

Probe and Matrix Diffusion of Polystyrene Particle and Labeled Polyallylamine Hydrochlorate

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Introduction

Particle-polymer interactions play an important role in industrial applications and they have been studied extensively.^{1,2} In recent to understand electrostatic interaction between charged particle and polyelectrolytes became more important due to development of LBL (layer-by-layer) technique that provides higher flexibility for surface property modification to materials used in electronics, optics, pharmacy fields.³ In the LBL technique, the formation of multilayer with polyelectrolyte is based on the consecutive adsorption of polymer with alternating charge. The particle-particle or particle-polymer interactions have a substantial effect on polymer conformation, charge on probe molecules or polymer chain in solution.² When interactions between particles and polymers occur, stabilization, destabilization can be occurred. When interactions between particles and polymers occur, stabilization, or destabilization can occur. In stabilization, there are two basic mechanisms namely charged and steric stabilization. When a solution is destabilized, colloidal particles can form aggregates.

We choose PS particles with a negatively charged surface (sulfate modified) as the probe particle and the positive charged polyelectrolyte PAH as the matrix to explore the effect of concentration and salt between particle and polyelectrolyte interaction. Because of dimension of PAH that strongly affected by matrix and salt concentration, sulfate PS and PAH solution showed different features at dilute and concentrated condition. We will discuss this phenomenon in terms of electrostatic interaction between the probe and matrix and contraction of the polymer with SE deviation through DLS, FPR, and viscosity experiments.

Experimental

Material. PS (200 nm, SD = 5.2 nm) particles with a negatively charged surface (sulfated modified) were purchased from Polymer Science, Inc. Poly(allylamine hydrochloride) (PAH; $M_w = 70,000$) and fluorescein isothiocyanate, isomer I (FITC; $M_w = 389.39$) were obtained from Aldrich. For the FPR experiment, PAH was labeled with FITC. 10 g of PAH solution was mixed in 10^{-4} M FITC that was dissolved in DI water.

Sample Preparation. Polyelectrolyte solutions were prepared by thoroughly mixing appropriate amounts (from 0.5 g/L to 100 g/L) of PAH powder in the desired solutions. The probe concentrations were kept as low as possible to lower interaction among probe particles. The final probe concentration of all solution was 2.5×10^{-3} %. NaCl salt was used to control the ionic strength of solutions.

Fluorescence Photobleaching Recovery. The FPR instrument was built with an Olympus Labshot microscope. To catch the fluorescence image, FITC filter cube was used. A satellite 2017 argon ion laser was used as the source beam (488 nm). The laser beam was passed through a NEOS 35085 acoustic modulator (AOM) driven by 31085-6DS radio-frequency source for the bleaching. The acquired signal through PMT was fed on to the lock-in amplifier (Signal recovery 7265). The data from the lock-in amplifier was saved on the computer through a GPIB card (National Instrument, GPIB-USB-B⁴).

Light Scattering Measurement. Dynamic light scattering experiments were performed using an ALV-5000/E/WIN multiple tau correlator with a JDS-Uniphase He-Ne ion laser with a wavelength of $\lambda_0 = 632.8$ nm. The intensity correlation function, $g^{(2)}(\tau)$, obtained at a 90° scattering angle $g^{(2)}(\tau)$ is related to the electric field correlation function, $g^{(1)}(\tau)$, by the following equation, $g^{(2)}(\tau) = B(1 + f |g^{(1)}(\tau)|^2)$. Here, τ is the lagtime, B is the baseline, and f is an instrumental parameter determined by deviation from an ideal correlation. The relaxation time distributions were obtained by analyzing $g^{(2)}(\tau)$ by a CONTIN algorithm, which was programmed by a ALV-5000/E/WIN multiple tau correlator with 288 exponentially spaced channels. Diffusion coefficients were obtained with non-linear algorithm.

Viscometry. Viscosities of the polyelectrolyte solutions were measured using Brookfield DV-III viscometers in a water bath kept at

$25 \pm 1^\circ\text{C}$. The experimental values were calibrated from measured DI-water viscosity. The measurement time for each sample was 30 s. Three measurements were made for each concentration, and the average and standard deviation (SD) were obtained.

Results and discussion

The adsorption behaviors of positively charged matrix (PAH) onto negatively charged probe (sulfate PS particle) were investigated using DLS (dynamic light scattering) and FPR (fluorescence photobleaching recovery) as view points of matrix and salt concentration.

Diffusion coefficients of sulfate polystyrene (Sul-PS) particles at three salt conditions (0 mM, 50 mM and 100 mM, respectively) were measured from dilute (0.5 $\mu\text{g/L}$) to high concentrate PAH concentration (100 g/L). The dynamic behaviors of the Sul-PS particles varied with the PAH and salt concentrations. In terms of the matrix concentration, flocculation occurred as diffusion coefficients of particles decreased from 0.5 $\mu\text{g/L}$ to 50 $\mu\text{g/L}$. Above 50 $\mu\text{g/L}$, the flocculation gradually removed. Probes were most stable at 0.1 g/L. Above at 0.1 g/L, diffusion coefficients gradually decreased as the polymer concentration was increased. As a point of NaCl salt concentration, slow diffusion coefficients were observed due to increased salt concentration in dilute polymer concentration (below 0.1 g/L) but reversed in semi-dilute concentration (from 0.1 g/L to 40 g/L), that is, slow diffusion coefficients were monitored as decreased salt concentration. These salt effects disappeared at concentrate polymer concentration (above 40 g/L) as shown in Figure 1.

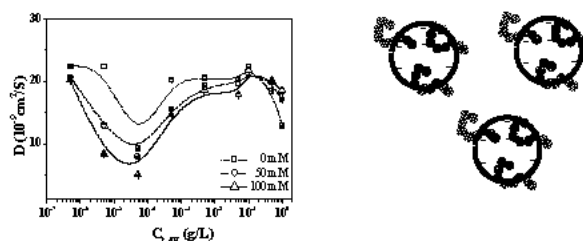


Figure 1. Diffusion coefficient for sulfate PS particles as a function of PAH concentration (from 0.5 mg/L to 1 g/L) at three NaCl salt concentrations: (square) 0mM, (circle) 50mM, (triangle) 100 mM. And the cartoon shows the interaction between the particles and the matrix polymers.

The system experienced sharp decrease of diffusion (flocculation) at dilute condition while the system underwent gradual decrease of diffusion above semi-dilute concentration. With FPR and viscometry experiments, we revealed the probe behaviors in polyelectrolyte solution were strongly affected by the coil overlap concentration (0.5 g/L PAH concentration). The hydrodynamic radius of matrix was about 30 nm that presents entanglement dimension of PAH at near the coil overlap concentration but the hydrodynamic radius after that concentration showed gradual decrease that means transition toward a network structure. In this system, salt acts as an obstacle preventing electrostatic interaction between the probe and matrix or a shrinker to contract matrix dimension. As a result of competition of two effects, the highest salt concentration presented maximum flocculation below the coil overlap concentration and the maximum electrostatic interaction was shown at a salt concentration of 50mM above that concentration. A weak positive Stokes-Einstein deviation in the system was observed near the coil overlap concentration.

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