Study of the colloidal glass transition in suspensions of highly polydisperse poly(*N*-isopropylacrylamide) microparticle

ISPCM-2017, ICTS

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Outline

- **Introduction**
- **Synthesis of highly polydisperse PNIPAM microparticles**
- **Characterization of size, thermoresponsivity and size distribution**
- **Glass formation dynamics - effects of polydispersity**
- **Conclusion**

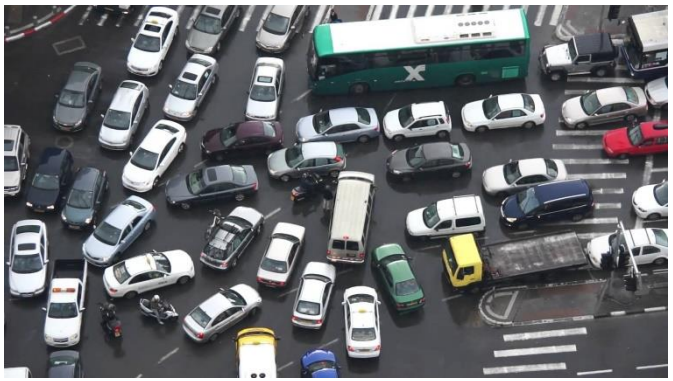
Glass

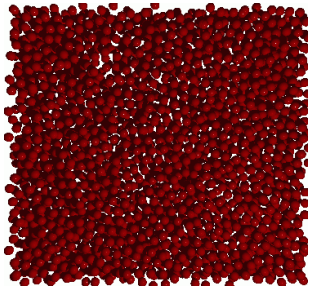
Window glass

Metallic glass

Molecular glass

Molecular glasses are formed cooling the molecular liquids at a faster rate





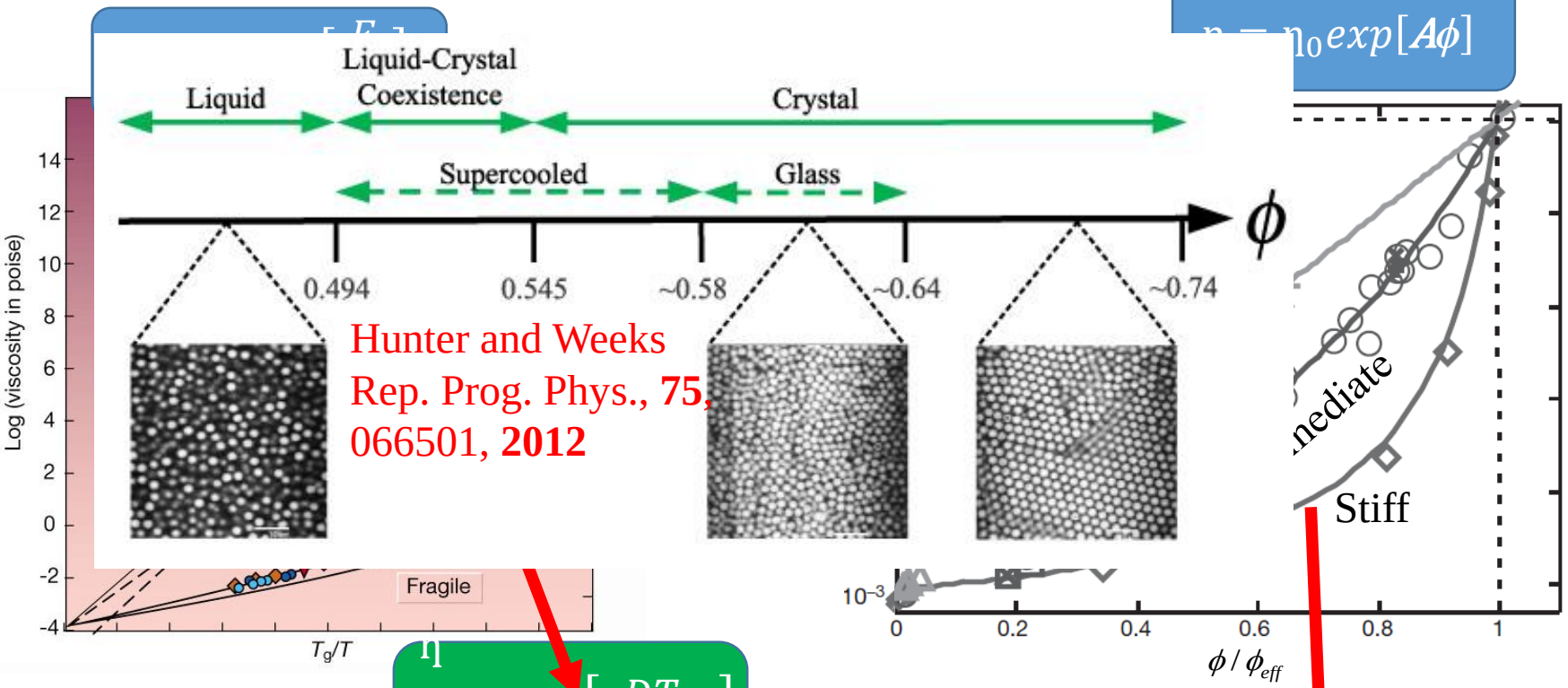
Colloidal glass

Colloidal crystal

Colliodal glasses are formed by increasing the volume fraction of colloidal particles

