

# Comparison of the $\text{Ca}^{2+}/\text{COO}^-$ Complexation Induced Controllable Aggregation of P(VCL-co-NaA) Spherical Microgels and Linear Chains

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*Received March 1, 2001; Revised Manuscript Received May 21, 2001*

**ABSTRACT:** The  $\text{Ca}^{2+}/\text{COO}^-$  complexation induced aggregation of poly(*N*-vinylcaprolactam-co-sodium acrylate) (P(VCL-co-NaA)) spherical microgels as well as linear chains under different conditions, such as the  $\text{Ca}^{2+}$  concentration, the  $\text{COO}^-$  content, and the aggregation temperature, was studied by a combination of static and dynamic laser light scattering. Using thermally sensitive P(VCL-co-NaA) enabled us to vary the chain conformation and the sticking efficiency of two collided spherical microgels or linear chains by temperature, so that the aggregation was controllable and reversible. The time evolution of both the weight-average molar mass ( $M_w$ ) and the average hydrodynamic radius ( $\langle R_h \rangle$ ) of the aggregates was simultaneously recorded. It showed that for the microgel aggregates  $M_w$  could be scaled to  $\langle R_h \rangle$  as  $M_w \propto \langle R_h \rangle^{d_f}$  and the average scattering intensity  $I(q)$  varied with the scattered vector  $q$  as  $I(q) \propto q^{-d_q}$  with  $d_f$  and  $d_q$  in the range 1.6–1.9, indicating a diffusion-limited process, while for the chain aggregates, both  $d_q$  and  $d_f$  decreased from  $\sim 2.5$  to  $\sim 1.6$  as the aggregation temperature increased from 32.5 to 50 °C, revealing, for the first time, that the structure of the resultant aggregates depends on the initial chain conformation. For both spherical microgels and linear chains, the aggregation rate and the aggregate size increased with the  $\text{Ca}^{2+}$  concentration, but the structures of the resultant aggregates remained.

## Introduction

The cation induced aggregation of colloid particles in a dispersion or polyelectrolytes chains in a solution is not only fascinating and interesting in basic research but also important in many applications,<sup>1</sup> such as the production of chemical toners, the treatment of wastewater, and the making of membrane filters. Numerous theoretical<sup>2–5</sup> and experimental<sup>6–9</sup> efforts have been devoted to the formation and structure of colloidal aggregates. Two limiting regimes have been identified as the diffusion-limited cluster–cluster aggregation (DLCA) and the reaction-limited cluster–cluster aggregation (RLCA).<sup>10,11</sup> One of distinctive features between DLCA and RLCA is different fractal dimensions ( $d_f$ ) of the resultant aggregates,<sup>12</sup> 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 the formation of aggregates with an open and less uniform structure and  $d_f \sim 1.75$ –1.80 for a three-dimensional system. The kinetics of DLCA is characterized by a power law  $R \sim t^\alpha$  with  $\alpha < 1$ , where  $t$  is the aggregation time.<sup>13</sup> On the other hand, the sticking probability in RLCA is so low that a number of collisions can only result in one sticking. The RLCA process often happens in hyperbranching polymerization. Experimental observation<sup>14</sup> and the computer simulations<sup>15,16</sup> have revealed a higher fractal dimension in the range  $\sim 2.0$ –2.5; namely, the aggregates have a more uniform structure because when a microgel collides with an aggregate, it can penetrate into the

“fjords” of the aggregate before they stick together.<sup>17</sup> Weitz et al.<sup>13</sup> suggested that the RLCA process follows an exponential kinetics, i.e.,  $R \sim e^{At}$ , where  $A$  is a constant, depending on the dispersion studied. A combination of different scattering techniques provides a possibility to study the formation and structures of colloidal aggregates over a wide size range.<sup>18–22</sup>

The study has been extended to the complexation of biopolymers because of its implications in ecology, biotechnology, and medicine.<sup>23,24</sup> In this aspect, the aggregation and complexation of much better defined synthetic polyelectrolytes can be used as a minimal representation of various processes related to biopolymers. The association kinetics and interaction mechanism of synthetic polyelectrolytes have been extensively studied.<sup>25–27</sup> 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.<sup>28,29</sup> It was suggested that the distribution of ionic groups on the chain backbone had no effect on the complexation.<sup>30</sup> Unfortunately, most of the past studies were conducted in a poorly controlled and irreversible fashion. To our knowledge, the influence of initial chain conformation on the formation and structure of the aggregates has not been thoroughly investigated.

In the present study, using thermally sensitive poly(*N*-vinylcaprolactam-co-sodium acrylate) (P(VCL-co-NaA)), we can use temperature to alter the chain conformation from coil to globule without changing the degree of ionization and the chain length. This is because PVCL is hydrophilic and soluble in water at the room temperature and gradually becomes hydrophobic and insoluble when the temperature increases from  $\sim 25$  to  $\sim 35$  °C.<sup>31</sup> The copolymerization of a few percent of NaA into PVCL makes the chain more hydrophilic. When the temperature is lower than  $\sim 30$  °C, PVCL is so hydrophilic that the strength of the

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complexation between  $\text{Ca}^{2+}$  and  $\text{COO}^-$  groups is not sufficient to pull different microgels or chains together. As the temperature increases, the balance between hydrophilic solvation and hydrophobic attraction is gradually broken so that the complexation leads to intrachain contraction and interchain aggregation. A comparative study of the complexation induced aggregation of P(VCL-co-NaA) spherical microgels and linear chains is conducted by using a combination of static and dynamic laser light scattering (LLS). The influence of temperature, charge density, and cation concentration on the formation and structures of the aggregates was studied.

