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Different Flocculation Behaviors Between Ternary-Amine Polystyrene Latex and Poly(styrenesulfonate): Probe Charge Effect

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Summary: The flocculation of strong polyelectrolyte, poly(styrene sulfonate), (PSS) with ternary amine-functionalized polystyrene particles was investigated by dynamic light scattering (DLS). Ternary amine particles that show stable dispersion in pH 10 undergo different flocculation in a low pH conditions. In pH 3 condition, particles present fast aggregation and irreversible process (coagulation) but in pH 7 solution particles show slow aggregation and reversible process (depletion-induced flocculation). By adding strong polyelectrolyte, aggregation rapidly removed in pH 7 but retained some concentration (about 5 mg/L) in pH 3. The homogeneity exponent λ to characterize the different flocculation behaviors presents not only difference as a function of pH but also distinction as a function of concentration in pH 3.

Keywords: flocculation; homogeneity parameter; polyelectrolyte; polymer adsorption; probe charge effect

Introduction

The interaction and formation of particle-polymer assembled thin films has been an active research area for a long time because they play an important role in industrial applications.[1–6] The particle-particle or particle-polymer interaction was severely influenced on polymer conformation in solution or charge on probe molecules or polymer chain.[6] When interactions between particles and polymers occur, stabilization and destabilization are generally occurred. In stabilization, there are two basic mechanisms namely charged and steric stabilization. When solution destabilized, colloidal particles can form aggregates. The destabilization phenomenon generated from polymer onto charged particle has been widely observed.[7,8] According to DLVO theory, the stability of charged colloidal system was governed by a competition between London-van der Waals forces of attraction and the electrostatic double-layer forces of repulsion.[9]

Another number of non-ideal behaviors of charged particles in polyelectrolyte solutions have been studied as a point of diffusion.[10–13] In general, the hydrodynamic radius, R_H of a particle with diffusion coefficient D is generally analyzed with the Stokes-Einstein (SE) equation, $R_H = k_b T / 6\pi\eta D_T$, where k_b is the Boltzmann constant, T is the absolute temperature and η is the solvent viscosity. Many researchers founded $D_T\eta/(D_{T0}\eta_0) > 1$ is usually attributed to the probe experiencing the microviscosity of the solvent rather than the bulk viscosity, whereas a deviation with $D_T\eta/(D_{T0}\eta_0) < 1$ is attributed either to particle aggregation or to polymer adsorption on the particles.

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In recent to understand electrostatic interaction between charged particle and polyelectrolytes became more important due to development of LBL (layer-by-layer) technique that provides higher flexibility to surface property modification used in electronics, optics, and pharmacy materials. In LBL technique, the formation of multilayer from polyelectrolyte is based on the consecutive adsorption of polyions with alternating charge. Since this technique was introduced by Decher et al.,[14] various cores like nanoparticle, biological cells, and dye molecules from nano to micron size have been used as templates for multilayer formation.[15–18] Among particles, especially, latex particles are receiving considerable attention in several field because they can serve as a support through physical adsorption or covalent binding.[2–5]

In this paper, we choose the polystyrene (PS) particles with a positively charged surface (ternary-amine modified) as probe particle and the strong polyelectrolyte, poly(styrene sulfonate), (PSS) as matrix to explore probe charge effect between particle and polyelectrolyte interaction. The pK of amine group in bulk solution is around pH 10.[9] Thus amine group can be charged positively at low and medium pH but high pH leads to the dissociation of H^+ ions and the formation of an uncharged amine group. First, by increased charges of particles as a function of pH, fast-aggregation and coagulation of aminated PS particle was observed. Second, by added polyelectrolyte in pH 3 condition, transition of flocculation rate was observed.

