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Studies of aggregation kinetics of polystyrene latices sterically stabilized by poly(*N*-isopropylacrylamide)

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The aggregation of polystyrene latices sterically stabilized by poly(*N*-isopropylacrylamide) has been studied using dynamic light scattering. The time dependence of the aggregate growth could be monitored under appropriate experimental conditions. The measured fractal dimension was found to increase with an increase in the aggregation rate and in the salt concentration, as well as the temperature. These unexpected observations do not conform to the predictions of the current models for aggregation of electrostatically stabilized particles. It was also inferred that the restructuring process was different from that reported in the literature. The hydrophobic interaction (or hydration), which is controlled by the salt concentration and temperature, is believed to play a crucial role in the present system in the aggregation process and in the nature of the aggregate structures formed. The results indicate that the fractal dimension increases with an increase in the hydrophobic interaction, i.e., with a decrease in the interparticle interaction energy. This is in good agreement with the predictions of the computer simulations of Shih, Aksay, and Kikuchi [Phys. Rev. A **36**, 5015 (1987)].

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I. INTRODUCTION

The aggregation of colloidal particles is an important phenomenon in physics, chemistry, biology, medicine, and engineering. Many studies [1–7] of this area, both theoretical and experimental, have been undertaken in recent times. Although the reasons for aggregation are complex and vary from one system to another due to different physical or chemical origins, it is now generally accepted that there are two limiting regimes of aggregation: (i) diffusion-limited cluster aggregation (DLCA), in which every collision between particles results in the formation of a permanent contact, and (ii) reaction-limited cluster aggregation (RLCA), in which only a small fraction of particle collisions leads to the formation of a contact. A fast aggregation process, in which the particles or clusters stick to each other upon contact as a result of diffusion, results in a loose, ramified structure with a fractal dimension of 1.78, in conformity with the predictions of the DLCA model. On the other hand, a slow aggregation process, in which more than one collision is required for particles and clusters to form permanent contacts, yields a more compact structure with a fractal dimension of 2.1, as predicted by the RLCA model. Although these two models have different values for the fractal dimension and different behavior for the kinetics of growth, both theory and experiment have shown that the two models share a common feature in that during the growth process, clusters are randomly positioned in space and there is no correlation between clusters at any time. The DLCA and RLCA models are also limited to certain ideal conditions. Both theory and experiment [8–11] have indicated that other regimes, which can be described as crossovers between DLCA and RLCA, exist. With respect to the relative mobility of aggregates, two limits exist: (i) particle-cluster aggregation [12], in which only the individual particles that come to make up aggregates are allowed to diffuse, i.e., aggregates grow by the addition of individual particles, and (ii) cluster-cluster aggregation [6,7], in which both individual particles and all of the aggregates are allowed to undergo diffusion and adhere to one another on collision. In the latter model, aggregates grow via the collision of two aggregates of any size. Furthermore, it has been found that in a fast aggregation process, aggregate structures with an initially lower fractal dimension of 1.75 can restructure after a certain time to more compact clusters with a higher fractal dimension 2.1 [13] or 2.4 [14]. The contact of aggregates in this case is considered to be reversible so that they can loosen and reform repeatedly after the first collision. Such a process would reach a steady-state distribution of aggregate structures. Shih, Aksay, and Kikuchi [15] (SAK) have studied by computer simulations the effects of energetic considerations on the restructuring of colloidal aggregates. They concluded that in a colloidal system with a finite interparticle attractive energy, the ramified aggregates would become more compact with time. Accordingly, the fractal dimension would increase with a decrease in the absolute magnitude of the interparticle attractive energy. Recently, Liu *et al.* [16] have reported that, for gold particles with finite interparticle attraction energies, the fractal dimension of aggregates varied from 1.75 to 2.7, depending on the surfactant concentration. Their observations are in good agreement with theoretical predictions of SAK.

Although aggregation behavior is now understood reasonably well, some questions remain open. For example, if hydrophobic solutes are introduced onto the surface of the particles, how does the hydrophobic interaction or hydration influence the aggregation kinetics and, in particular, the aggregate structures? Is there a restructuring process operative in that type of system? If so, how does the fractal dimension change with the experimental conditions, such as the salt concentration, temperature, and time? Experimental data along these lines are still lacking.

