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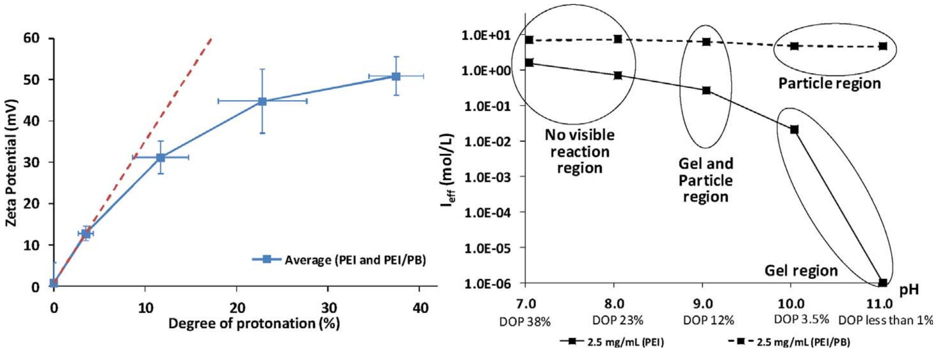
Effect of physical conditioning of pH responsive polyamine nuclei and their subsequent silication

Ahmad Seyfaee[a], Roberto Moreno-Atanasio[a], Frances Neville[b],*

[a] School of Engineering, The University of Newcastle, Callaghan, New South Wales 2308, Australia
[b] School of Environmental and Life Sciences, The University of Newcastle, Callaghan, New South Wales 2308, Australia

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, aqueous solutions of polymeric nuclei based on the polymer polyethyleneimine (PEI), were characterized as a function of pH. The viscosity and zeta potential values of the polymeric solutions were measured and have been related to the degree of protonation of PEI. In addition, the silication of the polymeric nuclei solutions was carried out using trimethoxymethylsilane and the products produced were characterised. The results demonstrate that the zeta potential of the silica particles made with the polymeric nuclei solutions coincides with the zeta potential of the polymeric nuclei solutions themselves, before their silication. Furthermore, a new parameter called the effective ionic strength, I_{eff}, was defined as the ratio of the ionic strength of the solution to the effective electrostatic nuclei packing. The I_{eff} values were compared with the silication product results for the different experimental conditions used. For the highest values of pH studied (10–11), silication of the PEI nuclei yielded particles if the effective ionic strength was high, otherwise, gel was formed. In contrast, a decrease in the value of pH to 9 was associated with a regime in which both particles and gel were observed simultaneously. A further decrease in pH (7–8) resulted in no visible reaction. It is expected that the understanding gained from this study should be applicable to other polyamines and silica precursors and therefore this information may be used to predict and control silica growth in general.

Abbreviations: PEI, polyethyleneimine; PB, phosphate buffer; TMOMS, trimethoxymethylsilane; DLS, dynamic light scattering; EEP, effective electrostatic nuclei packing

* Corresponding author.

E-mail address: Frances.Neville@newcastle.edu.au (F. Neville).

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1. Introduction

Silica particles have been found to be applicable in many technological innovations, namely catalyst design, protective coatings, paint additives and supports for biomolecular entrapment (especially in medical, biosensing or antifouling fields) [1–9]. There are several methods to produce silica, one of which is biomimetic synthesis [10–15], which draws inspiration from natural biosilication [16–17]. Biomimetic synthesis methods utilize an entrapped bio-inspired silica-tion-inducing catalyst in an aqueous environment, to exercise great morphological control of the silica particles produced [16]. One such bioinspired silication catalyst is the synthetic polybasic peptide mimic, polyethyleneimine (PEI), which, when combined in solution with phosphate ions, mimics the chemical activity of the biomolecule silaffin [13,18–20]. To induce silication, the entrapped PEI catalyst acts as an “in situ” surface modifier introducing an amine functionalization of the PEI-silica particles without the need for post synthesis modifying treatments [13,21–22]. Surface modified PEI-silica particles [21–24], may be used in carbon dioxide capture [25], medical applications [26] and gene delivery [27]. However, despite their vast range of applications, so far there has been no detailed study on the effect of the physical conditions of PEI on silica particle formation.

To fabricate PEI-silica particles with favoured characteristics such as shape and size, it is essential to know the effect of the reaction conditions and all the chemicals involved in the synthesis process. Seyfaee et al. [22] studied the effect of chemical concentration on PEI-silica particle formation [22]. The PEI-silica particles they fabricated used trimethoxymethylsilane (TMOMS) as the silica precursor in a mixture of PEI and phosphate buffer (PB) solution (PEI/PB solution) [22]. It was reported that the final particle diameter showed a stronger dependency on silica precursor concentration than on PEI/PB concentration. Although the values of Si/N molar ratios were not explicitly reported, the minimum and maximum Si/N ratios used were 0.43 and 6.88 respectively. Their results showed that even for a constant Si/N ratio, the final concentration of Si in the reaction needed to be higher than 25 mM in order to produce isolatable particles [22].

