6.1 Summary and conclusions

This chapter summarizes the investigations carried out on dense aqueous suspensions of thermo-responsive PNIPAM microgel particles using static/dynamic light scattering, cross-correlation static/dynamic light scattering, UV-Vis spectroscopy and Rheology techniques. As mentioned in Chapter 1, PNIPAM microgel particles are temperature sensitive, inhomogeneous density particles with core-shell structure having densely crosslinked core and thin shell (~ 30 nm) of dangling polymer chains. Earlier reports showed that in addition to the temperature, PNIPAM microgels also respond to osmotic pressure, where osmotic pressure on PNIPAM microgel was applied by addition of external polymer to the dilute suspension. In this thesis it is shown that PNIPAM microgels undergo compression in dense suspensions due to osmotic pressure from the surrounding particles of its own kind. In dense suspensions, where interparticle separations are of the order of particle diameter, the core-shell structure of the PNIPAM microgel particles is expected to influence their dynamics and shear deformation. Earlier reports have shown that PNIPAM microgel particle dynamics in liquid like ordered suspensions is affected by their core shell structure. In this thesis, it has been shown that, the dynamics and yielding behavior in the dense suspensions are affected by core-shell structure of PNIPAM microgels.

Towards the above studies, monodisperse PNIPAM microgel suspensions of various particle sizes have been synthesized using free radical polymerization by varying the surfactant and crosslinker concentration. Temperature response of the synthesized PNIPAM microgel particles have been characterized by measuring the
diameter of the particle as a function of temperature. Diameter of the PNIPAM microgel is found to decrease with increase in temperature, with sudden collapse at 34°C, which is identified as volume phase transition (VPT). Synthesized suspensions are purified and concentrated. PNIPAM microgel crystals have been prepared by heating the concentrated suspensions to temperatures above VPT followed by its slow cooling (0.5°C/hr). Upon repeated heating and slow cooling suspensions with \( \phi < 1.0 \) showed iridescence under visible light illumination indicating the crystallization of PNIPAM microgel suspensions. When cooled at faster rate, suspensions are found to exhibit glassy state. Details of the synthesis and sample preparation method have been presented in Chapter 2 of this thesis.

In order to study the osmotic compression of PNIPAM microgel particles in dense suspensions, PNIPAM microgel crystals with different volume fractions have been prepared by compressing the suspensions osmotically. Bragg diffraction of these crystals has been recorded using a UV-Vis spectrometer. Upon increasing the osmotic pressure, the Bragg peak is found to exhibit a blue shift. The Bragg peak has been used to determine the interparticle separation. Beyond a certain osmotic pressure, interparticle separation is found to be smaller than the size of PNIPAM microgel particle under swollen state (measured using DLS on dilute suspension). In dense PNIPAM microgel crystals, the observation of interparticle separation being lesser than the particle size measured under dilute conditions, provides direct evidence for shrinking (deswelling) of PNIPAM microgel particles under osmotic compression in the crystalline state. The experimentally observed swelling/ deswelling behavior of the PNIPAM microgel particles with temperature and pressure is understood using Flory-Rehner (FR) theory. Only qualitative agreement has been observed between theory and experiments. Results reported here suggest the need for improvement of the FR theory.
for obtaining quantitative agreement with the experiments. These results are reported in the Chapter 3 of the thesis.

