Effects of crosslinking on the viscoelastic response of industrial dual networks

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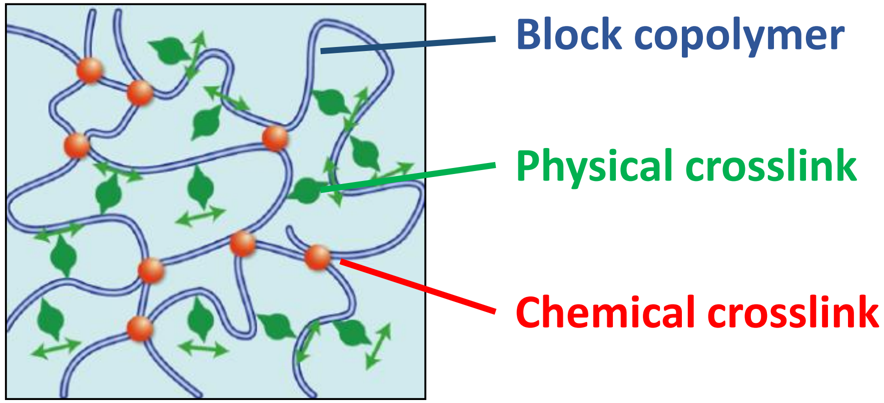
Introduction

Dual Network



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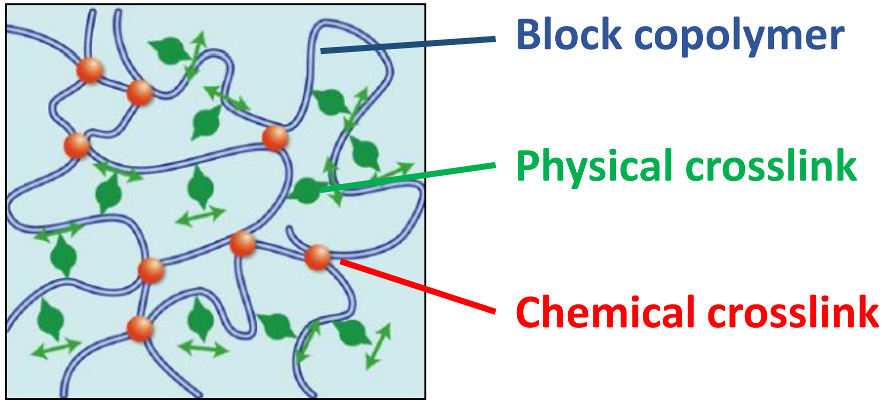

Pressure Sensitive Adhesive

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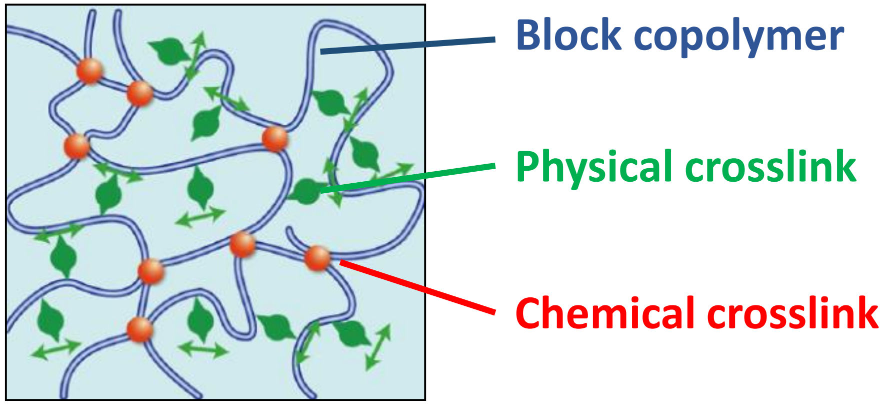

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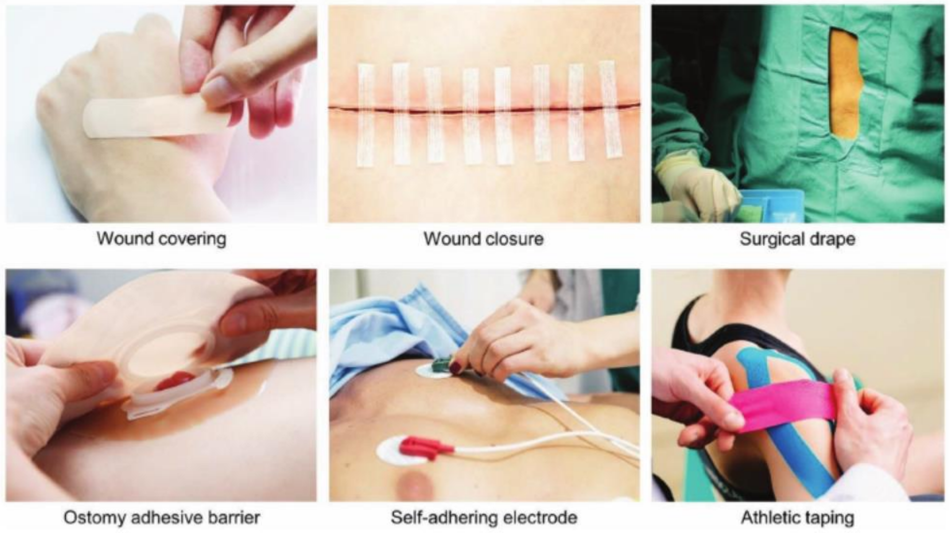

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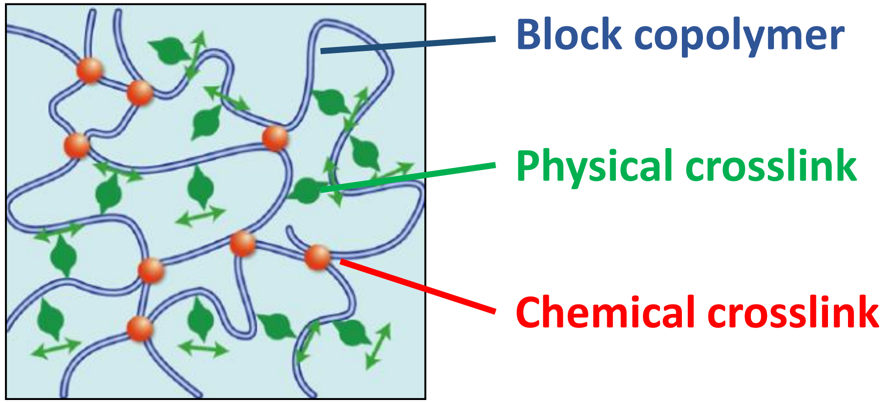
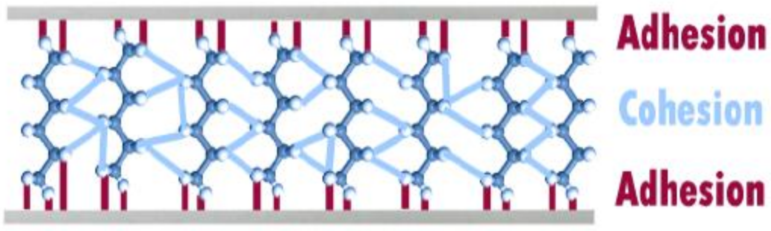


Pressure Sensitive Adhesive

ADHESIVE PROPERTIES



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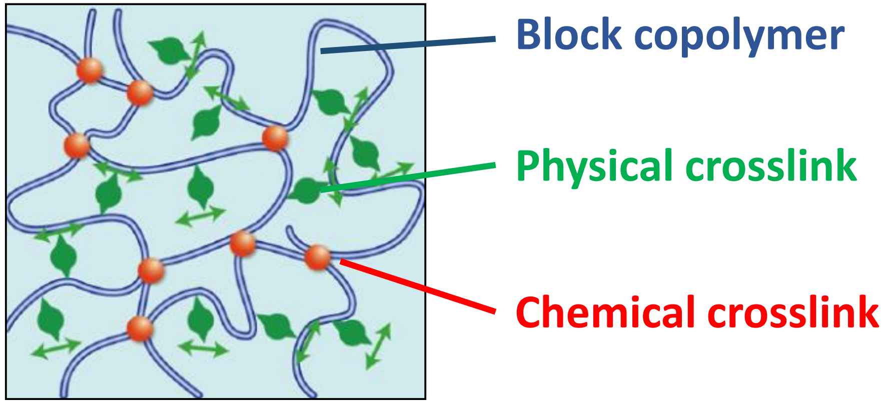

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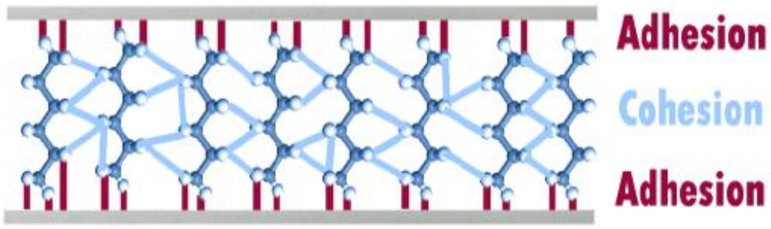

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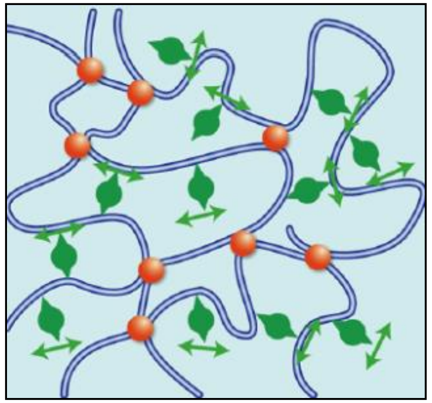
VISCOELASTIC PROPERTIES

Goal

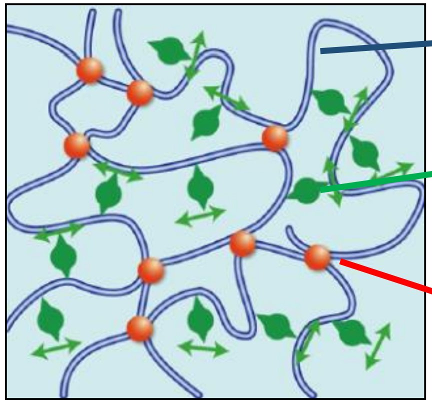
- Understand the rheological properties of industrial dual networks, linking them to the molecular structure.