In this paper, we report studies of the aggregation of polystyrene latex particles sterically stabilized by poly(*N*-isopropylacrylamide) (PNIPAM) in water. Aggregation was induced in two ways: (i) by the addition of an electrolyte at a fixed temperature, and (ii) by a change in temperature at a fixed salt concentration. Some characteristics of the system studied deserve mention at this point. First, it is assumed that there is no charge on the surface of core particles so that the particles are sterically, not electrostatically, stabilized as in previous studies. This means that the forces that are responsible for controlling the aggregation kinetics have been changed. Second, a polymer containing hydrophobic moieties is introduced into the interfacial layers of the particles, as well as amide groups capable of H bonding with water. The latter is very sensitive to both the salt concentration and the temperature [17,18]. The latter is manifest by the temperature of the PNIPAM coil-to-globule transition on the surface of polystyrene latex being observed on heating to about 31 °C in pure water [19].

II. EXPERIMENT

N-isopropylacrylamide (NIPAM) (monomer-polymer) was purified by recrystallization from a 65%-35% mixture of hexane and benzene. Styrene (AJAX Chemicals) was distilled at 55 °C under reduced pressure. H_2O_2 (BDH Chemicals) and $FeCl_2$ (Merck) were used as received. Azobisisobutyronitrile (AIBN, Fluka) was recrystallized. Water was doubly distilled.

The latex studied was prepared as follows. NIPAM (5 g) was polymerized at 65 °C in a 70%-30% benzene-acetone mixture (100 ml) using AIBN (0.5%) as the initiator under positive nitrogen pressure for about 20 h. The solvents were evaporated in a vacuum at room temperature. The resulting solid was crushed, vacuum dried, and then dissolved in the acetone. Poly(*N*-isopropylacrylamide) (PNIPAM) was obtained from precipitation by dropwise addition of the solution of hexane and was vacuum dried. The molecular weight of the PNIPAM sample was measured viscometrically in water at 25 °C and was found to be 3.6×10^5 as calculated from the Mark-Houwink equation [20]: $[[\eta]\ (\text{ml}\,\text{g}^{-1})]=2.26\times10^{-4}M^{0.97}$. Graft polymerization of PNIPAM (1.5 g) onto the styrene latex was accomplished by the slow addition ($\sim$40 min) of styrene (0.5 g) in the presence of redox initiator H_2O_2 $(5\times10^{-4}M)$–$FeCl_2$ $(3.5\times10^{-4}M)$ to yield a clear solution. Styrene (4.5 g) was then added quickly (<1 min) along with additional initiator (to final concentration of $2.5\times10^{-6}M$). After about 20 h, the latex was filtered and dialyzed by repeated changes using freshly distilled water for about 3 days. Nongrafted PNIPAM was removed by careful centrifugation and decantation of the supernatant. The latex particles were dispersed in doubly distilled water and filtered using 0.45 μm millipore.

The diameter of the core polystyrene particles was determined by transmission electron microscopy to be 140 nm, as shown in Fig. 1(b). The dynamic light scattering (DLS) measurements were performed at a particle concentration of about 5×10^{-5} (g/ml) with an argon ion laser operating at a scattering angle of $\theta=90°$ and a wavelength of $\lambda=488$ nm with a power of 150 mW. The autocorrelation function $G(\tau)$ was measured using a 4700*c* correlator. The diameter of sterically stabilized particles was determined by DLS in water at 25 °C to be 180 nm. A schematic illustration of the particles in water is shown in Fig. 1(a).

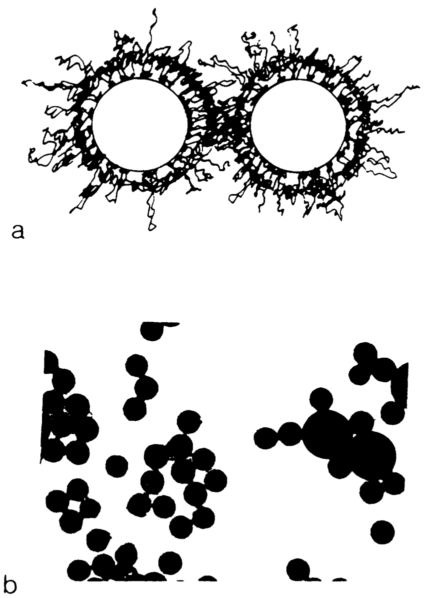

FIG. 1. (a) Schematic illustration of the sterically stabilized particles (not to scale); (b) the transmission electron microscopy of sterically stabilized particles (the smaller ones). The bigger particles are standard polystyrene samples with a diameter of 303 nm.