Molecular and colloidal system

$\eta = \eta_0 exp[A\phi]$



$\eta = \eta_0 exp\left[\frac{DT_0}{T - T_0}\right]$

Fragility=1/D

Viscosity or relaxatio molecular system incre decrease in temperature (*T*)

Viscosity or relaxat on time of colloidal sy increase in particles

$\tau_\alpha = \tau_0 exp\left[\frac{D\phi}{\phi_0 - \phi}\right]$

Fragility=1/D

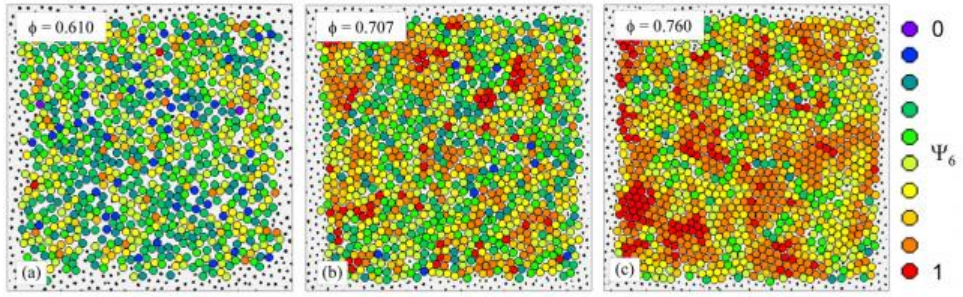
Vogel-Fulcher-Tammann (VFT) function

Debenedetti et. al, Nature, 410, 259 (2001)

J Mattsson *et al.* *Nature* 462, 83-86 (2009) doi:10.1038/nature08457

Fragility and dynamical heterogeneities (DHs)

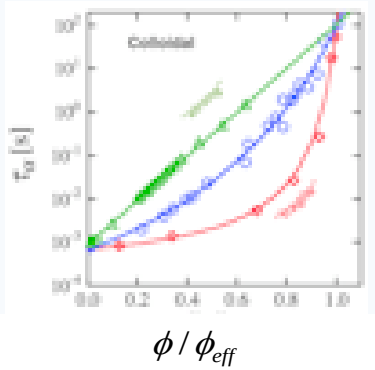
DHs arises because of the presence of fast and slow moving CR regions in polydisperse colloidal system at sufficient high volume fractions.



E. Tamborini, J. Phys. Condens. Matter, 27 (2015)

Intrinsic heterogeneity of the system increases with the increase of polydispersity, which enhances the dynamical heterogeneity at higher volume fractions in colloidal system.

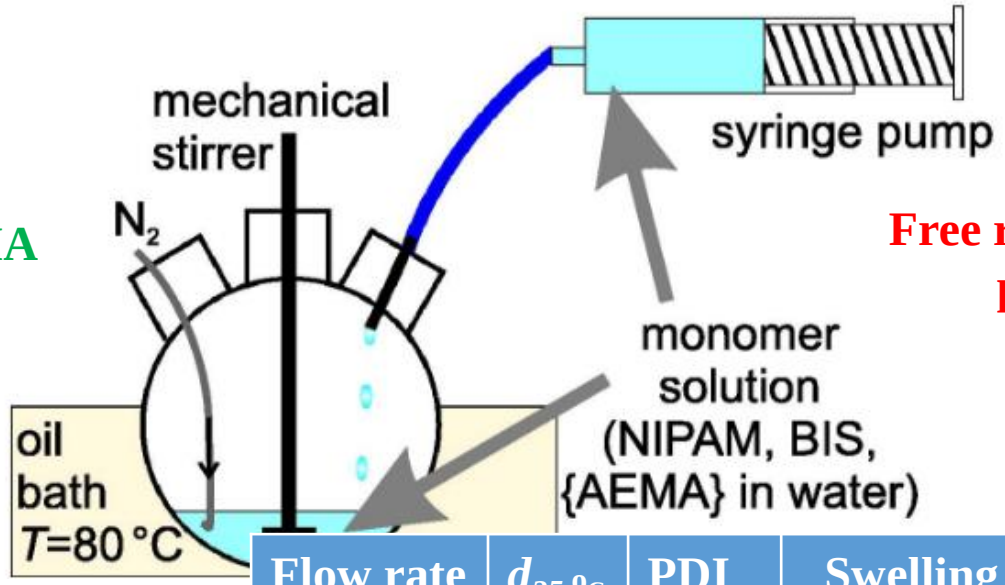
Fragility of colloidal glasses increases because of the increase of DHs



Motivation of this work:
Effect of polydispersity on glass transition of soft colloidal suspensions