- Develop predictive capabilities for the viscoelastic properties
  (extend the Time marching algorithm platform).



Materials

Dual Network



- **Main component** (without crosslinks)
N-butyl acrylate / 2-ethylhexyl acrylate / acrylic acid

- Network with only **physical crosslink (Aluminum-Chelate)**

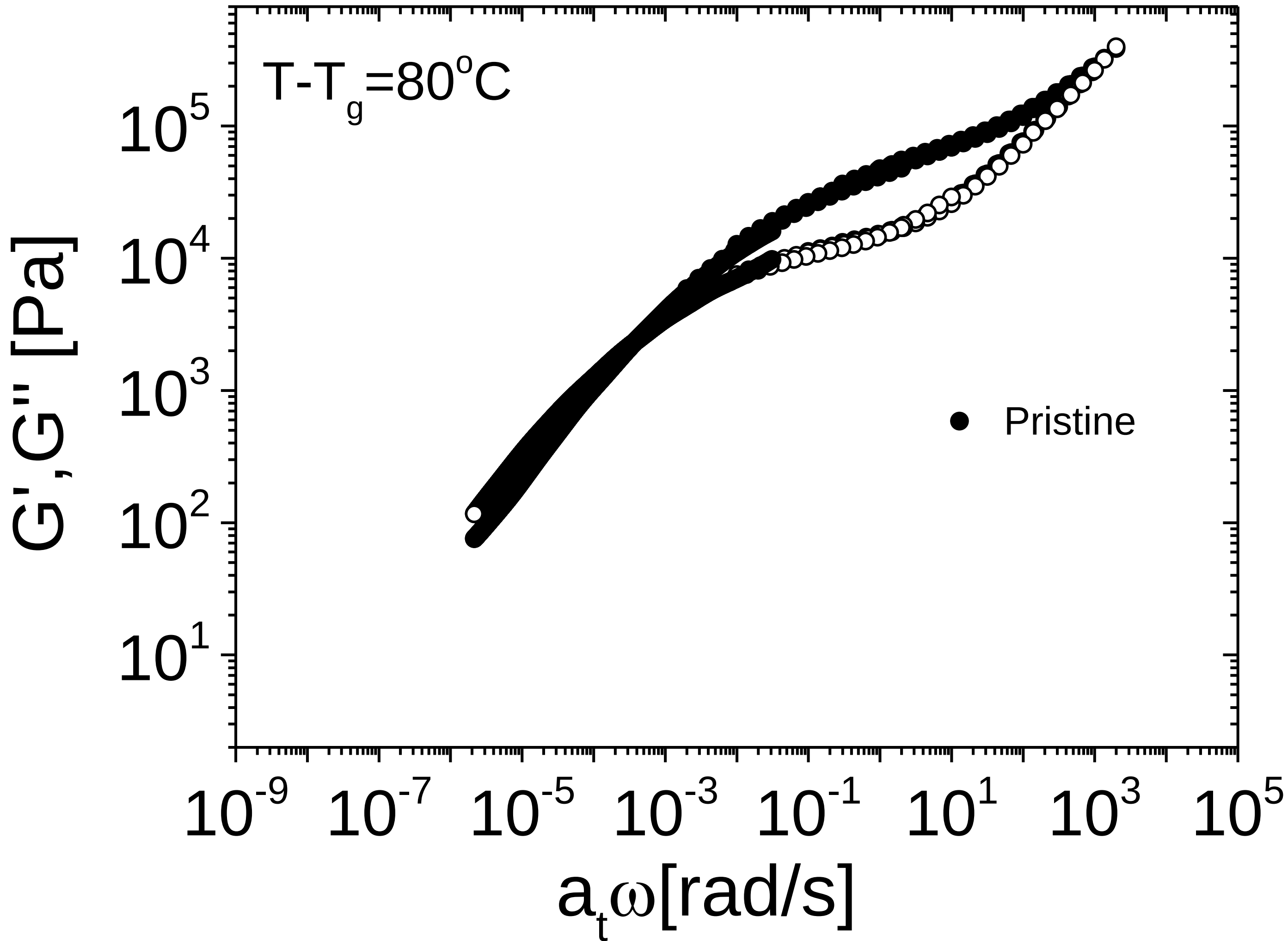
- Network with only **chemical crosslink (Epoxide)**

- Network with **dual crosslinks**

	Physical (%w/w)	Chemical (%w/w)
Pristine	/	/
Reversible I	0.075	/
Reversible II	0.106	/
Permanent I	/	0.035
Permanent II	/	0.118
Double	0.075	0.035
Double B	0.05	0.025

Rheological results

Rheological results of the different networks varying the amount and the type of crosslinkers.



Master curves obtained by:

- DFS at different T
- Creep in linear regime

	Physical (%w/w)	Chemical (%w/w)
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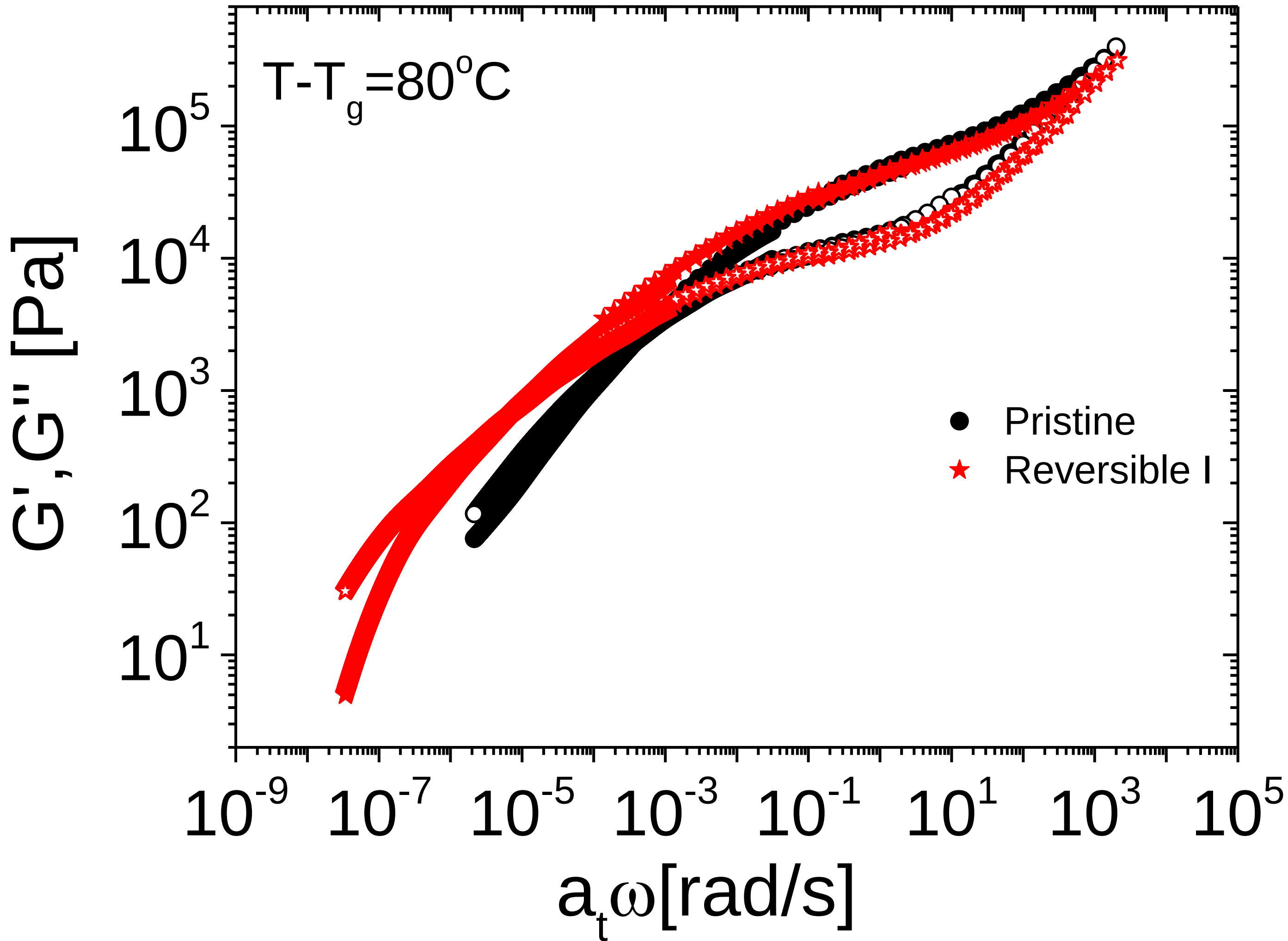

