Static and Dynamic Scattering from Polysulfobetaine Immobilized on Silica Nanoparticle in Ionic Liquid

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Abstract. Monodisperse silica nanoparticles were immobilized with poly[3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammonatopropanesulfonate)] (SiNP-PMAPS) by surfacinitiated atom transfer radical polymerization. SiNP-PMAPS was characterized in 1-hexyl-3-methylimidazolium chloride (HMImCl) solution by dynamic light scattering (DLS) and synchrotron small angle X-ray scattering (SAXS) measurements. The relaxation spectrum of DLS and SAXS profile for SiNP-PMAPS solutions showed a unimodal distribution attributed to the homogeneous dispersion of SiNP-PMAPS in the HMImCl without any aggregations. The scattering factor from the SiNP-PMAPS in HMImCl was described by the core-shell model considering interacting excluded-volume chains and assuming Schulz distributed core with the thickness of polymer layer of 56 nm.

1. Introduction

Sulfobetains are special classes of zwitterions having ammonium cation and sulfonate anion isolated with some methylene spacer, such as propyl and butyl group. The poly[3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammonatopropanesulfonate)] (PMAPS) exhibit a unique aqueous solution behavior in contrast with the conventional polyelectrolytes. For instance, the PMAPS are insoluble in pure water and can dissolve in above 60 mM NaCl aqueous solution at 30 °C [1]. The chain dimension of the PMAPS is dependent on the attractive polyampholyte effect (electrostatic attractive forces) between ammonium cations and sulfonate anions of the side chains, and also on the non-ionic excluded-volume effect between segments. The Ionic liquids (ILs) are interesting dispersion media for colloidal particles as well as aqueous solution. The ILs as novel classes of solvent are composed entirely of ions and are fluid at ambient conditions. The ILs exhibit the unique physicochemical properties, such as negligible vapour pressure, nonflammability, and distinguished thermal and chemical stabilities. However, the chain dimension of the PMAPS brush state on silica nanoparticle surface in ionic liquid is still unclear.

In this work, we carried out dynamic light scattering (DLS) and synchrotron small-angle X-ray scattering (SAXS) measurements of polymer-grafted silica nanoparticle (SiNP) in 1-hexyl-3-
methylimidazolium chloride (HMImCl) with high ionic strength (5.19 M) and high viscosity (155 g cm\(^{-1}\) s\(^{-1}\)) to investigate the chain dimension of PMAPS chains.

2. Experiments

SiNP (diameter of 108 nm; Nissan Chemicals) was dispersed in a mixture of ethanol/water/ammonia containing (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE) to immobilize alkylbromide on the surface [2]. The surface-initiated atom transfer radical polymerization of 3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammonatopropanesulfonate) (MAPS) mediated by a copper complex was carried out with the initiator-immobilized SiNP (SiNP-BHE) in 2,2,2-trifluoroethanol (TFE) containing a small amount of 1-hexyl-3-methylimidazolium chloride (HMImCl) at 60 °C [3]. The number-average molecular weight (\(M_n\)) and polydispersity index (\(M_w/M_n\)) of the cleaved graft PMAPS from the SiNP surface with HF aqueous solution were determined to be \(M_n = 2.06 \times 10^5\) g mol\(^{-1}\) and \(M_w/M_n = 1.21\) by size exclusion chromatography calibrated with a series of PMAPSs as a standard. The graft density of PMAS brush on SiNP surface was estimated to be 0.071 chains nm\(^{-2}\) using values of weight loss measured by thermogravimetric analysis of SiNP-PMAPS and \(M_n\) of PMAPS. The average number of graft PMAPS chain per SiNP was estimated to be 2550 by the graft density and the SiNP surface area.

DLS measurements of SiNP-PMAPS in HMImCl at 25 °C were carried out at scattering angle (\(\theta\)) range from 30 to 150 ° using a goniometer system purchased from ALV (Langen, Germany) employing a HeNe laser (wavelength \(\lambda = 632.8\) nm) with a power of 22 mW. The autocorrelation function is obtained by pseudo-cross-correlation of the signals from two photomultipliers to suppress noise. The DLS measured samples were four concentrations (\(C_p = 0.527 - 2.07\) mg cm\(^{-3}\)) of SiNP-PMAPS in HMImCl contained in 10 mm diameter glass cells. The scattering vector (\(q\)) was defined as \(4\pi n_0 \sin(\theta/2)/\lambda\), where \(n_0\) is the refractive index of HMImCl.

SAXS measurements of SiNP-PMAPS in HMImCl at room temperature was carried out at the BL03XU beamline of SPring-8 using an incident X-ray with a wavelength \(\lambda = 0.1\) nm and sample-to-detector distance of 6103 mm. The scattered intensity was detected by an imaging plate with 3000 × 3000 pixels over a scattering vector range from 0.013 to 1.5 nm\(^{-1}\). The scattering vector (\(k\)) as defined by \(4\pi \sin(\theta)/\lambda\) was calibrated by the average of 8 peaks of dry collagen. The SAXS measured samples were four concentrations (\(C_p = 1.03 - 1.81\) mg cm\(^{-3}\)) of SiNP-PMAPS in HMImCl contained in 2 mm diameter quartz capillaries.

