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Dichotomous behaviors of stress and dielectric relaxations in dense suspensions of swollen thermoreversible hydrogel microparticles

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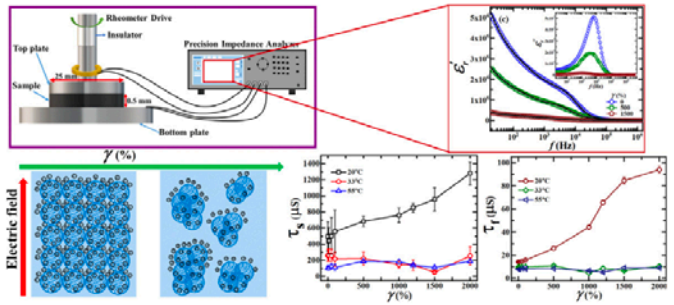
GRAPHICAL ABSTRACT



Chandeshwar Misra, Paramesh Gadige and Ranjini Bandyopadhyay
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RHEODLS Lab

Ranjini Bandyopadhyay,
RRI Bangalore, INDIA
ISPCM8, 1-3 February, 2023

PHYSICAL REVIEW MATERIALS 1, 055603 (2017)

Effects of polydispersity on the glass transition dynamics of aqueous suspensions of soft spherical colloidal particles

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(Received 16 June 2017; published 30 October 2017)

Thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) particles of a nearly constant swelling ratio and with polydispersity indices (PDIs) varying over a wide range (7.4%–48.9%) are synthesized to study the effects of polydispersity on the dynamics of suspensions of soft PNIPAM colloidal particles. The PNIPAM particles are characterized using dynamic light scattering (DLS) and scanning electron microscopy (SEM). The zero shear viscosity (η_0) data of these colloidal suspensions, estimated from rheometric experiments as a function of the effective volume fraction ϕ_{eff} of the suspensions, increases with an increase in ϕ_{eff} and shows a dramatic increase at $\phi_{\text{eff}} = \phi_0$. The data for η_0 as a function of ϕ_{eff} fit well to the Vogel-Fulcher-Tammann (VFT) equation. It is observed that increasing PDIs results in increasingly fragile supercooled liquidlike behavior, with the parameter ϕ_0, extracted from the fits to the VFT equation, shifting towards higher ϕ_{eff}. The observed increase in fragility is attributed to the prevalence of dynamical heterogeneities (DHs) in these polydisperse suspensions, while the simultaneous shift in ϕ_0 is ascribed to the decoupling of the dynamics of the smallest and largest particles. Finally, it is observed that the intrinsic nonlinearity of these suspensions, estimated at the third harmonic near ϕ_0 in Fourier transform oscillatory rheological experiments, increases with an increase in PDIs. Our results are in agreement with theoretical predictions and simulation results for polydisperse hard sphere colloidal glasses and clearly demonstrate that jammed suspensions of polydisperse colloidal particles can be effectively fluidized with increasing PDIs. Suspensions of these particles are therefore excellent candidates for detailed experimental studies of the effects of polydispersity on the dynamics of glass formation.

DOI: 10.1103/PhysRevMaterials.1.055603

I. INTRODUCTION

Thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel suspensions undergo a reversible volume phase transition above the lowest critical soluble temperature (LCST) of ≈32 °C in water [1,2]. This property of PNIPAM

glasses, therefore, T is replaced with $1/\phi$. The modified VFT equation $\eta = \eta_0 \exp\left(\frac{D\phi}{\phi_0 - \phi}\right)$ explains the rise in the viscosity of a colloidal suspension with ϕ and its dramatic increase at $\phi = \phi_0$ [14,16]. Here $1/D$ is the fragility and accounts for the deviation of the viscosity from an Arrhenius dependence on

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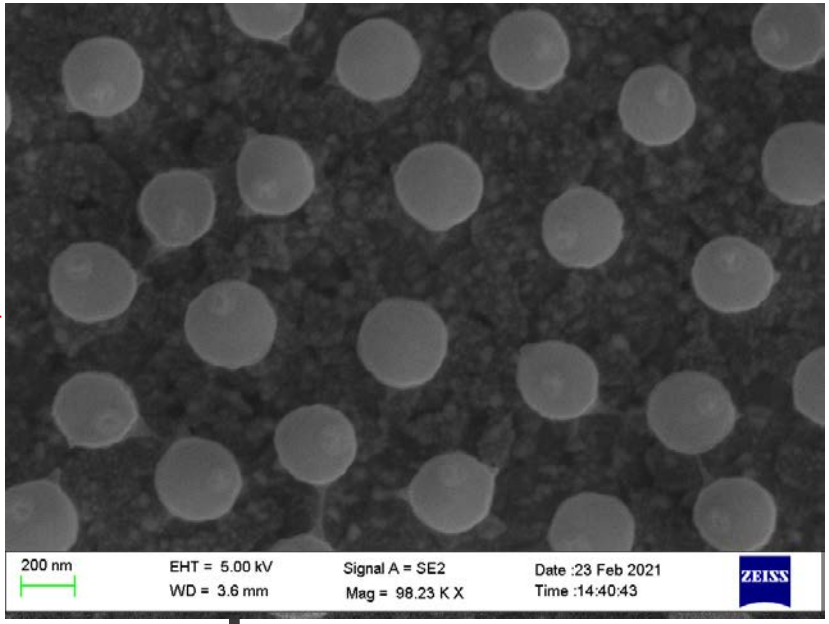
d by slow dynamics and aging

