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Journal:	<i>Langmuir</i>
Manuscript ID	la-2020-006195.R3
Manuscript Type:	Article
Date Submitted by the Author:	n/a
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Initial stage dynamics of flocculation of cationic colloidal particles induced by negatively charged polyelectrolytes, polyelectrolyte complexes and microgel studied using standardized colloid mixing

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Abstract

The initial stage dynamics of flocculation of positively charged latex particles induced by polyelectrolytes (PEs) and polyelectrolyte complexes (PECs), composed of linear polyacrylic acid (PAA) and a PAA-based hydrophilic microgel (PAA#) with a small amount of linear polycation, was comparatively analyzed by applying the standardized colloidal mixing procedure. Based on the rate of flocculation, this method allows us to investigate the dynamics of flocculation immediately after the onset. In addition to confirming the prediction made regarding the initial rate of flocculation with linear polyanions—which was mostly similar to that observed in negatively charged colloids with positively charged PEs—we have confirmed two important new results regarding the microgel: 1) the increase of the initial rate is less markedly affected by the microgel concentration than by the linear polymer concentration, which can be explained by the fact that the 3D crosslinked structure of the microgel that does not deform as easily as the linear structure upon touching the colloidal surface; 2) a remarkable increase of the initial rate due to the contribution of instant aggregation of the negatively charged microgel induced by the polycation adsorption. These results suggest the significance of state and formation dynamics of PECs prior to the reach to the surface of targeted colloidal particles for the intension of effective flocculation. These aspects are not treated so far in the dynamic process of flocculation so far.

Flocculation in turbulent flow, Polyelectrolyte adsorption, Dual polymer, Polyelectrolyte complex, Initial stage dynamics, Microgel at colloidal interface

INTRODUCTION

Water-soluble polymers with an affinity for colloidal surfaces have been used as flocculants of colloidal particles in many applications, such as mineral processing,¹ water and waste water treatment,^{2,3} pulp and paper production,⁴ and soil conditioner fabrication.^{5,38,55} It is empirically known that the degree of flocculation is remarkably enhanced by using an oppositely charged polyelectrolyte (PE) chain against the colloidal surface by means of effective palletization.⁶ Generally, two mechanisms of the polymer-induced flocculation are regarded. The first one is the formation of polymer “bridge” between more than two particles. That is, when the protruding part of the polymer chain adsorbed onto the surface of one colloidal particle attaches to the surface of another particle to form an adsorbing point will result in the formation of bridge.⁷⁻⁹ Additionally, adsorbed PEs may contribute to the flocculation, neutralizing the surface charges of colloidal particles.¹⁰ It was reported that PE chains of low charge density have a tendency to induce flocculation via bridging, and conversely, chains of high charge density induce flocculation via charge neutralization.^{11,12} In either case, flocculation is induced by the adsorption of polymers onto the surface of colloidal particles. Therefore, the state and the dynamics of the polymer or PE at colloidal interface¹³⁻¹⁶ are critically important when the dynamic process of flocculation is analyzed.

In our previous studies, we have established a method to evaluate the intensity of turbulent mixing in terms of the collision frequency between colloidal particles, detected by the rate of rapid coagulation. The rate of coagulation can be derived by the theory of collision frequency between rain droplets in clouds, considering the concept of isotropic turbulence,¹⁷ and taking into account that the capture efficiency is determined by the hydrodynamic and the colloidal interactions between two colloidal particles.¹⁸ This framework was first verified in the coagulation of polystyrene latex particle with simple salt in a fixed simple mixing setup.¹⁹ By measuring the rate of coagulation, a notoriously chaotic condition of mixing flow can be quantified in terms of collision frequency between colloidal particles. With this method, the progress of flocculation was analyzed in terms of collision process immediately after the onset of mixing with a time resolution of 1 s.

The rate of flocculation is the direct reflection of the interaction between colliding particles. The concept was applied to the study of flocculation of negatively charged sulfate latex particles with a neutral polymer²⁰ and positively charged PEs.^{21,22} The application of this method clearly revealed that the rate of flocculation is considerably enhanced by the application of polymer flocculants. In this enhancement, the size of the polymer in the solution phase is dominantly important, which can be confirmed by the results of molecular weight dependency and swelling behavior of PE chains as a function of the ionic strength.²³ In addition, the folding behavior of the polymer coil that attached onto the bare surface of a colloidal particle and changed into a flattened conformation was also analyzed as a function of the collision frequency of polymers toward the colloidal particle. Our recent result demonstrates that the co-presence of a relatively small polyanion will significantly inhibit the progress of flocculation with cationic flocculants.²⁴ This inhibitory effect is also ascribed to the decrease of effective collision radius by the shrinkage of the swollen polymer coil, as the result of the association of oppositely charged polymers. All these studies demonstrate the significance of polymer conformation in the solution phase and the re-conformation process of the polymer upon touching the surface of the colloidal particle when the flocculation begins. Thus, the effective size in the transient state that determines the dynamics from the collision to the metastable state of adsorption during the flocculation process should be analyzed more carefully. This aspect is particularly important when we consider the case in which two (or more) polymer species are involved.²⁵ This case is related to the formation of multilayer coating;²⁶ in principle, in a system composed of different chemical substances, many different types of protruding structures can be realized on the surface of colloidal particles.