III. RESULTS AND DISCUSSION

Before the experiments were performed with the addition of salt, the intrinsic stability of the colloidal dispersion in pure water was checked over a period of one week by repeated measurement of the average radius with DLS. This was found to be constant, implying that there was no aggregation. Although there are many studies that show that aggregation can occur rapidly, coagulation in sterically stabilized particles may or may not occur, depending on the experimental conditions. In order to study the kinetics of salt-induced aggregation in sterically stabilized particles, we first measured the minimum salt concentration necessary to induce aggregation. Figure 2 shows the average radius measured in the system as a function of $NaNO_3$ concentration in the range from $0.001-0.64M$ at 25 °C. As seen from this figure, the average size was independent of the $NaNO_3$ concentration over a wide concentration range until the concentration increased to about $0.63M$ when it increased dramatically. The aggregation process was therefore in-

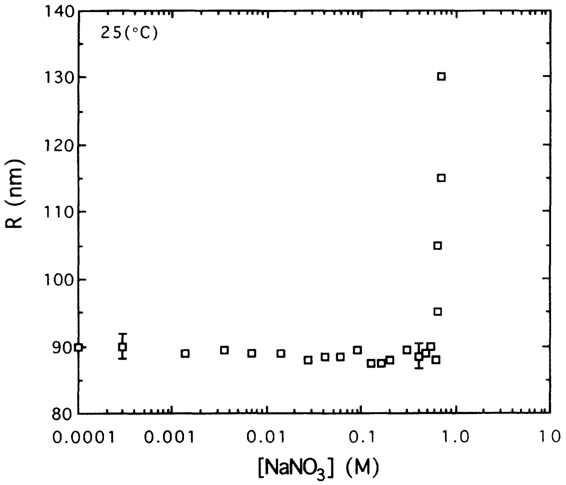

FIG. 2. Average radius R of the sterically stabilized particles as a function of NaNO$_3$ concentration at 25 °C.

vestigated in a range of electrolyte concentration above this critical value.

Figure 3 shows typical time dependencies of the average radius of aggregates after the addition of different NaNO$_3$ concentrations at 25 °C. The curves for sterically stabilized particles exhibit the same general aggregation behavior as that seen for electrostatically stabilized systems [1–5,11,21]. The rate of aggregation was found to be dependent on the salt concentration and to show different dynamic processes. From the data shown in Fig. 3, two regimes of colloid aggregation were apparent. When the NaNO$_3$ concentration was $0.66M$, slow aggregation occurred and the average aggregate radius reached was only about 130 nm in 400 min. Similar behavior was also observed at $0.74M$ electrolyte concentration. In contrast, when the NaNO$_3$ concentration was increased to $0.80M$, aggregation took place at a much faster rate. In fast aggregation, the average aggregate radius reached about 600 nm in only 60 min. It is worth noting that when salt was added, only a small increase in concentration of salt could lead to a dramatic increase in the rate of aggregate growth. In the present study, we focused on the fast aggregation process that was induced by salt concentrations in the range from $0.8-1.38M$.

It will now be assumed that in the fast aggregation process, the increase in average aggregate radius is mathematically described by the following simple power law:

$$R = R_0 t^{\beta} , \tag{1}$$

where t is time and R_0 and β are constants. The data obtained were fitted to Eq. (1) by using a least-squares regression analysis to obtain the constants R_0 and β. The straight line logarithmic plots shown in Fig. 4 imply that the power-law growth kinetics are applicable. A value for β greater than 1 indicates an autocatalytic aggregation rate while a value less than 1 indicates that the increase in rate of the average size decreases with time. The value of R_0 should physically be equal to the average

