Microstructure of Colloid-Polymer Mixtures Containing Charged Colloidal Disks and Weakly-Adsorbing Polymers

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Abstract

Structural arrest in an aging colloid-polymer mixture of charged colloidal disks and weakly interacting polymers is primarily governed by the spatial arrangement of microstructural domains in the system. Here we present a detailed ultra-small angle x-ray scattering (USAXS) study of the polymer induced microstructural changes occurring in systems containing laponite[®] and poly(ethylene oxide) (PEO). Laponite[®] suspensions are known to transition from a homogeneous fluid to an arrested phase as a function of time. USAXS results show that when polymer chains are added to this colloidal system, the microstructural changes are found to depend on (i) polymer-colloid size ratio, (ii) particle and polymer concentration. Large length scale structures (300-1000 nm) of non-uniformly varying size appear with increasing concentration of high molecular weight PEO ($R_g/R \sim 2.4$). However with shorter PEO chains ($R_g/R \sim 0.5$), we observe the formation of intermediary structures with a characteristic length scale of 50-60 nm. With increasing particle concentration, we observe a more compact structure for the high molecular weight PEO and no signature of a percolating network in the case of the low molecular PEO. We believe that these results add to our understanding of the complex aging behavior of clay-polymer systems.

Keywords: nanoparticle; USAXS; clay

Introduction

Particles in colloidal dispersions self-assemble under different conditions to form disordered, structurally arrested phases like colloidal glasses and gels. It is, thus of importance to understand the formation mechanism and the characteristic nature of these states as it helps in tuning material properties for a specific technological application and in determining the shelf life or long term stability of the material itself. Colloidal glasses and gels can form when the particle volume fraction is increased or when salts, surfactants or polymers are added to the system to modify interactions between particles. Hard-sphere colloidal systems are often used as simple models to understand the physics behind the formation of glasses and gels. For hard-sphere colloids at concentrations close to the fluid-glass transition ($\phi_c \sim 0.58$), the system transitions from a homogeneous liquid phase to an arrested glassy phase primarily due to increasing excluded volume effects[1, 2]. On the other hand, fluid-gel transitions can occur along a wider range of concentrations by increasing the range and strength of attractions between particles in the system. One way to achieve this is by adding salts to a charged repulsive colloidal system. The addition of salts increases attractions between particles by screening the electrostatic repulsive interactions. Fractal-like aggregates begin to form, and under certain conditions the fractal structure percolates to form a space-filling gel like network [3]. Colloidal gels can also form by the addition of non-adsorbing polymers to a hard sphere system, which causes a depletion attraction between particles. Recent studies have shown that the formation of this arrested phase is due to increasing strength of short-range attractions and can be precisely controlled by simply changing the length and the concentration of polymer chains in the

1 system[4, 5]. Experiments have also shown that the addition of non-adsorbing polymers to a
2 glassy colloidal system can shift the effective fluid-glass transition to a higher volume fraction,
3 thus making it feasible to work with a fluid phase at higher particle loadings[6]. Understanding
4 the formation of these states in suspensions containing aspherical colloids is however not
5 straightforward, as shape anisotropy and physical aging effects contribute to the existing
6 complexities in the problem.

7 Laponite[®] is a model system that is often used to study the structure, phase behavior and
8 dynamics of colloidal disks, as it exhibits a very rich physical behavior. Laponite[®] is a charged
9 synthetic clay (~25nm wide, ~1nm thick) with an empirical formula of
10 $\text{Na}^{+}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{22}(\text{OH})_4]^{-0.7}$. The particles carry a negatively-charged face which is
11 counterbalanced with the Na^{+} ions present in between layers and a pH-governed charge
12 distribution along the edges due to the formation of surface charges during hydration and
13 swelling. Extensive studies have been conducted using techniques such as rheology[7], light,
14 neutron and x-ray scattering experiments[8, 9] to probe the structure and phase behavior of
15 aqueous laponite[®] dispersions at different particle concentration, c_l , and salt concentrations.
16 Bonn and co-workers used light scattering and conductivity experiments to classify dispersions
17 of laponite[®] into three different arrested states; (i) Gels ($c_l < 1.5\text{wt}\%$), (ii) Repulsive glasses ($c_l >$
18 $1.5\text{wt}\%$) and (iii) Attractive glasses ($c_l < 1.5\text{wt}\%$, high salt conc.), based on the evolution of the
19 relaxation time parameters[10].

20 Colloidal glasses and gels of laponite[®] both exhibit solid-like rheological behavior, and
21 there are few experimental methods to distinguish between these two different arrested states. In
22 comparison with spherical colloids, the formation of glassy phases in laponite[®] occurs at a much
23 lower volume fraction of ~ 0.01 . The formation of colloidal glasses in most cases is driven by

1 dominant electrostatic repulsions between particles, and in other cases it is driven by weak inter-
2 particle attractions. Many refer to the latter condition as an “attractive glass,” as long lived
3 attractive bonds between particles exist in this structurally arrested phase, and the former state as
4 “Wigner” glasses, although there is still a considerable amount of debate on whether these are
5 gels or glasses[11-13]. Similar to the hard sphere system, colloidal gels in laponite[®] form when
6 clusters begin to span the volume to form a space-filling network. In rheological experiments,
7 glassy systems follow the framework of the SGR model[14] and gels can be identified by using
8 the Winter-Chambon’s criterion[15] where a single iso-frequency $\tan \delta$ point can be
9 correlated with the fractal dimensions in the system. Neutron and x-ray scattering measurements
10 are also used to identify these structures in the colloidal system. Colloidal glasses are
11 homogeneous at larger length scales and correlations are restricted to the interparticle distances,
12 whereas for the colloidal gel, correlations exist at larger distances with the structure factor
13 profiles showing fluctuations at low values of the scattering vector q [11].

