Colloidal Mikado: Rheology and Structure of Thermoreversible Gels of Sticky Rod-Like Particles

Naveen Krishna Reddy[1], *Zhenkun Zhang*[1], *M. Paul Lettinga*[2], *Jan Dhont*[2], *Jan Vermant*[1]

[1] *Department of Chemical Engineering, K.U. Leuven, W. de Croylaan 46, B-3001 Leuven, Belgium,* [2] *Institute for Festkorperforschung, Forschungszentrum, Juelich, D-52425 Juelich, Germany*

Abstract: The assembly of rod-like particles by weak attractive interactions is important for the properties of several soft biological materials as well as in tailoring the properties of colloidal gels in a variety of applications. Understanding the link between the physicochemical parameters such as size and aspect ratio, volume fraction, interparticle forces with the resulting microstructure and the rheological response remains however challenging. It is often difficult to obtain a good control over these parameters due to the lack of suitable model systems. In the present work a model rod-like fd-virus particle has been surface modified with a thermoreversible polymer poly(N-isoproplyacrlyamide). The repulsive and attractive contributions to the overall interaction potential can be varied independently by changing the ionic strength and the temperature. The effects of these changes on the strength and structure of the gel have been studied near the gel transition using a combination of rheological and scattering measurements. The results show that for these thermoreversible 'sticky' rod systems, the variations of the structure in the gelled state are relatively weak, with the gel strength mainly being controlled by the relative magnitudes between the attractive and repulsive contributions and the volume fraction, the anisotropic nature of the electrostatic interactions seems to have a minor effect.

Introduction: Anisotropic rodlike particles are effective basic building blocks for strong structures with low solid content. This property stems from the excluded volume effects which results in low percolation threshold to form networks [1, 2]. There are several examples from science and technology. Actin filaments and microtubules are used in strengthening the cytoskeleton of living cells [3], rod-like and disc-like clay particles were used for ages in pottery to induce plasticity and to make them permeable to air [4] and more recently anisotropic nanoparticles such as carbon nanotube or graphene are used to strengthen polymer composites [5]. The fundamental study of gels prepared using rodlike particles was hampered by the lack of suitable model systems. Typically the control over the interaction potential is poor and the particles were polydisperse. In the present work, the mechanical and structural properties of gels composed out of monodisperse rodlike particles are investigated. By restricting our observations to the region close to the gel transition, were a critical gel is observed, the effects of

changing the interactions on the strength and the structure of the gel can be investigated in detail.

Rheological and scattering studies of nearly critical gels made of *fd*-viruses (monodisperse, negatively charged rodlike particles) grafted with the thermoresponsive polymer poly(N-isoproplyacrlyamide) (hereafter referred as PNIPAM) [6] are presented. Control over the inter-particle interactions is achieved by changing the attractive interaction with temperature, by altering the hydrophobicity of the PNIPAM polymer, and changing the repulsive interaction by varying the ionic strength of the suspension.

Results and discussion: The phase diagram of the fd-PNIPAM suspensions is shown in figure 1.a. To make gels with low solid content and to exclude effects of liquid crystalline ordering, this study is limited to the isotropic regime. Suspensions were prepared in aqueous buffers of three different ionic strengths, i.e. 1, 5, 105 mM respectively. For each of these ionic strengths the particle concentration has been varied, as shown in figure 1.a. The effective diameter of the fd-PNIPAM particles is a function of the ionic strengths and temperature, as show in figure 1.b and c. For temperatures below the gel point the grafted polymer is in a coil state and acts as a stearic stabilizer. As the temperature is increased above the gel point, the PNIPAM chains collapse into a globular structure and the polymer becomes hydrophobic. Thus a short attractive interaction can be induced by increasing the temperature. Repulsive interactions are tuned by changing the electrostatic double layer thickness. For fd-PNIPAM particles in aqueous buffer solutions at 105 mM, the double layer thickness is smaller than the collapsed PNIPAM layer thickness, therefore the inter-particle potential is predominantly attractive. As the double layer thickness is made to be larger (low ionic strength) the electrostatic repulsions will also contribute significantly to the overall potential, leading to a repulsive system at low temperatures and a system with a weaker attractive interaction at high temperature. For fd-PNIPAM in a 1 mM ionic strength buffer, the electrostatic double layer is much larger than the collapsed PNIPAM polymer. This increases the gel temperature from 32^oC for fd-PNIPAM in 105 mM buffer to 35^oC in 1 mM buffer, see figure 1.d. The gelation point was determined by dynamic light scattering by measuring the transition from an ergodic to non-ergodic system, and by measurements of the linear viscoelastic properties, measuring where the phase angle, $\tan(\delta)$, becomes independent of frequency [7, 8]