Synthesis of polydisperse PNIPAM Particles

Monomer: NIPAM
Crosslinker: BIS
Co-monomer: AEMA
Initiator: APS



Free radical precipitation polymerization

T. Still et al., J. Colloid and Interface Science, 405, 96-102(2013).

(semi-batch s

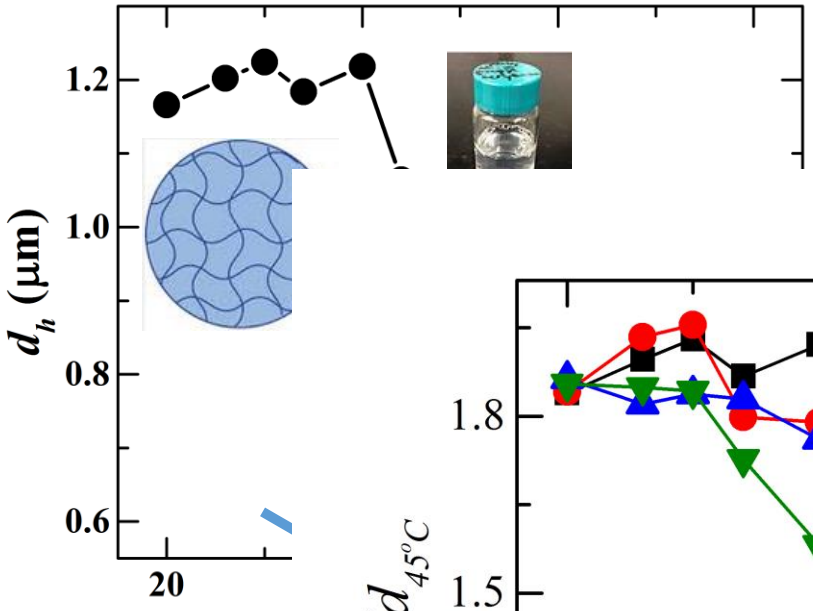
Flow rate (mL/min)	$d_{25\,^oC}$ (μm)	PDI (%)	Swelling ratio ($d_{25\,^oC}/d_{45\,^oC}$)
1.5	1.24	15.3	≈ 1.81
1.0	1.73	28.9	≈ 1.87
0.7	2.38	36.5	≈ 1.84
0.5	2.78	48.9	≈ 1.83

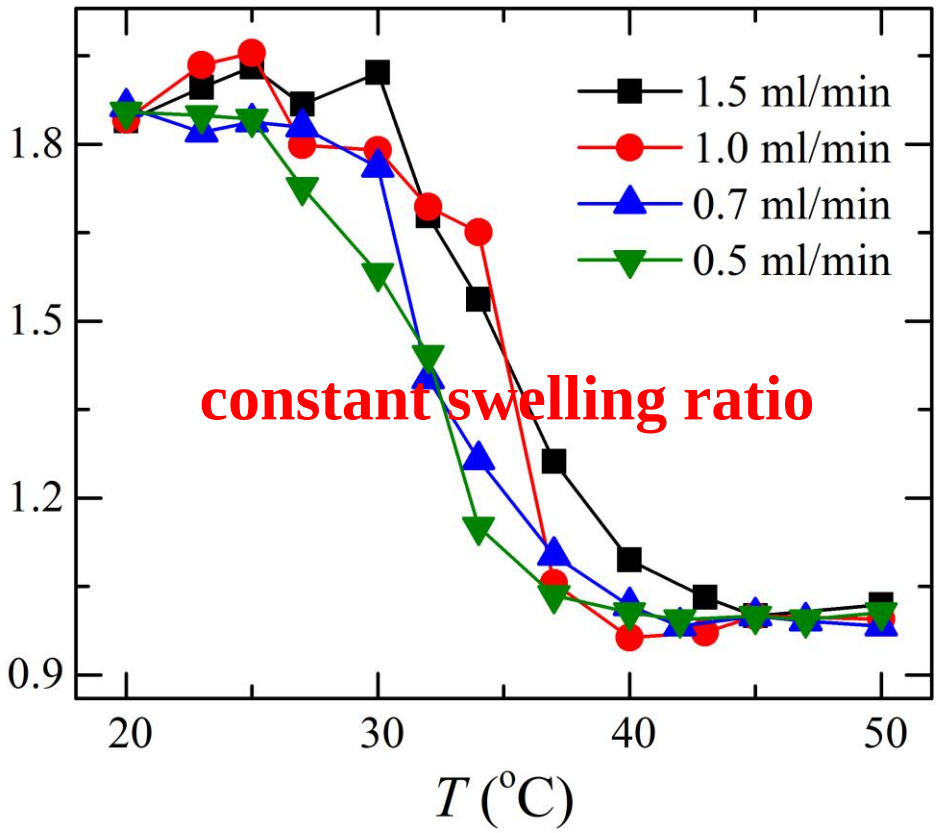
eously crosslinked AM particle

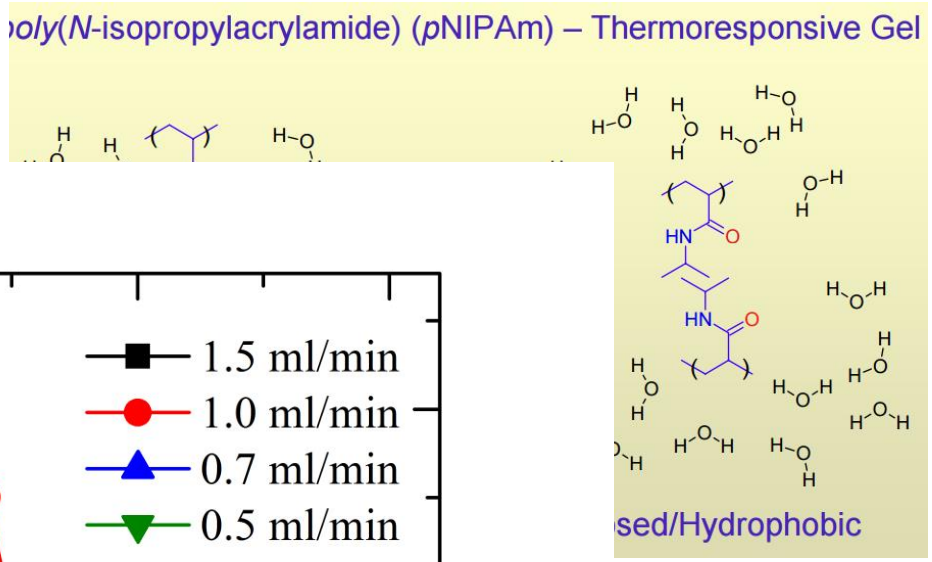
Polydispersity index (PDI) is defined as the ratio of mean and width of the size distribution

