

POLYMER COLLOIDS FORMED BY POLYELECTROLYTE COMPLEXATION OF VINYL POLYMERS AND POLYSACCHARIDES IN AQUEOUS SOLUTION*

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Abstract The polyelectrolyte complex formed from the polyanion and polycation was studied by turbidimetry, static and electrophoretic light scattering, and elementary analysis. Sodium salts of polyacrylate (PA) and heparin (Hep) were chosen as the polyanion, and hydrochloric salts of poly(vinyl amine) (PVA) and chitosan (Chts) as the polycation. Although these vinyl polymers and polysaccharides have remarkably different backbone chemical structures and linear charge densities, all the four combinations PA-PVA, PA-Chts, Hep-PVA, and Hep-Chts provide almost stoichiometric polyelectrolyte complexes which are slightly charged owing to the adsorption of the excess polyelectrolyte component onto the neutral complex. The charges stabilize the complex colloids in aqueous solution of a non-stoichiometric mixture, and the aggregation number of the complex colloids increases with approaching to the stoichiometric mixing ratio. The mixing ratio dependence of the aggregation number for the four complexes is explained by the model proposed in the previous study.

Keywords: Polyelectrolyte complex; Colloidal dispersion; Polyacrylate; Poly(vinyl amine); Heparin; Chitosan; Light scattering.

INTRODUCTION

Colloidal particles formed by polymers are often called as polymer colloids. Their size ranges from few nm to microns, depending on their preparation methods: emulsion and dispersion polymerization^[1, 2], micellization of amphiphilic block and random copolymers^[3, 4], phase separation in polymer solutions (*i.e.*, the meso-globule formation)^[5], as well as complexation of polyanion and polycation^[6]. Polymer colloids are utilized as drug delivery systems, nano reactors, and so on. For their usages, the size control of polymer colloids is an important factor.

Recently, Ueno *et al.*^[6] studied polyelectrolyte complexation of sodium polyacrylate (PA) and poly(vinyl ammonium chloride) (PVA) in aqueous solution (*cf.* Scheme 1). The growth and stabilization mechanism of this polymer colloid were just the same as those of hydrophobic colloids of low molar mass salts, *i.e.*, the growth by hydrophobic interaction among neutral complexes and the stabilization by adsorption of the excess charged component.

In this study, we have extended the previous work of Ueno *et al.* using sodium heparin (Hep) and PA as polyanions and hydrochloric salt of chitosan (Chts) and PVA as polycations. The chemical structures of Hep and Chts are also shown in Scheme 1. While linear charge densities σ of PA and PVA are identical ($\sigma = 4.0e \text{ nm}^{-1}$ where e is the elementary charge), those for Hep and Chts are significantly different ($\sigma = 6.6e \text{ nm}^{-1}$ for Hep and

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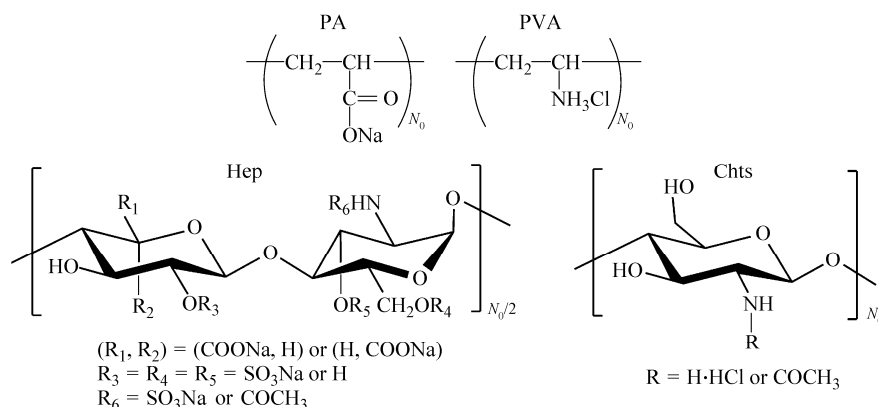
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$\sigma = 1.7e \text{ nm}^{-1}$ for Chts). Furthermore, chemical structures of the polymer backbone are also much different between the synthetic vinyl polymers and biological polysaccharides, leading distinctive hydrophobic interactions between polyanion and polycation in the two systems.



Scheme 1 Chemical structures of polyelectrolytes used in this study

We conducted measurements of static and electrophoretic light scattering (SLS and ELS), turbidimetry, and elementary analysis on the polyelectrolyte complexes formed by the four combinations of polyelectrolytes (Hep-Chts, Hep-PVA, PA-Chts, and PA-PVA) in water of neutral pH to characterize the colloidal dispersion. The experimental results for the four polyelectrolyte complexes were compared to elucidate the mechanism of the polyelectrolyte complex formation.

EXPERIMENTAL

Samples

A heparin (Hep) sample in the sodium salt form was purchased from Tokyo Chemical Industry Co., Ltd, and used as received without further purification. The aqueous solution of the Hep sample was checked to be neutral pH. A chitosan (Chts) sample was also purchased from Tokyo Chemical Industry Co., Ltd, and was used after dialysis against pure water, neutralization by addition of aqueous hydroxyl chloride, and freeze-drying.

