Assembling PNIPAM-capped Gold Nanoparticles in Aqueous Solutions

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Abstract

Employing small angle X-ray scattering (SAXS), we explore the conditions under which assembly of gold nanoparticles (AuNPs) grafted with the thermo-sensitive polymer Poly(*N*-isopropylacrylamide) (PNIPAM) emerges. We find that short-range order assembly emerges by combining the addition of electrolytes or polyelectrolytes with raising the temperature of the suspensions above the lower-critical solution temperature (LCST) of PNIPAM. Our results show that the longer the PNIPAM chain is, the better organization in the assembled clusters. Interestingly, without added electrolytes, there is no evidence of AuNPs assembly as a function of temperature, although untethered PNIPAM is known to undergo a coil-to-globule transition above its LCST. This study demonstrates another approach to assembling potential thermo-sensitive nanostructures for devices by leveraging the unique properties of PNIPAM.

Main

Poly(*N*-isopropylacrylamide) (PNIPAM) is an amphiphilic polymer comprising an alkyl-chain back-bone decorated with amide-isopropyl side groups. The amide side groups, common to protein chains, render hydrophilic properties to the polymer . PNIPAM has attracted attention across disciplines due to its unique thermally responsive behavior. The polymer exhibits a lower critical solution temperature (LCST) at ∼ 32 °C,[1,2] above which the chains expel water and undergo contraction to a cascade of globular conformations.[3] It has been established that the LCST phase transition is reversible. In addition, small angle neutron scattering of PNIPAM suspensions shows evidence of reversible assembly of the globular structures.[4] This unique property has been widely explored for drug delivery,[5,6]bio-sensors,[7,8] smart layers,[9,10] and microactuator.[11,12] The thermal properties of PNIPAM make it a suitable candidate for surface modifications of nanoparticles (NPs) to create stimuli-responsive self-assembly and crystallization.[13,14]

Recently, PNIPAM has been synthesized with a thiol end-group, making it suitable for grafting metallic NPs, particularly gold and silver.[15] Indeed, temperature-induced assembly PNIPAM grafted nanoparticles have been observed above the LCST by varying salinity, pH, and by photoexcitation.[16–20] Various dynamic light scattering (DLS) and ultraviolet-visible (UV-Vis) studies have shown that the hydrodynamic diameter (D_{H}) of PNIPAM grafted AuNPs in pure water decreases marginally above the LCST. However, upon adding sodium chloride to the solutions, aggregation emerges above the LCST.[16,17,19,21–23] Using block copolymer, poly(ethylene glycol)-b-poly(N-isopropylacrylamide) to graft AuNPs, it has been shown that self-assembly into one-dimensional (1D) or two-dimensional (2D) structures in salt solutions can be induced by raising the temperature above the LCST.[24] The same study emphasizes the significance of adding charged molecules to the grafted NP suspensions to achieve assembly. Other studies of grafted AuNPs with PNIPAM have been shown to exhibit assembly in two dimensions at air/liquid interfaces.[25–27] Although thermal effects have not been reported to achieve assembly, the polymer tends to respond to the salinity of the suspension in a similar manner as has been observed for poly-ethylene glycol (PEG) grafted AuNPs.[28,29]

Here, we extend these 2D studies to the three-dimensional (3D) bulk self-assembly and ordering by monitoring the combined effect of salinity and temperature. DLS studies have indicated assembly upon a variable salinity and temperature combination.[24] We employ *in-situ* synchrotron-based small angle scattering (SAXS) technique to determine the nature of the assembly upon adding electrolytes and varying the temperature.[30] As for electrolytes, we use salts such as potassium carbonate (K_2CO_3), sodium chloride (NaCl), or long-chain positively charged ploy-electrolyte Poly(diallyldimethylammonium chloride) (PDAC). PDAC has been shown to induce 2D crystallization of sodium do-decyl sulfide at the air/liquid interface, making it a potential electrolyte to facilitate assembly.[31] We also examine the effect of grafted PNIPAM molecular weight (∼ 3 vs. 6 kDa) on the characteristics of the assembly.