14 Laponite[®] gels and glasses have been studied extensively by several groups. However,
15 there is still a considerable amount of debate on whether these systems are really gels or glasses.
16 Several studies in the literature have reported the phase diagram of laponite[®] as a function of
17 both particle and salt concentration. There seems to be a large consensus on the observation that
18 laponite[®] particles phase separate at concentrations below 1% and when the salt concentration is
19 above 20mM[16]. It is also known that for concentrations between 1% and 2%, the suspensions
20 largely evolve to form colloidal gels. However, the final state and microstructure in systems at
21 and above 2% is largely unclear. Small-angle x-ray scattering experiments conducted by Ruzicka
22 and co-workers have found that systems above a concentration of 2% form glassy phases where
23 particles remain frozen and disconnected in the system[17]. Interestingly, results from a recent

1 study by the same group have indicated that while these exists as repulsive glasses during the
2 early aging period, the same system exhibited a repulsive glass – attractive glass transition due to
3 increasing attractions as aging proceeds in the system[18]. On the contrary, studies conducted by
4 Mongondry and Joshi have shown that the particles exist as colloidal gels where attractive bonds
5 do exist between particles[19, 20]. Comprehensive set of experiments conducted by Joshi and
6 co-workers have shown that structural arrest in laponite[®] systems is not driven just by repulsions
7 but also by attractive interactions between particles [20].

8 The kinetics of structural arrest in laponite[®] can be modified by the addition of salts to
9 the system. The addition of salts results in the screening of the electrostatic repulsions thereby
10 increasing the van der Waals attraction between particles. The rate of particle aggregation under
11 different salt conditions has been extensively studied by many groups. At very high salt
12 concentrations and at low concentrations of laponite[®], the particles begin to aggregate and phase
13 separate under the influence of gravity. Another way of modifying the interactions between the
14 particles is by adding polymers to the system. Several techniques like NMR, reflectometry, x-ray
15 and neutron scattering have been used to study the interaction of polymers with colloidal
16 surfaces[21-24]. Polymers are expected to contribute to a variety of interactions depending on
17 the nature of the polymer and on the way it interacts with the surfaces of a colloidal particle.
18 While non-adsorbing polymers trigger attractive interactions based on thermodynamic effects,
19 adsorbing polymers can contribute to both steric repulsions and, if chains are sufficiently long, a
20 bridging attraction between particles. Adding short polymer chains to a laponite[®] system is
21 known to slow down the aggregation process due to steric effects, and adding longer polymer
22 chains leads to the formation of large-scale clusters and space-filling gels in the system[25, 26].

Experiments using rheology were previously conducted to study the effect of chain length and concentration of polymers on the macroscopic properties of a laponite[®]-PEO system. Results from rheological experiments conducted for systems containing 2% laponite[®] with PEO have shown that two different behaviors exist when the polymer chain length is allowed to vary; (i) retardation in gelation kinetics for molecular weights below 83 kg/mol due to steric effects and (ii) accelerated gelation kinetics for molecular weights above 83 kg/mol because of polymer bridging[27, 28]. Studies have also shown that by changing the concentration of small PEO chains, the system transitions through a re-entrant behavior because of increasing depletion attractions in the system. More recently our group has recently studied the effects of varying the concentration of PEO on the macroscopic properties of the system[29, 30].

In this work, we have employed ultra-small angle x-ray scattering (USAXS) to investigate the microstructure of laponite[®] systems at particle concentrations of 2-3%, with poly(ethylene oxide), a weakly adsorbing polymer. In order to systematically examine microstructural changes, we consider two different polymer-colloid size ratios to highlight the effects of long ($R_g/R \sim 2.4$) and short ($R_g/R \sim 0.5$) polymer chains on the formation of structures in the system, where R_g is the radius of gyration of the PEO chains and R is the radius of the laponite[®] disc (~ 25 nm). In both cases, the concentration of PEO, c_p , was allowed to vary between 0.25% and 2.5% (w/w). For the longer PEO chain, this allows us to look at variations in the structure in the concentrated polymer regime. On the contrary, for the shorter PEO chains the range spans regions between dilute and semi-dilute polymer regimes.

1 **Materials and Methods**

2 Laponite[®] RD was procured from Southern Clay Products (Gonzales, TX, USA) and poly
3 (ethylene) oxide (PEO) with number-average molecular weight, M_w , of 20 and 300 kg mol⁻¹ were
4 purchased from Sigma Aldrich and used without any further purification.

5 **Sample Preparation**

6 Laponite[®] dispersions were first prepared by adding a calculated amount of clay to de-
7 ionized Millipore water with its pH adjusted to 10 using sodium hydroxide (NaOH) to ensure
8 stability against dissolution. A T25 UltraTurrax homogenizer was used for about 1 minute to
9 disperse particles thoroughly. The solutions were then agitated for 20 minutes and filtered
10 through a 0.45µm filter to remove large aggregates. PEO was then added to obtain the desired
11 concentration. The samples were stirred until the polymer completely dissolved. The samples
12 were then transferred immediately into a 1 mm capillary tube and stored at 25°C to allow them to
13 spontaneously age with time. The aging time is considered to be zero at the time the samples are
14 transferred to the capillary tube.

