istituto dei sistemi complessi

“Using molecular modeling and neutron scattering experiments to investigate PNIPAM microgels”

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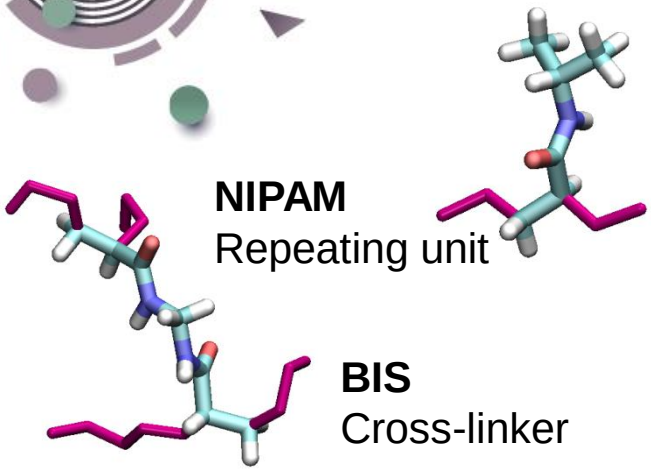
ESS/ILL User Meeting - Topical session on Atomic Scale Simulations in Neutron Scattering

PNIPAM microgels

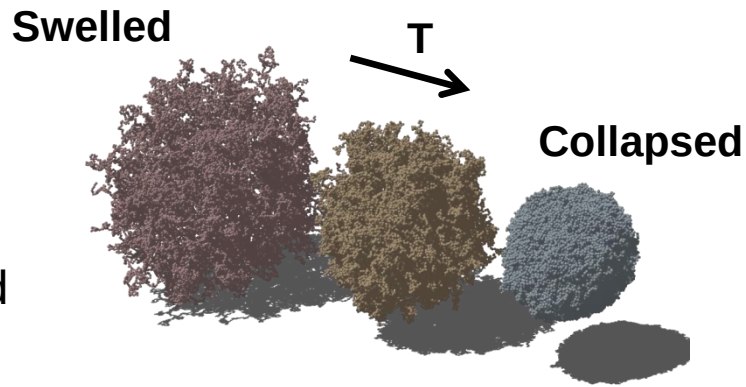


NIPAM
Repeating unit

BIS
Cross-linker

- Microgels are colloidal-scale particles with an intramolecular cross-linked polymeric network
- PNIPAM microgels are co-polymers of NIPAM (N-isopropylacrylamide) and BIS (bis-acrylamide)
- PNIPAM microgels share many features with proteins

- PNIPAM has a Volume Phase Transition in response to external stimuli at T_{VPT} ~32°C
- PNIPAM microgels are widely investigated around T_{VPT} because the tunability of chemical physical properties gives rise to a variety of applications



N. Gnan et al. *Macromolecules* 2017, 50, 8777

Protein dynamical transition

- It was first observed in 1989 for myoglobin. It takes place in hydrated protein suspensions at low temperature, typically ~220-240 K.

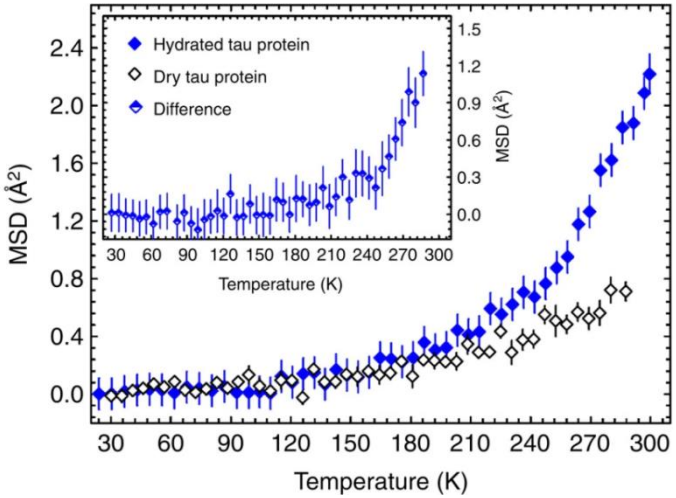
  W. Doster et al. *Nature* 1989, 337, 754

- It consists of a steep enhancement of the atomic mobility which has been associated to the activation of biological functionality.