PDI of PNIPAM microparticles suspension increases with the decrease in flow rate of the monomer solution

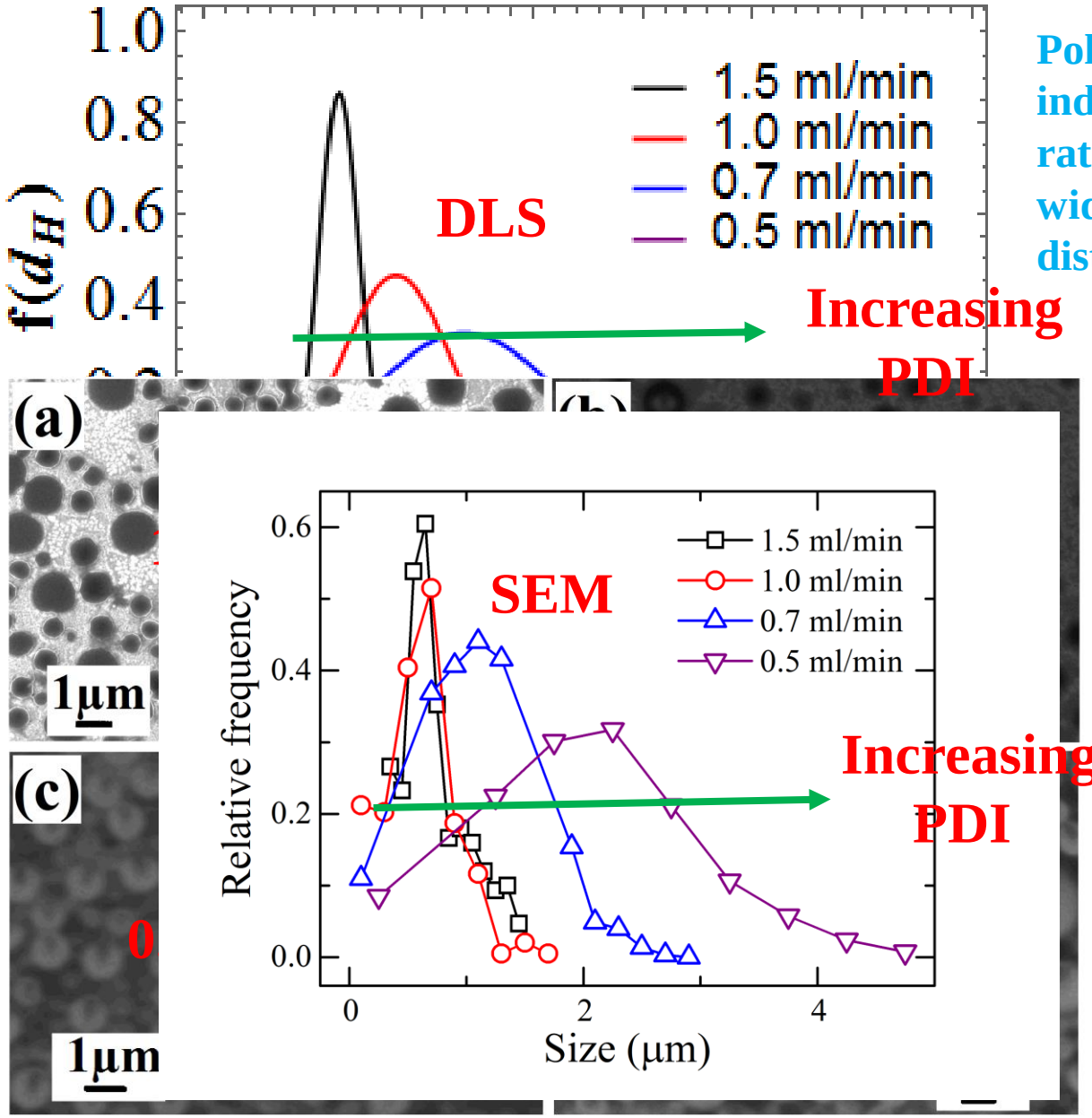
Size and Thermoresponsive behavior of PNIPAM Particle







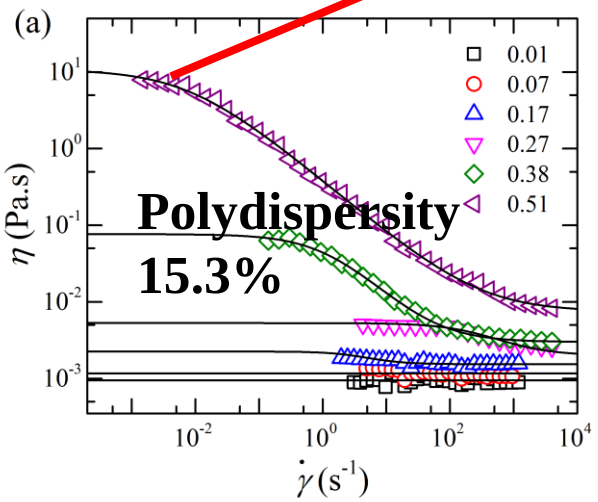
Particle size distribution of PNIPAM particle