In the present study, we analyzed the system which involved PEC,²⁷ anionic microgel, and further the microgel and an additional polycation. In the case of PEC, various types of adsorption dynamics can be expected in accordance with the physicochemical conditions due to the flexible nature of the PE chains⁴⁴. However, more interesting results can be expected for the case when the microgel is involved as a flocculant. So far, the microgel properties have been investigated in a series of studies,^{28-30,53} but no research

on the applicability of the microgel as flocculant has been reported. The application of microgel as flocculant is of interest for several reasons. The first is that the 3D crosslinked structure of the microgel is much less deformable upon touching the colloidal surface than the linear structure of polymer chains.⁴¹⁻⁴³ In this respect, the microgel can be considered a more stable flocculant upon adsorption onto the colloidal surface than a simple linear PE chain. Another reason is the adjustable potential of these systems to control surface properties. In the system where the microgel and oppositely charged PEs are involved, their potential to form microgel aggregates can substantially affect the flocculation process. So far, the surface property of microgels inducing different interfacial tension behaviors between the poly(N-isopropylacrylamide) microgel solution and the linear polymer solution has been reported.⁴⁹ In addition, the capability to retain toxic substances, such as organic dyes and heavy metal ions, within the structure of the microgel will be potentially advantageous when considering its application for environmental protection purposes.⁴⁶⁻⁴⁸

In order to verify and develop an effective method using microgel and polyelectrolyte complex (PEC), we designed the following set of experiments. In the first place, we confirmed the applicability of the normalizing procedure of colloid mixing to the analysis of flocculation of cationic colloidal particles with anionic PEs in the initial stage. Secondly, we compared the rates of flocculation with PEC and anionic microgel placing the emphasis on the initial stage of flocculation. Thirdly, we analyzed the effect of the polycation on the enhanced rate of flocculation with the anionic microgel.

KINETIC EQUATION OF INITIAL STAGE COAGULATION IN THE STANDARDIZED MIXING APPLIED TO THE ANALYSIS OF FLOCCULATION USING THE MODEL COLLOID

In the course of analysis, we use the term coagulation for aggregation of a colloid with inorganic salt, and the term flocculation for the aggregation of a colloid with an organic polymer and a microgel. Our idea to analyze the dynamics of flocculation is based on the comparison with results of standard salt-induced rapid coagulation realized with simple salt of sufficiently high ionic strength. For this standardization, we used mono-dispersed spheres of polystyrene latex particles rapidly coagulated in sufficiently high concentration of salt to induce rapid coagulation. Colloid mixing was fixed to the end-over-end rotation of the forked flask installed onto the rocking motion apparatus (Figure 1(a)). With this system, the rate of coagulation is equivalent to the collision frequency between the colloidal particles in the fluid under the mixing operation. If we apply the rate theory of coagulation in the turbulent flow taking into account the hydrodynamic interaction, we can use the following equation for the rate of salt-induced rapid coagulation of colloidal particles in the early stage, where most particles are regarded as mono-dispersed spheres.¹⁷⁻¹⁹

$$\frac{dN(t)}{dt} = -\alpha_T \sqrt{\frac{128\pi\varepsilon}{15\nu}} a_0^3 N(t)^2 \quad (1)$$

In this equation, $N(t)$ denotes the total number of flocs per unit of volume, and a_0 , ε , and ν are the radius of singlet, rate of energy dissipation per unit of mass, and kinematic viscosity, respectively. α_T is the capture efficiency and can be analyzed by taking into account the hydrodynamic interaction and the van der Waals attraction between two approaching colloidal particles. In the initial stage of coagulation, we can assume $N(t)^2 = N(t) N(0)$; thus Eq. (1) can be integrated as follows:

$$\ln \frac{N(t)}{N(0)} = -\alpha_T \sqrt{\frac{128\pi\varepsilon}{15\nu}} N(0) a_0^3 t \quad (2)$$

A simplified expression of α_T can be derived by substituting the effective shear rate of the turbulent mixing with the numerical result obtained by van de Ven for laminar shear flow⁵¹ as follows,

$$\alpha_T = \left(\frac{A}{36\mu\pi\sqrt{(4\varepsilon/15\pi\nu)a_0^3}} \right)^{0.18}. \quad (3)$$

where A is the Hamaker constant.

In practical terms, Eq. (2) is applicable to salt-induced rapid coagulation of latex particles carried out in the end-over-end rotation of forked flask mentioned above. The progress of salt-induced rapid coagulation is confirmed to be a linear plot of $\ln(N(t)/N(0))$ vs t as indicated in Figure 1(b). When the latex particles with a diameter of 1.356 μm were rapidly coagulated in the 1.1 M KCl solution, the value of α_T was estimated as 0.34 by using the values of $1.0 \times 10^{-21} \text{ J}$ and $8.2 \times 10^{-2} \text{ J kg}^{-1} \text{ s}^{-1}$ for A and ε , respectively.²⁰