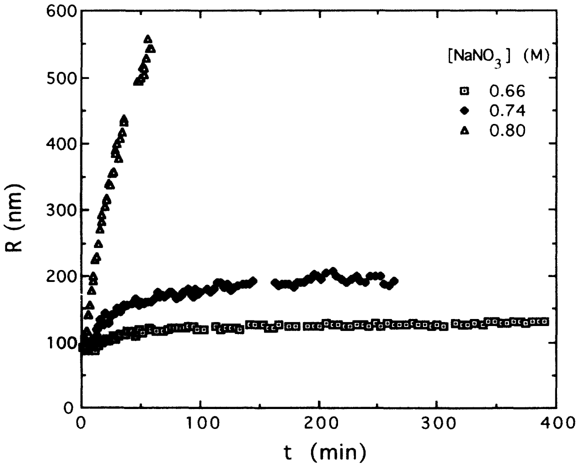

FIG. 3. Average radius R of the sterically stabilized clusters as a function of the time for different NaNO$_3$ concentrations at 25 °C.

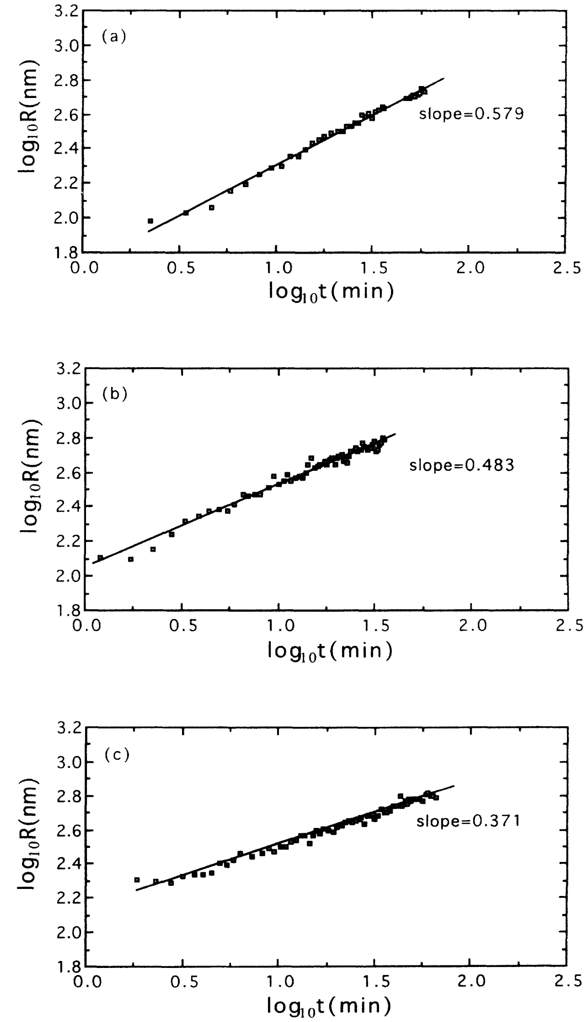

FIG. 4. Log-log plots of average radius R of the sterically stabilized clusters as a function of the time for different NaNO$_3$ concentrations: (a) $0.80M$, (b) $1.22M$, and (c) $1.38M$ at 25 °C.

aggregate size when the real time approaches zero. However, on the DLS time scale, R_0 should be thought of as a measure of average size at some arbitrary early time. In order to understand the observed behavior, it is assumed here that the growth of aggregates is due mainly to cluster-cluster aggregation and that the dispersion of cluster sizes is fairly narrow over the time studied. It is also assumed that the increase in the size of a cluster with a mass m is predominantly achieved by the aggregation of clusters with similar masses. The average time of the aggregation process can be considered to be inversely proportional to the concentration of clusters c, inversely proportional to the diffusion constant D, and inversely proportional to the capture radius [12] of the clusters $\langle R \rangle$. Under these assumptions, the aggregation process can be described by

$$\frac{\delta m}{\delta t} \propto D \langle R \rangle mc \ . \tag{2}$$

In terms of the conservation of mass $mc = m_0$, where m_0 is the total mass per unit volume of the sterically stabilized particles in the dispersion; moreover, we have $m \propto t$. Because $m \propto R^{1/d_f}$ [12], where d_f is the fractal dimension of the aggregates, we have the following relationship:

