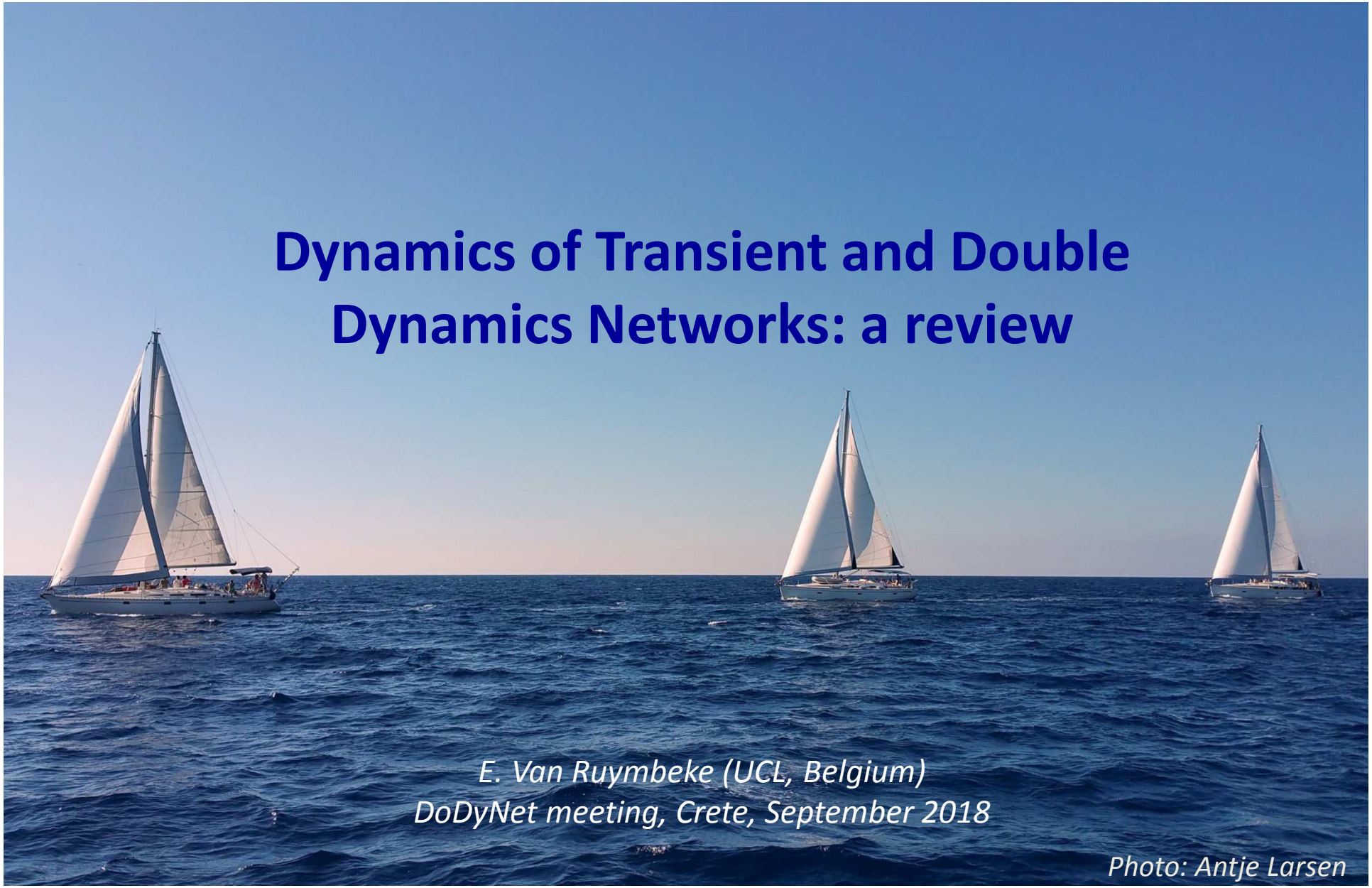
Dynamics of Transient and Double Dynamics Networks: a review



E. Van Ruymbeke (UCL, Belgium)

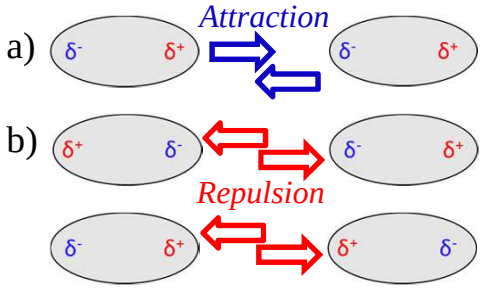
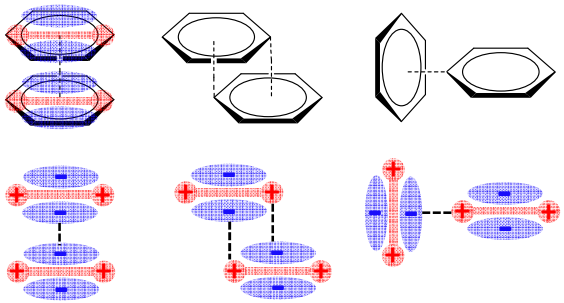
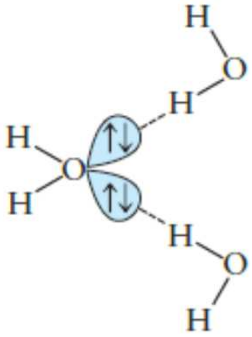
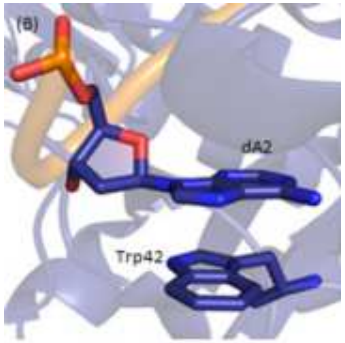
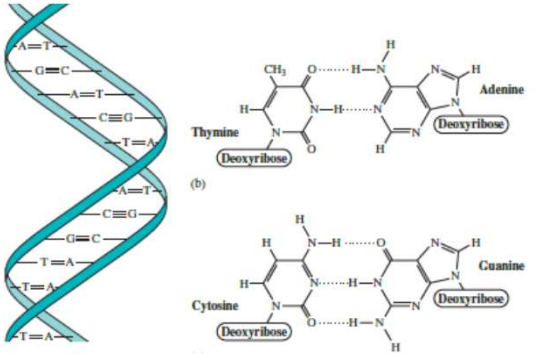
DoDyNet meeting, Crete, September 2018

Photo: Antje Larsen

INITIAL TRAINING NETWORK

Non covalent interaction

Non covalent interaction – Inspired by nature

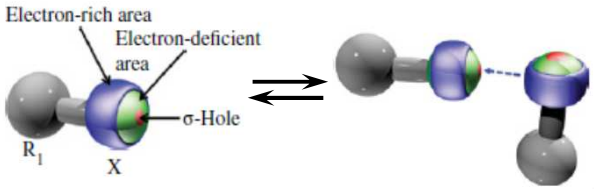
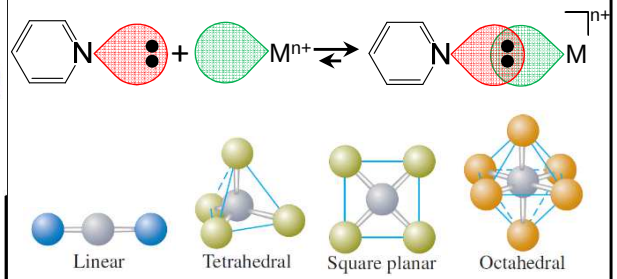
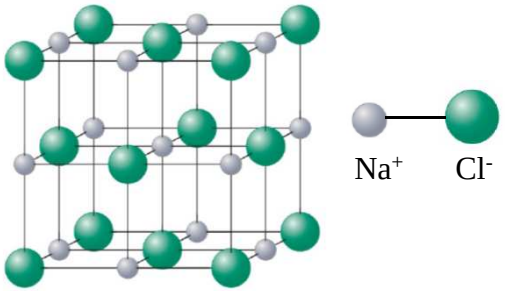
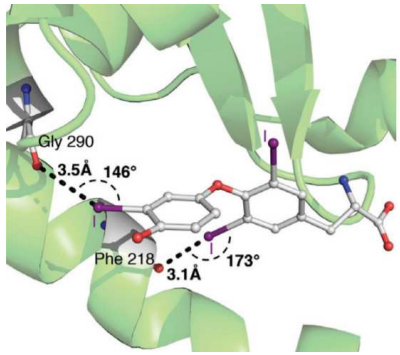
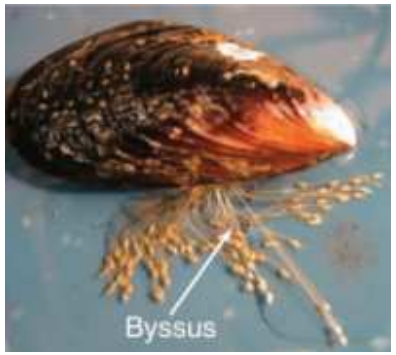
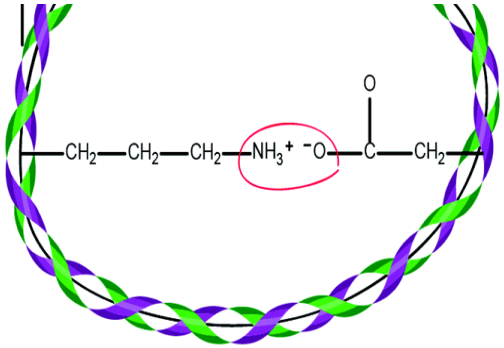
van der Waals	π- π stacking	Hydrogen bonding
		
Electrostatic interactions between e⁻ clouds Short-range, non-directional, extrem. Weak E < 5 kJ.mol^{-1}	Interactions between e⁻ rich/poor regions Within aromatics, directional, weak E = 2-50 kJ.mol^{-1}	e⁻ deficient H and electronegative atom Directional, from weak to strong E = 4-120 kJ.mol^{-1}
		
Gecko's amazing toes	*Nucleobase-amino acid*	*DNA double helix*

Chemical Principles, 8th ed.; Cengage Learning: Boston, **2015.**

Nucleic Acids Research, **2014**, *42*, 6726-6741.

Non covalent interaction

Non covalent interaction – Inspired by nature

Halogen bonding	Metal-ligand coordination	Ionic interactions
		
R_1: molecule with electrophilic region *X: halogen atom (F, Cl, Br, I or At)* Attractive interactions between e⁻ A/D Directional, from weak to strong E = 10-180 kJ.mol^{-1}	Transfer of lone electron-pair from D to A Highly directional, strong, labile E = 100-300 kJ.mol^{-1}	Electrostatic attractive interactions Directional, strong, easily disrupted E = 100-350 kJ.mol^{-1}
		
Hormone-protein recognition	*Mussel byssus*	*Salt bridge in protein*

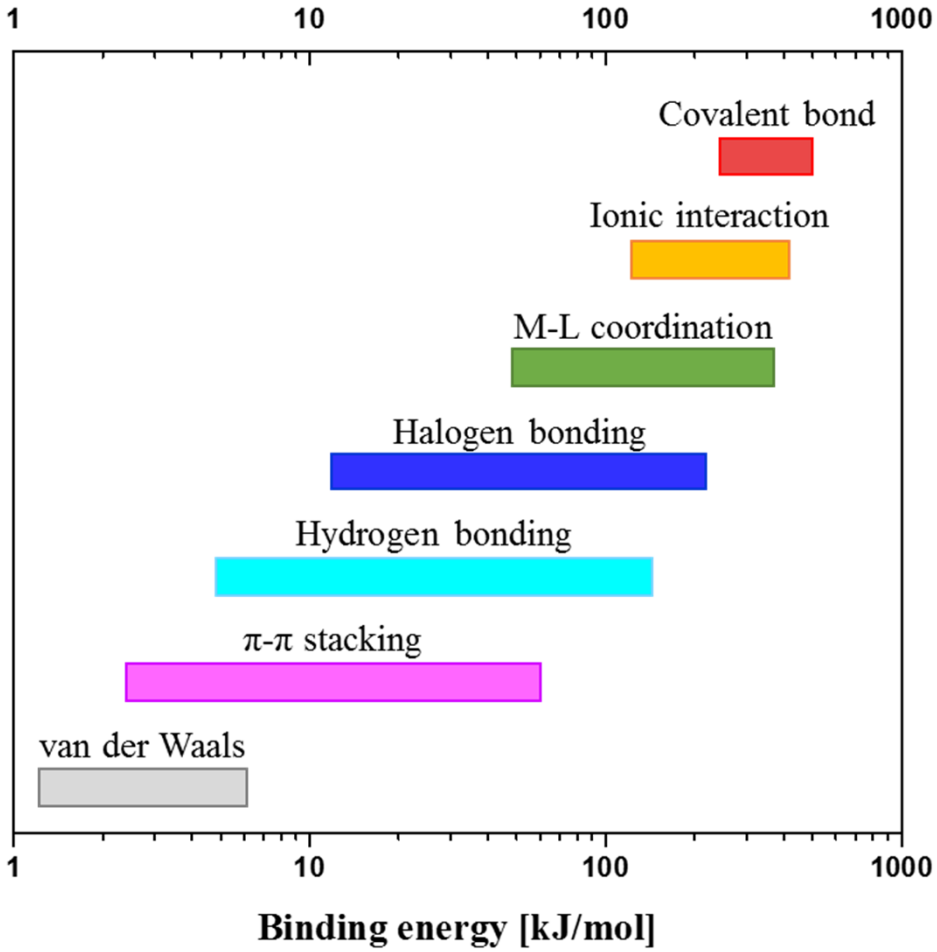
Protein Science, **2013**, *22*, 139-152.

Science, **2010**, *328*, 216-220.

Biomater. Sci., **2017**, *5*, 1699-1735.

Non covalent interaction

Non covalent interaction – Summary

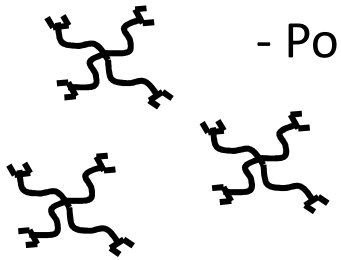


Interactions	Binding energy ($kJ.mol^{-1}$)
Covalent bonds	200 - 400
Ionic bonds	100 – 350
Metal-ligand bonds	100 – 300
Halogen bonds	10 – 180
Hydrogen bonds	4 – 120
π-π stacking	2 – 50
van der Waals	< 5

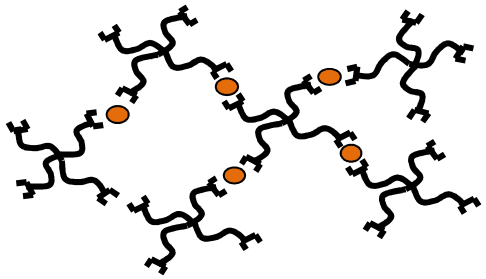
Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol. **2013**, *5*, 582−612.

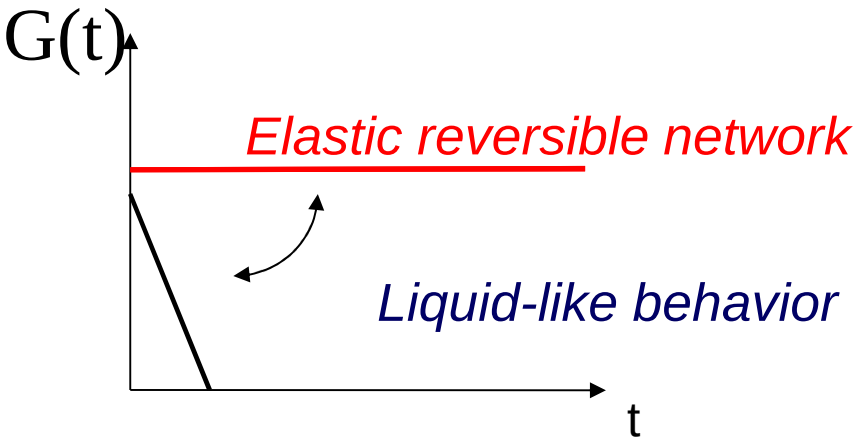
Unentangled vs entangled transient Network

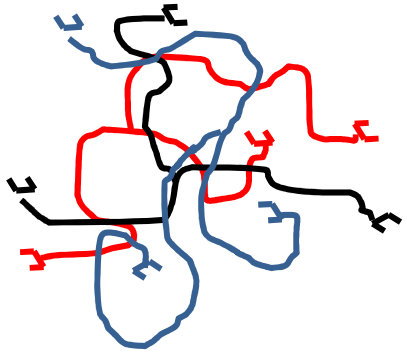
- Short blocks
- Polymer solution



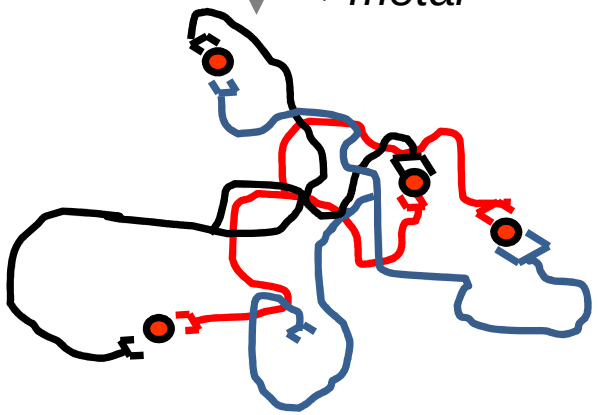
+ *metal*

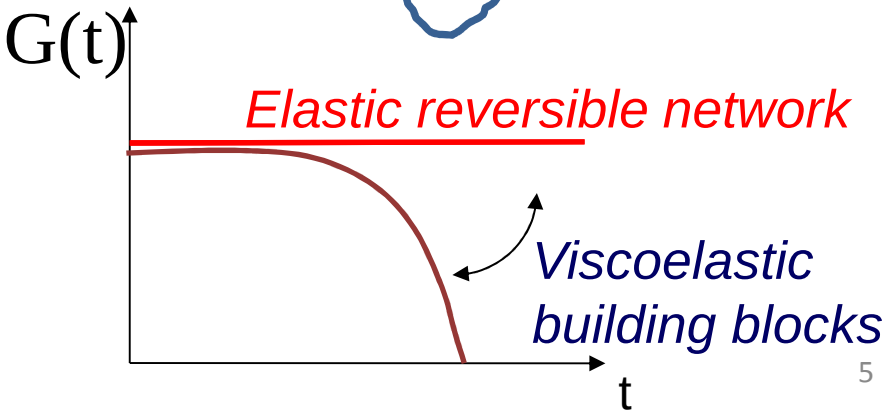




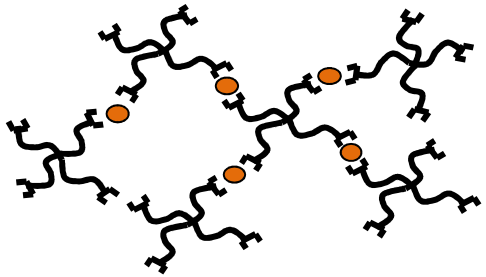


+ *metal*



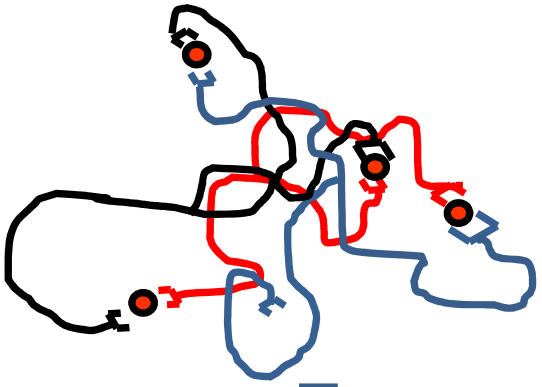


Unentangled vs entangled transient Network



Elastic plateau and relaxation time: fully governed by the supramolecular junctions

Many works in literature on this kind of supramolecular polymers



Elastic plateau:
also governed by the entanglement segments

Relaxation time:
Governed by both the supramolecular junctions and the entanglements dynamics

Ouline

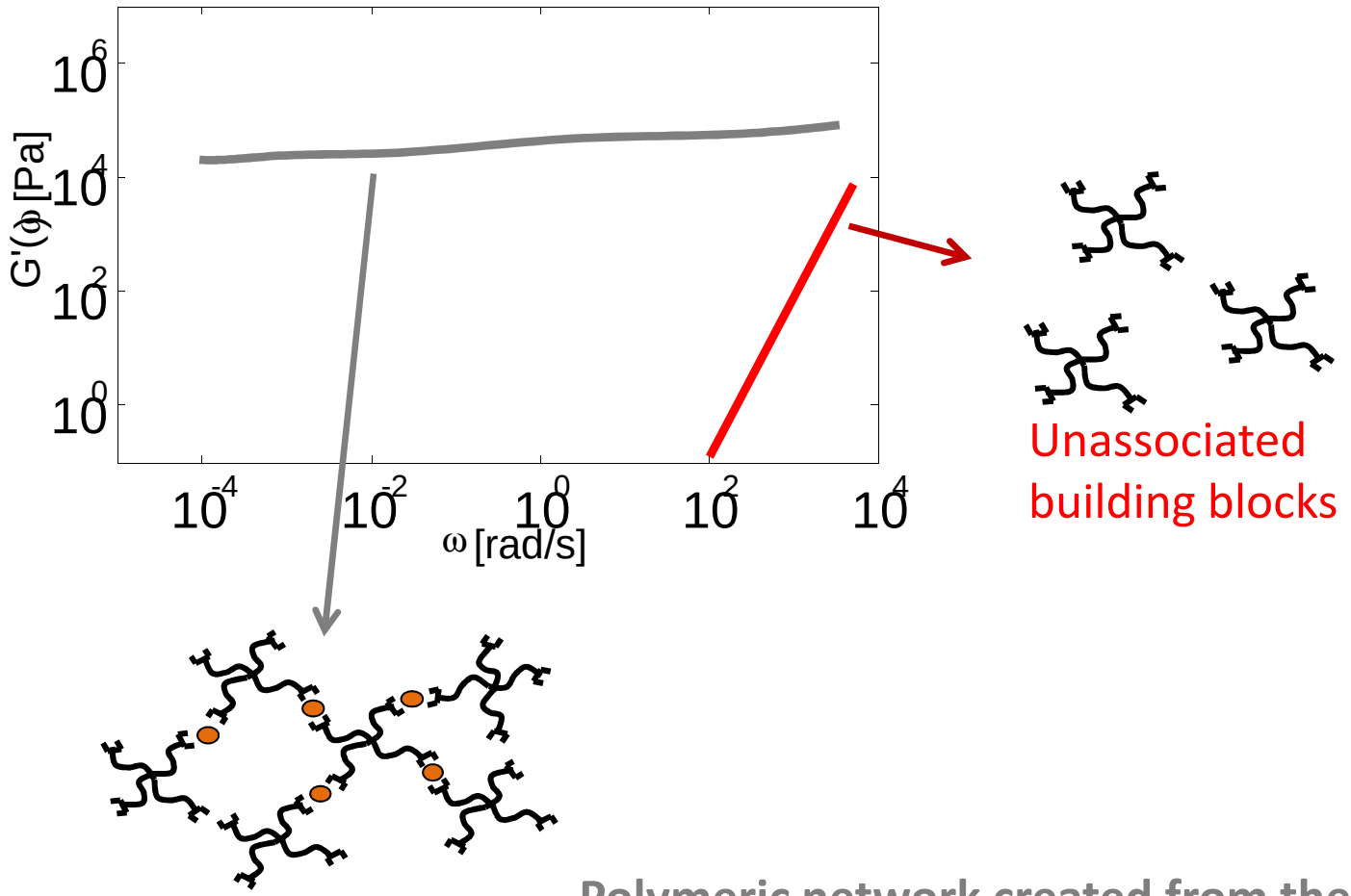
I) Dynamics of Transient Networks based on unentangled building blocks

II) Dynamics of Transient Networks based on entangled building blocks

II) Dynamics of Double Dynamics Polymer Networks

I) Dynamics of Transient Networks based on unentangled building blocks

Dynamics of unentangled transient Network



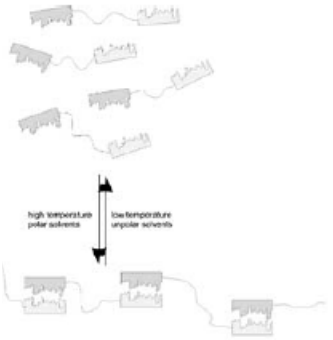
Polymeric network created from the association of the building blocks

Dynamics of unentangled transient Network

Systems based on hydrogen bonding (Upy groups)

Supramolecular Polymers from Linear Telechelic Siloxanes with Quadruple-Hydrogen-Bonded Units

J. H. K. Ky Hirschberg,† Felix H. Beijer,† Huub A. van Aert,† Pieter C. M. M. Magusin,‡ Rint P. Sijbesma,*,† and E. W. Meijer*,†



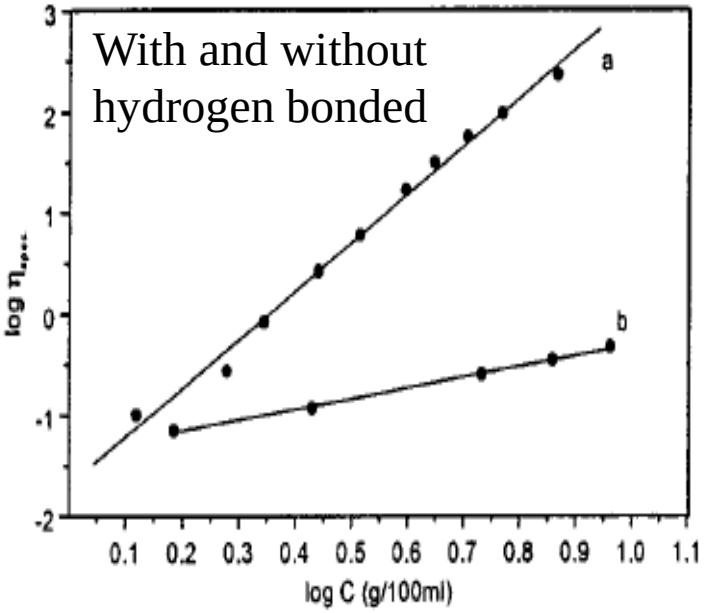
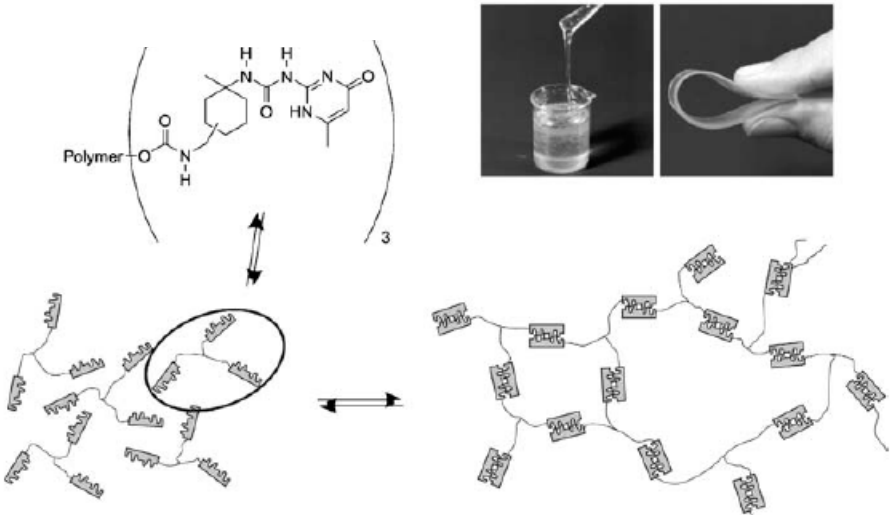


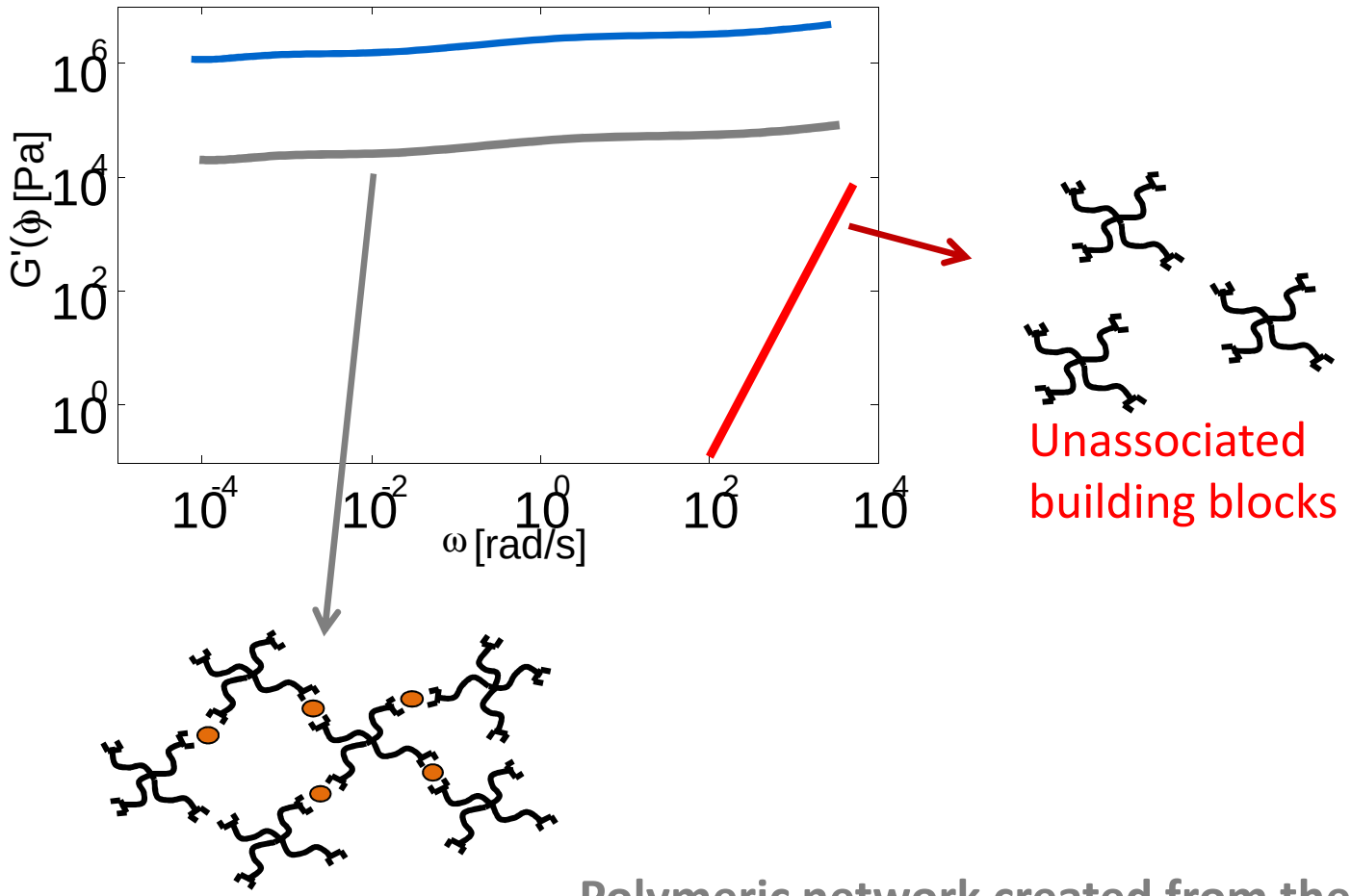
Figure 8. Specific viscosities of compounds 1 (a) and 1-Bn (b) in $CHCl_3$ as a function of concentration at 20 °C.



<u>Reversible network</u>: PEO- and PPO-telechelics + dimerizing ability of the ureidopyrimidine units (Upy)

Large viscosity increase, especially for concentrated systems

Dynamics of unentangled transient Network



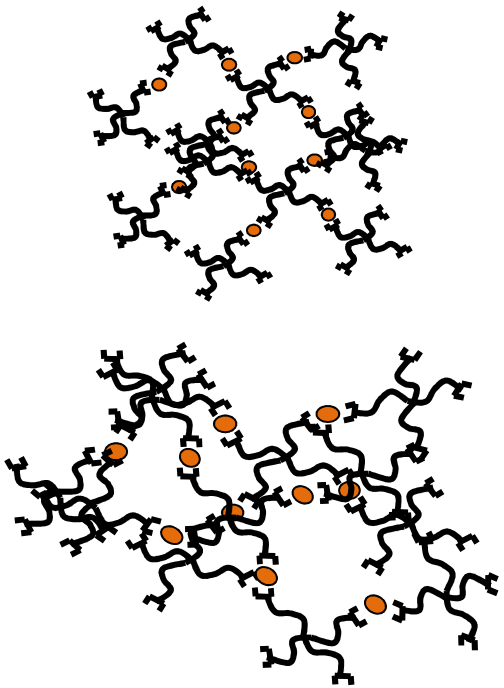
Polymeric network created from the association of the building blocks

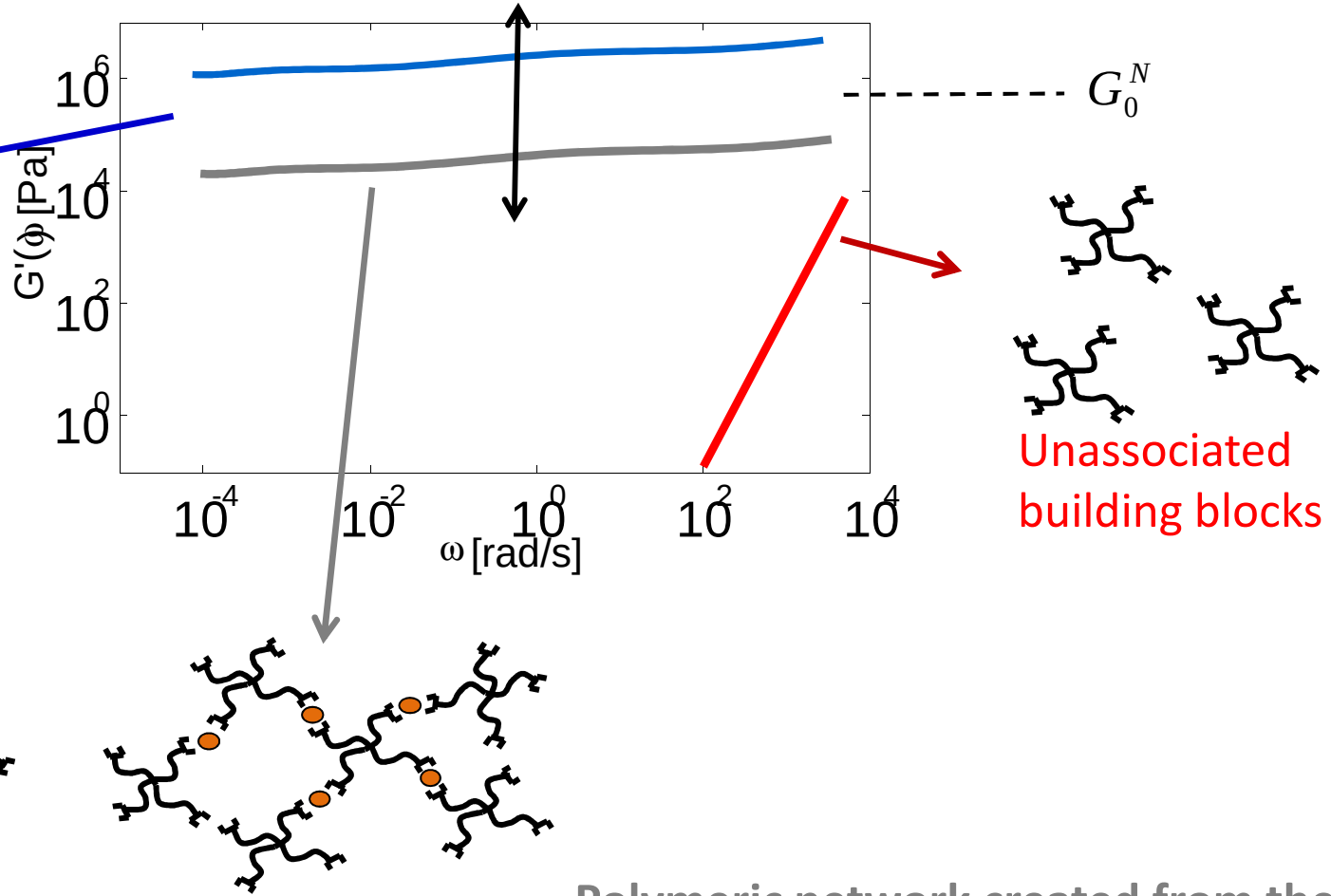
Dynamics of unentangled transient Network

Larger density of junctions between 2 reversible bonds

Or

Larger polymer concentration





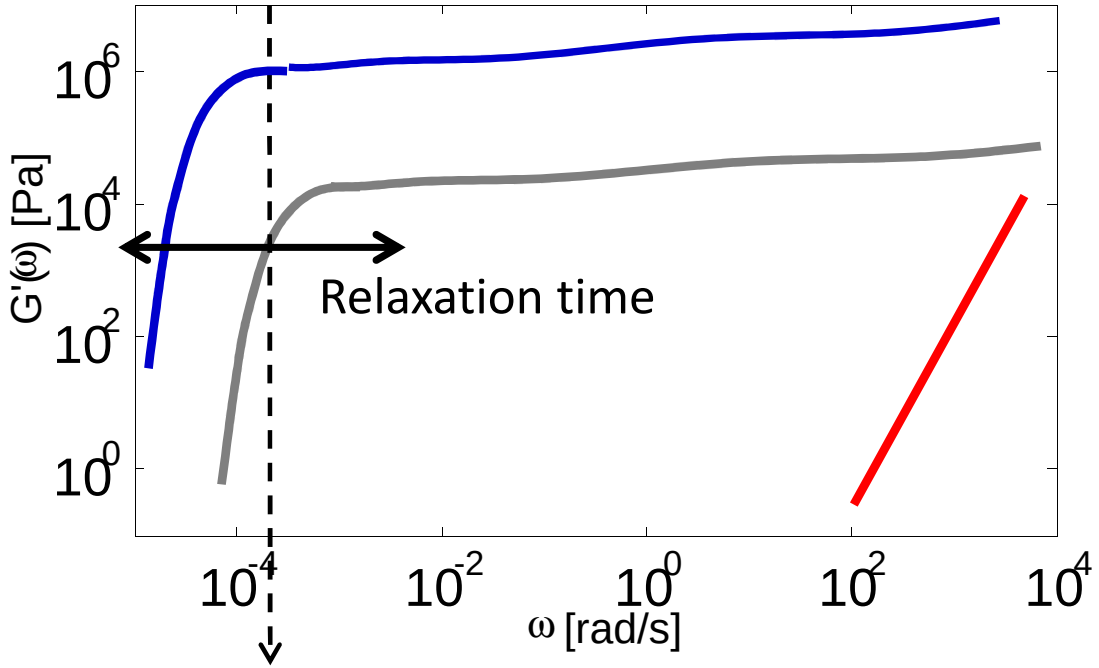
Unassociated building blocks

$$G_0^N = \frac{\rho RT}{M_{cross-links}}$$

Polymeric network created from the association of the building blocks

Dynamics of unentangled transient Network

Relaxation times:



