CHAPTER 5

DYNAMICS AND YIELDING BEHAVIOR OF DENSE PNIPAM MICROGEL GLASSES

5.1 Introduction

Glass is a disordered solid which is obtained by quenching or compressing the liquid within time smaller than the intrinsic structural relaxation time of the liquid [1-2]. Structural relaxation times in atomic systems are very small (~ 10^{-12} sec), hence these systems need very fast quenching rates and are difficult to probe directly. On the other hand, colloidal systems have slow relaxation times (~ 10^{-6} sec - 10^{3} sec) and hence accessible to dynamic light scattering technique to probe the dynamics in real time [3]. Colloidal suspensions of monodisperse hard sphere particles undergo glass transition at \( \phi = 0.57 \) [4-5]. Upon glass transition, structure of liquid remains almost same, whereas dynamics at longer time slows down drastically [5-6]. Slowing down of the particle dynamics at long times in hard sphere suspensions, on approaching the glass transition, is understood to occur due to kinetic arrest of the particles within cages formed by neighboring particles [5]. The particles start experiencing the effect of cage in a supercooled liquid state, even before it turns into the glass. The motion of a particle in the supercooled liquid state is diffusive at short times, becomes subdiffusive at intermediate times (due to cage effect) and again diffusive at long times (due to escape of the particle from the cage of neighbouring particles, the behavior of mean square displacement (MSD) of the particle is shown in Fig. 1.6(a)-3). Thus, the structural relaxation in the supercooled liquid occurs in two steps. The first step occur at short times (due to intra-cage dynamics of the particle) which is known as fast or beta relaxation and another at long times (due escape of the particles from the cages) is known as slow or alpha relaxation. On approaching the glass transition (i.e. with
increase in $\phi$, the cages from near neighbour particles becomes more and more rigid resulting into increase in alpha relaxation time (i.e. the suppression of long time diffusion of the particles). While alpha relaxation (long time dynamics) of hard sphere colloidal particles in the glassy state is ceased out, beta relaxation (short time dynamics) continues to exist with diffusive particle motion at short times [5].

Unlike hard spheres, PNIPAM microgels are soft particles having a dense core and a thin shell of polymer chains [7-8]. It is shown in Chapter 3 that, PNIPAM microgel particles undergo osmotic deswelling in dense suspensions with crystalline order of particles. Here, we report that the dense suspensions of PNIPAM microgels exhibit a glassy state with a reduction in the particle size upon osmotic compression. We also report here for the first time, subdiffusive dynamics at short times in the glassy state as well in the supercooled liquid state of microgel suspensions. Subdiffusive dynamics in the glasses and the super cooled liquids is argued to arise due to entanglement of dangling polymer chains of neighboring particles, similar to that reported in PNIPAM microgel crystals, discussed in Chapter 4.

Colloidal glasses are viscoelastic in nature and yield under application of the large shear [9]. The yielding behaviour of colloidal glasses has been found to depend on the interparticle interactions [10-11]. While the hard sphere colloidal glass has been found to yield in one step (Fig. 1.7) [10], attractive colloidal glasses have been found to yield in two steps (Fig. 1.9) [11]. In dense PNIPAM microgel glasses, interparticle interactions are soft repulsive [12] and there exists entanglements of dangling polymer chains between neighbouring particles (evidenced by short time subdiffusive dynamics). With an aim to know that how the soft repulsive glass with entangled polymer chains will respond to the applied shear, yielding behavior of dense PNIPAM microgel glasses has been studied by performing non-linear rheological measurements.
Results of non-linear rheological measurements are discussed in this chapter. Rheological measurements have revealed that dense PNIPAM microgel glasses yield in two steps (exhibiting two peaks in $G''$) in contrast to one step yielding observed in hard sphere glasses. Two step yielding behaviour is explained in terms of breaking of the bonds (entanglements) and breaking of near neighbour cage, similar to that in attractive glasses [11]. We also studied the effect of temperature on yielding behaviour. Two step yielding behaviour (two peaks in $G''$) of PNIPAM microgel glasses is found to transform into one step (one peak in $G''$) in supercooled liquid state upon increasing temperature and finally, in the liquid state, no peak in $G''$ is observed. Two step yielding of PNIPAM microgel glasses is also found to depend on the shear rate / oscillation frequency at which measurements are performed. Results of investigations on the shear rate dependence of yielding behaviour of dense PNIPAM microgel glasses are also discussed in this chapter.