$$R = R_0 t^{1/d_f} \ . \tag{3}$$

A comparison of Eqs. (1) and (3) leads to $\beta = 1/d_f$. The values of fractal dimension d_f were accordingly calculated from the slopes of the plots presented in Fig. 3. The values obtained are summarized in Table I. In Fig. 5, the fractal dimension d_f as a function of the $NaNO_3$ concentration at 25 °C is displayed. From these results, it is seen that the fractal dimension d_f in the range of $NaNO_3$ concentration from 0.8–0.985 M was approximately constant at 1.8 (any variation can be attributed to experimental uncertainty) but then increased from 1.8–2.7 with the further addition of the salt. It is interesting to note that the growth of aggregates at all salt concentrations studied apparently follows the same power-law behavior. We have repeated these measurements several times and have always observed behavior identical with that shown in Fig. 5. Although the fractal dimensions deduced in the range of $NaNO_3$ concentration from 0.80–0.985 M are numerically in good agreement with the predicted value of 1.78 in the ordinary cluster-cluster aggregation model (CCA) [6,7], the general behavior of the fractal dimension observed over the entire range of salt concentration studied cannot be explained by this model. It should also be emphasized that an aggregation rate dependence of the fractal dimension is contrary to what has been reported in the literature previously [13–15]. It would appear that the colloid aggregation in our system is more complicated than the aggregation which has been studied by computer simulations of DLCA and RLCA models. As will be discussed later, the unusual behavior observed in these studies can be ascribed to the restructuring of ramified colloidal aggregates, which is possible when the interparticle attractive energy is finite and possibly small; more importantly, it provides a deeper and physical insight into the origin of the restructuring.

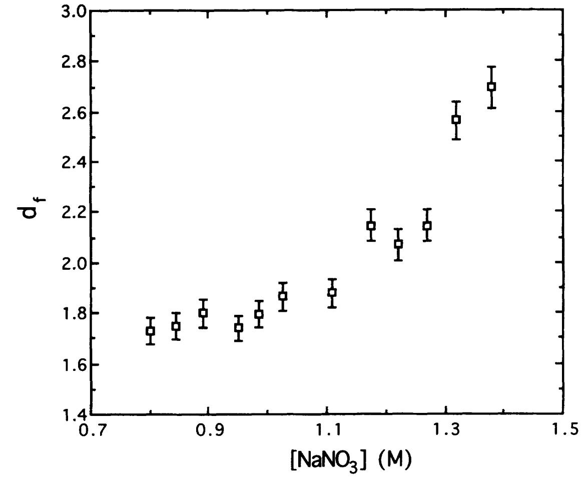

FIG. 5. Fractal dimension as a function of the $NaNO_3$ concentrations at 25 °C.

TABLE I. The parameters R_0, β, and d_f calculated in terms of Eqs. (1) and (3) at different $NaNO_3$ concentrations at 25 °C.

$[NaNO_3]$ (M)	R_0 (nm)	β (±0.05)	d_f (±0.05)
0.80	53.13	0.58	1.73
0.845	52.91	0.57	1.75
0.89	61.45	0.56	1.80
0.95	66.42	0.58	1.74
0.985	66.15	0.56	1.80
1.024	73.40	0.54	1.87
1.11	80.89	0.53	1.88
1.175	114.15	0.47	2.15
1.22	110.74	0.48	2.07
1.27	109.95	0.47	2.15
1.32	129.96	0.39	2.56
1.38	136.65	0.37	2.70

The growth behavior of aggregates at different temperatures but with fixed salt concentration was also studied. Figure 6 shows typical time dependencies of the average aggregate radius at different temperatures for 0.845 M electrolyte concentration. The rate of the aggregate formation was found to be quite sensitive to the temperature. A very slow aggregation occurred at 23.5 °C and as shown in Fig. 6, the aggregates grew to only about 230 nm in 200 min. At 24 °C, the average aggregate radius reached 530 nm in only 100 min. Even faster rates were measured at 26 and 30 °C. As known already [19], when the temperature is higher than 31 °C in pure water, the temperature-induced aggregation will occur due to the collapse of steric layers. Figure 7 shows log-log plots of the average aggregate radius versus the time. The temperature dependence of the fractal dimension is plotted in Fig. 8. The results are summarized in Table II. An effect of temperature on the fractal dimension of sterically stabilized particles was clearly observed. Somewhat surprisingly, a fractal dimension of 1.78 was obtained at lower temperatures and the value increased to 2.5 with increasing temperature. Thus, both the aggregation rate and the

