Light Scattering Study of the Formation and Structure of Partially Hydrolyzed Poly(acrylamide)/Calcium(II) Complexes

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ABSTRACT: The Ca\(^{2+}\) concentration and hydrolysis degree \([-\text{COO}^-]\) dependence of the self-complexation of partially hydrolyzed poly(acrylamide) (HPAM) chains in CaCl\(_2\) aqueous solution was systematically investigated by a combination of static and dynamic laser light scattering. We have, for the first time, revealed a transition between the intrachain and interchain complexations. For each given HPAM sample, there exists a critical Ca\(^{2+}\) concentration ([Ca\(^{2+}\)]\(_{agg}\)) at which the interchain HPAM complexation becomes dominant. [Ca\(^{2+}\)]\(_{agg}\) is related to \([-\text{COO}^-]\) by [Ca\(^{2+}\)]\(_{agg}\) = 7.46 \times 10^{-9} \text{[}[\text{COO}^-]\text{]}^{-1.4}, indicating that the complexation is not stoichiometric and many Ca\(^{2+}\) ions are free in water. We also found that even at [Ca\(^{2+}\)] = [Ca\(^{2+}\)]\(_{agg}\) the complexation at the initial stage was mainly an intrachain process, but gradually evolved into an interchain aggregation. The length of the initial stage increases as \([-\text{COO}^-]\) and [Ca\(^{2+}\)] decrease. Our results showed that in the complexation process, the weight average molecular weight (M\(_w\)) of the HPAM/Ca\(^{2+}\) complexes is scaled to the size (R) of the complexes as M\(_w\) \propto R^{2.11 \pm 0.04} for different [Ca\(^{2+}\)] and \([-\text{COO}^-]\), suggesting that the HPAM/Ca\(^{2+}\) complexes have a fractal structure. The fractal dimension of 2.11 \pm 0.04 shows that the complexation is a reaction-limited cluster aggregation (RLCA) process.

Introduction

The complexation of polyelectrolytes has been extensively studied.\(^{1-4}\) It is known that certain metal ions like Ca\(^{2+}\) can specifically interact with carboxylic groups. If the carboxylic groups are attached to a polymer chain backbone, such as partially hydrolyzed poly(acrylamide) (HPAM), the interaction could lead to a chain aggregation through the polyanion/metal "complexation.\(^{5}\) Flory and Osterheld\(^{6}\) showed, as early as 1954, that Ca\(^{2+}\) ions could change the chain conformation. Ohmine et al.\(^{7}\) and Ben Jar et al.\(^{8}\) studied the effects of monovalent and divalent cations on the collapsing of HPAM. Moreover, several attempts\(^{9,10}\) have been made to describe the polyelectrolytes aggregation in terms of a few mechanistic models. Michaeli\(^{11}\) interpreted the polyelectrolytes aggregation as a function of the ionization degree and of the inert monovalent electrolyte concentration in terms of a stoichiometric complex between divalent cations and anionic groups.

The aggregation kinetics has also been extensively studied.\(^{12}\) The observation that some colloidal clusters have fractal structures has sparked a renewed interest in the aggregation kinetics.\(^{13}\) Two distinct aggregation kinetic processes have been proposed and investigated. One is the diffusion-limited cluster aggregation (DLCA) controlled by the time taken for two clusters to collide via Brownian diffusion,\(^{15,16}\) and the other is the reaction-limited cluster aggregation (RLCA) in which the probability of forming a bond upon collision of two clusters is so high that the aggregation rate is chemically limited by its reaction rate. The RLCA has been observed in several colloid systems and modeled by computer simulation.\(^{17-20}\) In general, the fractal dimension d\(_f\) is defined as M \sim R\(^{d_f}\), where M is the molar mass and R is the cluster size.\(^{16}\) In RLCA, d\(_f\) \sim 1.55 and \sim 2, respectively, in 2-dimensional and hierarchical 3-dimensional simulations. The experimental values of d\(_f\) for the clusters formed in RLCA were \sim 2.1 \pm 0.1. Ball et al.\(^{21}\) pointed out that in RLCA, the slightly larger experimental d\(_f\) values were due to the cluster’s polydispersity.