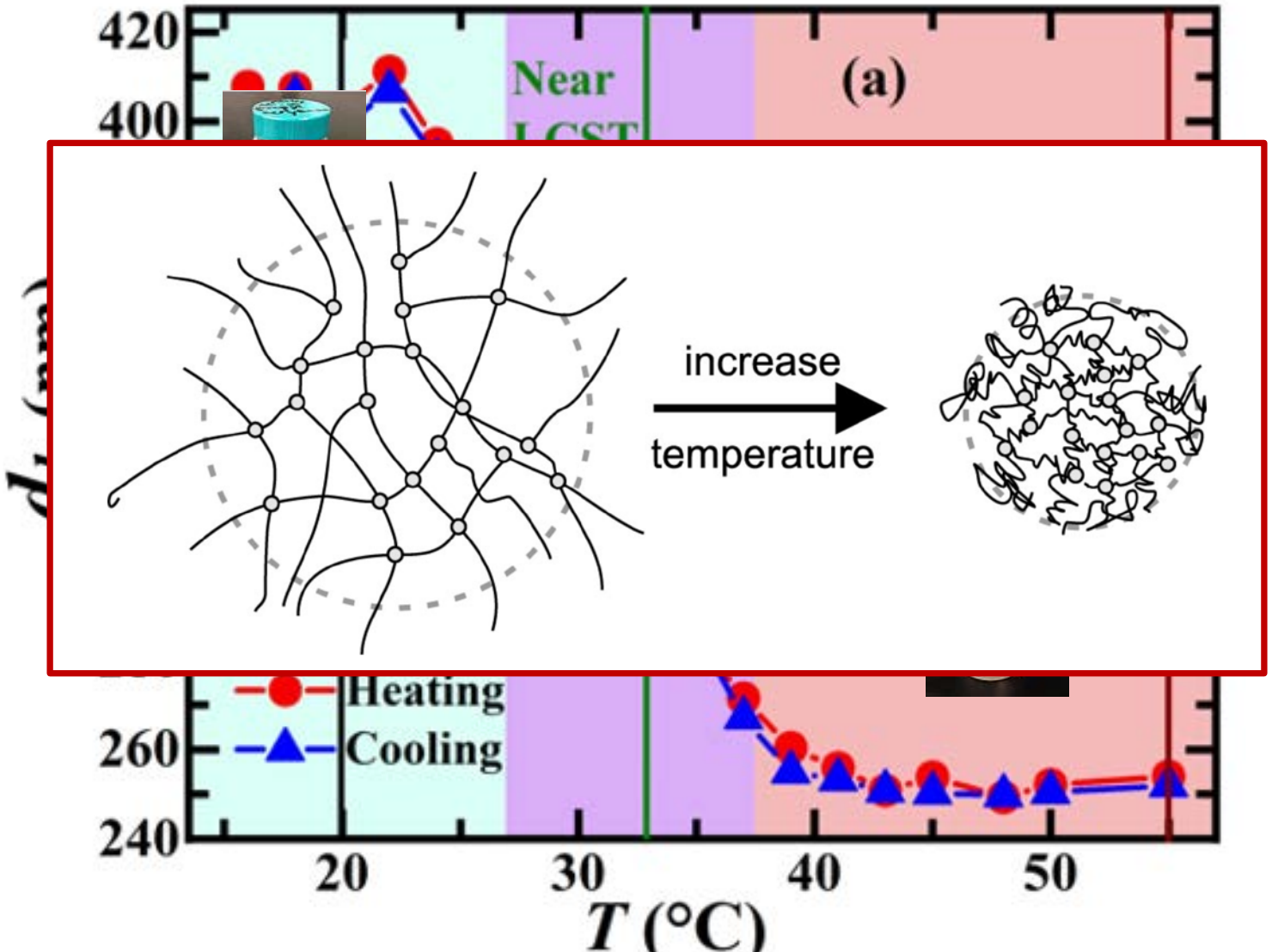


Homogeneously crosslinked

We can make particles having controlled stiffnesses and also of controlled particle size polydispersities (Behera, Saha, Gadige and Bandyopadhyay., PRM, 2017)

Thermoresponsive Poly(N-isoproplylacryliamide) PNIPAM Microgels

Thermoresponsive PNIPAM particles undergo a swelling-deswelling transition at LCST~ 32°C



Yunker et al., Reports in Progress of Physics, 77, 056601 (2014)

Maximally swollen particles < 20°C
Fully collapsed particles > 40°C

Rheo-dielectric setup

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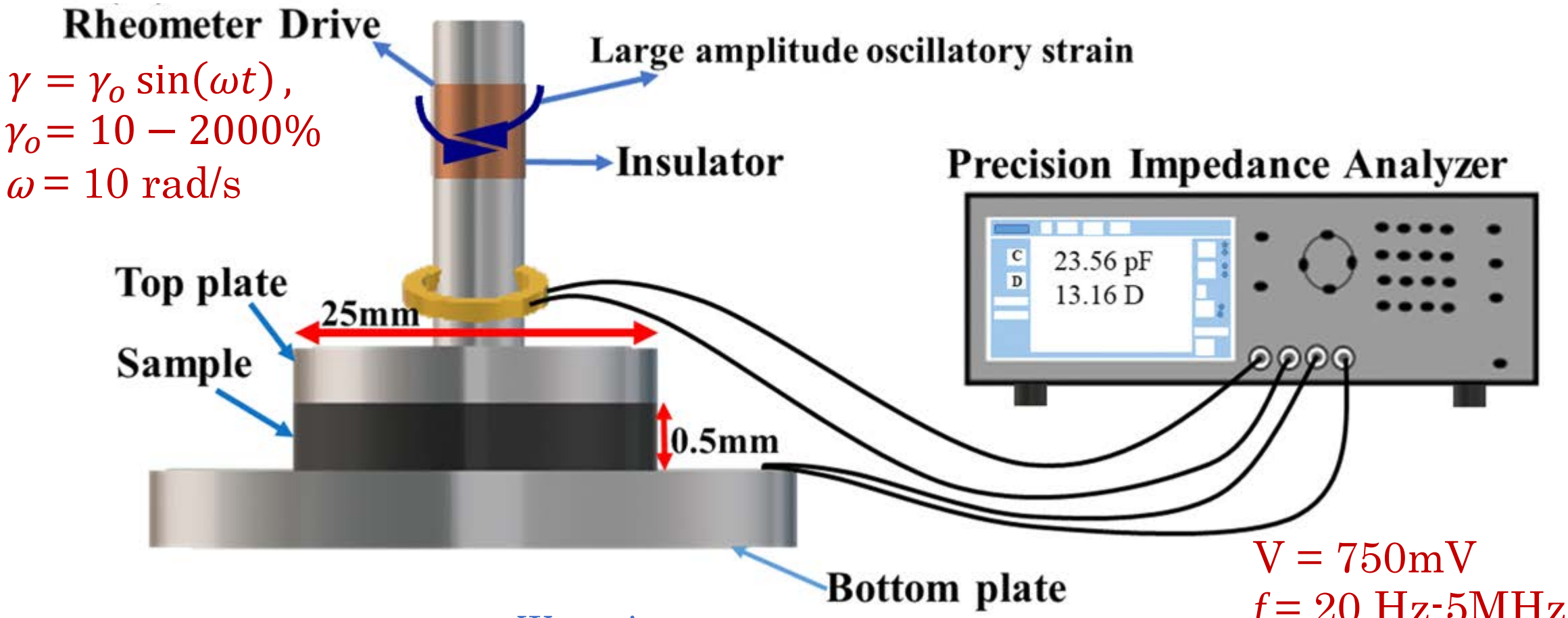