## Experimental Section

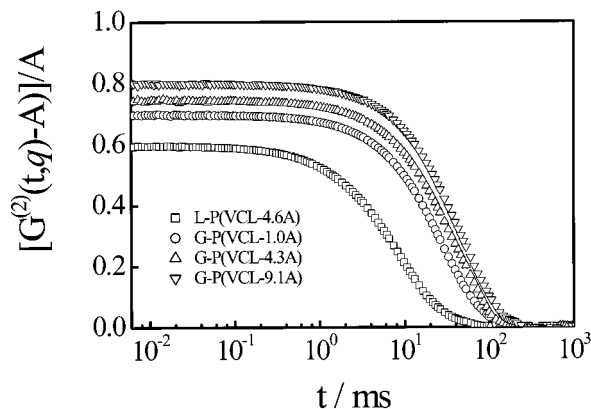
**Materials.** *N*-Vinylcaprolactam monomer (VCL, courtesy of BASF, Germany) was purified by reduced pressure distillation. Sodium acrylate monomer (NaA, from Lancaster) was used without further purification. Potassium persulfate as initiator (KPS, from Aldrich) and *N,N'*-methylenebis(acrylamide) as cross-linking agent (MBAA, from Aldrich) were recrystallized three times in methanol. Calcium chloride (anhydrous  $\text{CaCl}_2$ , from ACROS) was used without further purification.

**Sample Preparation.** Spherical poly(*N*-vinylcaprolactam-co-sodium acrylate) microgels were prepared by precipitation polymerization. Into a 150 mL three-neck flask equipped with a reflux condenser, a thermometer, and a nitrogen-bubbling tube were added VCL monomer (7.3 mmol), NaA comonomer, MBAA cross-linking agent (0.18 mmol), and deionized water (40 mL). The solution was stirred and bubbled by nitrogen for 1 h to remove oxygen before adding an aqueous solution of KPS (0.05 mmol) to start the polymerization at 60 °C for 24 h. The resultant P(VCL-co-NaA) microgels were purified by a successive four cycles of centrifugation (Sigma 2K15 ultracentrifuge, at 15 300 rpm and 40 °C), decantation, and redispersion in deionized water to remove unreacted low molar mass molecules. Three different kinds of microgels were prepared. On average, they contained 1.0, 4.3, and 9.1 mol % acrylic groups, denoted as G-P(VCL-1.0A), G-P(VCL-4.3A), and G-P(VCL-9.1A), respectively, where "G" stands for microgels. The weight-average molar masses of G-P(VCL-1.0A), G-P(VCL-4.3A), and G-P(VCL-9.1A) microgels were  $1.33 \times 10^9$ ,  $2.08 \times 10^9$ , and  $5.41 \times 10^9$  g/mol, respectively. The dispersions were diluted to  $1.00 \times 10^{-5}$  g/mL for the LLS study. Linear P(VCL-co-NaA) chains containing 4.6 mol % acrylic groups, denoted as L-P(VCL-4.6A), was prepared in a similar way without adding the cross-linking agent (MBAA). The weight-average molar mass of L-P(VCL-4.6A) was  $3.04 \times 10^6$  g/mol. The concentration of linear chains used in the LLS study was  $1.20 \times 10^{-5}$  g/mL.

**Laser Light Scattering.** A modified commercial light scattering spectrometer (ALV/SP-125) was used, which was equipped with a multi- $\tau$  digital time correlator (ALV-5000) and a solid-state laser (ADLAS DPY 425II, output power  $\approx 400$  mW at  $\lambda = 532$  nm). The detail of our laser light scattering spectrometer can be found elsewhere.<sup>32</sup> In static LLS, the angular dependence of the absolute excess time-averaged scattered intensity, known as the Rayleigh ratio  $R_{\text{vv}}(q)$ , is related to the weight-average molar mass ( $M_w$ ), the z-average root-mean-square radius of gyration ( $\langle R_g^2 \rangle_z^{1/2}$  or written as  $\langle R_g \rangle$ ) of the scattering objects, and the second virial coefficient ( $A_2$ ) of the dispersion or solution by

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

where  $K = (4\pi^2 n_1^2 / \lambda_0^4 N_A) (dn/dc)^2$  is a constant and  $q = [(4\pi n_1 / \lambda_0) \sin(\theta/2)]$  is the scattering vector with  $N_A$ ,  $dn/dc$ ,  $n_1$ ,  $\lambda_0$ , and  $\theta$  being Avogadro's number, the specific refractive index increment, the refractive index of solvent, the wavelength of the light in a vacuum, and the scattering angle, respectively.



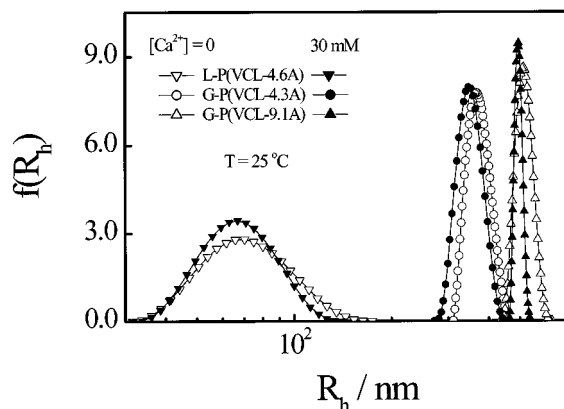
**Figure 1.** Typical measured intensity-intensity time correlation function of P(VCL-co-NaA) spherical microgels and linear chains in water at  $\theta = 15^\circ$  and  $T = 25^\circ\text{C}$ .