15 **Ultra-small angle x-ray scattering (USAXS)**

16 Ultra-small angle x-ray scattering measurements were conducted at the 9-ID-C beamline
17 of the Advanced Photon Source (APS) at Argonne National Laboratory. Samples for the USAXS
18 experiments were prepared by loading a calculated amount of dispersion from the samples that
19 were prepared as described in the earlier section, into a 1mm capillary tube. The capillary tubes
20 were then sealed and the mixtures were allowed to spontaneously age with time. The scattered
21 intensities were recorded over a broad range of q from $\sim 10^{-4} \text{Å}^{-1}$ to 10^{-1}Å^{-1} , and the background

scattering of pure water was subtracted. The experiment enables us to explore the presence of micron-sized domains at low q and the presence of individual disks at higher q .

Table 1 lists the experimental system used for this study. $c^* = 3M_w/4\pi R_g^3 N_A$ is the polymer overlap concentration. The amount of polymer needed to saturate a laponite[®] particle surface exhibits a weak power-law relationship with molecular weight ($\Gamma \sim M_w^{0.05}$). The concentration of PEO bound to the surfaces of a laponite[®] particle, estimated using NMR relaxation experiments, was found to be ~0.18%. This corresponds to a coverage of 0.4 mg/m², approximately. Additionally, laponite[®] has a specific surface area of 900m²/g. Therefore, for every gram of laponite[®] the amount of PEO at saturation can be calculated as (900 m²/g) x (adsorbed amount at saturation) x (1g/1000 mg). The concentration of PEO needed to saturate or bind to all available particle surfaces (c_{sat}) was estimated to be ~0.75% for systems containing 2% laponite[®] and 1.08% for systems with 3% laponite[®]. This is strictly based on the assumption that all adsorption surfaces are available to the polymer and that there is a perfectly monodisperse particle size distribution.

Table 1 : Experimental system used in this study. Polymer overlap concentration, c^* , size ratio R_g/R and the particle surface saturation concentration, c_{sat}

PEO M_w kg/mol	Critical overlap concentration, c^* (%)	Radius of gyration, R_g (nm)	Polymer-colloid size ratio R_g/R	Particle Saturation Concentration, c_{sat} (%)	
				2% laponite [®] ($\phi_c \sim 0.0075$)	3% laponite [®] ($\phi_c \sim 0.011$)
20	2.93	6.67	0.533	0.75	1.08
300	0.43	30.34	2.43		

Results and Discussion

USAXS experiments were carried out on systems containing laponite[®] RD with and without poly(ethylene oxide). The data reduction and analysis was done using the standard analysis macros that are available using the IGOR software platform[31].

Scattering from laponite[®] systems without PEO

Figure 1: USAXS spectra of neat laponite[®] systems at a particle concentration of 2% and 3%. Spectra show a low- q upturn with increasing laponite[®] particle concentration

Figure 1 shows the scattering profiles of 2% and 3% laponite[®] dispersions along with the form factor of a single disk with radius 125Å and thickness of 10Å. The form factor a disk shaped particle is as given below:

$$P(Q) = \int_0^{\pi/2} \sin\theta d\theta (V_p \Delta\rho)^2 \left\{ \frac{\sin[QH_p \cos\theta/2]}{QH_p \cos\theta/2} * \frac{2J_1[QR_p \sin\theta]}{QR_p \sin\theta} \right\}^2 \quad (1)$$

where R_p and H_p are the radius and the thickness of the particle respectively, V_p is the volume of one particle and $\Delta\rho$ is the difference in the scattering length densities of laponite[®] and the solvent, which in this case is water. The x-ray scattering length density of laponite[®] was calculated according the composition of the grade of laponite[®] and was estimated to be $2.25 \times 10^{-5} \text{ \AA}^{-2}$. The x-ray scattering length density of water $\rho_w = 9.46 \times 10^{-6} \text{ \AA}^{-2}$.

In order to estimate the particle size, the scattering from a 1% dilute suspension of laponite[®] was recorded. A Guinier analysis (Figure S1, Supplementary Information) was done to estimate the characteristic size and the particle radius was found to be ca. $12.07 \pm 0.25 \text{ nm}$. Generally, for a homogeneous suspension of single disks, the data in the Porod range, e.g. higher q values, ($q > 0.02 \text{ \AA}^{-1}$) typically exhibits a q^{-2} dependency. However, for the concentrations of laponite[®] used in this work, the value of slope was found to be less than -2. This is typically indicative of the presence of some polydispersity in the system. Along the intermediate regions of q ($0.002 \text{ \AA}^{-1} < q < 0.08 \text{ \AA}^{-1}$), we observe a plateau in the scattering intensity for both the 2% and the 3% laponite[®] system. At lower q values ($q < 0.002 \text{ \AA}^{-1}$), we observe an upturn in the intensity for the more concentrated laponite[®] suspension. A similar upturn in the low- q region was observed via USANS in neat laponite[®] suspensions at 6 wt% by Bhatia and co-workers[32]. Such low- q upturns are a characteristic feature of fractals or dense aggregates in the system and are commonly seen in colloidal gels.

Scattering of laponite[®] systems with High- M_w PEO

The addition of a high molecular weight PEO results in the formation of a gel-like network primarily due to bridging effects which begin to play an important role in gelation when the size of the polymer chains is close to the interparticle distance. There are a few studies in the

1 literature that discuss the phase behavior of laponite[®] with 300 kg/mol PEO[33] and the dynamic
2 responses of these systems to the application of different magnitudes of shear[34]. In a recent
3 work by Prasad and co-workers, static and dynamic light scattering experiments were conducted
4 to classify the phase behavior laponite[®]-PEO systems with different concentrations of laponite[®]
5 and PEO. They observed different types of behavior in these systems; (i) at concentrations below
6 the particle saturation, reversible shake gels formed on the application of a high amount of shear,
7 (ii) some systems shear thickened at high deformation rates and (iii) viscous samples remained
8 fluid-like and showed no shear thickening or shake gel like behavior[35]. All these studies
9 suggest that it is possible to control the gelation kinetics by effectively tuning the structure in the
10 system but lack a detailed analysis of the formation of structures over a wide range of polymer
11 concentrations in the system. So the discussion herein will aim to address these gaps by
12 analyzing the structures along a broader range of colloid-polymer compositions.