Weight average molecular weights M_w of the Hep and Chts samples were determined in 0.03 mol/L aqueous NaCl by static light scattering (see below). The results are listed in Table 1. Moreover, stock samples of sodium polyacrylate (PA) and poly(vinyl ammonium chloride) (PVA) were also used for the polyelectrolyte complexation experiment. Table 1 also lists their M_w .

Table 1. Molecular characteristics of polyelectrolyte samples used in this study

Sample	M_w	$M_{0,-}$ or $M_{0,+}$ ^a	N_0 ^b
Hep	9.2×10^3	155	59
Chts	6.0×10^5	250	2400
PA	2.5×10^4	94	270
PVA	3.0×10^4	79.5	380

^a Molar mass per elementary charge unit in units of g/cm^3 ; ^b Number of charges per chain

Preparation of Test Solutions

Each freeze-dried sample was dissolved into pure water separately to make dilute solutions of the same initial concentration c_0 at neutral pH. Then the solutions of polyanion and polycation with volumes V_- and V_+ respectively, were mixed at the room temperature to form the complex. In what follows, the polymer composition in the mixed solution or the mixing ratio is expressed in terms of the weight fraction $w_- [= V_-/(V_- + V_+)]$ of polyanion in the total polymers, and later it will be converted into the mole fraction x_- of negatively charged groups of polyanion in the total charged groups of both polyelectrolytes (cf. Eq. (5)).

Static Light Scattering

When the total polymer concentration c_0 was not higher than 3×10^{-4} g/cm³ and x_- was not very close to 0.5, aqueous solutions of polyelectrolyte mixtures were almost transparent, and did not yield any precipitates. Static light scattering (SLS) measurements were performed on these mixtures at 25°C using an ALV/SLS/DLS-5000 light scattering instrument (ALV, Langen, Germany) with a Nd:YAG laser operating at 532 nm. Each of polyanion and polycation solutions was filtrated with 0.20–0.80 μ m cellulose acetate membrane filters before mixing. The measurements were carried out at least 6 h elapsing after mixing, and it was checked that scattered light intensity did not change with time.

Polyelectrolyte mixture solutions may contain a polyelectrolyte complex (component 2) and the excess polyelectrolyte component (component 1). Assuming that scattering from the component 2 is much stronger than that from the component 1, we have the following equation for the dilute ternary solution^[7]:

$$\frac{Kc}{R_\theta} = \frac{1 + \frac{1}{6} \langle S^2 \rangle_z k^2 + O(k^4)}{w_2 M_w} + 2A_2 c + O(c^2) \quad (1)$$

On the left-hand side, K is the optical constant, c is the total polymer mass concentration, and R_θ is the excess Rayleigh ratio at the scattering angle θ of the mixture solution over that of the solution containing only the excess component, while on the right-hand side, w_2 , M_w , $\langle S^2 \rangle_z$, and A_2 are the weight fraction (in the total polymer), the weight average molar mass, z -average square radius of gyration, and the second virial coefficient respectively of the component 2, and k is the magnitude of the scattering vector. As mentioned below, the complex (the component 2) is turned out to be stoichiometric, so that the refractive index increment $(\partial n / \partial c)_2$ of the component 2 including in K was calculated from refractive index increments of polyanion $(\partial n / \partial c)_-$ and of polycation $(\partial n / \partial c)_+$ by:

$$(\partial n / \partial c)_2 = \frac{M_{0,-} (\partial n / \partial c)_- + M_{0,+} (\partial n / \partial c)_+}{M_{0,-} + M_{0,+}} \quad (2)$$

where $M_{0,-}$ and $M_{0,+}$ are molar masses of polyanion and polycation per charged group, respectively, which were estimated by ELS (see RESULTS section). By differential refractometry, $(\partial n / \partial c)_-$ of sodium Hep and $(\partial n / \partial c)_+$ of Chits chloride were determined to be 0.115 cm³/g and 0.152 cm³/g, respectively. Those for sodium PA and PVA chloride were reported previously^[6].

Electrophoretic Light Scattering

Electrophoretic light scattering (ELS) measurements on polyelectrolyte complex solutions ($c_0 = 1 \times 10^{-4}$ g/cm³) were carried out using an Otsuka Electronics zeta-potential analyzer ELSZ-1. From the Doppler shift frequency $\Delta\omega$ obtained by electrophoretic light scattering, the apparent electrophoretic mobility U_{app} was estimated using the equation

$$U_{app} = \Delta\omega / Ek \quad (3)$$

where E is the strength of the electric field applied and k is the magnitude of the scattering vector. The true electrophoretic mobility U was obtained after the correction of the electro-osmotic effect^[8]. The zeta potential of colloid surface ψ_ζ was calculated using the Smoluchowski equation^[9]

$$\psi_\zeta = \frac{\eta_s}{\varepsilon_0 \varepsilon_r} U \quad (4)$$

where ε_0 is electric constant, ε_r is relative permittivity of solvent, and η_s is the solvent viscosity.