  K. A. Henzler-Wildman et al. *Nature* 2007, 450, 913

- It has been connected to a strong to strong crossover of the protein hydration water dynamics.

  G. Camisasca et al. *J. Chem. Phys.* 2016, 145, 044503



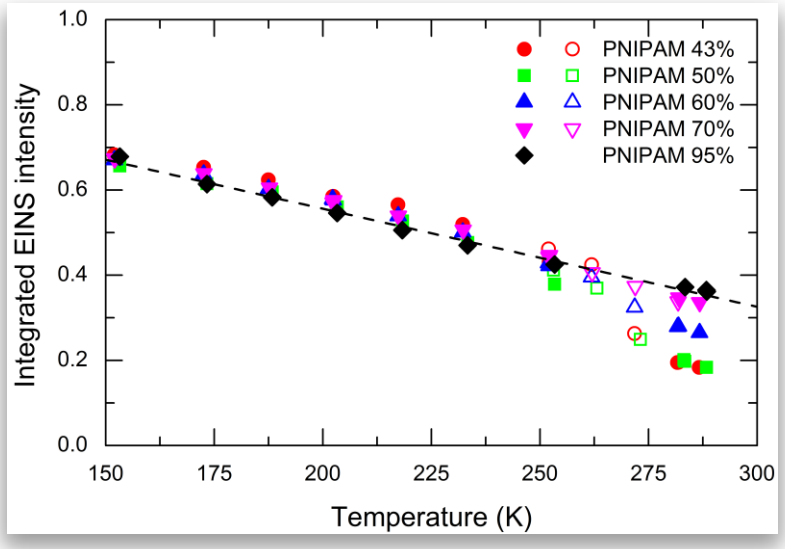
MSDs of the intrinsically disordered protein tau in a hydrated and dry state, measured by elastic incoherent neutron scattering.