The formation of PEI-silica particles occurs in three different stages: nucleation, growth and equilibrium [22–23]. During the nucleation stage (induction), particle diameter varies little with time and principally primary particles (< 25 nm) form. The growth stage, which is due to the aggregation of primary particles [23], is characterized by a rapid increase in particle diameter. This stage is followed by the equilibrium stage in which particle diameter does not change significantly. However, during this equilibrium region, particle surfaces become smoother as monomeric or dimeric silica molecules condense onto them [22–23].

It has been reported that the amine groups of biomimetic polyamines (*e.g.* PEI) attract hydrolysed silica precursor molecules [23,28–29] and may act as nucleation sites for the silication reaction [29]. Thus, they may be referred to as PEI nuclei. Further growth of silica around polyamine nuclei (entrapping PEI), results in a phase separation and primary particles are produced [30]. Aggregation of these primary particles as well as their production is highly influenced by the physical conditions of the PEI molecules and the reaction solution (e.g. ionic strength, pH). Despite the potential role PEI nuclei properties play on the silica product, there is yet to be a study focused on this matter. Thus, this work concentrates on the characterization of polyamine nuclei and their influence on the final silication products, which have also been modelled using a new parameter called the effective ionic strength.

2. Experimental section

2.1. Materials

Phosphate buffer (PB) consisting of sodium dihydrogen phosphate (NaH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) each at 0.58 M were mixed until the final pH was 7.4. Branched polyethyleneimine (PEI) with molecular weight of 25,000 g/mol and polydispersity index of 2.5, trimethoxymethylsilane (TMOMS) with final concentration of 0.2 M, hydrochloric acid (1 mM and 10 M), sodium hydroxide (10 mM and 2 M) and sodium nitrate (10 mM) were prepared using chemicals as supplied (Sigma-Aldrich). To prepare the desired concentration in all of the experiments, deionised water (18.2 Ω cm) was used.

2.2. Nuclei study

To characterize the polyamine derived nuclei, viscosity, dynamic light scattering (DLS) and zeta potential measurements on PEI and PEI/PB solutions of different concentrations (5, 10, 25 and 50 mg/mL) at different pH values (7, 8, 9, 10 and 11) were carried out. In all of the PEI/PB solutions the molar ratio of [PEI]:[PB] was kept constant at 1:290. After preparation of the desired concentrations of PEI and PEI/PB, small volumes of highly concentrated HCl (10 M) and NaOH (2 M) were added to the solution to adjust the pH values. Since the acid or base added was highly concentrated the amount added to the solutions to adjust their pH did not significantly vary the total volume of solutions. Hence, it was assumed that the concentration of PEI remained approximately constant. Each polymeric solution (PEI or PEI/PB) was given 48 h to equilibrate at 4 °C (before and after pH adjustments) prior to any measurements.

An Ubbelohde viscometer was used to measure the viscosity of the solutions. To maintain the solution temperature constant at 22 °C, a water bath was used. After loading the viscometer with the chosen solution, 15 min were given for the sample to reach thermal equilibrium with the water bath. Then, the time necessary for the solution to drain between two specific marks was recorded (drainage time). Three measurements of drainage time were made per sample, after which the viscometer was washed 3 times using water, followed by sonication with water for 15 min. Then, the viscometer was filled with acetone and sonicated for 15 min. To increase the efficiency of sonication, the ultrasonic water bath was filled with cold water (~4 °C). After the acetone-sonication washing step, the fluid inside the viscometer was drained and the viscometer was dried in the oven for 30 min at 70 °C. Each data point in the viscometry technique was reproduced by preparing three identical solutions for each concentration and pH.

In order to measure the diameter of polyamine nuclei or their zeta potentials, 1 mL of each solution (PEI or PEI/PB) was taken. Samples were characterized using a Malvern Zetasizer Nano ZS instrument. Plastic disposable cuvettes or zeta potential cells were used for mean intensity diameter or zeta potential measurements, respectively.

2.2.1. PEI viscosity and determination of nuclei hydrodynamic diameter

Knowing the viscosity of pure water and comparing the drainage time of the pure water with those of polymeric solutions, the viscosity of the polymeric solutions (PEI or PEI/PB) was calculated using Eq. (1),

$$\frac{\eta_s}{\eta_w} = \frac{t_s}{t_w} \tag{1}$$

where η (mm^2/s) and t (s) symbolize kinematic viscosity and drainage time respectively. The subscripts s and w represent the polymeric solution (PEI or PEI/PB) and pure water, respectively.

To determine the hydrodynamic diameter of polyamine nuclei (PEI) using the kinematic viscosity data (see results and discussion), the intrinsic viscosity, $[\mu]$ (cm^3/g), was calculated for each pH value, for both PEI and PEI/PB solutions. Then, using Eq. (2) the nuclei diameter was calculated [31–32].

$$d = \sqrt[3]{\frac{6\mathrm{M_w}}{2.5\pi}\frac{[\mu]}{\mathrm{N_a}}} \tag{2}$$

where M_w and N_a are the molecular weight (g/mol) of the solute (PEI)