We measure

Capacitance (C)
Loss Factor (D)

We estimate

$$\varepsilon_r' = C\left(\frac{d}{A\varepsilon_o}\right), \qquad \varepsilon_r'' = \mathrm{D}\,\varepsilon_r'$$

Dielectric relaxation

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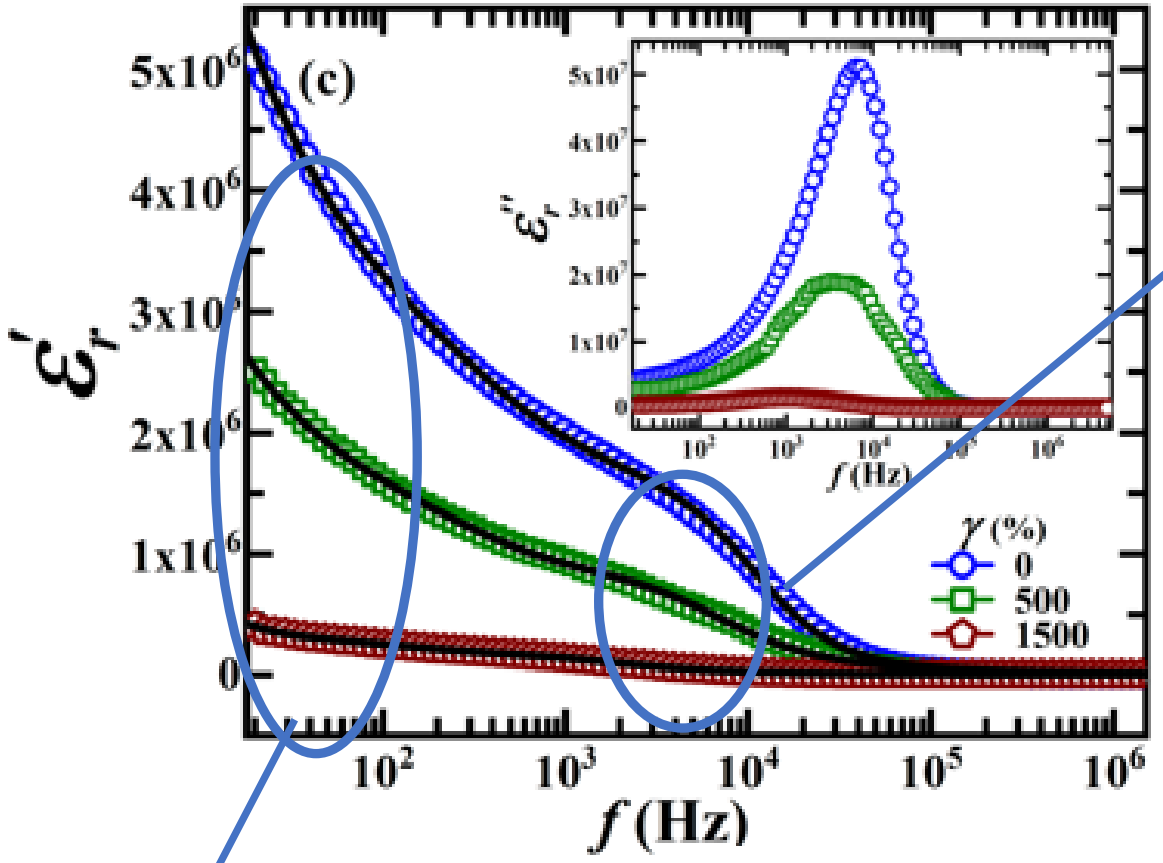


Fluctuation of the counterions below the LCST and interfacial polarization above the LCST

Interfacial polarization

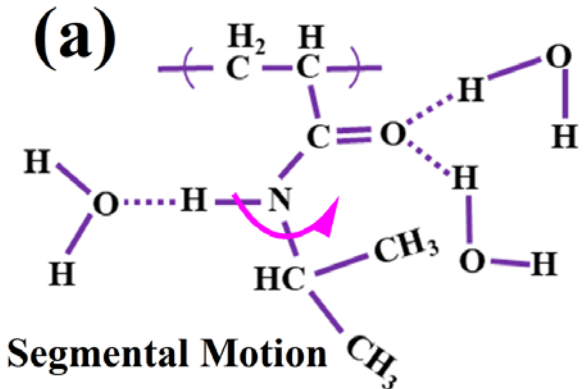
Cole-Davidson Relaxation model

$$\epsilon_r^* = \epsilon_h + \frac{\epsilon_l - \epsilon_m}{1 + (j\omega\tau_s)^{\beta_s}} + \frac{\epsilon_m - \epsilon_h}{1 + (j\omega\tau_f)^{\beta_f}} + A\omega^{-m}$$

$\Delta\epsilon_l \ (=\epsilon_l - \epsilon_m)$ and $\Delta\epsilon_h \ (=\epsilon_m - \epsilon_h)$

are the dielectric strength in low and high frequency regime respectively

Local segmental motion of the polymer and motion of counterions along the polymer chain over the entire temperature range