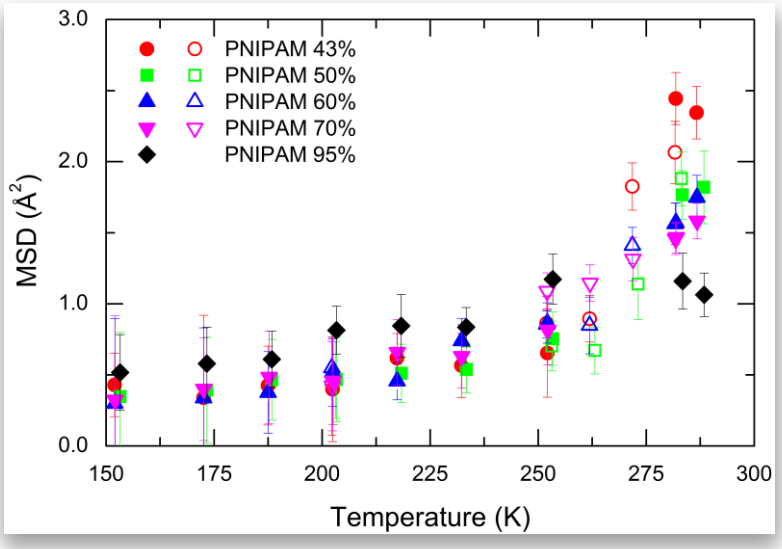
G. Schirò, *Nature Comm.* 2015, 6, 6490

Neutron scattering experiments

ILL (Grenoble) IN13 spectrometer

Probing motions faster than ~150 ps in a spatial region between 1 – 20 Å

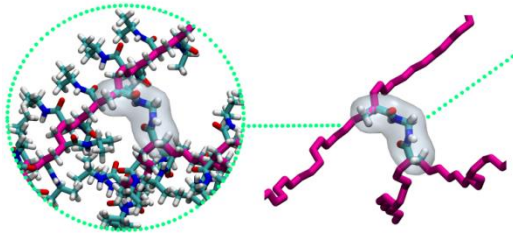


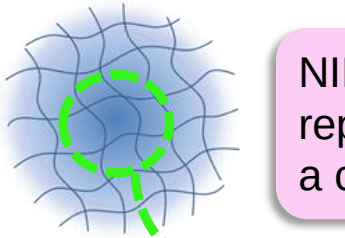


M. Zanatta et al. *Sci. Adv.* 2018, 4 : eaat5895

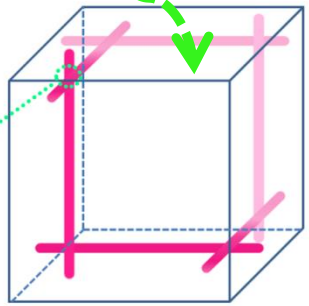
Microgel *in silico* model

Cross-linked atactic PNIPAM 30-mers chains





NIPAM/BIS ratio representing a core region

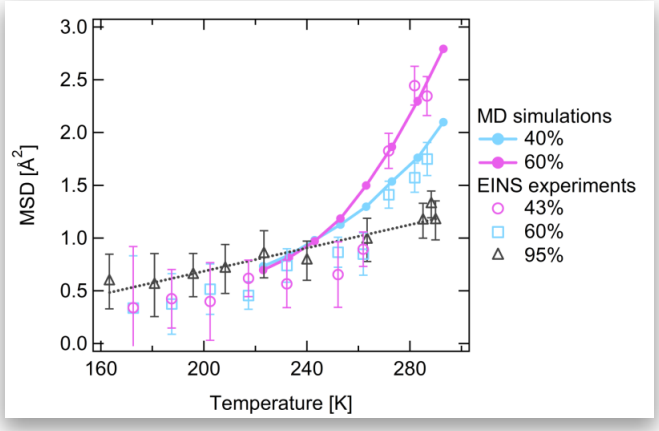


← 5 nm →

6 crosslinks and 3D percolation through infinite connectivity

Tip4p/ICE

Quantitative agreement between MD simulations and EINS experiments!



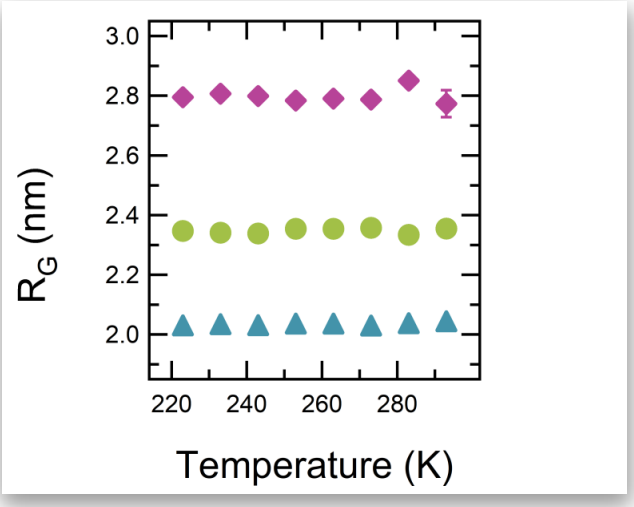
Microscopic origin

is this transition related to a structural rearrangement?