Figure 2 : USAXS spectra of suspensions with 2% laponite[®] and 300 kg/mol PEO. The scattering profiles have been vertically shifted for clarity. The dotted profiles (···) plotted against each spectrum is the scattering from the 2% laponite[®] without PEO and is shown for comparison.

Figure 2 shows the scattering profiles of suspensions with 2% laponite[®] and 300 kg/mol PEO. For comparison, the scattering spectra of 2% laponite[®] has been shown alongside each system's scattering profile. At low polymer concentrations, the scattered intensity profiles along the higher q region ($q > 0.02\text{\AA}^{-1}$) do not change by a large extent, which implies that the structural arrangement at the particle length scale is not altered greatly with increasing PEO content. The slope of the intensity profile along the higher q regions is $\sim -1.79 \pm 0.04$ (Figure S2(C)). This is less than what is expected for monodisperse disks, -2, which could indicate either

polydispersity or a contribution from PEO chains, even though the laponite[®] disks scatter more strongly than the PEO chains. As we approach the lower q region, the variations in the magnitudes of the scattering intensities from the 2% laponite system are larger and can be seen from the large error bars along this region. In laponite[®]-PEO systems at higher polymer concentrations, where $c_p/c^* > 1.5$, we observe that the magnitude of scattering is greater even at smaller length scales. Though the scattering spectra across the range of polymer concentrations considered for this system are qualitatively similar, the smaller scattering magnitude observed for the system at $c_p/c^* \sim 5.23$ is difficult to understand. However, multiple measurements were performed for on this sample, and the data were found to be reproducible. At higher polymer concentrations, it is expected that there will be some contribution from the scattering of the entangled polymer chains in the system. In order to verify this, we examined the scattering of polymer solutions both at the lowest and the highest concentration with water at pH 10 as the solvent at 25°C (Figure S3). The USAXS spectra obtained from these solutions were then analyzed using the correlation length model and the results show that the polymer chains in the system behave as though in a poor solvent.

For regions of $q < 0.02\text{\AA}^{-1}$ we observe that the scattering intensities are no longer flat, and they begin to exhibit a power law dependence with q . Small upturns in the intermediate q regions indicate the presence of structures at length scales greater than $\sim 300\text{\AA}$. As we increase the concentration of PEO in the system, we observe a non-monotonic variation in the slopes of the low- q upturn in the regions of $q < 0.001\text{\AA}^{-1}$. Typically, the structure in a colloidal gel is driven by the rate of aggregation in the system. As the strength of attraction increases, a fractal network begins to grow until it spans the entire volume of the system to form a gel that sustains its own weight. Depending on the mechanism and the rate of aggregation, fractals can either have an

open or a denser and closely packed structure. Particles interacting within a volume can either have fractal surfaces or form a mass fractal through clustering and the power law behavior, $I(q) = Aq^{-x}$, is used to identify and describe these structures in the system. Here, $-x$ is the power law slope along the low- q region. In the case of the structure of a mass fractal, the mass M of the structure of a certain dimension d_f scales as; i.e. $M \propto r^{d_f}$, where d_f is the scaling or power law exponent that describes the nature of these fractals and is equal to the fitting parameter x . The values of the exponent d_f ranges from 1 for weakly linked clusters to 3 for dense structures. On the other hand, surface fractals are compact with a surface area, SA , which scales as $SA \propto r^{d_s}$. The scaling exponent d_s is the surface fractal dimension and values ranges from 2 for smooth surfaces and 3 for highly folded or convoluted surfaces in the system. In the case of surface fractals, the power law exponent x is now equal to $6-d_s$ and thus the exponent of $I(q)$ ranges from 3 to 4.

To analyze and describe the scattering in the q range between $0.001\text{\AA}^{-1}$ and $0.0001\text{\AA}^{-1}$ we fit the curves with the power law $\sim Aq^{-x}$. The curves showing the fits are presented in Figure S4 (Supplementary Information) and the values of the power law slopes of these fits are shown in Figure 3. At an aging time of ~ 60 days (i.e within the full aging phase), 2% laponite[®] system does not exhibit a power law behavior at low- q ; instead, the scattering indicates that it is homogeneous at large length scales. However, with increasing concentration of 300 kg/mol PEO the exponents vary non-uniformly between 2.25 and 3.5. This non-uniform variation in the scattering along the low- q region indicates that the arrangement of the PEO chains and its interactions with the complexes play a very important role in **determining the spatial heterogeneity in the system at larger length scales.**

Figure 3 : Power law slopes obtained by fitting the low- q scattering region of the USAXS spectra of systems with 2% laponite[®] and various concentrations (c_p/c^*) of 300 kg/mol PEO, with Aq^{-x} . The horizontal dashed line along $y=0$ signifies the absence of a divergence at low- q . The fits to the spectra are shown in Figure S4 in the Supplementary Information.

The fractal structure is known to differ with the mechanism of aggregation taking place within the system. In the case of diffusion limited cluster aggregation (DLCA), particles while randomly diffusing through a medium collide and form aggregates or clusters of a bigger size. Such a mechanism has been observed in mixtures of PMMA-polystyrene where the fractal dimension is approx. 1.7 ± 0.2 [36, 37]. On the other hand, for a reaction limited cluster aggregation (RLCA) mechanism, the aggregation rate is governed by probability of clusters or particles forming strong long-living attractive bonds after collision. This type of aggregation is seen in latex systems under various salt conditions [38-40] and the fractal structure is more compact with a dimension of approx. 2.1. Now when we compare the values corresponding to such classical mechanisms with the laponite[®]-PEO system, it is obvious that the microstructural dimensions cannot be described entirely by either of these two aggregation mechanisms.