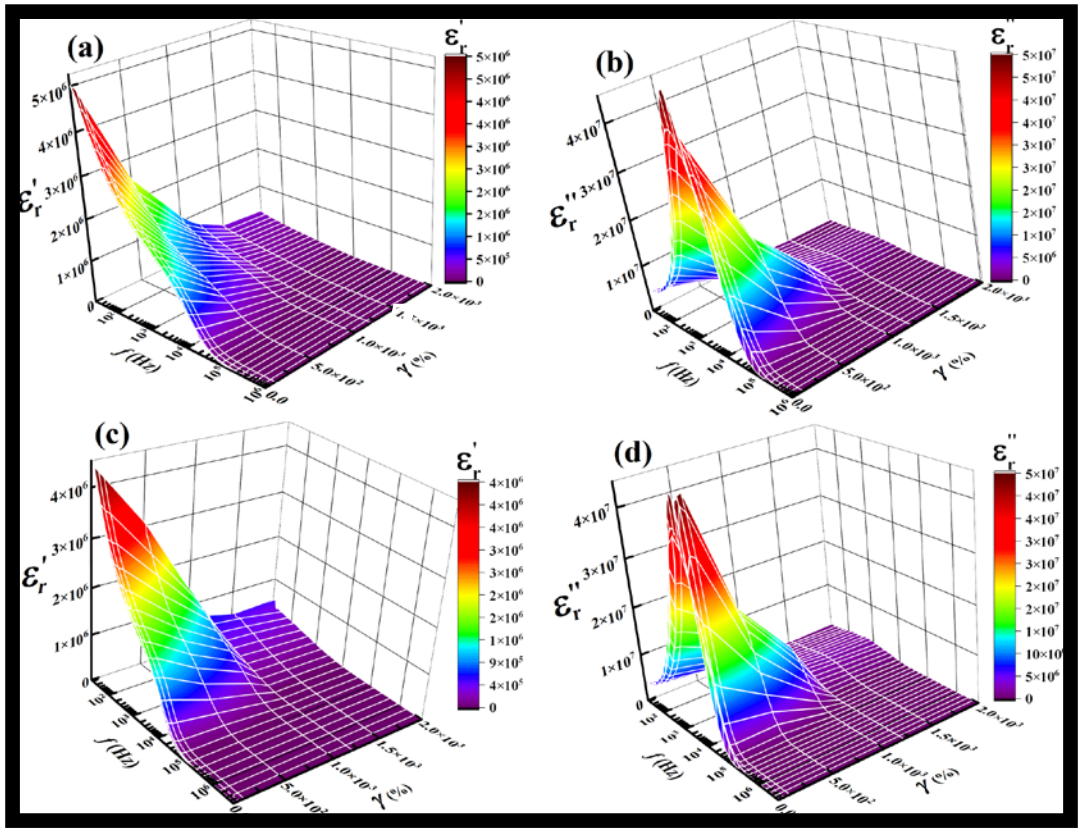


K. Asami, *Prog. Polym. Sci.* 27 (2002) 1617–1659

T below LCST

Dielectric permittivi

T at LCST



Densely packed

Loosely packed

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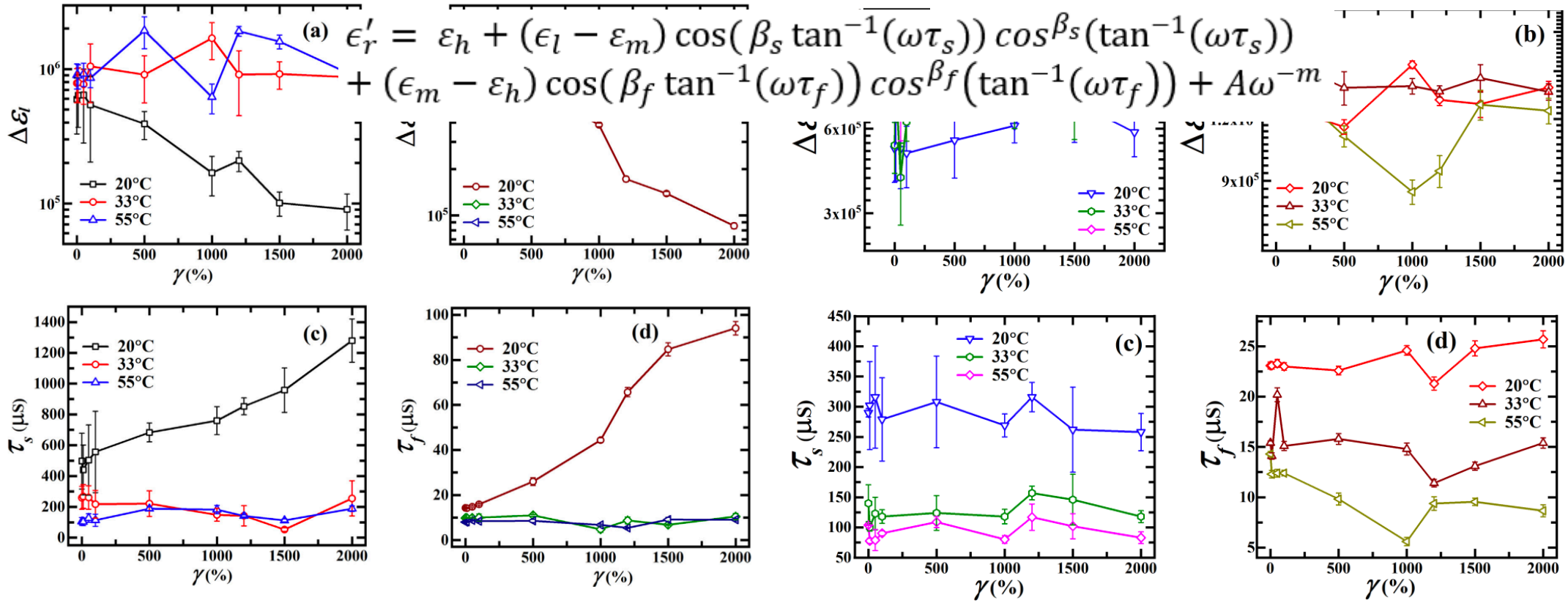
Estimating the orientation and dynamics of during shear flow

We fit the ϵ_r' data to the real part of the CD relaxation: $\varepsilon_r^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_m}{1 + (j\omega\tau_s)^{\beta_s}} + \frac{\varepsilon_m - \varepsilon_h}{1 + (j\omega\tau_f)^{\beta_f}} + A\omega^{-m}$

$$\epsilon_r' = \varepsilon_h + (\epsilon_l - \varepsilon_m)\cos(\beta_s \tan^{-1}(\omega\tau_s))\, cos^{\beta_s}(\tan^{-1}(\omega\tau_s)) + (\epsilon_m - \varepsilon_h)\cos(\beta_f \tan^{-1}(\omega\tau_f))\, cos^{\beta_f}(\tan^{-1}(\omega\tau_f)) + A\omega^{-m}$$