5.2 Experimental details

PNIPAM microgel particles having $d_h = 560$ nm and SPD = 6% at 25 °C were used to prepare glasses used for this study. Here, particles of larger diameter (560 nm), as compared to previous studies (discussed in Chapter 3 and Chapter 4) were used, in order to tune the first peak of the structure factor within the $q$ range of $0.68 \times 10^5 \text{ cm}^{-1}$ to $2.54 \times 10^5 \text{ cm}^{-1}$ of our DLS set up. The large sized particles of PNIPAM microgels have been synthesized using the procedure as described in Chapter 2, but without the addition of the surfactant and crosslinker during the synthesis. Dense PNIPAM microgel glasses having particle concentrations of $6.2 \times 10^{12} \text{ cm}^{-3}$ and $7.8 \times 10^{12} \text{ cm}^{-3}$ (determined using SLS) and labelled as S1 and S2, respectively have been used for the investigations. The $\phi$ values estimated using $d_h$ (measured using DLS under dilute conditions) are found to be 0.7 and 0.9, respectively for samples S1 and S2. At such a
high values of $\phi$ particle dynamics is expected to be slow due to kinetic arrest of particle within the cages formed by neighbouring particles, leading to a glassy state [5]. Kinetic arrest of the particles prevents crystallization of these suspensions, despite their SPD is low (6%) [4].

Since PNIPAM microgel particle’s size used for the present study is twice than that used for investigating dynamics across melting (Chapter 4), the scattering ability of these particles is quite high even below VPT (moderate turbidity as seen in Fig. 5.1(a)). With increase in temperature, suspensions become much more turbid (Fig. 5.1(b)), due to deswelling of the particles leading to increase in the polymer content within the particle [7].

![Fig 5.1](image)

**Fig 5.1** Photographs of dense PNIPAM microgel suspension (Sample S1) showing (a) moderate turbidity at 20 °C and (b) high turbidity at 31 °C.

In turbid suspensions, multiple scattering of light restricts the use of conventional static light scattering (SLS) and Dynamic light scattering (DLS) techniques for characterization of their structure and dynamics [13]. We have employed cross-correlation based light scattering techniques (3D DLS and SLS) for investigating the dynamics and structure in samples S1 and S2. As discussed in section 2.1.5, in 3D DLS experiments, two simultaneous light scattering experiments at identical scattering wave vectors are performed on the same scattering volume, but with detectors at different spatial positions. Under these conditions, when one correlates the intensities, only
singly scattered photon contributes to the correlation function. The uncorrelated multiply scattered light reduces the intercept of the correlation function. Thus, 3D DLS helps in probing the structure and dynamics when samples are turbid. 3D DLS and SLS measurements have been carried out on samples S1 and S2 placed in cylindrical glass cells with 8 mm path length. Details of the experimental set up, operation principle and analysis method are given in Chapter 2. Ensemble averaged intensity, $<I(q)>_E$ of the scattered light have been measured by rotating the sample cells about their cylindrical axis, at the speed of 1 rotation/90 sec. At each $q$, $<I(q)>_E$ is collected for 270 sec in a single run. The $<I(q)>_E$ from three such runs are found to be identical. Time averaged intensity cross-correlation, $g^{(2)}_{12}(q, t)$ have been measured at a sample location for 120 minutes in the glassy state of the samples and for 20 minutes in the liquid state of samples. At each temperature, results are obtained by averaging three such measurements. Ensemble averaged $f(q, t)$ has been obtained from the time averaged $g^{(2)}_{12}(q, t)$ by performing the non-ergodic analysis, which is discussed in the section 2.1.6.

Rheological measurements have been carried out using MCR 301 rheometer with a cone and plate geometry. Instrument and measurement details are described in Chapter 2. Upon loading the sample on the rheometer cell, the open area of the cell was sealed with silicon oil (viscosity ~ 99 cp) for preventing the evaporation of water during the measurements. Before performing the experiment, it is necessary to remove the shear history from the loaded sample, which it possesses due to the shear experienced by the sample while loading on the rheometer cell. To remove the shear history, temperature of the sample was raised well above the melting temperature of the glasses and then cooled back to the measurement temperature.
5.3 Static and dynamic light scattering results

5.3.1 Characterization of structural ordering in dense PNIPAM microgel suspensions

![Graph](image)

**Fig. 5.2.** Characterization of structural ordering and dynamics in samples S1 and S2. (a) ensemble averaged scattered intensity, $<I(q)>_E$ versus $q$, and (b) ensemble averaged $f(q,t)$ versus $t$, for samples S1 and S2 measured at 20 °C. Lines drawn are guide to the eye.