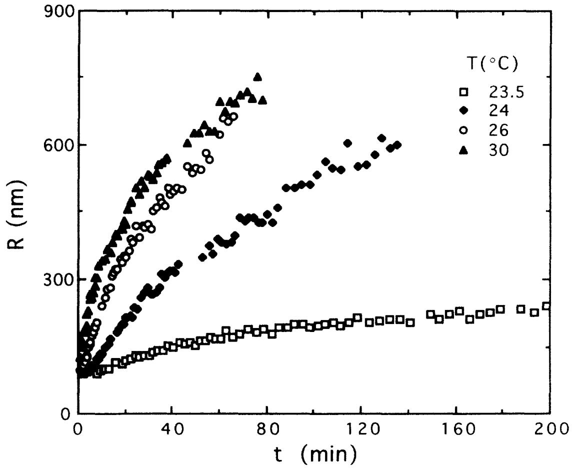

FIG. 6. Average radius R of the sterically stablized clusters as a function of the time for different temperatures at $0.845M$ $NaNO_3$.

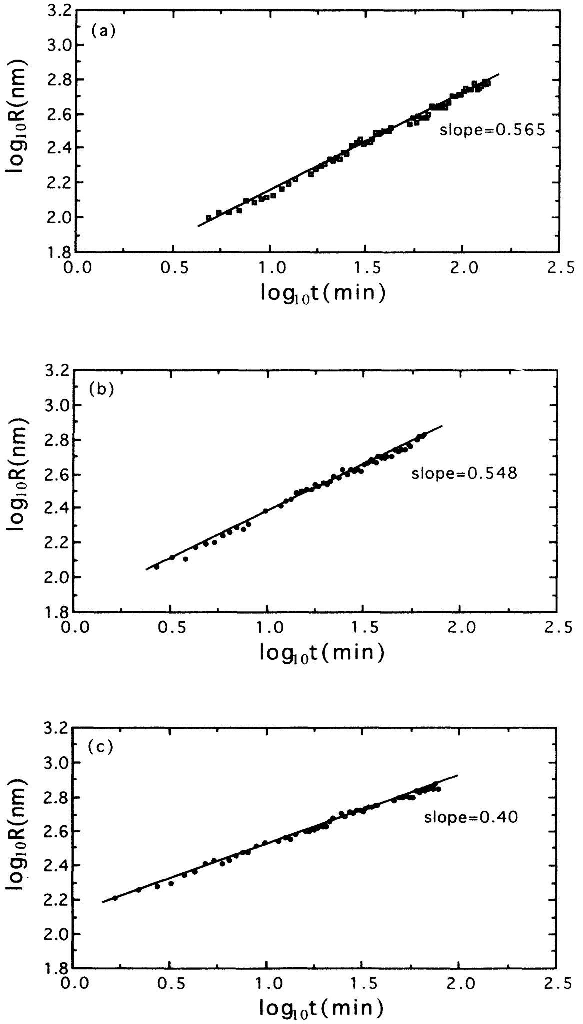

FIG. 7. Log-log plots of average radius R of the sterically stabilized clusters as a function of the time for different temperatures: (a) 24 °C, (b) 26 °C, and (c) 30 °C at $0.845M$ $NaNO_3$.

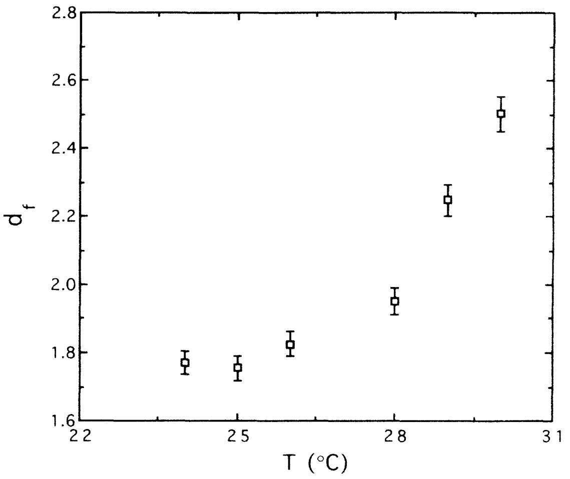

FIG. 8. Fractal dimension as a function of the temperature at $0.845M$ $NaNO_3$.

