Influence of initial chain conformation on the formation of mesoglobule phase in a dilute heteropolymer solution

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Abstract

We have observed, *for the first time*, that when the initial chain conformation changed from coil to globule, the association of linear poly(*N*-vinylcaprolactam-*co*-sodium acrylate) chains could gradually change from a reaction limited to diffusion limited process, reflected in a change of the fractal dimension of the resultant aggregates from ~ 2.5 to ~ 1.6. Such an influence of the initial chain conformation has been overlooked in past studies of the formation of the mesoglobule phase in a dilute heteropolymer solution.
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Keywords: Aggregation; Initial chain conformation; Fractal dimension

1. Introduction

As a fascinating subject, the aggregation of colloidal particles in dispersion has been extensively studied because it is important in both theory and practice [1–8], such as the production of chemical toners and the treatment of waste water. Two limiting regimes have been identified as the diffusion-limited cluster–cluster aggregation (DLCA) and the reaction-limited cluster–cluster aggregation (RLCA) [9, 10]. One of the distinctive features between them is the different fractal dimensions (d_f) of the resultant aggregates [11,12], i.e. different scalings between the mass (M) and size (R) of the aggregates, $M \sim R^{d_f}$. To which regime an actual aggregation process falls is essentially governed by the sticking efficiency between two collided particles. In DLCA, every collision leads to an irreversible sticking and the aggregation rate is limited solely by the time required for two particles to encounter each other by diffusion. The DLCA process leads to aggregates with an open and less uniform structure and d_f in the range $\sim 1.75-1.80$ for a three-dimensional system. On the other hand, the sticking probability in RLCA is so low that a number of collisions can only result in one sticking [13–15] and individual colloidal particles can penetrate into the 'fjords' of the aggregate before they stick together [16]. The resultant aggregates are more uniform with a higher fractal dimension of $d_f \sim 2.0-2.5$. Experimentally, a combination of static and dynamic laser light scattering (LLS) [17–19] is a particular useful method to study the aggregation process because it can continuously monitor the aggregation in a noninvasive manner, especially in dilute solution. In the study of the formation and structure of aggregates, LLS can provide not only the size of the aggregates but also the mass (aggregation number) and density distribution of the aggregates for a wide variety of colloidal systems.

The study has been extended to the association of synthetic and biopolymers, especially polyelectrolytes, in solution because of their implications in ecology, biotechnology and medicine [20,21]. It was found that the rate constant of the interaction increased sharply with decreasing the polycation ionic strength, but was independent of the polyanion chain length [22,23]. It was suggested that the distribution of ionic groups on the chain backbone had no effect on the complexation [24]. In general, the association of heteropolymer chains in a dilute solution can be placed

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under the framework of the formation of a mesoglobule phase [25]. To our knowledge, the influence of initial chain conformation on the association of linear heteropolymers has not been thoroughly investigated and the theoretical study in this aspect has been limited because linear flexible polymer chains with a variable conformation are much less defined than colloidal particles. The modeling of the chain aggregation is a remaining challenge.

In this study, by using thermally sensitive poly(*N*-vinylcaprolactam-*co*-sodium acrylate) (P(VCL-*co*-NaA)) chains, we were able to keep the same chain length and ionic distribution and only alter the initial chain conformation by a simple temperature variation because PVCL is hydrophilic/soluble in water and has a coil conformation at ∼25 °C or below. It gradually becomes hydrophobic/insoluble and collapses into a globule when the temperature increases from ∼25 to ∼35 °C [26]. Taking the advantage of this thermal sensitivity, we have studied the influence of the initial chain conformation on the Ca^{2+}/COO^- complexation induced aggregation. Our results showed that at 32 °C or below, PVCL is so hydrophilic that the strength of the complexation between Ca^{2+} and COO^- groups is not sufficient to induce interchain aggregation. Only at higher temperatures, the breakdown of the balance between hydrophilic solvation and hydrophobic attraction makes the interchain aggregation possible so that the aggregation is *controllable* and *reversible*.

2. Experimental

2.1. Materials

The P(VCL-*co*-NaA) sample was prepared by precipitation polymerization in water. Into a 150-ml three-neck flask equipped with a reflux condenser, a thermometer and a nitrogen-bubbling tube, were added *N*-vinylcaprolactam monomer (VCL), sodium acrylate (NaA) comonomer, and deionized water. The solution was stirred and nitrogen bubbled through for 1 h to remove oxygen before potassium persulfate (KPS) aqueous solution as initiator was added to start the polymerization at 60 °C for 24 h. The resultant P(VCL-*co*-NaA) was purified by a successive four times centrifugation (Sigma 2K15 ultracentrifuge, at 15,300 rpm and 40 °C), decantation and redispersion in deionized water to remove unreacted low molar mass molecules. On average, it contained 4.3 mol% acrylic groups with a weight average molar mass of 3.04×10^6 g/mol. The concentration used for LLS was 1.20×10^{-5} g/ml.