Materials and Experimental Procedure

Material and Sample Prepatration

Polystyrene (PS) particles with a positively charged surface (ternary-amine modified) of 60 nm in diameter (standard deviation = 5.2 nm) was purchased from Bangs, Inc. Poly(styrene sulfonate) (PSS; $M_w = 70{,}000$) was obtained from Polyscience. Inc. The citrate buffer solution of pH 3, phosphate buffer solution of pH 7 and borax buffer solution of pH 10 were purchased from Duksan. Inc, Seoul, Korea. All chemicals were used as received without further purification. Polyelectrolyte solutions were prepared by thoroughly mixing appropriate amounts (from 1 mg/L to 100 mg/L) of powder form of PSS in the desired PH solution. After PSS was dissolved in buffer solution, the solution was put into precleaned light scattering cell (13 mm × 100 mm test tube) using a 0.80 μm membrane filter. 10 μL droplet of amine PS from 10.2 % solution was added to 1 mg/mL of each concentration polyelectrolyte solution and sonificated for 10 minutes. The final probe concentration of all solutions was 10.2 mg/L.

Microelectrophoresis

The electrophoretic mobilies of bare carboxylate PS particles and each mixing solutions were determined by photon correlation spectroscopy on Zetasizer Nano ZS (Malvern Instruments, Malvern, U. K.). Three rounds of assays have been performed for average. All measurements were carried out at 25 °C. The mobility u was converted into ζ-potential by using the relation $\zeta = u\eta/\varepsilon$, where η is the viscosity of the solution and ε is the permittivity.

Light Scattering Measurement

A JDS-Uniphase He-Ne ion laser of $\lambda_0 = 632.8$ nm was used. The detector optics employed optical fibers coupled to an ALV/SO-SIPD/DUAL detection unit that employed an EMI PM-28B power supply and ALV/PM-PD preamplifier/discriminator. The correlator was an ALV-5000/E/WIN multiple tau correlator with 288 exponentially spaced channels. For check aggregation rate of aminated PS particles, the solution was exposed to ultrasonification for 10 minutes. And then the cylindrical scattering cell was located in a bath of index matching solvent (decaline) that was maintained at 25 °C. The scattered light was passed through 400 μm pinhole. Correlation functions and intensities were measured from $\theta = 90^\circ$ and the sampling time of the correlator gathered to 10 sec every

1 minute within 10 minutes and 20 sec every 2 minute after 10 minutes.

For dynamic light scattering studies, the intensity correlation function, $g^{(2)}(\tau)$, obtained by running dynamic light scattering instruments and $g^{(2)}(\tau)$ is related to the electric field correlation function, $g^{(1)}(\tau)$, by the following equation, $g^{(2)}(\tau) = B(1 + f|g^{(1)}(\tau)|^2)$. Here, τ is the lagtime, B is the baseline, and f is an instrumental parameter determined by deviation from an ideal correlation. In order to obtain diffusion coefficients, $g^{(1)}(\tau)$ was fitted to the relationship between $g^{(1)}(\tau)$ and decay rate (Γ), $g^{(1)}(\tau) = \exp(-\Gamma\tau)$. $g^{(1)}{}_{Vv}(\tau)$ is an exponential with a decay rate, Γ, which is related to the translational diffusion coefficient (D_T) through the following equation, $\Gamma = D_T q^2$. The hydrodynamic radius, R_H was obtained through the Stokes-Einstein equation, $D_T = k_b T/6\pi\eta R_H$, where k_b is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity.

Results and Discussions

Flocculation of Aminated PS Particle as Function of pH

The aminated PS particles exhibit flocculation as differenct pH conditions due to competition between electrostatic repulsion and van der Waals interaction. This phenomenon mainly occurs from the degree of protonation of NH_2 groups. The different feature as a function of pH of charged PS particles is reported by several researcher.[25] The macroscopic flocculation that was shown in pH 3 and 7 conditions disappeared with sonification but reformed within short time. Figure 1 that is intensity correlation function and inset that is relaxation time distributions determined by CONTIN analysis of $g^{(1)}(\tau)$ clearly shows destabilization state as different pH conditions. All spectra obtained after 10 min sonification because particle size varied with time.

As shown in Figure 1, the intensity correlation functions gradually shifted toward fast decay region with increase of pH. That is, particle size decreased as pH increased. The hydrodynamic radius of the aminated PS particles in pH 10 is 70 ± 2 nm, which is larger than the specification of the manufacturer (30 ± 5 nm). The small fast mode observed in pH 3 is similar with the mode in pH 10.