$1/\tau_{rel}$ ➡ Depends on the lifetime of the supramolecular junctions

Dynamics of unentangled transient Network

Few examples…

- Telechelic molecules
- Sticky chains

Dynamics of unentangled transient Network

Hydrogen-Bonded Supramolecular Polymer Networks

RONALD F. M. LANGE,[1,2] M. VAN GURP,[1] E. W. MEIJER[2]

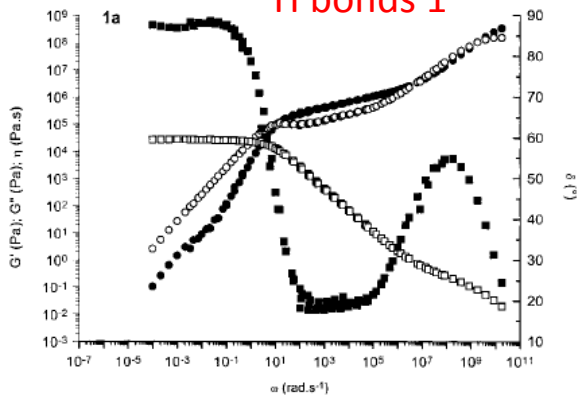
[1] DSM Research, P.O. Box 18, 61

[2] Laboratory of Macromolecular a
5600 MB Eindhoven, The Netherl

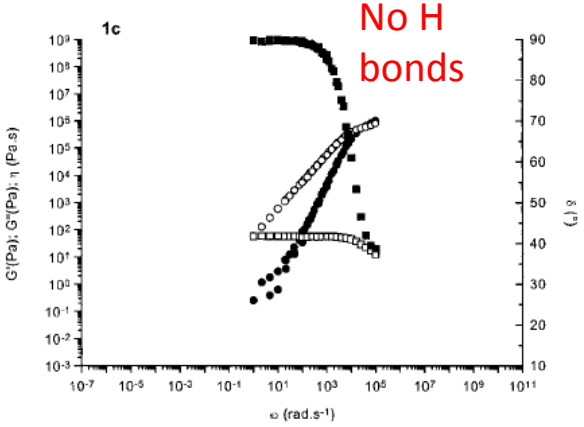
Received 12 February 1999; acc

In the melt state:

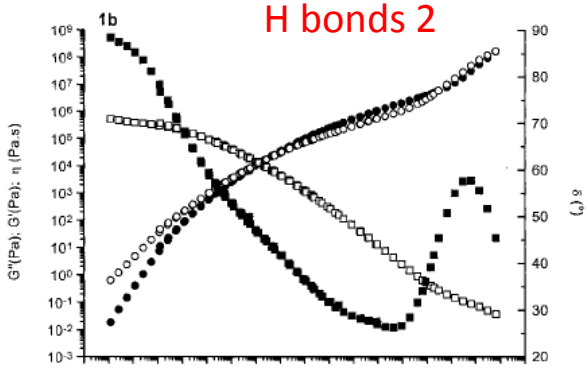
H bonds 1



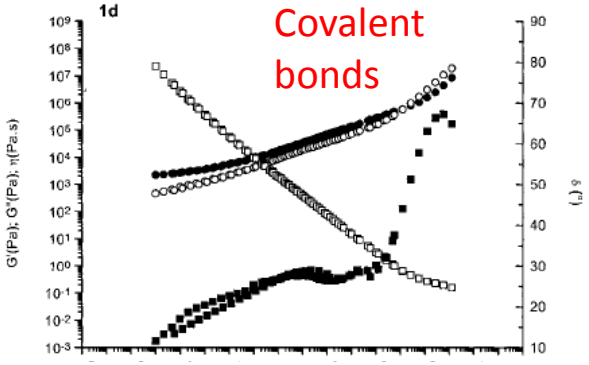
No H bonds



H bonds 2



Covalent bonds



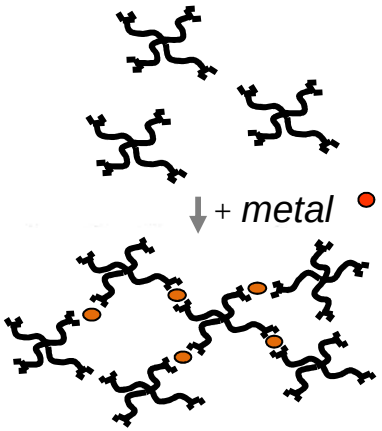
Viscosity increases in function of the lifetime of the supramolecular junctions

Dynamics of unentangled transient Network

Supramolecular Polymer Gels with Potential Model-Network Structure

Torsten Rossow[a,b] and Sebastian Seiffert*[a,b]

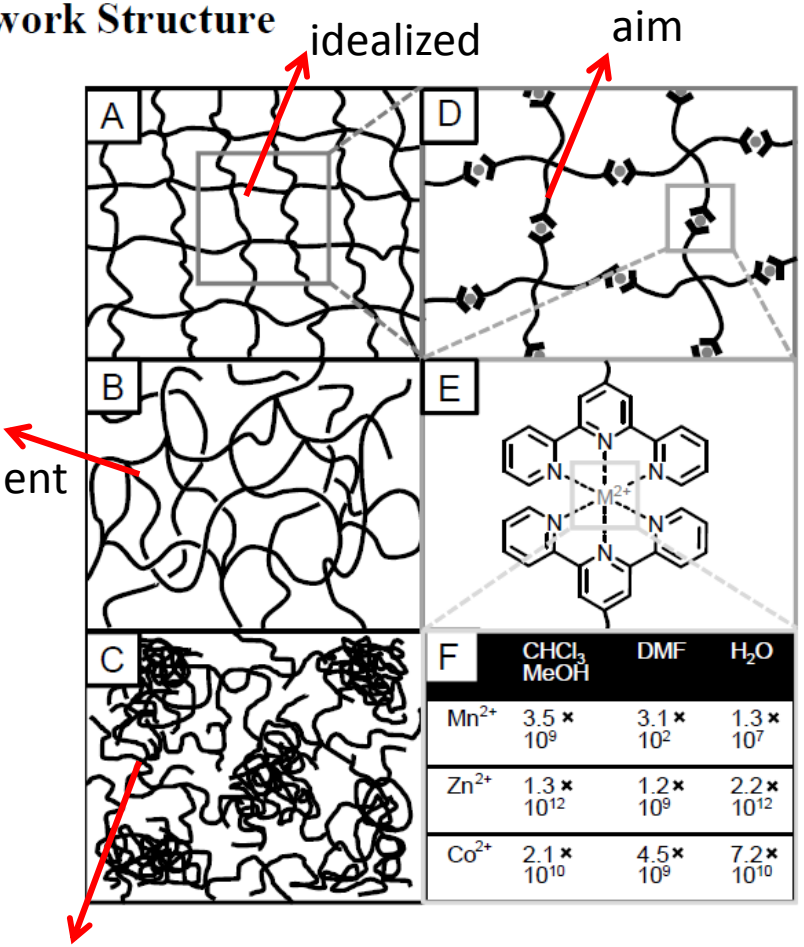
Narrow disperse building blocks (regular network), in solution



Longest relaxation times, in different solvents:

85

	$CHCl_3$–MeOH	DMF	H_2O
w/o X-Linking	τ = 0.012 s	τ = 0.008 s	τ = 0.014 s
Mn^{2+} Linking	τ = 0.055 s	τ = 0.010 s	τ = 0.008 s
Zn^{2+} Linking	τ = 317 s	τ = 13 s	τ = 4 s
Co^{2+} Linking	(τ not accessible)	τ = 1800 s	(τ not accessible)

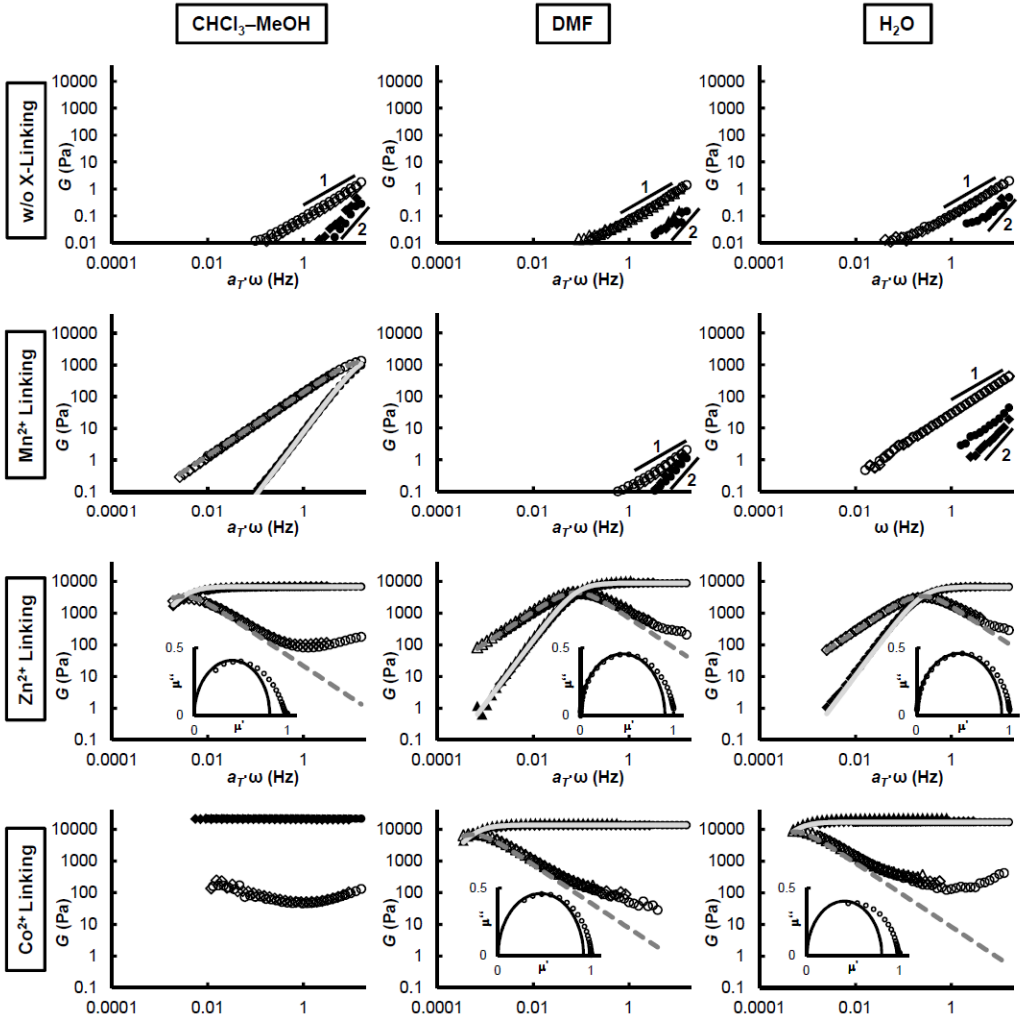


Relaxation times depends on the solvent and on the metal ions

Dynamics of unentangled transient Network

Supramolecular Polymer Gels with Potential Model-Network Structure

Torsten Rossow[a,b] and Sebast

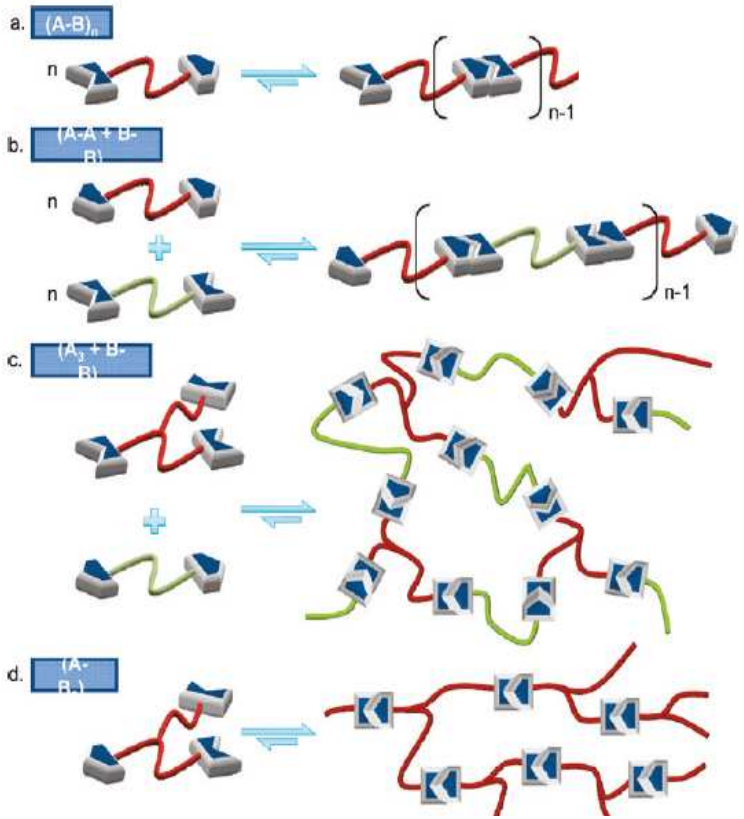


Relaxation times depends on the solvent and on the metal ions

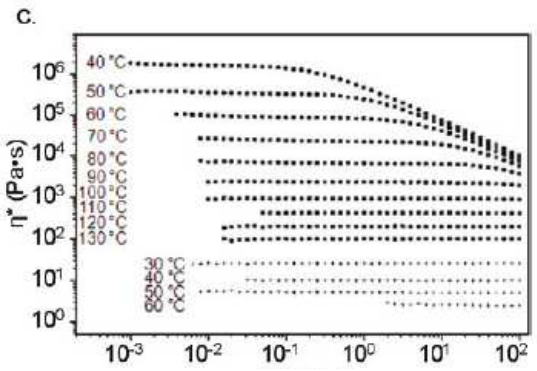
Influence of Temperature

Supramolecular Polymerizations and Main-Chain Supramolecular Polymers

D. Fox and Stuart J. Rowan*



H bonding



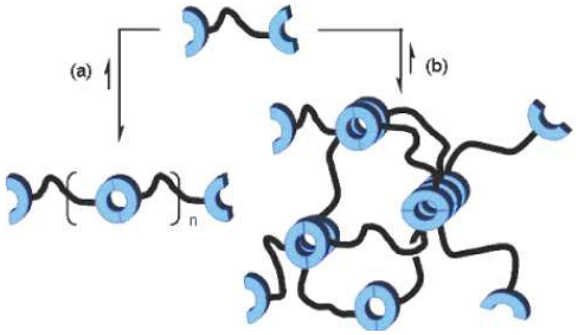
Relaxation times and plateau modulus depends on temperature

Additional effects of Upy groups

J|A|C|S
ARTICLES
Published on Web 11/30/2005

Utilization of a Combination of Weak Hydrogen-Bonding Interactions and Phase Segregation to Yield Highly Thermosensitive Supramolecular Polymers

Sona Sivakova,† David A. Bohnsack,‡ Michael E. Mackay,*,‡ Phiriyatorn Suwanmala,† and Stuart J. Rowan*,†



H bonding

Phase segregation

pTHF (2000 g/mol)

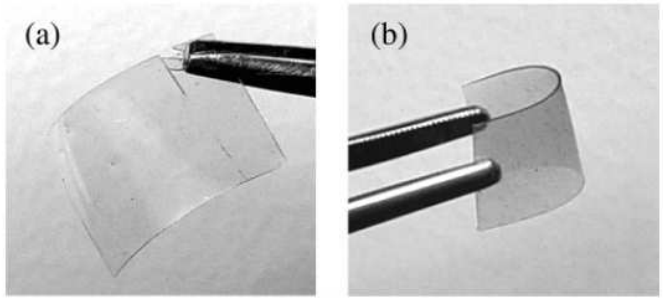
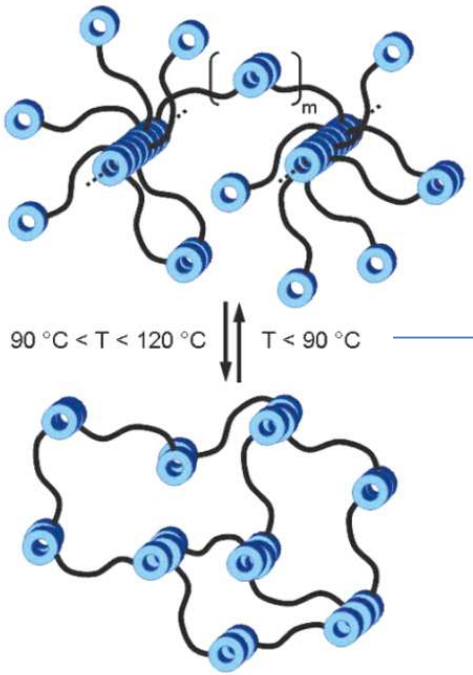
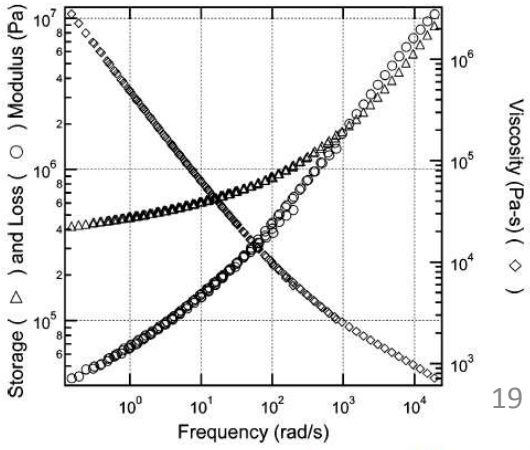


Figure 3. Pictures of the films formed from (a) $A^{An}3A^{An}$ and (b) $C^{Pbz}3C^{Pbz}$.

Temperature influence:

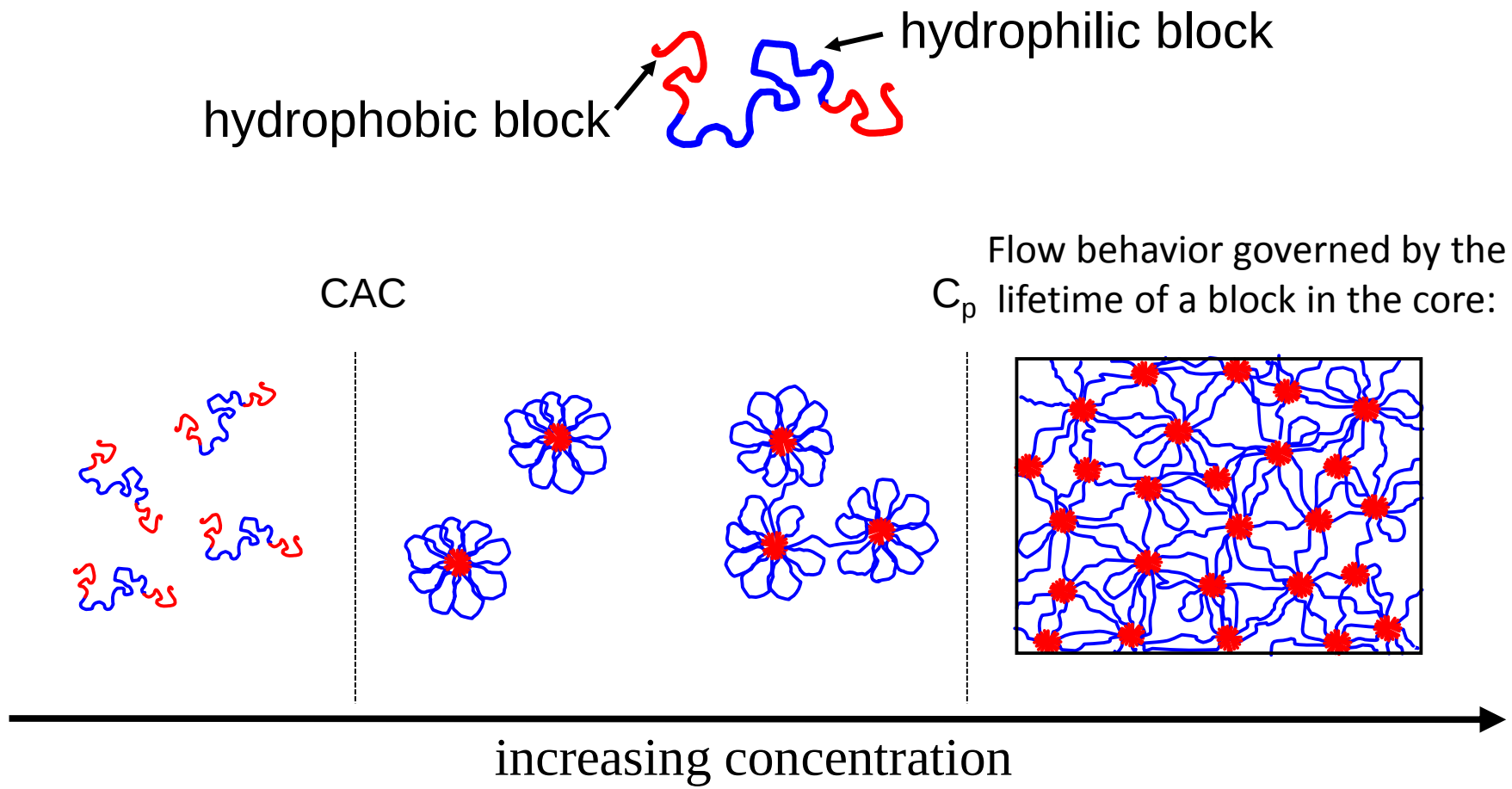


Up to 90C: The materials behaves like a normal (non relaxing) polymer



Self-assembly of triblock copolymers in solution

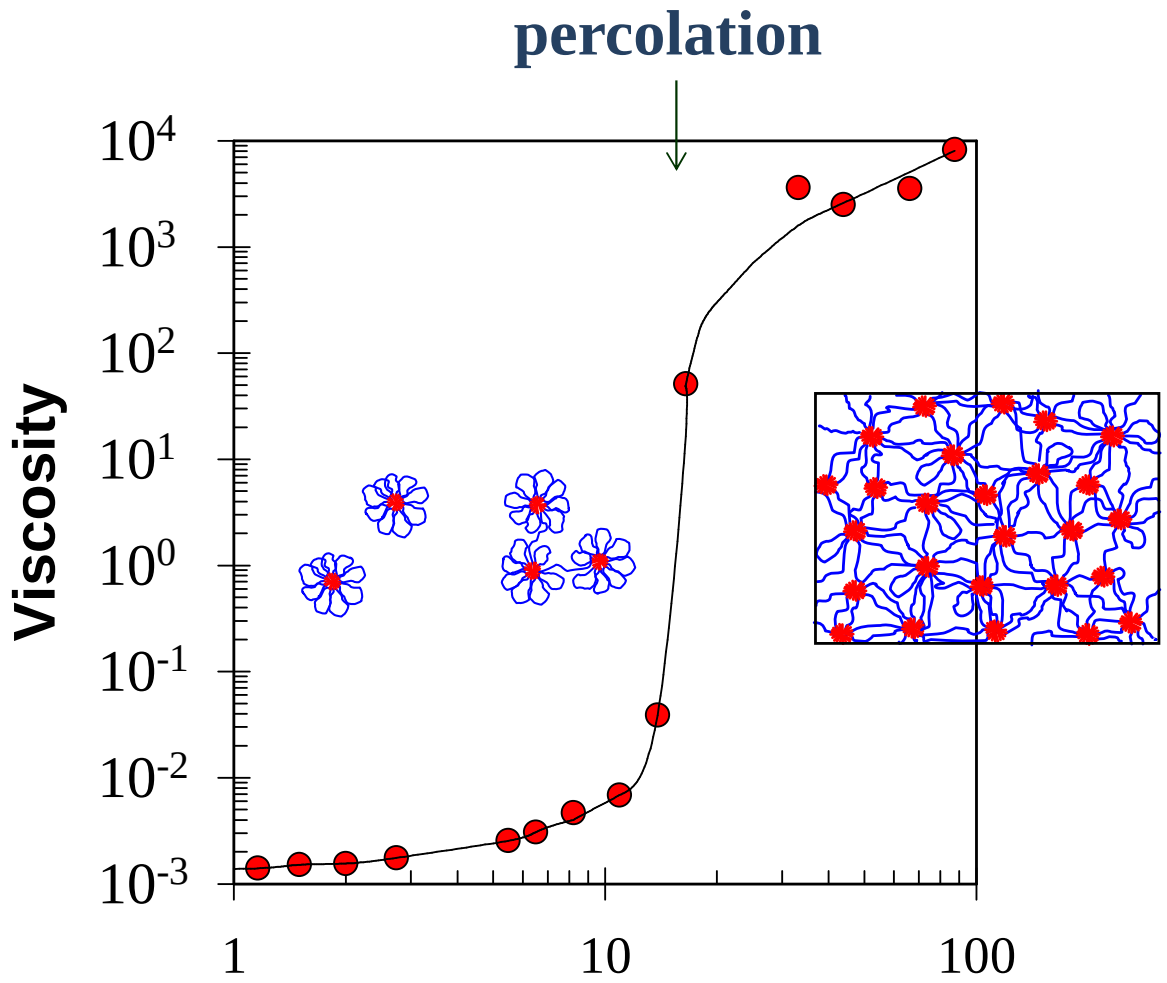
(from T. Nicolai)



The properties of this micellar network depends on the concentration, the association strength and the length of the triblocks

Self-assembly of triblock copolymers in solution

(from T. Nicolai)

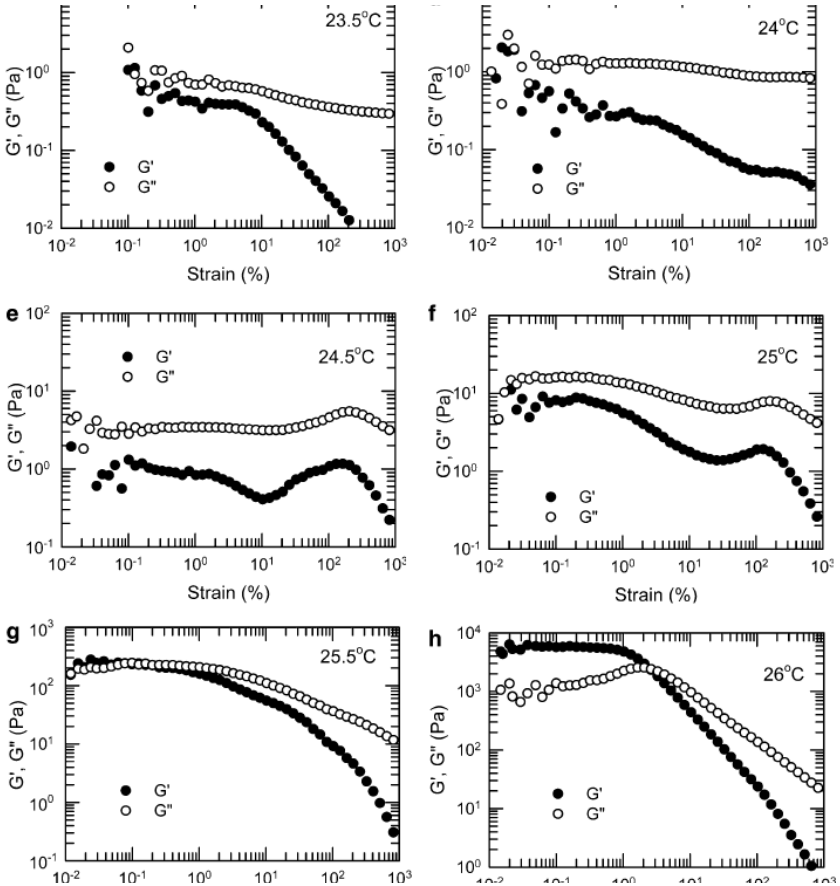


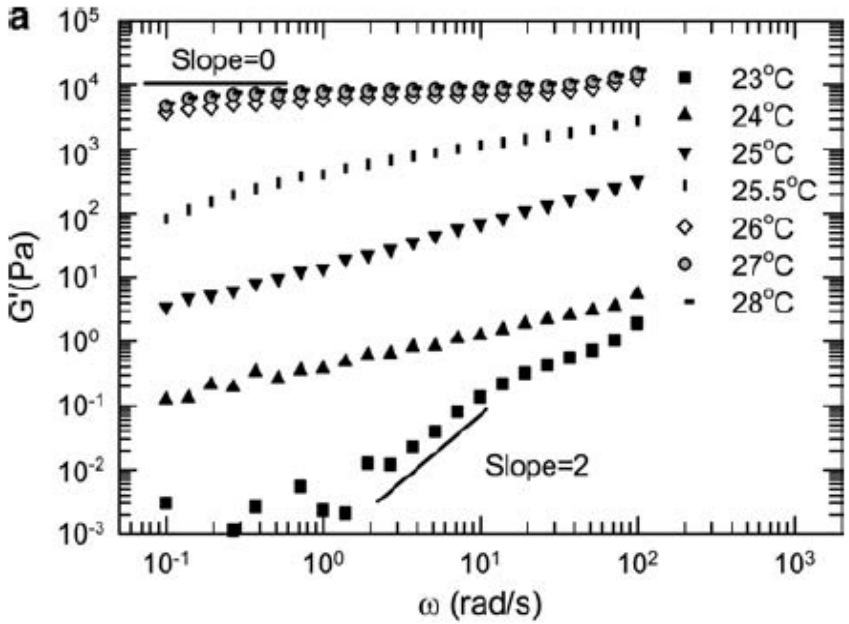
There is a minimum concentration needed to reach the percolation of the system

Shear thickening properties

Kyu Hyun
Jung Gun Nam
Manfred Wilhellm
Kyung Hyun Ahn
Seung Jong Lee

Large amplitude oscillatory shear behavior of PEO-PPO-PEO triblock copolymer solutions





Transient network can lead to shear thickening

Shear thickening properties

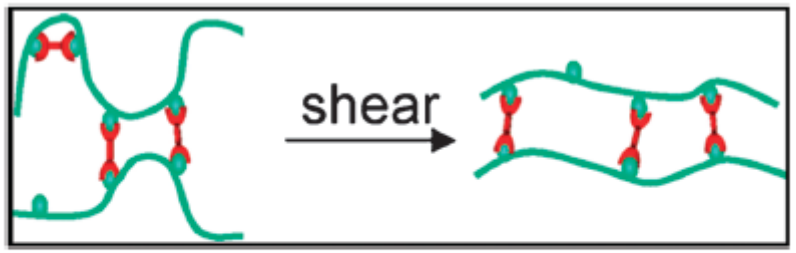
Mechanism of Shear Thickening in Reversibly Cross-Linked Supramolecular Polymer Networks

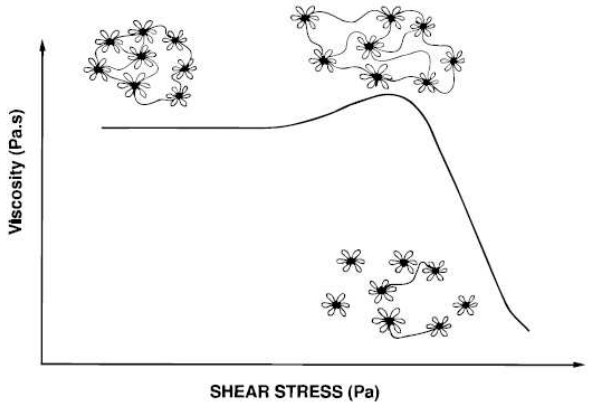
Donghua Xu, Jennifer L. Hawk, David M. Loveless, Sung Lan Jeon, and Stephen L. Craig*

There are mainly two propositions to explain the shear thickening:

- Non-Gaussian stretching effect within a network whose number of elastically active chains does not change during shear. This extended conformation partially relax when the chain end dissociates (Marrucci et al.)

- The shear thickening properties come from the coagulation of free chains into the existing network. (Wang et al.)





Shear thickening does not have a fully clear origin

Shear thickening properties

A new stochastic simulation for the rheology of telechelic associating polymers

Gun Woo Park[a] and Giovanni Ianniruberto

Strain hardening: FENE effect

(Brownian dynamics for HEUR solutions)

Deviation from Cox-Merz: persistence of bridge chains and flow-induced creation of new bridges

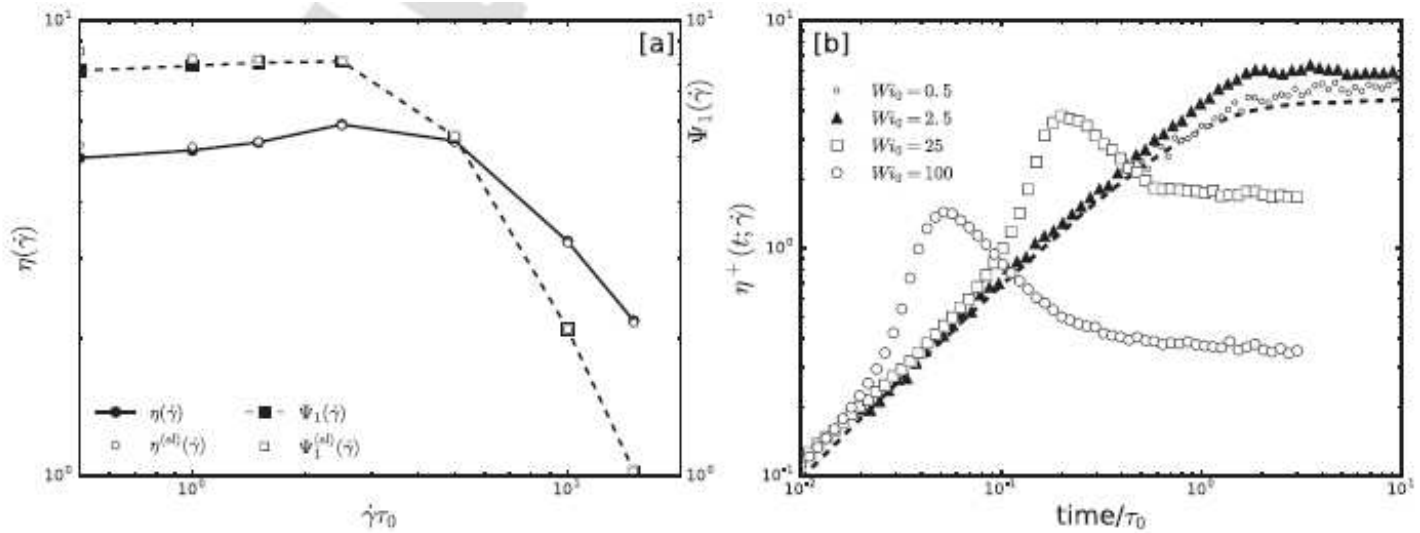


FIG. 12. Steady-state shear viscosity and first normal stress difference coefficient vs shear rate (a) and shear stress growth function during startup (b), for $n_c = 7$ and $\nu_m = 2$. Other parameters are as in Fig. 6.