Samples S1 and S2 did not show iridescence when left undisturbed for several days. Structural ordering and dynamics in the dense samples have been investigated by performing static and dynamic light scattering measurements using 3D DLS setup. For both samples S1 and S2, time averaged and ensemble averaged intensities of the scattered light (measured at a given $q$) are found to differ from each other, indicating non-ergodic nature of the samples. Figure 5.2(a) shows the ensemble averaged intensity of the scattered light, $<I(q)>_E$ for samples S1 and S2 at 20 °C. For both the samples, $<I(q)>_E$ shows broad peak, suggesting that the samples are disordered. In order to characterize that whether the disorder is liquid-like or glass-like, ensemble averaged dynamic structure factor, $f(q,t)$ have been measured and is shown in Fig. 5.2(b). It can be seen that $f(q,t)$ shows non-decaying behavior, suggesting the dynamical arrest of microgel particles in samples S1 and S2. The non-decaying $f(q,t)$, with broad peak in $<I(q)>_E$, suggest that both the samples are in the glassy state at
20 °C. The volume fraction of samples S1 and S2 in their glassy state has been estimated using relation \( \phi = \frac{n_p \pi d_h^3}{6} \) and found to be 0.70 and 0.90, respectively. Here \( n_p \) is the particle number density and is related to the position of first peak position, \( q_m \) in \( \langle I(q) \rangle_E \) as \( n_p = \left( \frac{4}{3\sqrt{3}} \right) \left( \frac{q_m}{2\pi} \right)^3 \) for fcc-like ordering. These volume fractions are greater than random closed packing fraction of hard spheres (\( \phi = 0.64 \)), suggesting that PNIPAM microgel particles have undergone osmotic compression, similar to that observed by us in dense PNIPAM microgel crystals (discussed in Chapter 3).

### 5.3.2 Identification of the glass transition

![Graphs](image)

**Fig. 5.3** (a) \( \langle I(q) \rangle_E \) vs. \( q \), (b) \( f(q, t) \) vs. \( t \) and (c) Mean square displacement of PNIPAM microgel particles, in units of average interparticle spacing (\( l \)), \( \langle \Delta r^2(t) \rangle / l^2 \), measured at 20 °C and 30 °C for samples S1 and S2. Lines drawn are guide to the eye.

Upon increasing the temperature, dense PNIPAM microgel suspensions are expected to transform from the glassy state into a liquid like state, due to decrease in the size of PNIPAM microgel particles and hence, \( \phi \) of the suspension. The \( \langle I(q) \rangle_E \)
measured at 20 °C and 30 °C for samples S1 as well as S2 are shown in Fig. 5.3(a). At both the temperatures, samples S1 and S2 show broad peaks indicating the presence of disorder. \( f(q, t) \) for the samples, at 20 °C and 30 °C, are shown in Fig. 5.3(b). At 20 °C, \( f(q, t) \) for both samples is non-decaying, whereas it decays to zero at 30 °C, indicating the transfer of microgel glass at 20 °C into microgel liquid at 30 °C. Mean square displacement (MSD) in units of the average interparticle separation (\( l \)), 
\[
\frac{\langle \Delta r^2(t) \rangle}{l^2},
\]
(obtained from corresponding \( f(q, t) \) using Eq. 2.24) at 20 °C and 30 °C for samples S1 and S2 is shown in Fig. 5.3(c). At 20 °C (in the glassy state) MSD shows tendency towards saturation at long times whereas at 30 °C (in the liquid state) it is observed to increase with time, \( t \). Since both the glass and the liquid are disordered structures, while undergoing from the glass to liquid transition, MSD is not expected to show a sharp discontinuity as observed for crystal to liquid transition [14]. MSD (monitored across the glass to liquid transition at a constant time in the long time regime) have been used to identify the glass transition [14], where it shows a change in the slope at the glass transition.

With an aim to identify the glass transition temperature, \( T_g \) for samples S1 and S2, detailed 3D DLS and SLS measurements as a function of temperature have been carried out. The MSD at constant delay time of \( t = 0.15 \) sec (a time in the long time regime) as a function of temperature for samples S1 and S2 is shown in Fig. 5.4 (upper panel). The MSD increases with increase in temperature exhibiting a change in the slope at \( \sim 25 \) °C for sample S1 and at \( \sim 26 \) °C for sample S2. The temperature at which change in slope occurs is identified as the glass transition temperature. Identification of the glass transition has also been reported in the literature through the structural studies, where the ratio \( g_{min}/g_{max} \) (known as Wendt-Abraham parameter) or its Fourier analogue \( S_{min}/S_{max} \) have shown to exhibit a change in the slope at glass
transition [15-16]. Here, \( g_{\text{min}} (S_{\text{min}}) \) and \( g_{\text{max}} (S_{\text{max}}) \) represents the minimum in the pair correlation function, \( g(r) \) (structure factor, \( S(q) \)) at higher \( q \) side near the first peak and the maximum value of the first peak in \( g(r)/S(q) \), respectively. Though we have monitored the \( <I(q)>_E \) as a function of temperature across the glass transition (Fig. 5.3(a)), which is related to the \( S(q) \) via form factor \( P(q) \) as \( <I(q)>_E = AP(q)S(q) \) with \( A \) being a constant (Eq. (2.9)), difficulty in determination of proper \( P(q) \) of PNIPAM microgel particles in dense suspensions (due to their soft and core-shell nature) restricts the estimation of \( S(q) \) from \( <I(q)>_E \).

