



Surface structure of stimuli-responsive polystyrene particles prepared by dispersion polymerization with a polystyrene/poly(L-lysine) block copolymer as a stabilizer



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ABSTRACT

A block copolymer composed of polystyrene and poly(α -L-lysine hydrobromide) (PLL) segments was used as a stabilizer for dispersion polymerization of styrene in water–methanol medium to give narrowly-distributed polystyrene particles in the size range from 0.36 to 1.09 μm , on which the PLL segment was grafted with a surface density of 0.2–3.4 L-lysine residue/ nm^2 . We investigated effects of polymerization time, stabilizer concentration, segmental composition of the block copolymer, and composition of the medium on surface structure and particle size of the affording particles. Interestingly, we obtained an experimental evidence that the surface density of the PLL clearly depends on structural parameters of the stabilizer and various polymerization conditions. Based on the dependence, it was possible to control the surface density of the narrowly-distributed particles within the range between the minimum and the maximum density limits of the graft chain by changing the structure of the stabilizer and polymerization conditions. Conformation of the PLL, which underwent a helix–coil transformation with an increase in water composition of the medium, had a strong effect on the surface structure, the size, and property of the resulting particles. Further modification of the particle surface was possible by utilizing the amino groups in the PLL graft.

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1. Introduction

Polymer particles play important roles in various fields of biomedical analysis, cosmetics, electronics, chemical industry, and so on. For further advanced applications, polymer particles should be prepared in a method which can afford them with well-defined surface structure, morphology, and size. One of the effective methods for preparation of such controlled polymer particles is dispersion polymerization using a certain kind of polymer as a “stabilizer”, which is covalently attached to the surface of a growing particle during the polymerization of a parent monomer and ensure the uniform growth of the particle by a sterically stabilizing effect to result in the formation of micrometer- or submicrometer-sized particles with narrow size distribution. In addition to the effect of giving uniform-sized particles, the stabilizers can be used for modification or functionalization of particle surface, because the covalently-attached stabilizer chains usually form a hairy layer on

the particle surface. Such dispersion polymerizations allow one-pot preparation of polymer particles having functional groups on its surface with a controlled size. Actually, among the reported examples of dispersion polymerization using a variety of homopolymers [1–11], macromonomers [12–16], macroinitiators [17–20], graft copolymers [21–23], and block copolymers [14,24–42] as a stabilizer, well-defined stimuli-responsive polymer particles have been prepared with a derivative of poly[(2-dimethylamino)ethyl methacrylate] [14,19,31], poly(α,β -aspartic acid) [15], or poly(*N*-isopropyl acrylamide) [16] in one-pot procedure.

Along with the above-mentioned polymers, a series of polypeptides can be a promising candidate as a stabilizer in preparation of functional polymer particles because of their well-known characteristics among an α -helix, a β -structure, and a random coil responding to external stimuli. Although polymer particle preparations with a polypeptide-containing stabilizer have been reported [15,43–46] and, in some examples, fine-control of the particle size has been achieved, the utilization of polypeptides for the purpose is the important objective to be explored in this field.

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Meanwhile, as for a design of an efficient stabilizer for dispersion polymerization, using block copolymers is a quite effective approach, especially when they have two segments with a different role: one segment imparts certain functionality as a hairy component existing on the particle surface, and the other acts as an anchor, which should be incorporated into the core of the particle. The advantage of using block copolymers is that we can control the performance of a block copolymer as a stabilizer by finely tuning the structure of each segment in terms of the choice of monomers, degree of polymerization, chain conformation, and so on. Furthermore, clarifying the detailed relationship between the block copolymer structure and performance as a stabilizer will eventually lead us to achieve a highly effective system for control of particle preparation, although such information has been quite limited so far.

With the background described above, we have been trying to investigate the ability of block copolymers of polystyrene and polypeptide as a stabilizer for preparation of polystyrene particles. As a first step for this project, we have reported in our previous paper, that a block copolymer composed of polystyrene and poly(α -L-glutamic acid) with well-defined structure can be useful as an effective stabilizer for dispersion polymerization of styrene, giving polymer particles with narrowly-distributed size [42]. In addition, we have succeeded in determining the amount of the poly(α -L-glutamic acid) on the particles. However, there remains a certain limitation in controllability of the poly(α -L-glutamic acid) block copolymer with respect to particle size and its surface structure. Thus, in this study, as a polypeptide segment in a block copolymer with polystyrene, we employ poly(α -L-lysine hydrobromide) (PLL), which has a cationically charged ammonium group in its side chain in contrast to the anionic carboxylic group in poly(α -L-glutamic acid), and investigate the performance of the block copolymer as a stabilizer for dispersion polymerization of styrene. In particular, we try to focus on the effect of the structure of the stabilizer and polymerization conditions on the structural parameters of resulting polymer particles, thereby aiming at revealing the adsorption behavior of the block copolymer onto the particle surface. Furthermore, a hairy surface layer of PLL will contribute to functionalizing the resulting particles as demonstrated in the antibacterial properties [47] and CO₂ capturing ability [48] of PLL-grafted silica nanoparticles. Although preparation and aggregation behavior in solution of the block copolymer of polystyrene and PLL (PS_{*n*}-*b*-PLL_{*m*}) have been reported [49], its application as a stabilizer for dispersion polymerization has not been investigated so far. The results described in this paper will extend the utility of well-defined peptide-containing block copolymers as an efficient stabilizer for control of particle preparation.