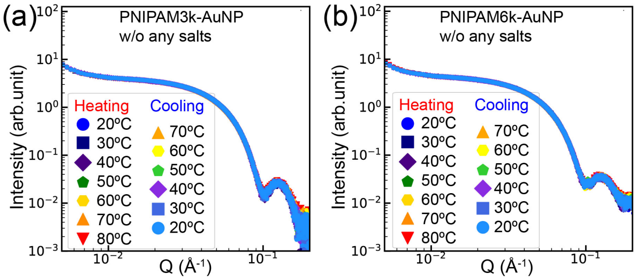

Figure 1: SAXS data for (a) PNIPAM3k-AuNPs (10 nm core) and (b) PNIPAM6k-AuNPs (10 nm core) in water (i.e., without any electrolytes) at various temperatures as indicated. The normalized intensities profiles $S(Q)$ are shown in SI Figure S7 and prove that no assembly occurs upon raising the temperature.

Raising the temperature above the LCST, without adding any electrolytes, the PNIPAM-AuNPs remain dispersed in the suspensions. Figure 1 shows SAXS patterns obtained from PNIAPM-AuNPs without salts at various temperatures (heating and cooling cycles). The pattern for PNIPAM3k-AuNPs in (a) and PNIPAM6k-AuNPs (b), up to 80 °C consists of the form factor of the core AuNPs (See Figure S5). We note that the SAXS intensities are dominated by the form factor of the AuNP core with little contribution from the PNIPAM corona. These results do not provide clear evidence for conformational change above the LCST of PNIPAM-AuNPs. We conclude that the particles remain dispersed in the suspensions even above the LCST. This is consistent with the globular shrinking conformation above the LCST,[3] where the polymer likely exposes its hydrophilic moieties to the aqueous medium. The absence of assembly in pure water above LCST can be rationalized by the repulsion between the hydrophilic (dipolar) moieties.[17,23] The lack of scattering from the PNIPAM corona in aqueous suspensions is due to a negligible electron-density (ED) contrast between the suspension (water) and the organic polymer. As a result, one cannot infer from SAXS measurements moderate changes in the conformations of the polymer in the corona. The normalized intensity profiles $S(Q)$ are shown in Figure S7 of the SI, confirming well-dispersed grafted AuNPs at all measured temperatures. More details on the form factor, the core size of AuNPs,