![Graphs showing MSD and I_min/I_max as a function of temperature](image)

**Fig. 5.4** Identification of the glass transition: Upper panel; MSD as a function of temperature, \( T \) (at the time of 0.15 sec) for samples S1 and S2. Lower panel; The ratio \( I_{\text{min}}/I_{\text{max}} \) as a function of temperature, \( T \). Lines drawn are guide to the eye. Arrows indicate the glass transition with corresponding temperature \( T_g \).
The ratio $I_{\text{min}}/I_{\text{max}}$, with $I_{\text{min}}$ and $I_{\text{max}}$ being the minimum in intensity at higher $q$ side near the first peak and the maximum intensity of the first peak in $\langle I(q) \rangle_E$ respectively, monitored as a function of temperature for samples S1 and S2 is shown in the Fig. 5.4 (lower panel). The ratio $I_{\text{min}}/I_{\text{max}}$ is also found show a change in the slope at the glass transition, though it is not a proper quantity to be monitored.

5.3.3 Subdiffusive dynamics at short times in dense PNIPAM microgel glasses

Upon identification of the glass transition, we have performed the analysis of MSD at the short time and the long time regime with the power law behavior ($\langle \Delta r^2(t) \rangle \propto t^\alpha$). The short time ($t \ll \tau_R$) and the long time ($t \gg \tau_R$) regimes are identified with the reference to $\tau_R = d_h^2/4D_0$. $\tau_R$ has been estimated by using $d_h$ and $D_0$ of PNIPAM microgel particles at the corresponding temperatures. MSD shows saturation tendency in the glassy state and increases with time for temperatures higher than glass transition temperature (as shown in Fig. 5.5). Analysis of the MSD at long times, for temperatures above the glass transition, suggested that it exhibits diffusive behavior ($\alpha = 1$), similar to that observed in hard sphere colloidal glasses [5].

At short times, MSD above as well as below $T_g$ is observed to increase with increase in time (Fig. 5.5). Interestingly, the value of $\alpha$ in the glassy state of samples, determined from the short time MSD, is found to be lesser than the unity ($\alpha = 0.67$ for sample S1 and $\alpha = 0.62$ for sample S2), indicating the subdiffusive dynamics of PNIPAM microgel glasses at short times. In the case of hard sphere glasses, short time dynamics is observed to be diffusive ($\alpha = 1$) [5], whereas we observe it to be subdiffusive for dense PNIPAM microgel glasses. Similar kind of subdiffusive dynamics at short time have been observed in dense PNIPAM microgel liquids close to their crystallization (as discussed in Chapter 4) and is understood to occur due to the
overlap / entanglement of dangling polymer chains of neighboring microgel particles. The subdiffusive dynamics of PNIPAM microgel particles indicate that entanglements of dangling polymer chains also exist in the glassy state of the dense suspensions. The smaller value of $\alpha$ ($= 0.62$) for sample S2 than that for sample S1 ($\alpha = 0.67$) is as expected, since sample S2 ($\phi = 0.90$) is expected to have more number of entanglements than sample S1 ($\phi = 0.70$) due to its high volume fraction.