By measuring  $R_{\text{vv}}(q)$  of a very dilute solution at a relatively small angle, we can estimate  $M_w$ . For a fractal object made of colloid particles, the scattered intensity  $I(q)$  is scaled to  $q$  as  $I(q) \sim q^{-d_f}$  in the range of  $R_{\text{aggregate}} > q^{-1} > R_{\text{particle}}$ , where  $d_f$  is the fractal dimension;  $R_{\text{particle}}$  and  $R_{\text{aggregate}}$  are the radii of primary particles and the resultant aggregate, respectively.<sup>19</sup> When  $q^{-1} < R_{\text{particle}}$ , the light probes internal structures of primary particles, and the intensity profile reflects the density distribution inside, while when  $q^{-1} > R_{\text{aggregate}}$ , the average size of the resultant aggregates and the correlation of the topological length between the aggregates could be determined.

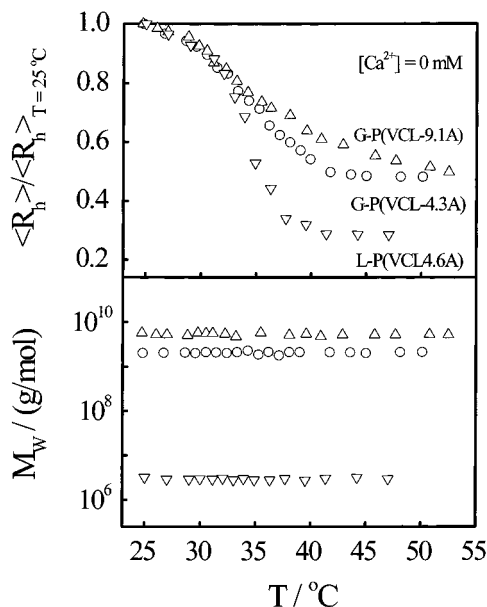
In dynamic LLS, the cumulant or Laplace inversion analysis of the measured intensity-intensity time correlation function  $G^{(2)}(q, t)$  in the self-beating mode can lead to an average line width ( $\Gamma$ ) or a line width distribution ( $G(\Gamma)$ ).<sup>33,34</sup> For a pure diffusive relaxation,  $\Gamma$  can be related to the translational diffusion coefficient  $D$  via  $\Gamma = Dq^2$  at  $C \rightarrow 0$  and  $q \rightarrow 0$ <sup>35</sup> or the hydrodynamic radius ( $R_h$ ) by the Stokes-Einstein equation,  $D = k_B T / (6\pi\eta R_h)$ , where  $k_B$ ,  $T$ , and  $\eta$  are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. Therefore,  $G(\Gamma)$  can be converted to a hydrodynamic radius distribution  $f(R_h)$ . All the dynamic LLS measurements were carried out at  $15^\circ$ .

## Results and Discussion

Figure 1 shows that a typical plot of the measured intensity-intensity time correlation function for spherical microgels and linear chains in water at  $T = 25^\circ\text{C}$ . From each correlation function, we were able to calculate an average line width by using the second-order cumulants fitting or the line width distribution (or the hydrodynamic radius distribution) by the CONTIN method. Figure 2 shows typical hydrodynamic radius distributions of spherical microgels and linear chains at  $25^\circ\text{C}$  before and after adding  $\text{Ca}^{2+}$ . It shows that both microgels and linear chains are reasonably narrowly distributed. The relative distribution width ( $\mu_2 / \langle \Gamma \rangle^2$ ) for spherical microgels and linear chains are  $\sim 0.05$  and  $\sim 0.18$ , respectively. The addition of  $\text{Ca}^{2+}$  led to the shrinking of both spherical microgels and linear chains. However, it should be stated that the addition of  $\text{Ca}^{2+}$  did not alter the scattering intensity. Therefore, the shrinking of spherical microgels and linear chains can be respectively attributed to the intraparticle and intrachain  $\text{Ca}^{2+}/\text{COO}^-$  complexation. For each  $f(R_h)$ , we were able to calculate one average hydrodynamic radius  $\langle R_h \rangle$  by using  $\langle R_h \rangle = \int_0^\infty f(R_h) R_h dR_h$ . Figure 3 shows that without  $\text{Ca}^{2+}$  spherical microgels and linear chains gradually shrink as the temperature increases, but no change in molar mass, clearly indicating that there exists no interparticle or interchain aggregation even



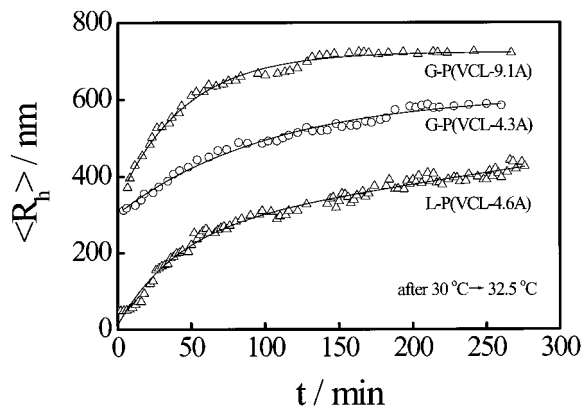
**Figure 2.** Hydrodynamic radius distributions of P(VCL-co-NaA) spherical microgels and linear chains at  $T = 25\text{ }^{\circ}\text{C}$  with and without the addition of  $\text{Ca}^{2+}$ .