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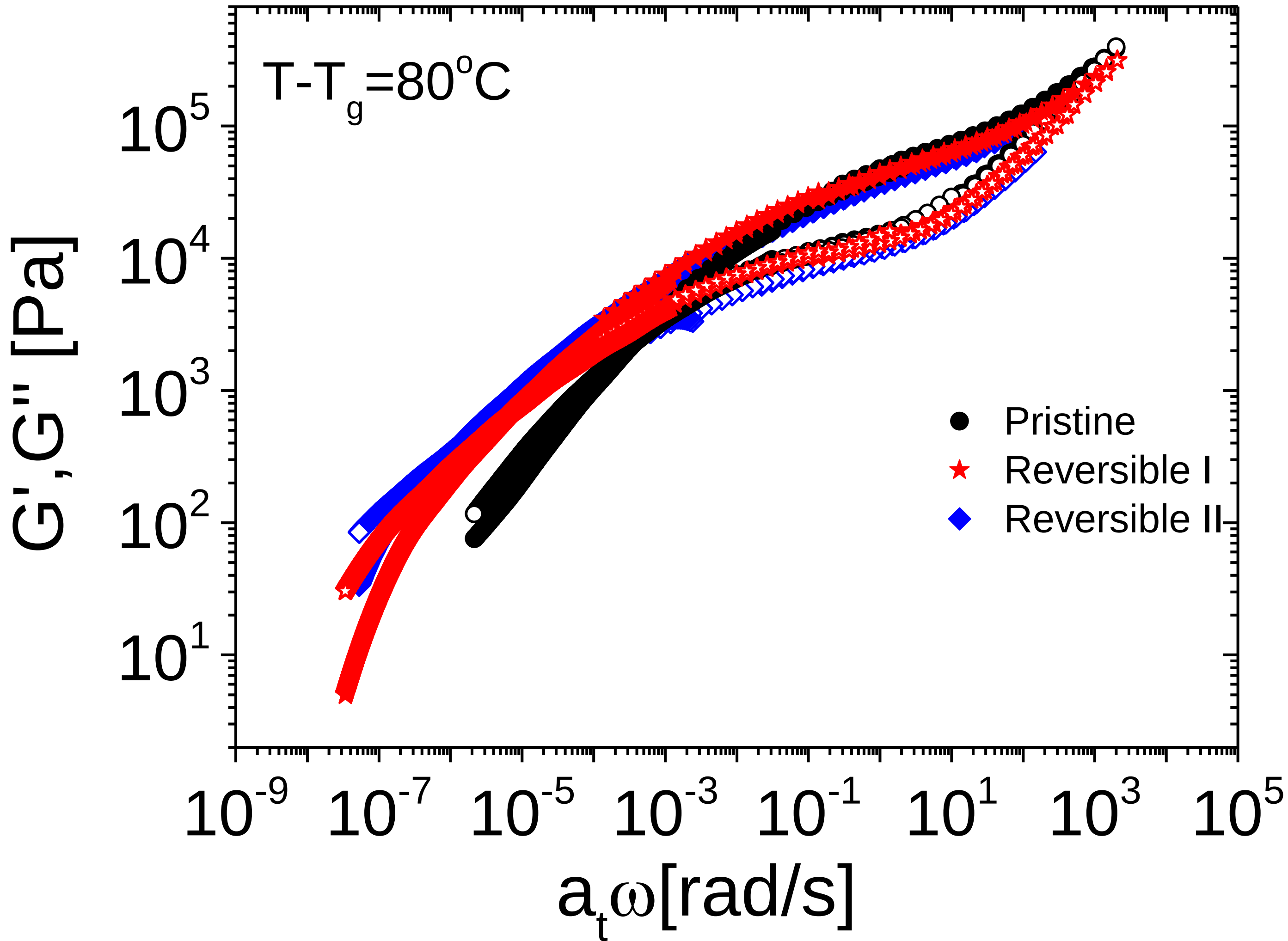

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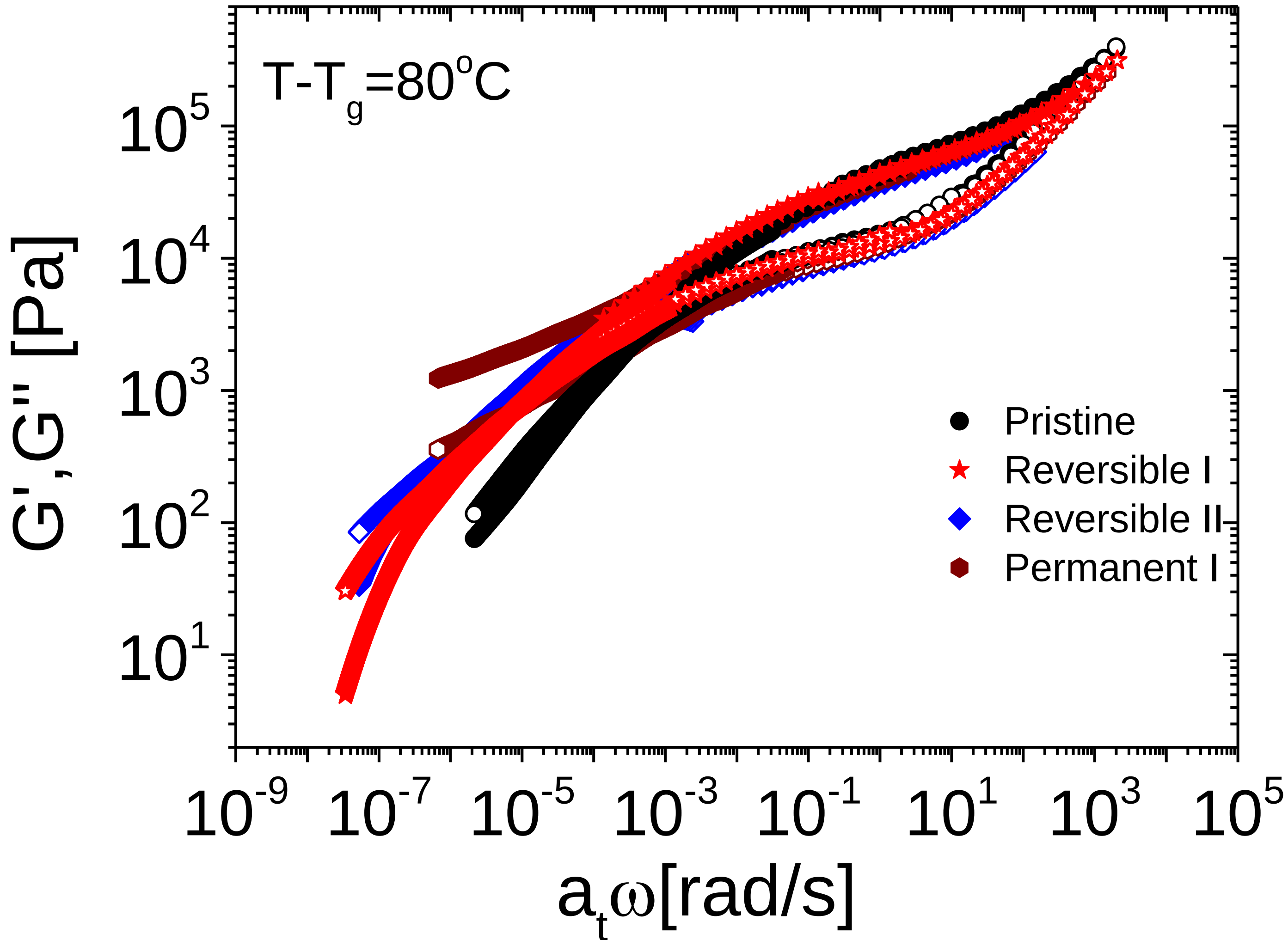

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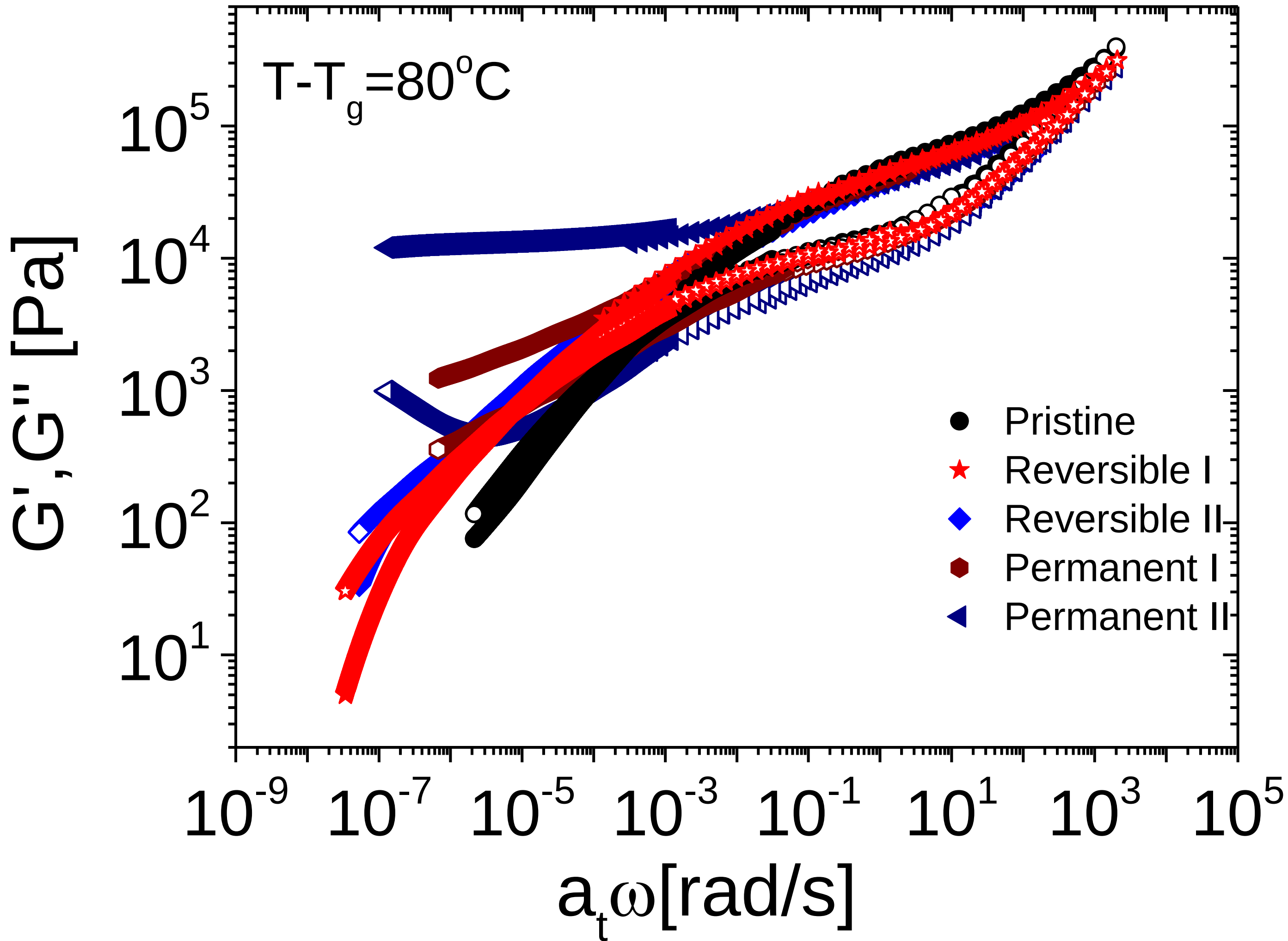