Figure 2.a shows the change in the average storage modulus (at a frequency of 6.28 rad/s) as a function of fd-PNIPAM particle concentration at $\Delta T =$

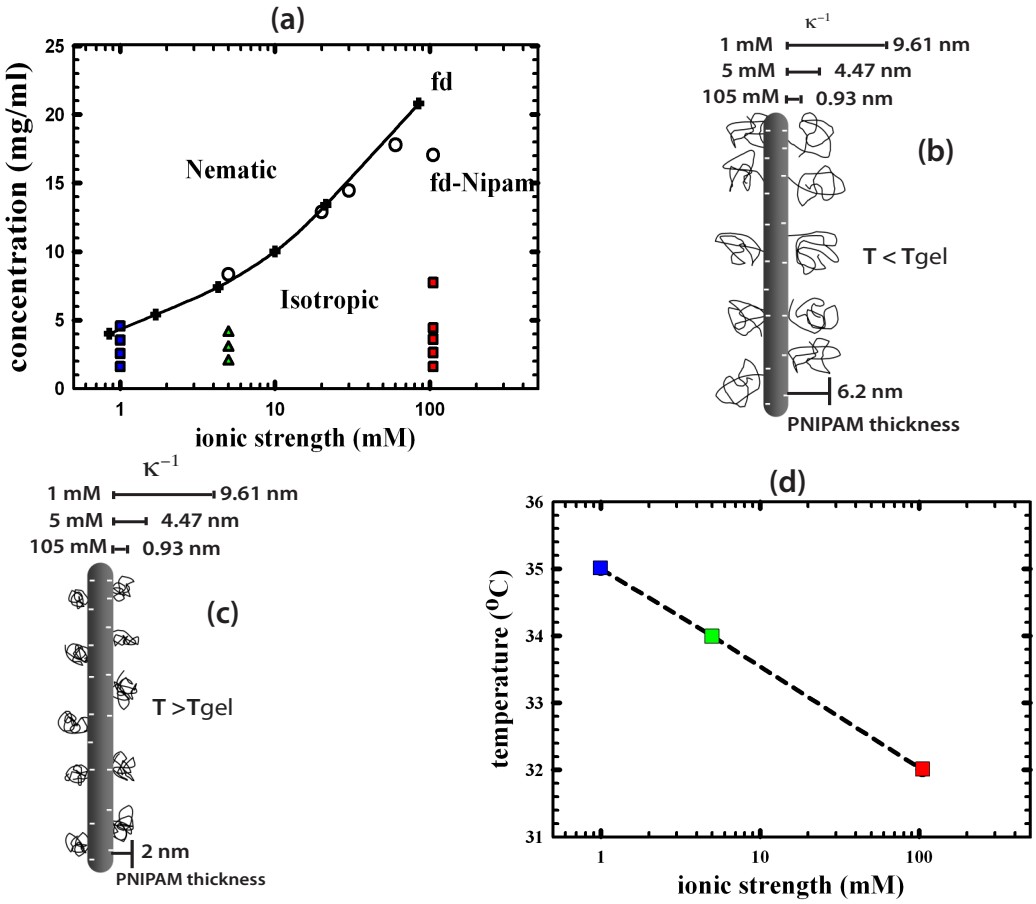

Figure 1: a) Phase diagram of modified *fd*-PNIPAM and wild type, bare *fd* virus suspensions at room temperature. Open circles and crosses represent the highest stable concentration of *fd*-PNIPAM and bare *fd* respectively, where the suspension was still isotropic. Squares and triangles represent the concentrations studied. b) and c) cartoons of the particles at temperatures below and above the gelation temperature, respectively with the thickness of PNIPAM polymer layer and the electrostatic double layer thickness as a function of ionic strength. d) Decrease in gelation temperature with increase in ionic strength from 35^{o}C for 1 mM buffer to 32^{o}C for 105 mM buffer.

$T - T_{gel} = 4^oC$ in a strain sweep experiment. It can be concluded that the strength of the gel increases with increases in particle concentration, and this for all ionic strengths. The gels formed by suspensions in buffers at high ionic strength have higher moduli compared to gels formed at low ionic strengths. The slopes from the fit to power law equation ($G \propto C^x$) decreases as a function of ionic strength, indicating that also the underlying structure of the gel changes with ionic strength. Increasing ΔT to 6^oC for fd-PNIPAM gel in 105 mM buffer increased the strength of the gel but did not change the structure of the gel as inferred from the slope from the power law fits for different ΔT). The critical strain values are shown in figure 2.b, as function of concentration, ionic strength and ΔT. The critical strain decreases as a function of concentration and ionic strength, indicating stronger gels to be more brittle.