Figure 2(a) is the time evolution of correlation functions in pH 7 and the inset is R_H obtained from Stokes-Einstein equation. The R_H moderately increased from about 150 nm to micro-meter within

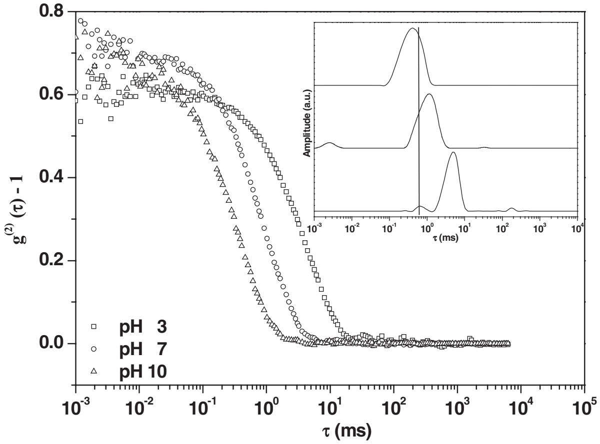

Figure 1.

Intensity correlation function of PS particles at different pH conditions. The inset is relaxation time distributions determined by CONTIN analysis of $g^{(1)}(\tau)$, whcih clearly shows destabilization state as different pH conditions.

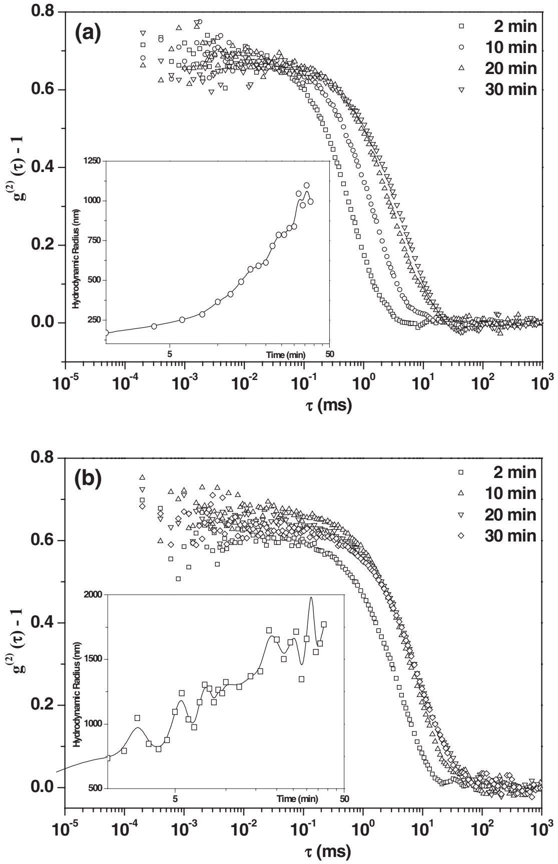

Figure 2.

Time evolution of correlation functions in (a) pH 7 and (b) pH3, and the inset is R_H obtained from Stokes-Einstein equation.

experimental time window. But as shown Figure 2(b), hydrodynamics radius in pH 3 rapidly increased with instability. Figure 1 and 2 apparently shows increased particle charges invoked destability of particles.

To describe the different flocculation feature with quantity, the dynamical scaling model that can show flocculation process in solution was used.[22]

$$R_h(t) \propto R_h(0)t^{z/D}, \quad Z = \frac{1}{1-\lambda}$$

Where $R_h(t)$ is the hydrodynamic radius at at given time, $R_h(0)$ is the size of the bare PS particles, D is the fractal dimension of the clusters, λ is the homogenity parameter and z is the kinetic exponent. It is known that the λ changed from 0 to 1 as fast-aggregation (diffusion-limited cluster-cluster aggregation (DLCA)) or slow-aggregation (reaction-limited cluster-cluster aggreagtion (RLCA)).[21]

Figure 3 shows aggregation kinetics of particle as different pH conditions. The linearity of slopes suggests that the data can be described by power laws and the intercept of slope presents particle size at early-time.

Intercepts of slopes are 1.9 in pH 7 and 2.8 in pH 3. Therefore, particle size at early-time is 631nm and 79 nm in pH 3 and 7, respectively. It means particles in pH 3 can form hard aggregates (coagulation) that can not break with sonification while particles in pH 3 forms weak aggregates that can easily break with sonification.