When colloidal particles are attached by polymer flocculants or microgels, the rate of colloidal aggregation will change accordingly. In the case of flocculation induced by a polymer flocculant, we have used the condition of overshooting. As illustrated in Figure 1(b), the progress of flocculation in this case is characterized by a remarkable enhancement of the rate of flocculation due to the increase of the collision radius (the first stage), followed by the abrupt decrease of the rate reflecting the approach of the saturated condition of polymer adsorption (the second stage). Flocculation is disturbed sterically or electrostatically by the effect of the adsorbed polymer flocculant. Basically, the initial stage dynamics of flocculation can be analyzed by the slope of the first stage. In the case of a polymer flocculant, when we increase its concentration, the rate of flocculation will increase and the duration of the first stage will decrease. The increase of the rate in the first stage can be regarded as the reflection of the effective increase of the collision radius, as depicted in Figure 1(c) and 1(d). If we draw a picture of the folding process of the polymer on the surface of the colloidal particle after adhesion, this result is consistent with the representation of non-equilibrium flocculation.⁵² The value of β , termed as the enhancement factor of the rate of flocculation by the application of polymer flocculant and defined as,

$$\beta = \frac{\text{Rate of flocculation induced with polymer flocculant}}{\text{Rate of salt induced rapid flocculation}}, \quad (4)$$

is the most significant index in the analysis. It is also possible to use this index for the crude estimation of the value of effective layer thickness, δ_{He} , as follows,

$$\beta = \frac{\alpha_p (a_0 + \delta_{He})^3}{\alpha_T a_0^3}, \quad (5)$$

where α_p is the capture efficiency of the particle coated with polymer or microgel. When we can assume that the reducing effect of capture efficiency due to hydrodynamic interaction upon collision of the colloidal particle is negligibly small when the particles are attached polymer flocculants with a highly porous structure, the value of capture efficiency between colloidal particles coated with the flocculant can be considered to be close to the unit. This assumption has been used in our previous investigations.^{20-24,45} Although we recognize that this assumption will sometimes overestimate the effect of permeability in the intermediate thickness of adsorption, we believe this crude estimation is worth to be tested to obtain the value of layer thickness in terms of collision process for the case of extremely high permeability.

EXPERIMENTAL

Colloidal Particle and Polymer

Mono-dispersed polystyrene latex particles with a diameter of 1.0 μm (standard deviation of 0.04 μm) and 3.1×10^6 cationic amidine groups per particle were purchased from Molecular Probes. Polyacrylic acid (PAA) with an average molecular mass (MM) of 250 kDa (FUJIFILM Wako Pure Chemical Co.) and the cationic poly(diallyl dimethylammonium chloride) (PDDA; MM = 200–350 kDa; Sigma-Aldrich) were used to generate PE complexes.

Preparation of the Microgels

All chemicals for the synthesis of the PAA-based hydrophilic microgel (PAA#) were obtained from commercial sources: N-isopropylacrylamide (NIPA) from KJ Chemicals Co. and acrylic acid (AA), *N,N'*-methylenebisacrylamide (bis, cross-linker), ammonium persulfate (APS, initiator), and sodium dodecylbenzene sulfonate (NaDBS, surfactant) from FUJIFILM Wako Pure Chemical Co. (Osaka, Japan).

Prior to usage, NIPA was recrystallized with a hexane/benzene mixture, and AA was distilled under reduced pressure. PAA# was synthesized using the chemicals mentioned above.³⁰ First, a solution of monomers, crosslinking agent, and surfactant was prepared by dissolving 6.34 g of NIPA, 1.73 g of AA, 0.12 g of Bis, and 0.1 g of NaDBS in 200 mL of distilled water. The molar ratio of NIPA and AA was 70% to 30%. The solution was placed in a reaction vessel assembled with a round bottom separable flask (500 mL) and separable cover, equipped with a reflux condenser and a magnetic stirrer, and maintained at 60 °C with constant stirring (300 rpm). The oxygen was removed from the solution by placing the latter under a stream of N_2 in a round-bottom flask for 1 h. Then, the reaction was initiated by adding of 1 mL of an aqueous solution of APS (5 w/w %). After 2 h, the polymerization was terminated by stopping the N_2 supply. The obtained microgel solution was dialyzed against 10 mM HCl and subsequently against distilled water, using a dialysis membrane with molecular weight cutoff of 12,000 Da (size 36; FUJIFILM Wako Pure Chemical Co., Osaka, Japan), and then treated by ion-exchange chromatography on columns filled with ion-exchange

1 AMBERLITE resins. Finally, the microgel was lyophilized. 0.2 g of PAA#
2 was placed in a glass vessel, to which 100 mL of bi-distilled water was added.
3 The PAA# were left to swell for 24 h. The PAA# solution was used for
4 preparation of PDDA-PAA# PECs and in experiments to characterize PAA#
5 and PDDA-PAA# PECs.
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10 11 12 **Characterization of PAA#**

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14 The overall content of acidic groups was determined by pH titration at
15 25 °C and in 1 mM and 0.1 M NaCl solution with 0.1 M NaOH as the
16 standard titrant. Hydrodynamic radius and weight-average molecular weight
17 (Mw) were determined by laser light scattering.
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22 **Preparation of PECs of the PDDA/PAA and PDDA/PAA#**

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24 PECs were prepared by addition of PDDA solution into PAA solution or
25 PAA# suspension at 25 °C. Before PEC preparation, the weight
26 concentration, pH, and KCl concentration of each PE solution was fixed to
27 0.1 g/L, pH 6.0, 1 mM, respectively.
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32 **Electrophoresis**

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34 Data of Electrophoretic mobility (EPM) are very useful in the analysis
35 of charging behavior of PECs and microgels, and also their adsorbing
36 behavior onto colloidal particles. Throughout this investigation, EPM was
37 measured with a laser microelectrophoresis (Malvern Zetasizer Nano, UK) at
38 25°C. Measurements were repeated three times and the average value was
39 considered representative of the data of the corresponding condition.
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46 **Dynamic Light Scattering (DLS)**

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48 The size of the particles dispersed in various aqueous solutions was
49 determined by dynamic light scattering at 25°C using DLS7000 (Otsuka
50 Electric Co., Japan). Each sample was measured twice and the average result
51 was determined.
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56 **Static Light Scattering (SLS)**

The same apparatus as that used in DLS was employed for SLS measurements. The calibration was made by using pure (>99.5%) toluene, and the optical alignment was ensured by less than $\pm 2\%$ over the range $30^\circ \leq \theta \leq 140^\circ$. We determined the Rayleigh ratio (R_θ) as the average of two different measurements for the same sample. Then, Zimm plots were obtained with a SLS data fitting program.