With increase in temperature, PNIPAM microgel particles shrink in size and their kinetic energy also increases, which could result into decrease in the overlap/entanglement of the dangling polymer chains between neighbouring particles. Thus, one expects a change of subdiffusive behavior ($\alpha < 1$) of short time MSD at 20 °C (glassy state) to diffusive type ($\alpha = 1$) at temperatures above glass transition. Variation of $\alpha$, from short time MSD of samples S1 and S2, as a function of temperature is shown in Fig. 5.6(a). Upon increasing the temperature, value of $\alpha$ (from the short time MSD) is indeed observed to rise gradually and tend towards the unity at temperatures close to VPT, suggesting the decrease in overlap/entanglement of dangling polymer chains between neighbouring particles with increase in temperature. The value $\alpha < 1$ for temperatures above the glass transition, suggests the presence of entanglement of dangling polymer chains between neighbouring particles even in the liquid state. $\alpha \sim 1$ at temperatures close to VPT indicates complete disentanglement of dangling polymer chains. At the glass transition, $\alpha$ is found exhibit a change in the slope (Fig. 5.6(a)), suggesting that $\alpha$ can also be used as a parameter to identify the glass transition. Schematics depicting the strong entanglements of dangling polymer chains at temperature well below glass transition (i.e. indicated by I in Fig. 5.6(a)) and disentanglement of dangling polymer chains at temperature close to VPT (indicated by II in Fig. 5.6(a)) are shown in Fig. 5.6(b) and (c), respectively.
Fig. 5.5 Mean square displacement ($<\Delta r^2(t)>$) expressed in units of average interparticle spacing ($l$), $<\Delta r^2(t)>/l^2$, for (a) sample S1 and (b) sample S2 in their glassy and liquid states. Values of $\alpha$, indicated on the MSD curves, are determined from the power law fit of the MSD data ($<\Delta r^2(t)> \propto t^\alpha$) over a time range indicated by continuous lines.

Fig. 5.6 (a) variation of $\alpha$ (obtained from short time MSD) as a function of temperature, $T$ for samples S1 and S2, (b) Schematic depicting the strong entanglements of dangling polymer chains at temperature well below glass transition (i.e. deep inside the glassy state indicated by I in (a)) and (c) Schematic depicting the disentanglement of dangling polymer chains at temperature close to the VPT (indicated by II in Fig. 5.6(a)). Lines drawn are guide to the eye.
5.4 Yielding behaviour of PNIPAM microgel glasses

As discussed in Chapter 1, hard sphere colloidal glasses are known to yield in one step, whereas attractive glasses show two step yielding under the application of shear, thus yielding behaviour of colloidal glasses depends on the nature of interparticle interactions. In PNIPAM microgel glasses, interparticle interactions are soft repulsive [12] and also there exists entanglement of dangling polymer chains of neighbouring microgel particles under dense conditions. With an aim to know, how dense PNIPAM microgel glasses with soft repulsive interactions responds to the applied shear, yielding behaviour of samples S1 and S2 have been studied by subjecting them to oscillatory rheological measurements. To remove shear history, loaded samples are melted by heating beyond the glass transition temperature and cooled back to the measurement temperature. Immediately after cooling, \( G' \) and \( G'' \) have been measured as function of time under the application of small \( \gamma_0 = 3\% \), at \( \omega = 10 \text{ rad/sec} \), are shown in Fig. 5.7. Both samples (S1 and S2) have been found to recover rapidly after cooling. It can be seen from Fig. 5.7 that a waiting time of 900 sec is sufficient for performing each measurement to ensure complete recovery of the sample for obtaining reproducible results.

![Fig. 5.7 Recovery of \( G' \) (solid symbols) and \( G'' \) (open symbols) measured at constant \( \omega (10 \text{ rad/sec}) \) and \( \gamma_0 (3\%) \), immediately after cooling the sample.](image)

\( T = 20 \, ^{\circ}\text{C} \)
Dense colloidal suspensions can experience wall-slip due to particle-wall interactions [17-18]. Presence of the wall-slip can affect the flow behavior of dense microgel suspensions considerably [18]. In order to verify, whether the wall-slip is present or not in samples S1 and S2, measurements have been performed with and without attaching a sand paper (grit size 1000) to the measuring tool and to the measuring plate. Figure 5.8 shows dependence of shear stress, $\sigma$ on shear rate, $\dot{\gamma}$ for measurements with and without the sand paper attached to the measuring tool and the measuring plate. The good overlap between the data obtained with and without sand paper suggests the absence of the wall slip in our samples (i.e. particle-wall interactions are negligible).

![Graph](image)

**Fig. 5.8** Shear stress, $\sigma$ versus applied shear rate, $\dot{\gamma}$ for samples S1 and S2 measured with and without the sand paper attached to the measuring tool and the measuring plate.

### 5.4.1 Linear viscoelasticity of dense PNIPAM microgel glasses

In the previous section on dynamics, it has been shown that the dynamics in dense PNIPAM microgel glasses at short times (i.e. intra-cage dynamics or beta relaxation behaviour) is subdiffusive. This observation constitutes evidence for the entanglement of dangling polymer chains between neighbouring particles.
Fig. 5.9 Linear Viscoelastic behavior of samples S1 (triangles) and S2 (circles) in their glassy state (at 20 °C). Arrows indicate the approximate position of minimum in $G''$ and the corresponding $\omega$ represents $\omega_\beta$.

