Experimental Report

15/01/2014

Proposal: **9-11-1585** **Council:** 4/2012

Title: NSE study of the collective dynamics of counterion presenting in solutions of polyelectrolyte with different conformation

This proposal is resubmission of: 9-11-1545

Researh Area: Physics

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Samples: polystyrene

Instrument	Req. Days	All. Days	From	To
IN15	11	7	19/07/2013	26/07/2013

Abstract:

Polyelectrolytes possess unique properties because of the presence of charges. Numerous commercial applications have been developed using these materials, mostly related to their capabilities of modifying flow and stability properties of aqueous solutions and gels. Generally, the small angle neutron scattering (SANS) intensity I(Q) obtained from polyelectrolyte solutions are characterized by the presence of an interaction peak. In addition, an upturn is always present in the low Q region. This low Q upturn cannot be predicted by any existing liquid theories or computer simulations. But they are possibly related to the stability and structure formation of a variety of ionic macromolecules in aqueous media. Understanding the origin of this phenomenon is critical in the development of charged polymers with desired functionality. The focus is placed on elucidating the correlation between the collective motions of counterion and the conformation of polyelectrolyte, which has been shown to greatly influence the large-scale density fluctuation of polyelectrolyte solutions.

Experimental Report of IN15

The properties of soft colloidal solutions have been known to exhibit a strong dependence on concentration c. Similar to the linear polymer systems, an overlap concentration c* for soft colloids has been used as a critical point to define different solution regimes characterized by distinct conformational and dynamical features. The physical size of an unperturbed soft colloid in solution is used to determine c* geometrically. Below c* each soft colloid is considered to be independent since the physical interpenetration and congestion between neighboring particles is minimal. Therefore, in this static picture, it is generally believed that within the dilute concentration region of c < c* their internal dynamics and conformation essentially remain unchanged. Using IN15, we explore the dynamical properties of Poly(amido amine) (PAMAM) dendrimers, an extensively studied soft colloid model system. Their dynamics in solutions is characterized by internal collective motion as well as center-of-mass diffusion. We demonstrate that the competition between the relaxation processes associated with these two degrees of freedom results in strong dependence of dynamics and structure on colloid concentration, c, well below the overlap concentration c* (Figure 1). Triggered by the increasing inter-particle collisions, resultant slow-down of internal dynamics occurs before actual colloidal overlap develops. Complementary D22 experiment reveals that this progressively sluggish internal dynamics in manifested by the substantial structural dehydration (Figure 2). This observation is surprising since it is generally believed that the internal dynamics and conformation of soft colloid essentially remain invariant below c*. The competition between these two competing relaxation processes gives rise to a dynamic crossover at a dynamically-defined dilute threshold concentration well below c*.

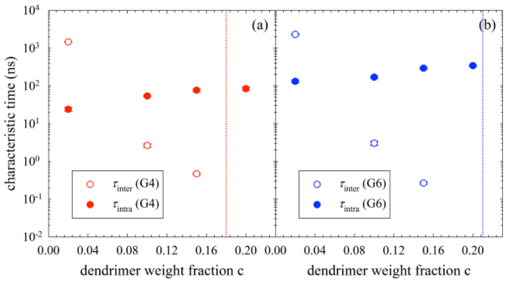

Figure 1. The average inter-dendrimer collision time $\boldsymbol{\tau}_{\text{inte}}$ (open circles) and internal relaxation time $\boldsymbol{\tau}_{\text{intra}}$ (filled circles) for G4 (a) and G6 (b) PAMAM dendrimers in water as a function of concentration. The dotted lines giv the *c** of PAMAM dendrimers. For both cases, a dynamical crossover is observed at *c* ~ 0.05 which is significantly less than *c** (dotted red and blue lines).

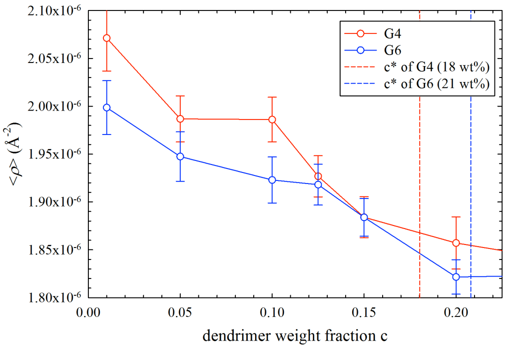

Figure 2. The average scattering length density of a single dendrimer $<\rho>$ for G4 and G6 PAMAM dendrimer in water as a function of concentration. Upon increasing *c*, a progressive decrease in $<\rho>$ is observed. Our data analysis demonstrates that this observation is the reflection of the decrease in intra-dendrimer hydration.