Characterization of sodium poly(4-styrenesulfonate)-grafted polymer fine particles synthesized by core-cross-linking of block copolymer micelles

Kozo Matsumoto*, Hirohiko Hasegawa, Hideki Matsuoka

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

Received 30 November 2005; received in revised form 24 March 2006; accepted 24 March 2006

Abstract

The detailed structure and unique characteristics of a sodium poly(4-styrenesulfonate)-grafted nanoparticle, CCL-SBS_{113-}b\text{-SSNa}_{208}, were investigated, where CCL, SBS, and SSNa represent a core-cross-linked micelle, 4-(1-methylsilacyclobutyl)styrene, and sodium 4-styrenesulfonate, respectively. The particle nanostructure was analyzed by small-angle neutron scattering (SANS), dynamic light scattering (DLS), and atomic force microscopy. SANS data suggested that the particle had a core–corona structure with a 14-nm core radius ($R_c$) and 2-nm radius of gyration ($R_g$) corona-forming chain in water. DLS analysis revealed that the hydrodynamic radius ($R_h$) of particle was 100 nm in water, which is much larger than the whole particle size evaluated by SANS, but the $R_h$ value gradually decreased with addition of NaCl and reached a constant value of 61 nm at an NaCl concentration above 0.2 M. Conductometric titration of the acidic form sample with NaOH suggested that the CCL-micelle had exactly the same content of sulfonate groups as the precursor block copolymer. The polySSNa-grafting particle showed high solution stability toward salt addition, which may be due to the electrostatic stabilization effect in addition to steric stabilization by the grafting polymer chains.

Keywords: Polyelectrolyte; Nanoparticle; Micelle; Graft polymer; Sodium poly(4-styrenesulfonate); Cross-link

1. Introduction

Polymers having sulfonate groups have been widely used as functional materials such as ion-exchange resins [1], separation membranes [2], and proton conductive membranes for polymer electrolyte fuel cells (PEFC) [3–11]. We consider that the design and control of micro and/or nanostructure of these materials are particularly important to improve their performance or to create novel materials with excellent functionalities for the next generations.

Recently, self-assembling of a diblock copolymer, which consists of two different polymer chains connected by covalent bonding, has been considered as one of the most powerful tools to fabricate nanostructures [12]. It is well known that a block copolymer forms nano-scale micelles when dissolved in a solvent selective for one of the blocks [13]. In the micelle, the core consists of the insoluble block and the hairy shell consists of the soluble block. Chemical cross-linking of the micelle core gives nanoparticles with soluble chain grafting from its surface [14–22].

Previously, we reported the synthesis of sodium poly(4-styrenesulfonate) (polySSNa)-grafted polymer fine particles starting from a diblock copolymer, poly(4-(1-methylsilacyclobutyl)styrene)-b-poly(neopentyl 4-styrenesulfonate) (polySBS-b-polySSPen), which has a sulfonate-ester-containing segment and a cross-linkable silacyclobutyl-containing segment in one molecule (Scheme 1) [23]. We first prepared block copolymer micelles whose core consisted of polySBS in acetone. Then we cross-linked a core of the micelle by platinum-catalyzed ring-opening reaction of silacyclobutyl moiety, and finally obtained particles of a polySSNa-grafting polymer, CCL-polySBS-b-polySSNa, by hydrolysis and neutralization of the neopentyl-ester protecting sulfonate segment, where CCL denotes the core-cross-linked micelle. This material has a unique structure, which is the strong ionic chains tethered on the nanoparticle...
surface, and can be expected to exhibit interesting properties. In this study, we characterized the structure of the polySSNa-grafted cross-linked particles by neutron scattering (SANS), dynamic light scattering (DLS), and atomic force microscopy (AFM) in detail, and examined the properties of the particles in aqueous media.