fractal dimension increased with increasing temperature. In other words, the aggregates were less and less ramified as the temperature increased. Although the kinetics of salt-induced aggregation of an electrostatically stabilized system have been extensively studied, the temperature dependence of the fractal dimension has been little studied. The origin of this temperature dependence could be very different from one system to another and each has to be discussed separately. It has been found [22] that the fractal dimension of TiH_2 aggregates in a CuTi matrix can increase from about 2.0 to 3.0 due to the increase in desorption of hydrogen with the increase in temperature.

According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability [23], the interparticle interaction energy between colloid particles plays an important role in an aggregation process for electrostatically stabilized particles. However, for the sterically stabilized systems studied, the total interparticle interaction is the sum of the steric repulsion and the van der Waals attraction. When the molecular weight of the steric layers is sufficiently high, the van der Waals attraction between the core particles is so small that it can be neglected [24]. The behavior of the steric layers is therefore of considerable importance for our understanding of the aggregation characteristics of sterically stabilized particles. The general rule [24] that governs the thermodynamic stability of sterically stablized particles is that when the dispersion

TABLE II. The parameters R_0, β, and d_f calculated in terms of Eqs. (1) and (3) at different temperatures at $0.845M$ $NaNO_3$ concentrations.

T (°C)	R_0 (nm)	β (±0.05)	d_f (±0.05)
24	38.27	0.57	1.77
25	51.90	0.57	1.75
26	67.04	0.55	1.83
28	92.90	0.51	1.95
29	113.95	0.45	2.25
30	131.22	0.40	2.50

medium is worse than a θ solvent, the steric layers become mutually attractive, which results in aggregation on collision. In addition, since in the present system PNIPAM contains hydrophobic groups, the characteristics of the hydrophobic solute in water should be emphasized. Generally speaking, the consequence of the introduction of hydrophobic groups in water can be summarized as follows [25]: (i) hydrophobic hydration in which the hydrophobic group is surrounded by water molecules with a cagelike structure, and (ii) hydrophobic interaction. The term hydrophobic interaction has been used in several related phenomena in the literature. The definition used here relates to the attractive interaction between nonpolar molecules in water. Any increase in temperature would impair the hydrophobic hydration and enhance the hydrophobic interaction because the total number of water molecules around the hydrophobic groups would be reduced as the temperature increases. On the other hand, Inomata *et al.* [18] have recently reported that the cloud points of PNIPAM in electrolyte solutions are strongly dependent on the anions and their concentrations, being significantly decreased with increasing anion concentration. They observed that the anions, which have negative values of the viscosity B coefficient (VBC), result in lower transition temperatures. It is known that the addition to aqueous solutions of an anion with a negative value of VBC weakens hydrated structures and decreases the viscosity of the solutions [18,26]. We also note that the hydrophobic interaction can be found to be about 10–100 times larger than the van der Waals forces [27].