As expected, the long time dynamics (alpha relaxation behavior) is diffusive and is unaffected by entanglements of dangling polymer chains between neighbouring particles. Once entanglements exist between neighboring particles in dense PNIPAM microgel glasses, their yielding behavior is expected to have the signature. Hence we subject samples S1 and S2 to non-linear rheological studies and results are discussed in sections below. As discussed in section 1.5, relaxation frequencies corresponding to the alpha and beta relaxations of colloidal glasses can be measured by performing the linear viscoelastic measurements. Alpha relaxation frequency, $\omega_\alpha$ is identified with the peak in $G''$ on the lower frequency side and beta relaxation frequency, $\omega_\beta$ with the minimum in the $G''$ on the higher frequency side. For determining $\omega_\beta$, linear
viscoelastic response of PNIPAM microgel glasses of samples S1 and S2 have been studied. Towards this, $G'$ and $G''$ have been measured by varying the $\omega$ between 0.1 to 100 rad/sec and applying small constant strain of amplitude $\gamma_o = 2\%$ (shown in Fig. 5.9). Notice in Fig. 5.9 that $G' > G''$, within the frequency range of 0.1 to 100 rad/sec, suggesting the solid-like nature of samples S1 and S2 at 20 °C. The minimum observed in $G''$ (shown with arrows) indicates $\omega_\beta$ for the samples [19]. The peak in $G''$, corresponding to alpha relaxation, falls out of the measurement window (0.1 to 100 rad/sec) due to very slow alpha relaxation process and hence is not visible. We have chosen $\omega = 10$ rad/sec to study yielding behaviour of samples S1 and S2, which is well above their $\omega_\beta$.

5.4.2 Non-linear rheological behaviour of dense PNIPAM microgel glasses

![Fig. 5.10 Yielding behavior of samples S1 and S2 in their glassy state showing two step yielding. Measurements have been carried out with $\omega$ fixed at 10 rad/sec. Arrows indicate the peak positions. $G'$ (open symbols) and $G''$ (solid symbols).](image)

Samples S1 and S2, in their glassy state, have been subjected to the non-linear rheological measurements by performing dynamic strain sweep (DSS) measurements,
where $\gamma_0$ has been varied over a wide range (1-1000%) by keeping $\omega$ constant at 10 rad/sec. Figure 5.10 shows the variation of $G'$ and $G''$ as a function of $\gamma_0$ for samples S1 and S2. In order to probe the intra-cage dynamics and hence the effect of entanglement of dangling polymer chains on the yielding behavior, $\omega$ is fixed at 10 rad/sec, which is higher than $\omega_\beta \sim 0.25$ rad/sec (Fig. 5.9). For lower values of $\gamma_0$, both $G'$ and $G''$ exhibit a plateau indicating the region of $\gamma_0$ over which PNIPAM microgel glasses show linear response to the applied $\gamma_0$. Notice that, in the plateau region, $G' > G''$, which suggests that the glasses behave as viscoelastic solid for low $\gamma_0$. For larger $\gamma_0$, $G'$ comes down indicating the yielding of glasses under the applied shear. With increase in $\gamma_0$, $G'$ further comes down and cross $G''$. The point at which $G'$ cross $G''$ is defined as the yield point and the corresponding value of strain, $\gamma_y$ and stress, $\sigma_y$ is defined as yield strain and yield stress, respectively. Beyond the yield point, Samples S1 and S2 behaves like a viscoelastic liquid (i.e. $G' < G''$) due to the applied shear (shear melting) of the glasses. In the non-linear response regime, $G'$ shows monotonic decrease with increase in $\gamma_0$. This behavior is similar to that of hard sphere glasses reported in the literature [10-11]. In contrast to hard sphere glasses [10-11], $G''$ shows two peaks (indicated by arrows in the Fig. 5.10) in dense PNIPAM microgel glasses. $G''$ exhibit two peaks at two values of $\gamma_0$, imply that two mechanisms are operational during the yielding of PNIPAM microgel glasses. This is the first observation of two step yielding in a dense PNIPAM microgel glass, where interactions are known to be soft repulsive [12].