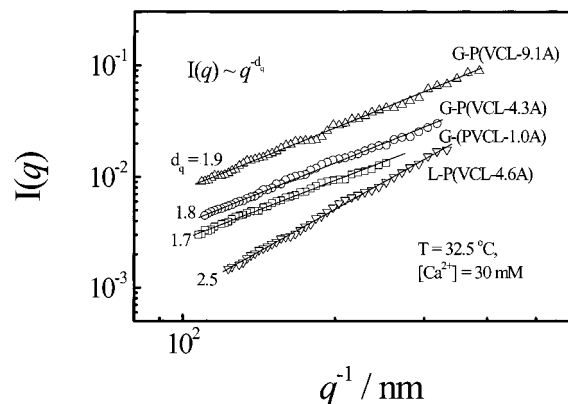
**Figure 3.** Temperature dependence of average hydrodynamic radius ( $\langle R_h \rangle$ ) of different microgels and linear chains in the absence of  $\text{Ca}^{2+}$  ions. The inset shows a corresponding temperature dependence of the weight-average molar mass  $M_w$ .

at higher temperatures. Relatively, microgels shrink less because they swell less at  $25\text{ }^{\circ}\text{C}$  due to the cross-linking. However, the situation was completely different after adding  $\text{Ca}^{2+}$ .

Figure 4 shows that the  $\text{Ca}^{2+}/\text{COO}^-$  complexation can induce an interparticle aggregation after the dispersion temperature was suddenly increased from 30 to  $32.5\text{ }^{\circ}\text{C}$ . As expected, the extent of the aggregation for a given  $\text{Ca}^{2+}$  concentration increases with the ionic content because each  $\text{COO}^-$  group acts as a "sticker" in the interparticle or interchain aggregation via the  $\text{Ca}^{2+}(\text{COO}^-)_2$  complexation. The aggregation slows down after a few hours and gradually approaches a plateau. It is worth noting that the resultant aggregates were very stable, and no precipitation was observed for a long time. For spherical microgels,  $\langle R_h \rangle$  can be scaled to  $t$  by  $\langle R_h \rangle \propto t^\beta$  with  $\beta$  in the range 0.16–0.20. However, the aggregation of linear chains has a different kinetics; namely, the increase of  $\langle R_h \rangle$  can be described by two exponential terms, representing two distinct processes. The initial fast process is related to the aggregation of individual chains and the formation of clusters, while the second slow process mainly involves the cluster–



**Figure 4.** Time dependence of average hydrodynamic radius ( $\langle R_h \rangle$ ) of the aggregates made of different spherical microgels and linear chains, where  $[\text{Ca}^{2+}] = 30\text{ mM}$  and  $T = 32.5\text{ }^{\circ}\text{C}$ .

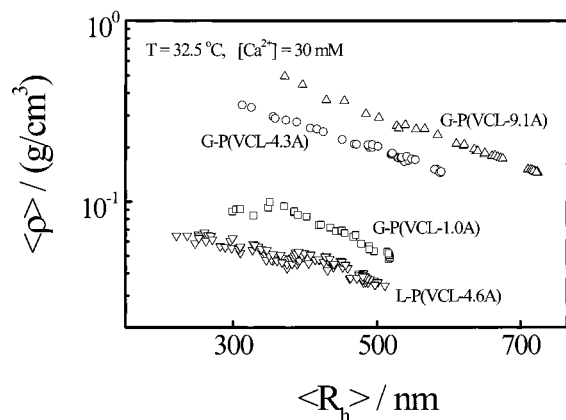


**Figure 5.** Double-logarithmic plots of scattering intensity  $I(q)$  vs scattering vector  $q$  for resultant aggregates made of different spherical microgels and linear chains, where  $[\text{Ca}^{2+}] = 30\text{ mM}$  and  $T = 32.5\text{ }^{\circ}\text{C}$ .

cluster aggregation. It should be noted that  $\langle R_h \rangle$  is a complicate parameter, and it involves not only the structure but also the hydrodynamic draining. To obtain the fractal dimension from the kinetics, one should measure the time dependence of radius of gyration ( $\langle R_g \rangle$ ). Unfortunately, the aggregation was so fast that we were not able to do it.

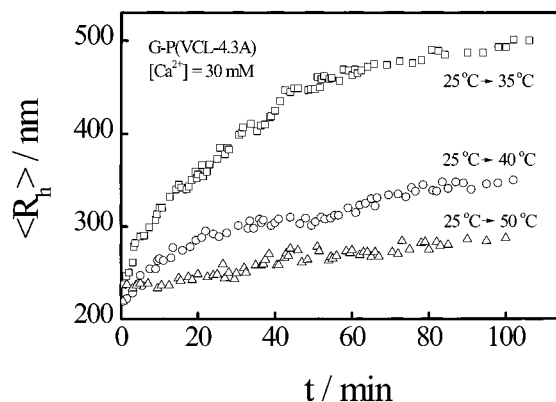
Figure 5 shows that the scattering intensity  $I(q)$  of the resultant aggregates is dependent on the scattering vector  $q$  as  $I(q) \propto q^{-d_q}$  with  $d_q = 1.7\text{--}1.9$  for spherical microgels and  $d_q = 2.4\text{--}2.5$  for linear chains, indicating that the aggregation of spherical microgels follows the DLCA process, but the aggregation of linear chains might be described by the RLCA mechanism. For spherical microgels, the slight decrease of  $d_q$  as the  $\text{COO}^-$  content increases indicates that the structure of the aggregates made of microgels with less  $\text{COO}^-$  groups is relatively more open and less uniform. Note that  $d_q$  for linear P(VCL-co-NaA) chains is higher than  $\sim 2.0\text{--}2.2$  observed in the aggregation/association of other linear chains, such as in the HPAM/ $\text{Ca}^{2+}$  system.<sup>14</sup> This is because, in addition to the interpenetration of different chains, the collapse of PVCL at higher temperatures leads to a more uniform structure. The packing of spherical microgels or linear chains in the resultant aggregates can be better viewed in terms of the size dependence of the average chain density ( $\rho$ ) defined as  $M_w / [(4/3)\pi \langle R_h \rangle^3]$ .