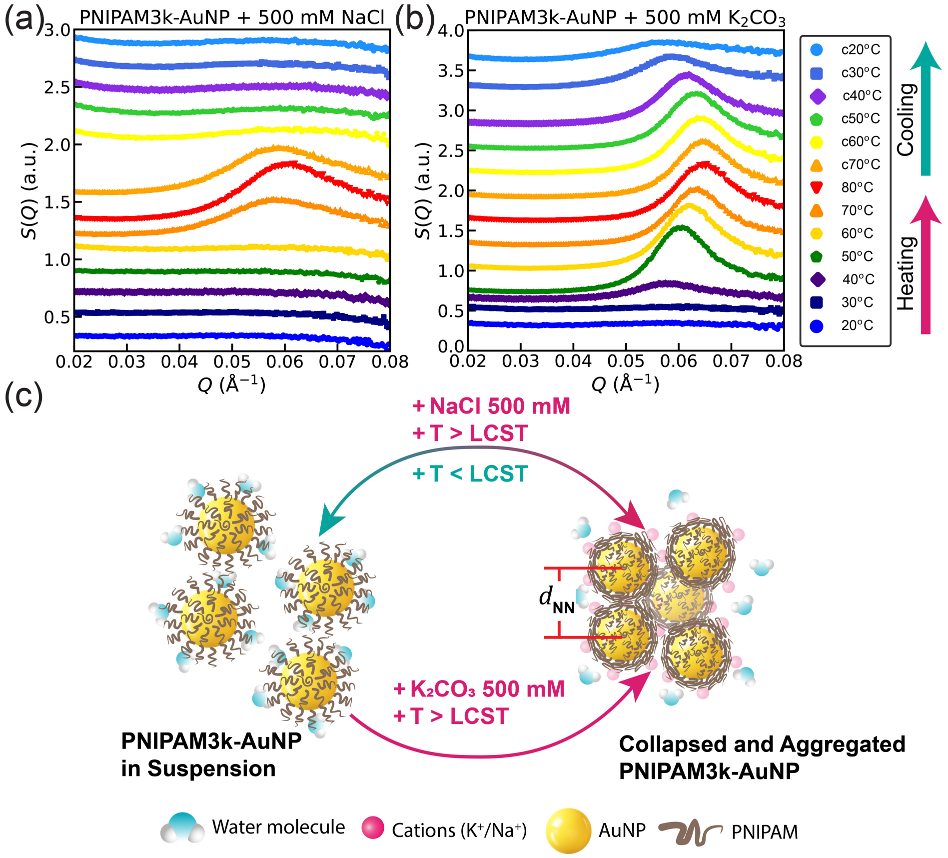

Figure 2: Normalized intensity $S(Q)$ data for PNIPAM3k-AuNPs with (a) 500 mM NaCl, (b) 500 mM K_2CO_3 at various temperatures, as indicated, showing the emergence of broad interference peak at $Q \simeq 0.055$ Å^{-1}. Such a lone broad peak indicates amorphous aggregation of particles with a characteristic nearest neighbor distance $d_{\rm NN} \sim 11.5$ nm. (c) Schematic illustration of the transition from dispersed nanoparticles to aggregates as the temperature is raised above the LCST in the presence of salts. The depicted aggregates show the particles with collapsed PNIPAM corona inferred from the value of $d_{\rm NN}$, which is close to the NP core diameter.

and the size distribution of the citrate-stabilized AuNPs are provided in the SI.

Raising the temperature above the LCST in the presence of salts induces aggregation of PNIAPM3k-AuNPs. At low salt concentrations (below 50 mM of NaCl or K_2CO_3), the SAXS data show that the particles are dispersed in the suspensions even at elevated temperatures above the LCST, as shown in Figure S9. Figure 2 shows SAXS $S(Q)$ patterns of PNIPAM3k-AuNPs at 500 mM (a) NaCl and (b) K_2CO_3. Adding K_2CO_3 or NaCl to the solution at room temperature yields SAXS patterns that are similar to those shown in Figure 1 (i.e., without salts). However, heating the same salinated suspensions above ~ 40 °C gives rise to the emergence of a prominent peak around $Q_0 = 0.06$ Å^{-1}, which gradually shifts to a higher Q value upon further increase in temperature. This stand-alone peak indicates random aggregation of NPs with a characteristic nearest-neighbor (NN) distance ($d_{\rm NN}$), indicating liquid-like order. The characteristic $d_{\rm NN} \simeq \frac{2\pi}{Q_0} \simeq 10.4$ nm is slightly larger than the diameter of the core AuNPs ($D_{\rm Core} = 8.7$ nm, see Figure S5). Such a small $d_{\rm NN}$ close to the $D_{\rm Core}$ suggests that the polymer is likely collapsed to its densely packed state (void of water) onto the NP surface. In the SI, we determine an upper limit to the grafting density, assuming such a densely packed collapsed corona. Furthermore, the shift in peak position to higher Q values as the temperature increases indicates smaller $d_{\rm NN}$ and further collapse of the grafted PNIPAM corona consistent with the globular behavior of pure PNIPAM in aqueous solutions.[3] We define collapse as a densely-packed dry polymer with its hydrophilic moieties exposed to the aqueous medium.[26] We hypothesize that the observed aggregation is induced by the presence of the cations and anions that lead to attractive interaction among the NPs. We argue that the ions