The storage modulus as a function of frequency and temperature for a 4.1 mg/ml fd-PNIPAM suspension in an aqueous 105 mM buffer solution is shown in figure 3.a. As the temperature is increased from 32^oC (gel point) to 36^oC, the gel strength increases due to the attraction between PNIPAM polymers. The solid lines in figure 3.a are fit to equation $G'(\omega) = \Gamma(n-1)cos(n\pi/2)S\omega^n$ [9]. The parameters S gives the gel strength and the power law exponent n reflects the structure of the gel, where $n = \dfrac{d(d+2-2d_f)}{2(d+2-d_f)}$ [10] can be used to relate the critical exponent n to fractal dimension d_f of the gel . Figure 3.b shows the decrease in n and the corresponding increase in d_f as the we go deeper into the gel regime (higher temperature). The fractal dimension of the gel increases rapidly from 2.2 to 2.4 for a 1^oC change in temperature and remains constant their after. The constant d_f explains the reason why their is no change in the structure of the gel as the temperature is changed beyond gel point. Table 1 shows the gel strength (S), critical exponent (n) and the fractal dimension (d_f) determined for fd-PNIPAM gels in buffers of 105 mM and 1 mM ionic strength at $\Delta T = 4^oC$. A can be seen from table 1, a small difference in the fractal dimension of fd-PNIPAM gels makes a huge difference in the magnitude of the moduli.

The structure of the gel can be inferred from rheological experiments, and showed only a small difference between the fractal dimensions of the gels formed in 105 mM and 1 mM ionic strength buffers. To confirm the above result we performed scattering experiments covering a wide range of scattering vectors (q) as shown in figure 4.a. The slope of the scattering curves, which gives the fractal dimension of the gels for $qL < 1$ is close to 2.5, confirming the order of magnitude obtained by the rheological results. As can be seen in figure 4.a there is not much change between the scattering of a fd-PNIPAM suspension and that for the gel. As the temperature is increased the particles in suspension are 'locked' into the