Elementary Analysis

Weight fractions of constituent elements in the Hep and Chts samples as well as in the Hep-Chts complex were determined by elementary analysis. The weight fraction of sulphur S was estimated from sodium fusion test. The Hep-Chts complex used for elementary analysis was prepared by mixing aqueous Hep and Chts solutions with a relatively high concentration ($c_0 = 5.0 \times 10^{-3} \text{ g/cm}^3$) with different w_- . Each mixed solution being slightly turbid was centrifuged at 9000 r/min for 1 h, and the obtained precipitate was dried in vacuo over night to make elementary analysis.

Turbidimetric Titration

Transmittance measurements on aqueous polyanion and polycation solutions ($c_0 = 1.0 \times 10^{-3} \text{ g/cm}^3$) titrated with aqueous polycation and polyanion solutions with the same c_0 , respectively, were carried out at the room temperature, using a Beckman PC920 probe colorimeter equipped with a 1 cm path length fiber optics monitored at 570 nm.

RESULTS

Solution Turbidity and Zeta Potential

Figure 1 shows the solution transmittance and zeta potential ψ_ζ for the four polyelectrolyte complexes as functions of the mixing ratio w_- . The solution turbidity becomes maximum at w_- where $\psi_\zeta = 0$ for all complexes examined. This mixing ratio is denoted as w_-^* in what follows. These results demonstrate that the polyelectrolyte complexes can grow without disturbance by the electrostatic repulsion among colloidal complex particles at w_-^* . This mixing ratio must correspond to the condition of equimolar charges between the polyanion and polycation, because the deviation from the equimolar condition may give charges to the complex by adsorption of the excess polyelectrolyte component.

The mole fraction x_- of the negative charges of the polyanion in the total polyelectrolyte charges in the solution can be related to w_- by

$$x_- = \frac{M_{0,+} w_-}{(M_{0,+} - M_{0,-}) w_- + M_{0,-}} \quad (5)$$

where $M_{0,-}$ and $M_{0,+}$ are the molar masses per elementary charge of polyanion and polycation, respectively. We know $M_{0,-}$ for PA and $M_{0,+}$ for PVA to be 94 g/mol and 79.5 g/mol, respectively, from the chemical structures. In fact, ψ_ζ for the complex of PA and PVA in water becomes zero at w_- which gives $x_- = 0.5$ from Eq. (5) along with the above values of $M_{0,-}$ and $M_{0,+}$ (see Fig. 1d). The values of $M_{0,-}$ for Hep and $M_{0,+}$ for Chts are determined so as for Eq. (5) with w_-^* given in Figs. 1(b) and 1(c) as well as $M_{0,-} = 94 \text{ g/mol}$ for PA and $M_{0,+} = 79.5 \text{ g/mol}$ for PVA, respectively, to give $x_- = 0.5$. The results were $M_{0,-} = 155 \text{ g/mol}$ for Hep and $M_{0,+} = 250 \text{ g/mol}$ for Chts. Using these results, Eq. (5) gives $w_-^* = 0.38$ at $x_- = 0.5$, which agrees with the experimental result shown in Fig. 1(a). The numbers of negative or positive charges per chain N_0 for Hep, Chts, PA, and PVA samples are listed in the last column of Table 1.

The result of $M_{0,+} = 250 \text{ g/mol}$ for Chts gives 0.94 as the degree of deacetylation and 0.191 as the weight ratio of nitrogen N to carbon C of the Chts sample used. From elementary analysis, the N/C ratio was determined to be 0.183, being in agreement within a 6% error. On the other hand, the result of $M_{0,-} (= 155 \text{ g/mol})$ obtained for Hep by ELS gives 2.3 of the degree of sulfate substitution (assuming all R_6 to be sulfated; see Scheme 1), and 0.515 as the weight ratio of sulfur S to carbon C of the Hep sample used. The elementary analysis gave 0.48 for the weight ratio of sulfur to carbon, which is also in agreement within a 6% error.