2.2. Laser light scattering (LLS)

The LLS spectrometer used was a modified ALV/SP-125 equipped with a multi-τ digital time correlator (ALV-5000) and a solid-state laser (ADLAS DPY 425II, output power ≈400 mW at $\lambda = 532$ nm). The details of the sample preparation and LLS spectrometer can be found elsewhere [27]. In static LLS, the scattering vector (q) dependence of the absolute excess time-averaged scattered intensity, known as the Rayleigh ratio $R_{vv}(q)$, can be related to the weight-average molar mass (M_w) and the *z*-average root-mean-square radius of gyration ($\langle R_g^2 \rangle_z^{1/2}$ or $<R_g>$) of the scattering objects and the second virial coefficient (A_2) of the dispersion or solution by,

$$\frac{KC}{R_{vv}(q)} \cong \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^2 \rangle_z q^2\right) + 2A_2C \qquad (1)$$

where

$$K = \left[\frac{4\pi^2 n_1^2}{\lambda_0^4 N_A}\left(\frac{dn}{dC}\right)^2\right]$$

is a constant and $q[= (4\pi n_1/\lambda_0)\sin(\theta/2)]$ is the scattering vector with N_A, dn/dC, n_1, λ_0 and θ being Avogadro's number, the specific refractive index increment, the refractive index of solvent, the wavelength of the light in vacuum and the scattering angle, respectively. By measuring $R_{vv}(q)$ of a very dilute solution at a relatively small angle, we can estimate M_w. For an aggregate with a fractal geometry and made of colloid particle, the scattered intensity $I(q)$ is scaled to q as $I(q) \sim q^{-d_f}$ in the range of $R_{aggregate}^{-1} < q < R_0^{-1}$, where d_f is the fractal dimension, R_0 and $R_{aggregate}$ are the radii of individual chains and the resultant aggregate, respectively [18]. When $q > R_0^{-1}$, the light probes internal structures of individual chains and the intensity profile reflects the density distribution inside, while when $q < R_{aggregate}^{-1}$, the average size of the resultant aggregates and the correlation of the topological length between the aggregates could be determined. In dynamic LLS, the cumulant or Laplace inversion analysis of the measured intensity–intensity time correlation function $G^{(2)}(q,t)$ in the self-beating mode can lead to an average line width ($\langle \Gamma \rangle$) or a line width distribution ($G(\Gamma)$) [28,29]. For a pure diffusive relaxation, Γ can be related to the translational diffusion coefficient D via $\Gamma = Dq^2$ at $C \to 0$ and $q \to 0$, or the hydrodynamic radius (R_h) by the Stokes–Einstein equation.

3. Results and discussion

Fig. 1 shows typical hydrodynamic radius distributions $f(R_h)$ of linear P(VCL-*co*-NaA) chains at 25 °C before and after adding Ca^{2+}. For each $f(R_h)$, we could calculate one average hydrodynamic radius $\langle R_h \rangle$ defined as $\int_0^\infty f(R_h)R_h \, dR_h$. It is noted that the addition of Ca^{2+} at room temperature leads to a slight contraction of the chains. On the other hand, the inset shows that there was no change in the scattering intensity. Therefore, the contraction can be attributed to the intrachain complexation between Ca^{2+} and COO^-. The inset also clearly shows that without Ca^{2+}, the chains gradually shrink ∼70% as the temperature increases
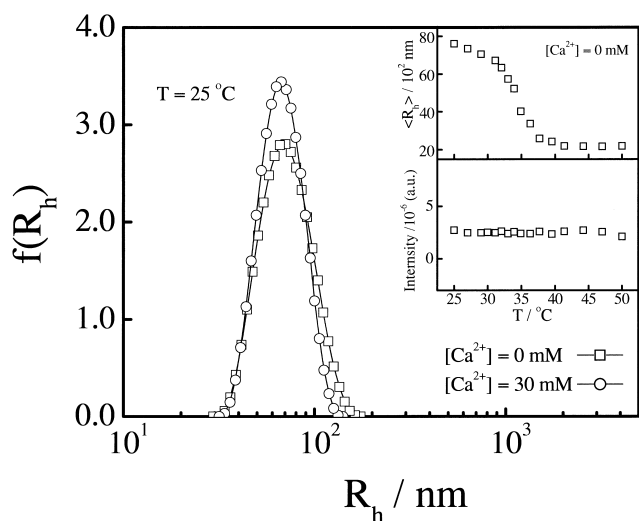
Fig. 1. Typical hydrodynamic radius distributions of linear P(VCL-*co*-NaA) chains in water at 25 °C with and without the addition of Ca²⁺. The inset shows the temperature dependence of average hydrodynamic radius $\langle R_h \rangle$ and the relative scattering intensity of linear P(VCL-*co*-NaA) chains in water without Ca²⁺.

from 25 to 40 °C and there is no interchain association even at 50 °C. However, the situation was completely different in the presence of Ca²⁺; namely, the chains started to associate when the temperature is higher than ~ 32 °C.