Densely packed suspensions

Loosely packed suspensions

Dynamical slowdown at the length-scale of the dipoles

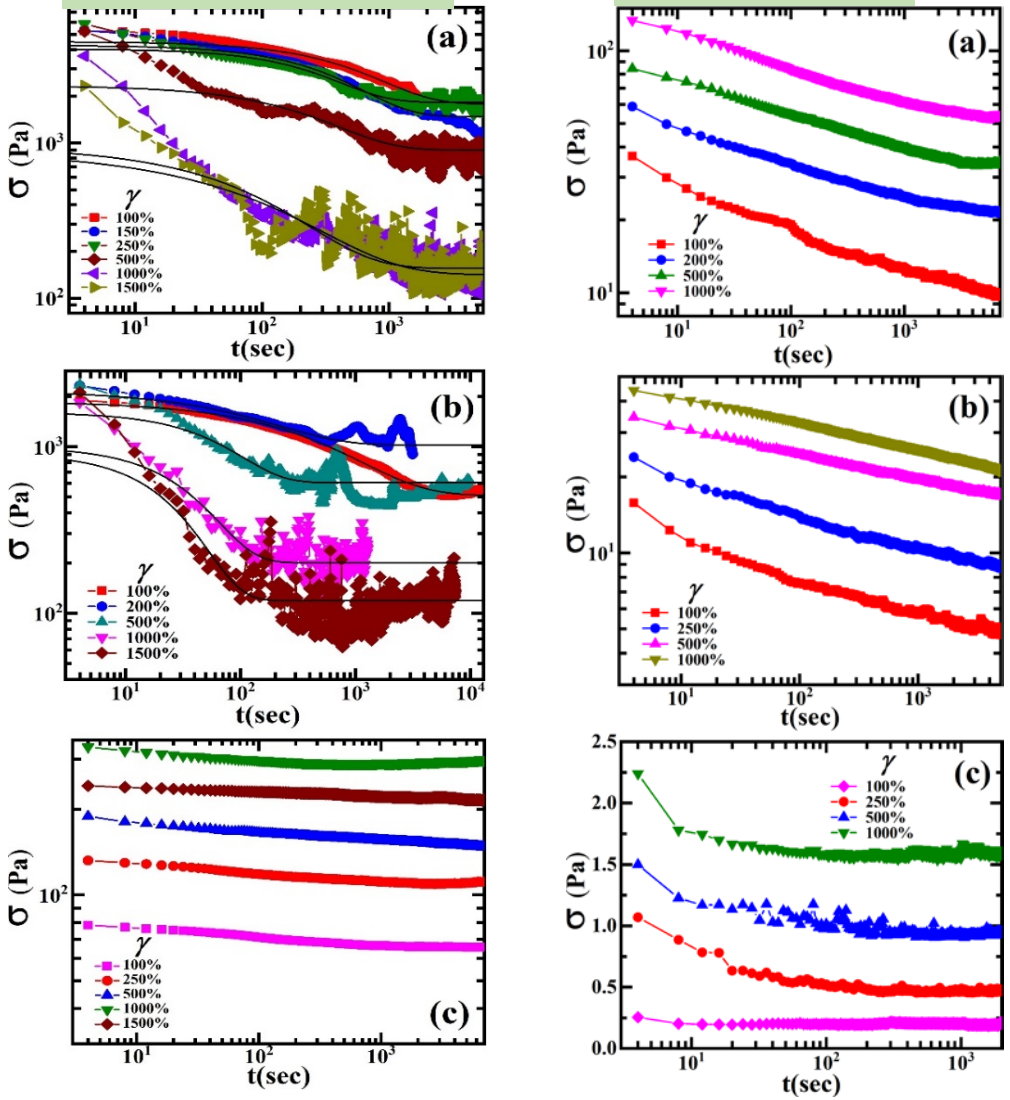
Bulk stress relaxation experiments at same oscillatory strain amplitudes