Laser light scattering (LLS) has been proved to be a particular useful method to study the aggregation process, especially in a very dilute solution in which a conventional viscometer does not have enough sensitivity. LLS is also a direct method to study fractal structures on the basis of the scattered intensity and the size dependence of the molar mass. It is worth noting that it is not trivial to prove a fractal structure, and the fractal concept has been abused in some cases. In this study, the complexation of the HPAM chains in CaCl\(_2\) aqueous solution was investigated. We focused on (1) the transition from the intrachain HPAM complex to the interchain aggregation over a wide range of the hydrolysis degrees and Ca\(^{2+}\) concentrations and (2) the structure of the HPAM/Ca\(^{2+}\) complexes.

Experimental Section

Sample Preparation. The ultrapure acrylamide from Beijing Chemical Reagent Co. was further purified by a three-time recrystallation. Poly(acrylamide) (PAM) was synthesized in water by a radical polymerization procedure detailed before.\(^{22}\) The resultant PAM sample was hydrolyzed in 10% NaOH and 10% Na\(_2\)CO\(_3\) aqueous solution at 60 °C.\(^{23}\) The hydrolysis was controlled by the reaction time. The hydrolysis degree (HD%) of five partially hydrolyzed polyacrylamide (HPAM) samples was in the range 4.7–17.9% which were determined by titration with a 0.10N HCl standard solution.\(^{24}\) The complexation was induced by adding dropwise a proper amount of dust-free CaCl\(_2\) aqueous solution into \sim 2 mL of dust-free HPAM aqueous solution. The initial concentration of the HPAM solution was kept at 1.00 \times 10^{-3} g/mL except otherwise specified. The resistivity of the deionized water used
in this study was 18.3 Ω cm. All the HPAM solutions used in LLS were clarified with a 0.5 μm Millipore filter, and the CaCl₂ aqueous solution was clarified with a 0.1 μm Whatman filter (Anotop 25) in order to remove dust.

**Figure 1**. Typical Zimm plot for poly(acrylamide) in 1 N NaCl aqueous solution at 25 °C.

**Figure 2**. Time dependence of the hydrodynamic radius distribution f(Rₜ) of the HPAM/Ca²⁺ complexes for the self-complexation of the HPAM chains in 0.05 M CaCl₂ aqueous solution.

**Figure 3**. Time dependence of the average hydrodynamic radius (Rₜ) of the HPAM/Ca²⁺ complexes for the self-complexation of the HPAM chains in different CaCl₂ aqueous solutions.

### Results and Discussion

Individual PAM and HPAM chains (i.e., unimer) were first characterized. **Figure 1** shows a typical Zimm plot of PAM in 1 N NaCl aqueous solution at 25 °C, where C ranges from 3.17 × 10⁻⁵ to 1.15 × 10⁻⁴ g/mL. The values of Mₗ, ⟨Rₜ⟩, and A₂ calculated on the basis of eq 1 are summarized in **Table 1**. The decrease of Mₗ as the hydrolysis degree (HD%) increases indicates a slight degradation of the PAM chains in the hydrolysis process.

The positive values of A₂ indicated that 1 N NaCl aqueous solution is a good solvent for both PAM and HPAM at 25 °C. The ratios of ⟨Rₜ⟩/⟨Rₜ⟩ ~ 1.5 are expected for linear flexible polymer chains in a good solvent.

**Table 1. Summary of LLS Results of Poly(acrylamide) and Partially Hydrolyzed Poly(acrylamide) in 1 N NaCl Aqueous Solution at 25 °C**
intrachain complexation in which individual HPAM chains contract before the interchain aggregation. For HPAM5, the intrachain complexation was dominant and the initial stage was too short to be observed, while for HPAM2, HPAM3, and HPAM4, the transition from the intrachain complexation to interchain complexation is very clear. To our knowledge, this transition is observed and reported for the first time. Figure 5 reveals that for a given Ca\(^{2+}\) concentration, the intrachain complexation is directly related to the hydrolysis degree because the carboxylic groups act as "stickers" to complex with the HPAM chains, similar to the results of the PMA/Ca\(^{2+}\) system reported by Yuko et al.\(^{31}\)

Figure 6 shows the Ca\(^{2+}\) concentration dependence of the maximum average hydrodynamic radius \((R_h)_{\text{max}}\), where \((R_h)_{\text{max}}\) is the plateau value as shown in Figure 3. In intrachain complexation, when individual HPAM chains contract before the interchain aggregation. For HPAM5, the intrachain complexation was dominant and the initial stage was too short to be observed, while for HPAM2, HPAM3, and HPAM4, the transition from the intrachain complexation to interchain complexation is very clear. To our knowledge, this transition is observed and reported for the first time. Figure 5 reveals that for a given Ca\(^{2+}\) concentration, the interchain complexation is directly related to the hydrolysis degree because the carboxylic groups act as "stickers" to complex with the HPAM chains, similar to the results of the PMA/Ca\(^{2+}\) system reported by Yuko et al.\(^{31}\)