The variations in the scattering profiles of suspensions containing a higher particle fraction of $\phi_c \sim 0.011$ were also examined. Figure 4 shows the USAXS spectra of 3% laponite[®] –

1 300 kg/mol PEO systems. Suspensions containing a higher particle concentration transition to an
2 arrested phase at shorter timescales. In the case of the 3% laponite[®] system, we observe a low- q
3 dependence for all compositions suggesting the existence of a network-like structure. With the
4 addition of PEO to this system, changes in the structure are observed through the variations in
5 this low- q dependence of the scattering intensities. A higher scattering intensity in systems with
6 PEO concentrations (c_p/c^*) between 2.5 and 5 is expected as we now have larger number of
7 scattering entities and as the concentration of PEO increases we expect that the number of
8 entanglements in the polymers is more. We analyze the low- q dependence by fitting the USAXS
9 spectra in the region of $q < 0.001 \text{ \AA}^{-1}$ with the power law $\sim Aq^{-x}$. The results of these fits are
10 presented in Figure 5 and the scattering profiles showing these fits are presented in Figure S5. As
11 shown in Figure 5, the variations in the power law exponents for systems with different PEO
12 concentrations is non-uniform and falls within a range of 2.2 and 3.8.

1

2

3 **Figure 4:** USAXS spectra of systems with 3% laponite[®] and various concentrations of the 300 kg/mol PEO. The
 4 scattering profiles have been vertically shifted for clarity. The dotted profiles (***) plotted against each spectrum is
 5 the scattering from the 3% laponite[®] without PEO and is shown for comparison.

6

7 **Figure 5:** Power law slopes obtained by fitting the low- q scattering region of the USAXS spectra of systems with
 8 3% laponite[®] and various concentrations (c_p/c^*) of 300 kg/mol PEO, with Aq^{-x} . The horizontal dashed line along $y=0$
 9 signifies the absence of a divergence at low- q . The fits to the spectra are shown in Figure S5 in the Supplementary
 10 Information.

The distinct feature in these scattering profiles is the strong q dependence in the low- q region. This type of scattering has been previously observed in laponite[®] PEO mixtures containing 3% laponite[®] and 2% PEO with molecular weights 100 kg/mol, 300 kg/mol and 600 kg/mol. In this work, SANS and USANS experiments showed that the low- q scattering scaled as $q^{-1.55}$ and this confirmed the presence of large-scale open structures where the polymer coated particles are tethered together to form a sponge-like network[33]. However, as we can see from the power law fits, the presence of free polymer chains does have some influence on the microstructure in the system.

Figures 3 and 5 indicate that several laponite[®]-PEO systems exhibit an excess scattering with power law exponents varying between -3 and -4. These values are indicative of surface scattering where a power law value of -3 corresponds to the scattering from very rough surfaces. On the other hand, a value of -4 is often described by a Porod like scattering from smooth objects. A similar q -dependence was observed in hard-sphere colloidal silica systems with a non-adsorbing polymer by Zukoski and co-workers. This unusually high q -dependence was attributed to the formation of dense, polydisperse aggregates with rough surfaces. Using various physical models, they were able to determine that the aggregates were 5-8 particle diameters in size[41].

With respect to the systems considered in this work, we observe large scale fluctuations from $\sim 0.002\text{\AA}^{-1}$ to $\sim 10^{-4}\text{\AA}^{-1}$. In real space, this corresponds to length scales between $0.31\mu\text{m}$ ($\sim 12D_p$) to $6.3\mu\text{m}$ ($\sim 250D_p$). The formation of large-scale structures in laponite[®]-PEO was previously investigated in systems containing 3% laponite[®] by Schmidt and co-workers. Cryo-TEM and SEM imaging of their laponite[®]-PEO systems showed the existence of clay-rich and clay poor regions in the systems[33]. This heterogenous distribution in the structure can be described by the Debye-Bueche model which is given by the following equation[42]:

$$I(q) \sim \frac{I_0}{(1 + q^2 \xi_v^2)^2} \quad (2)$$

where I_0 is the average mass which accounts for the differences in the number densities between the dense aggregates and the dilute spaces within the network. ξ_v is a correlation length that describes the distance between the dilute regions surrounding the dense aggregates in the system. In order to obtain values of the parameters I_0 and ξ_v , we rearrange the above equation to obtain an expression of the form $y = mx + c$ (shown in the Supplementary Information). We plot $I(q)^{-1/2}$ vs $(qD)^2$ and make a linear least square fit over a small range of q where a linearity is observed. Here, the observed slope $m = (\xi_v/D)^2 * I_0^{-1/2}$ and the intercept c is $I_0^{-1/2}$.

Figure 6 : Debye Bueche analysis for systems with laponite[®] and 300 kg/mol PEO that exhibit a low- q power law scattering with an exponent between 3.1 and 4. Values of the heterogeneity correlation length (ξ_v) were obtained by using a linear least square fit over regions of $(qD) < 0.245$. The Debye Bueche plots are shown in the Supplementary Information (Figure S6).