Figure 6 shows that during the aggregation ( $\rho$ ) decreases as the aggregation proceeds, clearly indicating



**Figure 6.** Aggregate size dependence of average chain density  $\langle \rho \rangle$  for different spherical microgels and linear chains, where  $[\text{Ca}^{2+}] = 30 \text{ mM}$  and  $T = 32.5^\circ\text{C}$ .

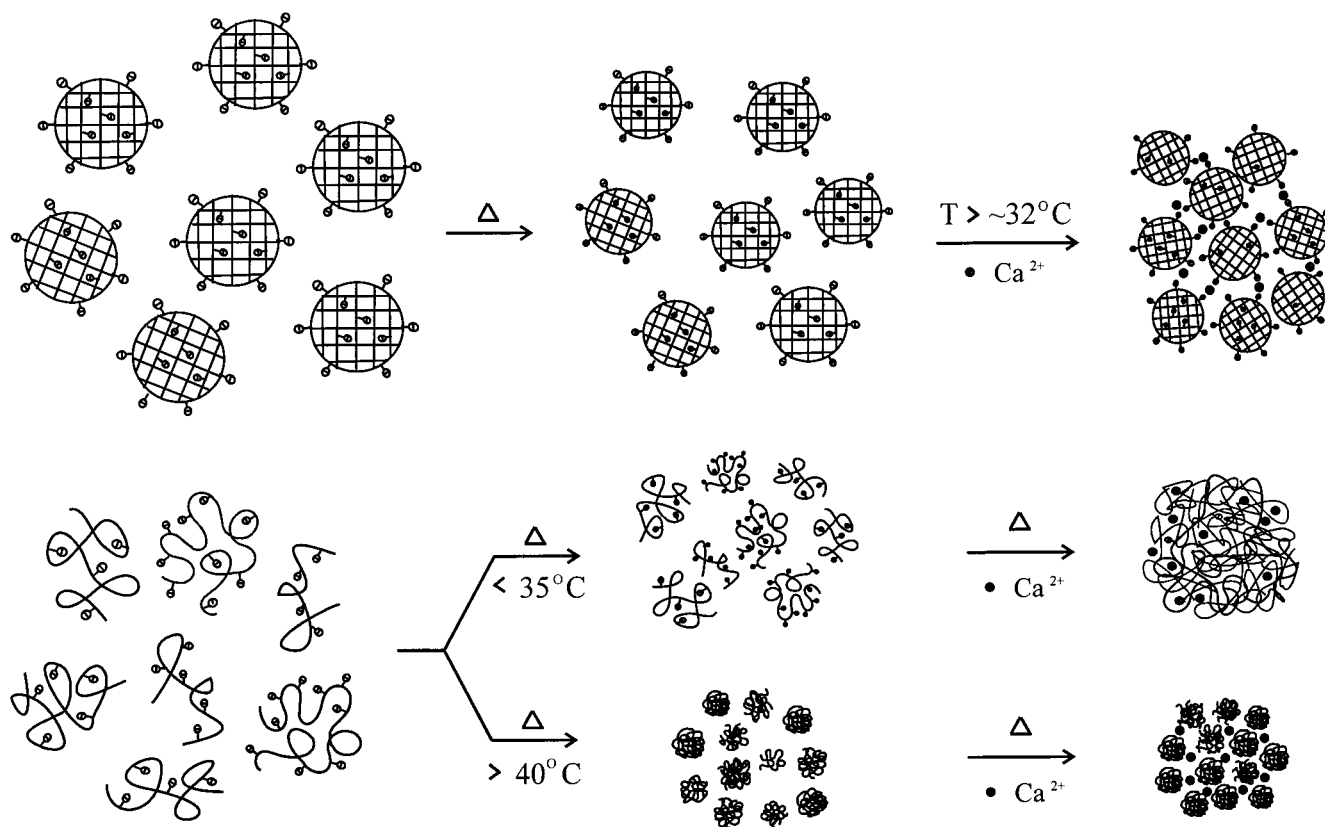
that the aggregates become loose and less uniform. Unfortunately,  $\langle \rho \rangle$  and  $\langle R_h \rangle$  only spread over a limited range. A combination of Figures 5 and 6 shows that for a given size the aggregates made of microgels have a lower  $d_q$  and chain density. It also shows that the aggregates made of linear chains have a much lower chain density but a higher  $d_q$ . This is because, in comparison with the microgels, there are no chemical cross-linking among different chains in the aggregates made of linear chains. Therefore, the interchain distance inside is larger so that the chain density is lower. Thermodynamically, there should be an entropy penalty when individual microgels are stick together, but the intertwining and knotting of linear chains could lead to a possible entropy gain. It is expected that the enthalpy change in the formation of each  $\text{Ca}^{2+}(\text{COO}^-)_2$



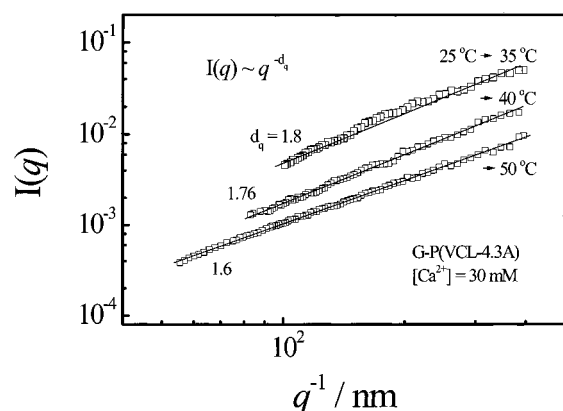
**Figure 8.** Time dependence of average hydrodynamic radius  $\langle R_h \rangle$  of microgel aggregates formed after the dispersion temperatures were suddenly increased to different aggregation temperatures.

complex is a constant. Therefore, the increase of entropy makes a process more favorable. Figure 7 shows a schematic of the  $\text{Ca}^{2+}/\text{COO}^-$  complexation induced aggregation of spherical microgels and linear chains at higher temperatures. The difference in the linear chain aggregation at different temperatures is presented and discussed as follows.