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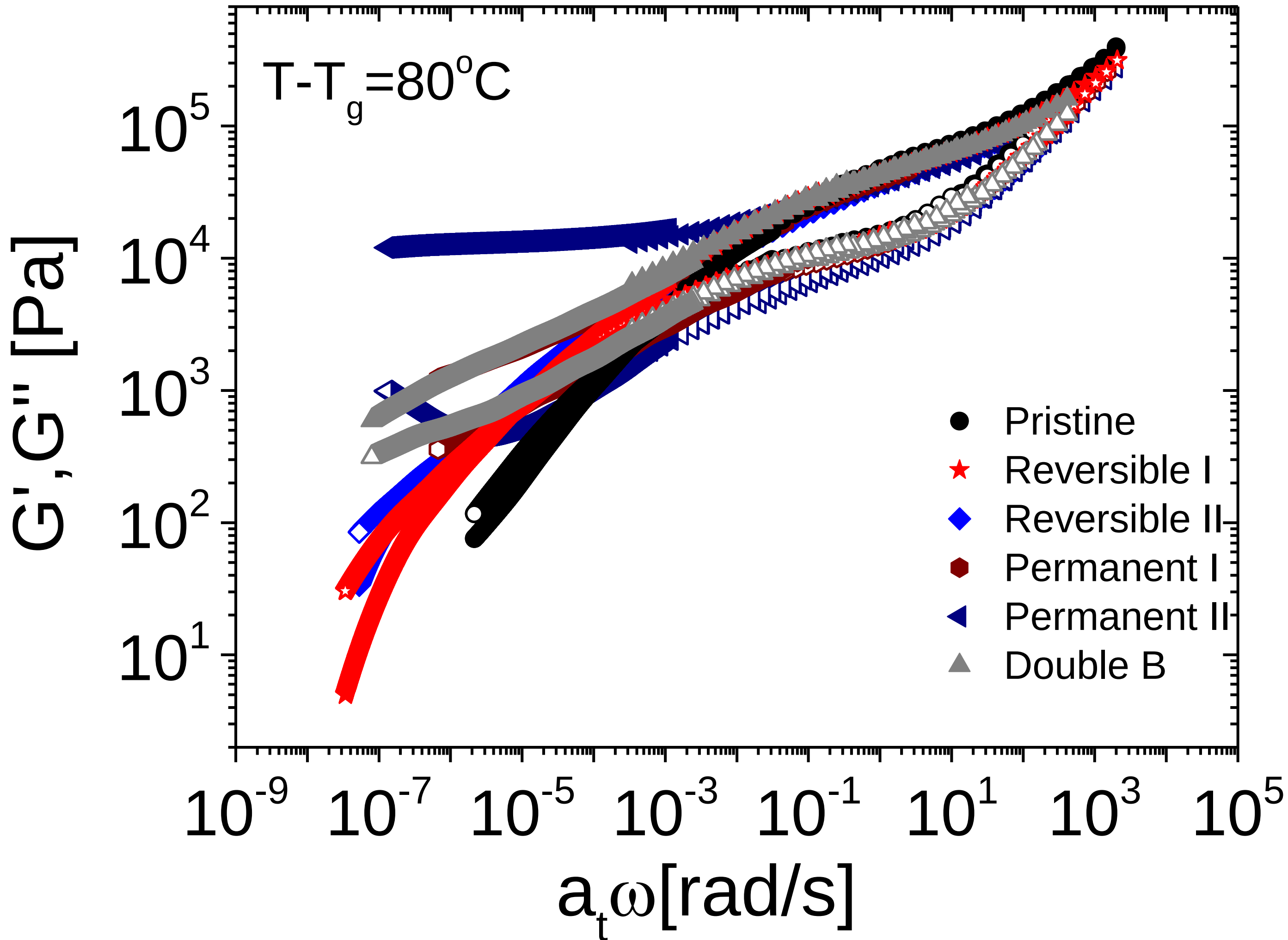

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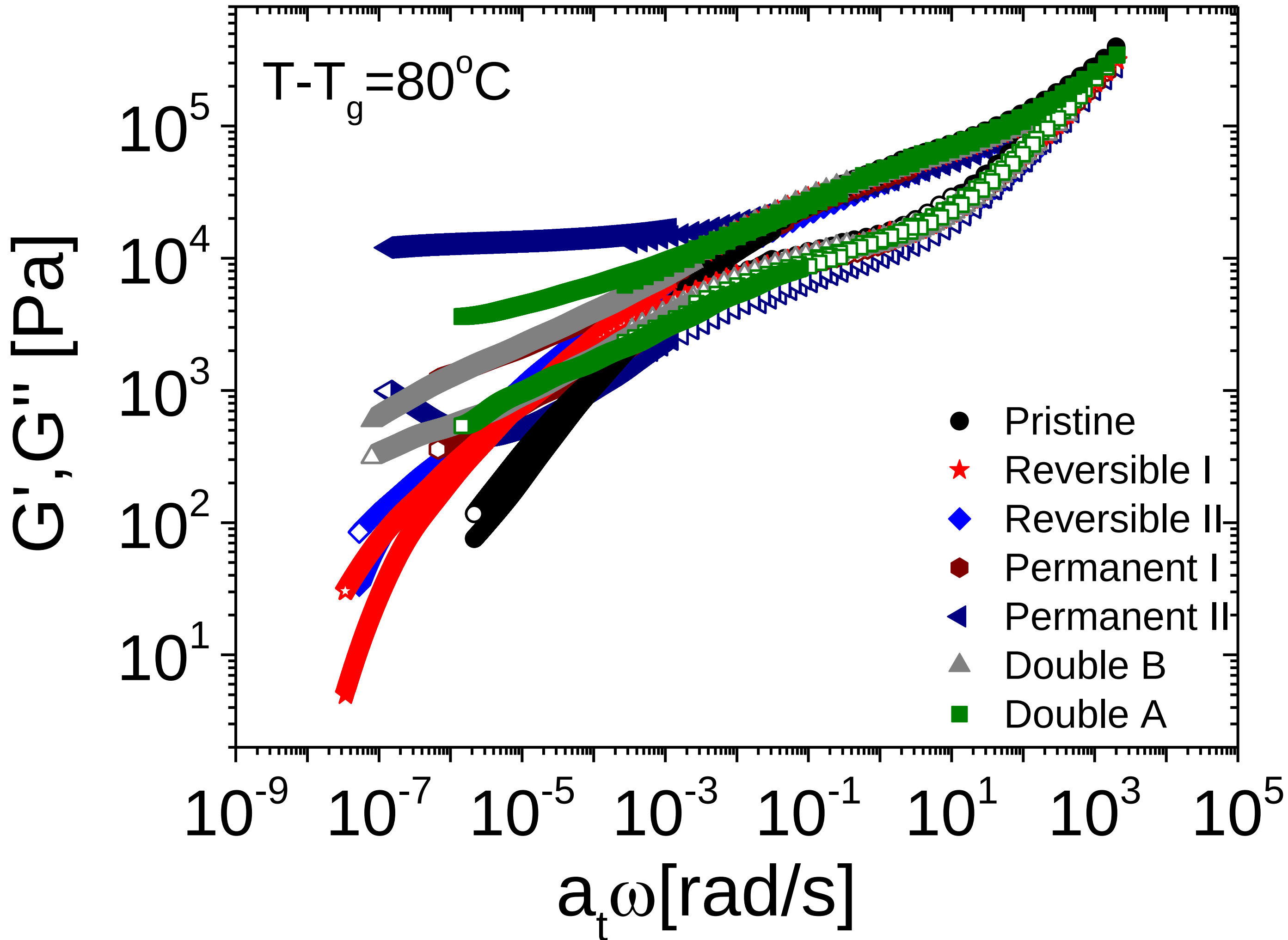

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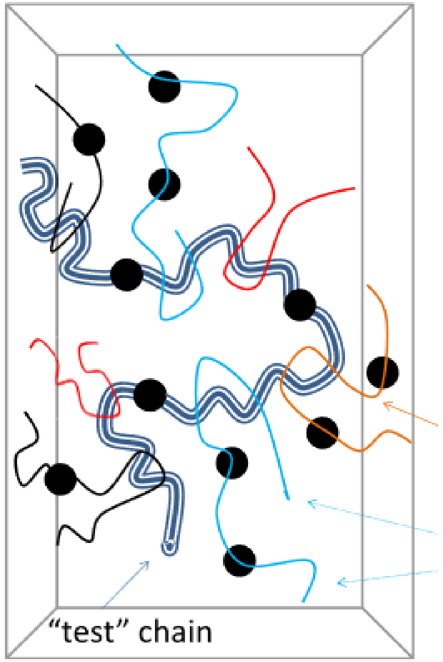
Double A	0.075	0.035

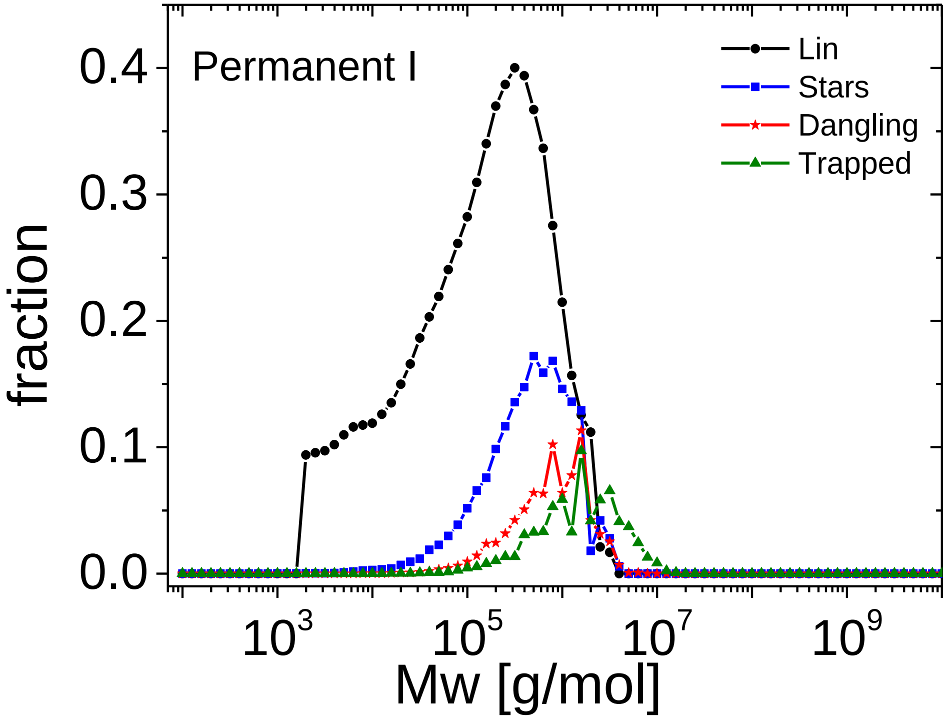
Time Marching Algorithm

- Develop predictive capabilities for the viscoelastic properties (extend the Time marching algorithm platform).