Figure 6 shows the changes in the heterogeneity parameter, ξ_v , for systems exhibiting a power law exponent greater than 3. For the series of samples containing 2% laponite[®], the parameter ξ_v were found to vary minimally with changes in the PEO concentration, and the

values were typically between $0.75\mu\text{m}$ ($\sim 30D_p$) and $1\mu\text{m}$ ($\sim 40D_p$). On the other hand, for the series of samples containing 3% laponite[®], this correlation length increases a little as the interparticle distance is smaller than when compared to the 2% laponite[®] system, and polymer bridging and any subsequent increase in the attractions results in the formation of more compact or tighter aggregates in the system. The results obtained from the Debye-Bueche analysis and the power law analysis (as shown in Figure 3 and Figure 5) thus clearly indicate that long polymer chains affect the spatial arrangement of particles within the system.

Scattering of laponite[®] with Low- M_w PEO

The addition of a lower molecular weight PEO changes the macroscopic properties of the laponite system in a different manner. In a recently published work from our group, we examined the rheological behavior of mixtures containing 2% laponite and PEO of molecular weights varying between 4.6 kg/mol to 35 kg/mol [30]. In addition to the typical re-entrant behavior observed when the polymer is dilute, we also see another onset of re-stabilization very close to the polymer overlap regime. We attributed these effects to polymer induced changes in the cluster or complex arrangements in the system. As the concentration of polymer increases in the bulk medium, polymer-particle and polymer-polymer interactions begin to play a more important role in altering the mechanisms of structural arrest. Additionally in another study, we used x-ray photon correlation spectroscopy (XPCS) to understand the dynamics in these systems at the same aging period [43]. Suspensions with 2% laponite[®] and various concentrations of PEO (M_w : 20-55kg/mol) were found to exhibit different dynamics depending on the polymer concentration in the system. As mentioned earlier, in addition to the re-entrant like behavior along the dilute polymer region, suspensions with intermediate concentration of PEO exhibited faster dynamics relative to a neat laponite[®] suspension. A third dynamic region was observed

1 close to the polymer overlap region and the onset into this regime was found to shift to lower
2 concentrations with increasing polymer molecular weight. The relaxations in the systems along
3 this region were found to remain unchanged with increasing polymer chain length. All these
4 observations suggest that the pathway to a structurally arrested phase is influenced by the nature
5 of the microstructures present in this system. It is, therefore, very critical to understand the type
6 of microstructure leading to such a behavior in the dynamics of the colloid-polymer system.

7 Figures 7 - 10 show the USAXS spectra of the colloidal system with low molecular
8 weight PEO. The polymer to colloid size ratio in this case is nearly 0.5. In contrast with the
9 systems containing long PEO chains, the USAXS spectra do not show any characteristic excess
10 scattering in the lower q -regions which suggests that there are no large domains or structures in
11 these systems. The intensity profile is flat along the intermediate ranges of q ($0.002\text{\AA}^{-1} - 0.02\text{\AA}^{-1}$)
12 and the slopes along the regions of q beyond $0.02\text{\AA}^{-1}$ range from -1.7 to -1.95 (Figure S2(A)),
13 which are close to the high- q scattering expected for disk-like objects. As above, the slope is a
14 little different than -2, but we expect these differences to occur because of two contributing
15 factors; (i) there may be some polydispersity in the system and (ii) polymer chains also
16 contribute to the scattering.

Figure 7 : USAXS spectra of suspensions containing 2% laponite[®] with varying concentrations of 20 kg/mol PEO. The scattered intensity profiles have been vertically shifted for clarity. The dotted profiles (***) plotted against each spectrum is the scattering from the 2% laponite[®] without PEO and is shown for comparison.

With the addition of a small amount of PEO in the system, we do not observe any remarkable change in the USAXS spectra. However, at a concentration of $c_p/c^* = 0.17$, there is an appearance of a weak correlation peak at a q -value of $0.001\text{\AA}^{-1}$ (as can be seen in Figure S7, Supplementary Information). Correlation peaks occur as a result of the formation of complexes in the system. In this case, this is expected to occur as interparticle distances decrease due to increasing local attractions in the system. At intermediate concentrations of PEO, we observe a scattering profile that is qualitatively different than what is observed in systems with smaller

amounts of PEO. For concentrations beyond 0.34, the profiles show the existence of two Guinier regions and one Porod region. Such features are often seen when the scattering arises either from non-spherical objects in the system or from two different populations of the same kind. The description of scattering from aspherical objects has been elaborately discussed by Hammouda, and a generalized model has been proposed[44].

According to the generalized Guinier Porod (GP) model:

$$I(q) = \frac{G_2}{q^{s_2}} \exp\left(\frac{-q^2 R_{g2}^2}{3 - s_2}\right) \quad q \leq q_2 \quad (3)$$

$$I(q) = \frac{G_1}{q^{s_1}} \exp\left(\frac{-q^2 R_{g1}^2}{3 - s_1}\right) \quad q_2 \leq q \leq q_1 \quad (4)$$

$$I(q) = \frac{D}{q^d} \quad q \geq q_1 \quad (5)$$

where s_1 and s_2 are dimensionality parameters; G_1 , G_2 and D are the scaling factors for the Guinier and the Porod regions respectively; and R_{g1} and R_{g2} describe the dimensions of the object. q_1 and q_2 are cut off values marking the transition between the three regions in the spectra and are calculated internally using the conditions of continuity. For spherical systems both s_1 and s_2 are 0 owing to its shape symmetry, and for cylindrical objects, $s_2 = 0$ and $s_1 = 1$. The Porod exponent usually describes the nature of the scattering inhomogeneities in the system; a Porod exponent of 2 represents the scattering from Gaussian polymer chains or can also represent the scattering from platelets or disks. An exponent of 5/3 represents the scattering from swollen polymer chains in a good solvent.