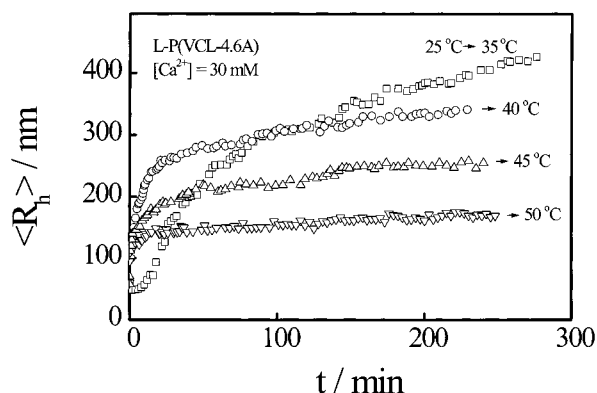
Figure 8 shows that for a given  $\text{Ca}^{2+}$  concentration the growth of  $\langle R_h \rangle$  is less pronounced as the aggregation temperature increases. This is different from what we expected. Originally, we thought that PVCL at a higher temperature was more hydrophobic so that the aggregation should be enhanced. However, we forgot that PVCL collapses more at a higher aggregation temperature. After a sudden temperature increase, individual microgels collapse before they have a chance to be stuck



**Figure 7.** Schematic of  $\text{Ca}^{2+}/\text{COO}^-$  complexation induced aggregation of thermally sensitive P(VCL-co-NaA) spherical microgels and linear chains at higher temperatures.



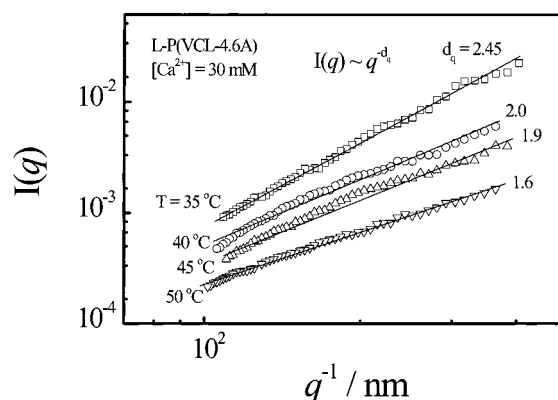
**Figure 9.** Double-logarithmic plots of scattering intensity  $I(q)$  vs scattering vector  $q$  for resultant microgel aggregates formed at different aggregation temperatures.



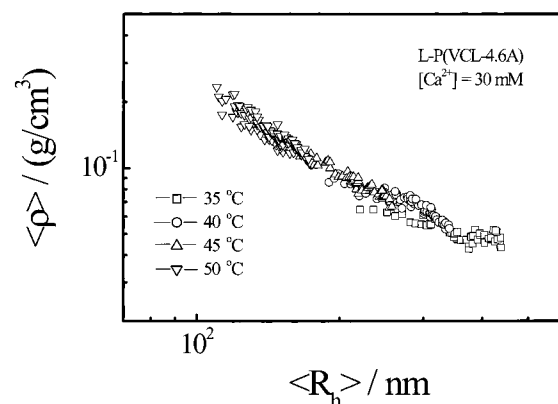
**Figure 10.** Time dependence of average hydrodynamic radius  $\langle R_h \rangle$  of linear chain aggregates formed after the solution temperatures were suddenly increased to different aggregation temperatures.

together by  $\text{Ca}^{2+}$ . The higher the temperature, the faster the collapse. It is expected that in a fast shrinking process more  $\text{COO}^-$  groups are trapped inside, so that the number of effective  $\text{COO}^-$  groups on the periphery decreases. Therefore, the binding probability between two collided microgels reduces. Further, we should consider the surface curvature of collapsed microgels. For less collapsed microgels, the surface is relatively flat so that two microgels can be stuck together via more  $\text{Ca}^{2+}(\text{COO}^-)_2$  complexation points, resulting in a stronger binding. For fully collapsed microgels, the surface curvature limits the number of the complexation between two microgels. Figure 9 shows that  $I(q)$  is scaled to  $q$  as  $I(q) \propto q^{-d_q}$  with  $d_q$  in the range 1.6–1.8. The slight decrease of  $d_q$  as the temperature increases reveals that the aggregates formed at higher temperatures are relatively more open and less uniform.

In comparison, Figure 10 shows the aggregation of linear chains at different temperatures. As in the case of microgels, the resultant aggregates become smaller when the temperature is higher. At 35 °C, there exists a short initial induction period in which there is no apparent interchain aggregation. Figure 11 shows a corresponding scaling between  $I(q)$  and  $q$  for the resultant aggregates made of linear chains.  $d_q$  decreases as the aggregation temperatures increase. At 45 and 50 °C,  $d_q$  is similar to those observed in the aggregation of spherical microgels. Note that the complexation of linear chains could be either intrachain or interchain. The intrachain complexation leads to the chain contraction,



**Figure 11.** Double-logarithmic plots of scattering intensity  $I(q)$  vs scattering vector  $q$  for resultant linear chain aggregates formed at different aggregation temperatures.

