Synthesis and Characterization of Polyectrolyte Grafted Charged Colloidal Particles

P. S. Mohanty, T. Harada, K. Matsumoto and H. Matsuoka Department of Polymer Chemistry, Kyoto University, Kyoto 615-8510, Japan

Novel polyelectrolyte grafted charged colloidal have been synthesized via emulsion particles polymerization method using block copolymer as an emulsifier and have been characterized by determining the surface charge (Z) number, chain density (σ) using conductometric titration, the size distribution, hydrodynamic (R_h) radius by dynamic light scattering and the core radius (R_c) by atomic force microscopy. The structural ordering and dynamics have been investigated in very dilute concentration and the effect of salt concentration (C_s) on hydrodynamic radius at dilute concentration have also been studied using dynamic light scattering.

Polyelectrolyte grafted charged colloidal particle have been the focus of a large number of experimental and theoretical studies [1]. It has been shown by both theoretically and experimentally [1] that majority of the counterions are confined within the corona of the brushes and give rise to an effective osmotic interaction. So at very low salt concentration, the chains may be stretched to nearly full length. Such systems can be generated by photo emulsion polymerization [2] and by emulsion polymerization using block copolymer as an emulsifier. So far the synthesis and characterization of these particles by the later method are very rare. Moreover block copolymer has advantage that it can readily form micelles in aqueous media [3] because of its hydrophobic and hydrophilic part and also can be used to understand the adsorption at air/water interface [3]. So block copolymer plays a major role in the stabilization of colloidal particles. Hence this motivates us to synthesize and characterize grafted charged colloidal particles.

Table 1:Characteristics of polyelectrolyte grafted latex particles

Samples	$R_{\rm h}$	σ	Z	$R_{\rm c}$
(wt %)	(nm)	(nm^{-2})		(nm)
S1(0.0005)	85±3	0.1	5×10^{5}	70
S2(0.0005)	80±3	0.035	1×10^{5}	65

These particle are synthesized via emulsion polymerization method using polystyrene – b – poly (sodium styrene sulphonate) (PSt-b-PSSNa) block copolymer (m: n = 90:65, M_w/M_n = 1.3) as an emulsifier. Potassium oxydisulfate was used as the initiator, and the polymerization was performed at 70 °C. Investigations are carried out at very dilute concentrations using light static and dynamic light scattering.

From the static light scattering, the structural ordering of these particles at 0.0005 wt % showed a gas-like disorder. The influence of salt concentrations (C_s) on R_h showed that after a certain critical salt concentration (C_s =

0.02 M, 0.01M for S1 and S2, respectively), the R_h decreases rapidly with the increase of C_s (Fig. 1). This is due to the electrostatic screening of the counterions by the salt ions [4]. In this salted regime, the R_h showed a scaling behavior (inset of Fig. 1) with the C_s ($R_h \cong C_s^{\alpha}$, $\alpha = -0.105$, -0.08 for S1 and S2, respectively). Further, the R_h measured at higher C_s for S1 and S2 showed a good agreement with the core radius measured by AFM (shown in Table 1).

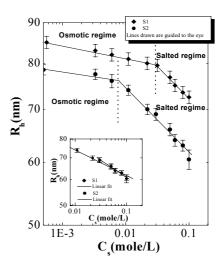


Figure 1: R_h vs C_s . The inset figure shows the linear fit to R_h in the salted regime.

In conclusion, newly synthesized polyelectrolyte grafted charged polystyrene colloidal particle are found to be highly stable against the salt concentrations compared to normal latex colloidal particle. The hydrodynamic radius is found to decrease after a critical salt concentration because of electrostatic screening of counterions with the salt ions. These results are in agreement with the recent theoretical prediction that most of the counterions are confined inside the brush region which led to stretching of the chains at low salt concentrations.

References

- [1] X. Guo, M. Ballauff, *Phys. Rev. E* **64** (2001) 051406.
 [2] X. Gao, X, A. Weiss, M. Ballauff, *Macromolecules* **32** (1999) 6043293.
- [3]H.Matsuoka, S. Maeda, P. Kaewasaiha, K. Matsumoto, *Langmuir*, **20** (2004) 7412.
- [4] P. S. Mohanty, T. Harada, K. Matsumoto and H. Matsuoka *Polymer Prep. Japan*, **45** (2005) 1081.