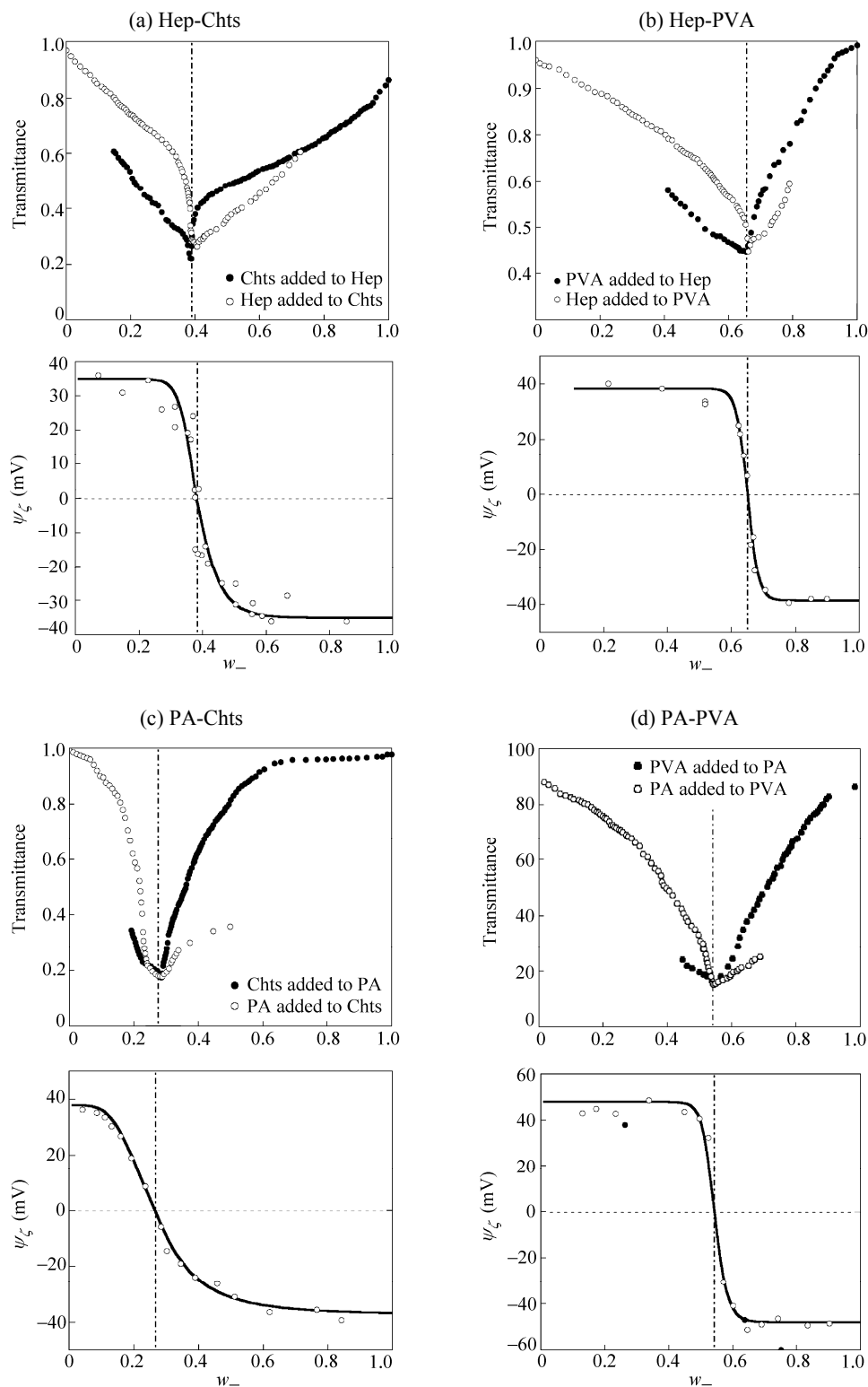


Fig. 1 Solution turbidity and zeta potential for complexes of (a) Hep and Chts, (b) Hep and PVA, (c) PA and Chts, and (d) PA-PVA
In panel d, filled circles are the results obtained in the previous study.

Stoichiometry of the Complex

The mole fraction X_- of negative charges in the Hep-Chts complex precipitated from aqueous solutions of Hep and Chts mixtures with different w_- or x_- can be calculated by elementary analysis. From weight fractions of S (w_S) and C (w_C) in the precipitate as well as weight fractions of S (w_{S-}) and C (w_{C-}) in the Hep sample and of C (w_{C+}) in the Chts sample, X_- is estimated by

$$X_- = \frac{1}{1 + [(w_{S-}w_C / w_Sw_{C-}) - 1](M_{0,-}w_{C-} / M_{0,+}w_{C+})} \quad (6)$$

where $M_{0,-}$ and $M_{0,+}$ have been already determined above. As shown in Fig. 2, the results of X_- are close to 0.5, irrespective of the mole fraction x_- of negative charges in the solution. This demonstrates that Hep and Chts form a stoichiometric complex in water.

Although the composition analysis was not made for the complexes of Hep and PVA and of PA and Chts, those complexes must be also stoichiometric because the turbidity becomes maximum and ψ_ζ becomes zero at $x_- = 0.5$ which is calculated from the $M_{0,-}$ and $M_{0,+}$ values same as those for the stoichiometric PA-PVA and Hep-Chts complexes.

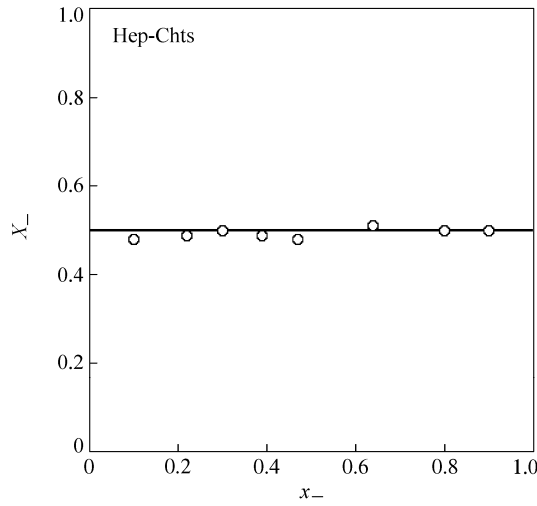


Fig. 2 The mole fraction X_- of negative charges in the Hep-Chts complex precipitated from aqueous solutions of Hep and Chts mixtures with different mixing ratios