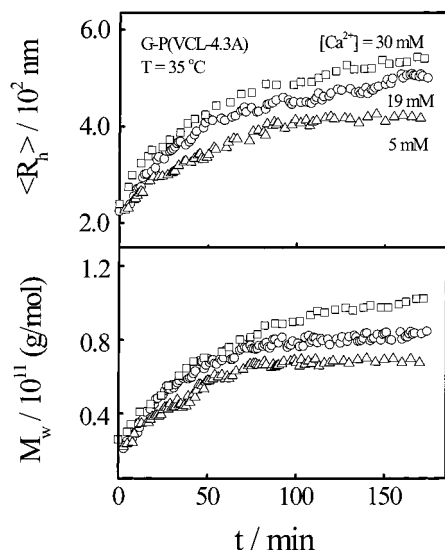


**Figure 12.** Double-logarithmic plots of aggregate size dependence of average chain density  $\langle \rho \rangle$  vs average hydrodynamic radius  $\langle R_h \rangle$  for resultant linear chain aggregates formed at different aggregation temperatures.

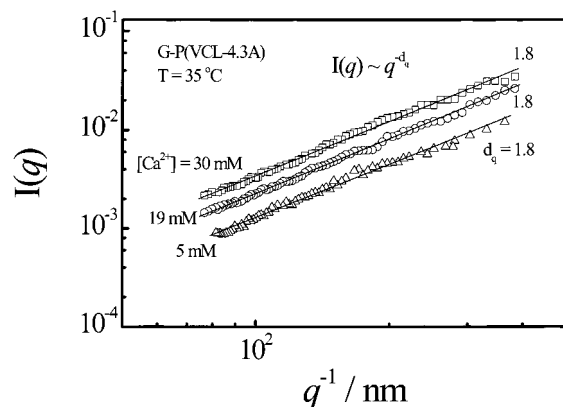
and only the interchain complexation results in the aggregation. The two processes always compete in a real experiment. At a lower aggregation temperature, individual crumpled chains are able to interpenetrate each other to form a more uniform structure. As the aggregation temperature increases, the collapse of individual chains becomes so fast that individual chains have less chance to undergo the interchain complexation in a dilute solution. Therefore, the complexation at higher temperatures mainly happens between highly collapsed small clusters, similar to the complexation between those collapsed microgels. Therefore, less interchain penetration occurs at higher temperatures, as illustrated in Figure 7.

Figure 12 reveals that, despite different values of  $d_f$  shown in Figure 11, the plots of  $\langle \rho \rangle$  vs  $\langle R_h \rangle$  for different temperatures collapse together. It is clear that in the initial stage small linear chain aggregates formed at 35 °C have a lower chain density. This is because linear chains were not fully collapsed at 35 °C, and the interpenetration of different chains at the initial stage was less. At higher temperatures, linear chains were more collapsed so that as the aggregation temperature increases, the chain density increases, but the size of the aggregates decreases, supporting the results in Figure 10, namely, a higher aggregation temperature leads to the aggregates with a more open and less uniform structure.

Figure 13 shows that, for the aggregation of microgels at 35 °C, the aggregation rate and the size and molar



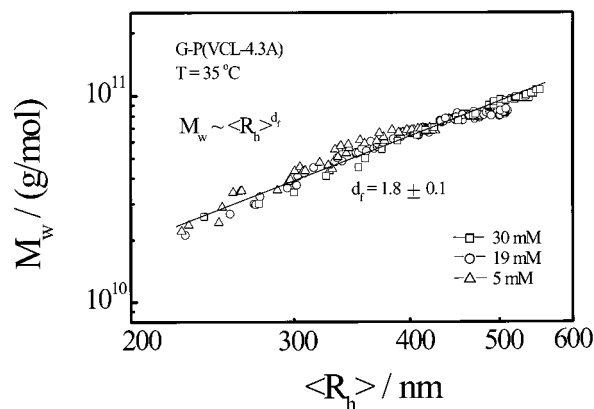
**Figure 13.** Temperature dependence of average hydrodynamic radius  $\langle R_h \rangle$  and weight-average molar mass  $M_w$  of microgel aggregates formed in the presence of different amounts of  $\text{Ca}^{2+}$ .



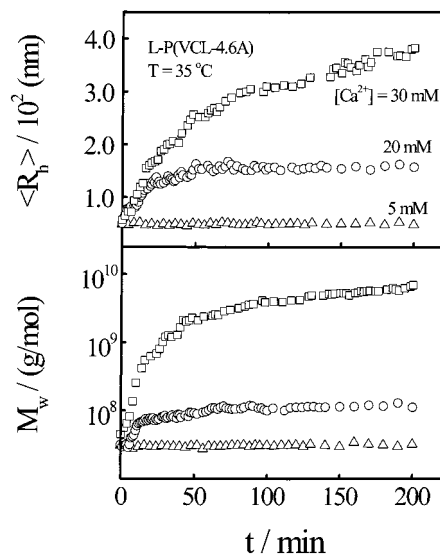
**Figure 14.** Double-logarithmic plots of scattering intensity  $I(q)$  vs scattering vector  $q$  for resultant microgel aggregates formed in the presence of different amounts of  $\text{Ca}^{2+}$ .