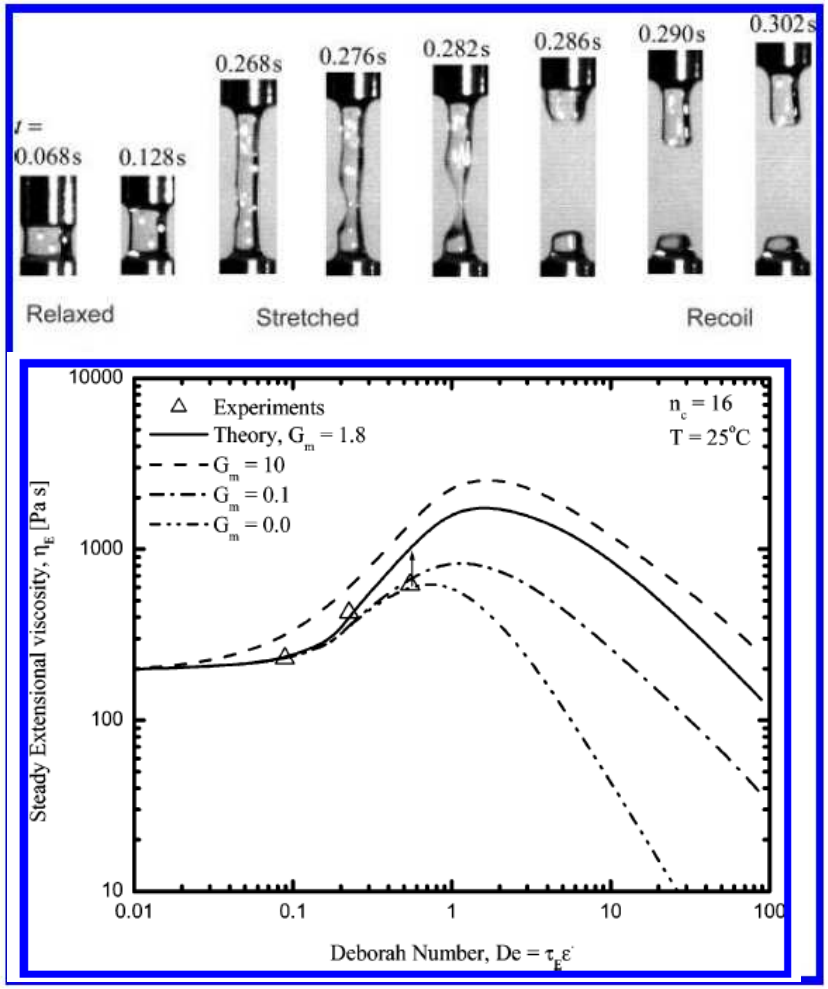
JOR, 2017

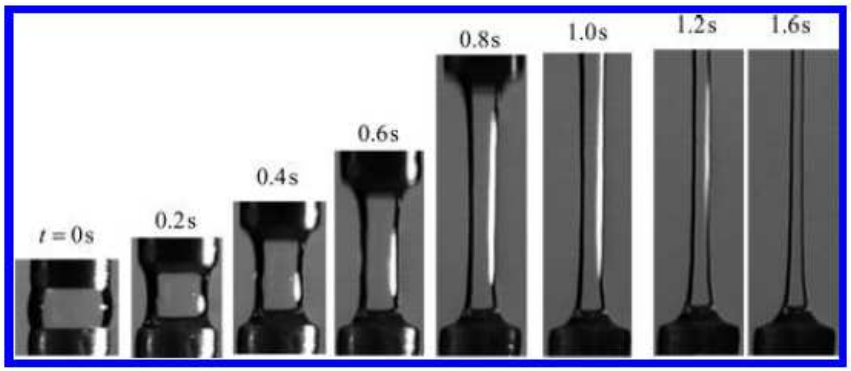
Elongation properties

Rheology and Dynamics of Associative Polymers in Shear and Extension: Theory and Experiments

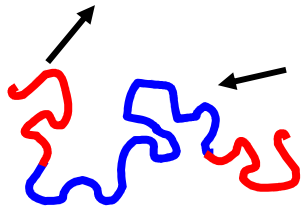
Anubhav Tripathi,*,† Kam C. Tam,‡ and Gareth H. McKinley§

Macromolecules **2006,** *39,* 1981−1999





hydrophobic block



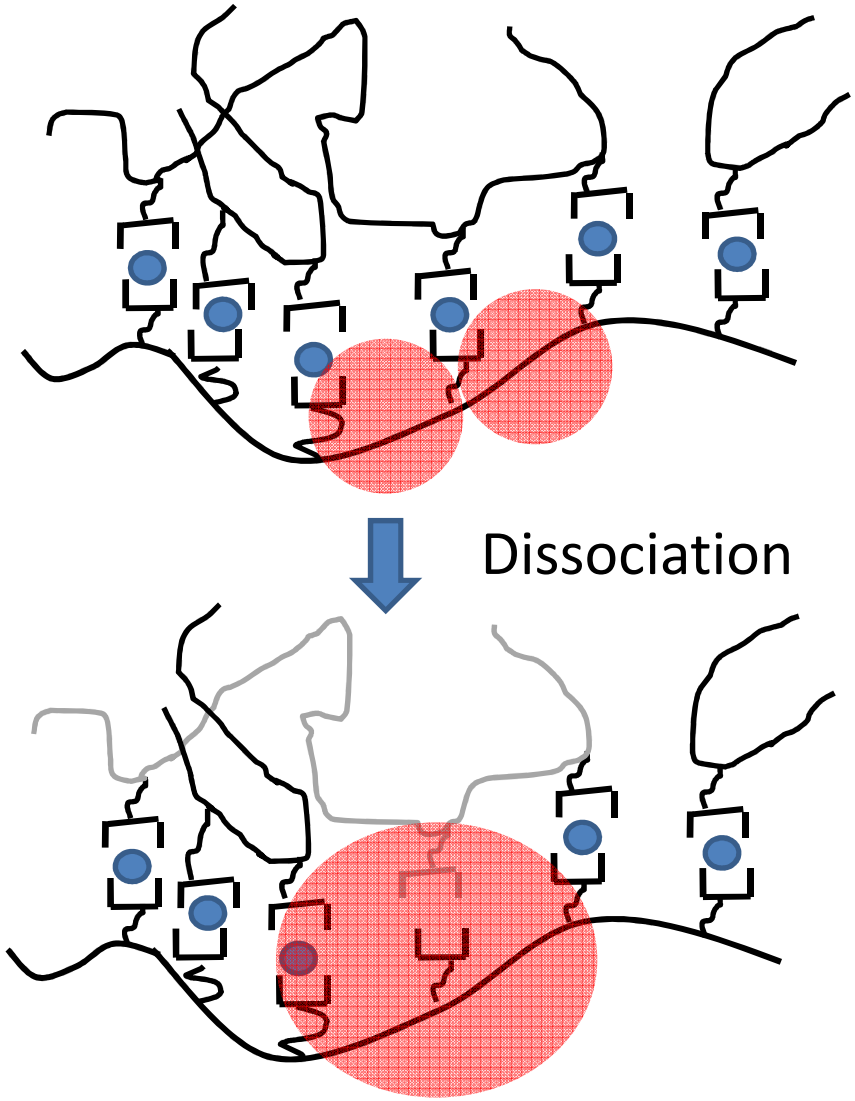
hydrophilic block

Dynamics of unentangled transient Network

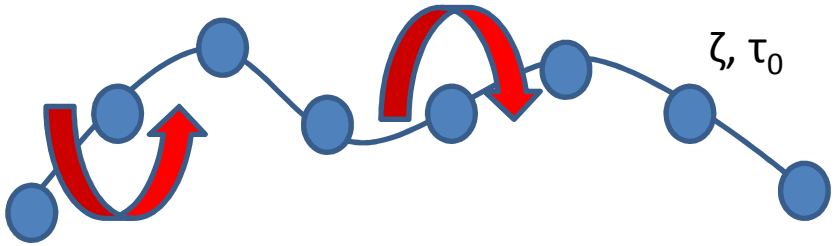
Few examples…

- Telechelic molecules
- Sticky chains

Unentangled sticky chains



Like a Rouse process, governed by the lifetime and number of the sticky groups (release of local constraint)



Sticky Rouse model
(Rubistein, Colby)

$$\tau_{rel} = \tau_{sticker} \#_{sticker}^{2}$$

Extra space to move (if not entangled)

Unentangled sticky chains: ionomers

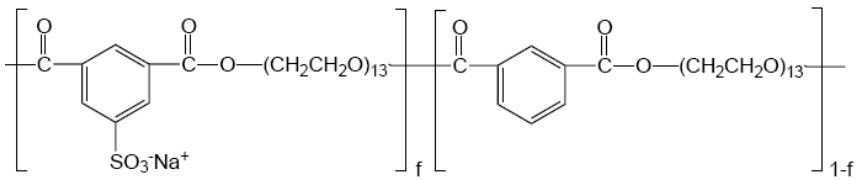
Sulfonated PEO and PTHF

Block copolymer:

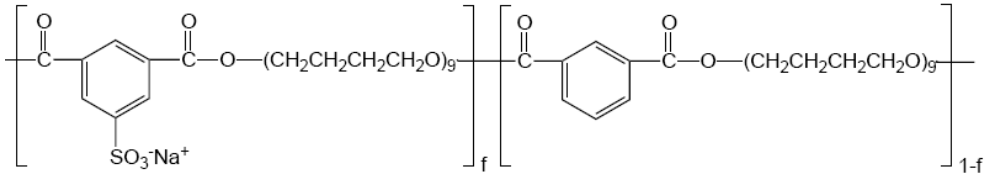
PEO (M= 400, 600 & 1100 g/mol)
PTHF (M=650 g/mol)

Mn ~ 4K-14K

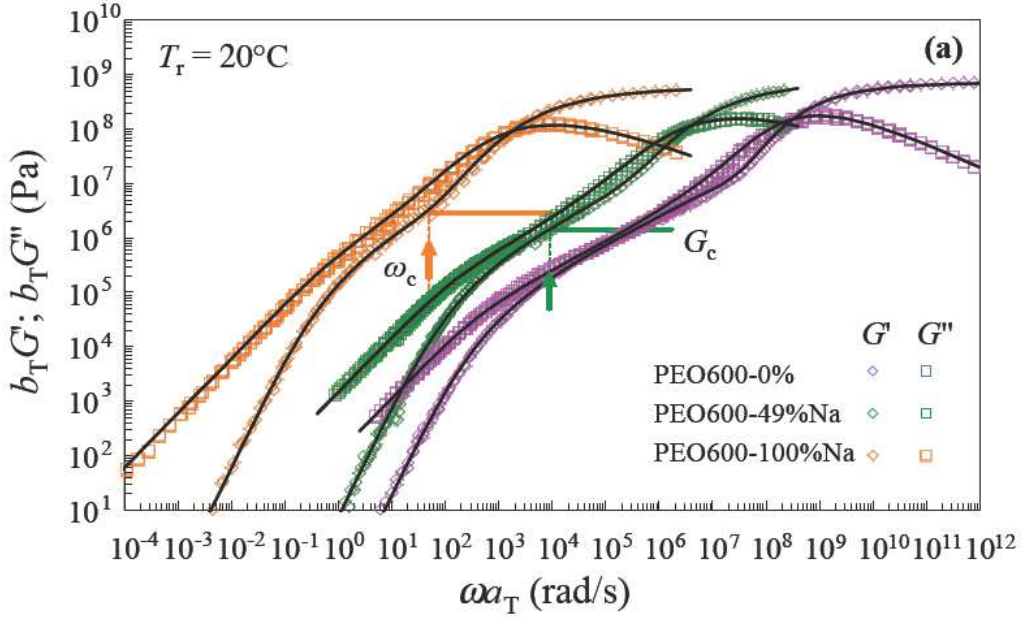
(a) PEO600-*f*Na



(b) PTMO650-*f*Na



Effect of Ion content:



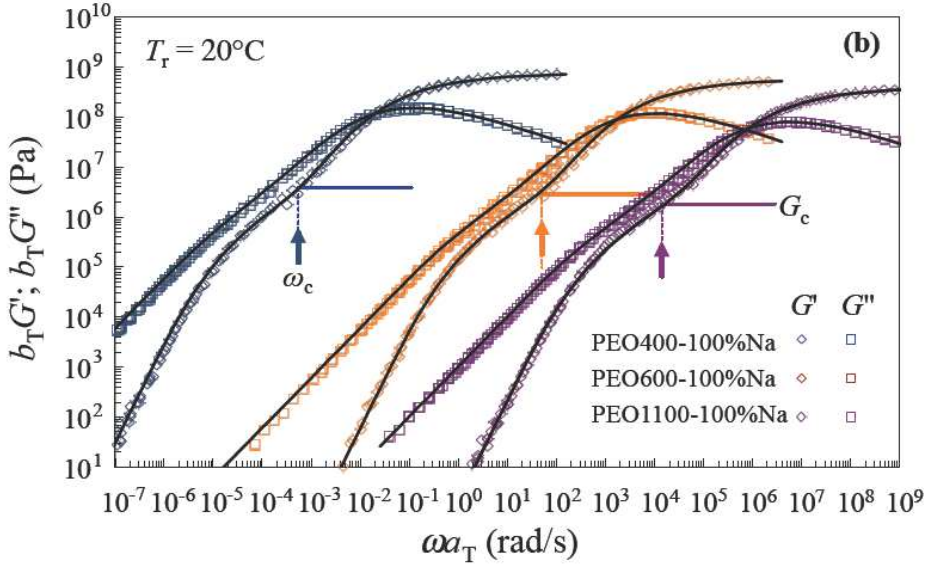
Both glassy and polymeric relaxations are delayed

Unentangled sticky chains: ionomers

Colby et al. J Rheol, 2013

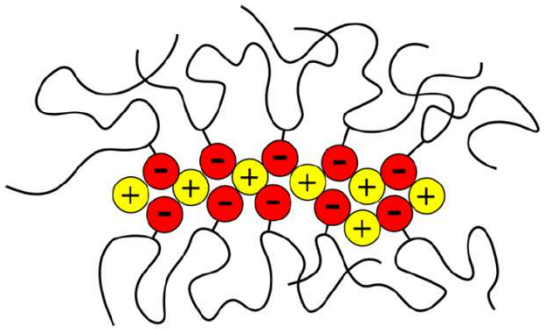
Effect of the length of the sulfonated PEO blocks:

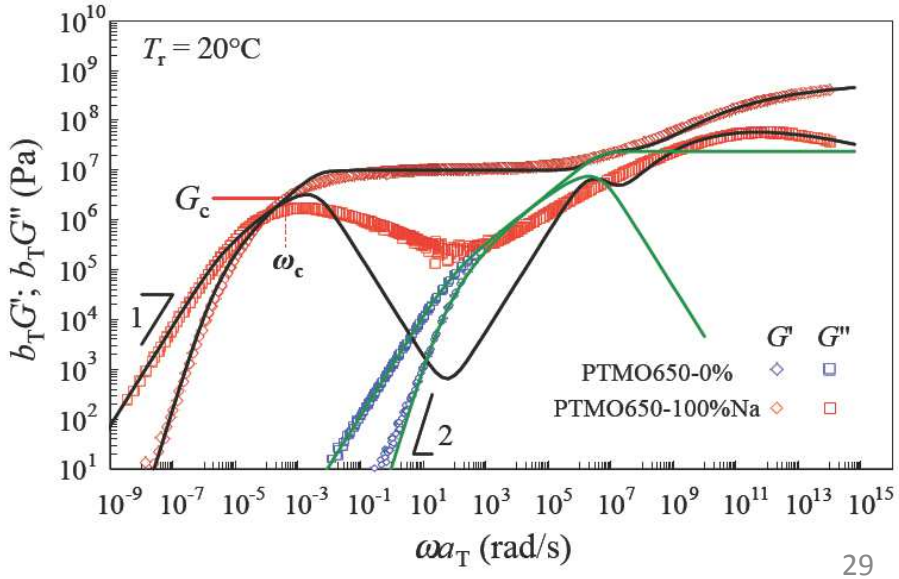
Both glassy and polymeric relaxations are delayed



Influence of the nature of the sulfonated blocks:

With PTMO: Lower ion solvation ability of PTHF, Higher activation energy of cluster dissociation





Chain dynamics against sticker dynamics

Association energy in strongly associative polymers

(unentangled)

Zhijie Zhang

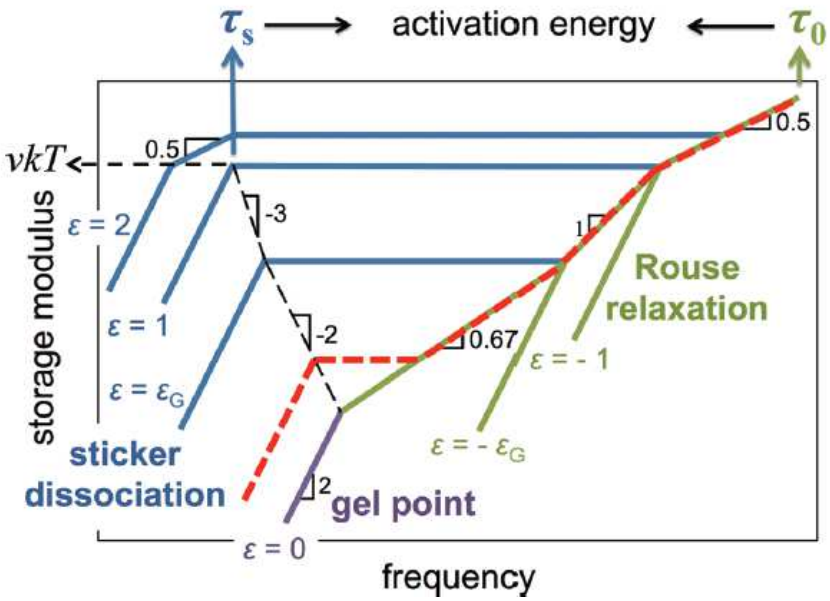
State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

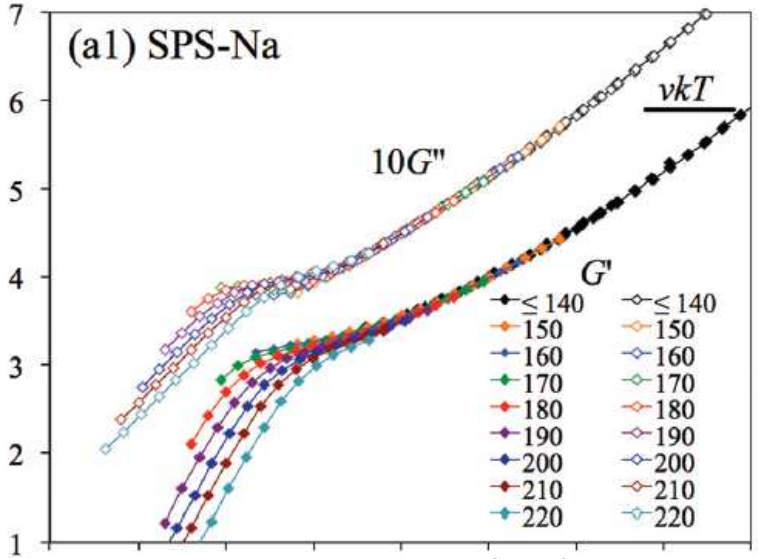
Chongwen Huang and R. A. Weiss

Department of Polymer Engineering, University of Akron, Akron, Ohio 44325

Quan Chen[a)]

JOR 2017





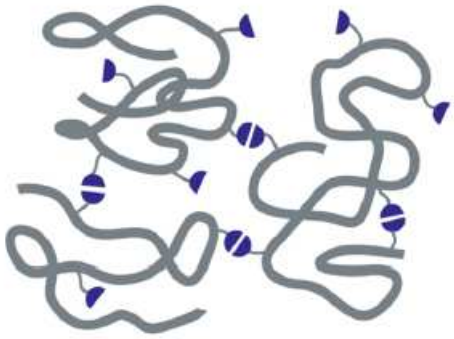
$$\tau_s = \tau_0 \exp\left(\frac{E_a}{kT}\right)$$

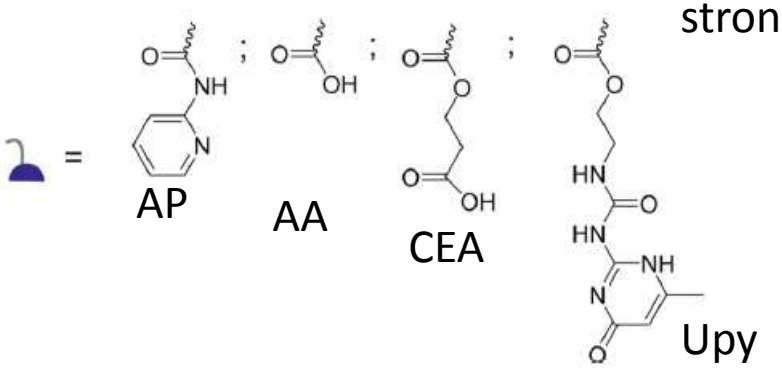
Unentangled sticky chains

The Influence of Hydrogen Bonding Side-Groups on Viscoelastic Behavior of Linear and Network Polymers

Christopher L. Lewis, Kathleen Stewart, and Mitchell Anthamatten*

From weak to strong bonds

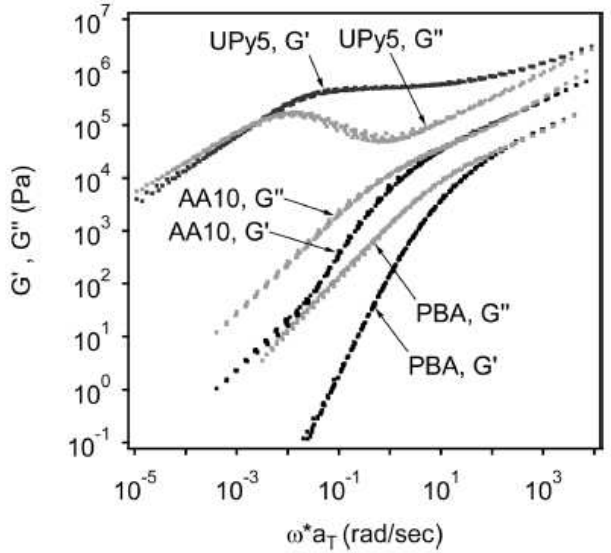




PBA polymer, Mn = 32 kg/mol

sample	H-bonding monomer feed [mol %]
PBA	0
AP5	5.4
AP10	10
AP15	15
AA6	7
AA10	13
AA23	25
CEA5	5
CEA12	12
UPy1	1
UPy2	2
UPy5	5

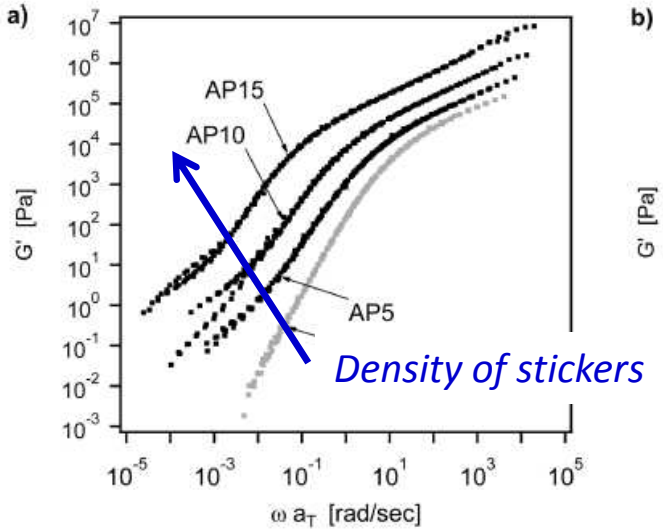
[a] x_{HB} is the mole fraction of H-bonding monomer,

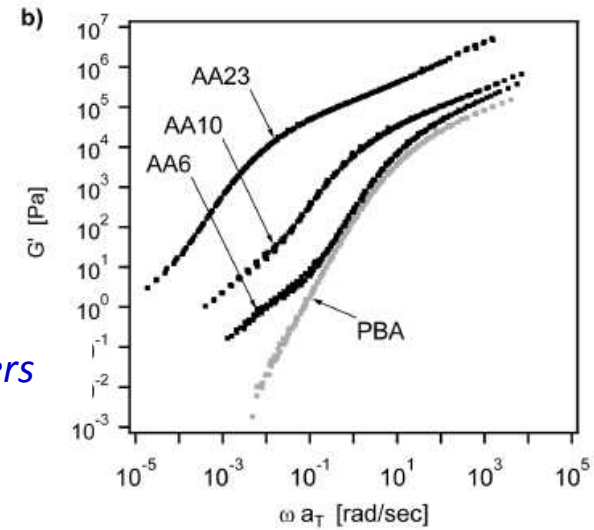


Strength of the side-groups strongly influences the flow properties

Unentangled sticky chains

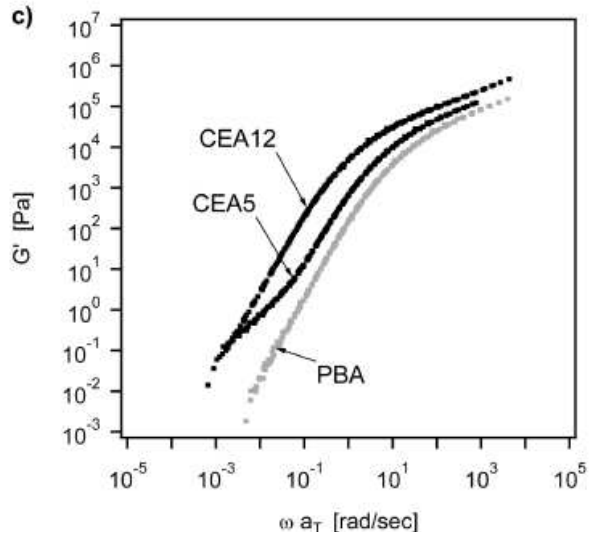
Increasing the density of supramolecular junctions:

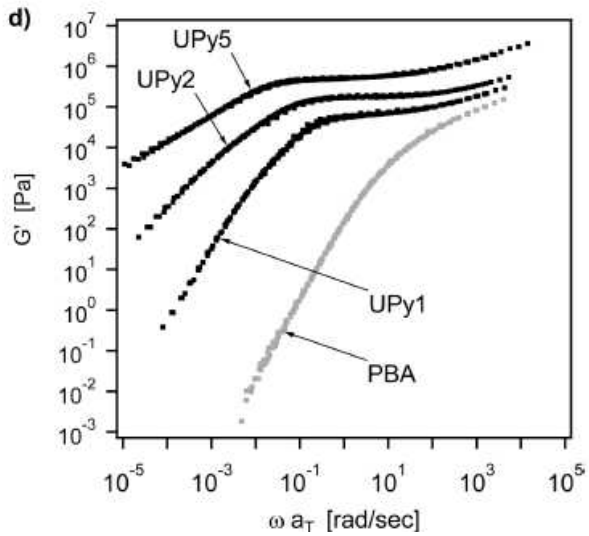




From weak to strong bonds

AP AA CEA Upy



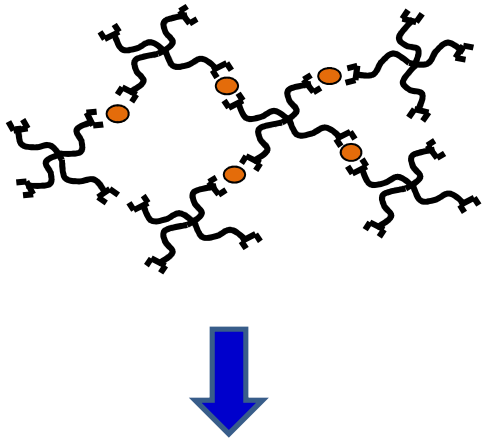


To be noted:
Tg varies according to the density of transient bonds

Density of the side-groups strongly influences the flow properties

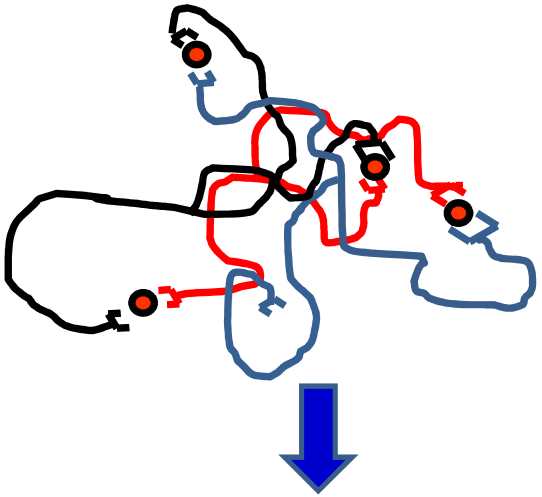
II) Dynamics of Transient Networks based on entangled building blocks

Unentangled vs entangled transient Network



Elastic plateau and relaxation time: fully governed by the supramolecular junctions

Many works in literature on this kind of supramolecular polymers

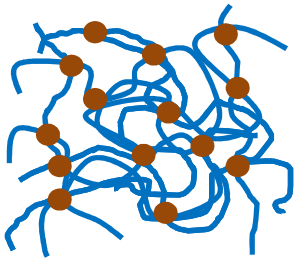


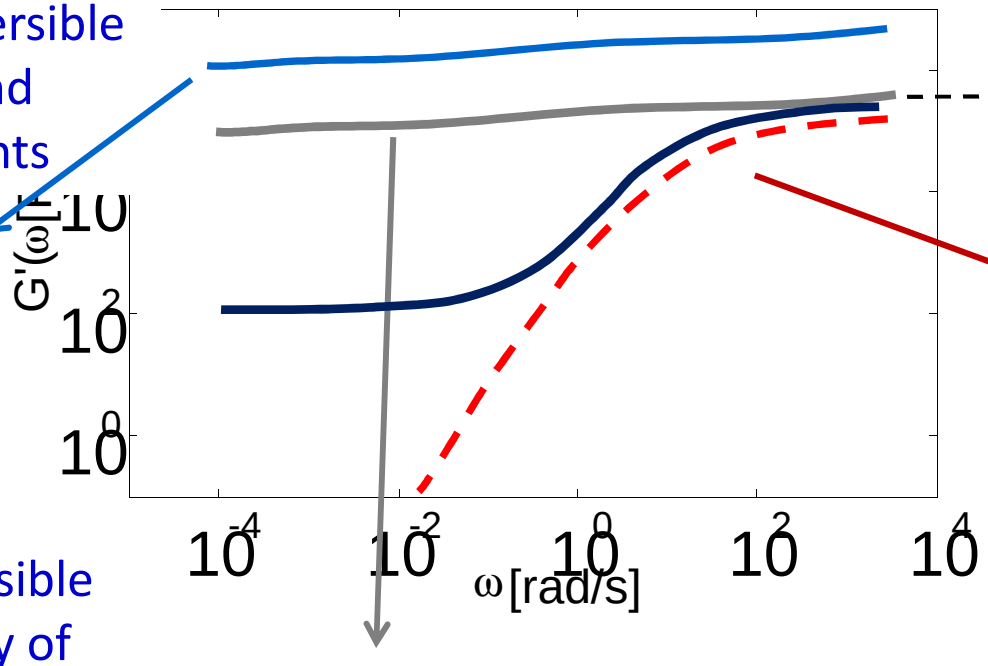
Elastic plateau:
also governed by the entanglement segments

Relaxation time:
Governed by both the supramolecular junctions and the entanglements dynamics

Entangled transient Network

Network governed both by the reversible junctions and entanglements



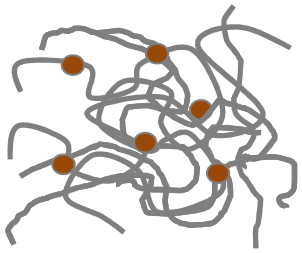


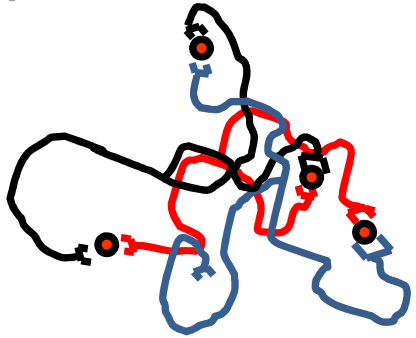
Entangled polymer melts

Density of reversible bonds > density of entanglements

$$G_0^N = \frac{4}{5}\frac{\rho RT}{M_e}$$

Entangled polymer melt unable to relax

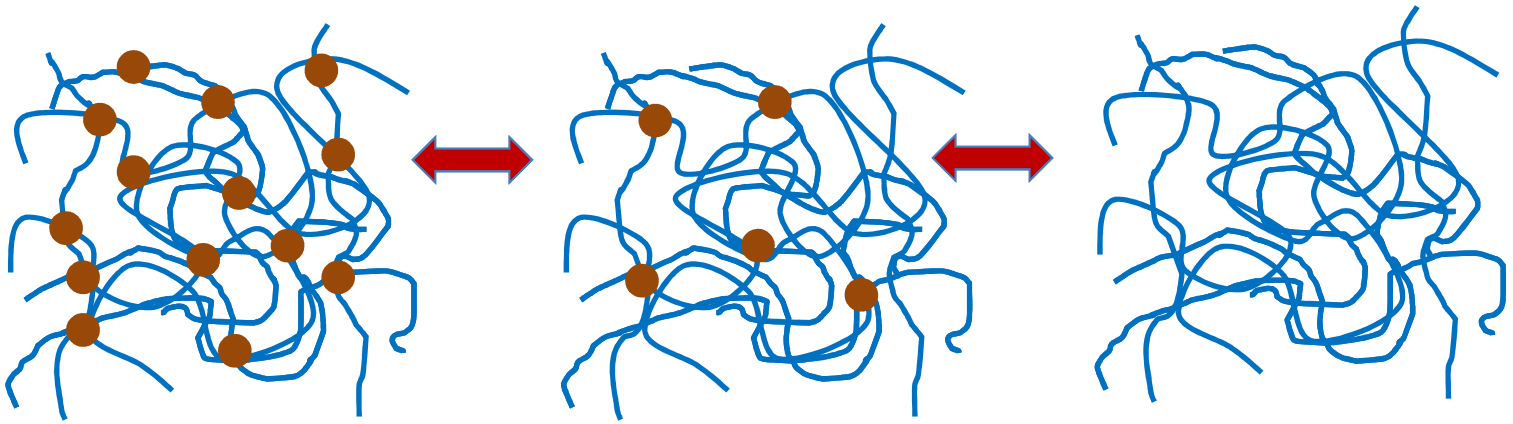




Density of reversible bonds << density of entanglements

Entangled transient Network

Depending on the density of supramolecular junctions:



Rubber

Non relaxing entangled polymer

Viscoelastic polymer melts

The relaxation time depends on:

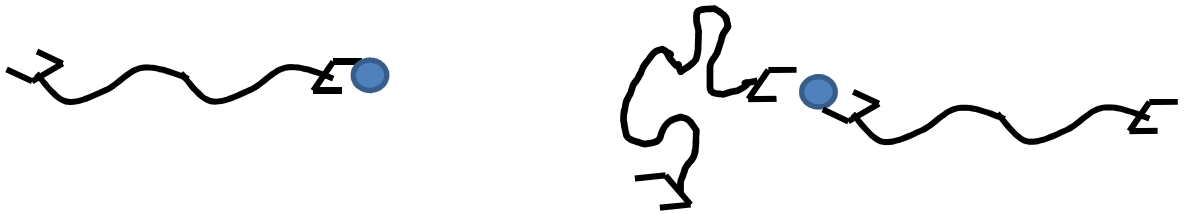
- Lifetime of the supramolecular junctions (stimuli responsive)
- Architecture of the building blocks (disentanglement time)
- M_e

Entangled transient Network from unentangled molecules

Dissociation

Reptation of the whole object

Relaxation of the building blocks



(see also the work of C. Ligoure and L. Ramos)

(see the model of Cates for living polymers)

Entangled transient Network from unentangled molecules

Humidity affects the viscoelastic properties of supramolecular living polymers

A. Louhichi and A. R. Jacob

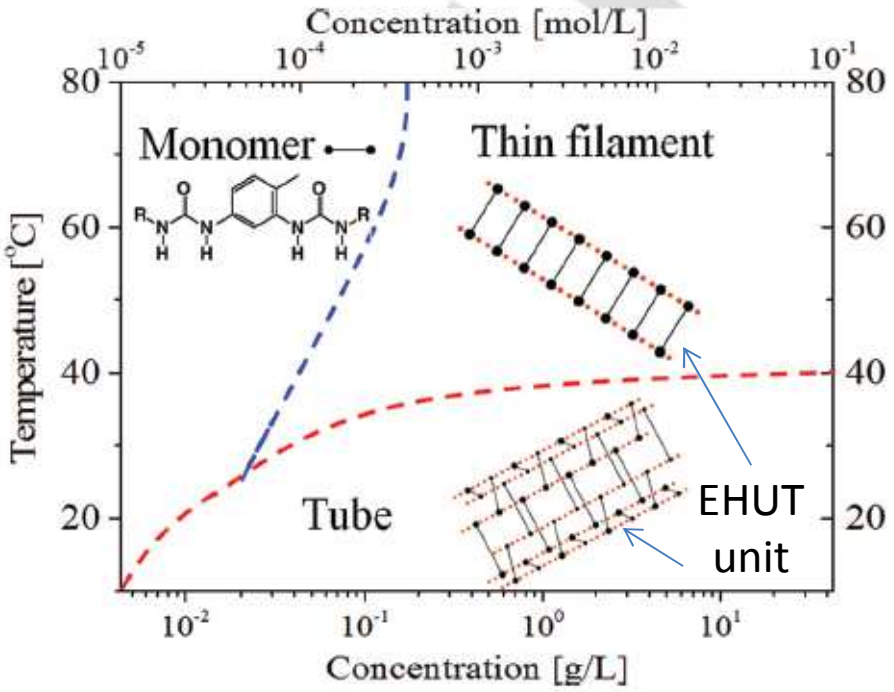
Institute of Electronic Structure and Laser, FORTH, Heraklion 70013, Crete, Greece and Department of Materials Science and Technology, University of Crete, Heraklion 71003, Crete, Greece

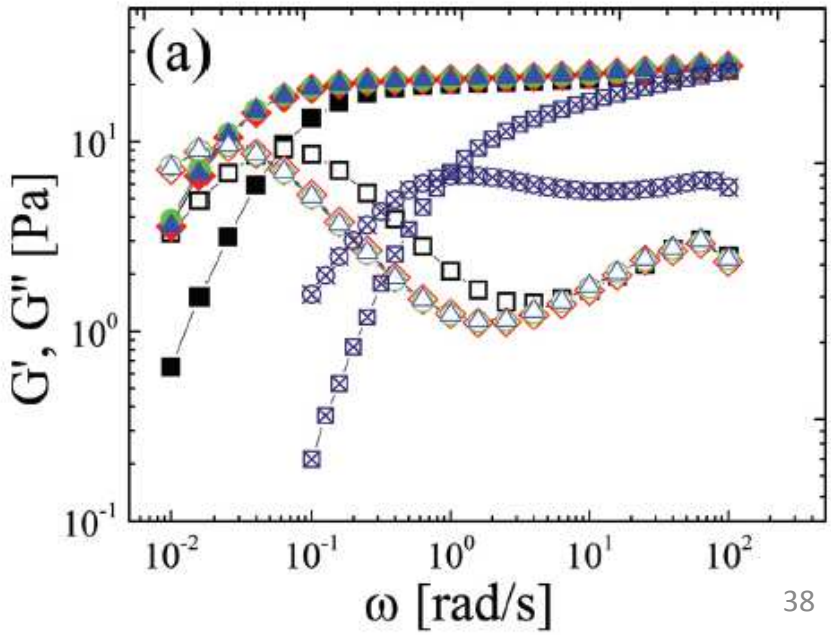
L. Bouteiller

Sorbonne Universités, UPMC Univ. Paris 06, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, 4 Place Jussieu, F-75005 Paris, France

D. Vlassopoulos[a)]

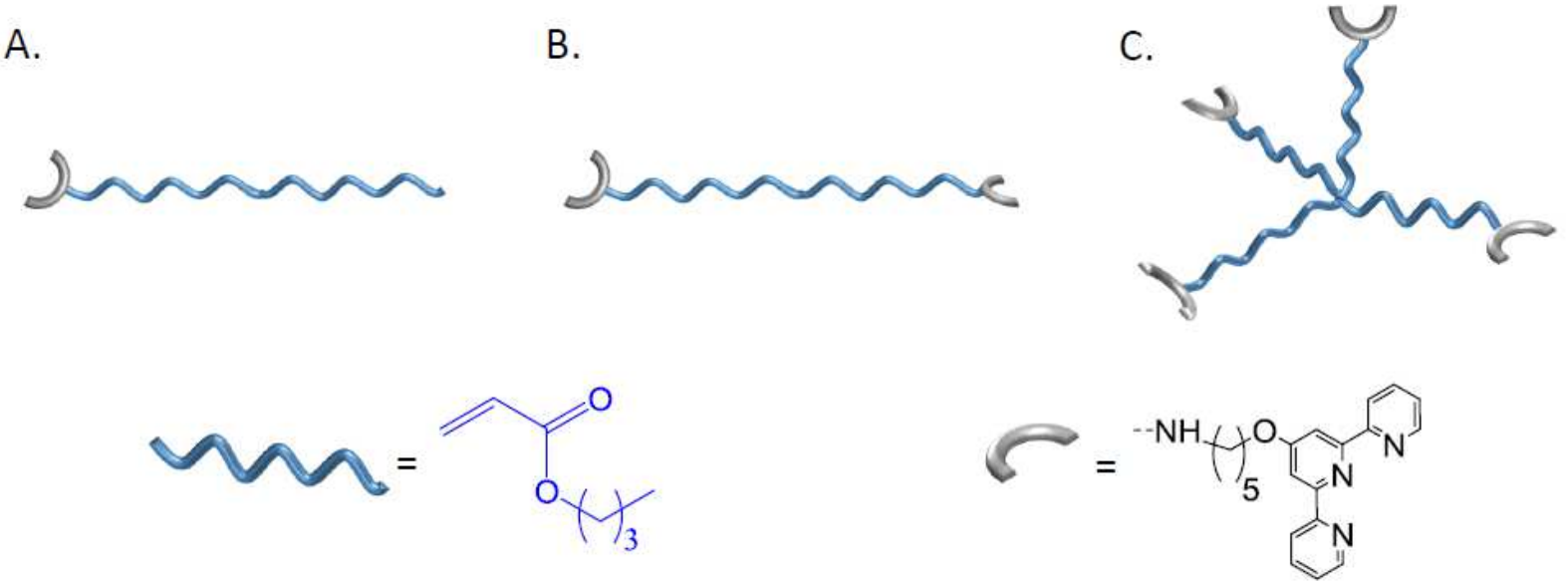
JOR2017





Metallo-supramolecular PnBA polymers

A. B. C.



	Sample	Mn*[a] (g/mol)	Ma†[a] (g/mol)	Đ[b]	Z	Tg[d] (°C)
A.	$PnBA_{100.9k}$-tpy	100 900	/	1.14	5.9	-52
B.	$PnBA_{113.2k}$-tpy_2	113 200	/	1.13	6.7	-53
C.	$PnBA_{107.3k}$-tpy_4	107 300	40 000	1.25	2.3/arm	-53

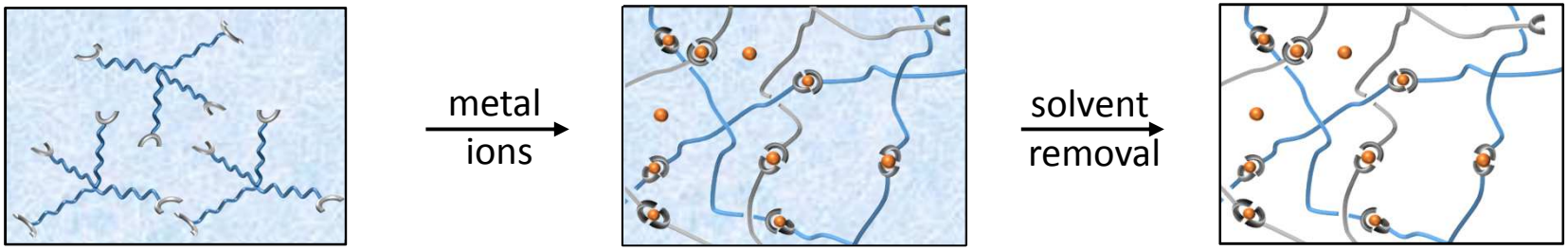
*Molecular weight of the whole system. †Molecular weight per arm.