2. Experimental section

2.1. Materials

Sodium poly(4-styrenesulfonate)-grafted polymer particle, that is, the core-cross-linked (CCL) micelle of polySBS-b-polySSNa, (CCL-SBS113-b-SSNa208), was synthesized as reported [23]. Water used for sample preparation was obtained by a Milli-Q system (Millipore, Pittsburg, PA) whose resistance was more than 18 MΩ cm. D2O (99.9% atom D) used for SANS experiments was purchased from Cambridge Isotope Laboratories (CIL). Polystyrene lattices, SS175 with a diameter of 130 nm and a surface charge density of 1.2 mC/cm², was prepared by emulsifier-free emulsion polymerization [24]. Sodium dodecyl sulfate (SDS) was purchased from Aldrich and used as delivered.

2.2. Small-angle neutron scattering (SANS)

The SANS measurements were performed with the SANS-U of the Institute for Solid State Physics, the University of Tokyo, in the research reactor JRR-3M, Tokai, Japan. The wavelength (λ) of neutron beam was 7 Å (Δλ/λ = 10%). Sample solutions (1.0 × 10⁻² wt%) were prepared by dialysis of the stock sample H2O solution against D2O, dilution with D2O, and filtered through a membrane (Millex-GV, Millipore, pore-size of 0.22 μm). Solutions were measured in quartz cells (Nippon Silica Glass Co., Tokyo) with a pass length of 4 mm at 25°C. Scattering data measured by a 2D detector were circular averaged to 1D and then corrected for electronic background, and the scattering of the empty cell was subtracted. The data were transformed to absolute intensities using a Lupolen® standard. From all scattering data of samples, we subtracted the scattering from solvent and the calculated incoherent scattering from the polymer. The SANS experiments were carried out at sample–detector distances of 1, 4, and 12 m, covering a range of the scattering vector (q) of 0.002 ≤ q ≤ 0.2 Å⁻¹, and the accumulation times at each distance was 1h, 3h, and 6 h, respectively.

2.3. Dynamic light scattering (DLS)

The DLS measurements were performed with a dynamic light scattering apparatus of Photal SLS-6000HL (Otsuka Electrics, Osaka Japan) equipped with a correlator (Photal GC-1000). He–Ne laser (wavelength, 632.8 nm) was used for the measurements. Sample solutions (1.0 wt%) were prepared by dilution of the sample stock solution and filtered through a membrane (Millex-GV, Millipore, pore size of 0.22 μm). The measurements were performed at 25°C. Typical measuring angles were 60°, 75°, 90°, and 105°. Cumulant fitting was applied for the data analysis. The diffusion coefficient was calculated from the slope of the straight line in the decay rate G versus q² plot, where q is the scattering vector.

2.4. Atomic force microscopy (AFM) measurements

AFM measurements were performed by Seiko SPI3800 probe station and SPA300 unit system of Scanning Probe Microscopy System SPI3900 series using a dynamic force mode (non-contact mode). The micro-cantilever (SI-DF-A, Seiko) was made of silicon and its spring constant was 2 N/m. For sample preparation, the aqueous solution of polymer particle was dropped on a micro-slide glass (IWAKI, Japan) and air-dried.

2.5. Conductometric titration

The CCL-SBS113-b-SSNa208 was converted to complete acid form of CCL-SBS113-b-SS208 by repeated treatment of the aqueous solution with an excess of cationic ion-exchange resin (Organo IR-120B), where SS represents 4-styrenesulfonic acid. The polymer aqueous solution was titrated with 0.01 mol/L NaOHaq while monitoring the electric conductivity with a conductivity meter DS-8 M (HORIBA, Kyoto).
3. Results and discussions