Characteristics of the Complex Colloids

Figure 3 shows an example of the Zimm plot for the Hep-Chts mixture of $w_- = 0.276$ ($x_- = 0.40$) obtained by SLS. As in the case of the PA-PVA complex formed at $c_0 = 3 \times 10^{-5}$ g/cm³ shown in the previous paper^[6], data points at each polymer mass concentration c obey straight lines in the Zimm plot, and the concentration dependence is weak. Similar Zimm plots were obtained for other mixtures of Hep and Chts with different mixing ratios and c_0 . According to Eq. (1), the common intercept and slopes of the plots at $c = 0$ and $k = 0$ give us w_2M_w , $\langle S^2 \rangle_z^{1/2}$ and A_2 of the polyelectrolyte complex. For the stoichiometric complex, w_2 can be calculated by

$$w_2 = \begin{cases} \frac{M_{0,-} + M_{0,+}}{M_{0,-}} w_- & (w_- < w_-^*) \\ \frac{M_{0,-} + M_{0,+}}{M_{0,-}} (1 - w_-) & (w_- > w_-^*) \end{cases} \quad (7)$$

Using this equation, we have calculated M_w from the intercept of the Zimm plot.

Figure 4(a) shows the mixing ratio dependence of the weight average number of charged groups per the

Hep-Chts complex $N_{0,w}$, which was calculated from M_w divided by the mean molar mass $\overline{M}_0$ per charged groups [$= (M_{0,-} + M_{0,+})/2$]. For all c_0 (the polymer concentration at mixing) examined, $N_{0,w}$ tends to diverge when x_- approaches to 0.5. Similar dependence was obtained for the colloidal complex of PA and PVA^[6]. The Hep-Chts complex formed in solutions with x_- very close to 0.5 was precipitated, and light scattering measurements were impossible. It is noted that $N_{0,w}$ at constant x_- increases with the polymer concentration c_0 .

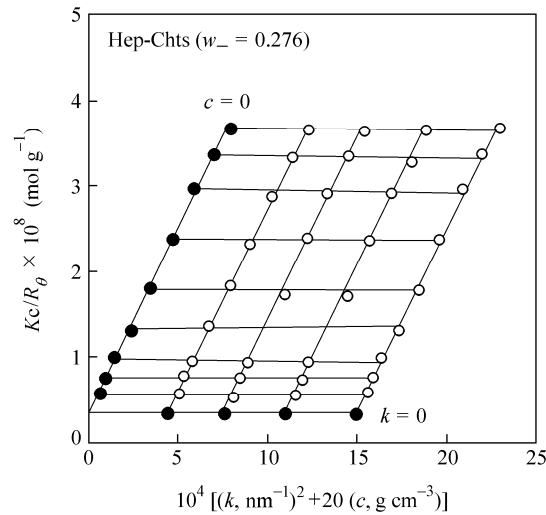


Fig. 3 Zimm plot for a Hep-Chts mixture obtained by SLS

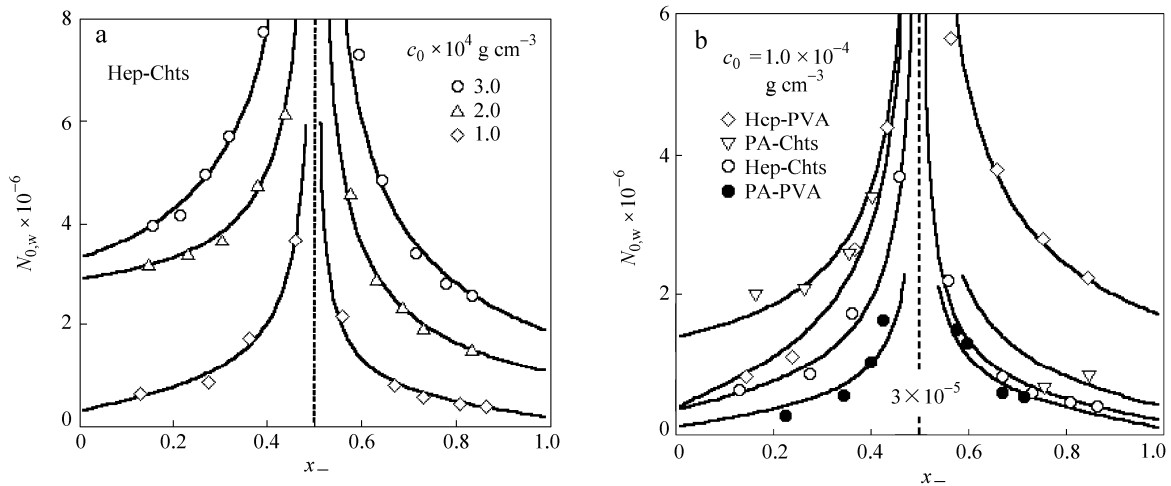


Fig. 4 Mixing ratio dependence of the weight average number $N_{0,w}$ of charged groups per the polyelectrolyte complex formed (a) in the mixture of Hep and Chts and (b) in the different polyelectrolyte mixtures