[a]Determined by ^{1}H-NMR. [b]Measured by SEC in DMF+NH_4PF_6 eluent. [c]Me(P*n*BA)=17 kg/mol). [d]Measured by DSC.

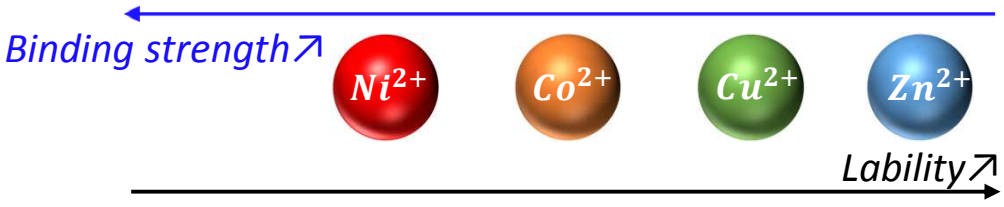
Flanco Zhuge, PhD project

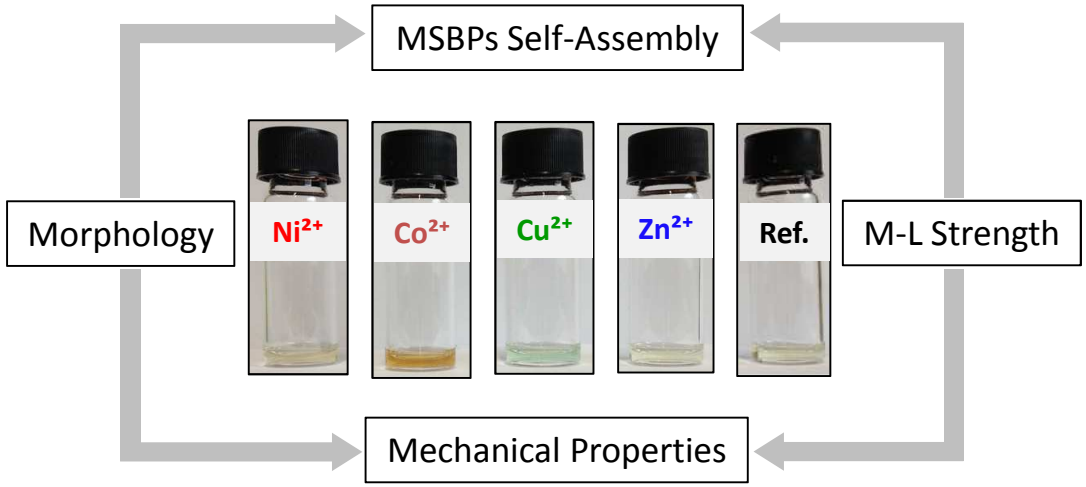
Metallo-supramolecular PnBA polymers

Sample preparation identical to organo-gel but at high concentration (C ≥ 400 g/L)

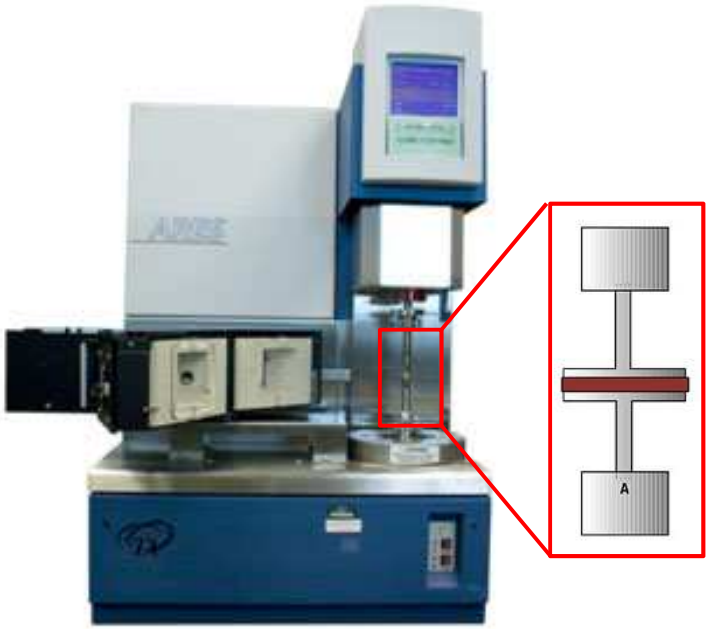


Transition metal ions



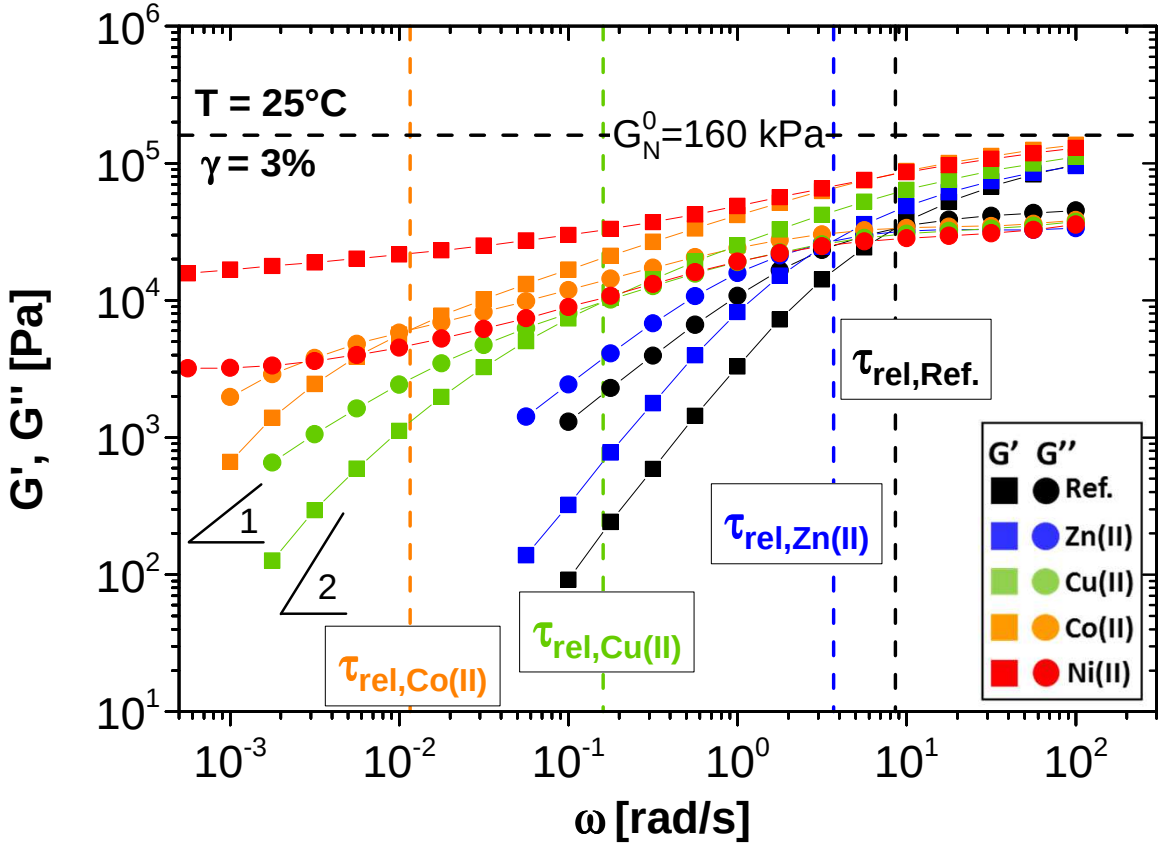


ARES Shear rheometer



⇨ Correlate Structure with Mechanical Properties

Influence of the metal ion nature

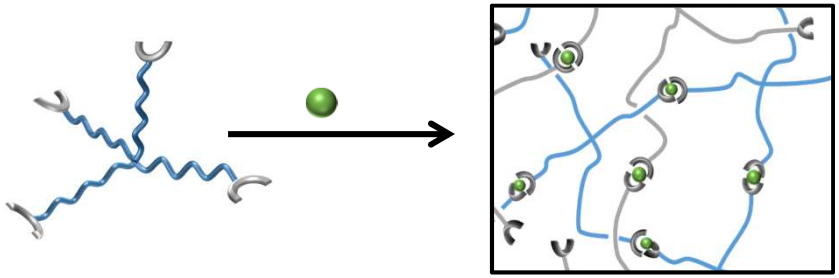


- ✓ $\tau_{rel} = 2\pi/\omega$ ↗ upon addition of metal ions
- ✓ Formation of M-L cross-links
- ✓ M : $Ni^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+}$

$$K = \frac{k_f}{k_{diss}}$$

Inorg. Chem. **1966**, *5*, 622–625

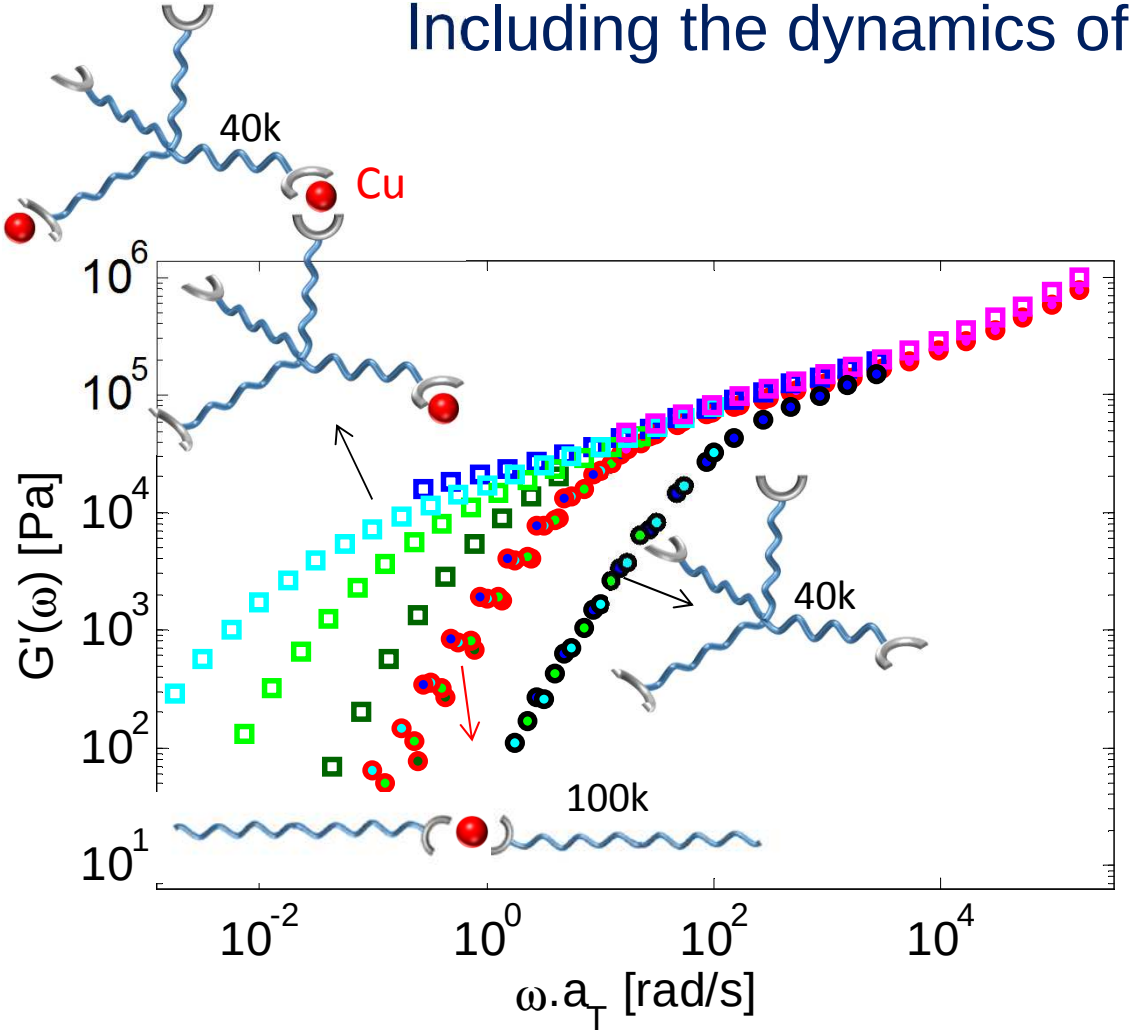
M_n = 249 kg/mol
Đ = 1.20
Z = 3.4/arm



Macromolecules **2017**, *50*, 5165-5175

Influence of the metal ion amount

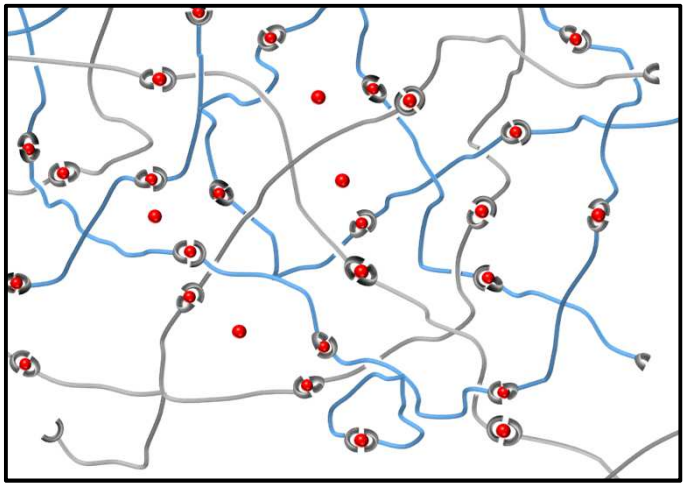
Including the dynamics of the stickers



0.5eq. Ions

At time t=0:
part of the arms are not associated and can relax

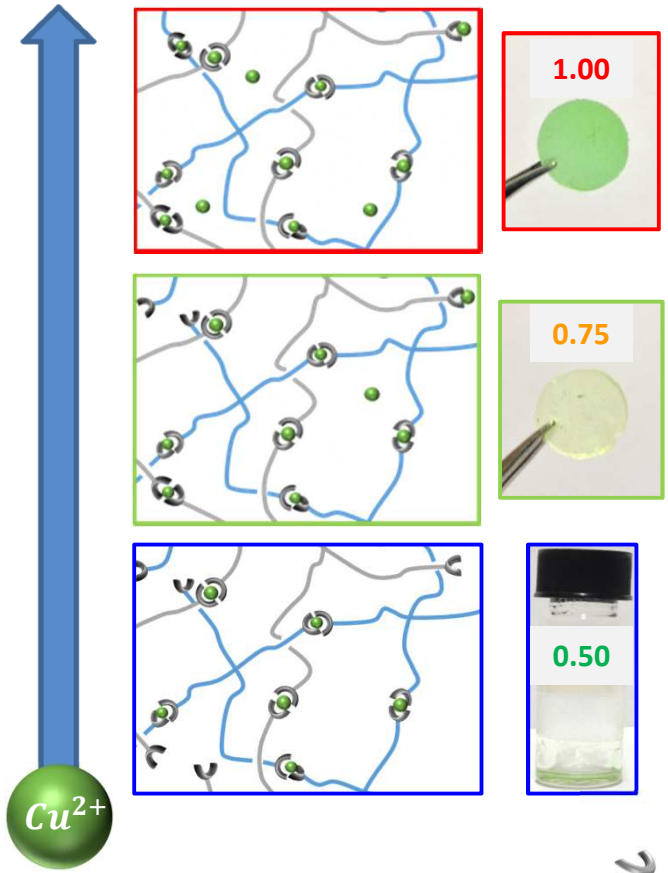
$\tau_{fluc} << \tau_{ass}, \tau_{exchange}$

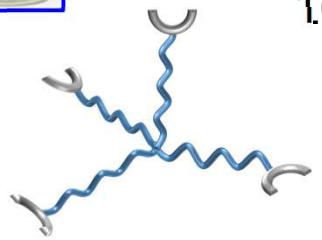


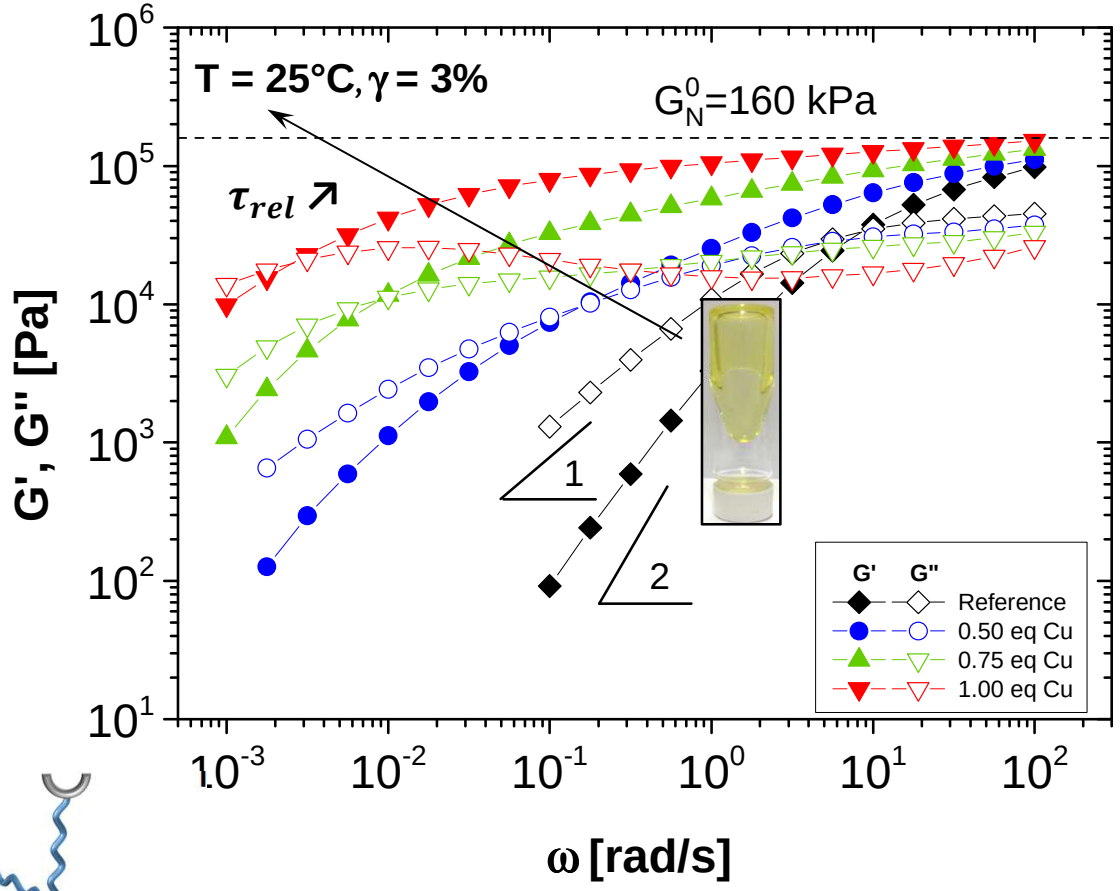
Dangling arms

Influence of the metal ion amount

eq. Cu(II) added ↗

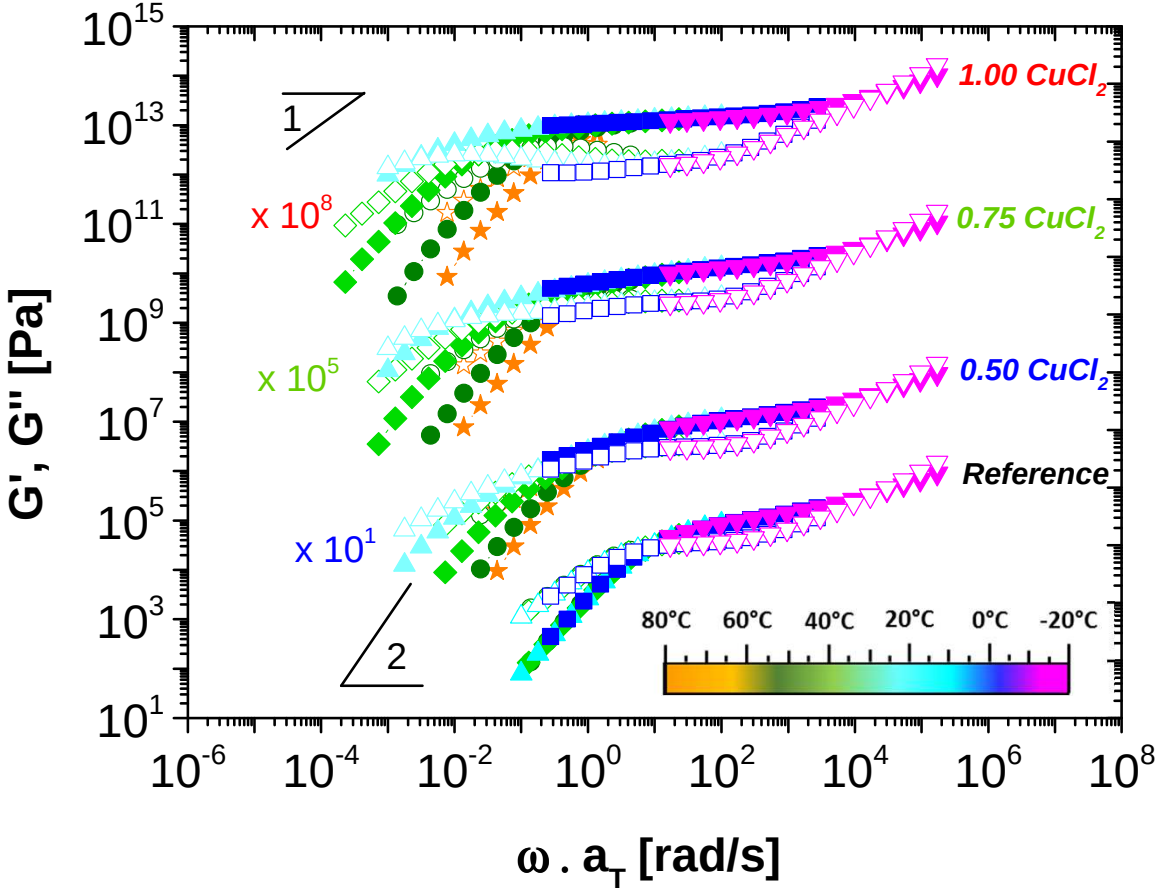






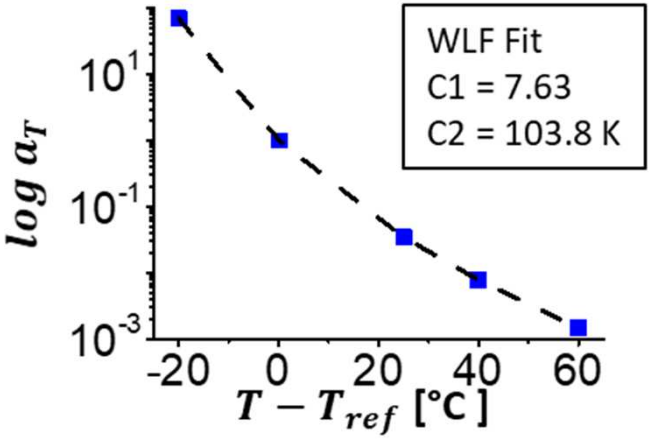
Journal of Rheology **2017,** *61,* 1245-1262

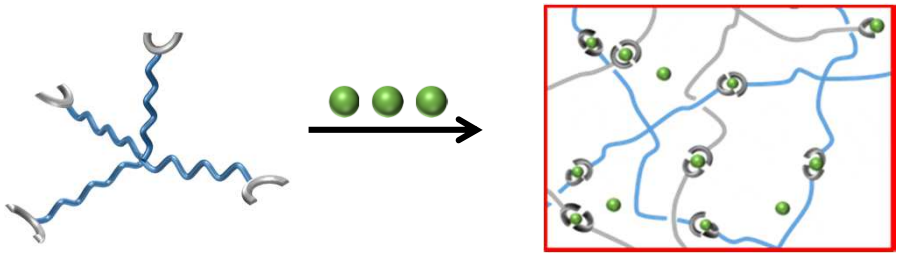
Influence of Temperature



⇨ **Thermo-rheological complexity**

- ✓ Thermo-rheological complexity
- ✓ Stickers temperature dependent
- ✓ No well fitted master curves

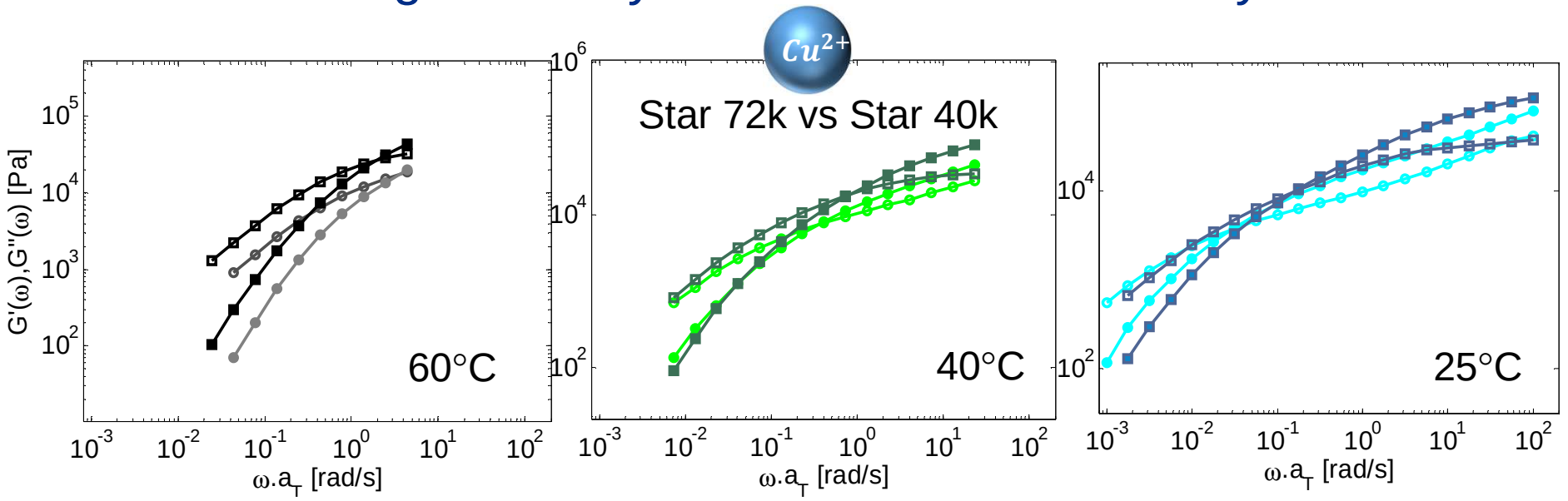


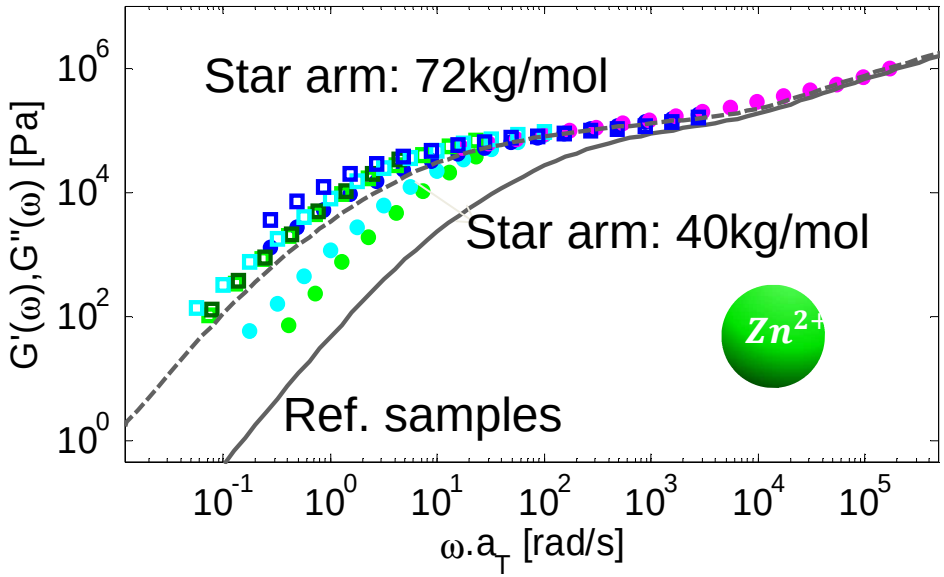


Macromolecules **2017,** *50,* 5165-5175

Metallo-supramolecular PnBA polymers

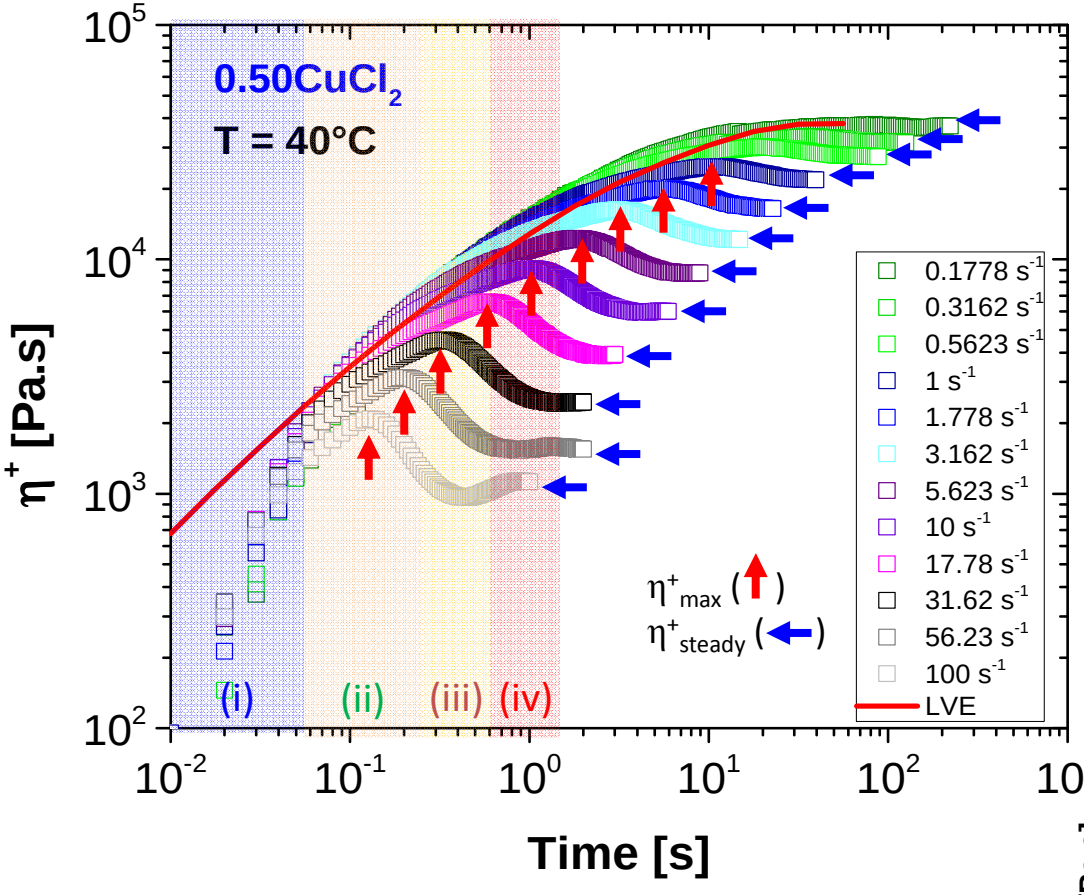
Disentanglement dynamics versus stickers dynamics

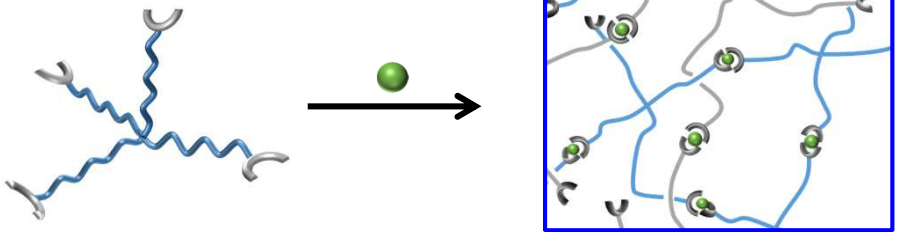




Terminal relaxation depends on both disentanglement and supramolecular dynamics

Nonlinear Shear rheology of PnBA stars





Measured with the CPP (S. Costanzo, D. Vlassopoulos)

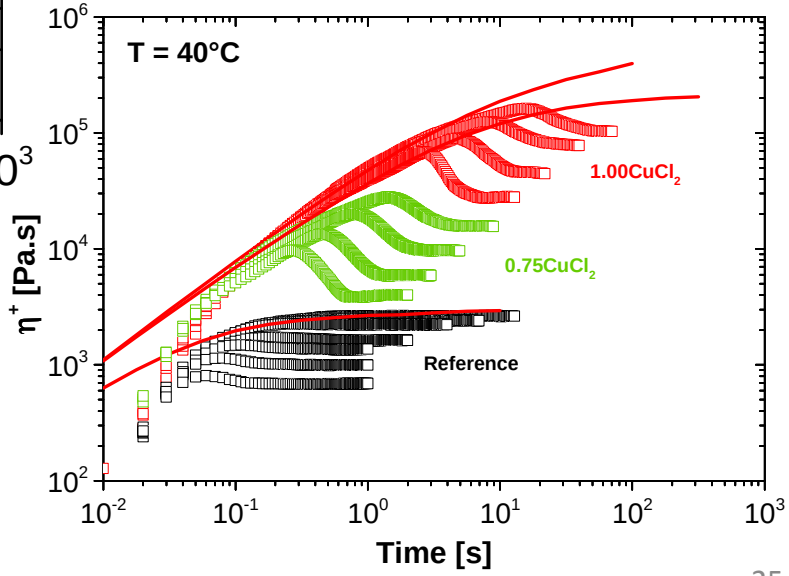
⇨ **Transient shear viscosity**

✓ Presence of four regions

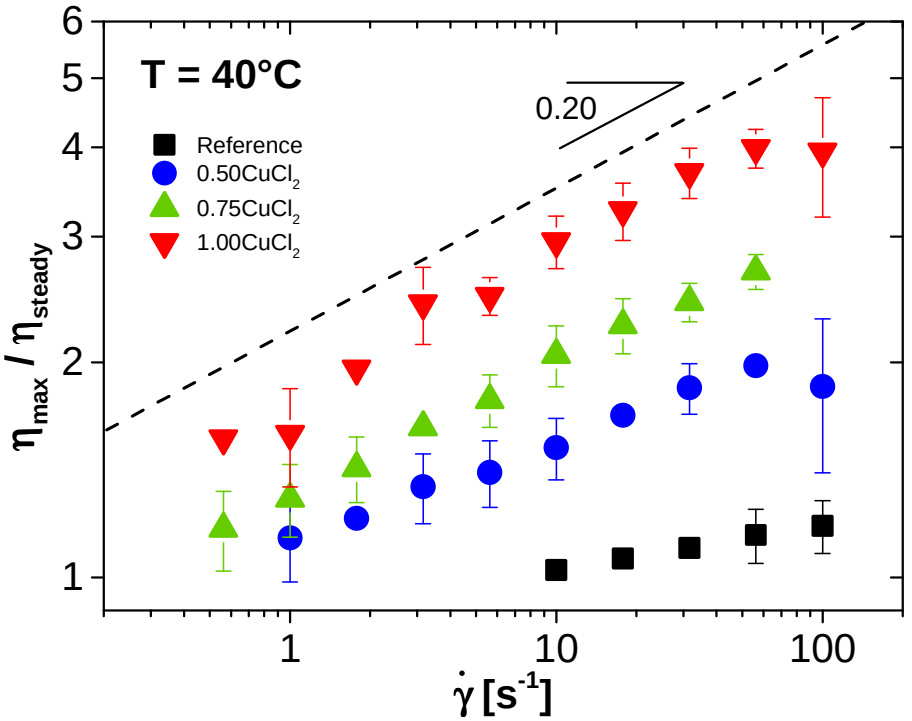
(i) Viscosity ↗ linearly
(ii) Overshoot (orientation, stretching)
(iii) Undershoot (tumbling effect)
(iv) Steady state