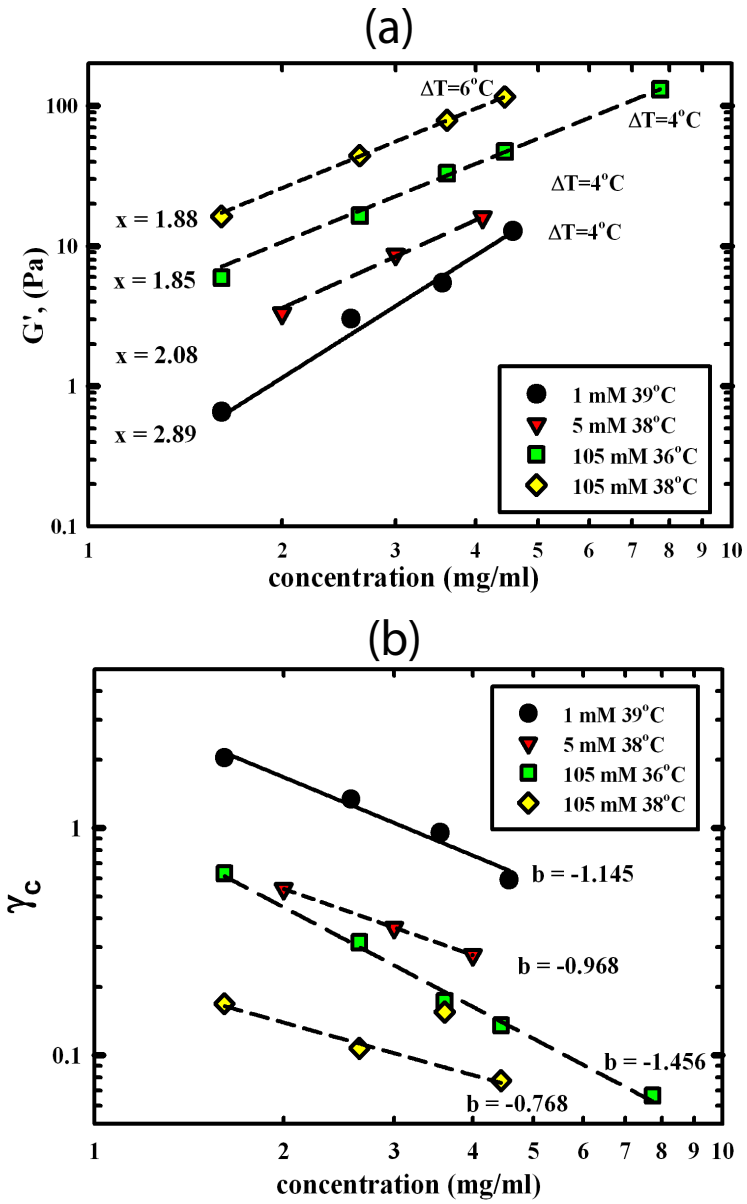

Figure 2: a) Average storage modulus and b) critical strain amplitude, obtained from strain sweep experiments at a frequency of 6.28 rad/s as a function of *fd*-PNIPAM concentration at $\Delta T = 4^oC$ for 1 mM, 5 mM and 105 mM ionic strength buffers. One set of data for *fd*-PNIPAM gels in 105 mM buffer at $\Delta T = 6^oC$ is also shown. Lines are power law fit to the data and the respective power law exponents are shown next to each line