Densely packed

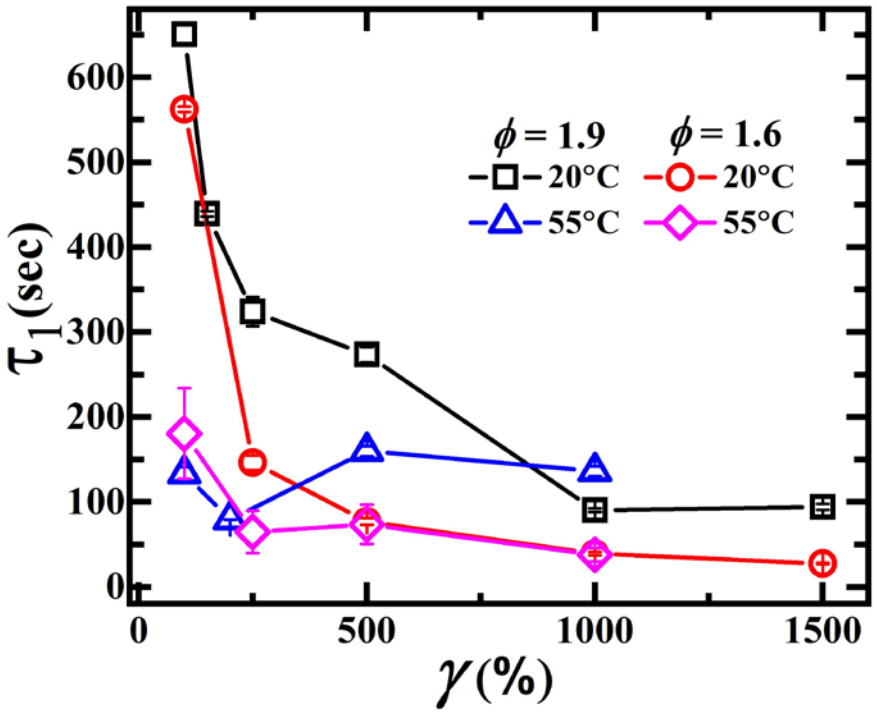
Loosely packed

T below LCST

T at LCST

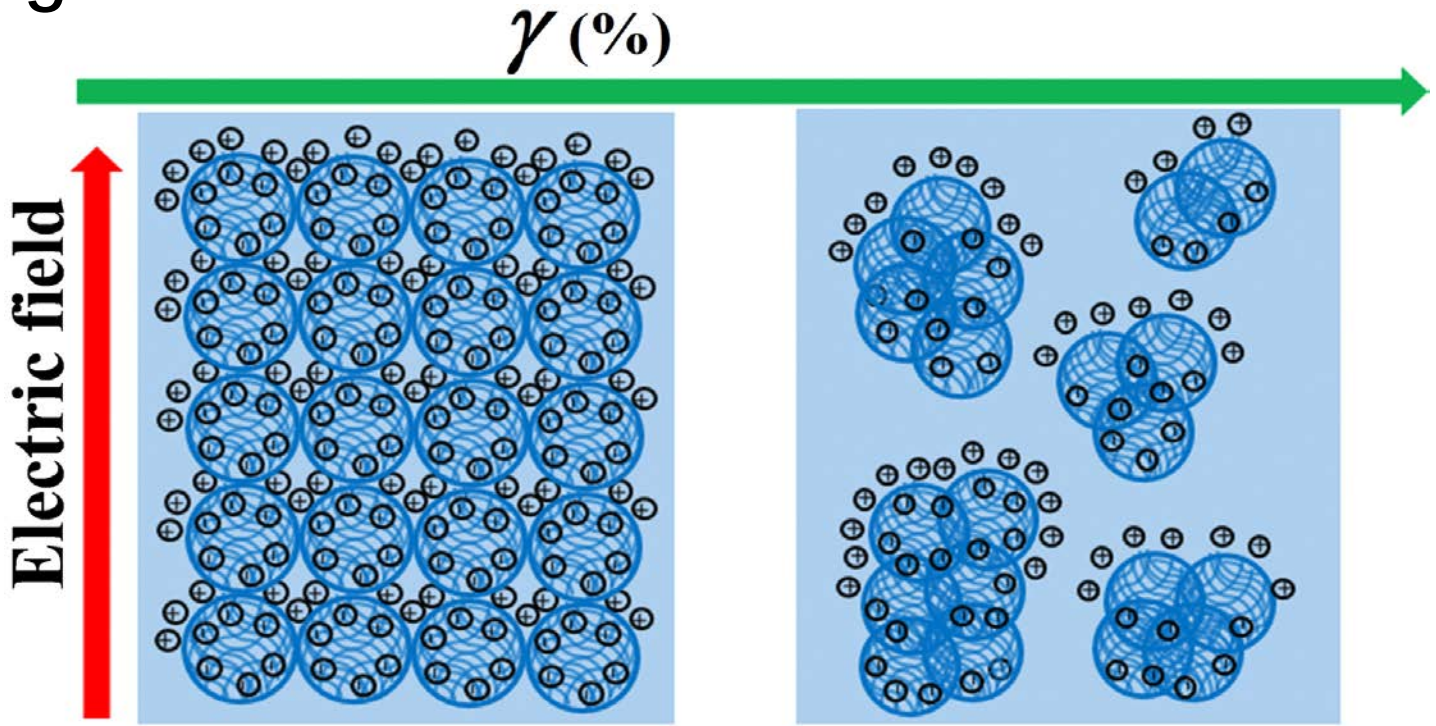


We fit the stress relaxation data for the densely packed suspensions below the LCST to the Kohlrausch-Williams Watts fitting function: $\boldsymbol{\sigma(t) = Ae^{-(t/\tau)^{\beta}}}$



Dynamics speed up in the bulk sample!

Connecting the data over decades in time and ler



To summarize:

1. Using a single technique we study the dynamics of PNIPAM suspensions over several decades of length and time scales

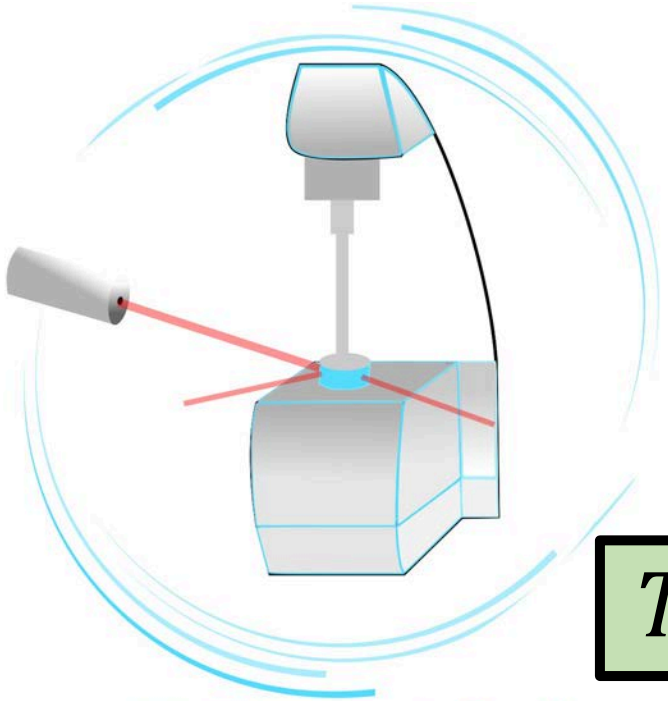
2. The dynamics of these suspensions are vastly different at different length scales (length-scale dependent rheology).

3. Since their rheology and self-assembly can be fine-tuned by changing shear and temperature, hydrogels are potentially good candidates for energy storage devices, stretchable flow capacitors and batteries

Acknowledgements

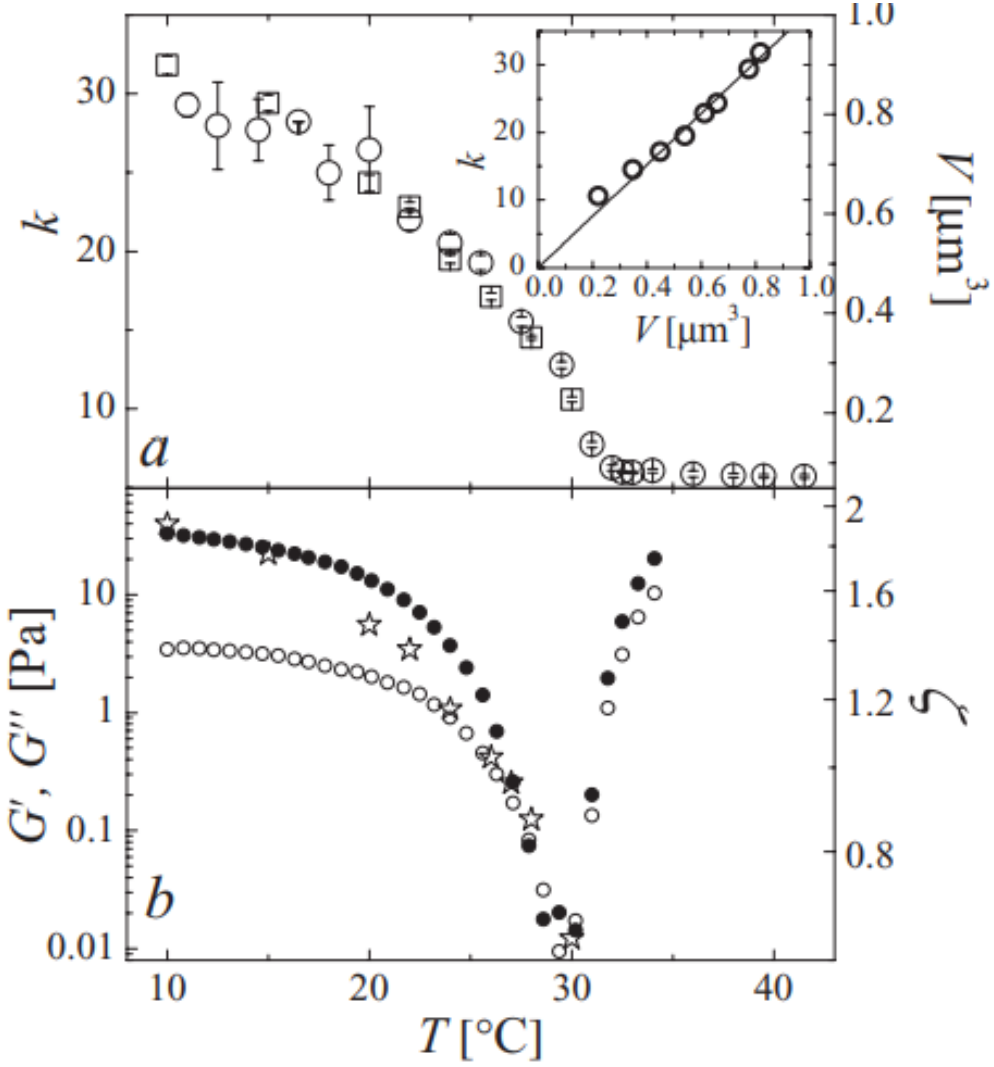
1. DST SERB (EMR/2016/06757) and RRI for funding
2. RRI workshop for technical support