3.1. SANS analysis

The small-angle scattering (SANS) technique is one of the most powerful methods to analyze the nanostructure of fine particles in solutions. SANS was measured for the D_2O solution at 25 °C. The dotted line in Fig. 1 is the SANS experimental profile obtained from a 1.0 × 10^{-2} wt% D_2O solution. Strong scattering in the low angle region indicated the existence of particles in the solution. To analyze the SANS profile in detail, we applied core–corona models [25] proposed by Pedersen et al. to our polymer-grafted particle without considering particle-size distribution. We calculated theoretical profiles of the models and fitted them to the experimental data. A solid line shown in Fig. 1 reproduced the experimental profile well. The deviation in the small angle region (q < 0.06 Å^{-1}) may be due to a trace amount of very large aggregates of the particles. Table 1 shows the fitting parameters thus obtained. The fitting results suggested that the particle consisted of a core with a radius R_c of 14 nm and hairy grafted polySSNa chains with a radius of gyration R_g of 2 nm. The R_c was reasonable, compared to the contour length of polySBS segment (28 nm), while the corona R_g was rather smaller than we expected for ionic polymer chains in aqueous media. We suppose that the polySSNa chain may take compact conformation to reduce a contact of the hydrophobic core with the solvent water. The width of the corona profile s was 9 nm, which represented the thickness of the shell. A sum of the core radius R_c and the width of corona profile s was 23 nm, which corresponded to the radius of the whole particle evaluated by SANS. From the core volume, the volume fraction of polySBS, and density of a SBS unit, we could calculate the number of polySBS chains in a core of the cross-linked micelle (N_agg), and then we could estimate the polySSNa graft density from N_agg and the surface area of the core. The graft density was estimated at 0.13 nm^{-2}. This value is practically lower than the highest graft density of ca. 0.7 nm^{-2} achieved in poly(methyl methacrylate)-grafted silica particle, which is prepared by surface initiated atom transfer radical polymerization [26]; however, it is sufficiently high compared to graft surfaces synthesized by other techniques such as grafting-onto [27] and grafting-from methods [28].

3.2. DLS analysis

To further analyze the particle, we measured the DLS of the particle in aqueous solutions. Fig. 2 shows a typical time-correlation function for the 1.0 wt% sample in pure water at a scattering angle of 90°. The time correlation functions obtained at different angles were analyzed by cumulant fitting and the decay rate (I) was plotted against q^2. As shown in Fig. 3, a linear relationship between I and q^2 was clearly observed, which indicates that the observed dynamic mode was translational motion. The translational diffusion coefficient (D) was evaluated from the slope of the straight line using the relation of I = Dq^2. A hydrodynamic radius (R_h) was then calculated from the diffusion coefficients using the Stokes–Einstein relation R_h = k_b,T/(6πη_0D), where k_b, T, and η_0 represent the Boltzmann constant, absolute temperature, and solvent viscosity, respectively. The R_h of the particle was determined as 100 nm (polydispersity: 0.10), which is much larger than the particle size evaluated by SANS. We assume that there are two reasons for this rather large R_h value. One is that the particle has some grafting polySSNa chains widely diffused into the solvent due to electrostatic repulsions between sulfonate ions, which is hardly detectable by SANS [29]. The other is that the particle has coronal structure at its surface, which increases a friction with the solvent to give the slow translational diffusion. These two assumptions were supported by the fact that the R_h of the particle significantly reduced by addition of NaCl to become 61 nm at salt concentration of 0.2 M, which was even slightly larger than the radius obtained from SANS.

![Fig. 1. SANS profiles of 1 × 10^{-2} wt% CCL-SBS_{113}\textsuperscript{b}-SSNa_{208} in D_2O. Dotted line: experimental data, solid line: fitting curve calculated by core-corona model.](image)
different salt concentrations. The decay rate became larger with the increase of the salt concentration and became constant above the concentration of 0.2 M. Table 2 summarized the $R_h$ values evaluated from the DLS analysis. As the salt concentration increased, the $R_h$ value decreased drastically at first, then reached ca. 60 nm above the salt concentration of 0.2 M. A double logarithmic plot of the $R_h-R_c$ values versus salt concentration is given in Fig. 5. $R_h-R_c$ corresponds to the brush thickness of the polySSNa-grafted particle. The slope of the plot in the region between 0.01 and 0.2 M is approximately $-0.12$, which agrees well with the reported value for the salt concentration dependence of the shell thickness for polySS-containing micelles ($-0.11$ to $-0.14$) [30,31]. These results indicate that the graft chains stretched by the electrostatic repulsions shrank due to the screening effect of the added salts.