Fig. 2 shows that as the temperature increases, the association rate becomes faster, but the average aggregation number $(N_{agg} \equiv M_{w,aggregate}/M_{w,polymer})$ decreases, where N_{agg} is determined from the ratio of the weight-average molar masses of the aggregates and chains. Higher temperatures led to smaller aggregates, which is partially due to the chain collapse at higher
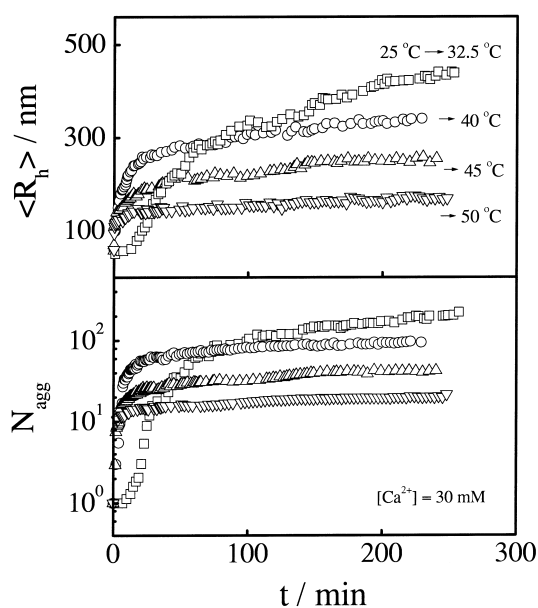

Fig. 2. Time dependence of average hydrodynamic radius $\langle R_h \rangle$ and aggregation number (N_{agg}) of resultant P(VCL-*co*-NaA) aggregates formed after the solution temperatures were suddenly increased to different association temperatures.

temperatures. Fig. 3 shows the scaling between $I(q)$ and q for the resultant aggregates formed at different temperatures after a long aggregation time. It is clear that d_f decreases as the aggregation temperature increases. Because $M_{w,aggregate}$ of aggregates is relatively larger for LLS measurement, the error of experiment is relatively small. We still repeated three measurements for each aggregate that have not difference in d_f. We also studied the Ca²⁺ concentration dependence of the association and found that for a given temperature, the increase of Ca²⁺ concentration could speed up the association and result in larger aggregates, but had no influence on the fractal dimension and structure of the resultant aggregates [26].

Note that for linear chains, the complexation could be either intrachain or interchain. The intrachain complexation leads to the chain contraction and only the interchain complexation results in the association. The two processes always compete with each other in a real experiment. At a lower temperature close to ~ 32 °C, P(VCL-*co*-NaA) is still hydrophilic and the chain only shrinks slightly, as shown in the inset of Fig. 1, so that the complexation is not sufficient to induce a high sticking probability when two chains collide with each other. Therefore, individual crumpled, but not collapsed, chains have more chance to interpenetrate each other to form a more uniform structure. The association follows a mechanism similar to a reaction-limited cluster aggregation (RLCA) process. When the association temperature is ~ 40 °C or higher, the chain becomes hydrophobic and fully collapsed, leading to a much higher sticking efficiency. The shrinking of the chain at higher temperatures is so fast that individual chains have much less chance to undergo the interchain knotting [30]. The complexation-induced aggregation in this case mainly happens between small collapsed clusters made of a single or few chains, very similar to that between those collapsed spherical microgels [31]. Therefore, the association becomes a diffusion-limited cluster aggregation (DLCA).