G(t) ⟷ p (probability that a chain unit is crosslinked)



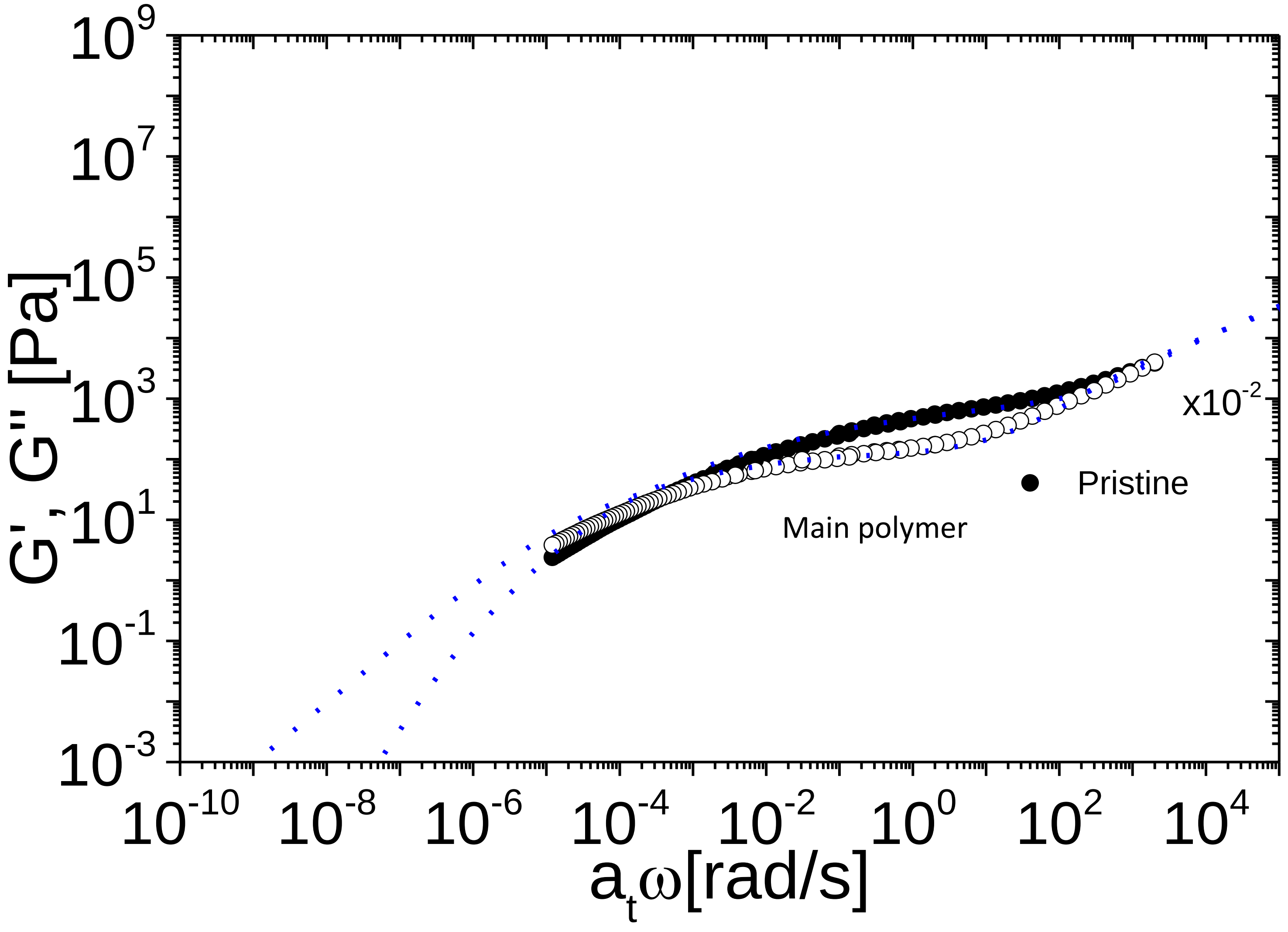
Linear chains
Star like chains
Dangling ends
Trapped strands



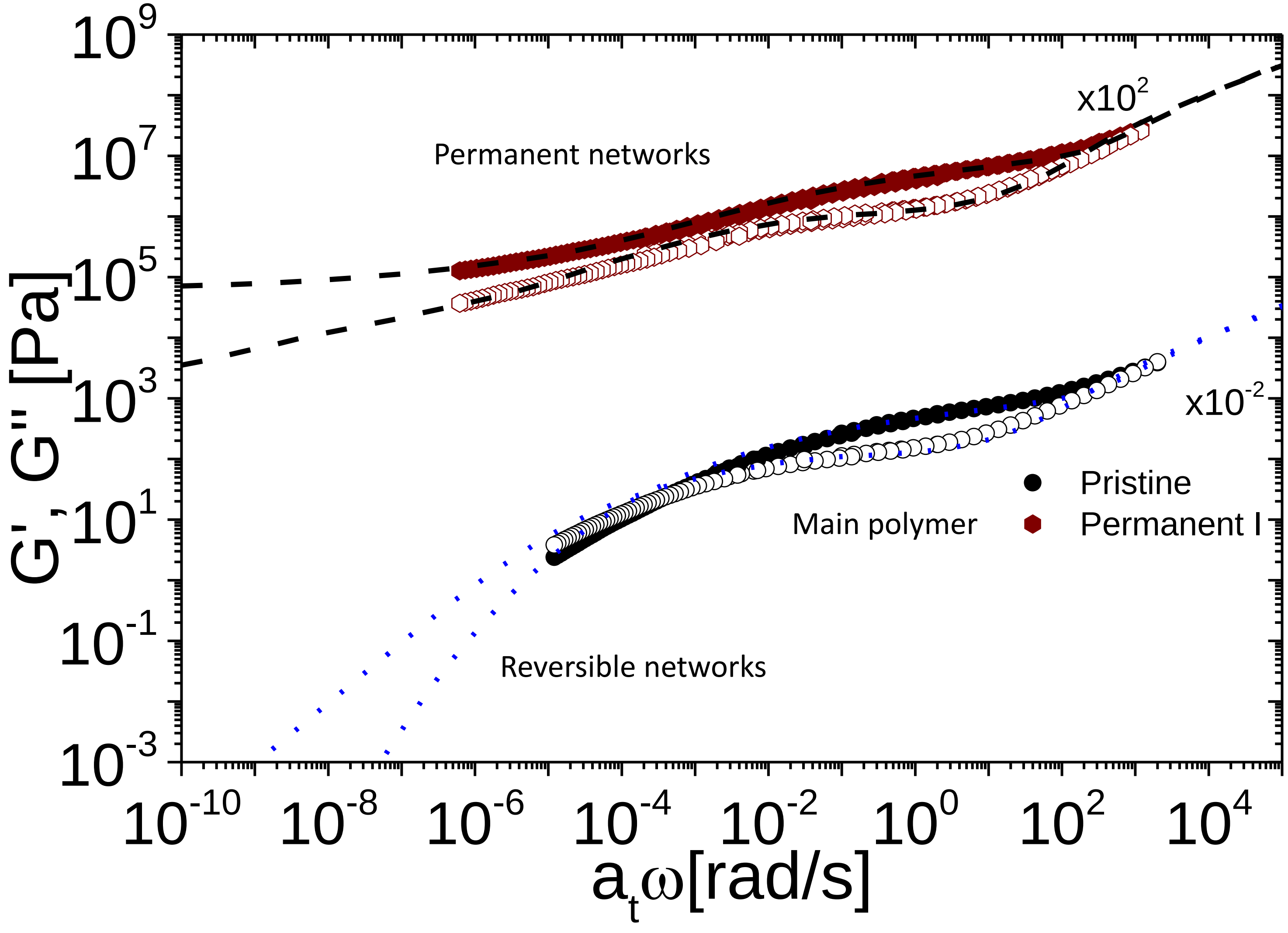
Hawke et al., JoR (60),2016

E. van Ruymbeke et al., J. Non-Newtonian Fluid Mech. (128),2005

TMA for Pristine



TMA for Permanent Network



Permanent network

The junction points are characterized by infinite friction.
(p_2)