A consistent interpretation of the experimental results obtained can be given with reference to the foregoing discussion. The growth of fractal aggregates is divided into two successive mechanistic steps: (i) a kinetic step for the diffusional approach of particles or aggregates, so as to be able to undergo collision, and (ii) a subsequent step to allow the aggregates so formed to pack more closely once they have come into contact, i.e., a restructuring process. The approach of particles or aggregates is promoted by the addition of $NaNO_3$. The repulsive force generated by PNIPAM is decreased or nearly extinguished, depending on the concentration of anion NO_3^-, which has a negative value of VBC [18] as a result of the weakening of the ordering effect of the hydration structure, as discussed previously. The decreasing hydration induced by increasing the NO_3^- concentration allows the attractive hydrophobic interactions to increase. The salt concentration dependence of the aggregation rate, as displayed in Fig. 3, is indicative of such behavior. Once aggregated, the polymer coating of the particles sticks or even interpenetrates each other through further hydrophobic interaction of the PNIPAM chains. The formation of the topological entanglements through closer contacts of PNIPAM chains has been observed [28]. Chemical reaction of the aggregates cannot be totally excluded but seems unlikely. When restructuring occurs, there must be a redistribution of the "filling" and "empty" areas on the surfaces of the aggregates after the onset of aggregation. At lower salt concentrations, the attractive hydrophobic interactions are not yet strong enough to produce a higher sticking probability because many hydrophobic groups would still be surrounded by water molecules. Compared with the aggregation occurring at higher salt concentrations, there is a smaller fraction of collisions between hydrophobic groups of different particles that form permanent contacts at lower salt concentrations. This results in a ramified structure of the aggregates. In contrast, at higher salt concentrations, more hydrophobic groups are freed from water molecules and the sticking of particles through hydrophobic interaction becomes stronger. Consequently, the resulting aggregate structure would be more compact and less ramified after collisions. As seen from the foregoing discussion, the restructuring postulated here would be completely irreversible and differs from that reported in the literature [13,14]. The salt concentration dependence of the fractal dimension, as shown in Fig. 5, serves as the evidence for this restructuring process. It can be seen from these results that since the hydrophobic attraction (which is very much larger than the van der Waals attraction) is so strong that a particle would never leave a cluster after contact, the restructuring process would make aggregative growth accelerative. Zhou, Wu, and Chu [11] also observed that faster aggregation rates produced a larger value of the fractal dimension in their study of cationic surfactant induced aggregation of negatively charged silica particles. The aggregation rate dependence of the fractal dimension was not, however, significant in their studies. Because a rise in temperature strengthens the hydrophobic interaction, as noted previously, a similar discussion can also be applied to the temperature dependence of the fractal dimension. Since the hydrophobic interaction reduces the energy barrier between particles, these results are in good agreement with the theoretical prediction [15] that the fractal dimension increases with a decrease in the absolute magnitude of the interparticle attractive energy. This model also predicts that the fractal dimension can change with time continuously or reach a constant after a long time, depending on both the interparticle attractive energy as well as the ratio of the diffusion time constant for Brownian motion of clusters τ_D, and the relaxation time constant for contact breaking after collision τ_R. However, no such change in the fractal dimension with time was measured in the range of the salt concentration studied. This could be a consequence of an unusually strong hydrophobic interaction [27], i.e., $\tau_R \gg \tau_D$, so that the fractal dimension is saturated so quickly that it cannot be followed by DLS. Actually, in the range of salt concentration studied, especially at higher concentrations, the relaxation time constant τ_R would approach infinity and discussion of this change becomes unnecessary. However, for the present system, a change in the fractal dimension with time may be expected at lower salt concentrations.

IV. CONCLUSION

In conclusion, we have extensively studied the aggregation of polystyrene latex particles sterically stabilized by poly(*N*-isopropylacrylamide) by using dynamic light scattering. There are several important findings in this work. Under appropriate experimental conditions, aggregation was observed and the time dependence of aggregate growth could be monitored. This growth followed a simple power law. The aggregation rate was found to increase with an increase in the salt concentration and with an increase in temperature. It was found however that the fractal dimension obtained increased with an increase in the salt concentration and thus in the aggregation rate. This finding was unexpected. These observations do not conform to the predictions of the normal models of aggregation of electrostatically stablized particles in which rapid aggregation yields clusters with a fractal dimension of 1.78, whereas slow aggregation results in clusters with a fractal dimension of 2.08. It is also different from the normal restructuring process in which aggregates with a fractal dimension of 1.78 restructure so that the fractal dimension increases to 2.08 after a sufficient period of time. The hydrophobic interaction (or hydration), which is controlled by the salt concentration and the temperature, is believed to play a crucial role in the aggregation observed in the present system. The results suggest that if there is a very strong attraction between particles or aggregates upon collision, the restructuring process renders the aggregation accelerative and fully irreversible. Because of the hydrophobic interaction, the aggregates formed in the present system occurred in a fairly low interparticle attractive energy. With respect to the energy, the results obtained are in good agreement with those predicted by computer simulations of SAK. Additional questions for the present system that remain unanswered are whether and how the aggregation kinetics and aggregate structures are influenced by the addition of flocculating agents ("structure breakers" of hydration), the core size, the molecular weight of steric layers, and the attachement density. Studies along these lines are planned.

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