In Chapter 4 of the thesis, results on the dynamics studied across the melting of dense PNIPAM microgel crystals using DLS technique are presented. Melting of the PNIPAM microgel crystals have been achieved by raising the temperature. At higher temperature, microgel particle size hence $\phi$ decreases, causing the melting. In order to identify the melting transition, Bragg peaks from PNIPAM microgel crystals were captured using SLS and the Bragg peak intensity was monitored as a function of temperature. The temperature at which the Bragg peak intensity showed sudden fall, which happen due to loss of the long range order, has been identified as melting transition. The study of dynamics across the melting of PNIPAM microgel crystals revealed the deviation of dynamical criterion at the melting of the PNIPAM microgel crystals ($i.e.$ $D_l/D_S < 0.1$). The deviation from 0.1 is found to be larger in the case of suspensions with higher $\phi$. Careful studies on the behavior of mean square displacement close to the melting transition showed that the particle motion to be subdiffusive at short times. The subdiffusive behavior observed at short times, is understood to arise from the entanglement of the dangling polymer chains between the shells of the neighboring PNIPAM microgel particles and argued to be the reason for the observed deviation ($i.e.$ $D_l/D_S < 0.1$). Hard sphere or charged colloidal systems undergoing freezing have showed the diffusive dynamics at short times. However, we have observed for the first time, the subdiffusive dynamics at short times in PNIPAM microgel liquids undergoing freezing. Since the dynamics at short times is subdiffusive, there exists no proper scale for long time diffusion, hence the inapplicability of dynamical criterion for the melting of PNIPAM microgel crystals (liquids) undergoing melting (freezing).
Chapter 5 report the results on light scattering and rheological behavior of dense PNIPAM microgel glasses carried out using 3D DLS and a rheometer, respectively. At elevated temperature (~ 30°C), PNIPAM microgel glasses have been found to transform into liquids. Upon rapid cooling of the microgel liquids to room temperature, they are found to freeze back into a glassy state. The glass transition temperature of dense PNIPAM microgel suspensions has been identified using 3D DLS. Non-ergodicity parameter, \( f(q, \infty) \) obtained from DLS studies showed a change from finite value to zero across the glass transition. Careful analysis of the mean square displacement of PNIPAM microgel particles at short times revealed subdiffusive behavior, similar to that observed in PNIPAM microgel liquids close to freezing. The observation of subdiffusive dynamics at short times in PNIPAM microgel glasses and in liquids before the glass transition is unique as, there are no reports of the subdiffusive dynamics at short times in hard sphere or charged colloidal glasses. Subdiffusive dynamics observed at short times in PNIPAM microgel glasses is interpreted as due to the overlap / entanglement of dangling polymer chains from shells of neighbouring microgel particles. Upon increasing the temperature, the glass turns into liquid and the subdiffusive behaviour \((\alpha < 1)\) is found to turn into diffusive behavior \((\alpha = 1)\), indicating the disentanglement of the dangling polymer chains at higher temperature. Non-linear rheological measurements on dense PNIPAM microgel glasses showed two step yielding by exhibiting two peaks in loss modulus, \( G'' \), in contrast to the one step yielding observed in hard sphere glasses. The two step yielding in PNIPAM microgel glasses is interpreted as : i) due to disentanglement of the dangling polymer chains giving a first peak at lower strain (first peak in \( G'' \)) and ii) breaking of near neighbour cages giving a second peak in \( G'' \) at large strain. Upon increasing the temperature, when the glass showed melting into super cooled liquid
state, yielding is observed to be single step (single peak in $G''$). The change of yielding from two step at low temperature to single step at higher temperature is understood to be due to the disentanglement of the dangling polymer chains existing between the shells of neighbouring PNIPAM microgel particles. Though two step yielding have been observed in attractive glasses, our experiments constitute first evidence for the observation of two step yielding in soft repulsive glasses.

The major findings of the thesis are as follows,

1. PNIPAM microgel crystals of different volume fractions have been prepared and Bragg diffraction from these crystals has been recorded using UV-Vis spectrometer. The interparticle separation in PNIPAM microgel crystals with $\phi > 0.74$, determined from the Bragg peak position, is found to be smaller than the diameter ($d_h$) of the PNIPAM microgel particles measured under dilute condition.

2. The observation of interparticle separation being lesser than the particle diameter ($d_h$), in dense ($\phi > 0.74$) PNIPAM microgel crystals, constitutes first evidence for deswelling of PNIPAM microgel particles under osmotic compression. PNIPAM microgel particles undergo osmotic compression as osmotic pressure on microgel particles exceeds their Bulk modulus (~ kPa).

3. Flory-Rehner (FR) theory is shown to provide the qualitative understanding for osmotic compression of PNIPAM microgel particles beyond a certain volume fraction.