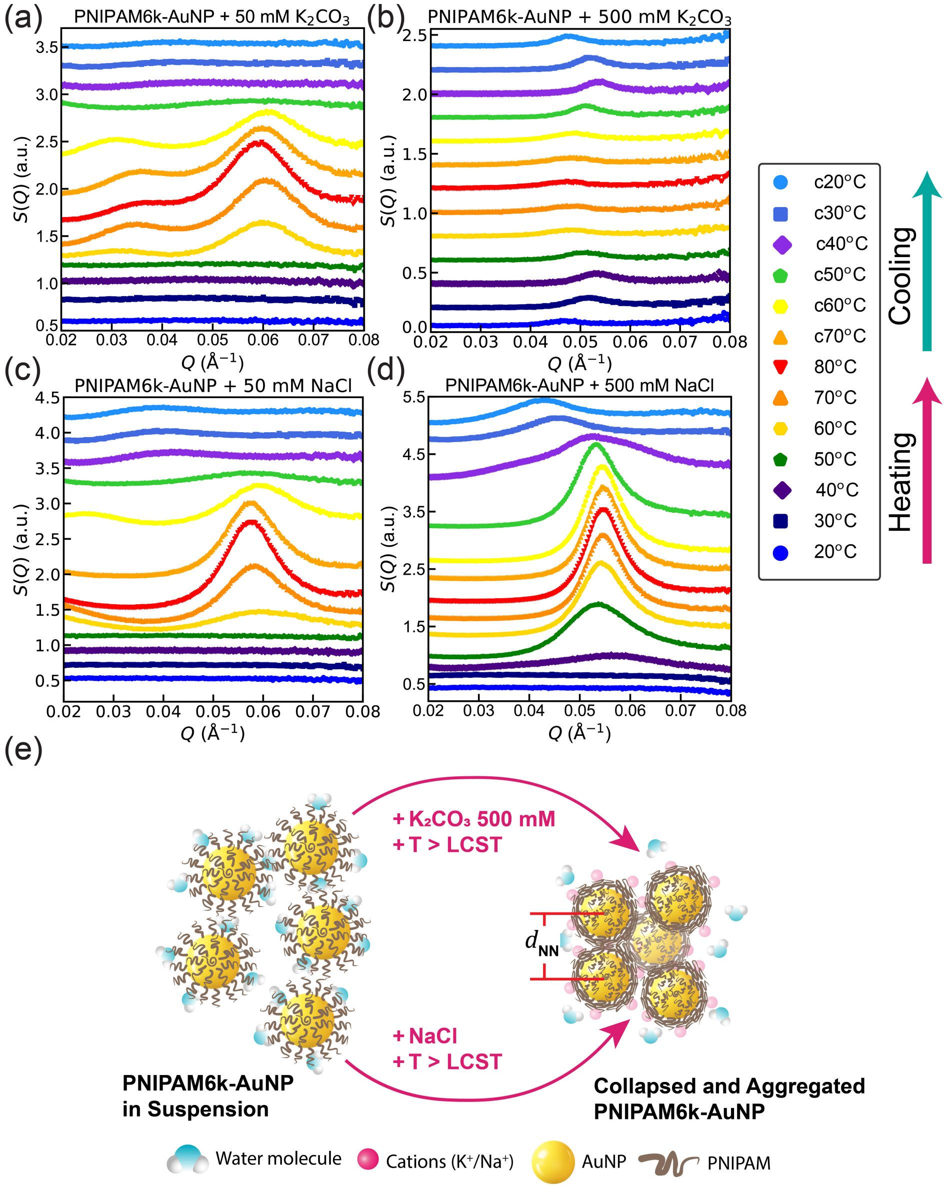

Figure 3: Normalized intensity $S(Q)$ patterns for PNIPAM6k-AuNPs with (a) 50 mM K_2CO_3, showing two broad diffraction peaks. In the SI (Figure S11), we show that the diffraction pattern is best-describing clusters with diamond-like motifs. Our conclusion is based on examining various other structural scenarios. (b) 500 mM K_2CO_3 shows a single weak peak corresponding to a $d_{NN} \simeq 12.5$ nm. It is also likely that at this concentration, precipitation occurs. (c) 50 mM NaCl, (d) 500 mM NaCl at various temperatures as indicated, showing a single peak as described in Figure 2. (e) Schematic illustrations of the assembly development from dispersed NPs to aggregated are presented. Note that in this case, the assembly process is irreversible.