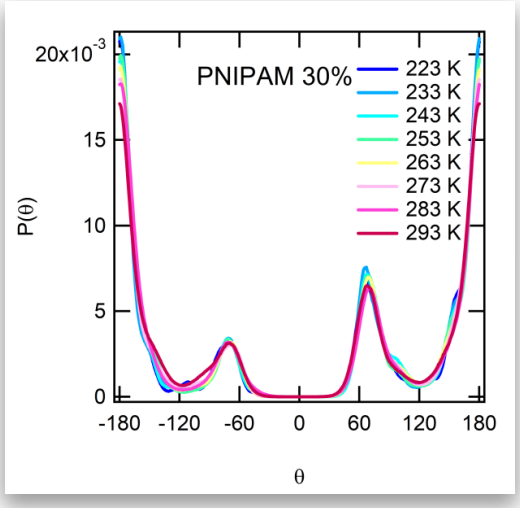
PNIPAM 30%

PNIPAM 40%

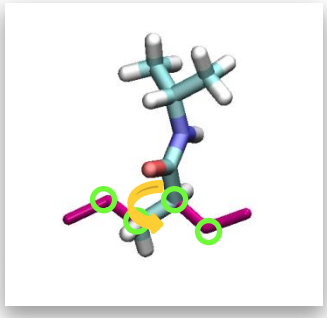
PNIPAM 60%



Temperature dependence of PNIPAM radius of gyration

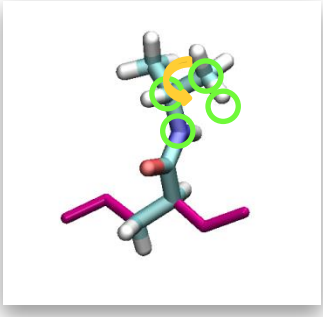


Distribution of backbone dihedral angles



No discontinuity is observed at ~250 K

PNIPAM dynamics

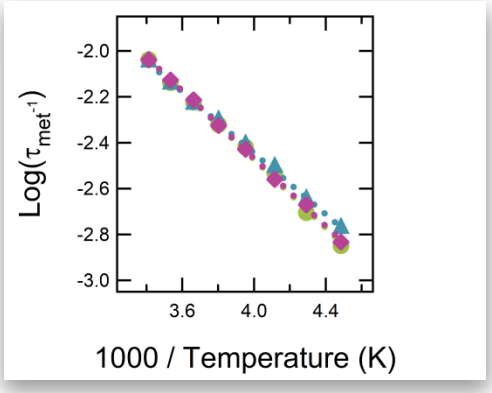


Methyl groups

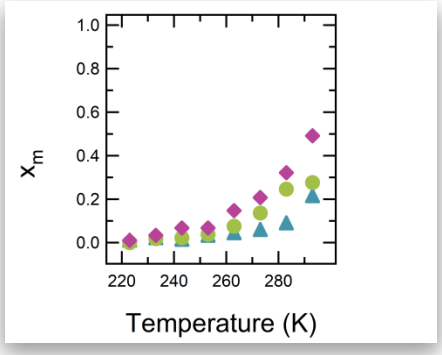
PNIPAM 30%

PNIPAM 40%

PNIPAM 60%



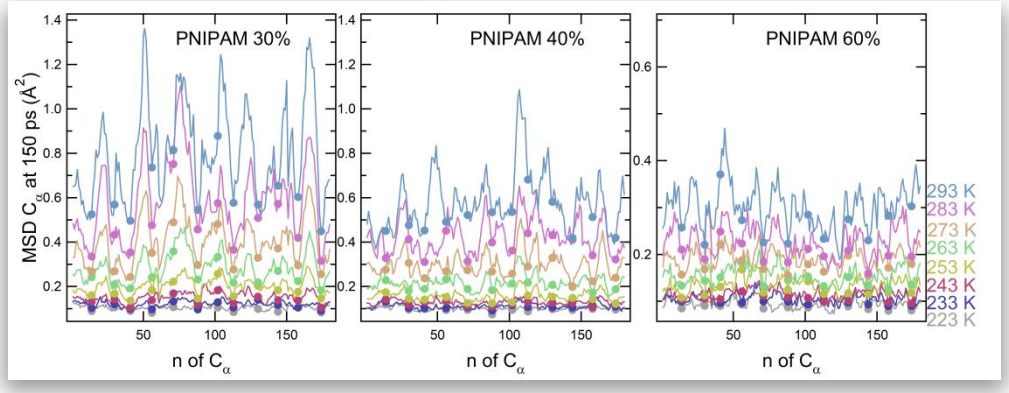
Lifetime of rotational states
E_a = 13.5 kJ mol^{-1}