The inset reveals that in spite of different values of d_f shown in Fig. 3, the plots of average chain density $(\langle \rho \rangle \equiv M_{w,aggregate}/[(4/3)\pi\langle R_h \rangle^3])$ versus $\langle R_h \rangle$ at different association temperatures collapse into a single curve. The initial lower chain density at 32.5 °C is due to less interpenetration among the crumpled chains at the initial stage. It is worth noting that on the one hand, the aggregates formed at higher temperatures have a higher chain density, but on the other hand, the low value of d_f suggests that they have a more open and less uniform structure. This apparent contradiction can be explained as follows. At higher association temperatures, the collapse of the chains results in a higher chain density, just imaging the approaching of such a collapsed chain toward an aggregate. The sticking efficiency at higher temperatures is so high that the arriving chain is more likely to attach to one of the tips of the aggregate than to penetrate deeply into the fjords of the aggregate without first contacting any surface sites [16],
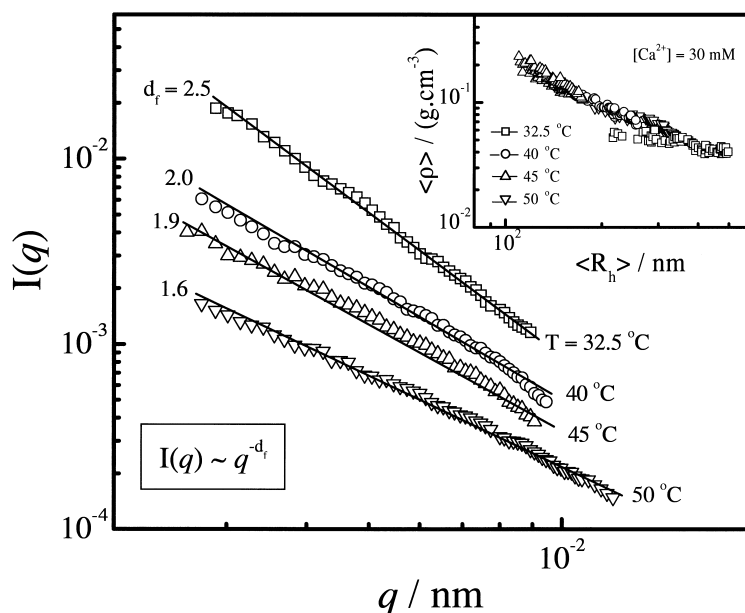
Fig. 3. Double logarithmic plots of scattering intensity $I(q)$ versus scattering vector q for resultant P(VCL-*co*-NaA) aggregates formed at different association temperatures. The inset shows the aggregate size dependence of average chain density $\langle\rho\rangle$ of resultant P(VCL-*co*-NaA) aggregates formed at different association temperatures, where $\langle\rho\rangle$ is defined as $M_{w,agg}/[(3/4)\pi\langle R_h\rangle^3]$.

resulting in a more open and less uniform structure. The aggregates have the fractal geometry with a self-similarity. At relatively lower aggregation temperatures, the chains are only crumpled and the low sticking probability permits an extensive interchain penetration, so that on average, each aggregate contains more chains and the resultant aggregates are more uniform. The influence of initial chain conformation on the Ca^{2+}/COO^- complexation-induced association of linear P(VCL-*co*-NaA) chains is schematically shown in Fig. 4.

4. Conclusion

A combination of static and dynamic LLS studies of the Ca^{2+}/COO^- complexation induced aggregation of linear (PVCL-*co*-NaA) chains has revealed, for the first time, that the initial chain conformation could greatly alter the formation of the mesoglobule phase of linear heteropolymer chains in a dilute solution. For the association of linear chains with an extended coil conformation at a relatively lower aggregation temperature, the association follows a reaction-limited process, resulting in a more uniform structure. As the aggregation temperature increases, the initial chain conformation becomes globule. Therefore, the Ca^{2+}/COO^- complexation mainly happens between highly collapsed small clusters, the association is mainly diffusion limited, leading to a more open and less uniform structure. The association of linear heteropolymer chains in solution has not only many practical implications, but also much richer physics than the aggregation of colloid particles.
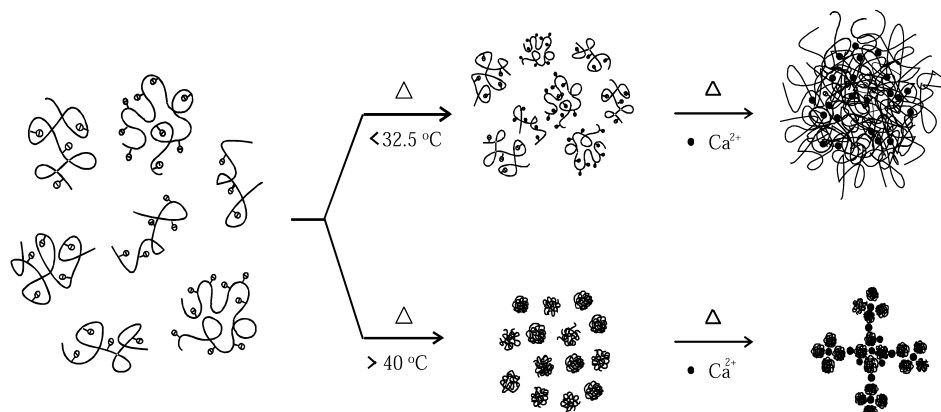

Fig. 4. Schematic diagram of influence of initial chain conformation on the Ca^{2+}/COO^- complexation-induced association of thermally sensitive linear P(VCL-*co*-NaA) chains.

Acknowledgements

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