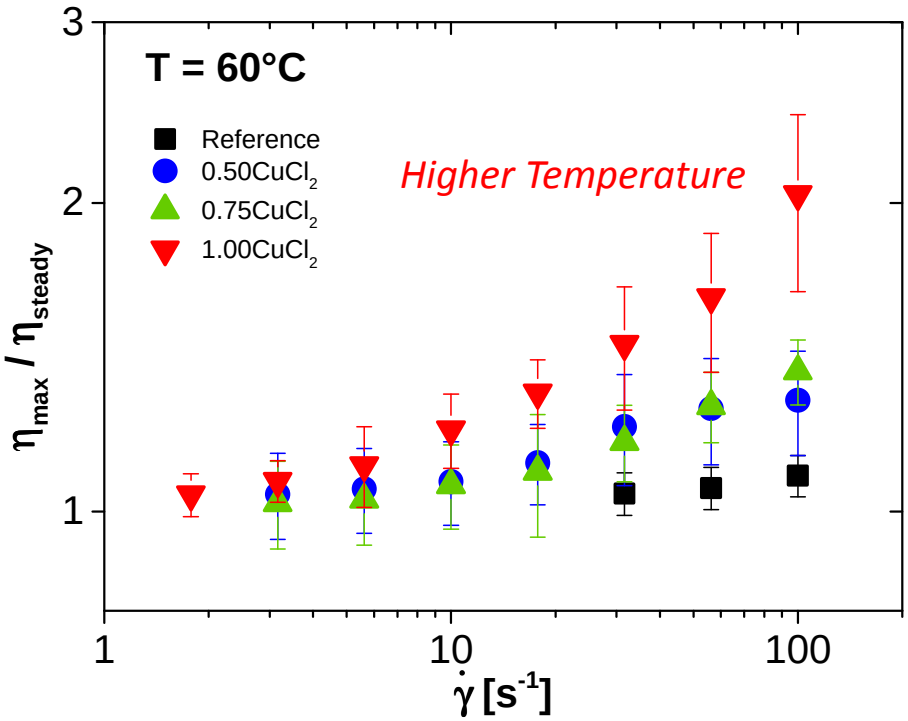
✓ Systematic investigation

(i) 0.1 $s^{-1} \leq \dot{\gamma} \leq$ 100 s^{-1} at 40°C



Nonlinear Shear rheology of PnBA stars





⇨ **Tailored resistance towards deformation**

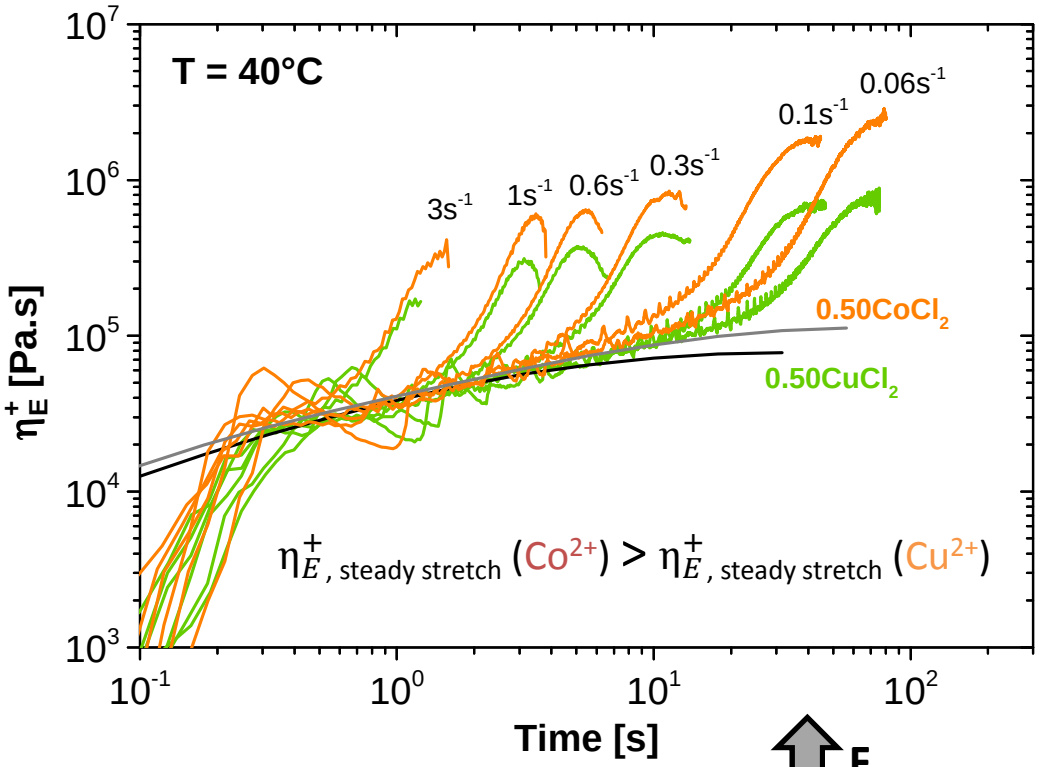
⇨ **Influence of temperature on M-L**

✓ M-L cross-links less stable and more labile

$$K = \frac{k_f}{k_{diss}} \quad , \quad K_{40°C} > K_{60°C}$$

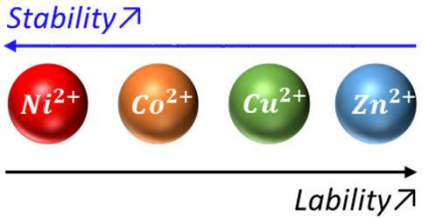
✓ M-L resistance capacity ↘ when T ↗

Nonlinear extensional rheology of PnBA stars



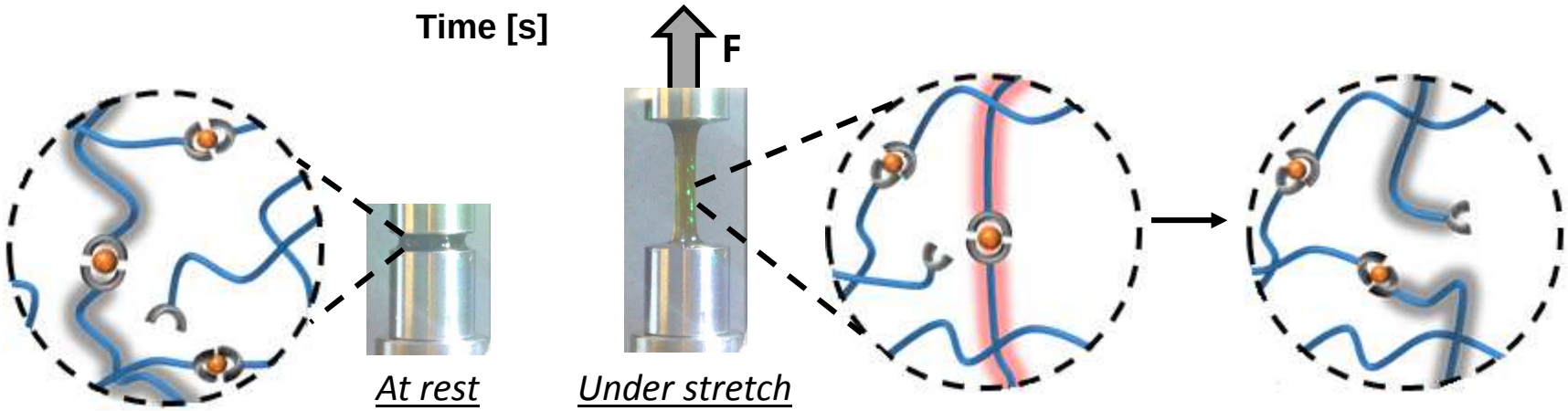
Influence of metal ion type

- ✓ Similar linear dynamic viscosity
- ✓ Difference in elongation viscosity



$$K = \frac{k_f}{k_{diss}}$$

- ✓ Highlight M-L cross-links (Co^{2+} > Cu^{2+})

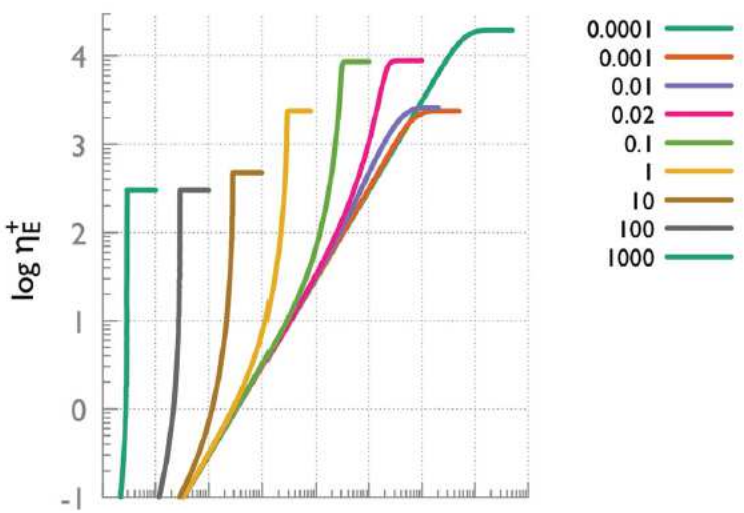


Nonlinear rheology of star polymers

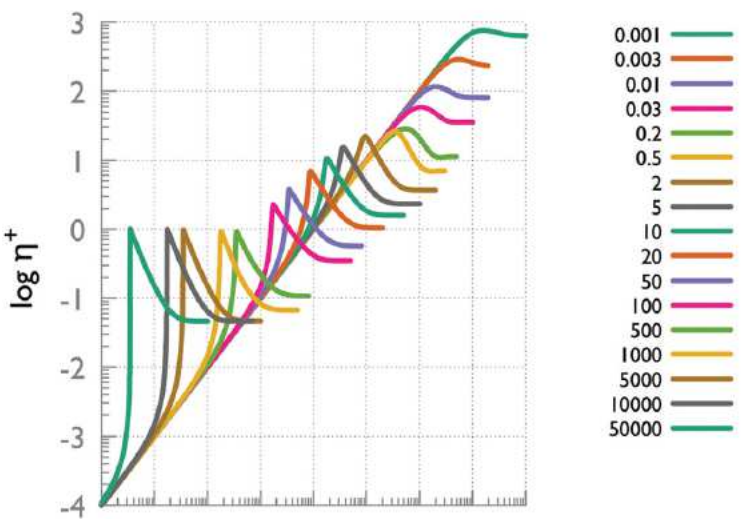
Stochastic and preaveraged nonlinear rheology models for entangled telechelic star polymers

Victor A. H. Boudara, and Daniel J. Read

Citation: Journal of Rheology **61**, 339 (2017); doi: 10.1122/1.4974908

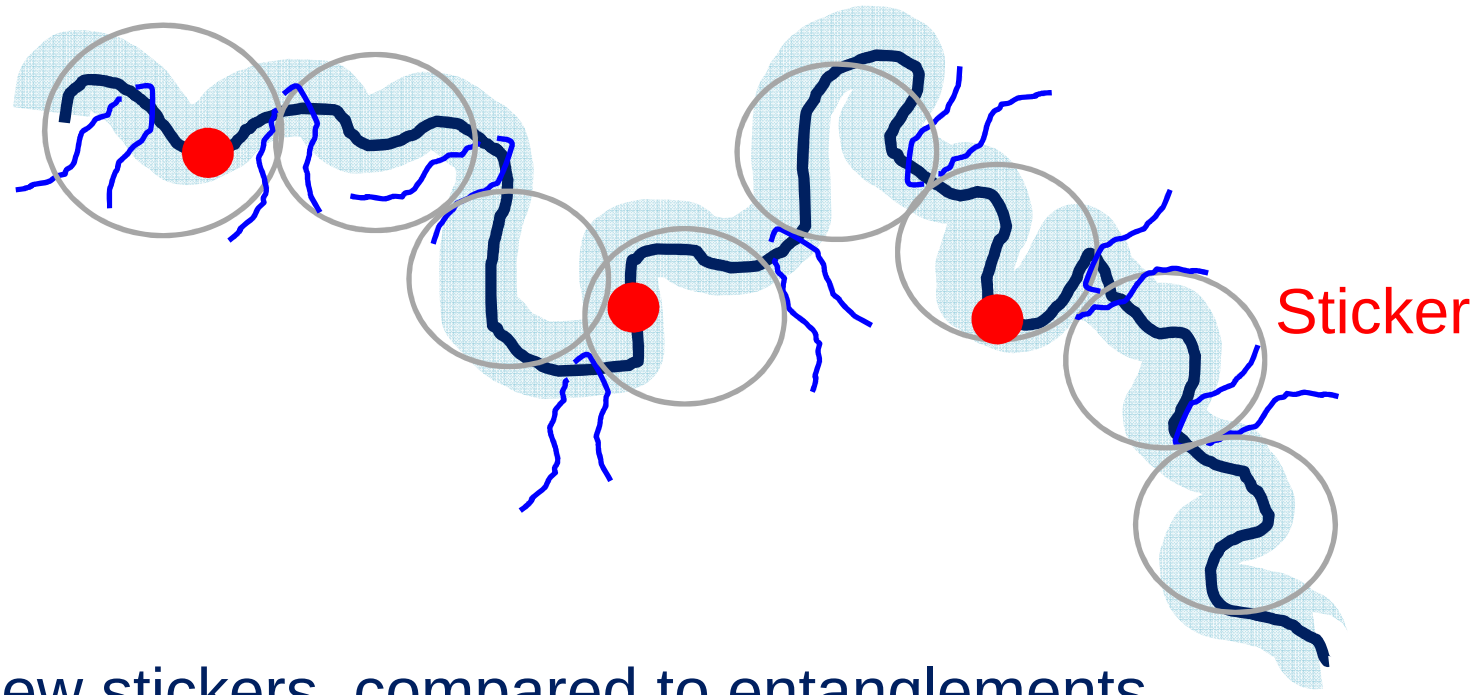


Elongation viscosity



Shear viscosity

Entangled sticky linear polymers



Case 1:

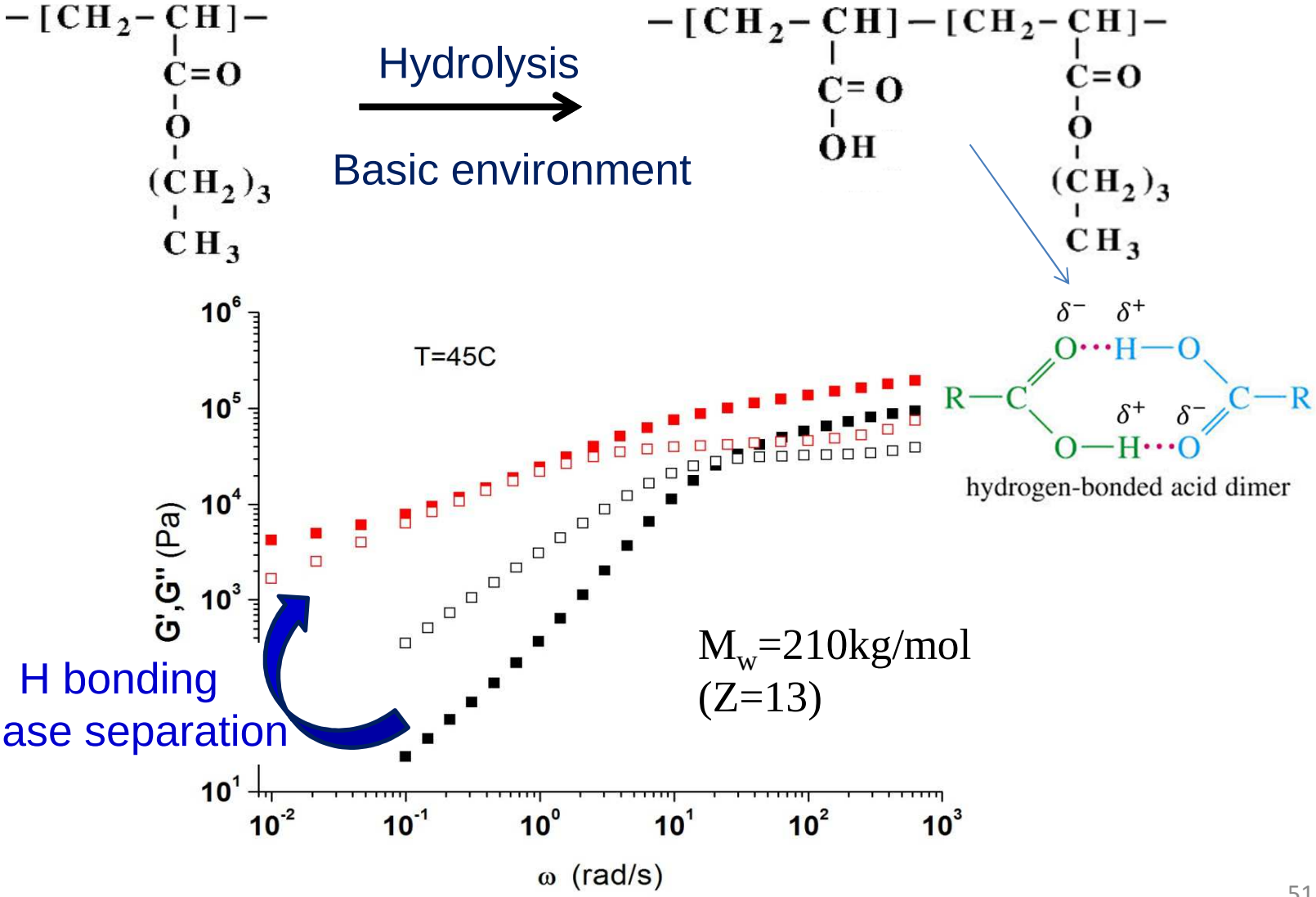
➡ Few stickers, compared to entanglements

$$M_{e,total}^{-1} = M_{e,ent}^{-1} + M_{e,XX}^{-1}$$

➡ Stickers with long lifetime

Viscoelastic properties of hydrolized PnBA chains

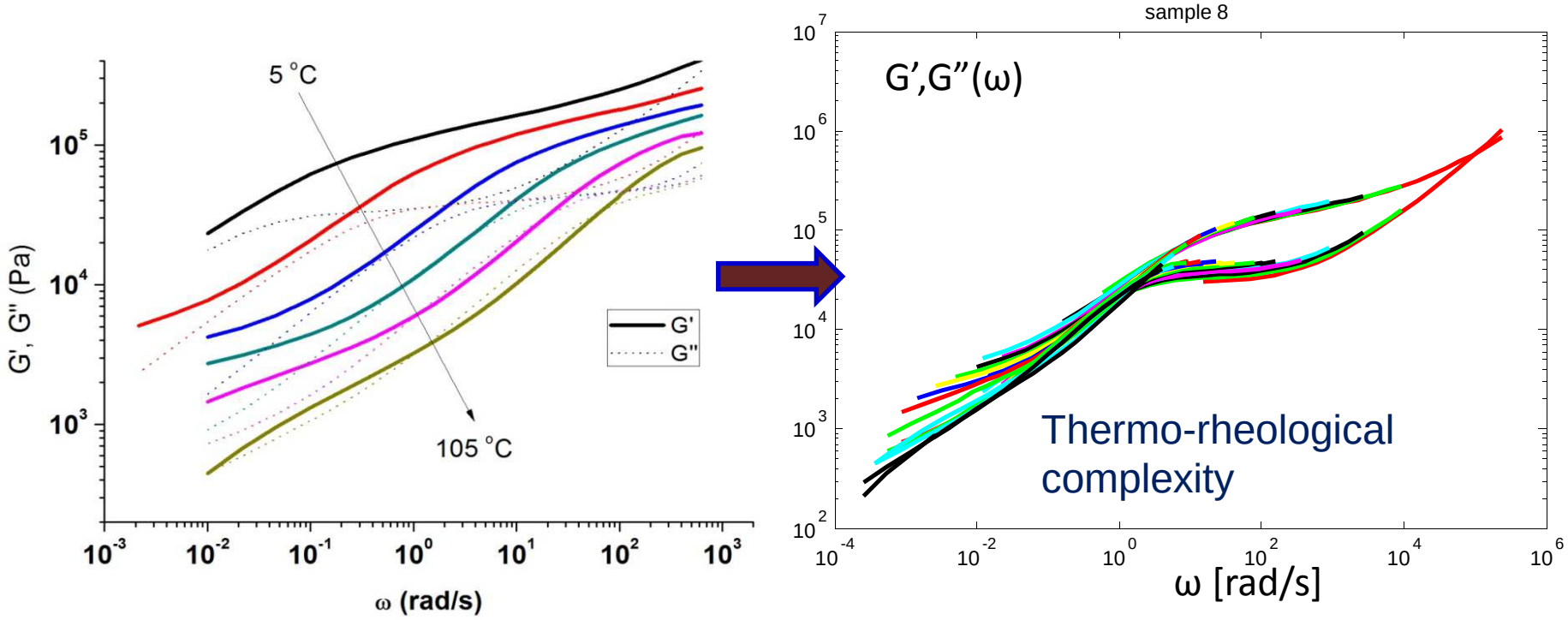
PnBA: Poly (n-butyl acrylate)



H. Goldansaz, C.A. Fustin, M. Wubbenhorst, E. van Ruymbeke, Macromol. 2016

Viscoelastic properties of hydrolized PnBA chains

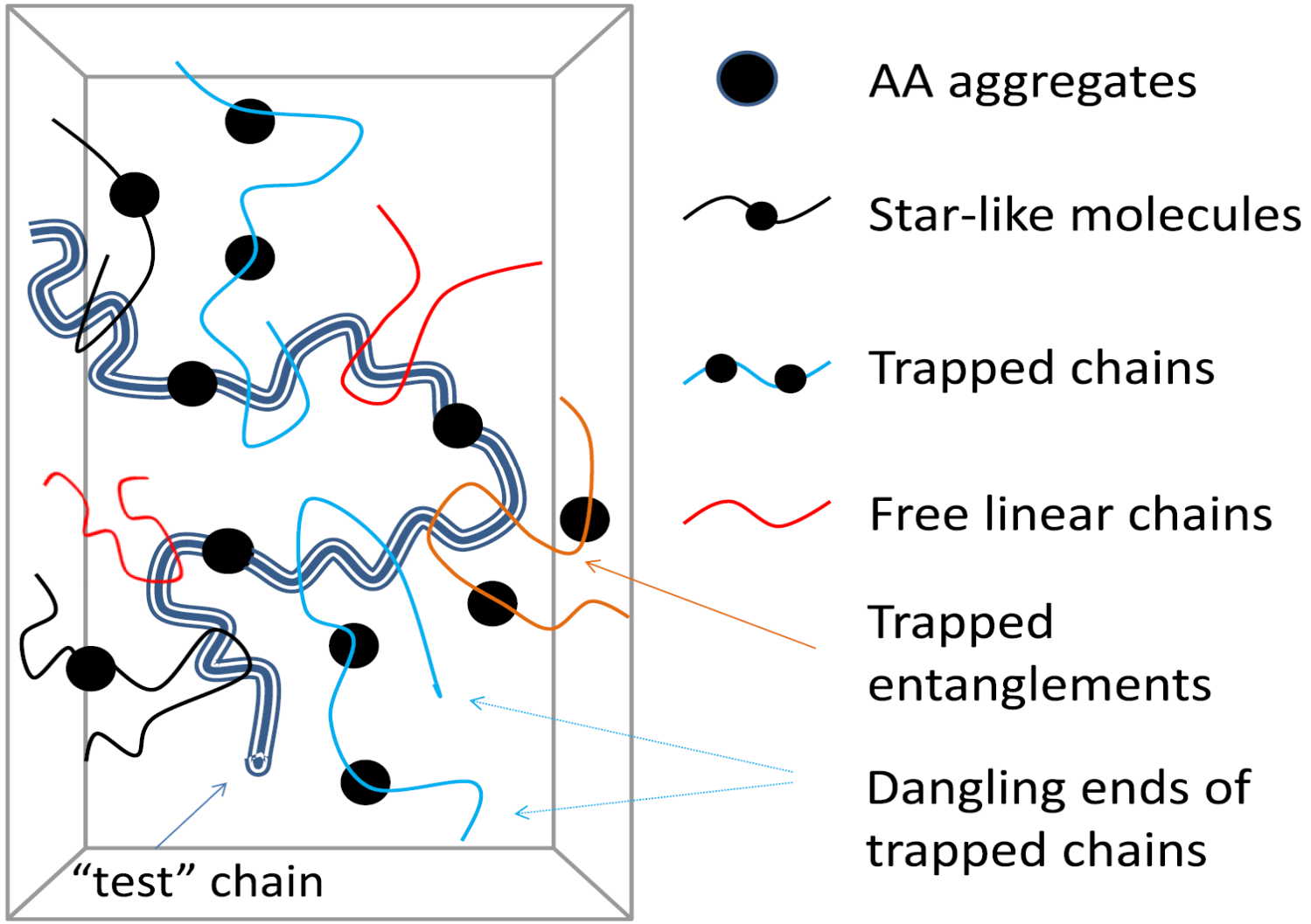
Influence of the temperature



The proportion of active stickers decreases with T

H. Goldansaz, C.A. Fustin, M. Wubbenhorst, E. van Ruymbeke, Macromol. 2016

Viscoelastic properties of hydrolized PnBA chains



At low frequency: only the trapped chains cannot relax

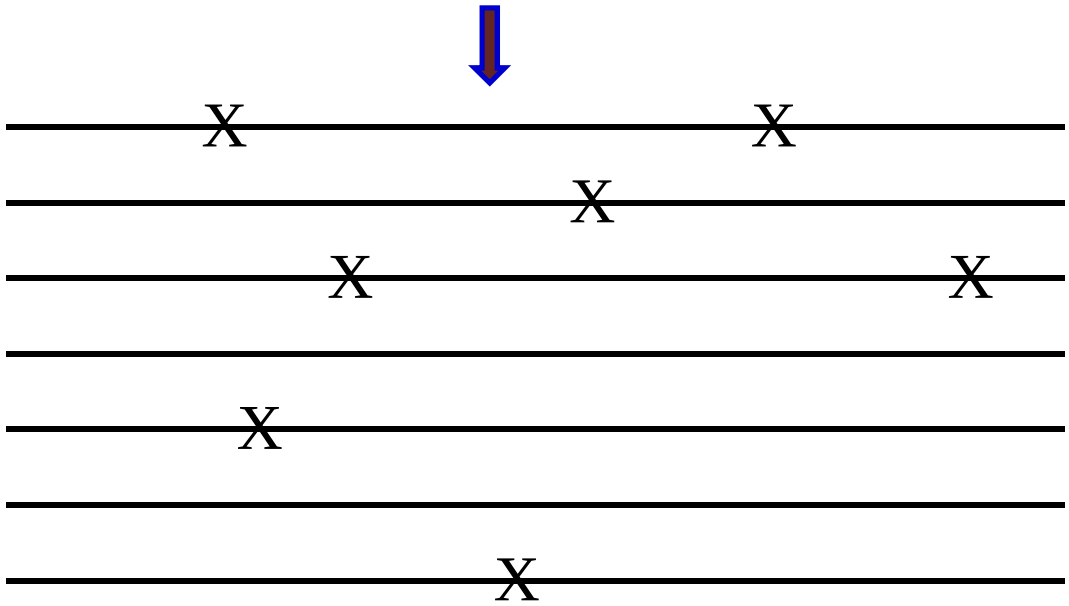
L. Hawke, M. Ahmadi, H. Goldansaz, E. van Ruymbeke, J. Rheol. 2016

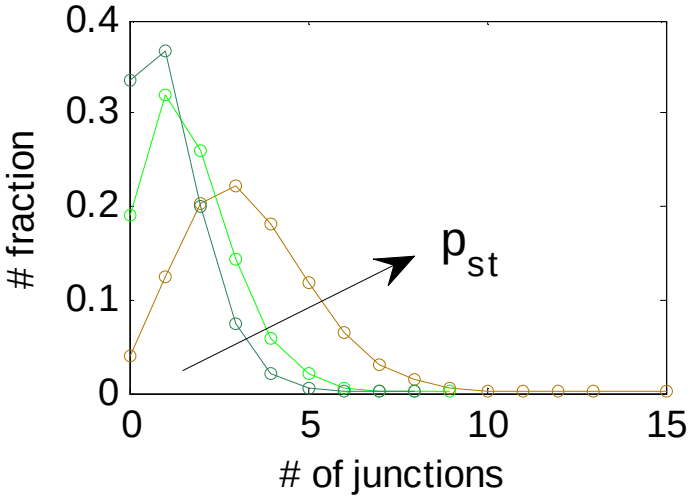
Viscoelastic properties of hydrolized PnBA chains

Statistical composition

Unknown:

p_{active_st} *the probability to find an active sticker along the chain*



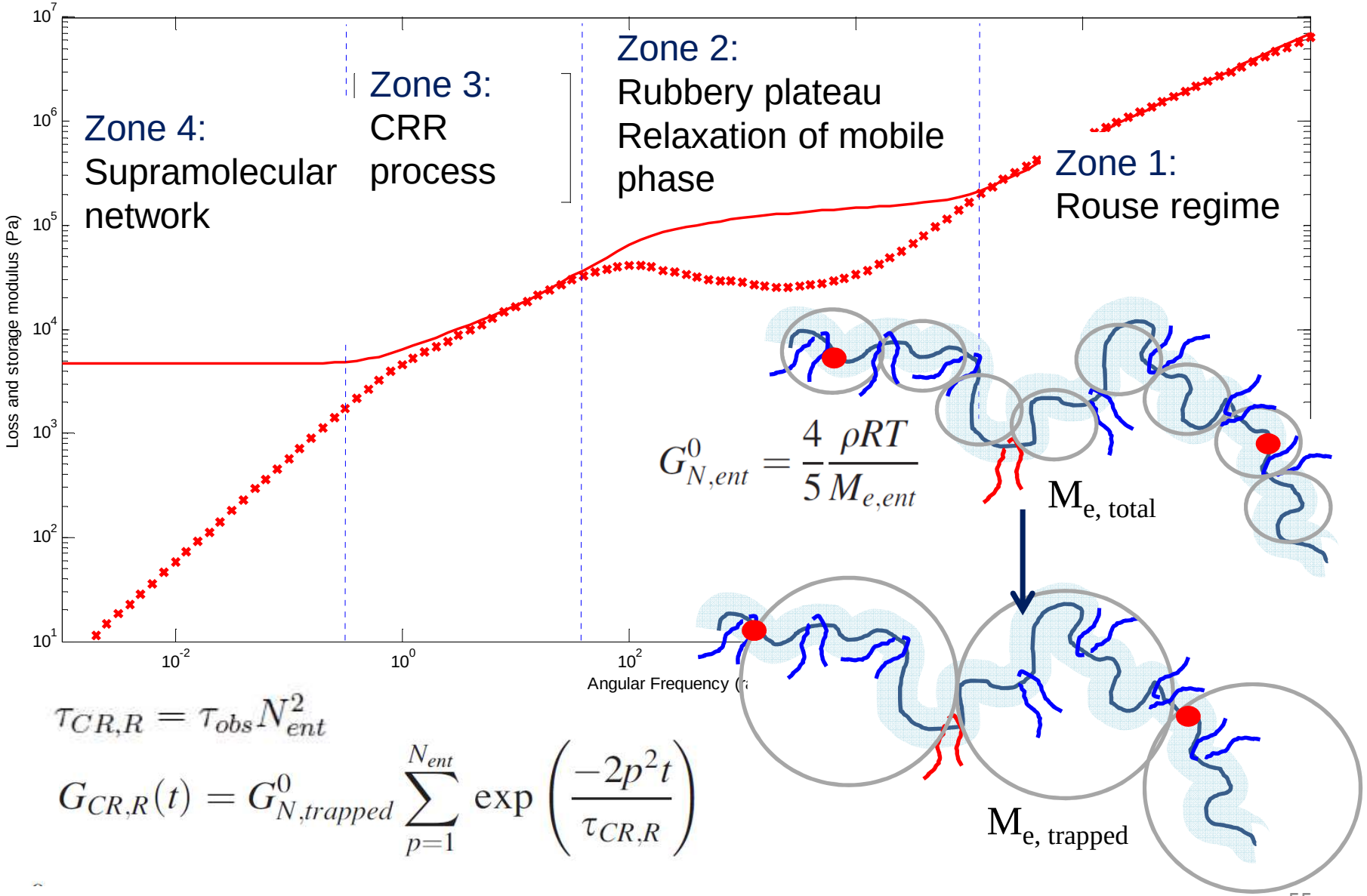


Analysis and classification of the chain segments

Building the sticky molecules

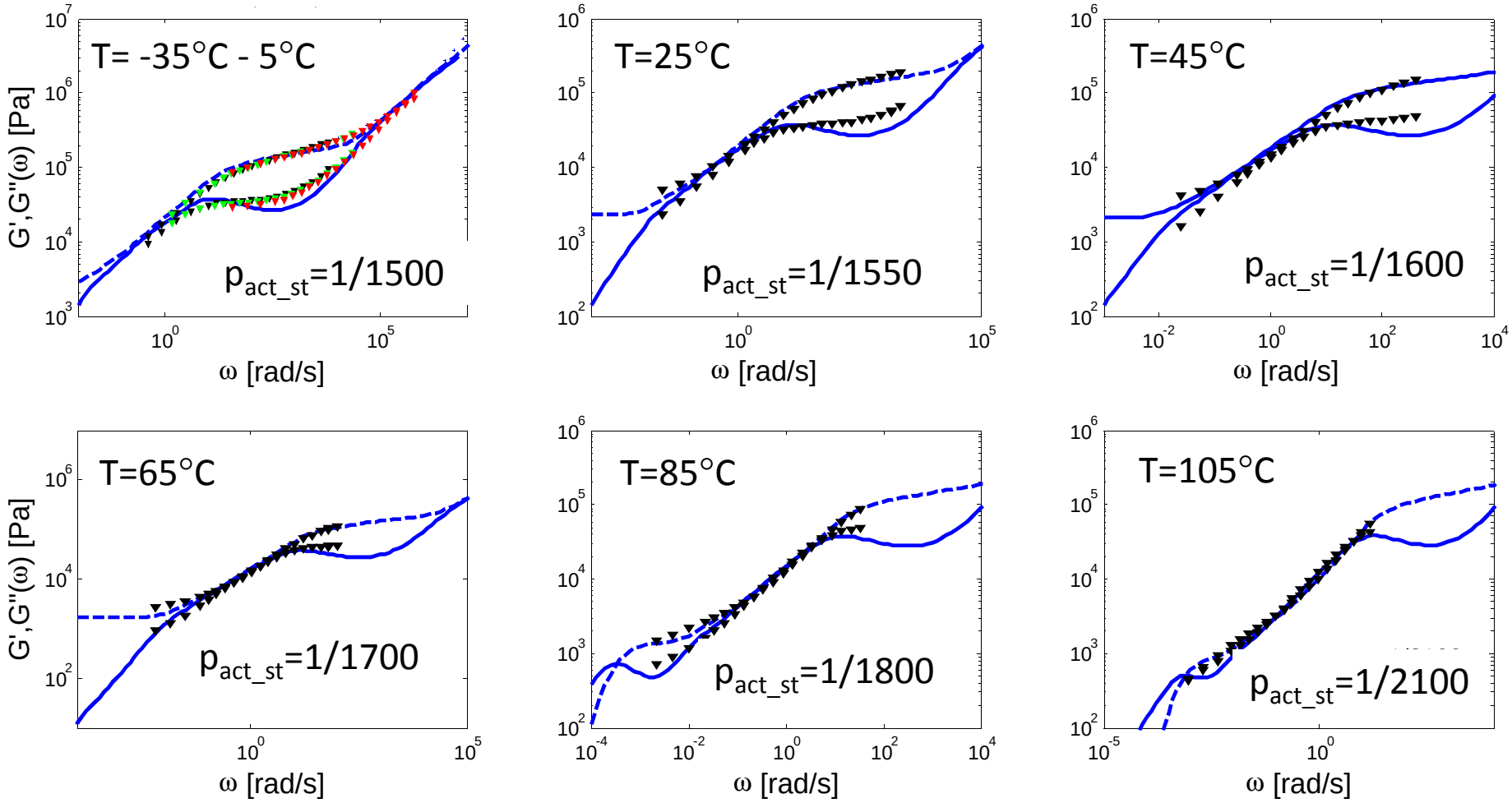
L. Hawke, M. Ahmadi, H. Goldansaz, E. van Ruymbeke, J. Rheol. 2016

Viscoelastic properties of hydrolized PnBA chains



L. Hawke, M. Ahmadi, H. Goldansaz, E. van Ruymbeke, J. Rheol. 2016

Viscoelastic properties of hydrolized PnBA chains

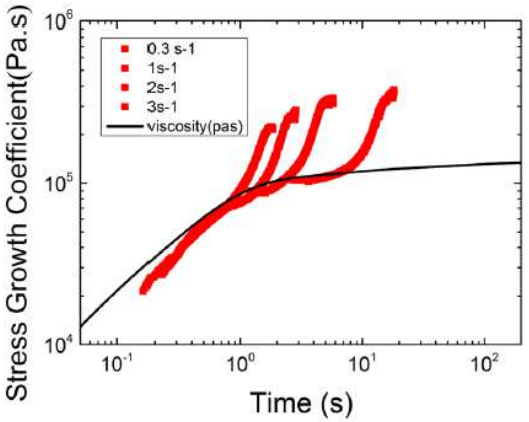


L. Hawke, M. Ahmadi, H. Goldansaz, E. van Ruymbeke, J. Rheol. 2016

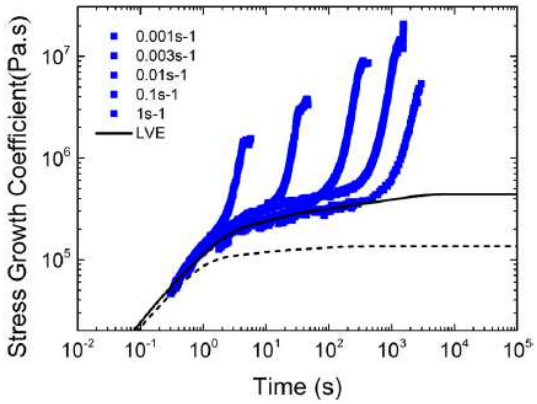
Viscoelastic properties of hydrolized PnBA chains

Effect of Hydrogen Bonding on Linear and Nonlinear Rheology of Entangled Polymer Melts

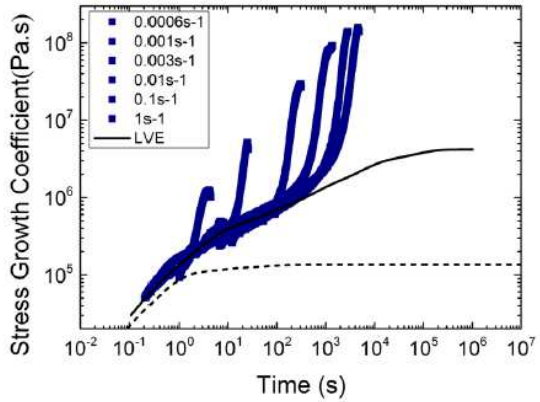
Aamir Shabbir,[†] Hadi Goldansaz,[‡] Ole Hassager,[†] Evelyne van Ruymbeke,[‡] and Nicolas J. Alvarez*[,§]



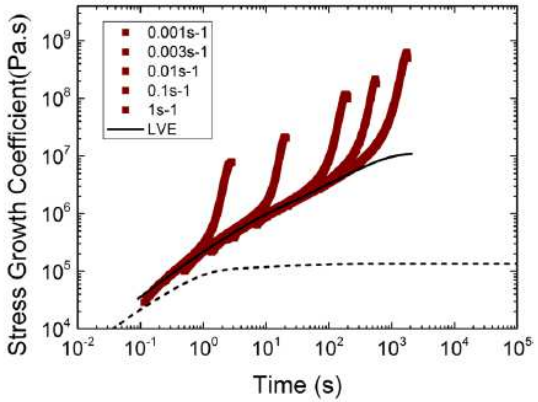
(a) PnBA



(b) AA6, 6% AA



(c) AA13, 13% AA

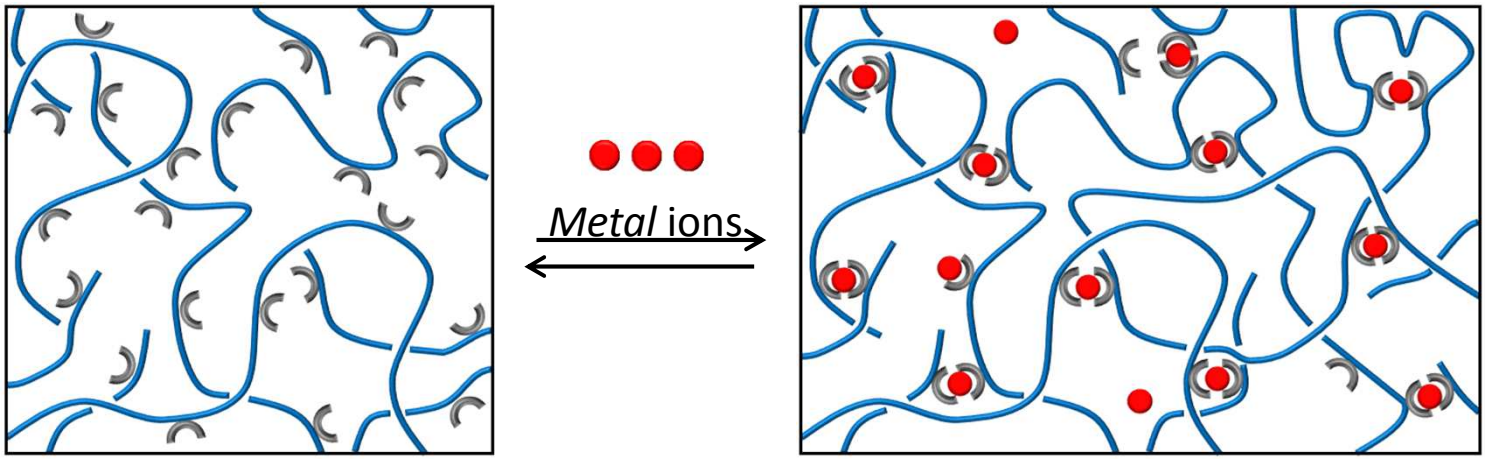


(d) AA38, 38% AA

Large strain hardening is observed

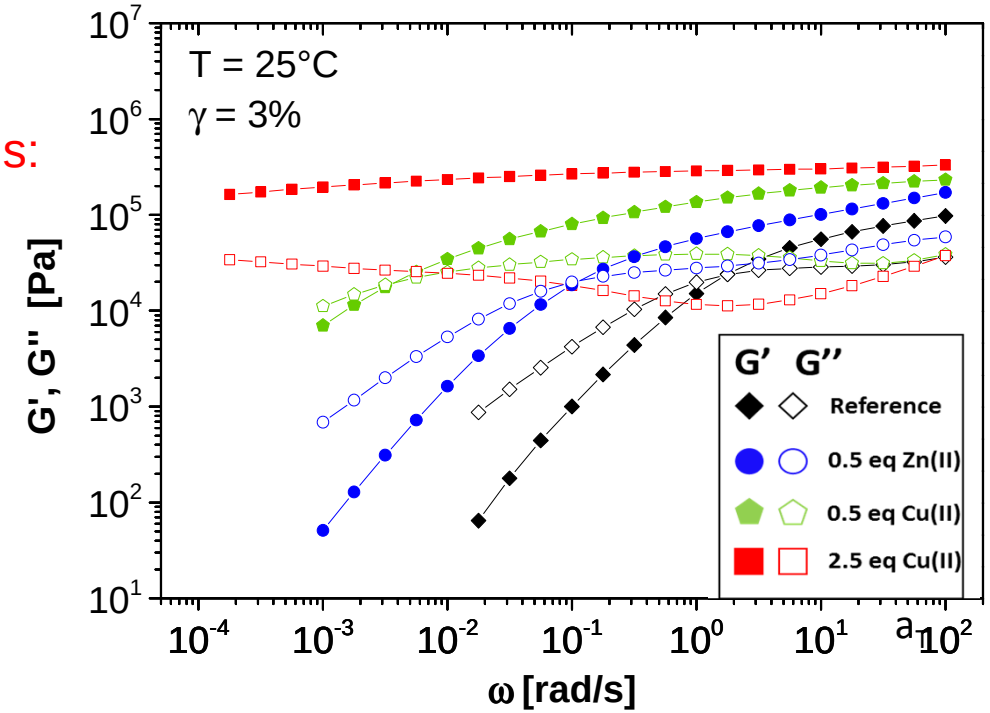
Entangled sticky linear polymers

Case 2: Short lifetime stickers



Plateau modulus:

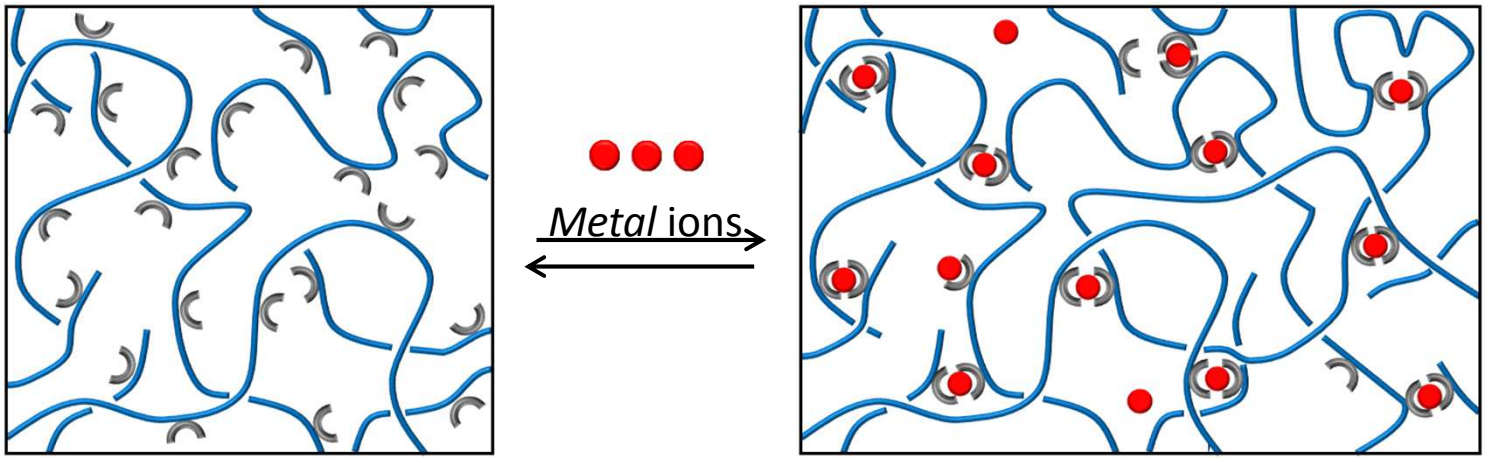
Dominated by entanglements



Entangled chains with extra friction

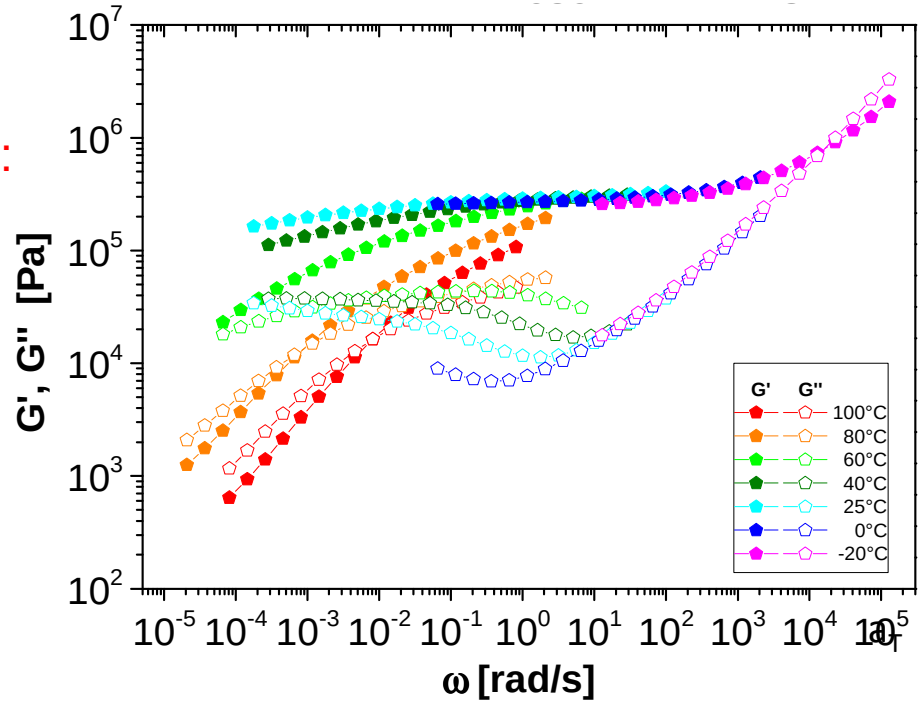
Entangled sticky linear polymers

Case 2: Short lifetime stickers



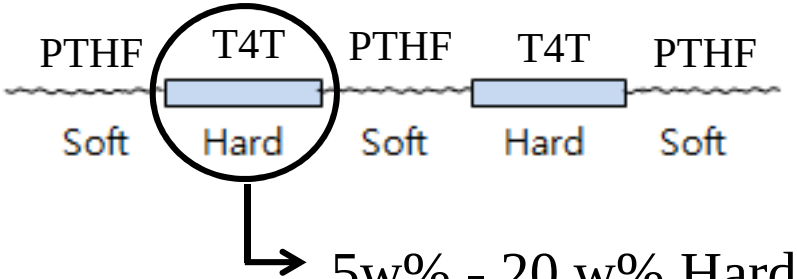
Plateau modulus:

Dominated by entanglements

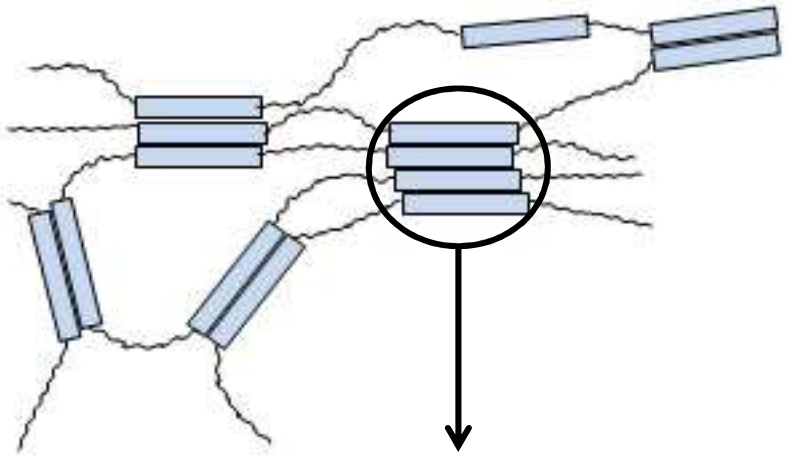


Entangled chains with extra friction

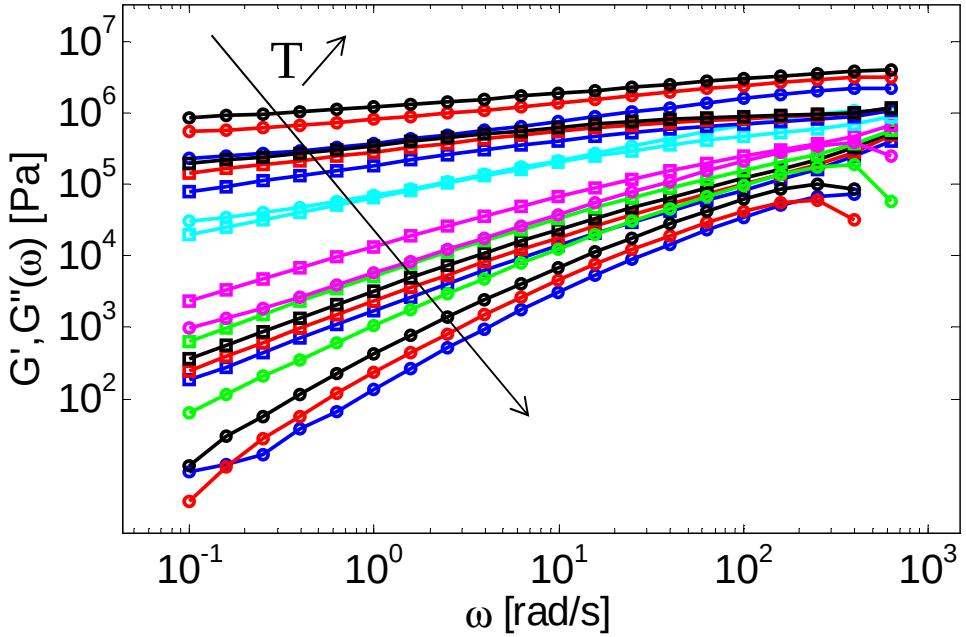
Viscoelastic properties thermoplastic elastomers

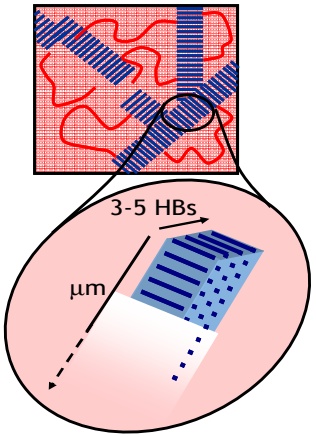


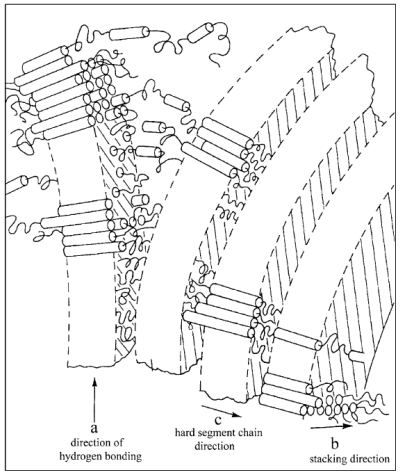
5w% - 20 w% Hard segments



H bonding and crystallization





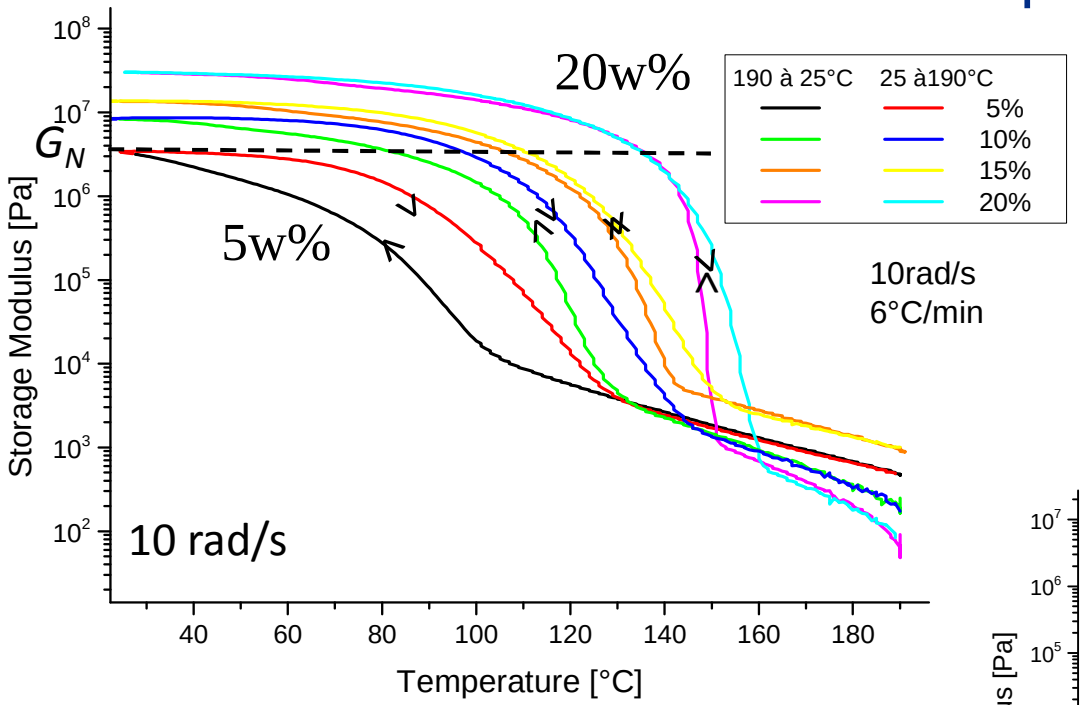


Large Mn (20 kg/mol) → Chains are entangled

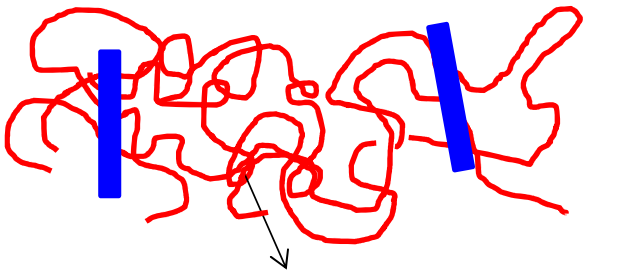
G.J.E. Biemond, J. Feijen, R.J. Gaymans, J. Applied Polym. Sci. , 2007; R.J. Gaymans, Progress in Polym. Sci., 2011

Viscoelastic properties thermoplastic elastomers

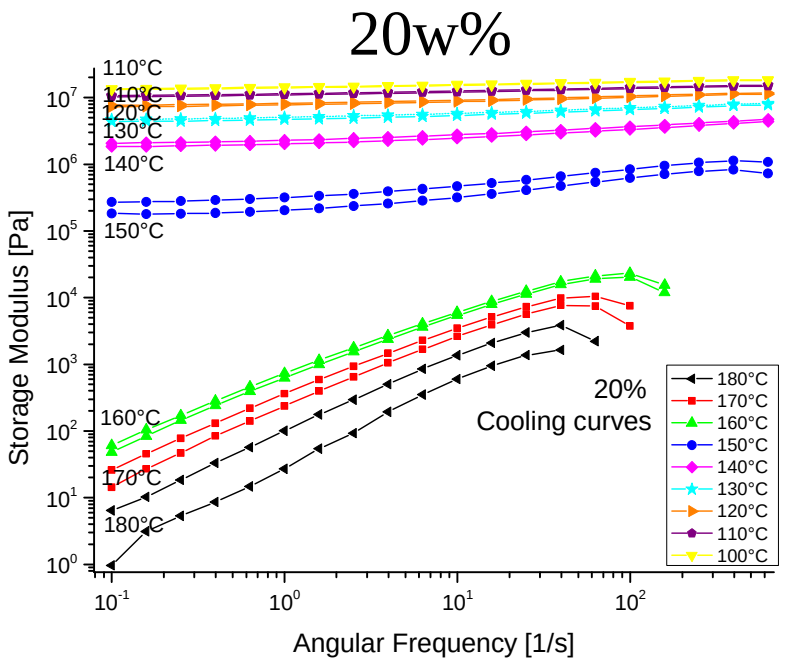
Influence of Temperature



- Large hysteresis
- Sharp liquid-solid transition
- Low module



Trapped entanglements

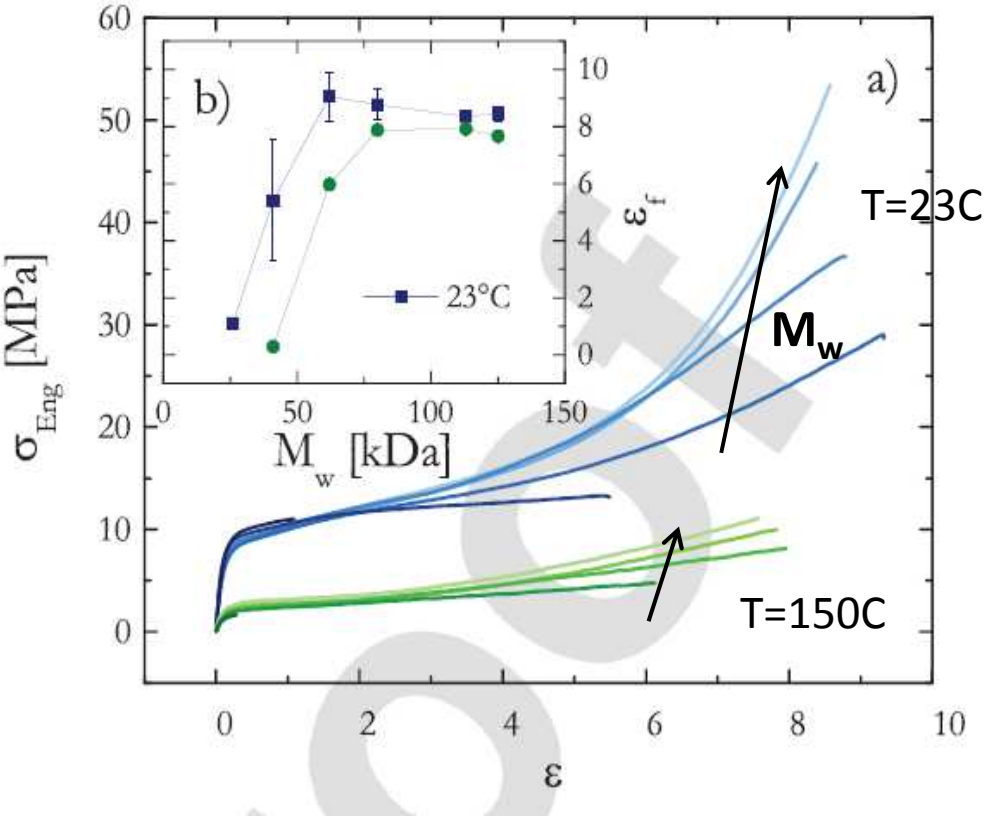


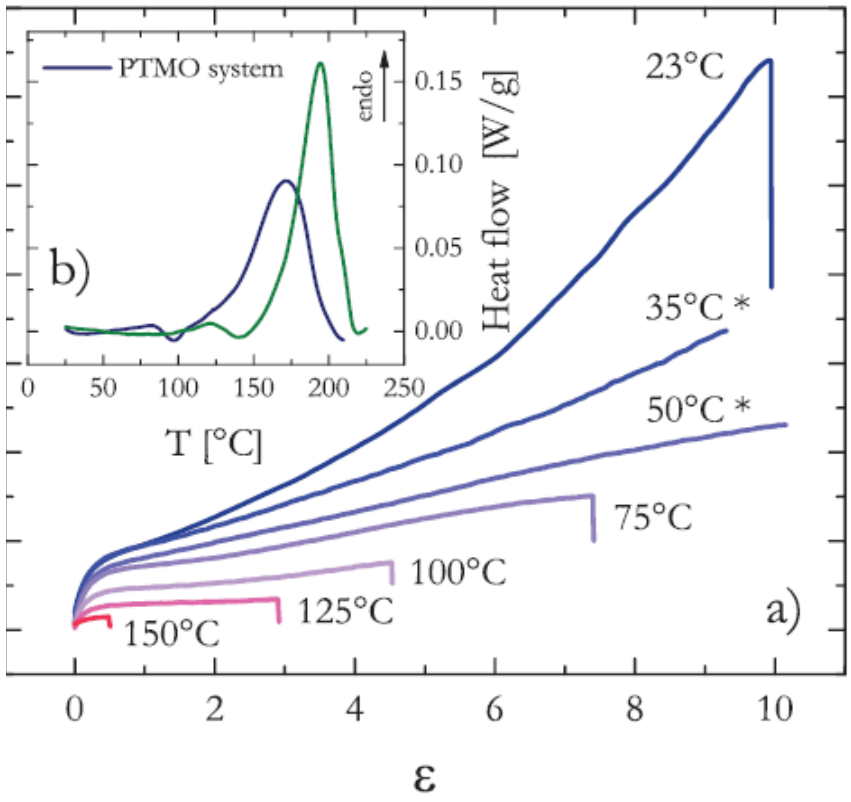
A. Sharma (DSM-UCL), G. Baeza (FORTH), Luna Imperiali (DSM), C. Fitie (DSM)

Viscoelastic properties thermoplastic elastomers

Role of the chain Architecture

S. Aime, N. Eisenmenger, T. Engels, JoR 2017





Weak mechanical properties at high T

Viscoelastic properties of block copolymers

Uniaxial Extensional Behavior of $(SIS)_p$-Type Multiblock Copolymer Systems: Structural Origin of High Extensibility

Yumi Matsumiya and Hiroshi Watanabe*

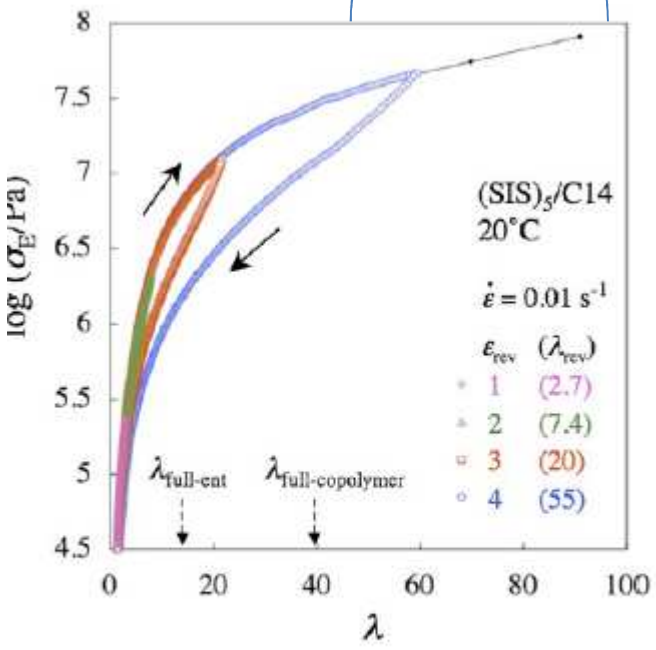
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

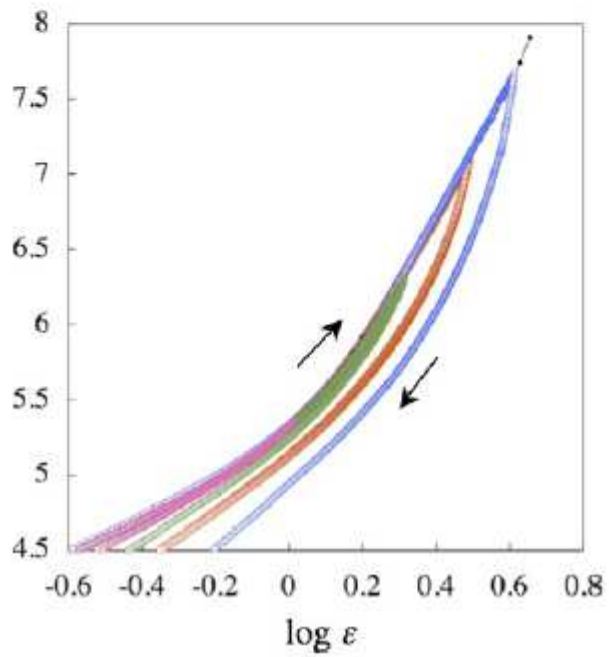
Atsushi Takano

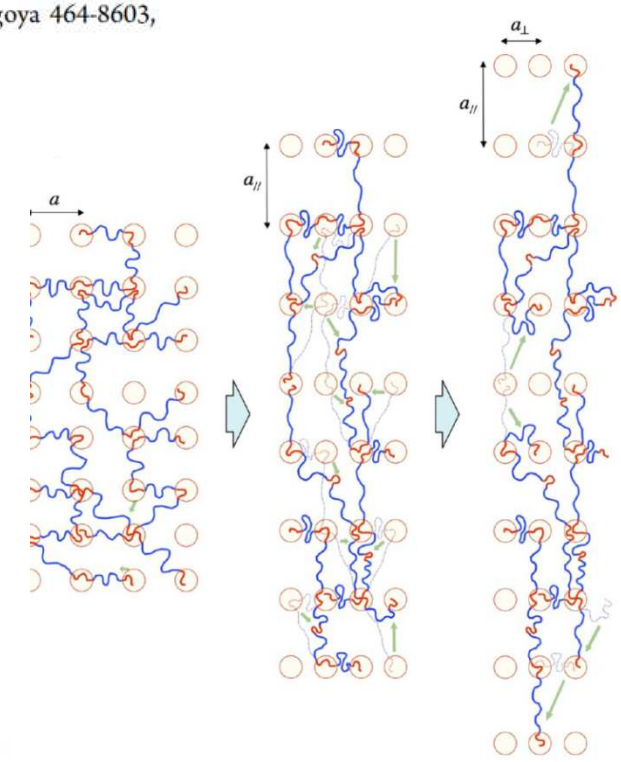
Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Yoshiaki Takahashi

Stretched above the full extension of a chain







Important recovery despite the large formation imposed

Viscoelastic properties of block copolymers

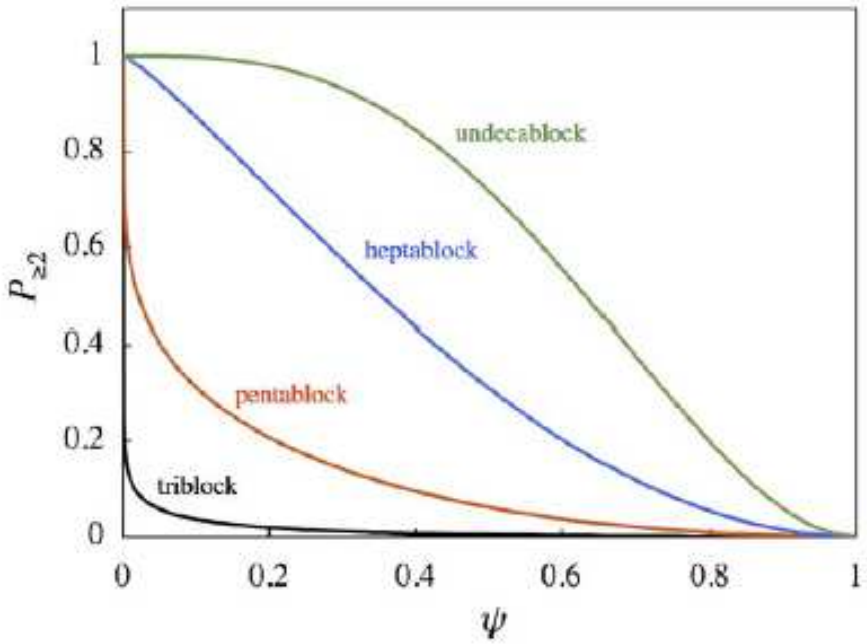
Block copolymers of different length:

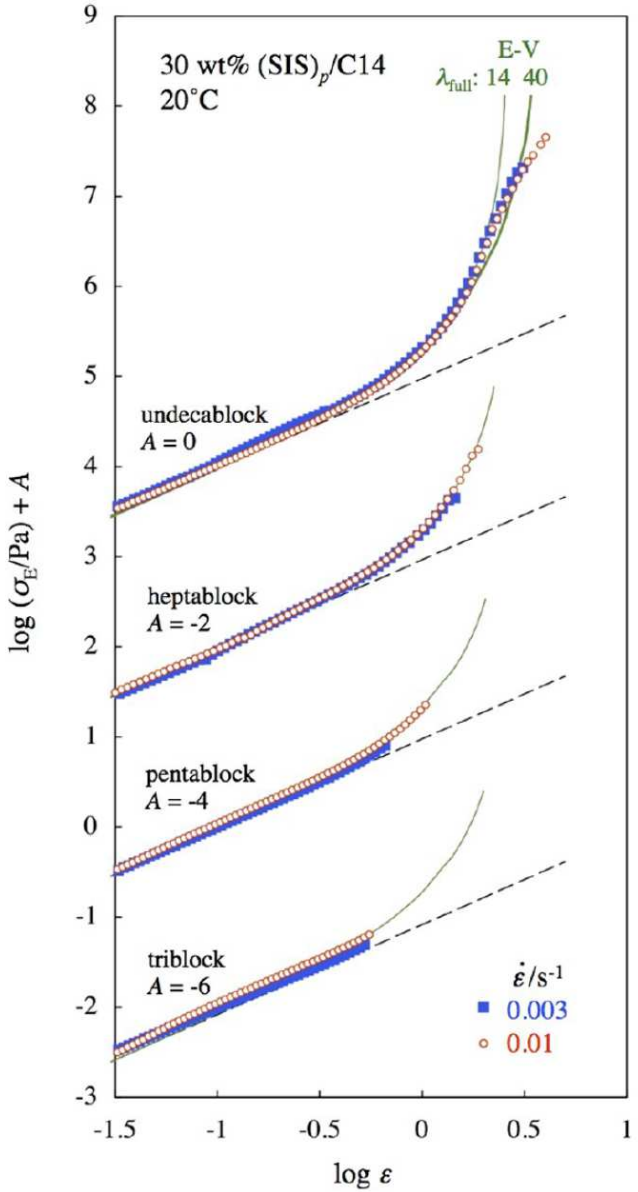
Same linear rheology, different extension behavior

M(I)=40kg/mol, M(S)=20 kg/mol

S domains: physical crosslinks

Probability to conserve connectivity versus Probability to dissociate a S block



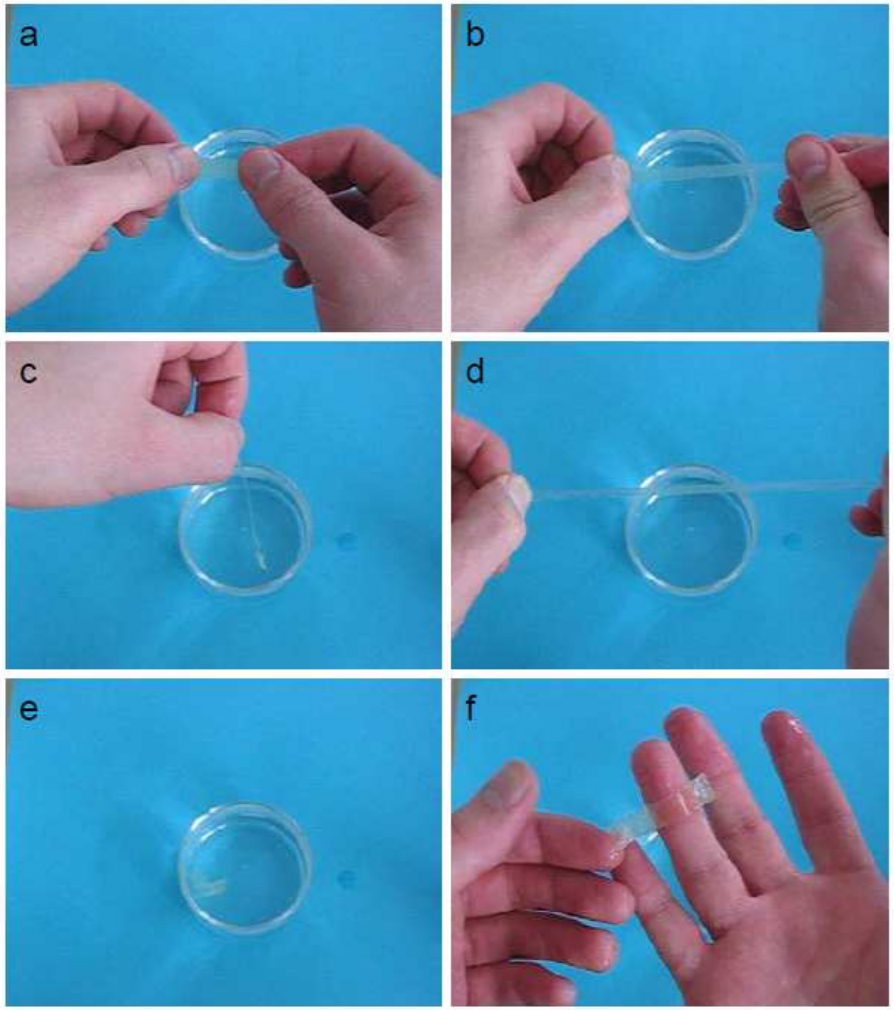


Matsumiya, Watanabe, Macromol. 2013

Viscoelastic properties of block copolymers

EFFECT OF CHAIN EXTENDERS ON SHAPE-MEMORY PROPERTIES OF SEGMENTED COPOLYMERS WITH ARAMID HARD SEGMENTS AND POLYCAPROLACTONE SOFT SEGMENTS

Arno Kraft, Louis Garnier



III. Double Dynamics Networks

Double Dynamics Networks

- Entanglements + stickers: See Section II
- Stickers 1 + Stickers 2
- Building blocks 1 + Building blocks 2

- Interpenetrated networks
- Dual networks

- Rheological behaviour
- Mechanical response

Blending two different stickers - unentangled sticky chains

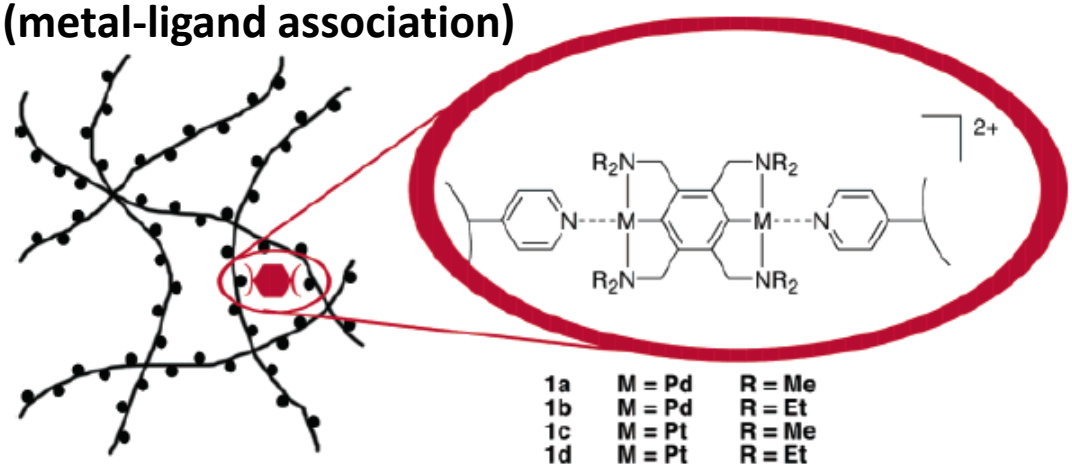
J|A|C|S
ARTICLES
Published on Web 09/22/2005

2005

Small-Molecule Dynamics and Mechanisms Underlying the Macroscopic Mechanical Properties of Coordinatively Cross-Linked Polymer Networks

Wayne C. Yount, David M. Loveless, and Stephen L. Craig*

Poly vinyl Pyridine + Bisfunctional cross-linker (metal-ligand association)



1a	M = Pd	R = Me
1b	M = Pd	R = Et
1c	M = Pt	R = Me
1d	M = Pt	R = Et

4 different cross-linkers of different strength:

complex	K_{eq} (M^{-1})	k_d (s^{-1})
1a·2	29[a]	1450[b]
1b·2	33[a]	17[b]
1c·2	8000[a]	0.026[a]
1d·2	4000[a]	0.0006[c]

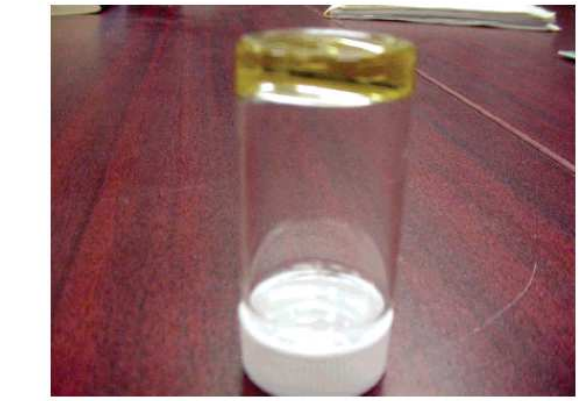


Figure 3. Gel formed from PVP and bimetallic compound **3b** (5% functional group equivalents) at 100 mg/mL in DMSO.

at 25 °C

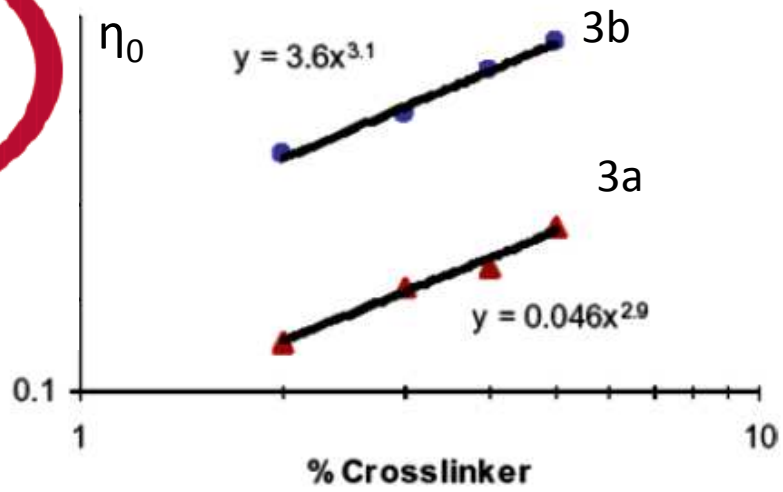
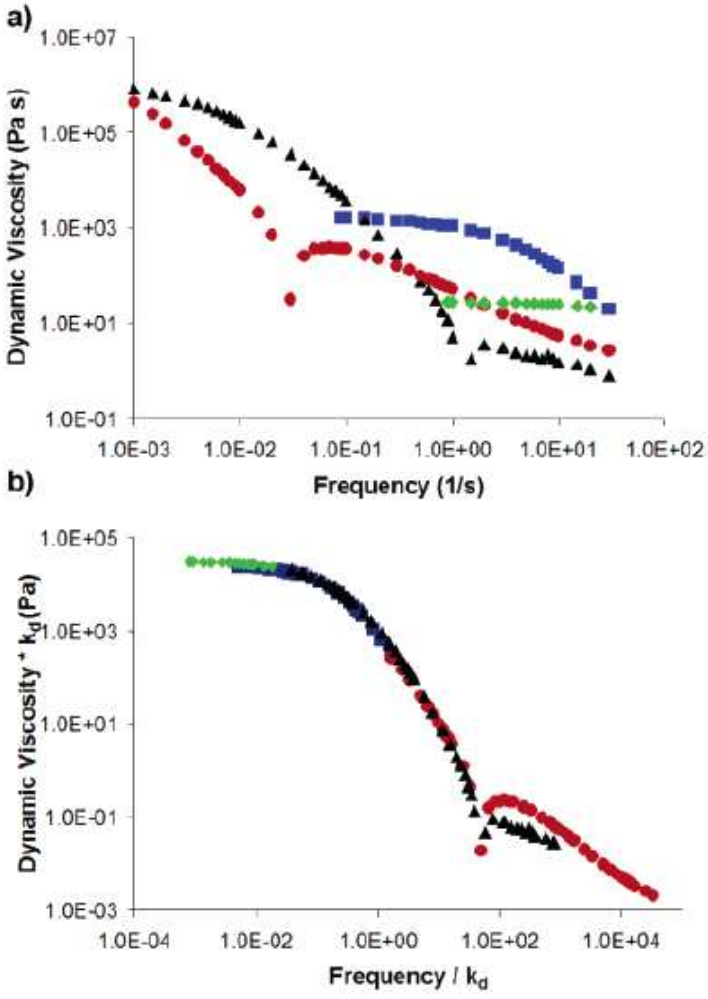
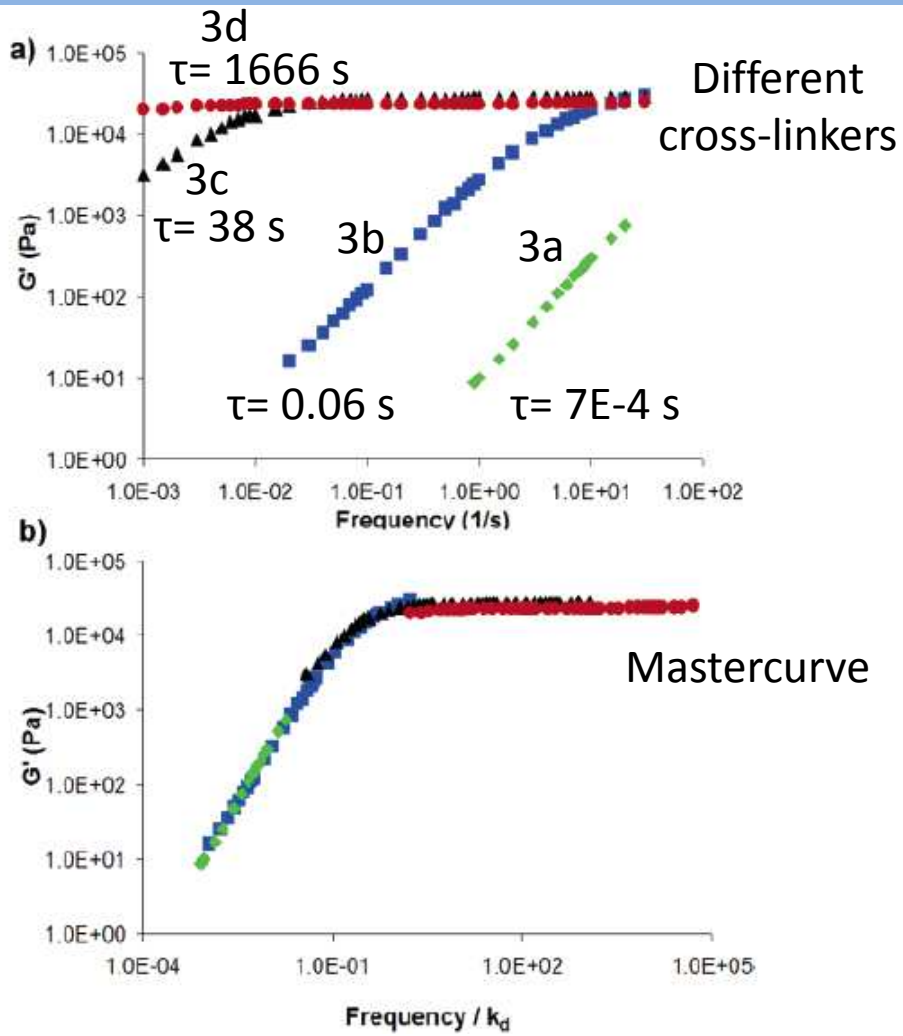


Figure 4. Steady shear viscosity as a function of density of cross-linker **3a** (red ▲) or **3b** (blue ●), expressed as functional group equivalents of metal relative to pyridine side group. 100 mg/mL **3**·PVP in DMSO.

