



Historical perspective

Effects of salt on intermolecular polyelectrolyte complexes formation between cationic microgel and polyanion



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ABSTRACT

The study of interpolyelectrolyte complex (IPEC) formation between cationic microgel and polyanion was presented. The size and molecular weight of cationic microgel are much larger than those of linear anionic polyelectrolyte. The resulting IPEC was divided by dynamic light scattering (DLS), static light scattering (SLS), and turbidity or spectrometry; (i) water-soluble *intra*-particle complexes consisting of one microgel to which linear polyelectrolytes bind; (ii) complex coacervates (*inter*-particle complexes composed of aggregated *intra*-particle complexes); and (iii) insoluble amorphous precipitates. These types depended on not only the mixing ratio of polyanion to cationic microgel but also salt concentration. This trend was discussed from IPEC's composition, thermodynamics of IPEC formation and the salt effect on intermolecular interactions which were expected in IPEC formation. The results obtained from the use of microgel in IPEC's study suggested that not only electrostatic interaction but also hydrophobic interaction play an important role in the aggregation or association of IPEC.

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1. Introduction

Interpolyelectrolyte complexes (IPECs) are formed by the interaction between oppositely charge polyelectrolytes in aqueous solution. IPECs have attracted attention for a long time since their first report in 1940s [1–4]. Because interpolyelectrolyte complex (IPEC) formation phenomena has been interested in not only application field such as water treatment due to flocculation [5], soil stabilization [6], the

formation of micro-capsules [7] and membranes [8–10], gene delivery [11,12], and layer-by-layer technique [10,13] but also a simple model of assembly-phenomena of molecules observed in biological system such as Histone–DNA complex [14].

Up to now, various combination of polyelectrolyte have been used in IPECs studies; oppositely charged polyelectrolytes [15–22], polyelectrolyte–micelle [23–26], polyelectrolyte–protein [27–30], oppositely-charged block copolymers [31,32], and so on. The resulting IPEC was categorized by dynamic light scattering (DLS), static light scattering (SLS), turbidity or spectrometry, and microscopy; (i) water-soluble complexes consisting of a few polycations and polyanions;

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(ii) complex coacervates of aggregated water-soluble complexes; and (iii) insoluble amorphous precipitates. The type of resulting complex depends on pH, ionic strength, mixing ratio and the nature of material (molecular weight and charge density). Among these three types, analyzing the structure of water-soluble complexes is believed to be important in order to study not only the conformation change of linear polyelectrolyte chain by IPECs formation but also the mechanism of aggregation of water-soluble complexes. Because water-soluble complex can be considered as “precursor” or “primary complex” [21] of coacervates in complex coacervation.

Generally, water-soluble complex can be formed more preferable under special conditions [19]: (i) a significant difference in molecular weights of oppositely charged polyelectrolytes, (ii) a high excess of long polyelectrolyte chains, and (iii) a relatively narrow range of mixing ratios. That is, water-soluble complex consists of long-chain component to which short-chain oppositely charged components bind uniformly, which can be observed in by light scattering in salt-containing system [15,16,19,26]. However, light scattering measurement of linear polyelectrolyte in salt-free solution is very difficult due to its weak light scattering [33,34].

In order to solve the difficulty, polyelectrolyte microgels [35–40], the size of which is larger than usual polyelectrolyte, have been used in IPECs system [38–40]. Polyelectrolyte microgel consists of lightly-crosslinked polymer chain and is available for light scattering measurement in salt-free system [35–40]. The resulting complex between linear polyelectrolyte and polyelectrolyte microgel is divided as mentioned in previous section: (i) water-soluble *intra*-particle complexes consisting of one microgel to which linear polyelectrolytes bind; (ii) complex coacervates (*inter*-particle complexes composed of aggregated *intra*-particle complexes); and (iii) insoluble amorphous precipitates. Analysis of this IPECs system by using light scattering is possible even in salt-free system [38–40]. This might make to discuss the mechanism of transition in detail, between the categories of resulting complex, in especially between (i) and (ii).

This review (i) presents the dependence of mixing ratio and salt concentration on the resulting type of IPECs between cationic microgel and strong polyanion, and (ii) discusses the mechanism of IPECs coacervation in molecular level.

2. Physical chemical properties of polyelectrolyte microgel

2.1. Morphological characteristics of polyelectrolyte microgel

Polyelectrolyte microgel presented in this review consists of lightly-crosslinked copolymer chain of N-isopropylacrylamide (NIPA), acrylic acid as anionic monomer, and N-vinylimidazole as a cationic monomer (Fig. 1(a)) [37,38,40]. Polyelectrolyte microgel was obtained by the polymerization in surfactant solution [35,37].