Similar light scattering experiments were made on polyelectrolyte complexes formed at mixing aqueous solutions of Hep and PVA and of PA and Chts with $c_0 = 1.0 \times 10^{-4} \text{ g/cm}^3$. The scattering function for the Hep-PVA complex was analyzed in terms of the Zimm plot as in the cases of the Hep-Chts and PA-PVA complexes, as shown in Fig. 3, but that for the PA-Chts complex was analyzed in terms of the Berry plot, where the extrapolation to the zero scattering angle was easier. The results of $N_{0,w}$ obtained are shown in Fig. 4(b). The panel also includes the results for the PA-PVA complex formed at $c_0 = 3.0 \times 10^{-5} \text{ g/cm}^3$, obtained previously using PA and PVA samples with $N_0 = 110$ and 930, respectively^[6]. For all the complexes, $N_{0,w}$ tends to diverge

when x_- approaches to 0.5, although the order of $N_{0,w}$ values depend not only on the species of the complex but also on the kind of the excess polyelectrolyte component; $N_{0,w}$ for the PA-Chts complex is larger than that for the Hep-PVA complex at $x_- < 0.5$ but opposite at $x_- > 0.5$.

Figure 5 shows the $N_{0,w}$ dependence of the radius of gyration $\langle S^2 \rangle_z^{1/2}$ of the colloidal Hep-Chts complex (filled symbols), as well as of the PA-Chts, Hep-PVA, and PA-PVA complexes (unfilled symbols), prepared at different x_- and c_0 . In the double logarithmic plot, most of the data points obey the line indicated with a slope of $1/3$. This dependence indicates that the colloids of all the polyelectrolyte complexes examined are spherical particles with a similar uniform internal polymer concentration. Scattering functions of the polyelectrolyte complexes showed better linearity in the Zimm or Berry plot than in the Guinier plot. The linearity may be due to the dispersity in the colloid particle size.

The internal concentration or the molar concentration of charged groups inside the colloidal complex $c_{0,in}$ is calculated by

$$c_{0,in} = \frac{3N_{0,w}}{4\pi N_A \left(\frac{5}{3} \langle S^2 \rangle_z \right)^{3/2}} \quad (8)$$

where N_A is the Avogadro constant. The straight line indicated in Fig. 5 gives us $c_{0,in}$ to be 0.15 mol/L. The corresponding mass concentration for the Hep-Chts complex ($c_{0,in}$ multiplied by the mean molar mass $\bar{M}_0$ per charged groups) is only 0.03 g/cm³, indicating that the complex contains a lot of water.

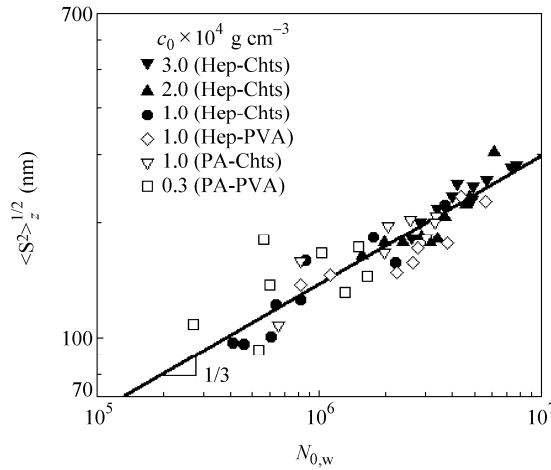


Fig. 5 $N_{0,w}$ dependence of $\langle S^2 \rangle_z^{1/2}$ of the colloidal complexes of Hep and Chts (filled symbols), of Hep and PVA (unfilled diamonds), of PA and Chts (unfilled triangles), and of PA and PVA (unfilled squares)

According to the Fujita-Hermans theory^[10], the zeta potential ψ_ζ for a spherical particle is written as

$$\psi_\zeta = \frac{n_c e}{4\pi \epsilon_0 \epsilon_r R_H} \frac{1 + e^{-2\kappa R_H}}{3 + (\kappa R_H)^2} \quad (9)$$

where n_c , e , and κ are the number of net charged groups in the spherical particle, the elementary charge, and the inverse of the Debye length, respectively, and R_H is the hydrodynamic radius of the particle. Approximating R_H by $\langle S^2 \rangle_z^{1/2}$ and using the relation between $\langle S^2 \rangle_z^{1/2}$ and $N_{0,w}$ shown in Fig. 5, we can calculate n_c as a function of $N_{0,w}$ from experimental ψ_ζ and Eq. (9), and then $|x_- - 1/2| = n_c/N_{0,w}$ for all the complexes. The results of $|x_- - 1/2|$ were less than 3%, which are consistent with the above elementary analysis for the Hep-Chts complex precipitate (see Fig. 2).