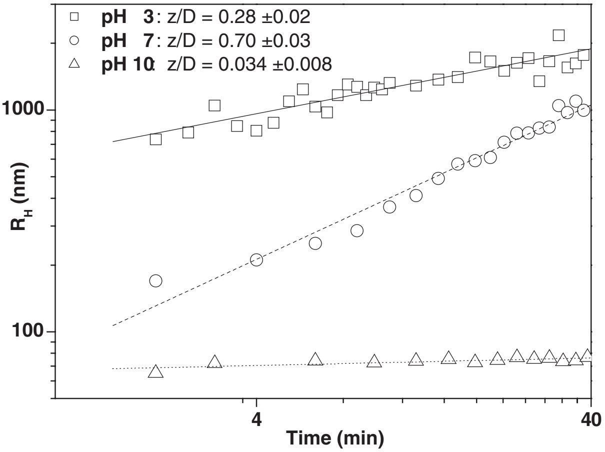

Figure 3.
Aggregation kinetics of PS particle as different pH conditions represented by the R_H vs. time plot.

The dynamic exponents obtained from slopes are $z/D = 0.28 \pm 0.02$, $z/D = 0.70 \pm 0.03$, and $z/D = 0.034 \pm 0.008$ in pH 3, 7 and 10, respectively. The exponent value in pH 10 is meaningless and just present stabilized colloid condition. The homogeneity parameters λ are determined from dynamic exponents. We used $D = 2.1$ because for polystyrene latex particles, Sandkuhler at al reported that fractal dimension of 2. 1 is good aggrement with polystyrene latex stablized with SDS.[22] From this value, λ is 0.32 ± 0.01 in pH 7, while -0.70 ± 0.05 in pH 3. The obtained values are corresponded with previous intercept results. That is, particles in pH 3 shows existence of coagulation and fast-aggregation[20] while that in pH 7 represents slow-aggregation (depletion-induced flocculation) that can define RLCA.

Induced Stability with Polyelectrolyte Solution

Destability of aminated PS colloid disappeared by adding opposite charged polyelectrolyte solution. Figure 4 shows apparent stabilization effect as a function of polyelectrolyte concentration. Colloidal stability of PSS solution in pH 3 can be achieved upto 10 mg/L. But flocculation in pH 7 removed as adding 1 mg/L PSS polyelectrolyte. The decreased hydrodynamic radius by adding polymer or absorbent was commonly observed by other researcher.[21,23]

Figure 4(b) shows the correlation functions at 90° and radius distribution of polyelectrolyte, PSS, as a function of pH. PSS does not affect within experimental pH condition because pKa values for HSO_4^- is about 1.9. The average diffusion coefficient of PSS in all pH condition is 3.01×10^{-7} cm^2s^{-1} and radius of gyration is 8.17 ± 0.02 nm.

To calculate polymer number for stabilized aminated particle, we used following equation

$$\text{Number of particles per ml} = \frac{6W \times 10^{12}}{\rho \times \pi \times \phi^3}$$

Where W is grams of polymer per ml in latex (0.1 g for 10% latex), ϕ is diameter in microns of latex particles (0.06 μm) and ρ is density of polymer in grams per ml (1.05 for polystyrene). By the equation, particle numbers in experiment are 8.42×10^{11} and polymer numbers in 10 mg/L are 8.60×10^{12}. From this calculation, we know that necessary polymer amounts to separate aggregate particle are about 1000 per particle.