Rate of Flocculation

The kinetics of flocculation was analyzed as the temporal decrease of the number of colloidal particles flocculating or coagulating in a standardized mixing flow. A latex suspension was mixed with a polymer flocculant solution in a forked flask connected to a homemade end-over-end rotation apparatus, which generated a turbulent flow with a fixed mechanical condition.^{19,20} Temporal evolution of the total number concentration of colloidal particles and flocs was monitored using a Coulter Counter (Multisizer III, Beckmancoulter Co. USA) as a function of the mixing steps that is equivalent to the elapsed time from the onset of flocculation. In the monitoring, after pre-determined number of mixing operation is reached, approximately 0.2 ml sample was sucked up and diluted into 20 times to freeze the size distribution. This sampling and dilution procedure was ruled to be carried out very gently and smoothly to finish exactly at 10 s. The validity of the same procedure can be referred to the reproducibility of flocculation in our previous studies^{20-24, 56}). In order to The kinetics of latex particle flocculation was represented as a “ $\ln(N(t)/N(0))$ vs. time” plot, where $N(0)$ and $N(t)$ are the initial particle count ($\sim 5 \times 10^7 \text{ ml}^{-1}$) and the particle count at a given time (t) per unit of volume, respectively. In the analysis, the slope of the plot in the limit of $t \rightarrow 0$ for each experimental condition was compared to reveal the possible conformation of the polymer or microgel attached on surface of colloidal particles.

RESULTS AND DISCUSSION

Characteristics of PAA#

Potentiometric titration of the swollen PAA# solution in 1 mM and 0.1 M NaCl at 25°C showed a $-\text{COOH}$ group density in the microgel of 2.85×10^{-3} mol/g. The molecular weight of PAA# was estimated to be 6.7×10^7 g/mol by SLS measurement of the swollen PAA# solution at pH 3 and at 25°C. The hydrodynamic radius of the swollen PAA#, measured with DLS, was 70 nm.

Characteristics of PEC of the PDDA/PAA and PDDA/PAA# Systems

PECs were prepared by controlling the ratio of the molar concentration of cationic quarternized PDDA groups and anionic carboxylic PAA/PAA# groups of both components—henceforth referred to as r_m —while keeping the final weight concentration of PEC constant at ~ 0.1 g/L. Binding of PDDA to PAA and PAA# was accompanied by neutralization of the polyanion charge, which was detected by the change of electrophoretic mobility (EPM) of the resulting PEC. Figure 2 shows the EPM of PEC of PDDA/PAA and PDDA/PAA# as a function of the molar ratio (r_m) of cationic to anionic groups. As shown in the figure, the EPM trend was similar in both systems, i.e., there was an increase in EPM up to the isoelectric point (EPM=0) followed by a change in charge from negative to a positive when PDDA was in excess. It should be noted that in both systems the EPM=0 was reached when $r_m < 1$: 0.37 for the PDDA/PAA system and 0.57 for the PDDA/PAA# system. Complexation of oppositely charged polymers has been investigated for a long time (see, for example, recent reviews³¹⁻³⁵). It has been shown, in particular, that the complexation is very strong, as both polymers are quantitatively bound to each other and no free (non-complexed) polymer can be found in the system.³¹ This allows the estimation of complex composition from the electrophoretic data. The cationic PDDA contains quarternized amino groups, and the total charge does not depend on the pH of the solution. In our study, this means that all cationic PDDA groups participated in electrostatic complexation with PAA and PAA# at pH 6. Contrastingly, PAA and PAA# are weak anionic polymers, whose total charges are governed by the pH of the solution.^{36,53} This fact is reflected in the data, which shows that only dissociated (deprotonated) carboxylic PAA and PAA# groups are

involved in the complexation with the PDDA amino groups and that the values of r_m at EPM=0 ($r_{m(0)}$) in PDDA/PAA and PDDA/PAA# systems are less than 1. The difference in the $r_{m(0)}$ value between PDDA/PAA and PDDA/PAA# is due to the ionization degree (α_i) of the carboxyl residue of PAA and PAA# in the solution at pH 6 and ionic strength 0.001 M. The α_i of carboxyl residue of PAA is 0.3³⁶ and that of PAA# is 0.5, as estimated from the results of pH titration. The fact that each $r_{m(0)}$ value is larger than each α_i suggests that extra ionized carboxyl groups appeared as a result of a cooperative displacement of protons from the carboxyl groups by the interacting cationic PDDA groups.^{38,54}