RRI



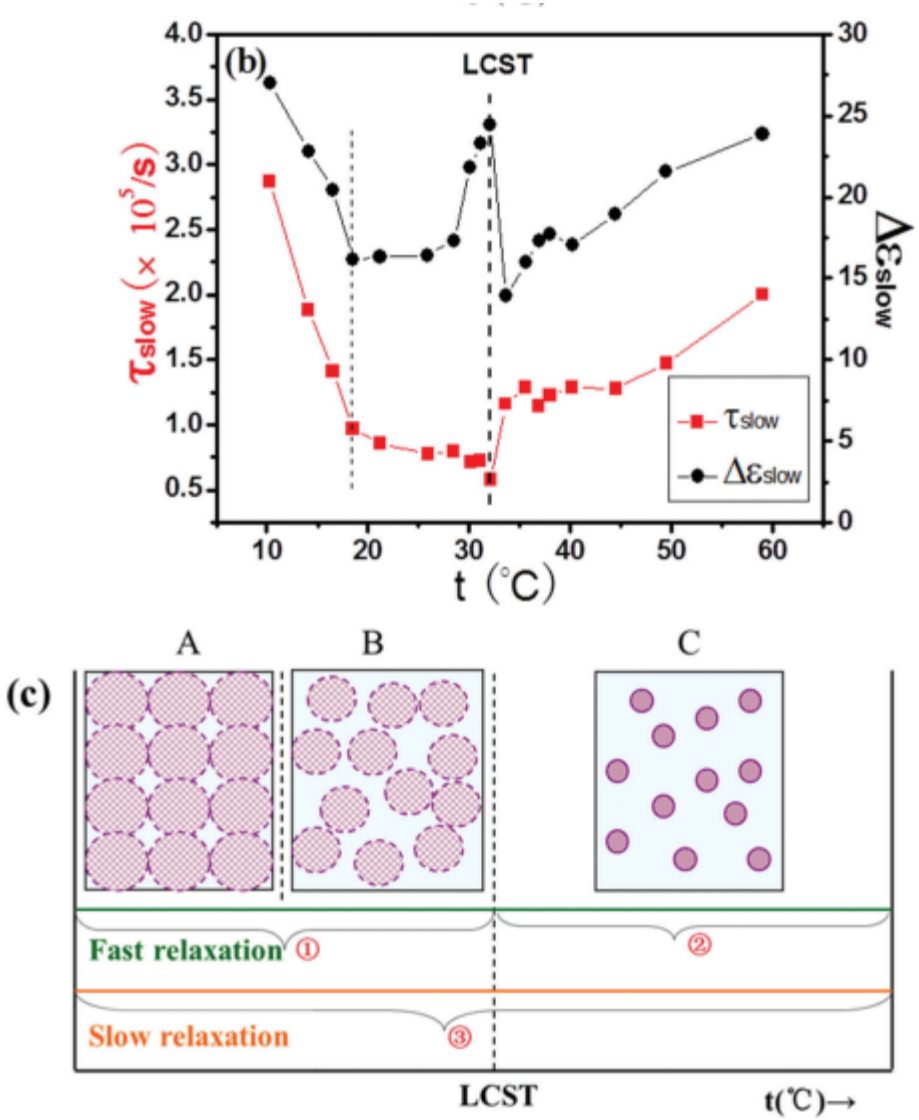
Thank you for your attention!

Rheological study



Adv. Mater. 2010, 22, 3441–3445

Dielectric study



Soft Matter, 2017, 13, 2663--2676

Effective volume fraction:

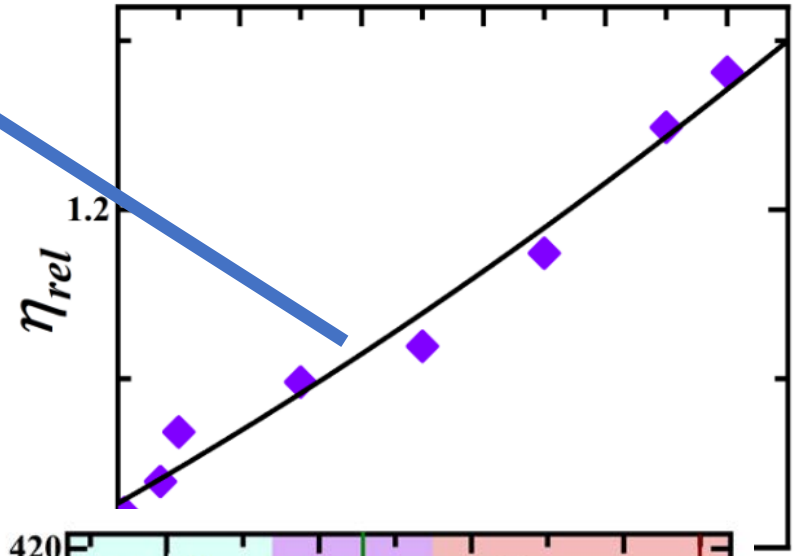
$$\eta_{rel} = 1 + 2.5(c/c_p) + 5.9(c/c_p)^2$$

