



Interpolyelectrolyte complex formation: From lyophilic to lyophobic colloids



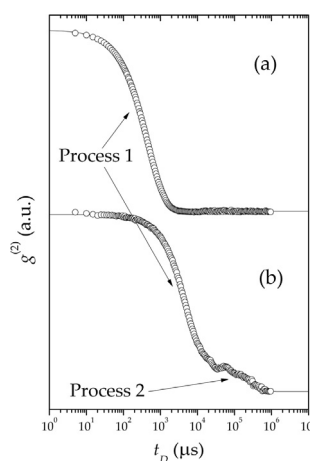
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HIGHLIGHTS

- IPEC particles were formed from chitosan (CS) and an anionic polyelectrolyte (PSSMA).
- Turbidity, conductivity, and viscosity indicated best PSSMA/CS ratio for PEC formation.
- At this very ratio zeta potential suggested IPEC system to be stoichiometric.
- ICF detected a second relaxation process and narrowing of relaxation rate distributions.
- SAXS suggested particles initially have a globular nature before phase segregation.

GRAPHICAL ABSTRACT



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ABSTRACT

Interpolyelectrolyte complexes (IPEC) have been used in different fields, ranging from biomedicine to oil exploration. Particle dimension is a key parameter for the use of an IPEC for a particular application. In this work, dynamic and static scattering (in the form of optical DLS and SAXS, respectively) were used to follow particle growth as a function of anionic/cationic polyelectrolyte mass ratio, w_{AC} , coupled to turbidimetry, conductometry, viscometry, and zeta potential measurements. Turbidimetry, conductometry, and viscometry showed that at $w_{AC} \cong 2$ the IPEC dispersions presented changes that were associated to a massive production of IPEC particles. At the same w_{AC} value, zeta potential measurements indicated an apparent isoelectric point, showing that this w_{AC} must be related to a stoichiometric point for IPEC formation. Double KWW equation was adjusted to data from DLS intensity correlation functions, and parameters related to the distribution of relaxation rates presented characteristic changes at the same value of w_{AC} . SAXS was used to follow particle growth until massive IPEC production. It showed that particles firstly were in the form of small, globular particles, tending to unfolded chain geometry, which can be related to the occurrence of flocculation, just at the point of massive IPEC production.

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1. Introduction

Interpolyelectrolyte complexes (IPEC) nanoparticles have already been used in (or proposed for) applications related to drug

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release [1–6], oil recovery [7], membranes [8] and environment remediation [9,10], among others [11–13]. In fact, dimensions of IPEC clusters may be so small that they may exist in the form of solubilized structures or solid IPEC particles dispersed in a continuous liquid phase [14,15]. This flexibility of behavior makes them, apart from being used as solid particles, to be used in the form of solutions, in order to obtain membranes [16,17].

IPEC's may be formed by simply mixing solutions of macro-ions [18]. These mixtures may be directly carried out, or they can be prepared using a dispersed aqueous phase, such as in emulsion-based process for IPEC preparation [19,20]. Examples of anionic polyions used in these systems are poly(acrylic acid) [21], sodium salt of poly(styrene sulfonic acid-co-maleic acid) [22,23], alginate [24,25], dextran sulfate [26], and carrageenan [27].

Chitosan has widely been reported to be used as a cationic macro-ion to obtain IPEC's [28–31]. This natural polymer has wide applicability [32–34] and has excellent physical and biological properties [35,36]: in fact, it has been shown that specific interactions with drugs make it an excellent candidate for effluent treatment of drug loading for posterior drug release [37–39]. The cationic nature and high density charge in acid solution make chitosan extremely adequate to form polymer networks in IPEC's with water-soluble polyanionic species [40].

Chitosan-based IPEC particles have initially been characterized as a result of electrostatic interactions between cationic groups from chitosan an anionic groups from the polyanion. A more representative, comprehensive mechanism of IPEC particle formation depicts it as being entropically driven by the delocalization of both polycation and polyanion counter-ions. In this manuscript, we intend to carry out a study on the formation of IPEC particles, following the approach already developed by Izmorudov et al. [41], involving the usual techniques of conductometry, zeta potential, viscometry, and static light scattering. In addition to this, we explore dynamic aspects of IPEC formation using DLS, correlating them with the deconvolution of pair-distance distributions from SAXS.