Backbone

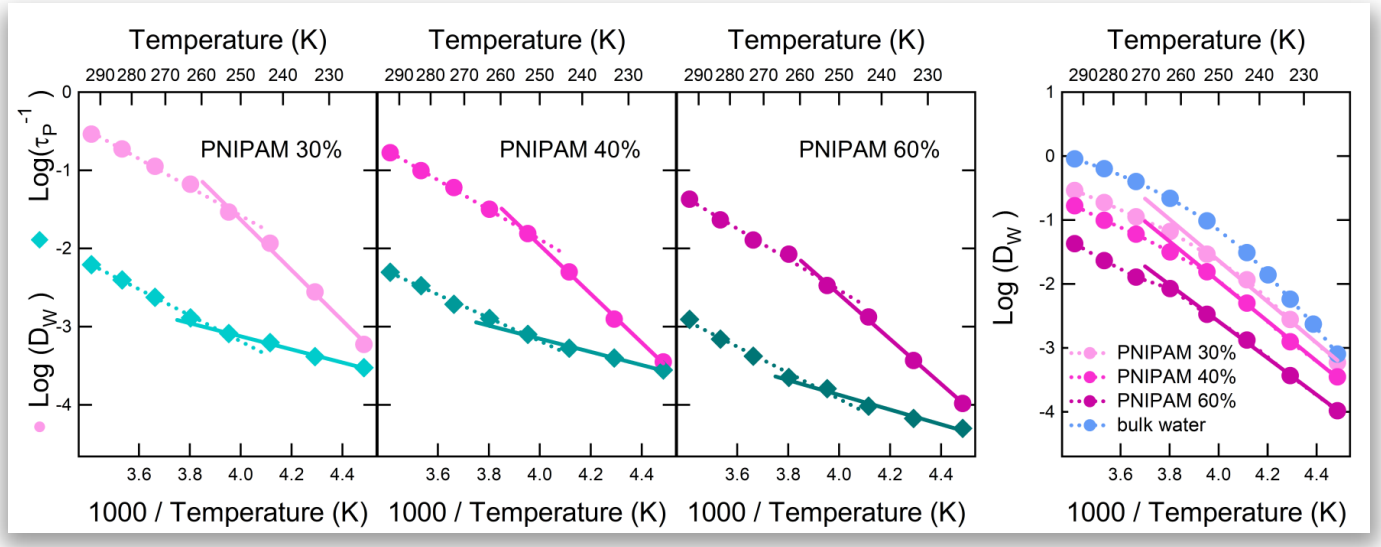
Fraction of mobile dihedrals

MSD at 150 ps of backbone carbon atoms Cα
(Dots are cross-linker atoms)