decorate different parts of the polymer corona, leading to weak mutual binding. As a result, upon cooling the suspension from 80 °C to room temperature, the NPs seem to re-disperse in the suspensions, as the hydrophilic moieties are less exposed. The evidence for re-dispersed clusters is that the prominent peak at Q_0 broadens significantly and almost diminishes upon cooling, indicative of the reversible nature of the collapsed state. We note that the addition of K_2CO_3 leads to a sharper $S(Q)$ peak and at larger Q values compared to those obtained by adding NaCl. This indicates that K_2CO_3, at elevated temperatures, leads to higher densely packed polymer corona with more well-defined d_{NN}. Our analysis of the diffraction patterns yields peak positions and line widths as shown in Table S1. The line widths indicate that the correlation lengths in the ordered states for 500 mM K_2CO_3 and NaCl is on the order of $\sim$90 and 60 nm, respectively (i.e., 8-5 correlated NN). In addition, the aggregation is not fully reversible in the presence of K_2CO_3. We note that K_2CO_3, unlike NaCl, releases a divalent anion, i.e., CO_3^{-2} whereas NaCl has a monovalent anion. More importantly, K_2CO_3 affects the pH (increases the alkalinity) of the suspension. We hypothesize that these differences affect the behavior of the assembled particles. In fact, assembling PEG-grafted AuNPs shows notable assembly differences between NaCl and K_2CO_3 in addition to the suspensions.[32]

Similar to PNIPAM3k-AuNPs, the addition of NaCl or K_2CO_3 to the suspensions of PNIPAM6k-AuNP has little effect below the LCST, even at concentrations of salt as high as 500 mM. A more noticeable effect of salt addition with temperature for PNIPAM6k-AuNPs is apparent at 50 mM K_2CO_3 above the LCST. As shown in Figure 3(a), two broad peaks ($Q_1 \sim 0.035$ and $Q_2 \sim 0.06$ Å^{-1}) appear upon heating the suspension above 50 °C. Although it is difficult to assign a definite structure from such a limited diffraction pattern, we rationalize our proposed structure based on the behavior of the polymer at different temperatures. In particular, we assume that above the LCST, the polymer corona collapses onto the core of the AuNP. This constraint limits the possible packings of assembled nanoparticles. In the SI, we examine various structural scenarios and conclude that the likely packing has diamond-like motifs,[33]albeit at very short-range order. The correlation length in the ordered states is of the order of 2-3 unit cells. Figure 4(a) shows $S(Q)$ profile of PNIPAM6k-AuNP10 at 50 mM K_2CO_3 and 80 °C, fitted to a relaxed diamond-like structure using the first three Bragg reflection peaks. Our model allows small variations in the lattice positions of the AuNPs. The model system accounts for lattice positions with which we calculate the structure factor. A similar diffraction pattern associated with diamond-like structures has been reported for assembled binary Au and Ag NP systems.[33] This interpretation yields a $d_{\rm NN}(\frac{3\pi}{2Q_{111}}) \simeq 13.1$ nm, which is consistent with the grafting density and the fact that the polymer is densely packed (collapsed). See Figure S11 and further discussions in the SI.

At a high concentration of K_2CO_3 (500 mM), the diffraction pattern consists of a single weak peak at $Q \sim 0.05$ Å^{-1} as shown in Figure 3(b).

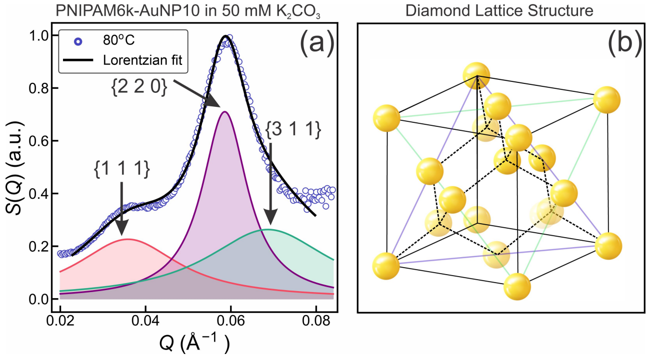

Figure 4: (a) $S(Q)$ profile of PNIPAM6k-AuNP10 at 50 mM K_2CO_3 and 80 °C, fitted to a relaxed diamond-like structure using the first three Bragg reflection peaks. The model system accounts for lattice positions with which we calculate the structure factor. The shaded peaks show the contribution of each Bragg reflection to the fitted data. (b) Schematic of a diamond-cubic lattice where the golden spheres represent the collapsed PNIPAM-AuNPs.