Since PNIPAM microgel particles shrink in the size with increase in temperature, entanglements of dangling polymer chains between neighbouring particles are expected to come down. This is expected to reflect in the yielding behavior of samples S1 and
S2. We have investigated the effect of temperature on the yielding behavior of samples S1 and S2 by performing DSS measurements at various temperatures and results are shown in Fig. 5.11. For the sake of clarity, only $G''$ behavior as a function of $\gamma_o$ at different temperatures are shown in Fig. 5.11. Notice in sample S1, two step yielding at 20 °C (two peaks in $G''$) changes to one step yielding (single peak in $G''$) at 24 °C and no peak upon further heating to 29 °C. In the case of sample S2, single peak in $G''$ is observed at higher temperature (27 °C) than that for S1 (24 °C) and no peak at 30 °C. These observations imply that upon shearing at elevated temperature, the entanglements between neighbours goes off leading to the appearance of single peak in $G''$, which is characteristic of most of the soft colloidal glasses. Upon further heating, the glass melt into a liquid which is evidenced by absence of peak in $G''$. For sample S2, single peak in $G''$ appearing at higher temperature than that in sample S1 is also understandable as, S2 is more dense and hence disentanglements are expected to occur at higher temperature.

Fig. 5.11. $G''$ measured using DSS measurements at various $T$ for samples S1 and S2. Arrows indicate the peak positions.
5.4.3 Understanding of two step yielding in dense PNIPAM microgel glasses

![Fig.5.12](image)

**Fig.5.12** Schematic representation of the two step yielding process in dense PNIPAM microgel glasses. State A represents the undeformed state configuration of PNIPAM microgel glass with $R$ as reference particle having entangled neighbors as 1,4,6,5 and topological neighbors 1-6. State B shows that, upon application of lower yield strain ($\gamma_1$), entanglements with 1,4,6,5 are broken leading to peak in $G''$ at $\gamma_1$. State C shows that, upon application of higher yield strain ($\gamma_2$), topological neighbors of $R$ changes due to cage breaking, which leads to second peak in $G''$ at $\gamma_2$.

Two step yielding in the form of two peaks in $G''$ as a function of $\gamma_o$ is reported by Pham *et al.* [11] in attractive glasses, prepared by introducing depletion attraction between hard spheres by the addition of a non-adsorbing polymer in dense hard sphere suspension. Pham *et al.* [11] have interpreted their observation of two step yielding (two peaks in $G''$) due to occurrence of two processes, i) breaking of the near-neighbor bonds arising from attractive interactions leading to the first peak in $G''$ to occur at low $\gamma_o$ and ii) breaking of the cages (topological constraints arising from neighbouring particles) leading to the second peak in $G''$ to occur at larger $\gamma_o$. The two step yielding reported in our dense PNIPAM microgel glasses is explained by drawing an analogy with attractive glass [11]. With this analogy, the observed two step yielding (two peaks in $G''$ in Fig. 5.10) in PNIPAM microgel glasses is interpreted through two processes: i) breaking of entanglements of dangling polymer chains between neighbouring
PNIPAM microgel particles giving a peak in $G''$ at lower strain ($\gamma_1$) and ii) breaking of the near neighbor cages giving a peak in $G''$ at higher strain ($\gamma_2$). These two processes are schematically shown in Fig. 5.12. Configurations A, B and C describe changes in the environment of a reference particle $R$, with respect to its entangled neighbors and topological neighbors under the application of shear. In unsheared state (A), the reference particle $R$ has topological neighbors (1 - 6) and entanglements neighbors (1, 4-6). When strain of increasing amplitude is applied, particles start moving in the direction of strain. At lower yield strain ($\gamma_1$), entanglements with its neighbours (1, 4-6) are broken (configuration B). This process of breaking of entanglements, while keeping the same topological neighbors, gives rise to first peak in $G''$. As $\gamma_o$ is increased further to higher yield strain ($\gamma_2$), cages break with changes in topological neighbors (configuration C). This breaking of cages results in the second peak in $G''$.

5.4.4 Yield strains of dense PNIPAM microgel glasses and their frequency dependence

The yield strain values $\gamma_1$ and $\gamma_2$ for sample S1 at 20 °C are found to be 18% and 40% (Fig. 5.10), whereas those for sample S2 at 20 °C are found to be 20% and 35% (Fig. 5.10), respectively. The yield stress values $\sigma_1$ and $\sigma_2$ corresponding to $\gamma_1$ and $\gamma_2$ for sample S1 are found to be 1.1 and 2 Pa, whereas those for sample S2 are found to be 4.6 Pa and 6.2 Pa, respectively. With increase in $\phi$, number of entanglements of dangling polymer chains are expected to increase due to increase in the overlap of dangling polymer chains, hence more energy is required to break entanglements in sample S2 than sample S1. The higher values of $\sigma_1/\sigma_2$ and $G''_{\gamma_1}/G''_{\gamma_2}$ for sample S2 than for sample S1 indicates that sample S2 has more number of entanglements than sample S1. Here $G''_{\gamma_1}$ and $G''_{\gamma_2}$ represent the peak amplitudes at $\gamma_1$ and $\gamma_2$, respectively.
Small increase in $\gamma_1$ and decrease in $\gamma_2$ for glassy state of sample S2 than that for sample S1 is understandable, because near neighbor separation in sample S2 is smaller than S1 due to its higher volume fraction. Due to decrease in $\gamma_2$ and increase in $\gamma_1$, peaks in $G''$ for sample S2 (Fig. 5.10) appear smeared as compared to that of sample S1.