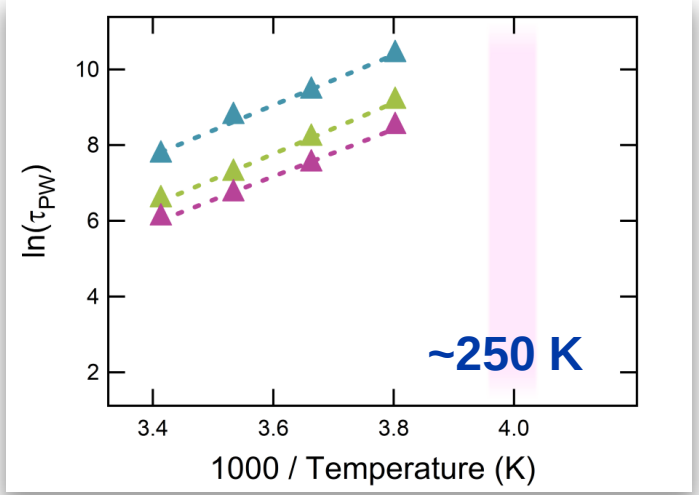
PNIPAM and water dynamics

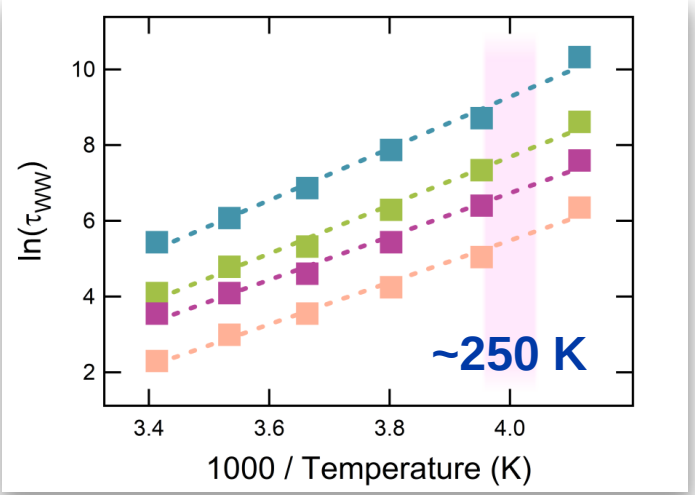
Coupling between water and polymer dynamics



Arrhenius plot of the long relaxation time of the self intermediate scattering function calculated for PNIPAM hydrogen atoms (τ_P) and water diffusion coefficient (D_w)

Macromolecule-water coupling

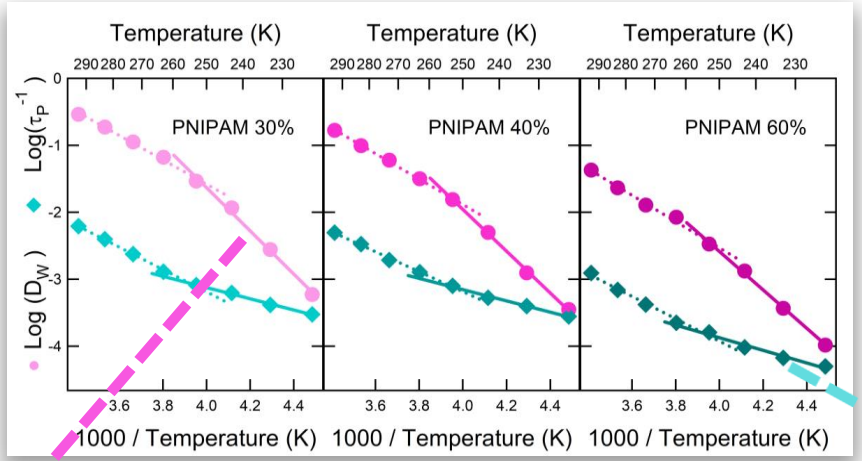




PNIPAM 30%
PNIPAM 40%
PNIPAM 60%
Bulk water

- we monitor the lifetime of PNIPAM−water τ_{PW} and water−water τ_{WW} hydrogen bonds
- τ_{PW} is considerably longer than τ_{WW}
- τ_{PW} and τ_{WW} follow an Arrhenius behavior with activation energies of about 55 kJ mol^{-1} irrespective of hydration level