As mentioned above, a single peak can only provide minimal information on the characteristic length scale of $d_{\rm NN}$; in this case, $d_{\rm NN} \sim 12.5$ nm. It is also possible that better quality crystals are formed and precipitate out of the suspension and, therefore, are not detected in our bulk solution SAXS measurements. In the SI, we show the assembly of PNIPAM6k-AuNP at the liquid/vapor interface in the presence of 100 mM K_2CO_3. The 2D diffraction pattern (grazing-incidence small-angle X-ray scattering; GISAXS) in Figure S12 shows two broad diffraction peaks similar to those observed in the bulk SAXS, however, at slightly smaller Q values. This suggests that the packing at the liquid/vapor interface is similar to that in bulk, and the $d_{\rm NN}$ is slightly larger at the surface. This is expected as the GISAXS measurements are performed below the LCST. We also note that the threshold for ordering in 2D is less strict than in 3D. In 2D, it is sufficient to achieve surface assembly with increased salinity even below the LCST at room temperature. By contrast, 3D assembly is induced by the combination of salinity and elevated temperature. More evidence on the 2D assembly of PNIPAM6k-AuNPs is established with X-ray reflectivity measurements and their analysis as shown in Figure S12.

The addition of 50 and 500 mM NaCl to the PNIPAM6k-AuNPs suspension has a similar effect on the assembly. As shown in Figure 3 (c) and (d), the addition of salt has little effect below the LCST. Upon heating, a single peak at about $Q \sim 0.055$ Å^{-1} emerges and grows in intensity up to 80 °C and decreases in intensity and shifts to lower Q values (at 20 °C the peak is centered around $Q \sim 0.045$ Å^{-1}) demonstrating the reversibility of collapsed state. The observed peak above the LCST is associated with a $d_{\mathrm{NN}} \sim 11.5$ nm and below the LCST $d_{\mathrm{NN}} \sim 14.1$ nm consistent with the globular shrinking of the PNIPAM above the LCST and expanding below it. For NaCl at 50 and 500 mM, we find that the Correlation length is in order of 50 and 100 nm, respectively.

To generalize the effect of assembly using polyelectrolytes, we use PDAC as an additive to the suspension to induce assembly. Figure S6 (a) shows the normalized intensity vs Q for the grafted AuNPs in the presence of ~ 1 wt % PDAC. Unlike the simple salts, the polyelectrolyte induces assembly below the LCST (See Figure S6). At room temperature, the SAXS pattern has a broad peak at about $Q_0 = 0.04$ Å^{-1} which, upon raising the temperature above 35 °C, shifts to $Q_0 = 0.053$ Å^{-1}. As discussed above, the single peak indicates $d_{\mathrm{NN}} = 11.8$ nm, consistent with a collapsed PNIPAM corona. More details are provided in the SI.

In summary, we have successfully grafted AuNPs with PNIPAM to achieve temperature-induced assembly and ordering of the NPs. Using synchrotron-based SAXS, we find that temperature has little effect on the nanoparticle assembly in the absence of salts. In fact, the SAXS provides clear evidence that in the absence of salts, the grafted AuNPs are well dispersed in the suspension, even upon heating above LCST. This may be due to the fact that above the LCST, PNIPAM exposes its hydrophilic moieties in the aqueous medium and becomes more soluble. By adding electrolytes (such as K_2CO_3, NaCl, or long chain polyelectrolyte PDAC) to the solution, aggregation emerges. We hypothesize that the mutual attractive interaction among NPs is due to the accumulation of cations and anions on the surfaces of the polymer corona. These interactions lead only to very short-range order assembly such that the SAXS diffraction patterns resemble those of liquids. Our results suggest that the longer the PNIPAM chain, the better organization in the assembled clusters.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxx/yyyyy.

Experimental section; Additional DLS data; Additional SAXS data; Structural analysis; 2D XRR and GISAXS data; Calculation of grafting density; Calculation for molarity

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Author contributions

WW, DV, and SM conceived and supervised the project. HK, SN, DV, and WW designed, conducted the experiments and analyzed the data. BN, HK, WW, and DV wrote the manuscript. WB supported in X-ray scattering experiments, data acquisition, and data processing at NSF's

ChemMatCARS. SM, DV, and WW secured the funding for the project. All co-authors read and reviewed the manuscript.

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