mass of the resultant aggregates increase with the  $\text{Ca}^{2+}$  concentrations. This is because more  $\text{Ca}^{2+}$  ions can enhance the sticking probability of two collided microgels via the  $\text{Ca}^{2+}/\text{COO}^-$  complexation. However, a similar scaling of  $I(q)$  vs  $q$  shown in Figure 14 reveals that the structure of the resultant aggregates is independent of the  $\text{Ca}^{2+}$  concentration. The aggregation at  $35^\circ\text{C}$  leads to a structure with  $d_f$  in the range 1.7–1.9, which agrees well with the DLCA model. Figure 15 shows that the plots of  $M_w$  vs  $\langle R_h \rangle$  in the presence of three different amounts of  $\text{Ca}^{2+}$  ions collapse into a single line of  $M_w \propto \langle R_h \rangle^{d_f}$  with  $d_f = 1.8 \pm 0.1$ , further indicating that the  $\text{Ca}^{2+}$  concentration has no influence on the structure of the resultant aggregates. A combination of Figures 13–15 shows that, despite different aggregation rates and the aggregate sizes, the aggregation mechanism and the aggregate structure are not influenced by the cation concentration as long as the ratio of  $[\text{Ca}^{2+}]/[\text{COO}^-]$  is much higher than the stoichiometric ratio (1:2).

In comparison, Figure 16 shows that for linear chains both the complexation rate and the aggregate size also increase with the  $\text{Ca}^{2+}$  concentration. Note that when  $[\text{Ca}^{2+}] = 5 \text{ mM}$ , there is no apparent interchain complexation even though the ratio of  $[\text{Ca}^{2+}]/[\text{COO}^-]$  is



**Figure 15.** Double-logarithmic plots of weight-average molar mass  $M_w$  vs average hydrodynamic radius  $\langle R_h \rangle$  of resultant microgel aggregates formed in the presence of different amounts of  $\text{Ca}^{2+}$ .

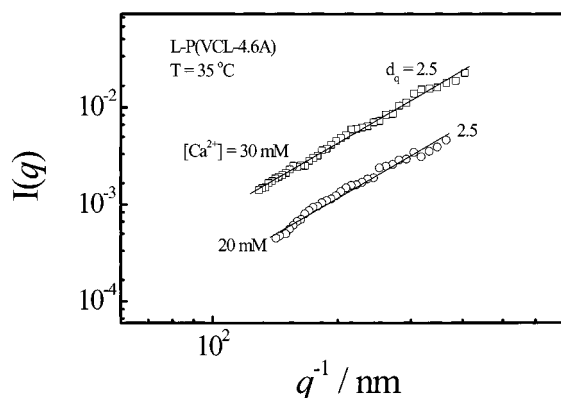


**Figure 16.** Time dependence of average hydrodynamic radius  $\langle R_h \rangle$  and weight-average molar mass  $M_w$  for resultant linear chain aggregates formed in the presence of different amounts of  $\text{Ca}^{2+}$ .

already hundreds times higher than the stoichiometric one (1:2). In comparison with the aggregation of spherical microgels under the same conditions, the  $\text{Ca}^{2+}/\text{COO}^-$  complexation induced aggregation of linear chains is less effective. Note that at  $35^\circ\text{C}$  each linear chain is not fully collapsed, and the  $\text{COO}^-$  groups are uniformly distributed in its hydrodynamic volume, while the shrinking of microgels forces more  $\text{COO}^-$  groups on surface. Therefore, it is much easier for two collided microgels to stick together. Figure 17 shows that the scaling of  $I(q)$  to  $q$  is similar, revealing that the structure of the resultant aggregates is also not affected by the  $\text{Ca}^{2+}$  concentration. The higher fractal dimension  $d_f$  of the linear chain aggregates has been discussed before.

## Conclusions

We have shown that the  $\text{Ca}^{2+}/\text{COO}^-$  complexation induced aggregation of thermally sensitive poly(*N*-vinylcaprolactam-co-sodium acrylate) spherical microgels is essentially governed by the diffusion-limited cluster–cluster aggregation (DLCA) mechanism, leading to the aggregates with a fractal dimension  $d_f$  in the range 1.7–1.9. The chain density of the resultant aggregates increases with the sodium acrylate content.



**Figure 17.** Double-logarithmic plots of scattering intensity  $I(q)$  vs scattering vector  $q$  for resultant linear chain aggregates in the presence of different amounts of  $\text{Ca}^{2+}$ .

The increase of  $\text{Ca}^{2+}$  concentration can speed up the aggregation and result in larger aggregates but has no influence on the aggregation mechanism and the aggregate structure. We also found that the fractal dimension and the chain density of the resultant aggregates slightly decreased as the aggregation temperature increased. As for poly(*N*-vinylcaprolactam-co-sodium acrylate) linear chains, the situation is more complicated because the chain conformation varies with the aggregation temperature. We have revealed, for the first time, that the fractal dimension of linear chain aggregates was dependent on the initial chain conformation. At a relatively lower aggregation temperature, the contraction of individual chains was accompanied by an extensive interchain penetration and aggregation. The resultant aggregates are more uniform. As the aggregation temperature increases, the collapse of individual chains is much faster they have less chance to undergo the interchain aggregation. Therefore, the  $\text{Ca}^{2+}/\text{COO}^-$  complexation mainly happens between highly collapsed small clusters, resulting in a more open and less uniform structure, similar to that formed in the aggregation of spherical microgels. The fractal dimension of the resultant linear chain aggregates decreases from 2.5 to 1.6 as the aggregation temperature increases from 35 to 50 °C.

**Acknowledgment.** The financial support of the Special Funds for Major State Basic Research Projectors (G1999064800), the CAS Bai Ren Project, the NNSFC projector (29974027), and the HKSAR Earmarked RGC Grants (CUHK 4266/00P, 2160135) is gratefully acknowledged.

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MA010376C