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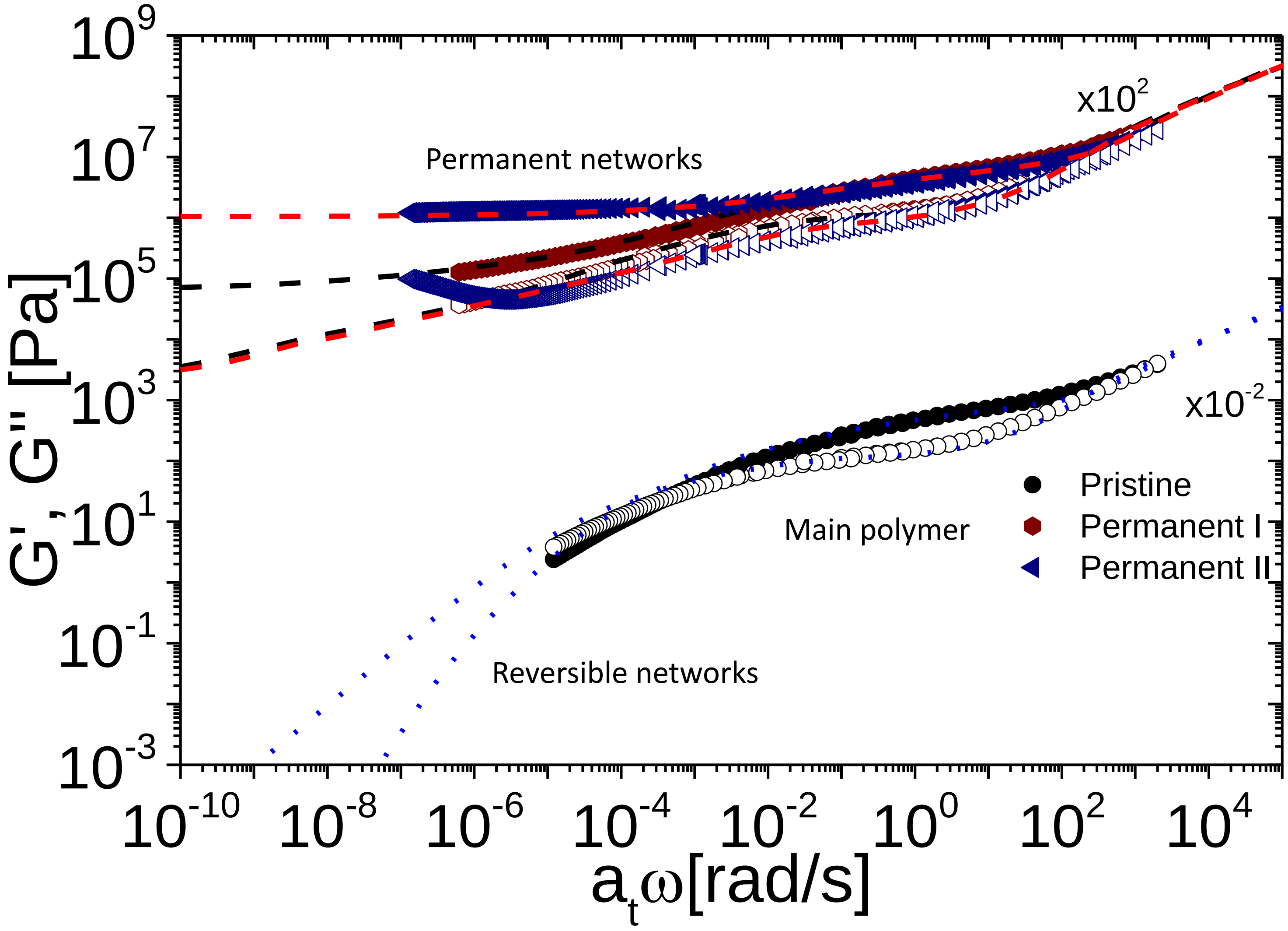

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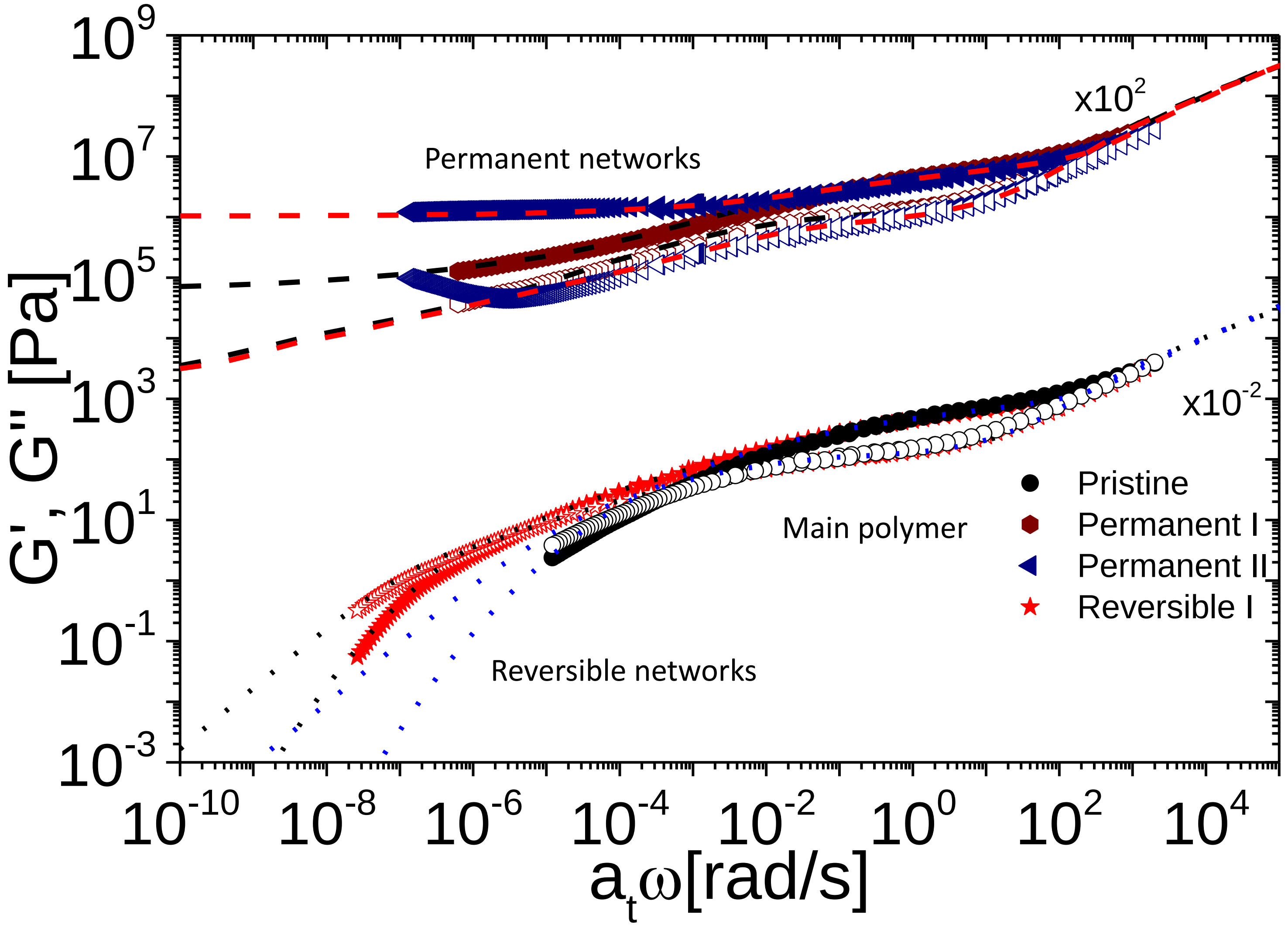
TMA for Reversible Network



Permanent network

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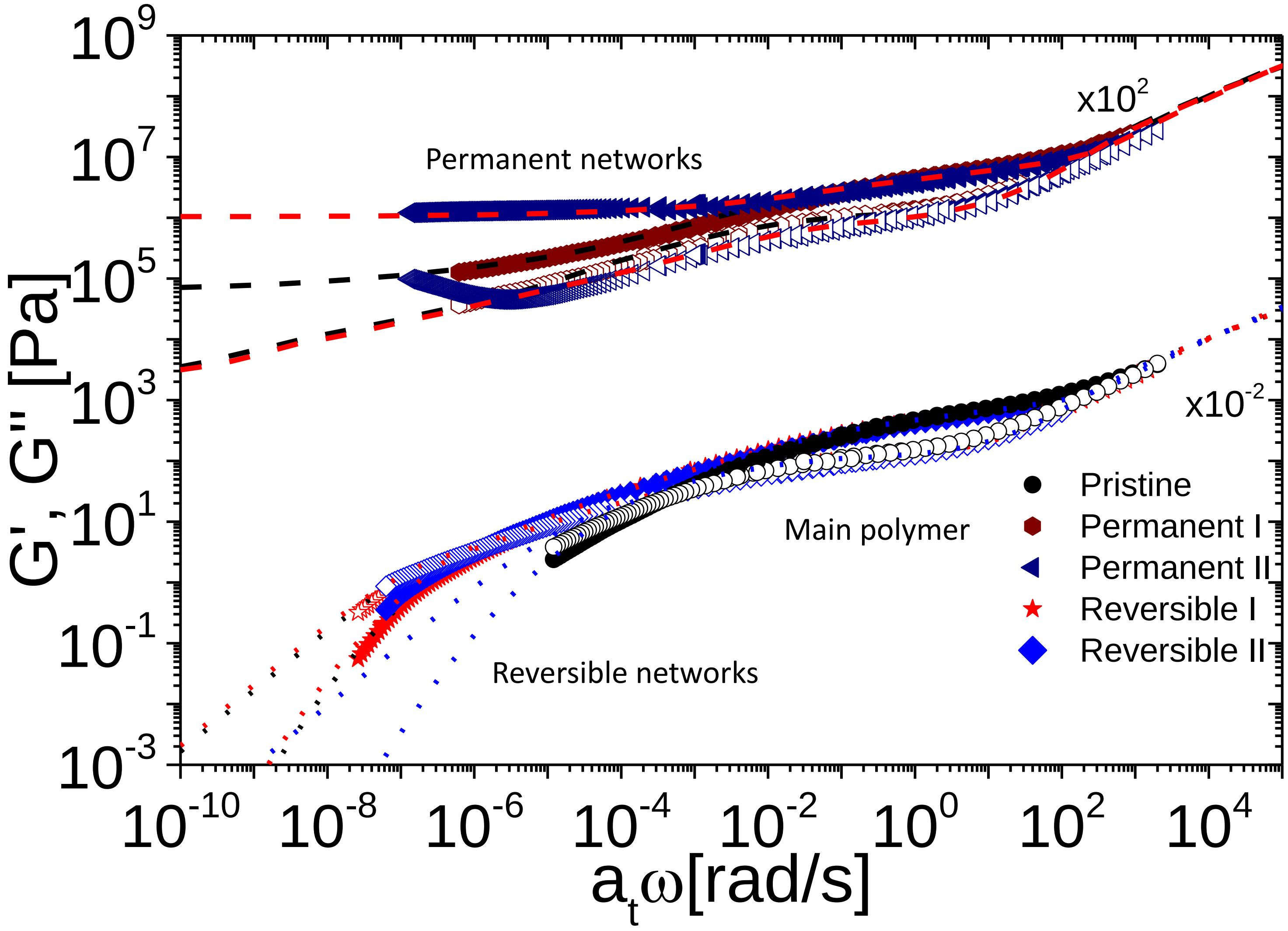
Reversible network