The scattering spectra (for $q > 0.003 \text{ \AA}^{-1}$) of systems with 2% laponite[®] and intermediate concentrations of PEO were successfully fit with the GP model using the non-linear least square

fitting method and is shown in Figure 8. Table 2 lists the values of the parameters obtained by fitting the data with the generalized GP model. For all of the systems that were examined using this model, the dimensionality parameter s_I was neither 1 nor 0 indicating that the scattering objects were of some intermediary structure. Assuming the extreme limit of this being a cylinder, as a first guess we estimate the radius R as $R_{gl} \cdot 2^{1/2}$ and the length L as $12^{1/2} / (R_{g2}^2 - R_{gl}^2)^{1/2}$.

Figure 8 : USAXS spectra of 2% laponite[®] systems with 20 kg/mol PEO at different concentrations ($c_p/c^* \sim 0.4$ -0.8). Open symbols indicate scattering data, while solid lines indicate the fit of the data with the Guinier Porod model.

Table 2 : Best fit parameters obtained by fitting data to the Guinier-Porod model.

laponite [®] - PEO (c_p/c^*)	s_I	R_{gl} (nm)	R (nm)	R_{g2} (nm)	L (nm)
0.43	0.78 ± 0.006	3.13 ± 0.034	4.42 ± 0.07	17.53 ± 0.10	59.66
0.51	0.75 ± 0.006	3.22 ± 0.035	4.55 ± 0.07	18.96 ± 0.12	64.73
0.63	0.64 ± 0.0065	3.67 ± 0.038	5.19 ± 0.08	18.10 ± 0.03	61.40
0.68	0.62 ± 0.0069	3.79 ± 0.039	5.36 ± 0.08	18.36 ± 0.18	62.24
0.77	0.47 ± 0.008	4.61 ± 0.048	6.52 ± 0.10	16.42 ± 0.22	53.88

1 The results from fitting the spectra to the GP model indicate very small changes in the
2 microstructure at length scales beyond the particle size. Considering the fact that the scattering
3 objects are not cylindrical but some intermediate structures between a spherical and a cylindrical
4 object we make an attempt at quantifying these structures using the Elliptical cylindrical
5 model[45].

6 **Elliptical Cylinder (EC) Model**

7 The Elliptical Cylinder (EC) model considers the scattering to be originating from a
8 cylindrical object with an elliptical cross section[46]. In this model, an elliptical cylinder of
9 length L has a minor radius and a major radius and the ellipticity parameter (ν) which is the ratio
10 of the major over the minor radius is always greater than 1. The scattering spectra of the same set
11 of systems that were analyzed using the generalized GP model were successfully fit with the EC
12 model (Figure 9) and the reduced chi-squared (χ^2) parameter was found to be less than 3.8.
13 Results of the fit of this model to the spectra are shown in Table 3.

Figure 9 : (a) USAXS spectra of 2% laponite[®] systems with 20kg/mol PEO at different concentrations ($c_p/c^* \sim 0.4$ -0.8). Open symbols indicate scattering data, while solid lines indicate the fit of the data with the Elliptical Cylinder model and (b) schematic representation of the intermediate structure seen in these systems.

Table 3 : Best-fit parameters obtained by fitting data to the Elliptical Cylinder Model

20 kg/mol PEO (c_p/c^*)	Minor Radius (nm)	Ellipticity Parameter, ν $\sim \frac{\text{Major Radius}}{\text{Minor Radius}}$	Major Radius (nm)	Length (nm)	Bkg (cm^{-1})	Reduced χ^2
0.43	0.75 ± 0.002	5.76 ± 0.034	4.32	59.06 ± 0.23	0.21 ± 0.001	2.77
0.51	0.709 ± 0.002	6.09 ± 0.036	4.32	60.69 ± 0.25	0.21 ± 0.001	2.68
0.63	0.742 ± 0.002	5.80 ± 0.03	4.30	52.31 ± 0.21	0.22 ± 0.001	3.09
0.68	0.744 ± 0.002	5.49 ± 0.03	4.08	53.49 ± 0.213	0.19 ± 0.001	3.72

1 The results from fitting the spectra to the EC model suggest that these are fairly
2 consistent with the results derived from fitting the spectra to the GP model. The major and the
3 minor radii do not vary greatly with increasing PEO concentration. The major radius was found
4 to be ca. 4nm for all the systems. However, we observe that the lengths of these objects vary
5 non-uniformly between 52nm and 61nm.

6 Given the above results, how do we exactly understand the reason behind the formation
7 of such structures in these systems? Let us first consider a system with neutral (uncharged) disks
8 alone in a suspension. As we keep packing the system with more particles, they will most
9 preferably stack against each other resulting in the formation of a rod or tactoid like structure
10 with two or more particles. Now, the same type of configuration can be achieved by the addition
11 of excess non-adsorbing polymer chains to a suspension containing particles at concentrations
12 below the close packing fraction. Polymer chains in the bulk increase the attractions as a result of
13 increasing depletion forces in the system[47]. However, in our case this formation does not seem
14 plausible because of the existing asymmetric electrostatic repulsions within the system and due
15 to the fact that the adsorbed PEO chains contribute to the repulsions through steric forces. For a
16 freshly prepared laponite[®] suspension in a salt-free condition the Debye screening length is
17 approx. 4.8nm [48] so there will be long ranged electrostatic repulsions. Additionally, the
18 adsorbed layer thickness estimated using contrast matched small angle neutron scattering and
19 dynamic light scattering techniques was found to be c.a 1.6nm[23, 24]. The steric force arising
20 due to the presence of the polymer layer will be short-ranged and highly repulsive within smaller
21 distances of approach. Hence, the depletion effects along the intermediate concentrations of
22 PEO, does not permit the formation of stacked structures in the system.