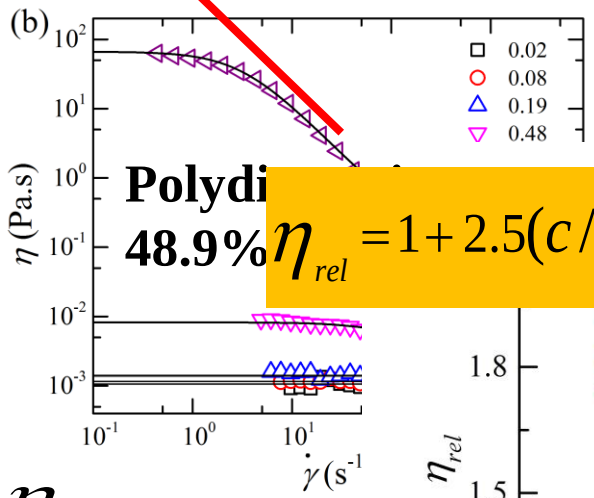


Polydispersity index (PDI) is the ratio of mean and width of the size distribution

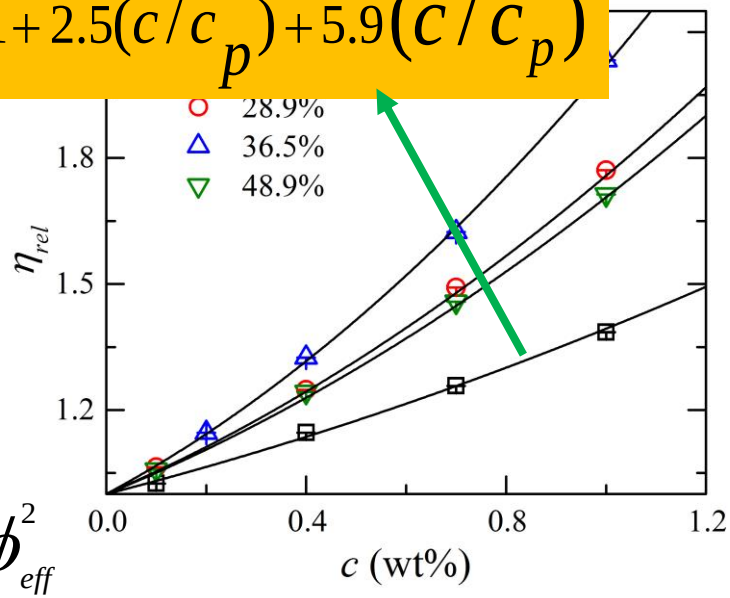
Zero shear viscosity (η_0):

Cross model: $\dfrac{\eta-\eta_\infty}{\eta_0-\eta_\infty}=\dfrac{1}{1+\left(k\dot{\gamma}\right)^m}$





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



$$\eta_{rel}=\frac{\eta_o}{\eta_s}$$

Effective volume fraction:

Batchelor's equation: $\eta_{rel}=1+2.5\phi_{eff}+5.9\phi_{eff}^2$

c_p = polymer mass concentration inside each particle in swollen state

c = polymer mass concentration of the suspension wt%

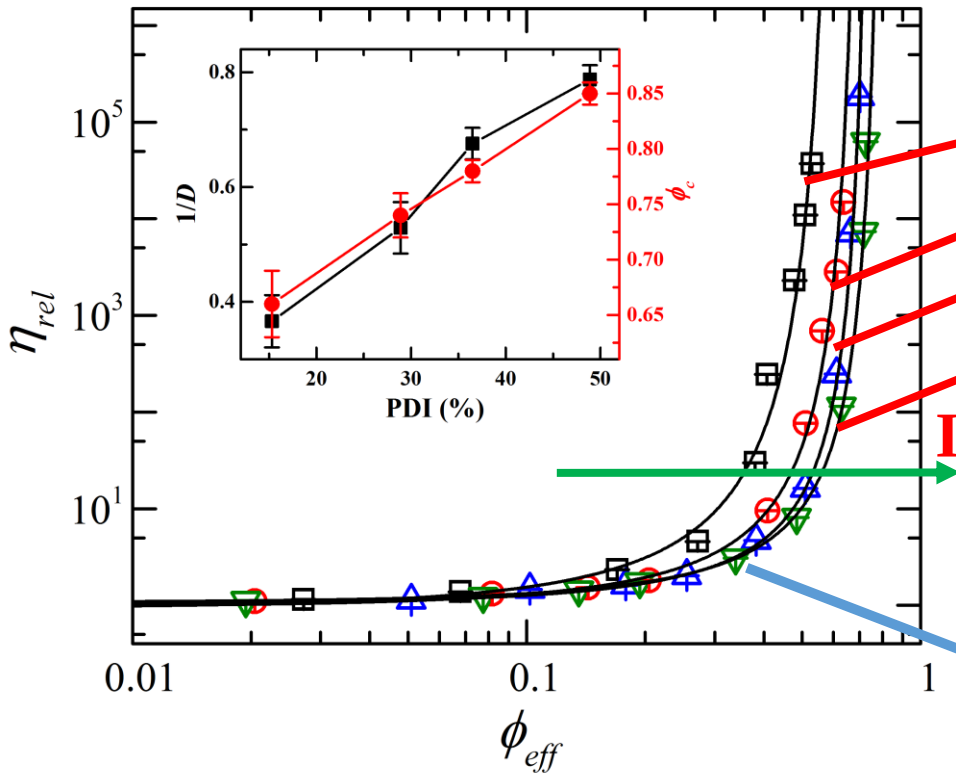
$$\phi_{eff}=nV_d=c/c_p$$

$$c_p=m_p/V_d$$

$$V_d=4\pi R_d^3/3$$

Lorenzo et. al., Macromolecules, **46**, 1962-1972 (**2013**).