2. Experimental

2.1. Materials

Chitosan (CS) used in this work was purchased from Polymar LTD (Brazil) and was purified as reported in the literature [39]. It had a deacetylation degree of 88%, determined by CHN elemental analysis and conductometric titration as described elsewhere [42], and average viscometric molar mass, $\bar{M}_V = 1.6 \times 10^5 \text{ g mol}^{-1}$, was determined using Mark-Houwink-Sakurada equation [43,44]. Sodium salt of poly(styrenesulfonic acid-co-maleic acid) (PSSMA, $\bar{M}_W = 2.0 \times 10^4 \text{ g mol}^{-1}$, styreneulfonic/maleic acids ratio of 1:1, Aldrich, Brazil) and acetic acid (P.A., Cromato Produtos Químicos LTD, Brazil) were used as received. Bi-distilled water was used in all experiments.

2.2. Interpolyelectrolyte complex preparation

Interpolyelectrolyte complexes were prepared by mixing positively charged CS and negatively charged sodium salt of PSSMA. 15 mL of aqueous solution of polyanion, with concentrations ranging between 0.1 and 0.5 g L^{-1} , were added to 15 mL polycation aqueous solution with concentration 0.2 g L^{-1} . Both CS and PSSMA were solubilized in acetic acid 2%. The resultant dispersion was kept at room temperature (25°C) for 18 h before any experiment. The

parameter analyzed in this study was the ratio between the mass of anionic PSSMA and cationic chitosan, w_{AC} , defined as:

$$w_{AC} = \frac{m_{PA}}{m_C} = \frac{V_{PA}C_{PA}}{V_C C_C} = \frac{C_{PA}}{C_C}, \quad (1)$$

where m_C is the mass of chitosan, m_{PA} is the mass of polyanion, $C_C = 0.2 \text{ g L}^{-1}$ is the chitosan solution concentration, C_{PA} is the polyanion solution concentration, and $V_C = V_{PA} = 15 \text{ mL}$ are, respectively, chitosan and polyanion solution volumes.

2.3. Analyses carried out with the dispersions

2.3.1. Turbidimetry

Turbidimetry was carried out using a Hatch turbidimeter (model 2100P, USA). The instrument was equipped with a tungsten-filament lamp, and a 90° detector to monitor scattered and transmitted light. According to manufacturer, the lamp yielded white light with a continuous spectrum. The instrument's micro-processor calculated the ratio of the signals from the 90° and transmitted light detectors, correcting interferences from color and/or light absorbing materials. All the measurements were taken at room temperature [$(25 \pm 1)^\circ\text{C}$] and the turbidity values were averages of six repeated measurements.

2.3.2. Conductometry

The conductivity of the dispersion was measured using an MCE-105 conductivimeter (MS Tecnopon, Brazil). All the analyses were carried out at room temperature [$(25 \pm 1)^\circ\text{C}$].

2.3.3. Zeta potential measurements

The determination of electroforetic mobility, μ_E , was carried out using a Zeta-Meter System 3.0+ (Zeta-Meter Inc., USA). Zeta potential, ζ , was calculated from μ_E by employing the Smoluchowski relationship [45,46]:

$$\zeta = \frac{\mu_E \eta}{\epsilon_0 \epsilon'}, \quad (2)$$

where ϵ_0 is the permittivity of vacuum; ϵ' is the dielectric constant of water; and η is the viscosity of the medium. All measurements were taken at room temperature [$(25 \pm 2)^\circ\text{C}$].

2.3.4. Viscometry

Viscometry of the resultant dispersions was carried out using a Cannon-Fenske viscometer (size 100), previously calibrated with different fluids in a thermostatic bath. The temperature used in these experiments was $(25.0 \pm 0.1)^\circ\text{C}$.

2.3.5. Dynamic light scattering (DLS)

DLS can be used to probe dynamic processes occurring in dispersions using the intensity correlation function, $g^{(2)}(t_D)$ [47–49]:

$$g^{(2)}(t_D) \equiv g^{(2)}(t_D, q) = \frac{\langle I(0; q)I(t_D; q) \rangle_t}{\langle I(0; q) \rangle_t^2}, \quad (3)$$

where t_D is the delay time, $I(t_D; q)$ is the scattered intensity at time t_D , q is the scattering vector modulus, $\langle \cdot \rangle_t$ denotes a time average of \cdot , and $g^{(2)}(t_D)$ is the scattering field time-correlation function. The intensity correlation function (ICF) $g^{(2)}$ is related to $g^{(1)}$, the theoretical field autocorrelation function, according to

$$g^{(2)}(t_D) = 1 + \beta [g^{(1)}(t_D)]^2, \quad (4)$$

where β is a constant that depends on the optical properties of the system. If there is a well defined, discrete, relaxation process, $g^{(1)}$ is

$$g^{(1)}(t_D) = e^{-\Gamma t_D}, \quad (5)$$

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