Non-entangled solutions (10%) + 5% (Metal to Nitrogen) cross-linkers

Blending two different stickers - unentangled sticky chains



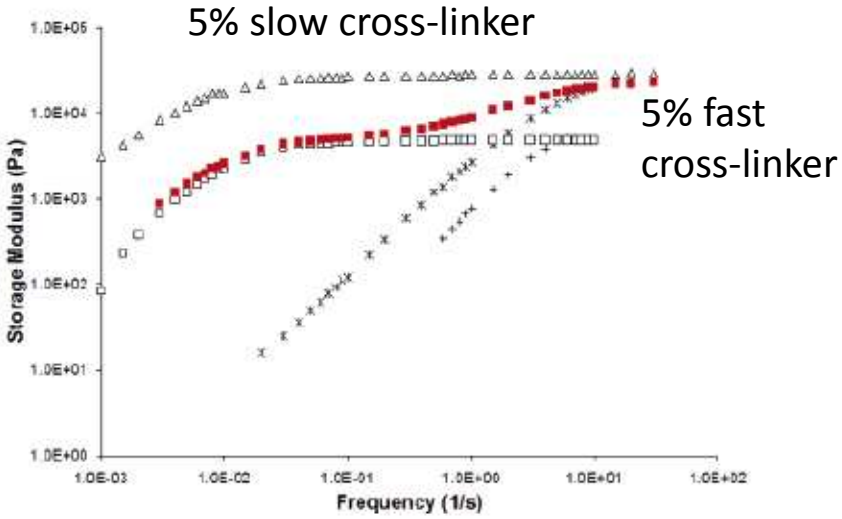


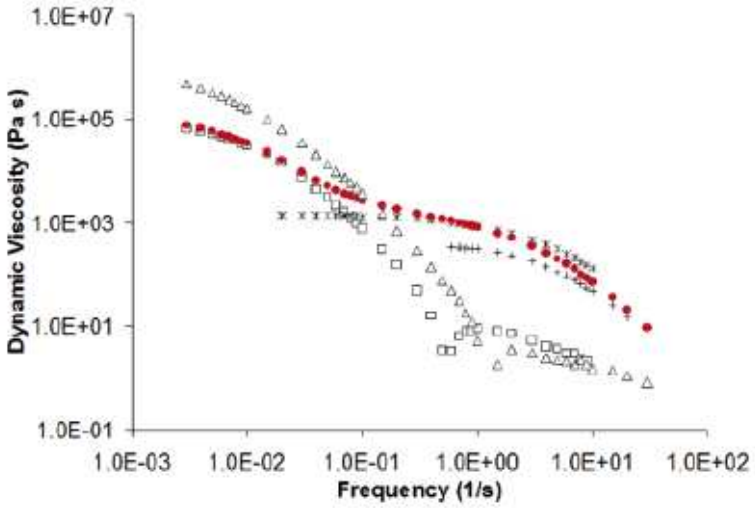
Reduced master-curve proofs that no dynamics except the crosslinkers

The dissociation process fully dominates the flow properties

Blending two different stickers - unentangled sticky chains

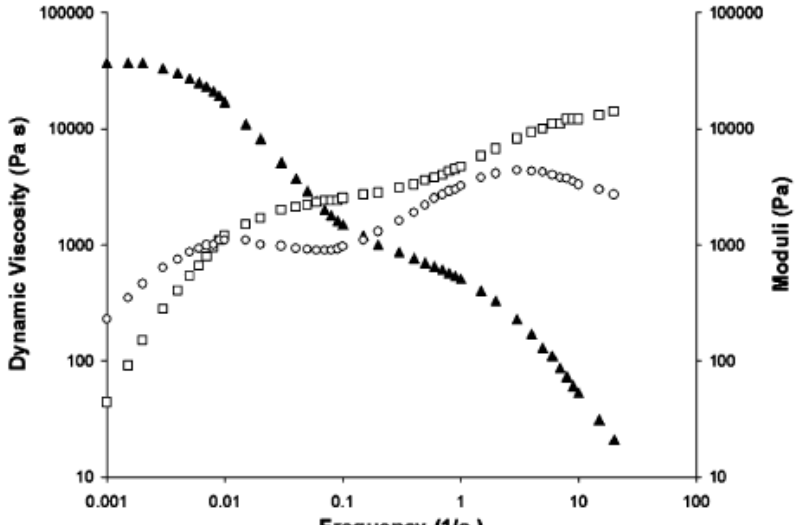
Rational control by introducing **2.5% of fast and 2.5% of slow** crosslinker





@ low frequency follows 2.5% of slow sample
@ high frequency follows 5% of fast sample

1.66% of fast, 1.66% of slow & 1.66 of intermediate crosslinker



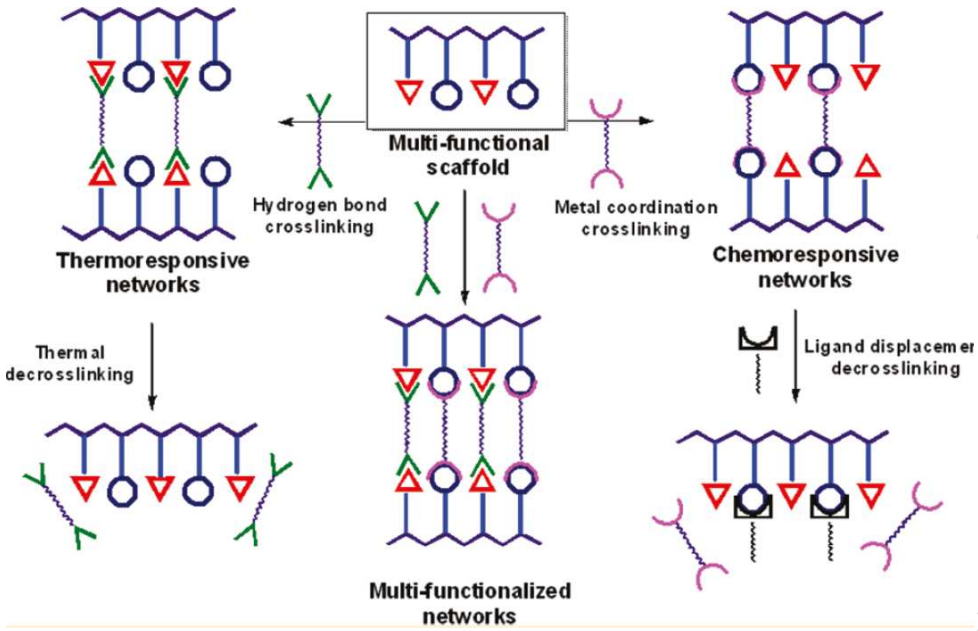
Simple mixing law based on the lifetime of the cross-linkers

Blending two different stickers - unentangled sticky chains

Multiresponsive Reversible Polymer Networks Based on Hydrogen Bonding and Metal Coordination

Kamlesh P. Nair,[†] Victor Breedveld,[*,‡] and Marcus Weck[*,§]

Starting point:



Dissociation by T increase

Dissociation by adding a decrosslinker

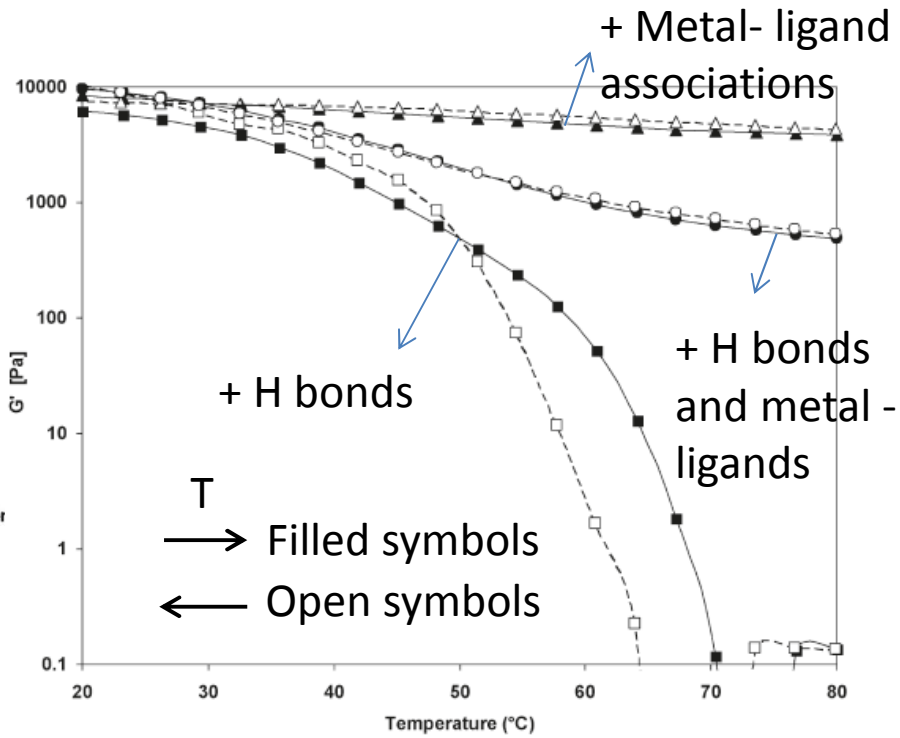


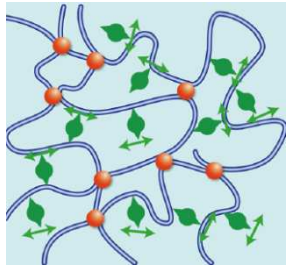
Figure 9. Thermal recovery of G': (1) 20 to 80 °C (heating cycle: filled symbols) and (2) 80 to 20 °C (cooling cycle: empty symbols) for Poly-123-4 (rectangles), Poly-123-5 (triangles), and Poly-123-45 (circles). G' was measured at ω = 6.3 rad/s and a strain of 0.1.

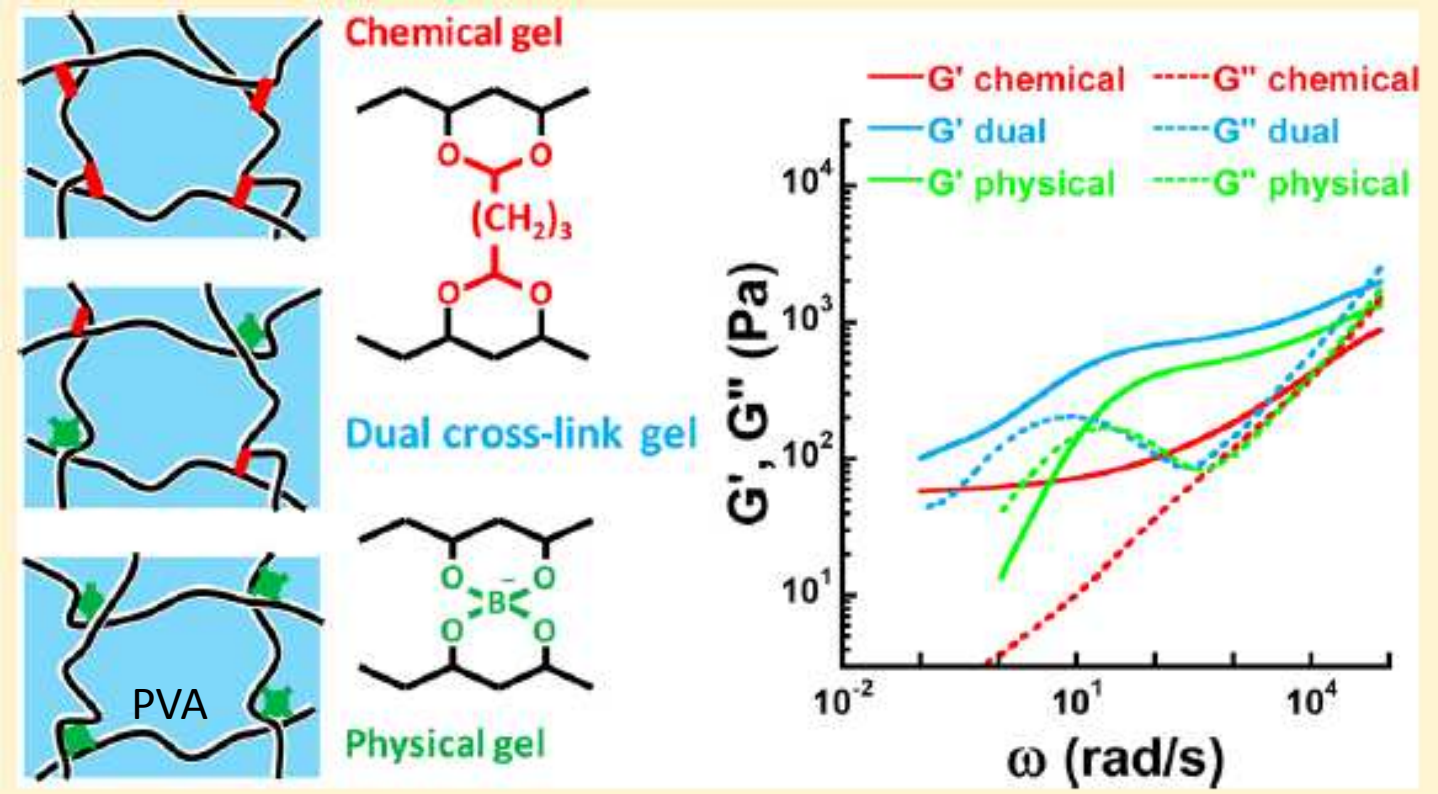
Double networks: H junctions are very sensitive to T.

Blending covalent and transient stickers

Viscoelastic Properties of Poly(vinyl alcohol) Hydrogels Having Permanent and Transient Cross-Links Studied by Microrheology, Classical Rheometry, and Dynamic Light Scattering

Tetsuharu Narita,[†,*] Koichi Mayumi,[†] Guylaine Ducouret,[†] and Pascal Hébraud[‡]





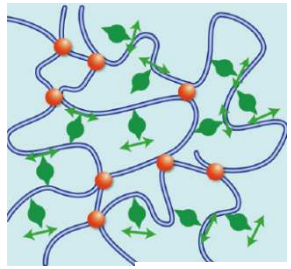
Additive effects of transient and permanent bonds

Blending covalent and transient stickers

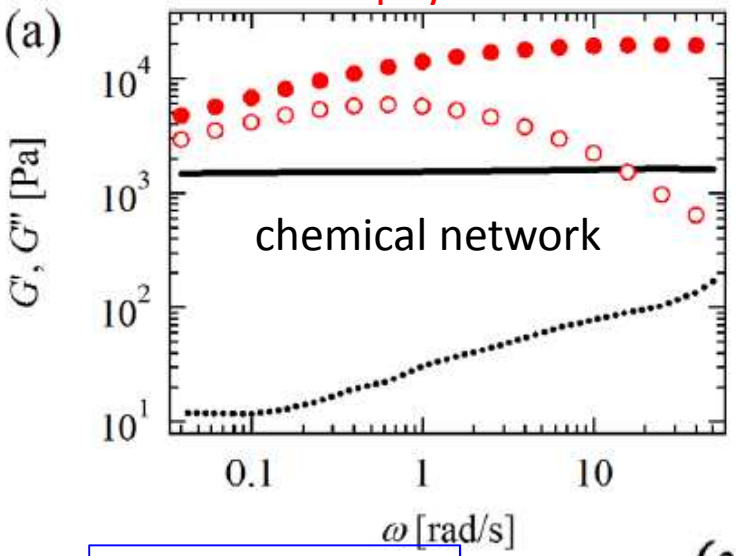
Stress–Strain Relationship of Highly Stretchable Dual Cross-Link Gels: Separability of Strain and Time Effect

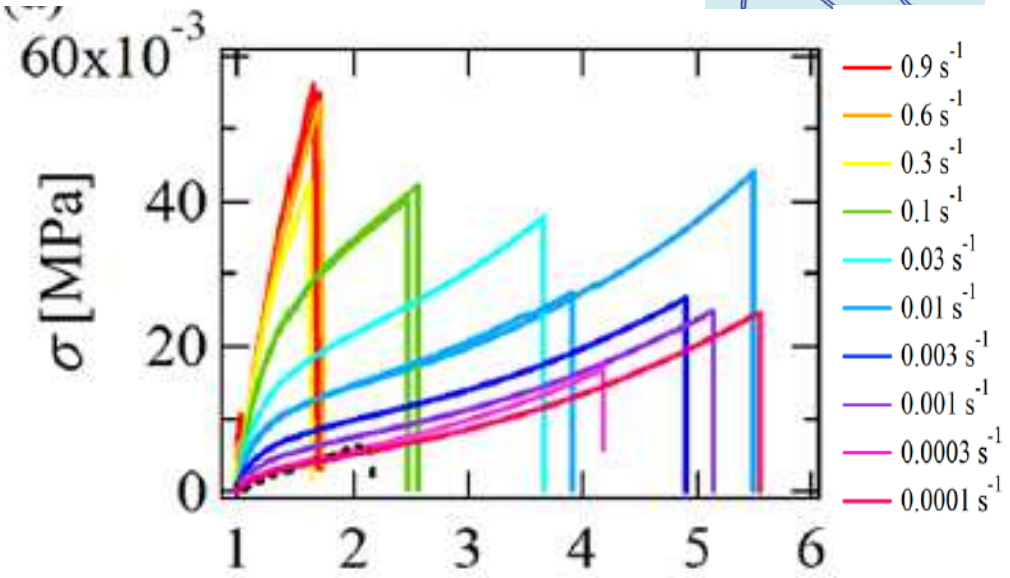
Koichi Mayumi, Alba Marcellan, Guylaine Ducouret, Costantino Creton, and Tetsuharu Narita*

Laboratoire SIMM-PPMD, UMR7615, ESPCI ParisTech – UPMC - CNRS, 10 Rue Vauquelin, 75231 Paris, Cedex 05, France



Chemical + physical network





Unentangled network:

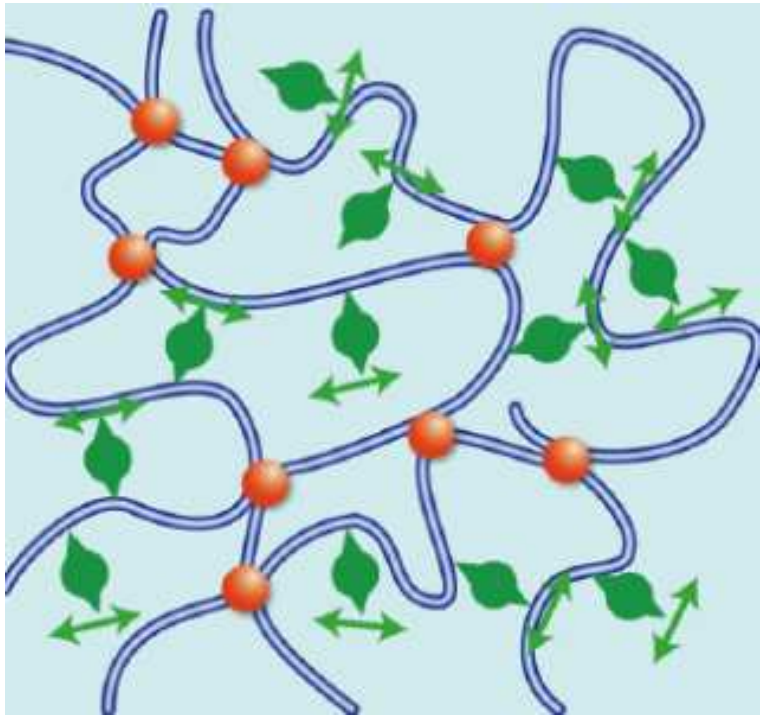
$$\sigma = \left(\lambda - \lambda^{-2}\right) \cdot f^*(t)$$

strain dependent (rubber elasticity) — time dependent (shear modulus)

Stretch — from the chemical network

from the supramolecular bonds — Higher modulus

Blending covalent and transient stickers



Comment:

At high deformation rate:

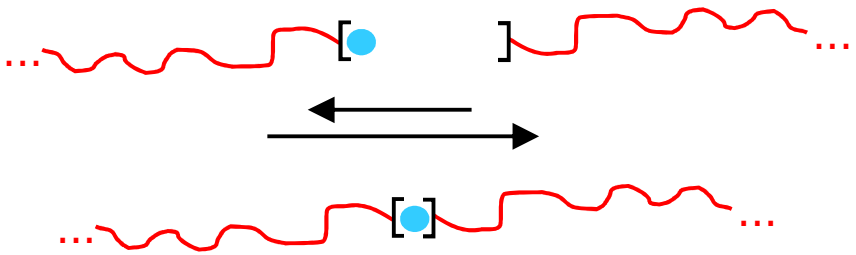
Reversible bonds act similarly as covalent bonds.

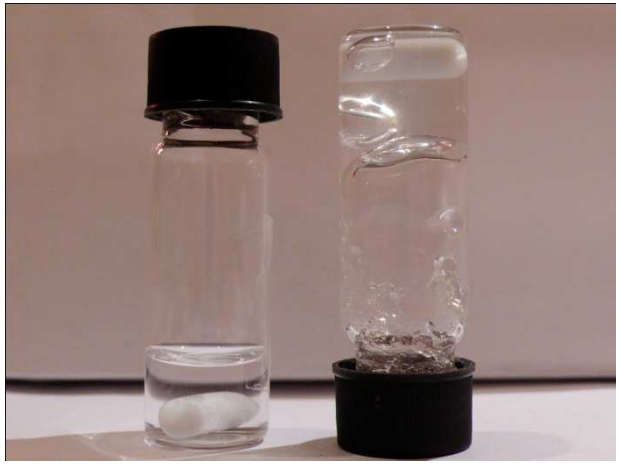
⇒ Limited extensibility

Blending two different stickers - unentangled telechelic chains

Combining block copolymers and metal-ligand associations

Fustin, Gohy et al., *Adv. Mater.* **2007**, *19*, 1665
Stadler et al., Soft Matter, **2009**

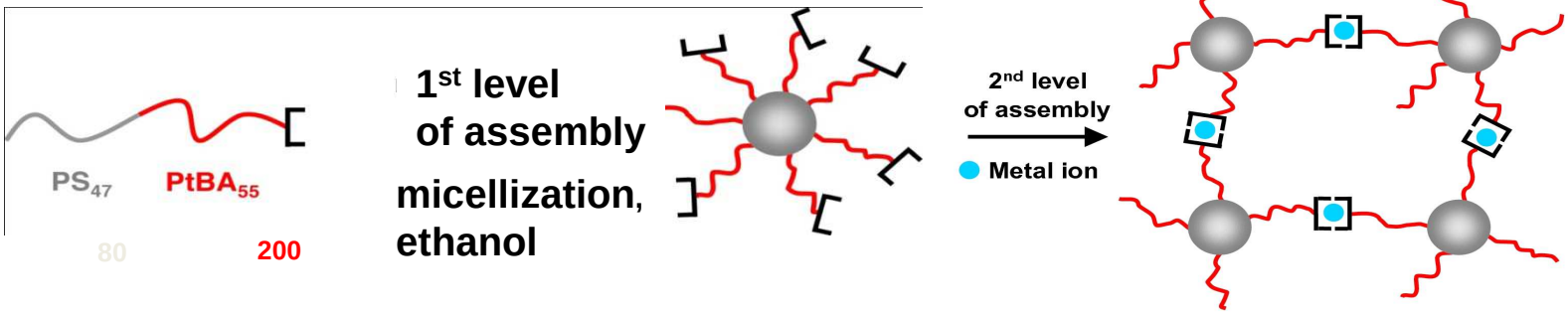




15 w%

15 w%+Ni^{2+}-salt (0.5 equ.)

(Interesting non-linear properties: see later)

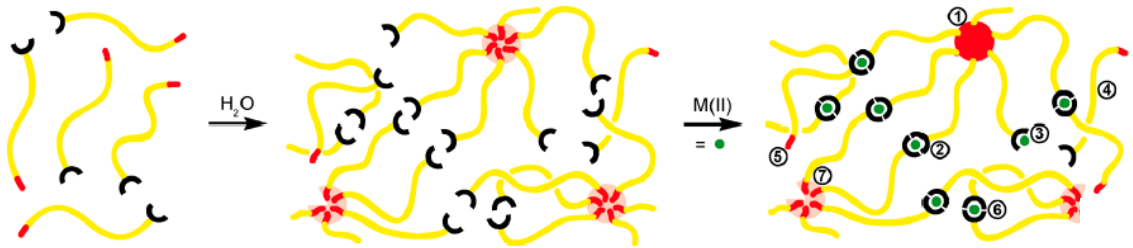


Supramolecular network obtained based on two reversible mechanisms: micellization + metal-ligand association

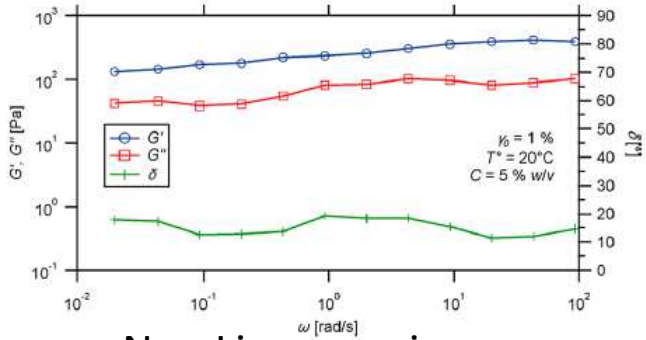
Blending two different stickers - unentangled telechelic chains

Hydrogels with Dual Relaxation and Two-Step Gel–Sol Transition from Heterotelechelic Polymers

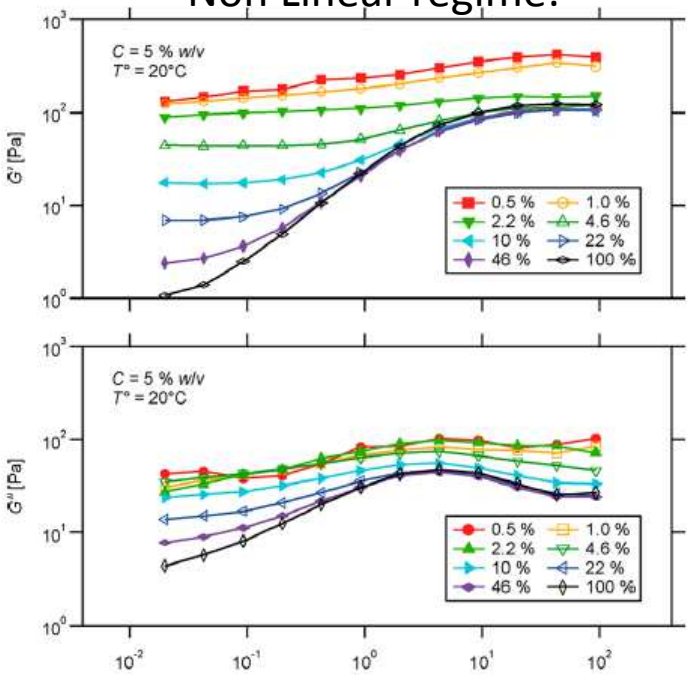
Jérémy Brassinne, Arnaud M. Stevens, Evelyne Van Ruymbeke, Jean-François Gohy and Charles-André Fustin*

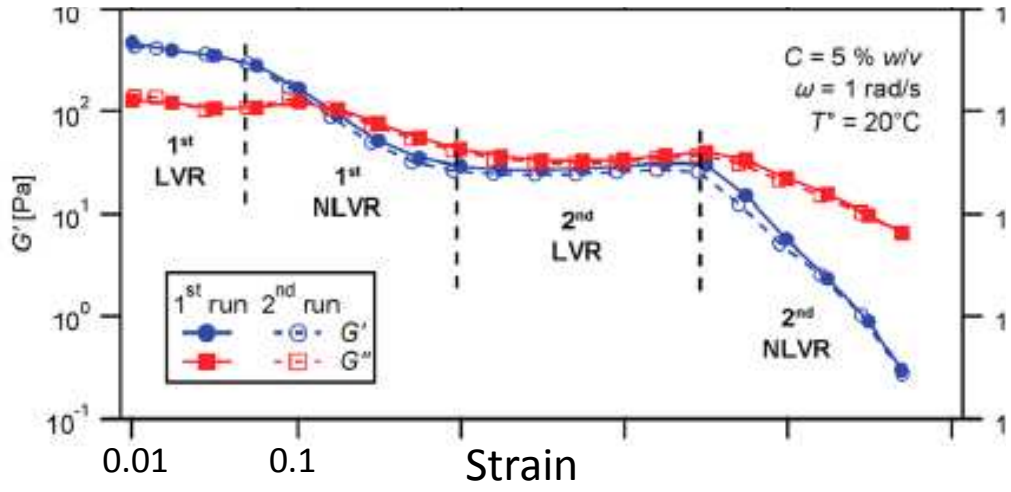


Linear regime:



Non Linear regime:



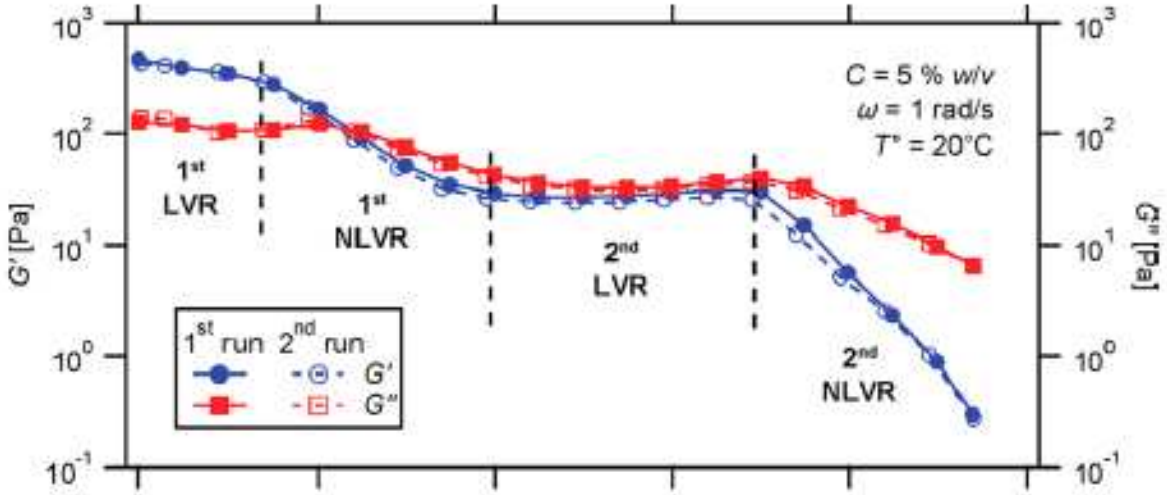


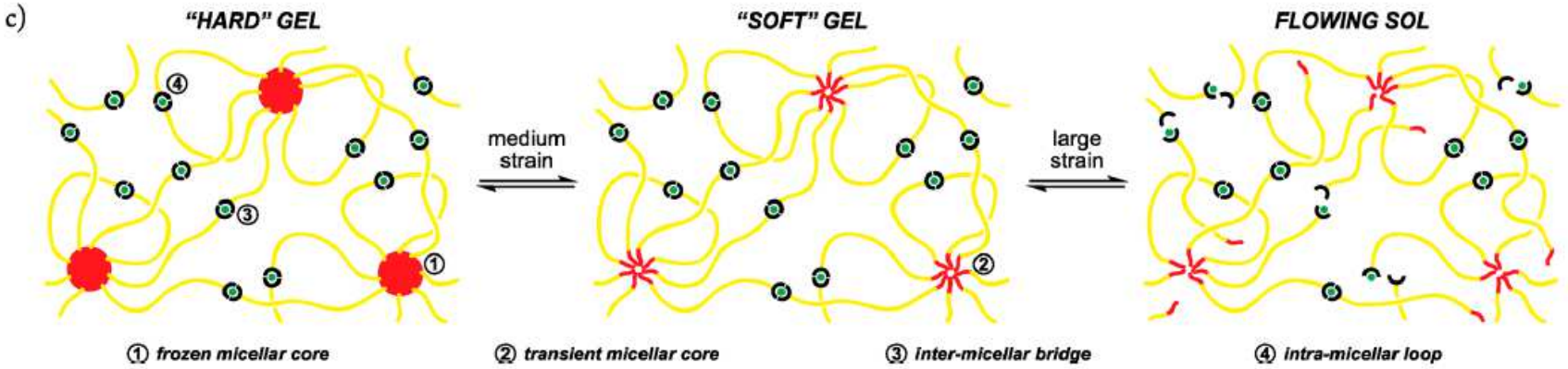
Two linear plateaus are observed

Blending two different stickers - unentangled telechelic chains

Hydrogels with Dual Relaxation and Two-Step Gel–Sol Transition from Heterotelechelic Polymers

Jérémy Brassinne, Arnaud M. Stevens, Evelyne Van Ruymbeke, Jean-François Gohy,* and Charles-André Fustin*





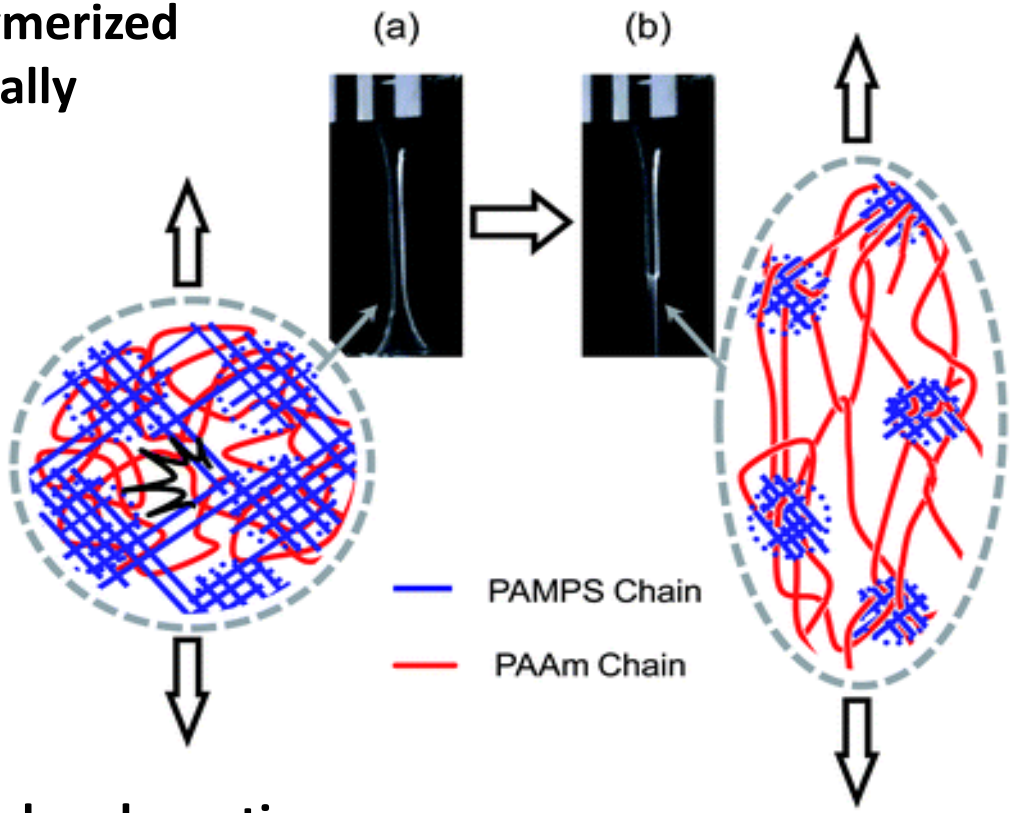
Interpenetrated polymer networks

Gong and co-workers

Two interpenetrating networks polymerized and chemically crosslinked sequentially