In parallel, the hydrodynamic radius of PECs was monitored using DLS. The results of PEC of PDDA/PAA complexes 180 min after preparation are represented as a function of r_m in Figure 3. For reference, the signal of scattering intensity reflecting the density of the scattering object is plotted in the right ordinate. As indicated this figure, the hydrodynamic diameter, as well as the scattering intensity, goes through a maximum as a function of r_m . The appearance of the maximum corresponds to the aggregate formation near isoelectric point ($r_{m(0)} = 0.37$) which was shown in Figure 2 (curve 1). Such profile is typical of polycation-to-polyanion complexation^{38,39} with the stable PECs with excess of either component, rendering negative and positive charge to the particles, and aggregates at a r_m close to the mutual neutralization point. However, the result for the microgel PDDA-PAA# complex is very different (Figure 4). Binding of PDDA to a swollen microgel at pH6 whose radius is about 200 nm and three times larger than at pH 3 caused a continuous decrease in the microgel size up to $r_m = 0.5$ as demonstrated in curve 1. In turn, the decrease in size was accompanied by an increase in the intensity, implying the increase of polymer density of PDDA-PAA# complex particles, but as indicated in curve 2, the signal abruptly decreased due to partial precipitation of PDDA-PAA# complex at $r_m = 0.6$ close to isoelectric point. The behavior represented in this curve is similar to that reported for other microgels;²⁸ aggregation occurs due to the charge neutralization of anionic PAA# with bounded cationic PDDA in the process of the precipitation of complex at $0.5 < r_m < 0.6$ near the isoelectric point.

Based on the electrophoresis and DLS measurements, PECs of anionic flocculant for the positively charged amidine latex particles were selected; PDDA-PAA complex with $r_m = 0.1$ and PDDA-PAA# complex with $r_m = 0.2$ were evaluated. These complexes contain hydrophobic blocks²⁷ with mutually neutralized positive and negative charges.

Electrophoretic Behavior of Cationic Latex Particle adsorbed with Anionic Polymer, Microgel, and Their PECs

Prior to the use of PAA, PAA#, and their PECs for application to flocculation, the investigation of the adsorption behavior of these anionic PECs on cationic latex particle is necessary. Figure 5 shows electrophoretic mobility (EPM) of cationic colloidal particle adsorbed with PAA (data 1), PDDA-PAA PEC ($r_m = 0.1$) (data 2), PAA# (data 3), PDDA-PAA# PEC ($r_m = 0.2$) (data 4) respectively as a function of weight concentration of PAA or PAA# or PECs. Each EPM sample was obtained by mixing equal volumes latex suspension and solution (PAA or PAA# or their PECs). The number concentration of cationic latex suspension before mixing was fixed at $\sim 10^8$ ml^{-1} . As shown in Figure 5, adsorption behavior of not only PAA and PAA# but also these PECs on cationic latex particles due to electrostatic interaction was confirmed by the decrease of EPM. On the other hand, there was difference in isoelectric point between samples due to the difference in charge density; (i) PAA with higher charge density reached $\text{EPM}=0$ at lower weight concentration compared with PAA#, (ii) complex formation of PAA and PAA# with PDDA lead the shift to higher isoelectric point. The same phenomenon as (ii) observed in previous study.³⁸ These results indicated that PAA# and anionic PECs as well as linear PAA would be applicable to flocculants whose driving force is neutralization of surface charges of colloid particles.

Kinetics of Flocculation of Cationic Latex Particles Induced by Anionic Polymers and Their Polyion Complex with Linear Polycation

The results for the case of flocculation induced by the application of PAA and PDDA-PAA complexes are shown in Figure 6. The conditions for material preparation are summarized in Table 1, together with the ratio ($R_{a/c}$)

of the concentration of anionic polymer groups to the that of cationic groups on latex surface in the mixture solution. Two flocculation regimes were tested. In the first, a concentration of anionic polymer groups was close to a concentration of cationic groups on the latex surface. In the second, the former was taken in an excess to the latter. The plot of data 1 obtained by the rapid coagulation induced by the electrolyte solution of 1.0 M KCl can be fitted as a straight line in the “ $\ln(N(t)/N(0))$ vs. t ” plot, which confirms the validity of our method using the normalized mixing in terms of collision frequency also for the case of positively charged latex particles; this has been confirmed for many times for negatively charged latex particles.¹⁹⁻²³ Using the result obtained for the particles with diameter of 1356 nm, the application of Eq. (3) yields an α_T value of 0.4 for these particles. We see that in all PAA-containing systems, the kinetics consists of two stages: the initial stage with a faster flocculation and the plateau where the flocculation slows down owing to saturation of the latex particle surface with polymer macromolecules. This result is consistent with the schematic image in Figure 1(b).

The application of PAA 0.04 mg/L (data 2 in Figure 6) was found to yield a steep slope initially that abruptly slows down after 2.0 s. Compared with the polymer concentration of 0.04 mg/L, the increase of polymer concentration to 0.2 mg/L (data 3) resulted in a shorter duration of the first stage and a steeper slope. This is the typical result observed for polymer flocculation under overshooting conditions, that is, in the case of 0.2 mg/L PAA (data 3), the saturation is finished earlier than the first monitoring point. The crude estimation using data 2 is 0.4 s which is significantly shorter than 1.0 s. In this case, the initial fast rate cannot be detected and only the slow flocculation after the bending point indicated in Figure 1(b) is considered to be recorded.

