

Clusters, Aggregates, Networks or Nanostructures

Strong dependency with their environment

A wide diversity of applications

Stimuli-responsive Materials


Self-healing by simple contact at RT

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?

\[ K = \frac{k_a}{k_d} \]

**Strength of Stickers**

- Chemistry of stickers
- Polarity of Polymer Matrix
Background


Poly(butylacrylate) Copolymers

Weak or Strong Stickers

![Diagram showing chemical structures and graph with Ea vs. (Tref - Tg) in °C]

- Weak Stickers
- Strong Stickers
Background


Poly(butylacrylate) Copolymers

\[ \text{Weak Stickers} \quad \text{or} \quad \text{Strong Stickers} \]

\[ \text{Weak Stickers} \quad \text{or} \quad \text{Strong Stickers} \]

E\(_a\) [kJ/mol]

\[ \text{Strong Stickers} \]

\[ \text{Weak Stickers} \]

\[ (T_{\text{ref}} - T_g) \, [^\circ C] \]

"\(T_g\) effect"

"\(T_g\) effect" + supramolecular network
Center-functionalized Polymers?

**Self-assembly** of stickers into **filaments** is favored


**Predictable shape** of the aggregates

**Link the rheology and the supramolecular Chemistry**
Center-functionalized Polymers?

**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.

**Self-assembly** of stickers into filaments is favored

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

\[ 5 \text{ kg/mol} \leq M_w \leq 100 \text{ kg/mol} \quad \text{and} \quad 4\% \geq \text{Sticker (w\%)} \geq 0.2\% \]
Key-molecular parameters

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

   - **Bis-urea Xylene**  
   "**Weak Sticker**"  
   2nd Part

   - **Tri-Urea Toluene**  
   "**Strong Sticker**"  
   1st Part

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

   - **PnBA**  
   \[ I_p \leq 1.4 \]

   \[ 5 \text{ kg/mol} \leq M_w \leq 100 \text{ kg/mol} \quad \leftrightarrow \quad 4\% \geq \text{Sticker (w\%)} \geq 0.2\% \]
T_g and Nanostructure for Strong Stickers

- No variation of T_g with M_n (between 5 and 100kg/mol): T_g = -49 ± 1°C (DSC)
$T_g$ and Nanostructure for **Strong** Stickers

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

**SAXS Investigation**

No peak for $M_n \geq 40 \text{ kg/mol}$
**T_g and Nanostructure for Strong Stickers**

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

### SAXS Investigation

- $I$ (u.a)
- $q$ (nm$^{-1}$)
- No peak for $M_n \geq 40$ kg/mol

#### Self-assembly of stickers into filaments

- $M_n \leq 40$ kg/mol
  - Randomly Oriented Rods

- $M_n \geq 40$ kg/mol
  - Oriented Filaments
Rheology for Strong Stickers

\[ b(T)G', b(T)G'' \text{ (Pa)} \]

- \( G' \) and \( G'' \) represent storage and loss moduli, respectively.

- \( a(T)w(\text{rad/s}) \) is the angular frequency.

- The graph shows different behaviors for material properties based on molecular weight:
  - \( M_n \leq 40\text{kg/mol} \)
    - Oriented Filaments
    - Dissipative
  - \( M_n \geq 40\text{kg/mol} \)
    - Randomly Oriented Rods
    - Viscoelastic Fluid

- Specific markers indicate different molecular weights:
  - 5kg/mol \( \times 1.6 \)
  - 20kg/mol \( \times 1 \)
  - 60kg/mol \( \times 0.5 \)
Shifts

Frozen Aggregates

Dissipative Relaxation of the side chains

Log (a_T)

\[ T - T_{ref} (°C) \]

+ PnBA3U
- WLF PnBA

\[ +5 \text{ kg/mol} \times 1,6 \]
\[ +20 \text{ kg/mol} \times 1 \]
\[ +60 \text{ kg/mol} \times 0,5 \]
$\omega \neq f(M_w)$

$\approx 0.5$

$G'' \geq G'$

$G'' \leq G'$

$5\text{kg/mol} \times 1.6$

$20\text{kg/mol} \times 1$

$60\text{kg/mol} \times 0.5$
Self-assembly of Stickers

Polymer Matrix

Gel / Fluid  Rouse / Entanglements  $T_g$

Comb-shaped Aggregates
≈ Comb-shaped Polymers

$G'' \geq G'$
$G'' \leq G'$

$\omega \neq f(M_w)$

$\approx 0.5$

$G' \times 1$
$G'' \times 0.5$

$G' \times 1.6$
$G'' \times 1$

$5\text{ kg/mol} \times 1.6$

$20\text{ kg/mol} \times 1$

$60\text{ kg/mol} \times 0.5$
Strong Stickers vs Weak Stickers ?

Molecular weight dependency ?
Strong Stickers vs Weak Stickers?

Molecular weight dependency?

$\eta^* (1 \text{rad/s}, T=25^\circ \text{C})$

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.

**Strong Stickers vs Weak Stickers ?**

Molecular weight dependency ?

[Graph showing viscosity (η*) against molecular weight (M_n) with data points for Strong, Weak, and PnBA stickers.]

Critical Molecular weight (M_c) ?

Stickers’ Regime
\( M_n \leq M_c \)

Entanglements’ Regime
\( M_n \geq M_c \)

\( M_c \approx 40 \text{kg/mol} \)
\( M_c \approx 20 \text{kg/mol} \)

Strength ↗, M_c ↗

**Strong Stickers vs Weak Stickers?**

Stability of the nanostructure (below $M_c$)?

$M_n = 5$ kg/mol

**Strong Sticker**

$T_{ref} = 7^\circ C$

$G' G'' PnBA3U5$
**Strong Stickers vs Weak Stickers?**

Stability of the nanostructure (below $M_c$)?

\[ T_{ref}=7^\circ C \]

\[ M_n = 5\text{kg/mol} \]

**Strong Sticker**

- $M_n = 5\text{kg/mol}$

**Weak Sticker**

- $G'$
- $G''$
Strong Stickers vs Weak Stickers?

Stability of the nanostructure (below $M_c$)?

$T_{\text{ref}} = 7^\circ C$

$M_n = 5\text{kg/mol}$

Strong Sticker

Weak Sticker

$T \leq T_{ODT}$

$T \geq T_{ODT}$
Strong Stickers vs Weak Stickers?

Stability of the nanostructure (below $M_c$)?

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

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

$M_n = 5\text{kg/mol}$

Strong Sticker

Weak Sticker

$G'$ $\triangleleft G''$
Conclusion on linear rheology of center-functionalized Polymers

$G'$

$G''$

Gel / Fluid

Entanglement / Rouse

Monomer Friction

$\omega$
Conclusion on linear rheology of center-functionalized Polymers

Fine Control of the viscoelasticity via the chemical structure

Density and Strength of Stickers

$T_{ODT}$ and $M_c$
Thank you for all People in Project ANR SUPRADHESION

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