The bonded stickers introduce in the system a delay of the reptation time.
(p_1, $\tau_{stickers}$)

$$\tau_{early}(x) = \frac{9\pi^3}{16}\left(\frac{\left(\frac{M}{2}\right)}{M_e}\right)^2 \tau_{Rouse}\, x^4\, c^2 + \frac{3\pi}{8}\#_{stickers}\left(\frac{\left(\frac{M}{2}\right)}{M_e}\right)^3 \tau_{sticker}\, x^4\, c^3$$

$$\tau_{rept} = 3\tau_e Z^3\, c + \frac{2\#_{stickers}\,\tau_{sticker}}{\pi^2} Z^2\, c^2$$

TMA for Reversible Network



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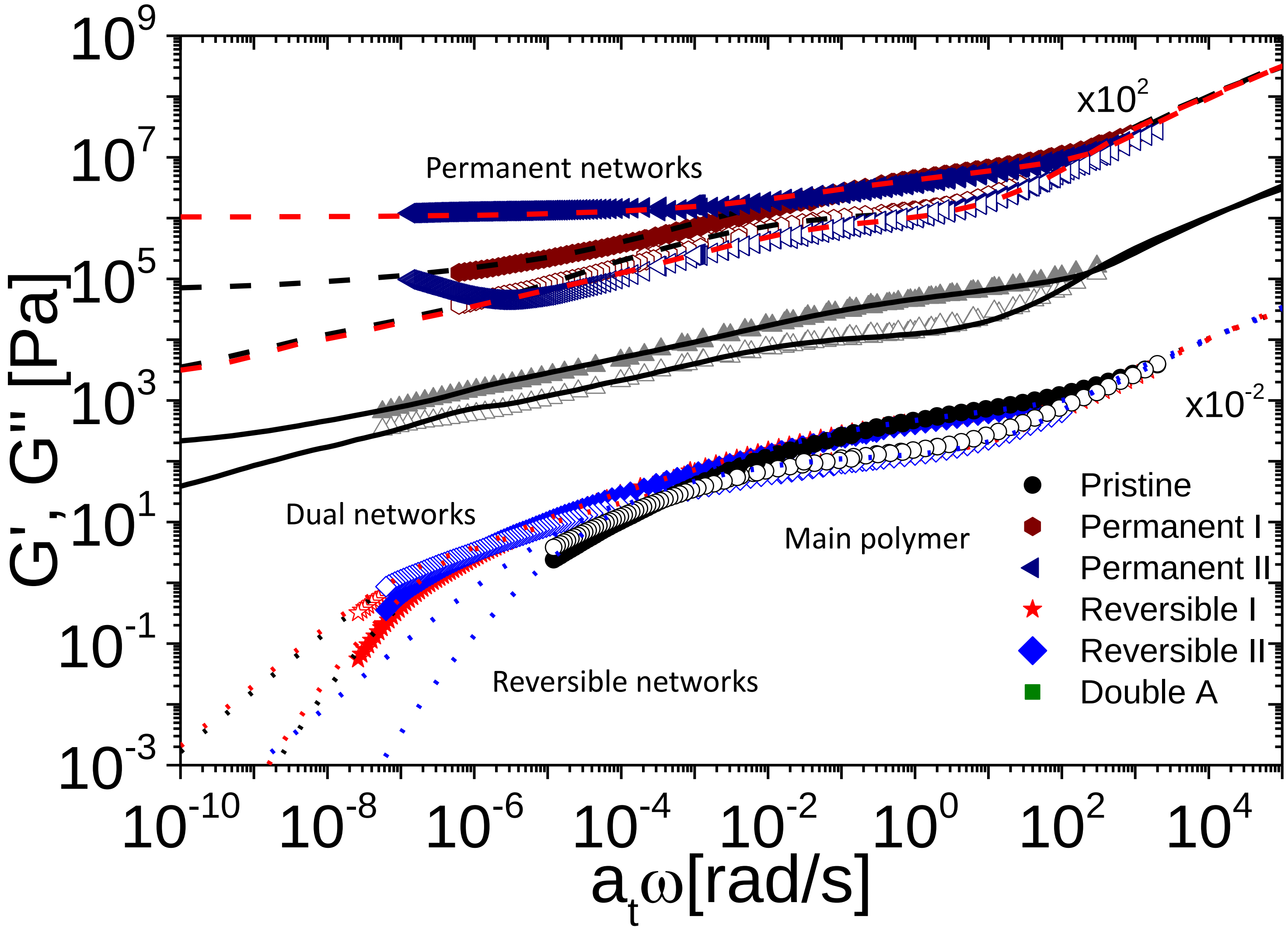
TMA for Dual Network



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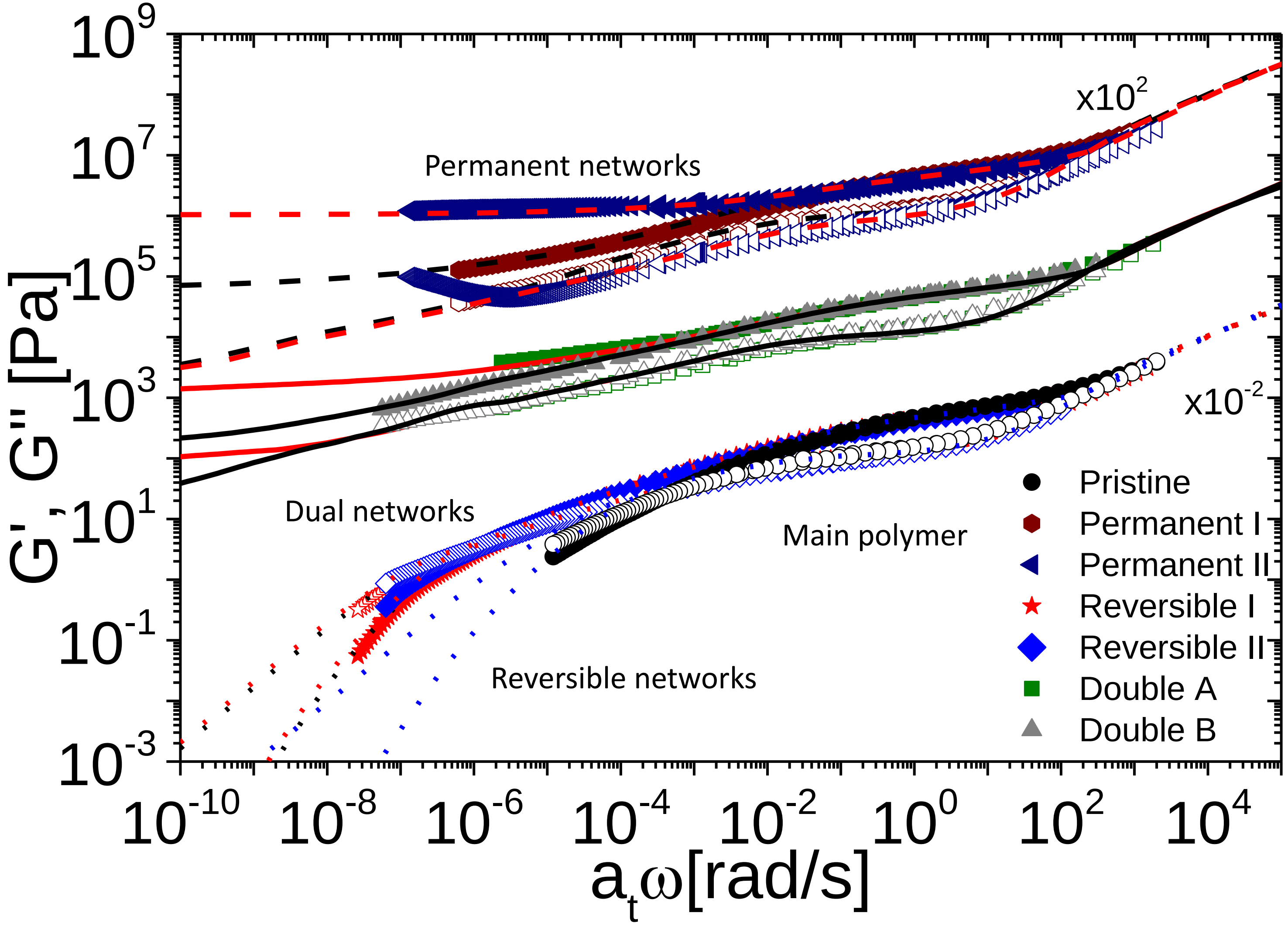
Dual network

The polymer network is only formed by the permanent stickers, but a delay in their relaxation is added in order to account for the influence of the reversible stickers.