2. Experimental section

2.1. Materials

Dimethylformamide (Nacalai Tesque, Kyoto, Japan, 99%) and tetrahydrofuran (Nacalai Tesque, 98%) were dried over calcium hydride and sodium/potassium alloy, respectively, and distilled before use. Styrene (Nacalai Tesque, 98%) was washed with 5 wt % aqueous sodium hydroxide to eliminate inhibitor, dried over magnesium sulfate and then calcium hydride, and distilled before use. 2,2'-Azobisisobutyronitrile (AIBN; Nacalai Tesque, 98%), buffer solution standard (Wako Pure Chemical Industries, Osaka, Japan, pH 9.18), diethyl ether (Wako Pure Chemical Industries, 99%), hydrazine monohydrate (Nacalai Tesque, 80%), 25% hydrogen bromide–acetic acid solution (Wako Pure Chemical Industries), methanol (Wako Pure Chemical Industries, 99%), N^ε-carbobenzoxy-L-lysine (Tokyo Chemical Industry, Tokyo, Japan, 98%), phthalimide

potassium salt (Nacalai Tesque, 98%), pyrene (Tokyo Chemical Industry, 97%), 1-pyrenebutyric acid *N*-hydroxysuccinimide ester (Aldrich, MO, US, 95%), trifluoroacetic acid (Nacalai Tesque, 99%) and triphosgene (Tokyo Chemical Industry, 98%) were used as received.

2.2. Methods

¹H nuclear magnetic resonance (¹H NMR; 400 MHz) spectra were recorded in a Bruker Avance 400 spectrometer (Bruker, Rheinstetten, Germany). The ¹H NMR measurements for block copolymers were taken in a 20% trifluoroacetic acid–chloroform-*d* mixture or a dimethylsulfoxide-*d*₆ solution. From the ¹H NMR measurement, *M*_n of the PLL segment was determined on the basis of *M*_n of the polystyrene macroinitiator which was used for the block copolymerization.

Molecular weight (*M*_n) and molecular weight distribution (*M*_w/*M*_n) of polystyrene homopolymers were determined using a gel-permeation chromatography on a Jasco-Borwin system (version 1.50; Jasco, Tokyo, Japan) equipped with polystyrene-calibrated Tosoh TSKgel (G3000H_{HR}, G4000H_{HR} and G6000H_{HR}; Tosoh, Tokyo, Japan) using tetrahydrofuran as an eluent.

Scanning electron microscopic studies were conducted using a JEOL JSM-5310 (Japan Electron Optics Laboratory, Tokyo, Japan). Average diameter of particles (*D*_n) and particle size distribution (*D*_w/*D*_n) were determined by following equations:

$$D_n = \frac{\sum_{i=1}^n D_i}{n},$$

$$D_w = \frac{\sum_{i=1}^n D_i^4}{\sum_{i=1}^n D_i^3},$$

where *D*_{*i*} is the diameter of the *i*th particle measured by using MacView software (version 4; Mountech, Tokyo, Japan) and *n* is the number of particles (>100).

Titration of the particles was carried out by a TOADKK AUT-701 automatic titrator (TOA-DKK, Tokyo, Japan). In a typical case, polystyrene particles (100 mg) were added to 5.0 mM HCl (8 mL) and sonicated to obtain turbid mixture and titrated with 10 mM NaOH. On the assumption that the junction of the two segments in the PS_{*n*}-*b*-PLL_{*m*} is located at the particle surface, density of surface L-lysine unit (σ), surface area occupied by one PLL chain (*S*), and the ratio of the PS_{*n*}-*b*-PLL_{*m*} consumed for surface coverage to that used for the reaction mixture (θ) were determined from the following equations:

$$\sigma = \frac{C_{\text{NaOH}} D_n \rho_{\text{PS}} V_T N_A}{6W_{\text{p0}}},$$

$$S = \frac{m}{\sigma},$$

$$\theta = \frac{C_{\text{NaOH}} V_T M_{n,\text{block}}}{mW_{\text{p0}} Y C_{0,\text{block}}},$$

where *C*_{NaOH} is the concentration of the NaOH aqueous solution used for the titration (10 mM), ρ_{PS} is the density of the PS particles (1.05 g cm⁻³), *V*_T is the difference of the titer between the two inflections in the titration curve, *N*_A is the Avogadro number, *W*_{p0} is the weight of particle feed for titration, *m* is the number of repeating units in the PLL segment, *M*_{n,block} is the total molecular weight of the PS_{*n*}-*b*-PLL_{*m*}, *Y* is the yield of the PS particles, and

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