3. Results and Discussion

The typical autocorrelation function (\(g^{(2)}(t)-1\)) and relaxation spectrum (\(A(\tau)\)) measured by DLS for the SiNP-PMAPS in HMImCl are shown in Figure 1 (a). The concentration of the SiNP-PMAPS and the scattering angle were 2.07 mg cm\(^{-3}\) and 90 °, respectively. On the ordinate, the \(A(\tau)\) at relaxation time (\(\tau\)) was calculated from the intensity of \(g^{(2)}(t)-1\) at time (\(t\)) by CONTIN analysis. The \(A(\tau)\) was observed as a single and sharp peak. The \(A(\tau)\) of all concentrations and scattering angles for the SiNP-PMAPS solutions showed a unimodal distribution and sharp peak indicating the homogeneous dispersion of SiNP-PMAPS in HMImCl without any aggregations.

The mutual diffusion coefficient (\(D_m\)) and hydrodynamic radius (\(R\)\(_H\)) calculated from \(A(\tau)\) are expressed by the following equations:

\[
D_m = \lim_{q \to 0} \left[ \frac{\Gamma q^{-2}}{\sum \frac{A(\tau)}{\tau^2}} \right] \quad \text{where} \quad \sum_{\tau \to 0} A(\tau) = 1
\]

\[
R_H = \frac{k_B T}{6 \pi \eta_0 D_0}
\]

where \(\Gamma\), \(k_B\), \(T\), \(\eta_0\), and \(D_0\) are the first cumulant, the Boltzmann constant, the absolute temperature, viscosity of the solvent, and the diffusion coefficient at an infinite dilution, respectively.
Figure 1 (b) shows concentration dependence of the $D_m$ at the zero scattering vector for the SiNP-PMAPS in HMImCl at 25 °C. By extrapolating to $C_p = 0$, the $D_0$ and $R_H$ for the SiNP-PMAPS in HMImCl at an infinite dilution were estimated to be $1.57 \times 10^{-12}$ cm$^2$ s$^{-1}$ and 89.8 nm, respectively.

The SAXS profile for the SiNP-PMAPS in HMImCl (2) with $C_p = 1.81$ mg cm$^{-3}$ showed smooth minima in the SiNP-PMAPS form factor which was slightly shifted to a low $k$ region in comparison with that of the SiNP-BHE form factor. The SiNP-PMAPS in HMImCl is expected to form core-shell structure, as shown in the inset of Figure 2 (a). Here we estimated radius of SiNP-PMAPS from the SAXS profile using the core-shell model analysis considering interacting excluded-volume chains [5]. The scattering form factor for core-shell model containing four terms is expressed by

$$P(k) = \left\{ \frac{N^2\Delta Z_{e,core}^2P_{core}(k)}{1 + 2N\Delta Z_{e,core}\Delta Z_{e,chain}S_{core-chain}(k)} \right\} + N\left[ N - P_{PWC}(0) \right] \frac{\Delta Z_{e,chain}^2S_{chain-chain}(k)}{N^2(\Delta Z_{e,core} + \Delta Z_{e,chain})^2}$$

where the $N$ is the number of graft polymer chain, $\Delta Z_e$ is the excess electron density, $P_{core}(k)$ is scattering function for rigid sphere with assuming Schulz distribution, $P_{PWC}(k)$ is scattering function for infinitely thin perturbed wormlike chain [6], $S_{core-chain}(k)$ is structure factor between the core and chains, and $S_{chain-chain}(k)$ is structure factor between different chains.

The theoretical curve calculated by equation 3 with the radius of core $R_c = 53.5$ nm, the polydispersity of core $p = 0.06$, the radius of polymer layer of $s = 28$ nm is shown in Figure 2 (a). The experimental SAXS profile for SiNP-PMAPS in HMImCl was close to the calculated values based on from core-shell model and $P(k)$ function, which related with $\Delta I(k)/\Delta I(0)$.

Figure 2 (b) shows the radial profiles for SiNP-PMAPS in HMImCl estimated from the SAXS profile and the core-shell model with interacting excluded-volume chains. The $M_w$-dependence of $z$-average mean-square radius of gyration ($<S_z^2>$) for the free linear PMAPS in 74 mM aqueous NaCl solution at 25 °C as a theta state is given by the following equation:
The value of polymer layer (2s = 56 nm) was larger than the 2\langle S^2 \rangle^{1/2} for free linear PMPAS chain with same molecular weight and polydispersity in theta state (noninteracting) calculated from equation (4), as shown in Figure 2 (b). The ratio of radius of gyration (56 nm) measured by SAXS to hydrodynamic radius (36.3 nm) measured by DLS for PMAPS layer of SiNP-PMAPS in HMImCl was estimated to be 1.54. Thus, chain conformation of PMAPS brush on SiNP surface is behaved as Gaussian coil.

4. Conclusion

The relaxation spectrum of all concentrations and scattering angles for SiNP-PMAPS solutions by DLS showed a unimodal distribution and sharp peak attributed to the homogeneous dispersion of SiNP-PMAPS in the HMImCl without any aggregations. The scattering factor from the SiNP-PMAPS in HMImCl is described by the core-shell model considering interacting excluded-volume chains and assuming Schulz distribution core with the thickness of polymer layer of 56 nm. The thickness of polymer layer estimated from SAXS profile is larger than the radius of gyration for the free PMAPS chain with same molecular weight in theta state. From the ratio of radius of gyration to hydrodynamic radius for PMAPS layer of SiNP-PMAPS in HMImCl, chain conformation of PMAPS brush on silica surface is behaved as Gaussian coil.

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