Figure 6 shows the Ca\(^{2+}\) concentration dependence of \((R_h)_{\text{max}}\) for five different HPAM samples. The inset shows an enlargement of the low [Ca\(^{2+}\)] range in which \((R_h)_{\text{max}}\) decreases as [Ca\(^{2+}\)] increases, indicating the intrachain complexation. Figure 6 shows that at higher [Ca\(^{2+}\)] concentrations, \((R_h)_{\text{max}}\) increases sharply as [Ca\(^{2+}\)] increases, revealing a Ca\(^{2+}\)-induced transition between the intrachain and interchain complexations. The [Ca\(^{2+}\)] concentration at which \((R_h)_{\text{max}}\) starts to increases is defined as the aggregation concentration [Ca\(^{2+}\)]\(_{agg}\).
chains under different experimental conditions.

Figure 9. Schematic of the self-complexation of the HPAM chains under different experimental conditions.

Figure 10. Double logarithmic plots of the weight average molar mass ($M_w$) vs the average hydrodynamic radius ($R_h$) for the HPAM5 chains in the presence of different amounts of Ca$^{2+}$ ions.

These clusters further collide with each other or with individual HPAM chains, leading to larger clusters. Finally, when either Ca$^{2+}$ ions or $-COO^-$ groups are consumed, the complexation stops. In the process, clusters with different size were formed as shown in Figure 2. Note that the intrachain $-COO^-$ groups are closer than those interchain $-COO^-$ groups. For the HPAM chains with a low hydrolysis degree in the presence of small amounts of Ca$^{2+}$ ions, the intrachain complexation is expected to be easier, while in the case of a high hydrolysis degree and a high Ca$^{2+}$ concentration, the interchain complexation becomes dominant, as shown schematically in Figure 9. In the medium range of [Ca$^{2+}$] and [-COO$^-$], the HPAM chains first undergo the intrachain complexation through the neighboring carboxylic acid groups on the same chain before the interchain complexation becomes apparent.

Figure 10 shows double logarithmic plots of the weight average molar mass ($M_w$) of the HPAM/Ca$^{2+}$ complexes vs their average hydrodynamic radius ($R_h$) for a given HPAM sample but different Ca$^{2+}$ concentrations. Figure 11 shows double logarithmic plots of $M_w$ vs ($R_h$) for a given Ca$^{2+}$ concentration but different HPAM samples, where the values of $M_w$ were calculated from the measured Rayleigh ratio on the basis of eq 1. It should be stated that the ratio of $(R_g)/(R_h)$ was close to a constant of ~1.35 in the measurable range of $(R_g)$. Figures 10 and 11 clearly demonstrate that $M_w$ can be scaled to $(R_h)$, i.e., $M_w \propto (R_h)^{2.11 \pm 0.04}$, for different Ca$^{2+}$ concentration and different HPAM samples. This suggests that the HPAM/Ca$^{2+}$ complexes have a fractal structure with a dimension of $d_f = 2.11 \pm 0.04$, which is in a good agreement with the value predicted for RLCA.$^{32,33}$

Figure 11 shows double logarithmic plots of the scattering intensity $I(q)$ vs the scattering vector $q$ for the HPAM5 chains in two different CaCl$_2$ aqueous solutions after the maximum complexation was reached. The slope of $\sim 2$ also indicates that the HPAM/Ca$^{2+}$ complexes have a fractal structure.

In summary, a systematic study of the self-complexation of partially hydrolyzed poly(acrylamide) (HPAM) chains in CaCl$_2$ aqueous solution at 25 °C shows, for the first time, that there is a transition between the intrachain and interchain complexations. The complexation can be well controlled by both the hydrolysis degree and Ca$^{2+}$ concentration. For a given HPAM sample, there exists a Ca$^{2+}$ concentration ([Ca$^{2+}$]) at which the interchain complexation becomes dominant and the size of the complexes increases as [Ca$^{2+}$] increases. On the other hand, for a given Ca$^{2+}$ concentration, the size of the complexes increases as the hydrolysis degree increases. The HPAM/Ca$^{2+}$ complexes have a fractal structure with a dimension of 2.11 ± 0.04, indicating that the self-complexation is a reaction-limited cluster aggregation process.

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References and Notes

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