DISCUSSIONS

Figure 6 illustrates the schematic model previously proposed for the mechanism of polyelectrolyte complexation^[6]. When aqueous solutions of polyanion and polycation are mixed, they first form neutral complexes N by the electrostatic interaction (step 1), and then the neutral complexes aggregate by the hydrophobic interaction (step 2). If the system is a non-stoichiometric mixture of polyanion and polycation, the excess component chain E may adsorb on the growing aggregate N_m to make charged colloids $N_mE_{m_E}$ (step 3, where m and m_E are the aggregation numbers of N and E), and when the net charge n_C of $N_mE_{m_E}$ attains a critical value n_C^* , the growth of $N_mE_{m_E}$ stops^[11] (step 4). The value of n_C^* should depend on the strength of the hydrophobic interaction of $N_mE_{m_E}$ and also on the ionic strength. The steps 2 and 3 occur simultaneously.

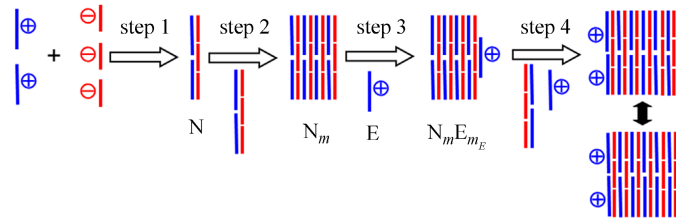


Fig. 6 Schematic diagram illustrating the mechanism of polyelectrolyte complexation

The step 1 must occur rapidly just after mixing the polyanion and polycation solutions. We do not consider this step, choosing the end of this step as time $t = 0$, and assuming N at $t = 0$ to be monodisperse spheres of a molar mass M_N . The step 2 may be treated as the rapid coagulation process of colloidal particles, which was formulated by the Smoluchowski theory^[12]. According to the theory, the weight average number of charged groups per the polyelectrolyte complex $N_{0,w}$ grows in the step 2 by the equation

$$N_{0,w} = N_{0,N} + \frac{4N_A k_B T c_0 (1 - |1 - 2x_-|)}{3\eta_s [M_{0-} x_- + M_{0+} (1 - x_-)]} t \quad (10)$$

where N_A is the Avogadro constant, $k_B T$ is the Boltzmann constant multiplied by the absolute temperature, c_0 is the total polymer mass concentration, and η_s is the solvent viscosity. (The previous paper missed the factor $(1 - |1 - 2x_-|)$ in the equation, which eliminates the excess component E from the growing N.)

In the step 3, the excess component E adsorbs on the growing colloidal particle surface. The rate of adsorption dm_E/dt should be proportional to the surface area $4\pi R^2$ of the colloidal particle and to the molar concentration c_E of the E chain:

$$\frac{dm_E}{dt} = 4\pi k_{ads} R^2 c_E \quad (11)$$

where R is the radius of the colloidal particle and the rate constant k_{ads} . The radius R is related to $N_{0,w}$ by

$$\frac{4\pi}{3} R^3 c_{0,in} = \frac{N_{0,w}}{N_A} \quad (12)$$

where $c_{0,in}$ is the number concentration of the total charged groups inside the particle. The amount of the adsorption is so small that we neglect the time change of c_E . Then Eq. (11) along with Eqs. (12) and (10) can be integrated to obtain the time dependence of m_E as

$$m_E = \frac{3\sqrt[3]{36\pi k_{ads} c_E}}{5\lambda (N_A c_{0,in})^{2/3}} \left(\left\{ N_{0,N} + \frac{4N_A k_B T c_0 (1 - |1 - 2x_-|)}{3\eta_s [M_{0-} x_- + M_{0+} (1 - x_-)]} t \right\}^{5/3} - N_{0,N}^{5/3} \right) \quad (13)$$

In the late stage, both the colloidal growth and E chain adsorption should slow down because of the charging of the colloidal particles (the slow coagulation). Although Eq. (10) is for the rapid coagulation, we approximately use the same relation between m_E and $N_{0,w}$ in the slow coagulation, assuming the same decelerations of the colloidal growth and E chain adsorption. Finally, in the step 4, the colloids stop growing when the net charge n_C ($= m_E$ multiplied by the degree of polymerization $N_{0,E}$ of the E chain) attains the critical value n_C^* . The $N_{0,w}$ of the stable colloid particle is then given by

$$N_{0,w}^{5/3} = N_{0,N}^{5/3} + A \left(\frac{1}{|1-2x_-|} - 1 \right) \quad (14)$$

where the parameter A is defined as follow

$$A \equiv \frac{N_A^{5/3} k_B T n_C^* c_{0,in}^{2/3}}{450^3 \sqrt{36\pi} \eta_S k_{ads}} \quad (15)$$

To obtain Eq. (15), we have used the relation $c_E = 10^3 |1 - 2x_-| c_0 [x_- M_{0,-} + (1 - x_-) M_{0,+}] N_{0,E}$. It can be seen from Eq. (14) that $N_{0,N}$ is the value of $N_{0,w}$ at $x_- = 0$ or 1 where the solution contains infinite amount of the excess polyelectrolyte component. The other parameter A in Eq. (15) represents the degree of growth of the neutral complex N after the step 1.