Study of glass formation dynamics of PNIPAM particles



PDI	*1/D*	ϕ_c
15.3%	0.37 ± 0.05	0.66 ± 0.03
28.9%	0.53 ± 0.04	0.74 ± 0.02
36.5%	0.68 ± 0.03	0.78 ± 0.01
48.9%	0.79 ± 0.02	0.85 ± 0.01

Increasing PDI

Vogel Fulcher Tammann Equation

$$\eta_{rel} = \exp\left(\frac{D\phi_{eff}}{\phi_c - \phi_{eff}}\right)$$

Dynamical heterogeneities (DHs) explains well the fragility of these highly polydispese system

Glass transition of soft and highly polydisperse PNIPAM particles occurs at volume fraction well above the random close packing volume fraction of monodisperse hard sphere

D **= fragility parameter, the inverse of fragility**

ϕ_c **= The critical volume fraction**

Decoupling of dynamics between smallest and largest particles explains well the ϕ_c behavior with PDI

Conclusions

- **PNIPAM micropartcles of different PDIs (15.3%-48.9%) are synthesized in a controlled manner.**
- **Flow behavior of concentrated polydisperse PNIPAM microparticle suspensions studied using rheology**
- **Increasing PDI increases the fragility of the system**
- **Increasing PDI shifts the φ_c to high φ**
- **Tunability of rheology while controlling the polydipsersity of PNIPAM hydrogels**
- **We are now studying the nonlinear stress response to the first higher harmonic (3ω) for a sinusoidal perturbation (ω) to quantify the intrinsic nonlinearities of the microparticle suspensions characterized by varying PDIs.**

Acknowledgements

- **A. Dhason and K. M. Yatheendran for their help with SEM and cryo-SEM imaging**
- **Chemistry Lab@RRI**

Thank you!

Importance of our study

- **It's very difficult and challenging to synthesize highly polydisperse spherical colloidal particles and to control polydispersity of these particles**

- **Effect of polydispersity on the glass transition of colloidal system is not clearly understood**

- **To explore new physical phenomena present in highly polydisperse system**

- **Other than stiffness, polydispersity can also affect fragility (rapidity of approach towards glass transition) of soft colloidal system.**

Stimuli Responsive Polymers

Temperature, pH, Light

Hydrophilic state → Hydrophobic state

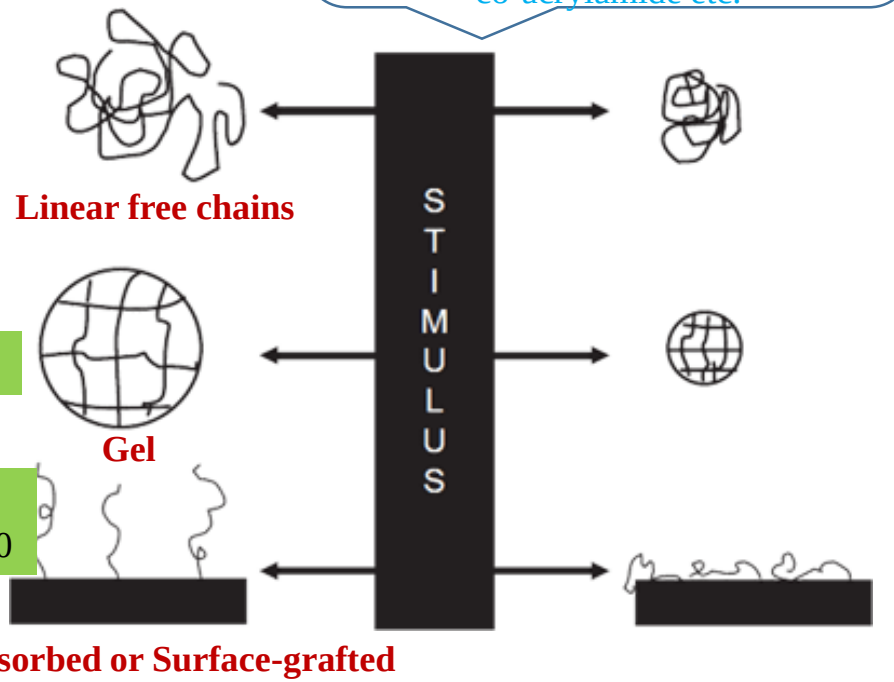
Magnetic and electric field

Crosslinked poly(vinyl alcohol) chains entangled with polyacrylic acid, poly(*N*,*N*-dimethylaminoethyl methacrylate), Chitosan, ferromagnetic materials PNIPAmm-co-acrylamide etc.