Batchelor's equation:

$$\eta_{rel} = 1 + 2.5\varphi_{eff} + 5.9\varphi_{eff}^2$$

$$\varphi_{eff} = c/c_p$$

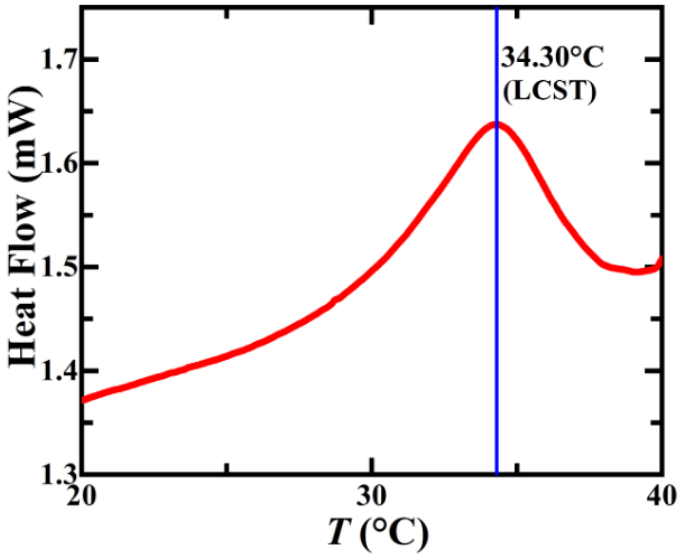
$c_p(wt.\%)$	$c((wt.\%))$	ϕ_{eff}
12.18	23.14	1.9
12.18	19.49	1.6
12.18	15.83	1.3

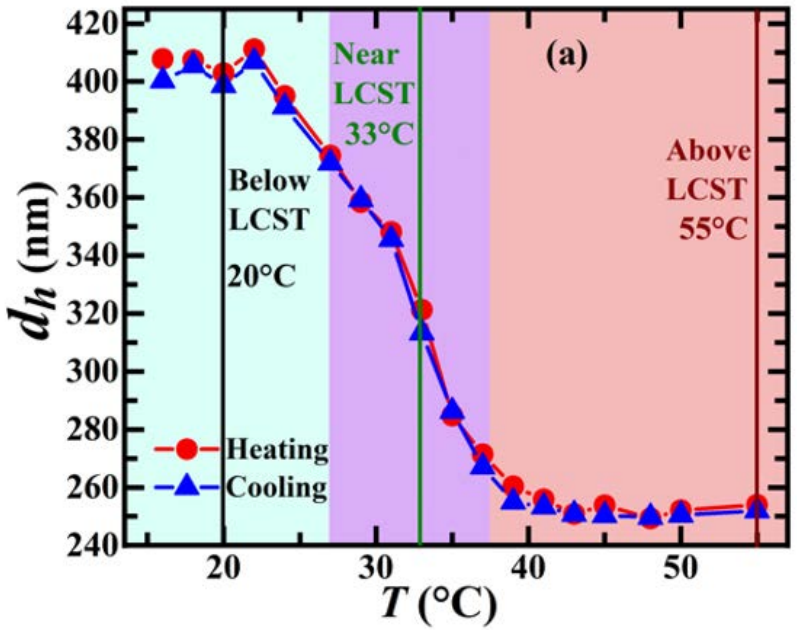


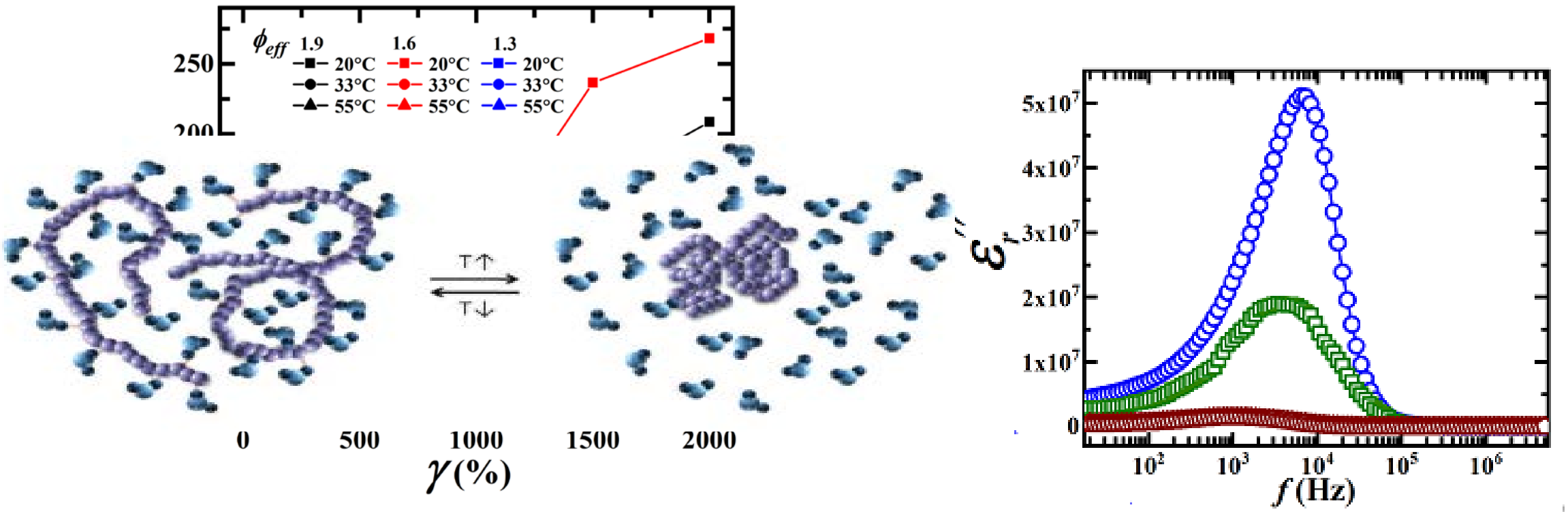
c_p = polymer mass concentration inside each particle in swollen state

c = polymer mass concentration of the suspension wt%

Differential Scanning Calorimetry(DSC)







$$\tau = 1/2\pi f_{peak}$$

C. Misra *et al. J. Colloid Interface Sci.* (accepted)