In case PAA is associated with PDPA, its effectiveness as a flocculant is considered to be decreased due to the decrease of the size of the chain in solution and the decrease of effective charge of the chain. As illustrated in Figure 7(b), the resulting progress of flocculation was assumed to be the smallest, as suggested by the plot of data 4. In this case, the system is

governed by slow coagulation in respect to ionic strength of background solution. We have observed a similar behavior in a previous study, and confirmed that it is an inhibitory effect of negatively charged polymer on the bridging enhancement of the positively charged flocculant.²⁴ However, as indicated in the data of 5, the effect as a flocculant appears again following a fivefold increase of the concentration of the PDDA-PAA complex. This behavior can be explained in two ways. One is the change of the charging behavior of the colloidal particles covered with the oppositely charged complex. That is, the increase of negatively charged complex favors the reduction of the electrostatic repulsion between colloidal particles. However, we expect a more important factor to enhance the flocculation: it can be induced by the formation of PDDA-PAA complex aggregates as illustrated in Figure 7(c). It should be noted that the collision frequency is proportional to the square of the concentration; thus, the rate of aggregate formation of the PEC can increase significantly by a concentration increase of up to five times. A similar effect will be discussed in the result of flocculation induced with microgel-PDDA complex in the next section. Systematic research on the effective size of PEC as a function of PEC concentration is necessary to quantify this effect.

Flocculation in the Presence of Microgels

In the presence of PAA microgels (PAA#), the flocculation (Figure 8) follows the trends as described above in the results of the PDDA-PAA complex, but with more pronounced effects. In Figure 8, three results draw attention by themselves. First, we recorded a higher rate of flocculation for PAA# than for the linear PAA, which is obvious because of the much greater size of microgels (PAA#) in comparison with that of linear macromolecules (PAA). Secondly, the initial slope observed for different concentrations of microgel (plotted data 6 and 7) is nearly the same, probably owing to the 3D crosslinked structure of the microgel (Figure 9(a)). In general, a microgel is considered to be much less deformable than a linear PE in regards to the surface of particles. That is, in terms of degree and rate, the re-conformation behavior of a microgel into a flattened shape on the colloidal surface is much smaller and slower than that of a linear polymer, considering the non-

equilibrium flocculation with a linear polymer or PE, which is schematically illustrated in Figure 1(d). Thirdly, the initial slope obtained for PDDA-PAA# complexes demonstrated the strong dependency of flocculation on the concentration of PDDA-PAA# complexes. The decrease of the initial slope of data 8 (Figure 8) occurred for two reasons: one is that the reducing effect of the positive charge of the amidine group on the latex particle is not completely shielded; and the second is the decrease of the effective size by the shrinkage of the microgel induced by the adsorption of PDDA.

Remarkably, at high concentration (0.5 mg/l) the initial slope of data 9 sharply increased. We have observed the similar effect in the case where flocculation was induced by polyethylene oxide with nominal molecular weight of 5 million g/mol.⁴⁵ Such remarkable increase can be explained by the formation of aggregates (Figure 9(b)). We term this mechanism as instant pre-aggregation. This mechanism can be considered to be triggered in the dispersion of PDDA-PAA# complexes by the presence of positively charged PSL particles under turbulent mixing condition. However, the progress of flocculation of this type is considered to be induced only when the surface of PSL particles is not saturated. The duration of this period is very short only after the start of mixing because of the concentration of the complex is sufficiently high to bring about charge reversal. After this period the colloidal surface is saturated with adsorbed PDDA-PAA# complexes which will induce negative charge on the colloidal surface. With this condition, PSL suspension is considered to be electrostatically stabilized. Further systematic analysis along with this picture will elucidate the mechanism. It is conceivable that the same effect of the increase of effective collision radius due to aggregation occurs in the case of a linear polyelectrolyte-based complex, similarly to the effect mentioned in the previous section.

Protruding Length of Adsorbed Polymer, PEC, Microgel, and Their Aggregates on the Surface of Colloidal Particles

In the present study, we measured the rate of flocculation in the initial stage in dual polymer flocculant systems. We ascribe the difference in the rate of flocculation in the initial stage to the analysis of collision frequency in which the collision radius is dominantly important. We summarized the

enhancement factor of the initial rate of flocculation compared with salt-induced rapid coagulation (Table 2) for different conditions in each experiment. In this table, we also include some results of δ_{He} obtained from Eq. (5) assuming α_p is close to the unit. Presumably, this assumption is only valid for data 9, but for the other cases, the estimated values are smaller than the actual ones. Obviously, values can be estimated closer when we introduce the value of capture efficiency between colloidal particles covered with a porous material in Eq.(5). Although the ambiguity of this factor posed limitations to this study and prevented us from making more progress, future research would be warranted.

CONCLUSION

In the present study, we have compared the difference of initial stage dynamics of flocculation of positively charged latex particles induced by negatively charged PEs, PEC of linear PEs and PEC of negatively charged microgels, and positively charged linear PEs. This is the first report on the measurement of the flocculation enhancement factor for different types of PEC, highlighting the importance of the less deformable nature of microgel compared to the linear polymer, and the contribution of the aggregation of PEC on the enhancement of the rate of flocculation. Application of the normalizing procedure colloid mixing in terms of collision frequency of colloid was confirmed to demonstrate the critical information on the state and transient dynamics of flocculant not only for single linear polymer of polyelectrolyte but also of dual polymer system including microgel.

CRedit authorship contribution statement

Leonid O. Ilyasov: Conceptualization, Methodology, Investigation, Writing - original draft, Funding acquisition.

Kazuyoshi Ogawa: Resources, Methodology, Investigation.

Irina Panova, Writing - original draft

Alexander A. Yaroslavov: Writing - original draft. Funding acquisition.

Yasuhisa Adachi: Writing - original draft, Supervision, Project administration, Funding acquisition.