Poly(N-isopropylacrylamide), polyvinylmethylether, PEO, polyhydroxyethylmethacrylate, PS, PE, PMMA

PEG, poly(lactic acid)

Polymers with acidic group(-COOH, -SO_3H) and basic group(-NH_2)



H. Almeida et al., JAPS, **2(6)**, 1-10, (2012)

Applications

- Controlled and self-regulated drug delivery
- Bio-conjugation
- Tissue engineering
- Biosensors
- Bio-separation
- Liquid chromatography

Zheng et al., Act Polym. Sinica, **8**, 2011
A. S. Hoffman, Clinc. Chem., **46(9)**, 2000

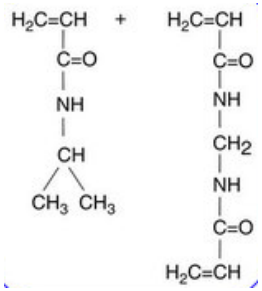
Free radical polymerisation is a method of polymerisation by which a polymer forms by the successive addition of free radical building blocks.

Types of Initiation

1. **Thermal decomposition:** The initiator is heated until a bond is homolytically cleaved, producing two radicals.
Examples: peroxides or azo compounds
2. **Phtolysis:** Radiation cleaves a bond homolytically producing two radicals.
Examples: metal iodides, metal alkyls and azo compounds.

$$I - I \rightarrow 2I^{\cdot}$$
$$I^{\cdot} + M \rightarrow I - R_i^{\cdot}$$
$$I - R_i^{\cdot} + M \rightarrow I - R_{i+1}^{\cdot}$$
$$I - R_i^{\cdot} + I - R_j^{\cdot} \rightarrow I - R_i - R_j - I$$
$$I - R_i^{\cdot} + I^{\cdot} \rightarrow I - R_i^{\cdot} - I$$

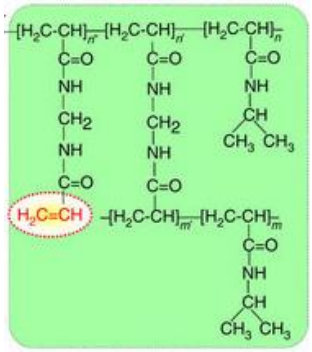
NIPA Monomer

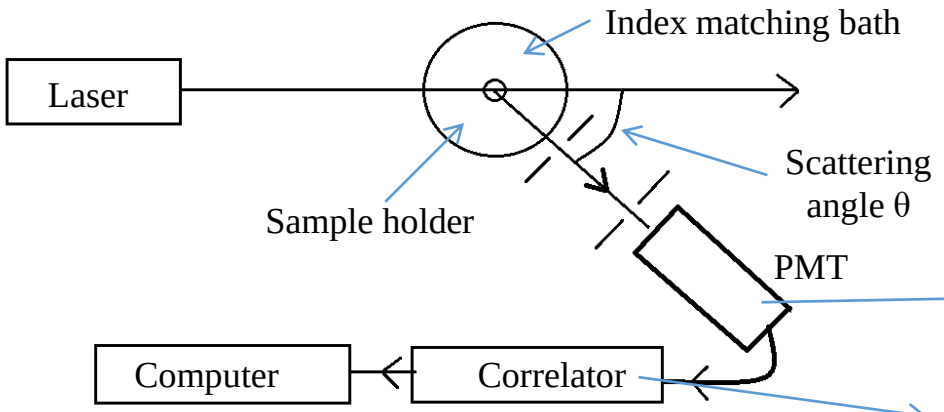


MBA Crosslinker

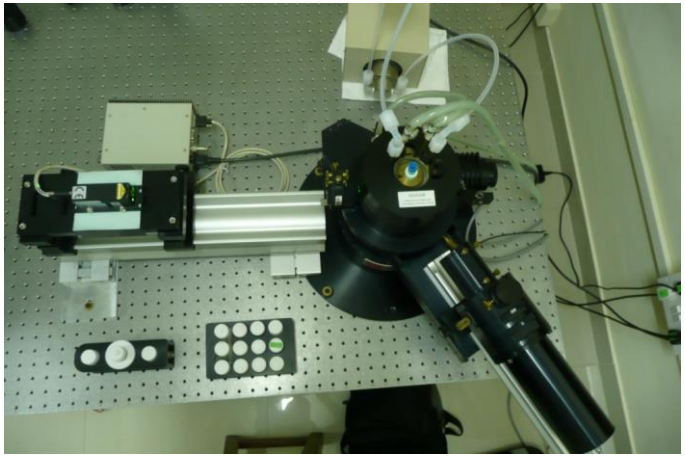
KPS or APS

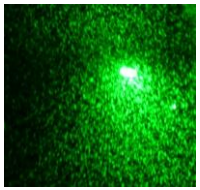
80^0C





Dynamic Light Scattering set up





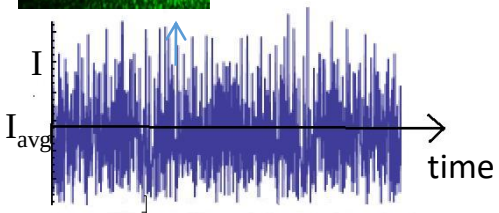
$$g_1(t) = \exp\left[\frac{-t}{\tau}\right]^{\beta}$$ → **polydisperse spherical particles**