(p_1, p_2, $\tau_{stickers}$)

TMA for Dual Network



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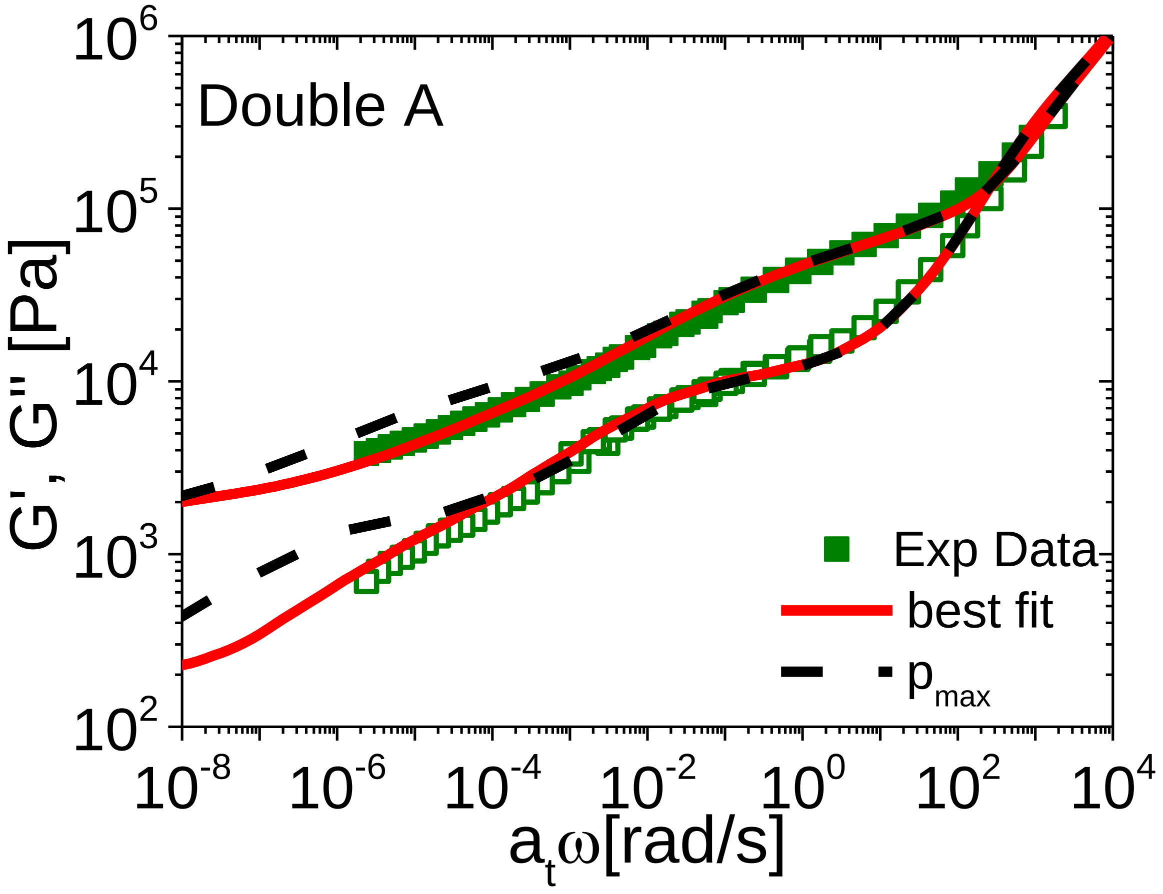
Model predictions



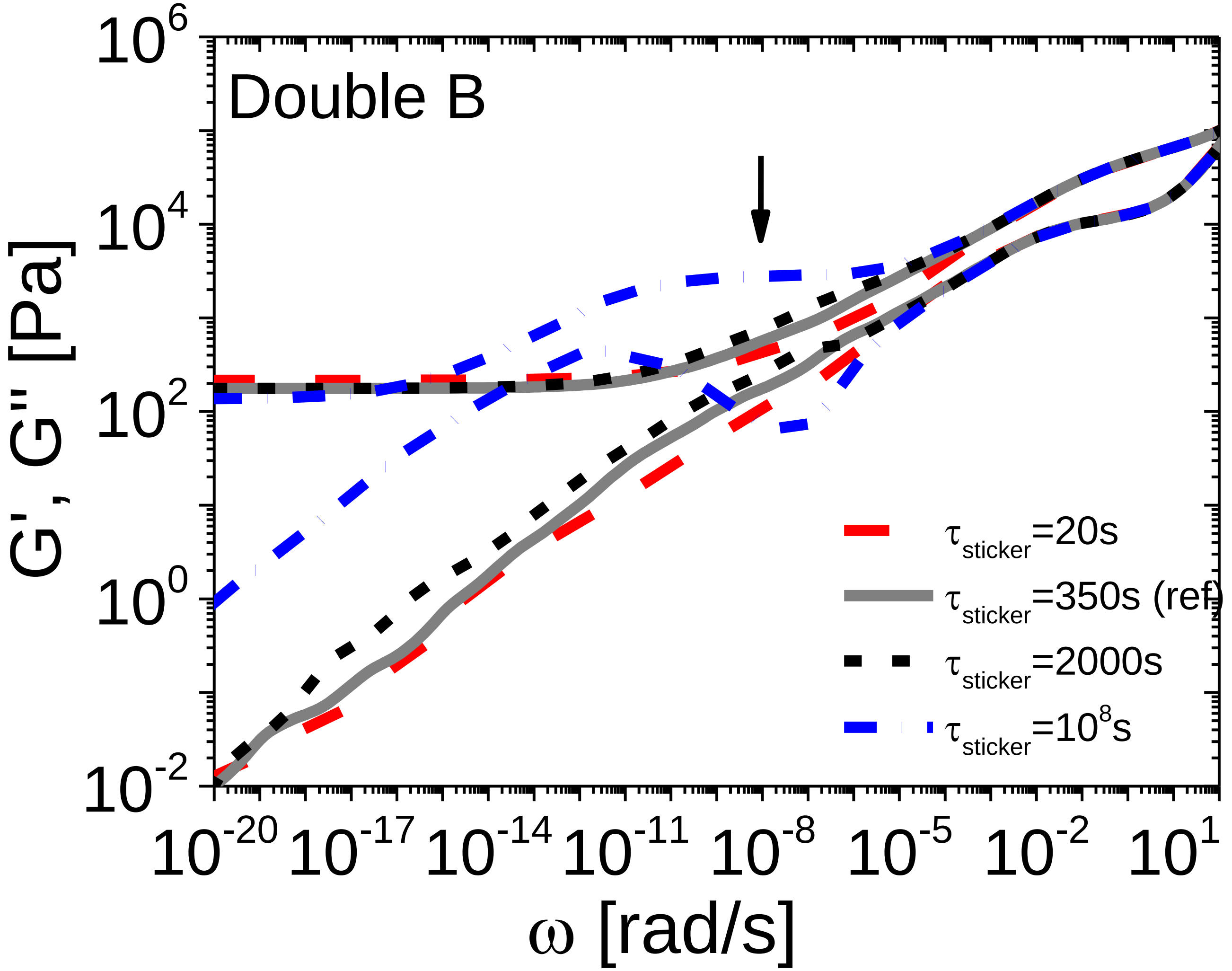
Comparison of the experimental data with predictions obtained considering the best fit values and $p_{max.}$

p_{max} were determined considering the network chemical composition.

Model predictions

The model can be used to predict the viscoelasticity of the networks considering different molecular features.

- Mw distribution
- **Lifetime of bonds**
- Density of stickers



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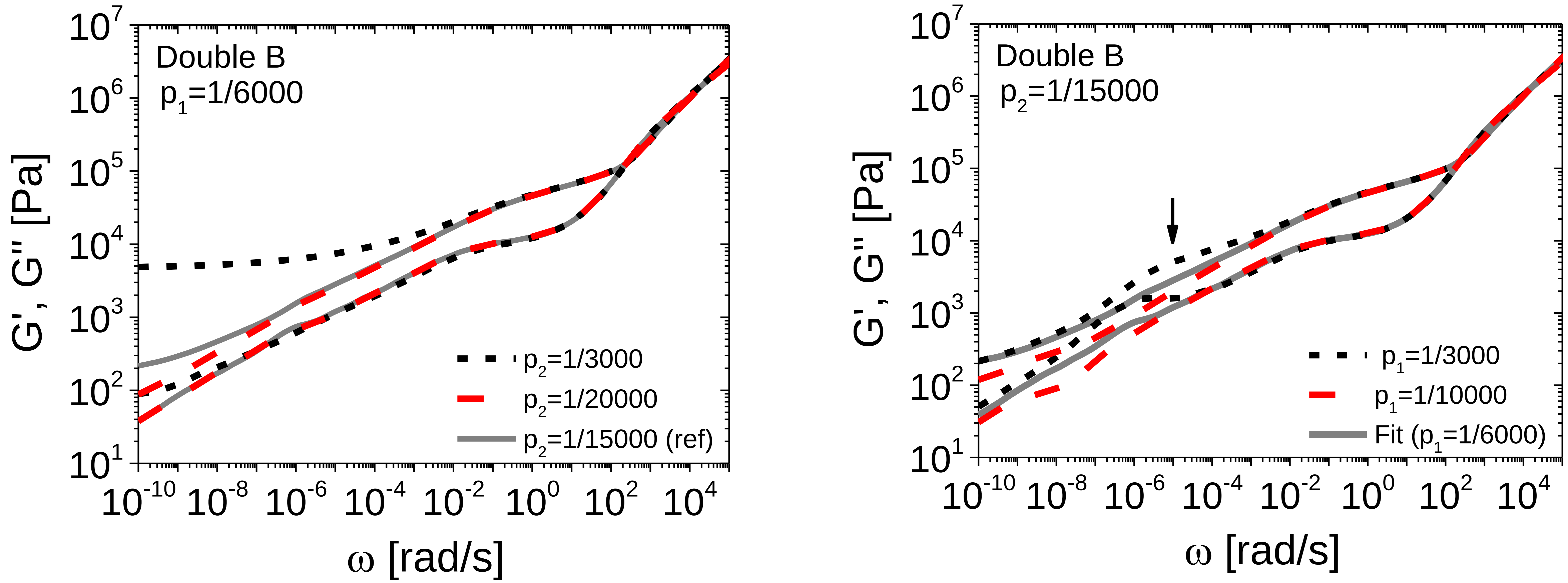

Conclusions

Quantitative analysis of linear viscoelasticity of industrial double networks (using TMA)

Parametric analysis (molecular weight distribution, strength and density of bonds) offers clues for tailoring properties

Crosslinkers highly affect the rheological response of the networks at long times.

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Double dynamics for designing new responsive polymer networks and gels

THANK YOU