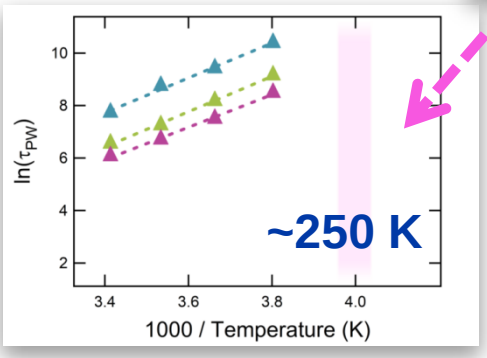
Molecular mechanism



Water dynamics

PNIPAM-water HBs

E_a = ~55 kJ mol^{-1}



PNIPAM 30%

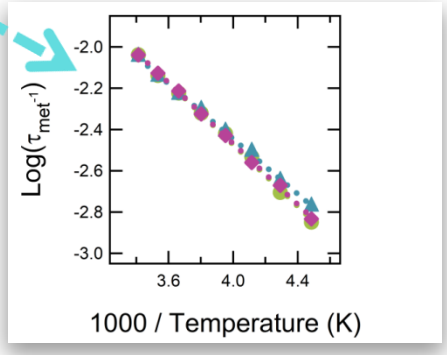
PNIPAM 40%

PNIPAM 60%

PNIPAM dynamics

Rotation methyl groups

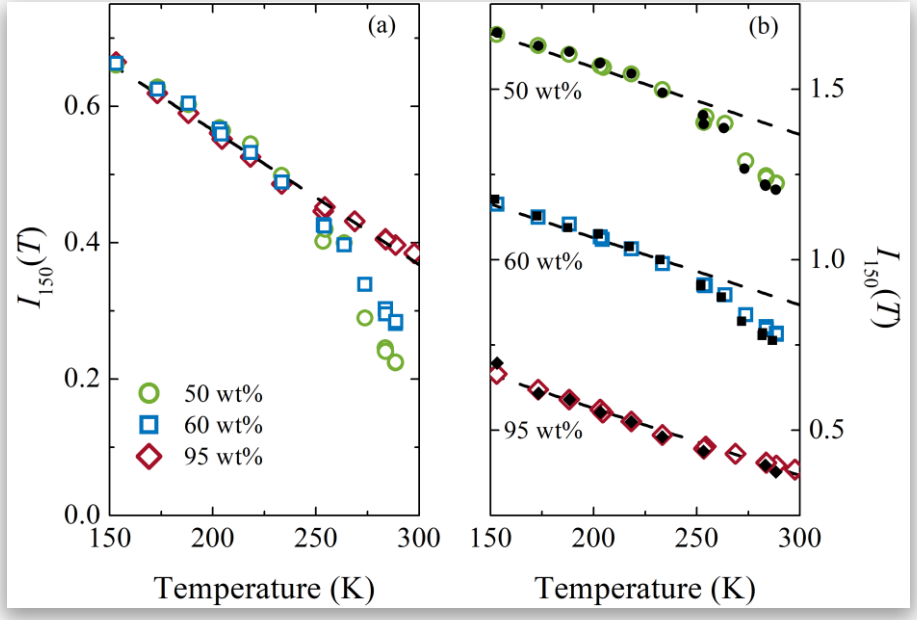
E_a = 13.5 kJ mol^{-1}



L. Tavagnacco et al. *J. Phys. Chem. Lett.* 2019, 10, 4, 870-876

Role of the architecture

ILL (Grenoble) IN13 spectrometer



IN13 integrated elastic intensity as a function of temperature for:

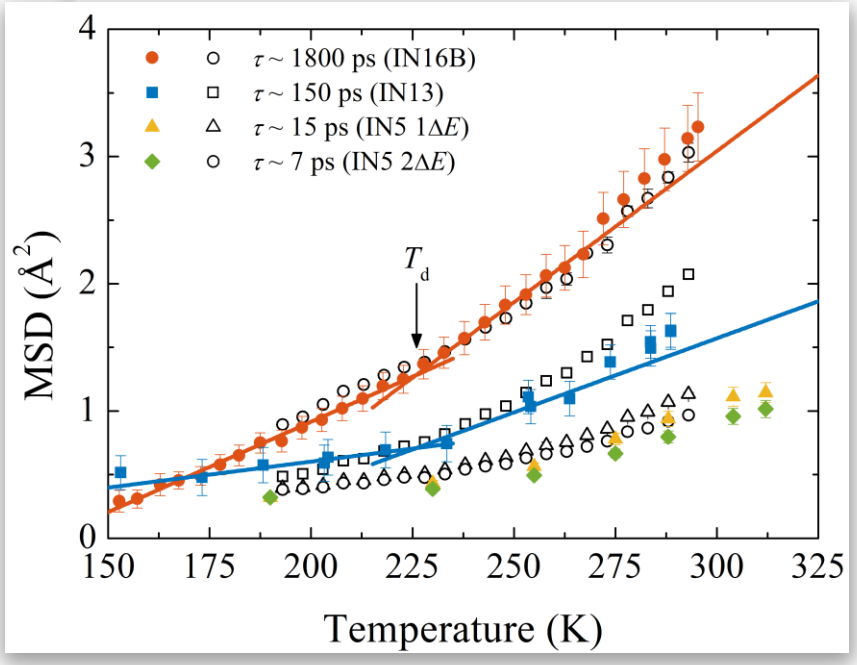
(a) linear polymer chains as a function of PNIPAM concentration

(b) linear chains (open symbols) compared to microgels (filled symbols)

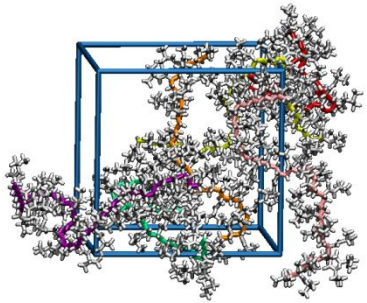
L. Tavagnacco et al. *Phys. Rev. Res.* 2021 in press

PNIPAM linear chains

ILL (Grenoble) IN13, IN16B and IN5 spectrometers

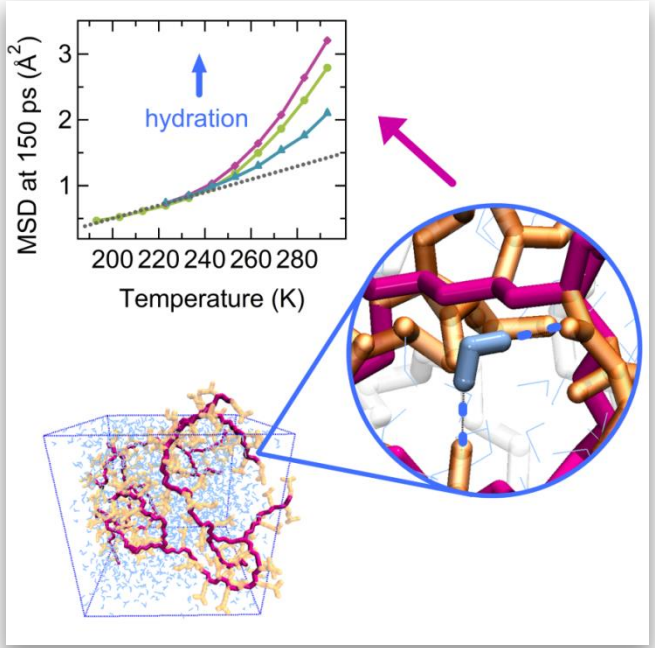


Comparison between experimental MSDs (filled symbols) and numerical MSDs (open symbols) at different timescales



L. Tavagnacco et al. *Phys. Rev. Res.* 2021 in press

Summary



- Evidence of a “protein-like” dynamical transition in non-biological macromolecules, independently on the polymer topology
- At $T<T_d$ PNIPAM dynamics is governed by the rotation of the methyl groups and a sudden increase of the polymer segmental dynamics occurs at T_d
- Hydrogen bonds between PNIPAM and water play a primary role in determining water dynamics below T_d
- Macromolecule−water coupling is a driving ingredient of the dynamical transition

In collaboration with…

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CNR-ISC Rome

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