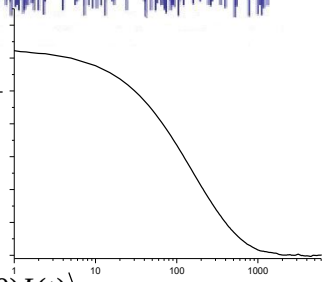
$$\langle \tau \rangle = \frac{\tau}{\beta}\Gamma\left(\frac{1}{\beta}\right)$$

$$\langle \tau^2 \rangle = \frac{\tau^2}{\beta}\Gamma\left(\frac{2}{\beta}\right)$$

$$\sigma = \sqrt{\langle \tau \rangle - \langle \tau^2 \rangle}$$

$$polydispersity(\%) = \left(\frac{\sigma}{\langle \tau \rangle}\right) \times 100$$





$$g_2(t) = \frac{\langle I(0)I(t)\rangle}{\langle I(0)\rangle^2}$$ → **Intensity auto-correlation**

$$g_2(t) = 1 + A\left|g_1(t)\right|^2$$

$$g_1(t) = \exp\left[-\frac{t}{\tau}\right]$$ → **monodisperse spherical particles**

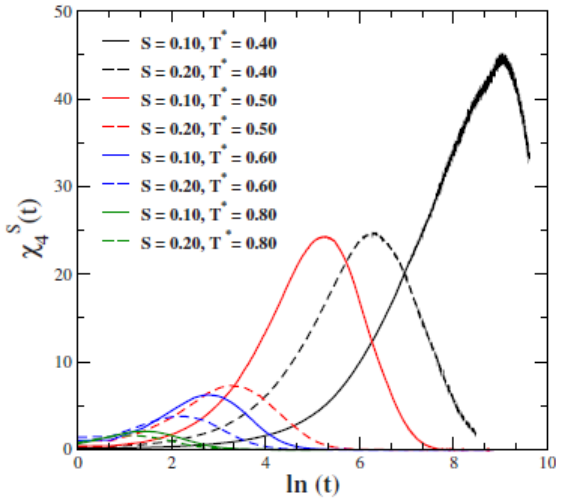
$$\frac{1}{\tau} = Dq^2 \qquad D = \frac{k_B T}{6\pi\eta r_h} \qquad q = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

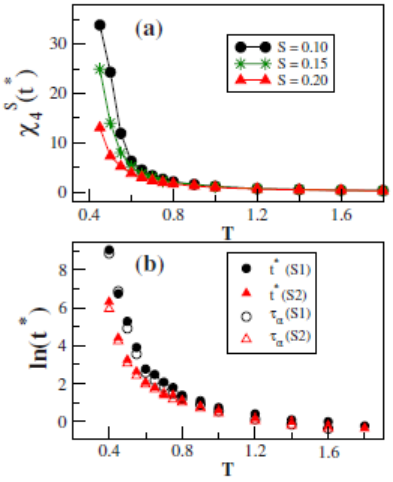
$$g_1(t) = \int G(\tau)\exp\left[-\frac{t}{\tau}\right]dt$$

No.	Material name	T_K (K)	T_0 (K)	T_K/T_0	D	No.	Material name	T_K (K)	T_0 (K)	T_K/T_0	D
1	GeO_2	418[a]	199[a]	2.1	113[a]	10	Ethylene glycol	115	109	1.05	16.0
2	SiO_2	876[a]	529[a]	1.66	63[a]	11	$Cu_{47}Ti_{34}Zr_{11}Ni_8$	573[k]	500[e]	1.15	12[e]
3	$ZnCl_2$	250	180–236	1.39–1.06	32	12	Glycerol	135	127	1.07	10.6[l]
4	Butyronitrile	81.2	58	1.26	32	13	Sorbitol	236	224	1.05	8.6
5	Vit4[b]	560[c]	372[d]	1.5	22.7[e]	14	Toluene	96	103	0.93	5.6
6	$Mg_{65}Cu_{25}Y_{10}$	325[f]	260[f]	1.25	22.1[f]	15	*o*-terphenyl	200	184	1.09	5.0
7	Vit1[g]	558[h]	413[h]	1.35	20.4[e]	16	Propylene carbonate	125.8	130	0.97	2.9
8	$Pd_{40}Ni_{40}P_{20}$	500[i]	390[j]	1.28	18.1[j]	17	Triphenyl phosphite	166	183	0.91	2.9
9	1,2-propane diol	127	114	1.11	17.8	18	Sucrose	283	290	0.98	0.154

Tanaka et. al, PRL, **90**, 055701, 2003

Polydispersity and dynamical heterogeneity



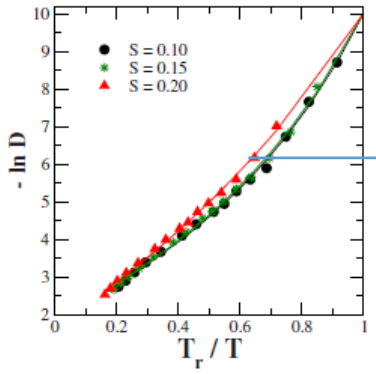


$$\chi_4^s(t) \propto \left\langle Q_s^2(t) \right\rangle - \left\langle Q_s(t) \right\rangle^2$$

Where

$$Q(t) = \int\int d\vec{r}_1 d\vec{r}_2 \rho\left(\vec{r}_1, 0\right)\rho\left(\vec{r}_2, t\right) w\left(\left|\vec{r}_1 - \vec{r}_2\right|\right)$$

Here, $Q(t)$ is the time dependent order parameter



Increasing polydispersity at fixed volume fraction decreases the fragility of the system

VFT fit of the diffusivity data

$$D = D_0 \exp\left(\frac{E_D}{T - T_0}\right)$$

Intrinsic heterogeneity of the system Increases with the increase of polydispersity , which suppress the dynamical heterogeneity..

S. E. Abraham et al., PRL, **100**, 167801 (2008)

S. E. Abraham et al., PRE, **78**, 051501 (2008)