![Fig. 5.13](image)

**Fig. 5.13** (a) $G''$ for samples S1 and S2 in their glassy state (at 20 °C) measured using DSS measurements for various $\omega$ values, (b) Variation of peak strain, $\gamma_p$ (i.e $\gamma_1$, $\gamma_2$) with $\omega$ for samples S1 and S2 at 20 °C. Continuous lines are the power law fits ($\propto \omega^m$) giving $\omega$ dependence of $\gamma_1$ and $\gamma_2$, with values of $m$ written over the corresponding curve. Arrows indicate the peak positions.
In the case of hard sphere glasses, the yield strain is known to depend on the value of $\omega$ at which measurements are performed [20]. In order to know the $\omega$ dependence of $\gamma_1$ and $\gamma_2$ in dense PNIPAM glasses, DSS measurements have been performed at various values of $\omega$ and the results are shown in Fig. 5.13(a). For sake of clarity of the peaks, only $G''$ at different $\omega$ values are shown. Upon approaching $\omega_\beta$ (from higher frequency side), peak due to disentanglement is found to disappear, which is expected, since for $\omega \leq \omega_\beta$ intra-cage dynamics becomes insignificant. Variation of $\gamma_1$ and $\gamma_2$ with $\omega$, for sample S1 is plotted in Fig. 5.13(b). Both $\gamma_1$ and $\gamma_2$ are found to show the power law dependence on $\omega$ (i.e. $\propto \omega^m$) with values of exponent $m$ for samples S1 and S2 given in Fig. 5.13(b). As $\omega$ increases, $\gamma_1$ and $\gamma_2$ are found to shift to higher strain values. This is understandable from the increase in $G'$ with increase in $\omega$ as shown in Fig. 5.9.

5.5 Summary

We have prepared dense suspensions of thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) microgel particles with different volume fractions by subjecting them to the different osmotic compressions. Structural investigations, carried out using 3D DLS and SLS measurements, have suggested that at low temperatures dense suspensions of PNIPAM microgels exists in glassy state. PNIPAM microgel glasses have been found to transform into the liquid like order upon increasing the temperature. The glass transition temperatures of dense PNIPAM microgel suspensions have been identified by observing the change in the slope of the long time value of mean square displacement (MSD) plotted as a function of temperature. The ratio of the minimum in intensity at higher $q$ side near the first peak and the maximum intensity of the first peak in $\langle I(q) \rangle_E$, also showed a change in the
slope at the same temperature exhibited by long time value of MSD. For the first time the MSD behavior at short times is found to be subdiffusive \((i.e. \langle \Delta r^2(t) \rangle \propto t^\alpha\), with \(\alpha < 1\)) in dense PNIPAM microgel glasses. Subdiffusive behavior at short times is due to the overlap/entanglement of dangling polymer chains from shells of neighbouring particles. Subdiffusive behaviour observed at short times is found to change gradually into diffusive \((\alpha = 1)\) upon increasing the temperature, suggesting disentanglement of dangling polymer chains at higher temperature. Non-linear rheological measurements showed that dense PNIPAM microgel glasses, yield in two steps (exhibits two peaks in \(G''\) as a function \(\gamma_0\)) in contrast to the one step yielding observed in hard sphere glasses. The two step yielding in PNIPAM microgel glasses is interpreted due to occurrence of two processes: i) due to the breaking of entanglements of dangling polymer chains, giving rise to the first peak at lower strain and ii) due to the breaking of the near neighbour cages giving rise to the second peak at larger strain. At higher temperature, due to disentanglement, yielding behavior is observed to be single step (one peak in \(G''\)). Two step yielding behaviour of the dense PNIPAM microgel glasses is also found to depend on the oscillation frequency/shear rate at which measurements have been performed. Two peaks in \(G''\) are apparent only for \(\omega > \omega_\beta\). For \(\omega \leq \omega_\beta\) only single peak in \(G''\) is observed, since at these frequencies intra-cage dynamics becomes insignificant. Our measurements suggest that the inhomogeneous structure of PNIPAM microgel particles play an important role in governing the dynamics and shear flow behavior in dense PNIPAM microgel suspensions.

References