Table 1 shows the several characteristics of the NIPA-based polyelectrolyte microgel. From DLS and SLS data, polymer density (ρ) was calculated by

$$\rho = M_w / \left((4/3)\pi R_h^3 N_A \right) \quad (1)$$

where M_w is molecular weight (g/mol), R_h is hydrodynamic radius, and N_A is Avogadro's number. This ρ values (~ 0.01 g/cm³) suggested that microgel seems to be formed via cross-linking and have an obscure surface due to a lot of dangling chains (Fig. 1(b)) [37]. This figure shows that morphological characteristic of this microgel seems to be different from that of spherical “hard” colloids such as poly(styrene) latex and proteins.

2.2. Light scattering behavior of polyelectrolyte microgel

The interesting property of such microgels is to show the volume change or dispersion-aggregation in response to the change of pH,

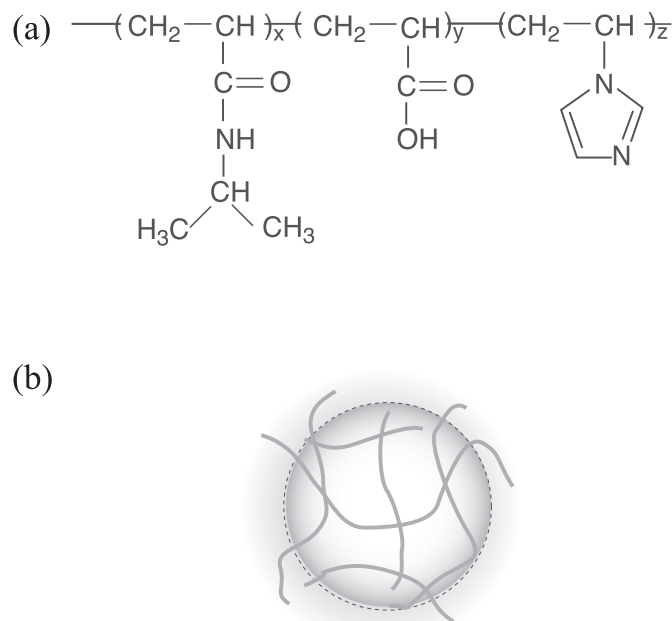


Fig. 1. Polyelectrolyte (polyampholyte) microgel presented in this review: (a) structural formula of copolymer of N-isopropylacrylamide, acrylic acid as anionic monomer, and N-vinylimidazole as cationic monomer which is component of microgel; (b) schematic illustration which was expected from the results of SLS and DLS (Table 1). This drawing (b) was adapted from [37]. Reprinted from [37] with permission. Copyright 2003 American Chemical Society.

temperature and salt concentration in solution [37]. These behaviors are due to the change of the *intra*- and *inter*particle interactions, that is, hydrogen-bonding, hydrophobic interaction, and electrostatic interaction. Volume change and dispersion-aggregation of microgel can be detected by R_h in light scattering measurement and turbidity in the spectrometry, respectively. Generally, it is very difficult to measure R_h of linear polyelectrolyte in salt-free solution due to its weak light scattering [33,34]. On the other hand, polyelectrolyte microgels have strong light scattering intensity to measure R_h even in salt-free solution. The microgels with such properties were used in the formation of IPECs.

3. The dependence of mixing ratio and salt concentration on the resulting type of IPECs between cationic microgel and polyanion

3.1. Combination of polyelectrolyte microgel and linear polyelectrolytes

The combination of potassium polyvinyl sulfate (KPVS; $M_w = 4.19 \times 10^5$ g/mol) (Fig. 2) and polyampholyte microgel mentioned in previous section (Fig. 1) was used in IPECs formation system [38]. This complex formation is due to electrostatic interaction between anionic KPVS and cationic microgel whose imidazole residue was fully protonated at pH 3. The complex was prepared by titration of KPVS solution (pH 3) to 50 mL of microgel dispersion (pH 3) in the absence and the

Table 1
Several characteristics (25 °C) of the polyelectrolyte (polyampholyte) microgel. Reprinted from [37] with permission. Copyright 2003 American Chemical Society.

Charge density (mmol/g dry weight)		$10^{-5}M_w$ (g/mol) ^b	R_g (nm) ^{b,c}	R_h (nm) ^d	pI ^e
Carboxyl ^a	Imidazole ^a				
1.36	1.12	149	81	87	5.3

^a Determined by potentiometric titration in 0.5 M KCl solution at 25 °C.

^b Determined by static light scattering (SLS) in 0.1 M KCl at pI solution at 25 °C.

^c Radius of gyration (R_g).

^d Determined by dynamic light scattering (DLS) in 0.1 M KCl at pI solution at 25 °C.

^e Determined by electrophoretic light scattering (DLS) in 0.01 M KCl solution at 25 °C.

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