3.3. AFM analysis

We observed the particle in a dried state on a glass substrate by AFM. Fig. 6 shows the typical AFM image for CCL-SBS$_{113}$-$b$-SSNa$_{208}$. Many spherical particles with diameter of ca. 60 nm (estimated from lateral images) were observed. We consider that this particle size (radius of ca. 30 nm) is in good agreement with the particle size estimated by SANS, if we admit that the particle may be somehow flattened when it was dried, and also that the AFM lateral image is often larger than the real object due to the convolution effect of a cantilever.
3.4. Conductometric analysis

Conductometric titration of the aqueous solution was performed for CCL-SBS\(_{113-b}\)-SS\(_{208}\) by 0.01 mol/L NaOH\(_{aq}\). Fig. 7 shows the titration curve obtained from 18.6 mg of the CCL-SBS\(_{113-b}\)-SSNa\(_{208}\) sample. An interesting feature is that the conductivity once decreased and then slowly increased with the addition of NaOH\(_{aq}\), and the endpoint was indistinct. This is in good contrast to the normal titration curve for linear polySS solutions, in which a clear titration endpoint is observed. This rather gentle curve is presumably because of the structural restriction of the polySS chains in the corona and confinement of counter ion by the grafting polymer chains. Detail of this peculiar titration curve for polySSNa-grafted particles will be discussed elsewhere [32]. The intersection of the two tangent lines in the figure should be the endpoint of the titration. From the titration endpoint, it was suggested that exactly the same content of the sulfonate groups existed in the cross-linked particle (99 mol\%) as that estimated by \(^1\)H NMR spectrum in the precursor block copolymer, SBS\(_{113-b}\)-SSPen\(_{208}\).

3.5. Solution stability

The polySSNa-grafted particle showed particularly high solution stability in the presence of salt. Fig. 8 shows photographs for the particle solution before and after salt addition. For comparison, photographs of a colloidal suspension of polystyrene lattices (SS175) having sodium sulfate groups at the particle surface (a diameter of 130 nm and a surface charge density of 1.2 mC/cm\(^2\)) and of a micelle solution of low molecular weight anionic
or new drug carriers for controlled drug delivery and release systems.

Acknowledgments

This work was financially supported by a Grant-in-aids (A15205017 and 15750104 for young scientists) and the 21st century COE program, COE for a United Approach to New Materials Science, of the Ministry of Education, Culture, Sports, Science, and Technology, Japan. We are deeply grateful to Professor Shibayama and Master Okabe (University of Tokyo) for their kind support for SANS measurements at Tokai, which is adopted as Proposal 03. 061.

References

[1] N.J. Slater, in: Ion Exchange Advances, Elsevier, Amsterdam, 1992.
[2] R.v. Klitzing, B. Tieke, Adv. Polym. Sci. 165 (2004) 177.
[3] K.D. Kreuer, Chem. Mater. 8 (1996) 610.
[4] K. Miyatake, E. Shouji, Yamamoto, E. Tshuchida, Macromolecules 30 (1997) 2941.
[5] E. Vallejo, G. Pourcelly, C. Gavach, R. Mercier, M. Pineri, J. Membr. Sci. 160 (1999) 127.
[6] F. Wang, M. Hickner, Y.S. Kinm, T.A. Zawodzinski, J.E. MacGrath, J. Membr. Sci. 197 (2002) 231.
[7] J. Ding, C. Chuy, S. Holdcroft, Macromolecules 35 (2002) 1348.
[8] X. Guo, G. Fang, T. Watari, K. Tanaka, H. Kita, K. Okamoto, Macromolecules 35 (2002) 6707.
[9] J. Fang, X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, Macromolecules 35 (2002) 9022.
[10] K. Miyatake, H. Zhou, U. Uchida, M. Watanabe, Chem. Commun. (2003) 368.
[11] X. Guo, M. Ballauff, Phys. Rev. E 64 (2001) 051406.
[12] S. Förster, V. Abeutz, A.H. Müller, Adv. Polym. Sci. 166 (2004) 173.
[13] S. Förster, N. Hermsdorf, C. Böttcher, P. Lindner, Macromolecules 35 (2002) 4096.
[14] K. Matsumoto, H. Hasegawa, M. Matsukawa, Tetrahedron 60 (2004) 7197.