The first network:
Highly crosslinked and stretched, "sacrificial minority network"

The second "majority" network:
Large deformability (hence coherence of the overall structure)



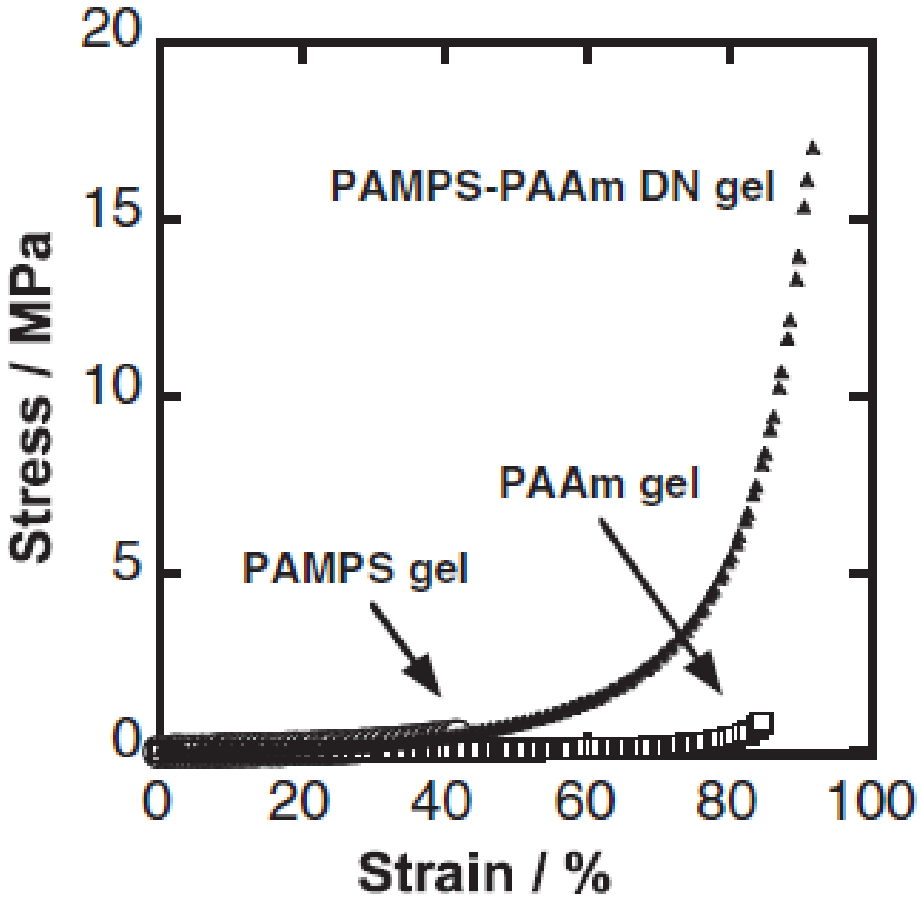
→ **Permanently damaged under elongation**

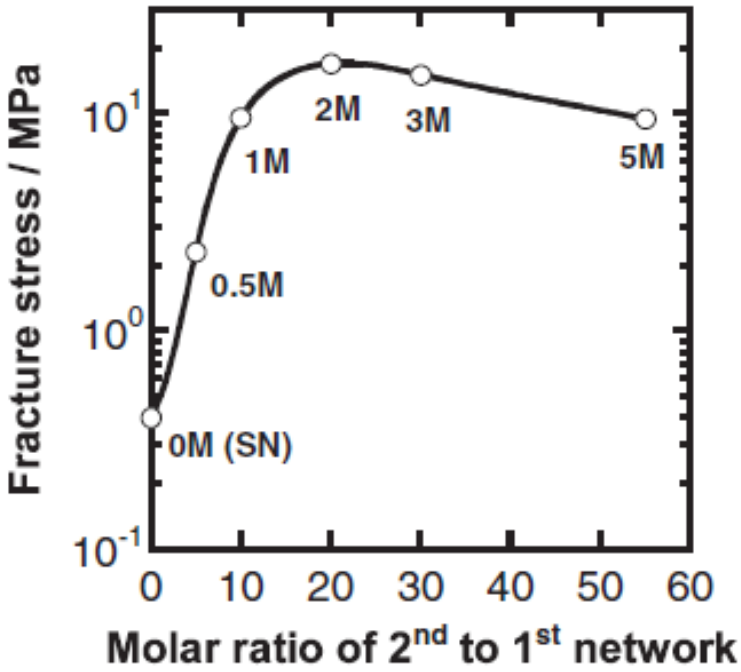
→ **Hybrid DNs: covalent bonds of the stiff network are replaced by reversible bonds**

Viscoelastic properties has hardly been addressed

Interpenetrated polymer networks

First rigid network: PAMPS
Second soft network: PAAm

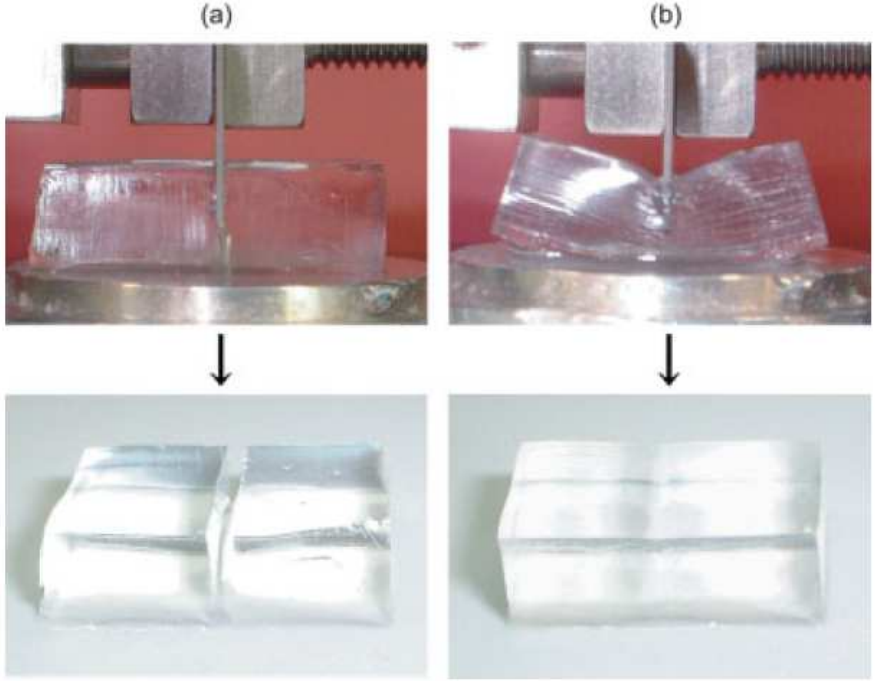




Interpenetrated polymer networks

Double-Network Hydrogels with Extremely High Mechanical Strength**

By *Jian Ping Gong,* Yoshinori Katsuyama, Takayuki Kurokawa,* and *Yoshihito Osada*



ADVANCED MATERIALS

Fig. 3. Photographs demonstrating how a DN gel sustains a high compression. a) PAMPS-1-4 SN gel, b) PAMPS-1-4/PAAm-2-0.1 DN gel. Fracture stress: PAMPS SN gel, 0.4 MPa, PAMPS/PAAm DN gel, 17.2 MPa.

Interpenetrated polymer networks

Large Strain Hysteresis and Mullins Effect of Tough Double-Network Hydrogels

Rebecca E. Webber and Costantino Creton*

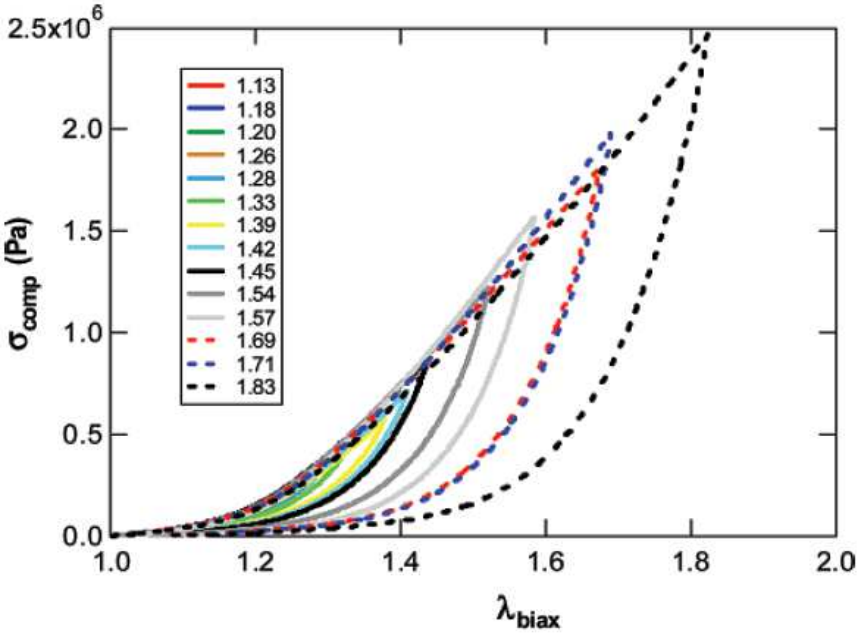
Laboratoire de Physico-Chimie des Polymères et Milieux Dispersés, UMR 7615 CNRS−UPMC-ESPCI, 10, Rue Vauquelin, Paris, France

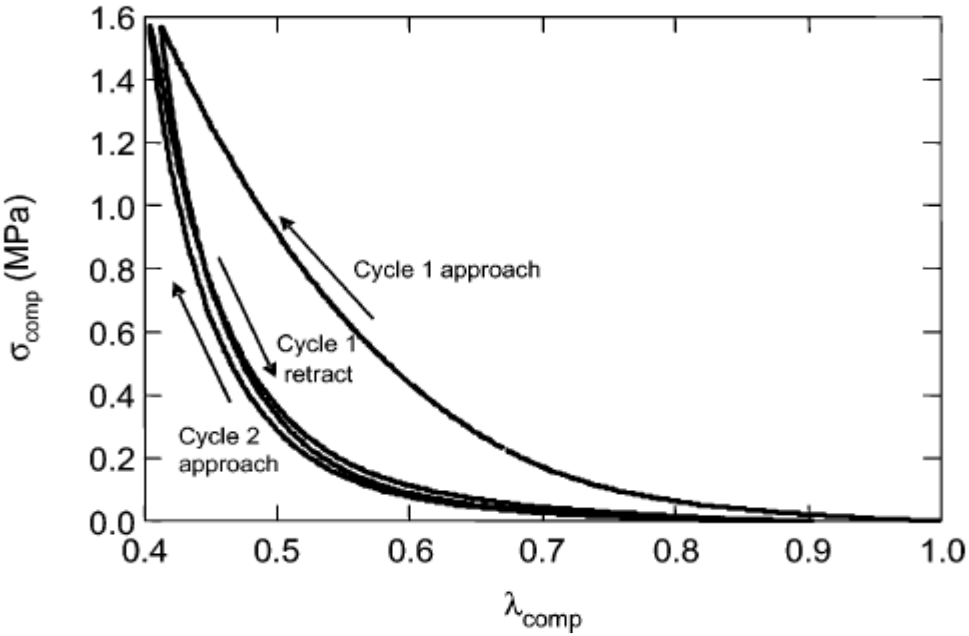
Hugh R. Brown

Faculty of Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

Jian Ping Gong

Laboratory of Soft and Wet Matter, Department of Biological Sciences, University of Hokkaido, Japan



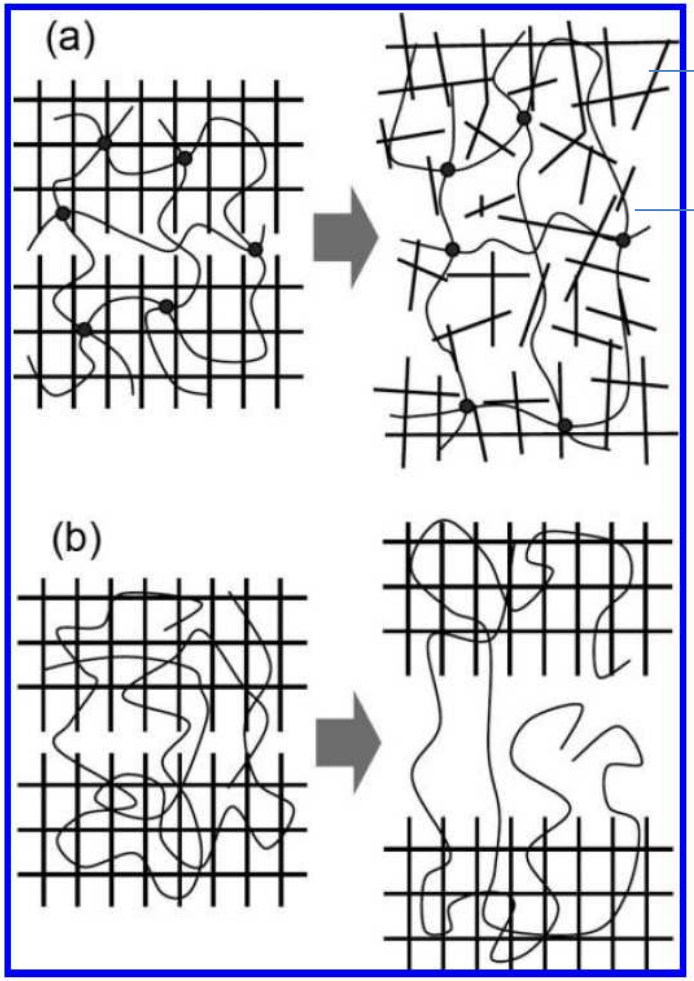


Large hysteresis: permanent damage of the highly crosslinked network

Interpenetrated polymer networks

True Chemical Structure of Double Network Hydrogels

Tasuku Nakajima, Hidemitsu Furukawa, Yoshimi Tanaka, Takayuki Kurokawa, Yoshihito Osada, and Jian Ping Gong*



PAMPS

PAAm

Under deformation, cracks appear.

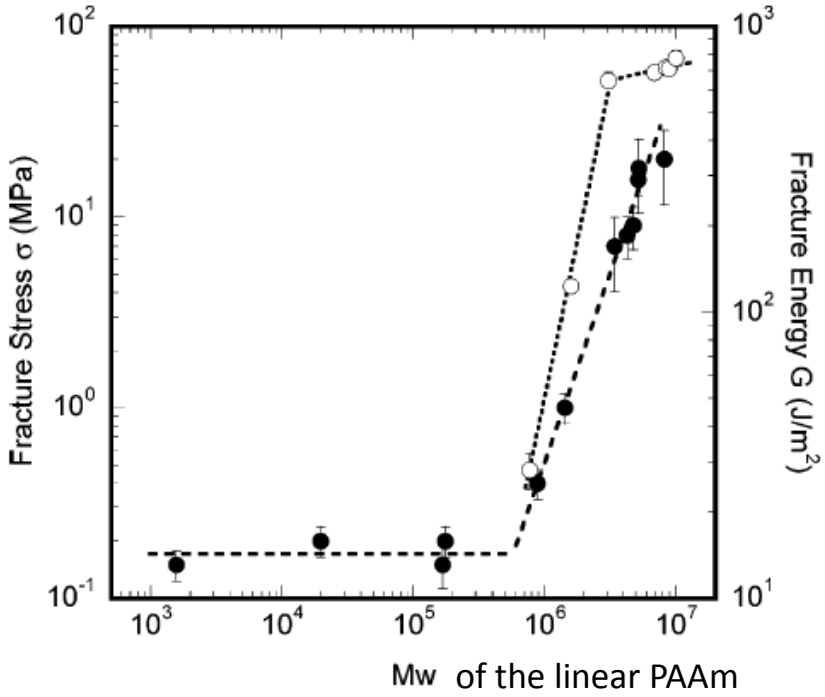
Chemically crosslinked PAAm network:
The crosslinks play the role of anchors: the force can be transferred to PAMPS network far from the crack, by elongation of the PAAm network.

Entangled PAAm:
The force transfer depends on the length of the chain

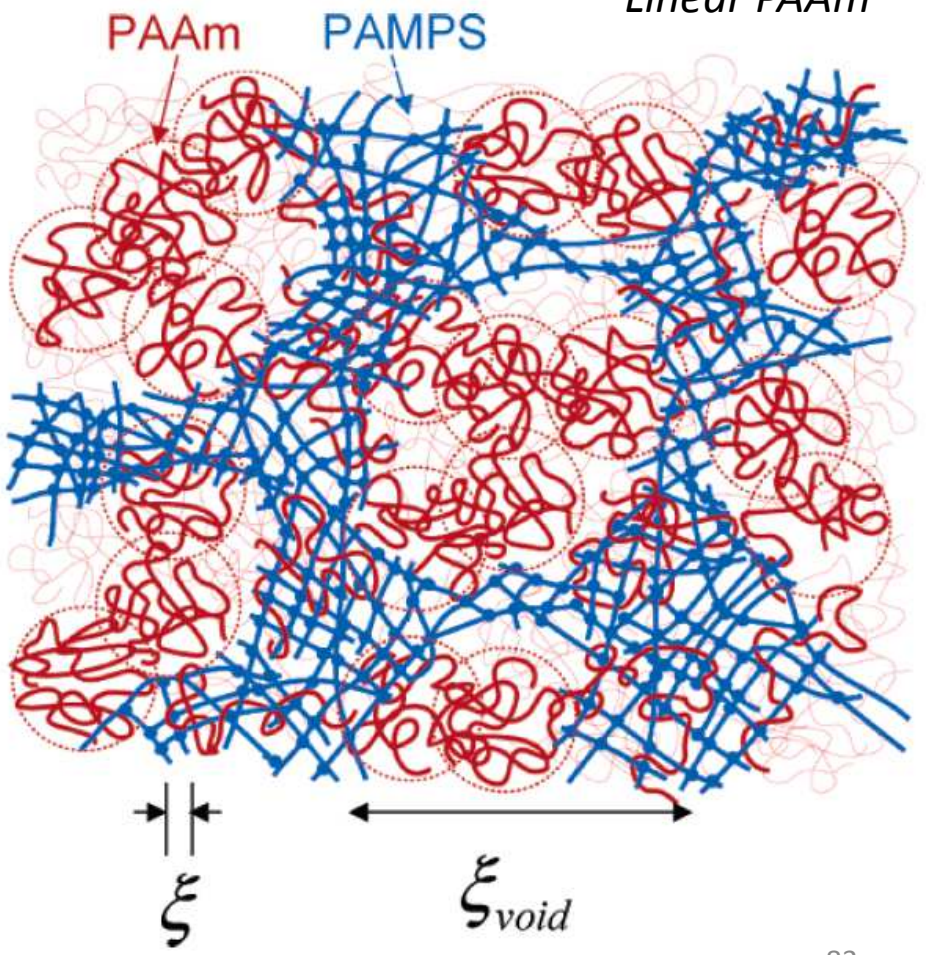
Interpenetrated polymer networks

Effect of Polymer Entanglement on the Toughening of Double Network Hydrogels

Hiroyuki Tsukeshiba,[†] Mei Huang,[†,||] Yang-Ho Na,[†] Takayuki Kurokawa,[†] Rikimaru Kuwabara,[†] Yoshimi Tanaka,[‡] Hidemitsu Furukawa,[†] Yoshihito Osada,[†] and Jian Ping Gong*,[†,§]



Linear PAAm

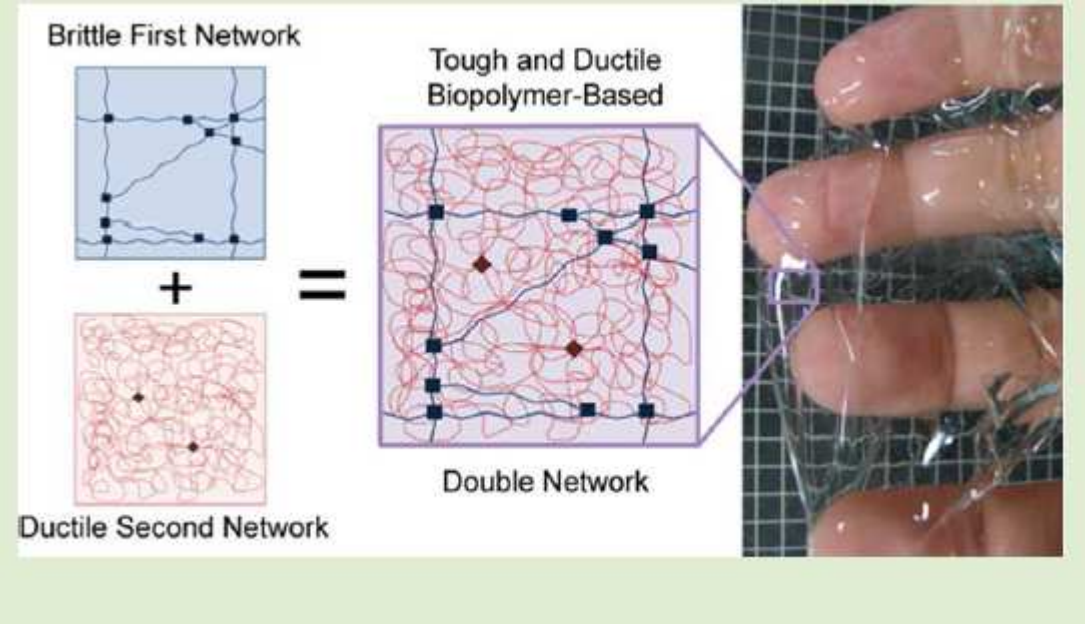


Entanglements are important to increase the fracture stress

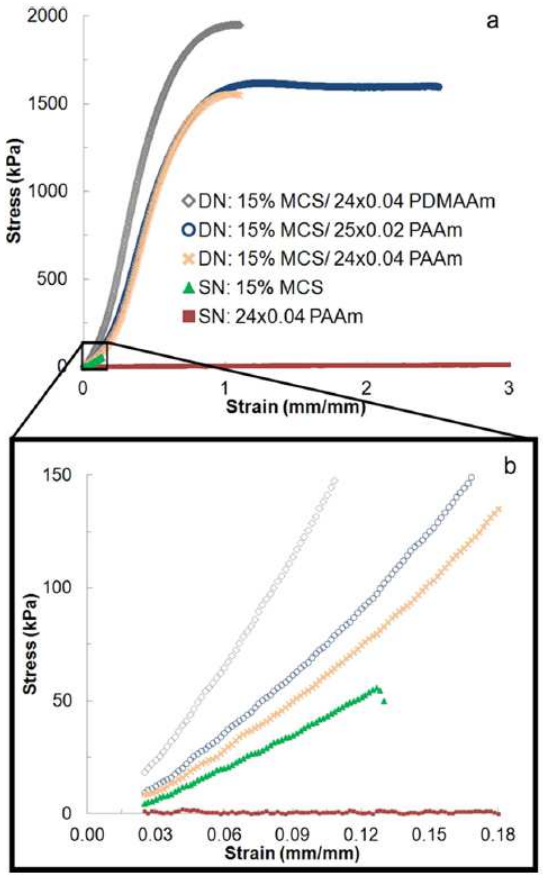
Interpenetrated polymer networks

Double-Network Strategy Improves Fracture Properties of Chondroitin Sulfate Networks

Tiffany C. Suekama,† Jian Hu,‡ Takayuki Kurokawa,‡ Jian Ping Gong,‡ and



Biopolymer-based hydrogel

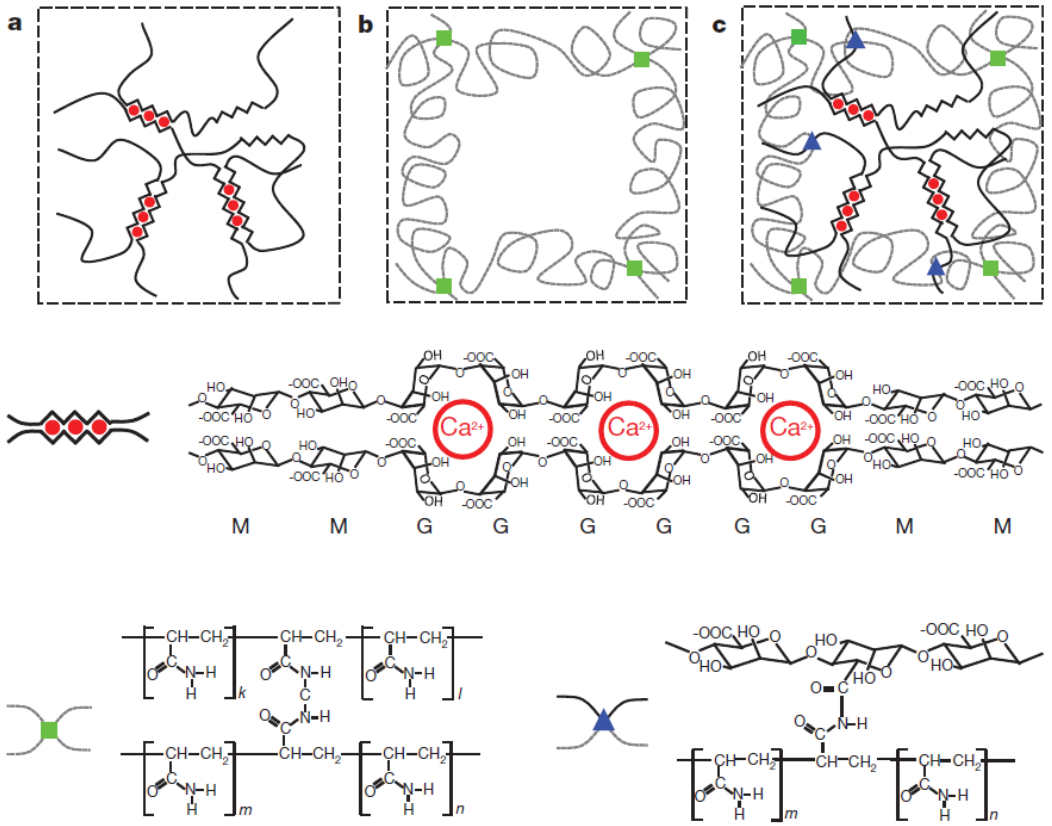


Combination of tough and ductile networks is needed to observe enhanced properties

Interpenetrated polymer networks

Highly stretchable and tough hydrogels

Jeong-Yun Sun[1,2], Xuanhe Zhao[3], Widusha R. K. Illeperuma[1], Ovijit Chaudhuri[1], Kyu Hwan Oh[2], David J. Mooney[1,4], Joost J. Vlassak[1] & Zhigang Suo[1,5]



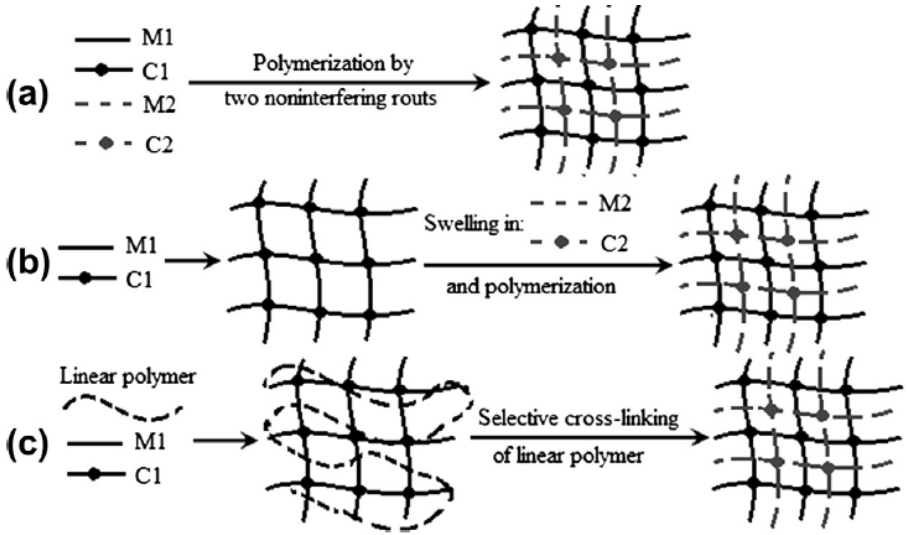
Combination of tough and ductile networks is needed to observe enhanced properties

Interpenetrated polymer networks

Review

Design and applications of interpenetrating polymer network hydrogels. A review

Ecaterina Stela Dragan * (2014)



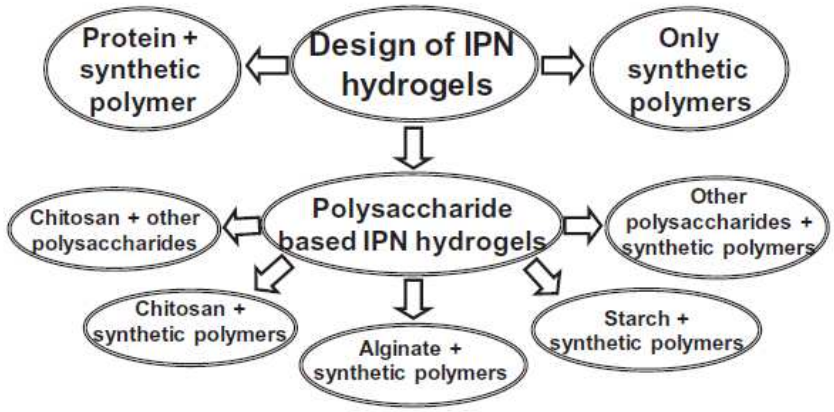


Fig. 2. Possible combinations of hydrophilic polymers used to prepare IPN hydrogels.

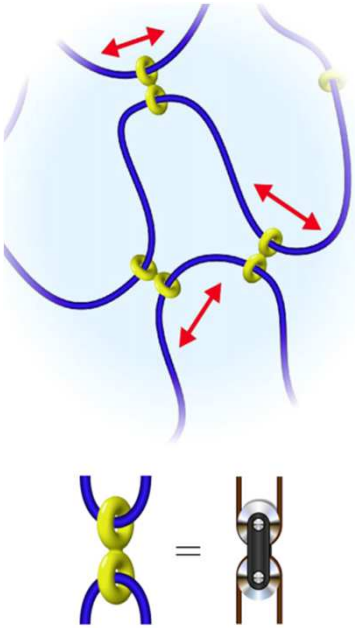
Combination of tough and ductile networks is needed to observe enhanced properties

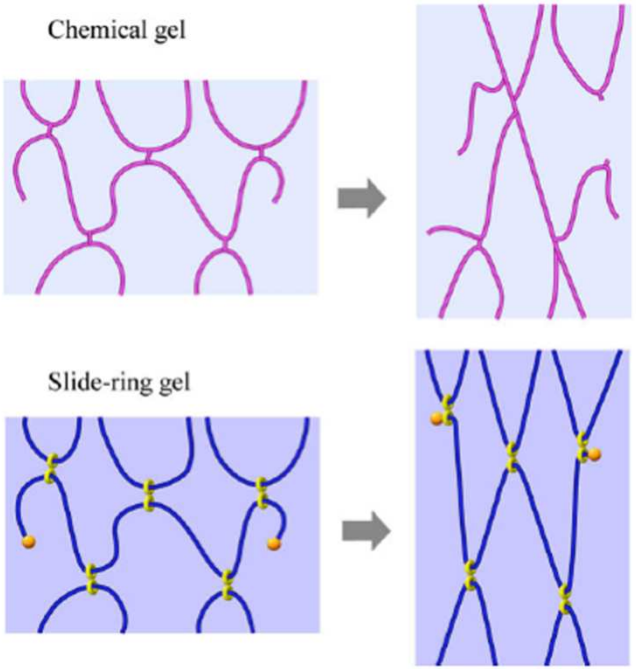
Dynamics of slide-ring gels

Slide-ring materials using topological supramolecular architecture

Kohzo Ito

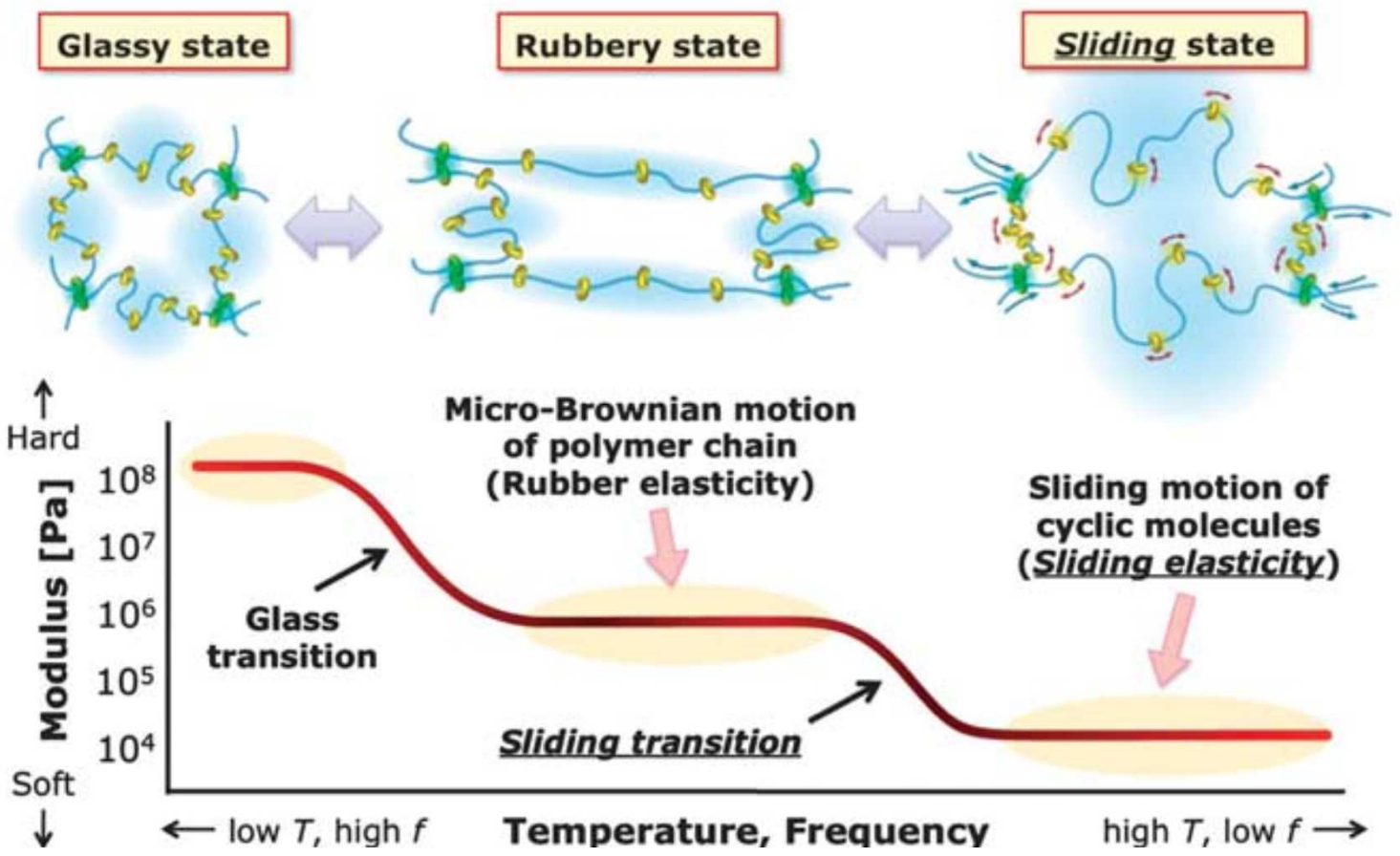
- Gels based on freely movable (topological) crosslinks
- Equilibration of tensions along the chains (pulley effect)





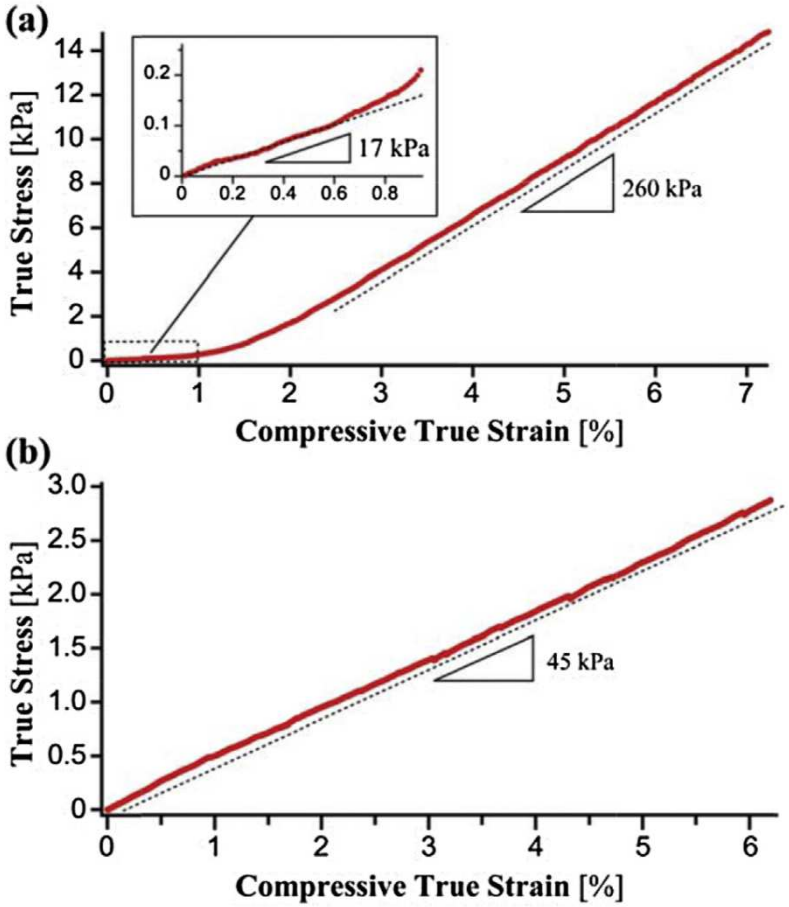
huge swelling capacity, extreme softness, and ability to equilibrate internal tension of the chain in a manner similar to pulleys

Dynamics of slide-ring gels



Ito et al.

Dynamics of slide-ring gels



Slide-ring gels

covalent gels

Such a J shape response has been observed in many biomaterials such as mammalian skin, vessels and tissues, and is responsible for their toughness: their low modulus drastically reduces the energy released in a fracture while the gradual increase in stiffness prevents elastic instability.


INITIAL TRAINING NETWORK
net