We can fit Eq. (14) to the experimental results shown in Fig. 4, choosing suitable values for the two adjustable parameters $N_{0,N}$ and A . The solid curves in both panels of Fig. 4 show the fitting results. We chose different values of $N_{0,N}$ and A at $x_- < 0.5$ and > 0.5 . Values of $N_{0,N}$ chosen are shown in Fig. 7(a), where unfilled and filled symbols indicate values chosen at $x_- < 0.5$ and > 0.5 , respectively. We can see that $N_{0,N}$ increases with c_0 for the Hep-Chts complex, and also that $N_{0,N}$ values are considerably different at $x_- < 0.5$ and > 0.5 for most of the complexes.

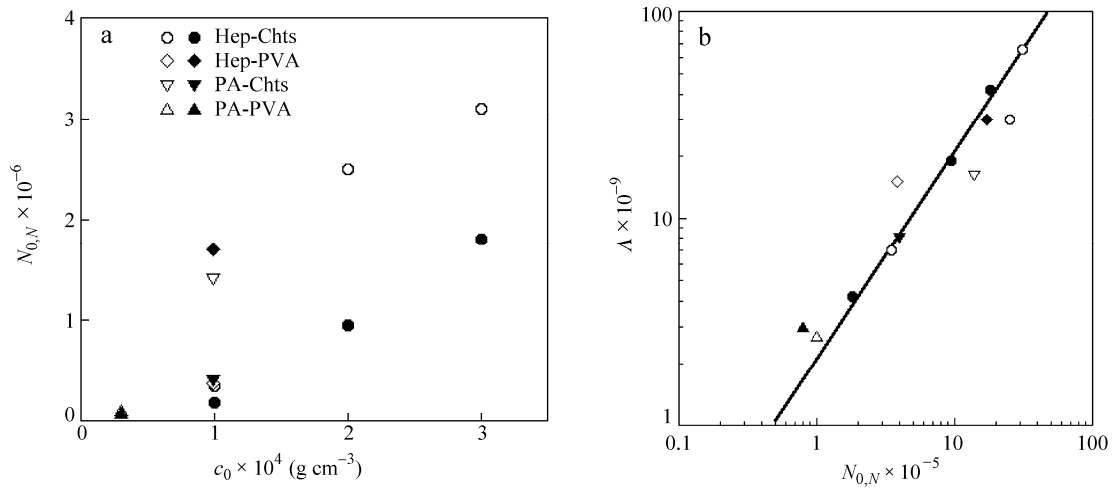


Fig. 7 Adjustable parameters $N_{0,N}$ and A chosen to fit experimental results of $N_{0,w}$ for the four polyelectrolyte complexes

When solutions of polyanion and polycation are mixed, both polyelectrolyte concentrations in the solution must be very inhomogeneous at the beginning. Negatively and positively charged complexes are formed in polyanion-rich and polycation-rich domains, respectively, and those charged complexes grow at traveling oppositely charged polyelectrolyte-rich domains. This growth mechanism continues until the solution becomes homogeneous (the end of the step 1), and the complexes become almost neutral. Each neutral complex contains $N_{0,N}$ charged groups on average in this stage. Therefore, $N_{0,N}$ should depend on the homogenization process in the mixed solution. In fact, the previous study demonstrated that aggregation numbers of the PA-PVA complexes prepared by the rapidly and slowly mixing methods were more than ten times different. At present,

we have little molecular information about the homogenization process in polymer solutions.

Figure 7(b) displays the relation between Λ and $N_{0,N}$ chosen at the fitting. The points almost obey a universal line with the slope of 1 indicated in the panel. The parameter Λ depends on n_C^* , $c_{0,in}$, and k_{ads} in Eq. (15). Among them, $c_{0,in}$ is essentially constant for all complexes examined as seen from Fig. 5, and k_{ads} is not expected to depend on $N_{0,N}$, so that the relation of Λ and $N_{0,N}$ in Fig. 7(b) indicates the proportionality of n_C^* to $N_{0,N}$. The inter-particle force may increase with the particle size, so that more net charges are necessary to stabilize the larger complex. This empirical but universal linear relation between Λ and $N_{0,N}$ is useful, because using this relation $N_{0,N}$ becomes only the single adjustable parameter in Eq. (14).

CONCLUSIONS

We have investigated the colloidal polyelectrolyte complexation using charged polysaccharides heparin (Hep) and chitosan (Chits) and vinyl polyelectrolytes polyacrylate (PA) and poly(vinyl amine) (PVA) in water at neutral pH. Although the main-chain chemical structure, linear charge density and degree of polymerization are quite different among the vinyl polymers and polysaccharides, all polymer colloids formed by the complexation of the Hep-Chits, Hep-PVA, PA-Chits, and PA-PVA pairs obey universal equations. The weight average number $N_{0,w}$ of charged groups per colloid and the radius of gyration $\langle S^2 \rangle_z^{1/2}$ of the colloid for the four complexes obey Eqs. (14) and (8), where $\Lambda = 2.1 \times 10^4 N_{0,N}$ (cf. Fig. 7b) and $c_{0,in} = 0.15$ mol/L (cf. Fig. 5), within our experimental condition examined. Only the parameter characterizing the system is $N_{0,N}$, the number of charged groups of the neutral complex formed just after mixing the oppositely charged polyelectrolyte solutions

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