Acknowledgments

L.O. Ilyasov acknowledges the University of Tsukuba for financial support in the form of a JASSO scholarship, and Professor Usuyama Toshinobu for the support. This work was financially supported by the JSPS KAKENHI (16H06382) and Russian Foundation for Basic Research (project №19-29-05036).

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Figure Legends

Figure 1. Schematic illustration of the methodology used to study the initial stage dynamics of flocculation induced by polyelectrolytes, polyelectrolyte complexes, and microgels. (a) The normalized mixing procedure of colloid mixing. (b) Typical temporal evolution of the total number concentration of colloidal particles and flocs for salt-induced coagulation (dashed line) and flocculation induced by a polymer in overshooting conditions. (c) The rate of flocculation is largely affected by changes in the collision radius of a colloidal particle coated with polymers or complexes. (d) In the case of a polymer flocculant, an increase in polymer concentration will result in a short-lived first stage of flocculation and in a thick layer on the particle surface, reflecting the situation where it is possible to find high amounts of polymer on the colloidal surface upon collision. This representation is consistent with that of non-equilibrium flocculation [52].

Figure 2. Electrophoretic mobility (EPM) of PDDA-PAA (curve 1) and PDDA-PAA# complex (curve 2) as a function of r_m . The aqueous solution consisted of 1 mM KCl at pH 6 (25 °C). At $r_m \geq 0.6$ in the case of PDDA-PAA# complex, the supernatant solution was measured because precipitation was observed.

Figure 3. Hydrodynamic radius (R_h) of PDDA-PAA complex (curve 1) and intensity of light scattering of the solution (curve 2) as a function of r_m . The aqueous solution consisted of 1 mM KCl at pH 6 (25°C).

Figure 4. Hydrodynamic radius (R_h) of PDDA-PAA# complex (curve 1) and intensity of light scattering (curve 2) as a function of r_m . A KCl aqueous solution (1 mM, pH 6, 25°C) was used. At $r_m = 0.6$, the supernatant solution was measured because precipitation was observed.

Figure 5. Electrophoretic mobility (EPM) of cationic colloidal particle adsorbed with PAA (data 1), PDDA-PAA PEC ($r_m = 0.1$) (data 2), PAA# (data 3), and PDDA-PAA# PEC ($r_m = 0.2$) (data 4) respectively as a function

of weight concentration of PAA or PAA# or PECs. Number concentration of mono-dispersed polystyrene latex particles used for the preparation of EPM samples is 5×10^7 /mL. The aqueous solution consisted of 1 mM KCl at pH 6 (25 °C).

Figure 6. Kinetics of latex flocculation induced by 1 M KCl (data 1), 0.04 mg/L PAA (data 2), 0.2 mg/L PAA (data 3), 0.04 mg/L PDDA-PAA PEC ($r_m = 0.1$) (data 4), and 0.2 mg/L PDDA-PAA PEC ($r_m = 0.1$) (data 5). Polymer and latex suspensions except for data 1 were prepared in 1 mM KCl solution at pH 6.

Figure 7. Possible inhibitory effects induced by the addition of the second polymer. One is to reduce the effective layer thickness to induce the shrinkage of the first polyelectrolyte. The formation of PEC essentially decreases the size of the polymer flocculant and thus reduces the effective collision radius from (a) to (b). However, by increasing the concentration, pre-aggregation is considered to be induced near the surface of colloidal particle thus increasing the effective collision radius as depicted in (c).

Figure 8. Kinetics of latex flocculation induced by 1 M KCl (data 1), 0.2 mg/L PAA# (data 6), 0.5 mg/L PAA# (data 7), 0.2 mg/L PDDA-PAA# ($r_m = 0.2$) (data 8), 0.5 mg/L PDDA-PAA# ($r_m = 0.2$) (data 9). Except for data 1, polymer and latex suspensions except for data 1 were prepared in 1 mM KCl solution at pH 6.

Figure 9. Schematic of the flocculation induced by the microgel. Owing to the less deformable nature of the microgel, its re-conformation on the surface of the colloid is not considered to change the rate of flocculation (a). However, the effective thickness will increase remarkably as a result of the aggregation induced by the increase of adsorption of PDDA prior to attachment onto the surface (b); the increase in thickness is more likely to occur when the microgel concentration is increased.

Table 1List of flocculants and $R_{a/c}$ of each data number described in Figure 6 and 8.

	Flocculants	$R_{a/c}$
1	1 M KCl	
2	0.04 mg/L PAA	0.80
3	0.2 mg/L PAA	3.99
4	0.04 mg/L PDDA-PAA PEC ($r_m = 0.1$)	0.58
5	0.2 mg/L PDDA-PAA PEC ($r_m = 0.1$)	2.92
6	0.2 mg/L PAA#	1.26
7	0.5 mg/L PAA#	3.15
8	0.2 mg/L PDDA-PAA# PEC ($r_m = 0.2$)	0.92
9	0.5 mg/L PDDA-PAA# PEC ($r_m = 0.2$)	2.31

$R_{a/c}$ in the case of the anionic polymer and anionic PEC was calculated from Eq. (5) and Eq. (6), respectively.

$$R_{a/c} = \frac{D_{AP} \times C_{AP} \times r_{m(0)}}{N_{latex} \times N_0 \times 10^3 / N_A} \quad (5)$$

$$R_{a/c} = \frac{D_{AP} \times \frac{\frac{1}{r_m} \times \frac{D_{PDDA}}{D_{AP}}}{\frac{1}{r_m} \times \frac{D_{PDDA}}{D_{AP}} + 1} \times (1 - r_m) \times C_{PEC} \times r_{m(0)}}{N_{latex} \times N_0 \times 10^3 / N_A} \quad (6)$$

where N_{latex} denotes the number of cationic amidine groups per particle (3.1×10^6); N_A , Avogadro's Number; C_{AP} and C_{PEC} , weight concentration of anionic polymer and anionic PEC in g/L; D_{AP} and D_{PDDA} , charge density of anionic polymer and PDDA, respectively (mol/g).