Now we can calculate approximate surface area of the bare particle ($A_{ps} = 4 \times \phi(R_h)^2 = 61675$ nm^2) and PSS ($A_{pss} = 4 \times$

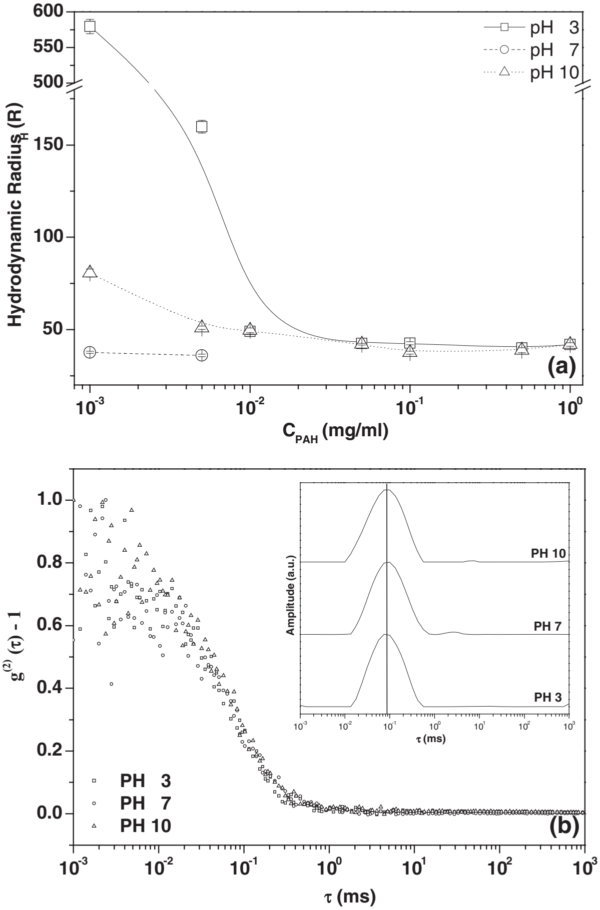

Figure 4.

(a) Apparent stabilization effect as a function of polyelectrolyte concentration, (b) correlation functions at 90° and radius distribution of polyelectrolyte, PSS, as a function of pH.

$\phi(R_h)^2 = 839$ nm^2). Then we got $A_{ps}/A_{pss} = 74$. It means PSS adsorbed PS particle have rather hairy structure than entanglement conformation. Hairy structure of polymer or surfactant on opposite charged particle is generally founded.[24]

Flocculation Kinetics of Aminated PS Particle in Polyelectrolyte Solution

Figure 5(a) is time evolution of R_H obtained from Stokes-Einstein equation as a function of concentration in pH 3. As shown in Figure 5(a), particle size gradually decreased by increasing PSS concentration. The log-log plot of growth of hydrodynamics radius showed in Figure 5(b) to get quantitative characterization of the kinetics of the flocculation behaviors. Intercepts of slopes are 2.74, 2.84 and 2.04 at 1 mg/L, 2.5 mg/L and 5 mg/ml PSS concentration, respectively. Therefore, particle size at early-time is 589 nm, 692 nm and 109 nm. It means coagulation in pH 3 can not break until particles are fully stabilized.

The dynamic exponents obtained from slopes are $z/D = 0.36 \pm 0.03$, $z/D = 0.21 \pm 0.02$ and $z/D = 0.080 \pm 0.01$ in 1 mg/L, 2.5 mg/L and 5 mg/L PSS concentration. Above 10 mg/L concentration, aminated PS particle present stable colloid state regardless time. Homogeneity parameter,