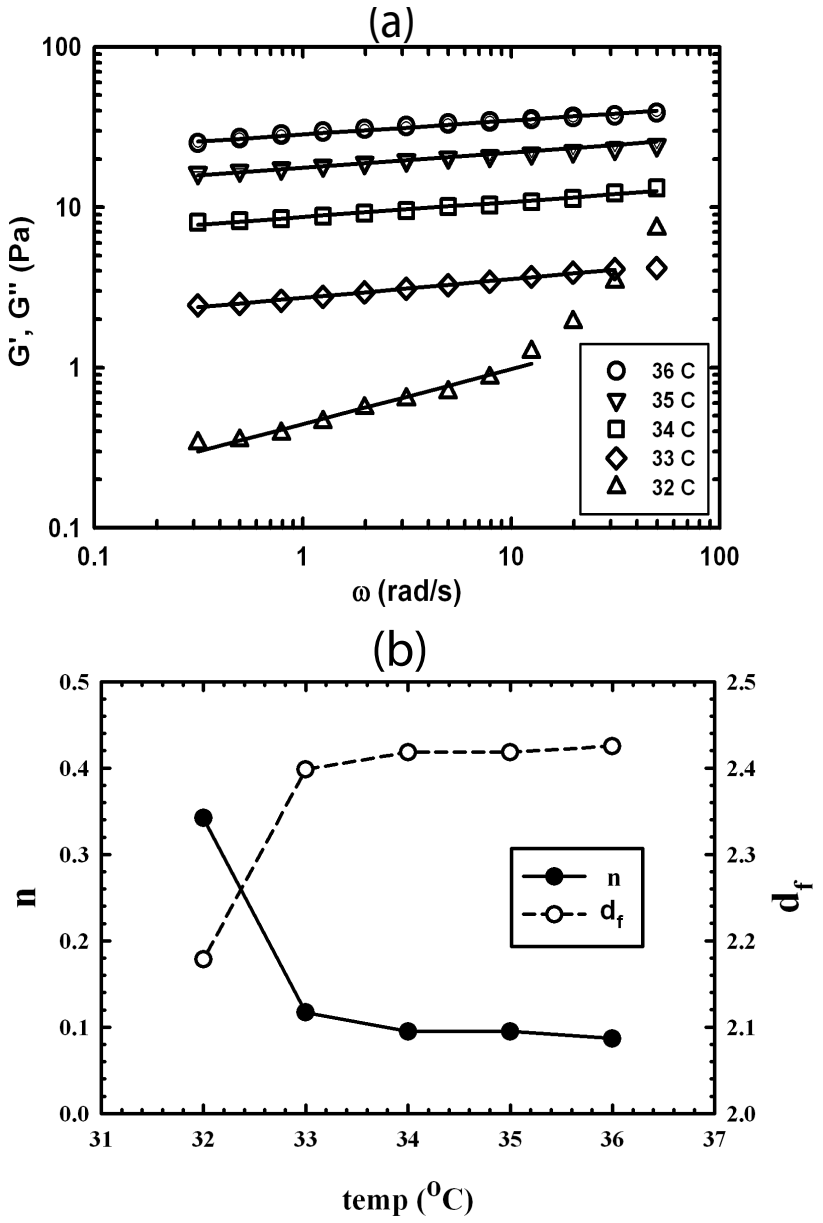

Figure 3: a). Storage modulus as a function of frequency at different temperatures above gel point for 4.1 mg/ml fd-PNIPAM in 105 mM ionic strength buffer. Solid lines are fits to the data using equation $G'(\omega) = \Gamma(n-1)cos(n\pi/2)S\omega^n$. b). The change in critical exponent n and the inferred change in fractal dimension as a function of temperature.

Table 1: Gel strength (S), critical exponent (n) and fractal dimension (d_f) for fd-PNIPAM gels in 105 mM and 1 mM ionic strength buffers at $\Delta T = 4^oC$

105 mM				1 mM			
Conc. (mg/ml)	S (±0.5)	n (±0.005)	d_f	Conc. (mg/ml)	S (±0.05)	n (±0.005)	d_f
1.61	6.5	0.13	2.38	1.61	0.15	0.22	2.30
2.64	17.0	0.09	2.42	2.56	1.7	0.26	2.26
3.61	32.0	0.08	2.43	3.55	5.0	0.18	2.34
4.44	46.0	0.085	2.42				
7.74	120.0	0.08	2.43				

gel state. There is only a small difference in intensity between the sol and the gel state due to the formation of clusters, as is shown in figure 4.b.