In order to investigate the effects of particle concentration on the microstructure in these systems, a similar set of experiments were conducted for systems with 3% laponite[®]. It is known that the time taken to reach a structurally arrested phase in a laponite[®] system decreases with increasing particle concentration. A suspension with 3% laponite[®] ($\phi_c \sim 0.011$) evolves with time and transitions from a homogeneous fluid to a repulsive glass where particles become increasingly localized due to the dominant electrostatic repulsions in the system. The scattering spectrum of the neat laponite[®] suspension is flat along the intermediate- q region and diverges at low- q with a slope of -3.6. As seen in the case of systems with long PEO chains, the slope along the regions of q greater than $0.02\text{\AA}^{-1}$ (Figure S2(B)) is smaller than -2 for all the systems. With the addition of small amount of PEO ($c_p/c^*:0-0.26$), we observe a weak peak in the scattering intensity at $q \sim 0.005\text{\AA}^{-1}$ ($d \sim 2\pi/q \approx 125.66\text{nm}$) (Figure S7). However, as we keep adding more polymer chains to the system the correlation peak is no longer observed in this region and a flat intensity plateau is observed at higher concentrations of PEO. At intermediate concentrations of PEO ($c_p/c^*:0.4-0.8$), contrary to the 2% laponite[®]-PEO series, we do not observe the formation of intermediate structures in the samples. Attempts to fit the USAXS spectra to a polydisperse core-shell cylinder model failed as the parameter fit results yielded unphysical values. This is expected as the system is concentrated and increasing interference effects will render it difficult to extract meaningful values of the radial and face side shell thicknesses.

1

2

Figure 10: USAXS spectra of suspensions containing 3% laponite[®] with varying concentrations of 20 kg/mol PEO. The scattered intensity profiles have been vertically shifted for clarity. The dotted profiles (---) plotted against each spectrum is the scattering from the 3% laponite[®] without PEO truncated at $q \sim 0.001 \text{ \AA}^{-1}$ for a better comparison.

3

4 The scattering spectra for both the higher M_w and lower M_w PEO indicate that the
5 formation of intermediate structures in the system is definitely influenced by the concentration of
6 particles within the volume. The interparticle distances are expected to decrease as the
7 concentration of laponite[®] increases. Now with the addition of PEO to the system, the effective
8 volume fraction decreases because formation of complexes. In the case of the series of samples
9 containing 2% laponite[®] and 300 kg/mol PEO, the adsorbed polymer chains initially contribute
10 to the formation of dense complexes that are approx. 3-4 times the size of the particle. As more
11
12
13

polymer is added to the system, particles begin to add up to the edges of the cluster and this is probably why the structure of the objects along intermediate and particle length scales do not vary with the addition of PEO. With the addition of PEO, increasing repulsions between polymers and between polymer coated complexes result in formation of denser clusters. In the case of systems with 3% laponite[®], the interparticle distances are now shorter so this results in the formation of denser aggregates. For the series of samples containing the 20 kg/mol PEO, the short and weak attraction strengths result in the formation of very small structures. In the case of the 2% laponite[®] series, the ellipsoidal structures that form at intermediate PEO concentrations are almost 2 particle diameters long and the thickness is about 4nm which is basically the lateral thickness that takes into account the polymer shell thickness.

The results discussed in this work elicit some major differences in the structure of a laponite[®] system in the presence of long or short polymer chains. When the chains are small, in addition to steric repulsions arising from the adsorbed polymer chains, free chains also contribute to a weak depletion attraction. The re-structuring of particles within the system at this stage occurs at a much smaller length scale. At these length scales, the polymer chains do not drive in enough attraction to cause the formation of large-scales structures in the system. Systems with longer polymer chains may also contribute to some weak depletions at very low polymer concentrations but the chains are so long that particle-polymer bridging effects are more dominant than the other. This is true when the interparticle distances are comparable to the length of the polymer chain and can be seen from the apparent decrease in the lower q power law scaling in systems with 3% laponite[®]. On the other hand, at polymer concentrations close to a point where the chains begin to overlap and beyond this limit, the distribution of structures in the

system seems to be driven by the formation of polymer-particle complexes and its interaction with the long polymer chains remaining in the bulk medium.

Conclusions

A systematic study of the influence of polymers on the microstructure in laponite[®]-PEO systems has been conducted using ultra small-angle x-ray scattering (USAXS). The focus was to understand how the microstructure contributed to the formation of an arrested phase in an aging colloid-polymer mixture. Two specific cases were considered; (i) polymer-colloid size ratio was 0.5 and (ii) polymer-colloid size ratio was 2.5 with the particle concentration fixed either at 2% ($\phi_c \sim 0.0075$) or 3% ($\phi_c \sim 0.011$). As the polymer concentration is allowed to increase, we find:

- (i) there is no systematic increase or decrease in the excess scattering at low- q for systems with 300 kg/mol PEO at both particle fractions and the effective size of the cluster is about 3-6 times the effective diameter of the particle,
- (ii) the shorter polymer chains do not remarkably change the structure at large length scales but influence the formation of ellipsoidal or prolate objects of smaller sizes at intermediate concentrations,
- (iii) at higher particle fractions, the formation of intermediate structures is avoided because the interparticle distances between particle are initially shorter and thus a more closely packed structure is expected to form at higher polymer concentrations.

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PEO 300 kg/mol
 $R_g/R \sim 2.4$

$$0 < c_p/c^* < 5.8$$

PEO 20 kg/mol
 $R_g/R \sim 0.5$

$$0 < c_p/c^* < 1.0$$