Table 2

The value of the initial slope of each data number in Figure 6 and 8 and the estimated value of β and δ_{He}

	1	2	3	4	5	6	7	8	9
Slope (/s)	0.0049	0.0172	0.0026	0.0030	0.0121	0.0194	0.0171	0.0140	0.1311
β	1.00	3.44	0.52	0.60	2.42	3.88	3.42	2.80	26.2
δ_{He}		56	—	—	—	79	53	—	590

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Fig.1

Figure 1. Schematic illustration of the methodology used to study the initial stage dynamics of flocculation induced by polyelectrolytes, polyelectrolyte complexes, and microgels. (a) The normalized mixing procedure of colloid mixing. (b) Typical temporal evolution of the total number concentration of colloidal particles and flocs for salt-induced coagulation (dashed line) and flocculation induced by a polymer in overshooting conditions. (c) The rate of flocculation is largely affected by changes in the collision radius of a colloidal particle coated with polymers or complexes. (d) In the case of a polymer flocculant, an increase in polymer concentration will result in a short-lived first stage of flocculation and in a thick layer on the particle surface, reflecting the situation where is possible to find high amounts of polymer on the colloidal surface upon collision. This representation is consistent with that of non-equilibrium flocculation [52].

254x190mm (96 x 96 DPI)

Fig.2

Figure 2. Electrophoretic mobility (EPM) of PDDA-PAA (curve 1) and PDDA-PAA# complex (curve 2) as a function of r_m . The aqueous solution consisted of 1 mM KCl at pH 6 (25 °C). At $r_m \geq 0.6$ in the case of PDDA-PAA# complex, the supernatant solution was measured because precipitation was observed.

254x190mm (96 x 96 DPI)

Fig.3

Figure 3. Hydrodynamic radius (R_h) of PDDA-PAA complex (curve 1) and intensity of light scattering of the solution (curve 2) as a function of r_m . The aqueous solution consisted of 1 mM KCl at pH 6 (25°C).

254x190mm (96 x 96 DPI)

Fig.4

Figure 4. Hydrodynamic radius (R_h) of PDDA-PAA# complex (curve 1) and intensity of light scattering (curve 2) as a function of r_m . A KCl aqueous solution (1 mM, pH 6, 25°C) was used. At $r_m = 0.6$, the supernatant solution was measured because precipitation was observed.

254x190mm (96 x 96 DPI)

Fig.5

Electrophoretic mobility (EPM) of cationic colloidal particle adsorbed with PAA (data 1), PDDA-PAA PEC (rm = 0.1) (data 2), PAA# (data 3), PDDA-PAA# PEC (rm = 0.2) (data 4) as a function of weight concentration of PAA or PAA# or PECs. Number concentration of mono-dispersed polystyrene latex particles used for the preparation of EPM samples is 5×10^7 (/mL). The aqueous solution consisted of 1 mM KCl at pH 6 (25 °C).

254x190mm (96 x 96 DPI)

Fig.6

Kinetics of latex flocculation induced by 1 M KCl (data 1), 0.04 mg/L PAA (data 2), 0.2 mg/L PAA (data 3), 0.04 mg/L PDDA-PAA PEC ($rm = 0.1$) (data 4), and 0.2 mg/L PDDA-PAA PEC ($rm = 0.1$) (data 5). Polymer and latex suspensions except for data 1 were prepared in 1 mM KCl solution at pH 6.

254x190mm (96 x 96 DPI)

Fig.7

Possible inhibitory effects induced by the addition of the second polymer. One is to reduce the effective layer thickness to induce the shrinkage of the first polyelectrolyte. The formation of PEC essentially decreases the size of the polymer flocculant and thus reduces the effective collision radius from (a) to (b). However, by increasing the concentration, pre-aggregation is considered to be induced near the surface of colloidal particle thus increasing the effective collision radius as depicted in (c).

254x190mm (96 x 96 DPI)

Fig.8

Kinetics of latex flocculation induced by 1 M KCl (data 1), 0.2 mg/L PAA# (data 6), 0.5 mg/L PAA# (data 7), 0.2 mg/L PDDA-PAA# ($rm = 0.2$) (data 8), 0.5 mg/L PDDA-PAA# ($rm = 0.2$) (data 9). Except for data 1, polymer and latex suspensions except for data 1 were prepared in 1 mM KCl solution at pH 6.

254x190mm (96 x 96 DPI)

Fig.9

Schematic of the flocculation induced by the microgel. Owing to the less deformable nature of the microgel, its re-conformation on the surface of the colloid is not considered to change the rate of flocculation (a). However, the effective thickness will increase remarkably as a result of the aggregation induced by the increase of adsorption of PDPA prior to attachment onto the surface (b); the increase in thickness is more likely to occur when the microgel concentration is increased.

254x190mm (96 x 96 DPI)