Conclusion: A model gel made of monodisperse and thermoreversible rodlike particles has been studied in the critical gel regime. Rheological experiments indicate that the structure of the gels is set in the critical gel regime and does not change as it is quenched deeper into the gel regime. A small difference in fractal dimensions of the gels causes significant differences in gel strength. Scattering experiments confirm results of fractal dimension analysis obtained from rheology.

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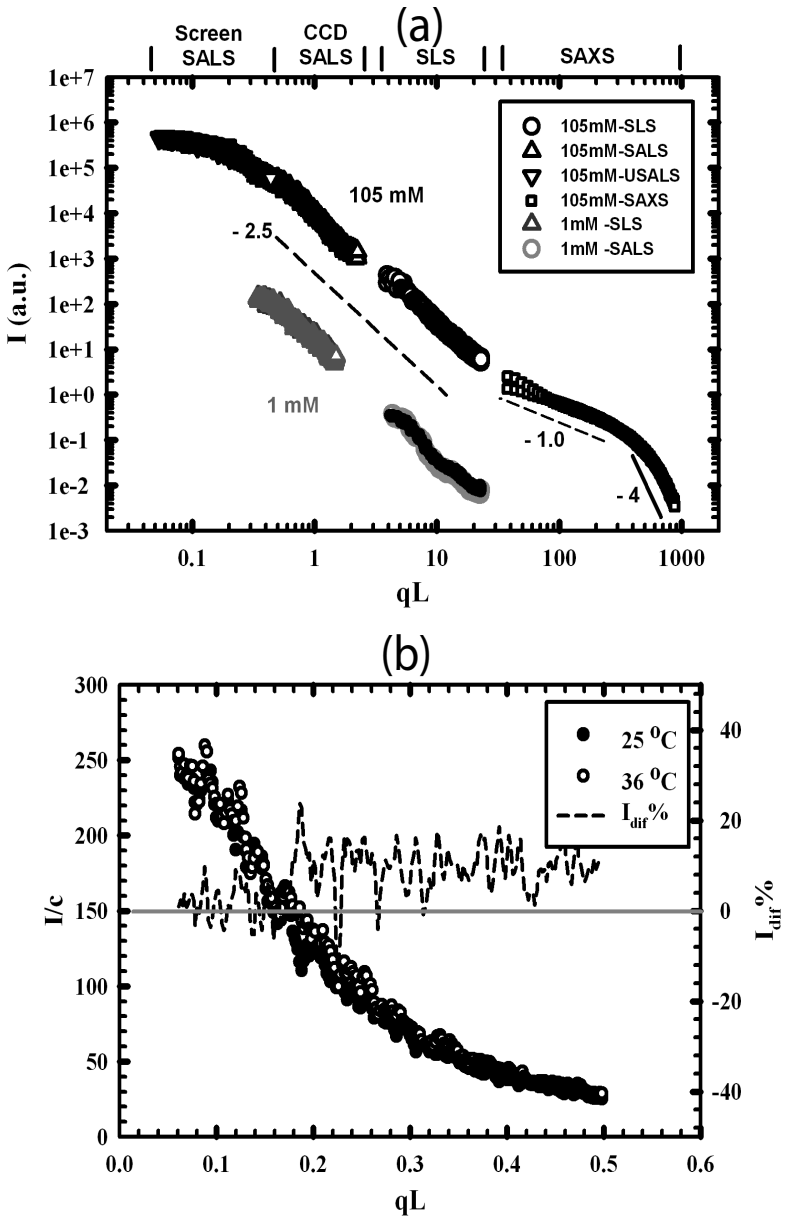

Figure 4: a) Combined light scattering and x-ray scattering data (Intensity versus scattering vector) for 3.5 mg/ml *fd*-PNIPAM in buffers solutions of 1 mM and 105 mM ionic strength at temperatures below and above gel point. b) Intensity difference between fd-PNIPAM suspension and the gel in 105 mM ionic strength buffer.

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