4. DLS has been employed to study the dynamics across the melting of dense PNIPAM microgel crystals. Careful analysis of mean square displacement showed for the first time that dynamics of PNIPAM microgel particles, close to melting of the crystals, is subdiffusive at short times. The subdiffusive dynamics
at short times is argued to arise due to the entanglements of dangling polymer chains of neighbouring PNIPAM microgel particles. Observation of subdiffusive dynamics at short times implies the deviation of the dynamical criterion for melting of PNIPAM microgel crystals.

5. Upon sudden cooling, dense PNIPAM microgel liquids are shown to freeze into a glassy state. The glass transition temperatures of dense PNIPAM microgel liquids have been identified using 3D DLS technique. Non-ergodicity parameter, $f(q, \infty)$ is shown to show discontinuity across glass transition.

6. The dynamics in dense PNIPAM microgel glasses is shown to be subdiffusive at short times, suggesting the existence of the entanglements of the dangling polymer chains between neighbouring PNIPAM microgel particles in the glassy state as well as in the super cooled liquid state (i.e. above the glass transition temperature).

7. Non-linear rheological measurements on dense PNIPAM microgel glasses have shown that these glasses yield in two steps by exhibiting two peaks in $G''(\omega, \gamma_0)$. It is the first report of two step yielding in a soft repulsive glass. Earlier reports of the two step yielding are in attractive colloidal glasses.

8. Two step yielding observed in dense PNIPAM microgel glasses is argued to arise i) due to breaking of the entanglements of dangling polymer chains between neighbouring particles and ii) due to breaking of topological cages formed by neighbouring particles.

6.2 OUTLOOK FOR THE FUTURE WORK

Present studies have shown that dense PNIPAM microgel suspensions exhibit distinct dynamics and yielding behavior as compared to that of hard sphere or charged colloidal suspensions, which is attributed to the overlap / entanglement of
dangling polymer chains from the shells of neighbouring PNIPAM microgel particles. The presence of entanglements has been evidenced by observation of subdiffusive dynamics at short times. In order to support the idea of entanglement of dangling polymer chains and to provide more evidences about the entanglements, following studies will be carried out.

a) **Dynamics in dense suspensions of charged PNIPAM microgels:** PNIPAM microgel particles are as such a neutral and can be made charged by copolymerization of NIPAM with ionic monomers like acrylic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid. Dynamics in dense suspensions of charged PNIPAM microgels will be studied. Addition of the electric charges is expected to prevent the entanglements of dangling polymer chains due to electrostatic repulsion and hence short time dynamics is expected to be diffusive rather than subdiffusive.

b) **Structural investigations in dense PNIPAM microgel suspensions using SLS:** In dense suspensions overlap / entanglement of dangling polymer chains may result into the local clustering of PNIPAM microgel particles and the formation of networks, which can affect their structure. The structure of dense PNIPAM microgel suspensions will be investigated (from analysis of scattering profiles measured using SLS by assuming PNIPAM microgel as fuzzy spheres), to look at the presence of local clustering and hence the entanglement of dangling polymer chains.

c) **Direct imaging of the dense PNIPAM microgel suspensions using atomic force microscope:** Density of polymer within the core of PNIPAM microgel particles is very high as compared to that of the shell. Therefore, in imaging of microgel particles in dilute suspensions (where there is no overlap of the
shells), only core of the microgel becomes apparent and shell stays invisible. On the other hand, overlap of the shells should lead to increase in polymer density within shells and make them visible. Typical thickness of the shells is ~ 20-30 nm, which can be resolved using atomic force microscope (AFM). Dense suspensions of PNIPAM microgel particles will be imaged using AFM with liquid cell to look at the overlap of the polymer chains via rise in the polymer density of the shells.

d) Immobilization of the PNIPAM microgel crystals in a gel matrix: Ordered crystalline arrays of PNIPAM microgel particles serve as sensors for temperature, pH, various chemicals etc. But the PNIPAM microgel crystals are fragile and lose their ordering against even smaller mechanical shocks, hence non portable. PNIPAM microgel crystals will be immobilized within a gel matrix, in order to make them portable.