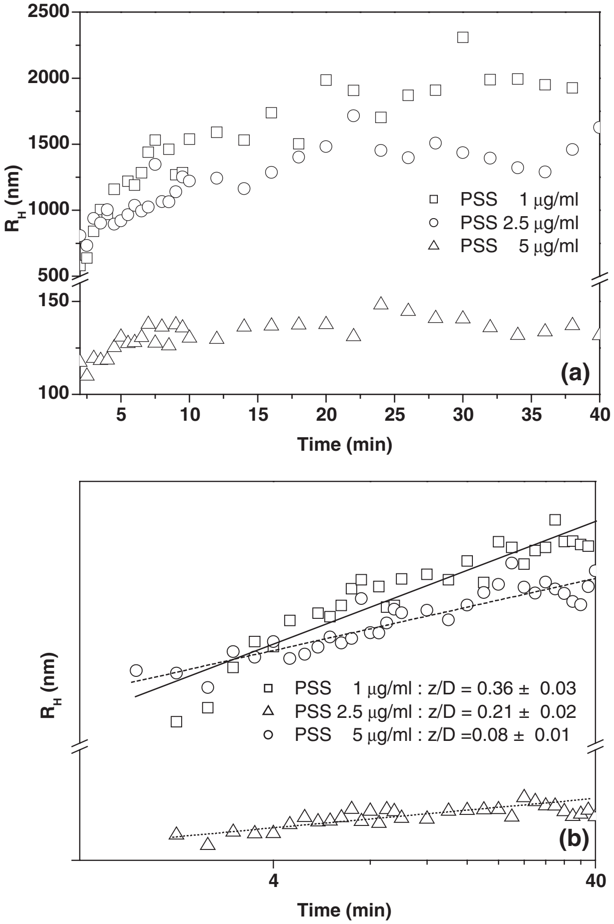

Figure 5.
(a) Time evolution of R_H obtained from Stokes-Einstein equation as a function of concentration in pH 3 and (b) The log-log plot of growth of hydrodynamics radius.

λ, is -0.32 ± 0.03, -1.26 ± 0.01, and -4.95 ± 0.06 for each concentration solution.

The concentration dependence of the homogeneity parameter in pH 3 is presented in Figure 6. Remind kinetic behaviors of bare aminated PS particle. Particles in pH 3 go through fast aggregation (coagulation) while particles in pH 7 undergo slow aggregation (depletion-induced flocculation). In general, depletion flocculations are weak interaction between non-adsorbing molecules such that particle aggregation process is a reversible phenomenon. $R_{(0)}$ in pH 7 is 79 nm, that is, similar with value in pH 10 but $R_{(0)}$ in pH 3 is 631nm. Depletion flocculation in pH 7 is weak interaction so immediately disappeared by adding small polyelectrolyte because added polymers reduce London-van der Waals interaction by screening effect. While desorption (breakage of coagulation) was known as slow process as a result of the large energy needed to remove a chain from a surface.[25]

In Figure 6, the homogeneity parameter at 1 mg/L shows that the coagulation of particles was interrupted by added polymers making the slow aggregation transit. It was also known that when added polymer adsorbs onto the particles, and bridging

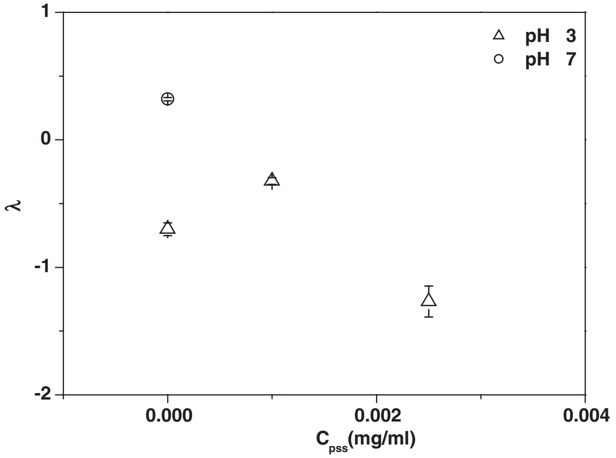

Figure 6.
The homogeneity parameter as a function of polyelectrolyte concentration.

flocculation can be occurred. Therefore, there are still fast-aggregations in pH 3 condition. It is hard to say difference between coagulation and bridging flocculation because we can not check initial particle size accurately with 2 min due to thermal stabilization of solution after sonification. From Figure 6, we carefully say bridging flocculation have the large value of homogeneity parameter than that of coagulation. But the coagulation still exist. In summary, bridging flocculation or coagulation have the – sign of homogeneity parameter while depletion flocculation has the + sign.

Conclusion

The kinetic processes of aminated PS particle as a function of pH and PSS onto aminated PS particle as a function of concentration were investigated. Time-evolved dynamic light scattering of ternary amine PS particle as function of pH shows two different flocculation behaviors. Particles show fast aggregation and irreversible process (coagulation) in pH 3 but in pH 7 show slow aggregation and reversible process. By adding strong polyelectrolyte, aggregation rapidly removed in pH 7 but showed two-step process in pH 3. (1) Breakage of coagulation due to induced particle-polymer interaction. (2) co-existence of coagulation and bridging flocculation. Finally through simple geometric calculation, we found PSS onto charged particle has hairy conformation.

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