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Surface structure and composition of narrowly-distributed functional polystyrene particles prepared by dispersion polymerization with poly(L-glutamic acid) macromonomer as stabilizer





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ABSTRACT

A novel macromonomer composed of $poly(\alpha-L-glutamic acid)$ was used as a stabilizer for dispersion polymerization of styrene in DMF–water medium with AIBN initiator, giving narrowly-distributed functional polystyrene particles on which the $poly(\alpha-L-glutamic acid)$ was grafted. The resultant particles had 0.54–2.12 µm in size and 0.2–2.6 residue/nm² in surface density and showed a pH-responsive colloidal behavior associated with a helix–coil transformation of the surface $poly(\alpha-L-glutamic acid)$. Not only the particle size but also the surface density were controlled with macromonomer concentration, macromonomer length, DMF composition, and styrene concentration, while no consistent trend for AIBN concentration was observed. A gel-permeation-chromatography curve of the particles was separated into three components. We tentatively identify the origin of each component and propose a possibility that unstable particles, which were generated even after the growing particles were stabilized, took an important role in particle growth and size distribution of the resultant particles.

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1. Introduction

There has been a growing interest in functional particles because of their fascinating properties for application in various fields such as biomedical analysis, electronics, and chemical industry. Particle surface has a strong effect on particle function, so that functionalization and precise control of the particle surface are demanded. Dispersion polymerization is a useful technique to prepare polymer particles with well-defined size, morphology, and surface structure. In order to achieve colloidal stability, the dispersion polymerization requires a steric stabilizer which is covalently attached to particle surface to provide a stericallystabilizing effect. A variety of homopolymers [1-5], macroinitiators [6,7], graft copolymers [8–11], block copolymers [11–17], and macromonomers [18-26] have been reported as effective stabilizers as well as macromolecular chain-transfer agents for reversible addition-fragmentation chain transfer (RAFT) polymerization in recent studies [11,27–29]. Taking advantage of the steric stabilizer adsorbed on the surface, narrowly-distributed stimuli-responsive polymer particles have been prepared by using functional stabilizers such as poly[(2-dimethylamino)ethyl methacrylate] [7,13,25], poly(*N*-isopropyl acrylamide) [6,23,24], and polypeptide [15–18]. In particular, use of a macromonomer as a stabilizer is attractive to prepare functional polymer particles because of a wide variety of its synthetic routes. For example, Armes et al. synthesized a poly[(2-dimethylamino)ethyl methacrylate] macromonomer by oxyanionic polymerization [25], and Akashi et al. prepared a poly(*N*-isopropyl acrylamide) macromonomer by free radical polymerization with 2-mercaptoethanol as a chain-transfer agent [23]. Postpolymerization modification was also available for preparation of a poly(*N*-isopropyl acrylamide) macromonomer by combination of RAFT polymerization and Michael addition of 3-(acryloyloxy)-2-hydroxypropyl methacrylate [24]. In addition, Ono and Tomita prepared a poly(sodium α,β aspartate) macromonomer by polycondensation of aspartic acid followed by a reaction with acryloyl chloride [18]. These macromonomers successfully gave uniform-sized surface-functional particles.

For advanced applications of the particles, not only surface functionalization but also control of size, surface structure, and

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composition of functional polymer particles are important subjects. These subjects are strongly related to formation mechanism of narrowly-distributed particles, that of surface structure, and polymerization kinetics. Particularly, adsorption behavior of a stabilizer is a key element to control size and surface structure of particles. The particle formation involving two periods of stabilization and growth is explained as follows [2,19]. Dispersion polymerization starts from a homogeneous solution of monomer, initiator, stabilizer, and dispersion medium, while oligomeric radicals and dead polymers are generated and aggregated to form unstable particles which coalesce each other in the dispersion medium. When a minimum amount of the stabilizer required for colloidal stability is adsorbed, the unstable particles stop the coalescence and then no further stable particle is newly formed. The stabilization is completed within a few percent conversion [3,4], and, in the subsequent period of particle growth, each particle has an equal chance to grow. Further stabilizer chains are adsorbed on the particles which enlarge their surface area along with their growth. Unless the particle surface becomes scarce or overcrowded with the stabilizer, the dispersion polymerization gives narrowly-distributed polymer particles. Therefore, final size of the resultant particles is determined by adsorption behavior of the stabilizer in the very early stage, while surface structure reflects the stabilizer adsorption in the growth period.

In order to precisely control particle function, it is of great importance to study surface structure of functional particles. For a macromonomer-stabilizing dispersion polymerization, Kawaguchi and Ito reported an excellent model where particle size and surface structure were theoretically controlled with monomer concentration, macromonomer concentration, molecular weight of macromonomer, and initiator concentration [19]. The theoretical exponents for the particle size were validated with experimental data. However, those for surface structure have not been numerically compared since no experimental value has not been available. Previously, we carried out a dispersion polymerization stabilized by a polystyrene-block-poly(1-glutamic acid) or a polystyrene-blockpoly(L-lysine), and measured the amount of surface-adsorbed stabilizer by a pH titration to provide a power law dependence on polymerization conditions for surface structure [16,17]. This technique can be applied to a macromonomer-stabilizing dispersion polymerization.

Polymerization kinetics of dispersion polymerization is another important subject for the precise control of functional particles. However, the kinetics is still controversial because of following mechanistic complexities. During particle growth, bulk and solution polymerizations take place in particle phase and in dispersion medium, respectively, in the same period. Oligomeric radicals generated in the dispersion medium cause bimolecular termination or transfer into the particle phase. Although stable particles are not newly generated under the colloidal stability, unstable particles are still generated in the dispersion medium and incorporated into the stable ones before stabilized as secondary particles. For a poly(Nvinylpyrrolidone)-stabilizing dispersion polymerization, Paine et al. reported that molecular weight of particles had an inverse correlation to particle size because, in the case of small particles, large surface area of total particles could cause efficient capture of solution-initiated oligomeric radicals [1]. In contrast, El-Aasser et al. found that polymerization rate was not dependent on particle size but on medium composition due to partitioning behavior of initiator, oligomeric radicals, and monomer between dispersion medium and particle phase [30–32]. While they discussed a value of molecular weight, we found that a GPC curve of the resultant particles was successfully separated into three components in the study of a block-copolymer-stabilizing dispersion polymerization [16]. We have expected that a careful consideration of particle components will lead us to useful information of the polymerization kinetics in dispersion polymerization.

We try to focus on fine control of size, surface structure, and composition for functional polymer particles prepared by dispersion polymerization stabilized with a functional macromonomer. As an example, we use a polypeptide-based macromonmer as a functional stabilizer for the study of the particle control. Polypeptides are typical multi-functional polymers having stimuli responsibility, biocompatibility, biodegradability, and side-chain functionality. Therefore, polypeptide-functional polymer particles are promising candidates for a broad range of application of stimuli-responsive material [16-18,33-35]. First, in this study, a novel functional macromonomer of $poly(\alpha-L-glutamic acid)$ (mPLGA_n) was synthesized by ring-opening polymerization of an amino acid N-carboxy anhydride, which is a controlled polymerization to give well-defined polypeptide [36-38]. Then, the mPLGA_n was used as a stabilizer for dispersion polymerization of styrene to give pH-responsive narrowly-distributed polystyrene particles. The use of the well-defined mPLGA $_n$ enabled us to clarify the surface structure of the resultant particles on which the mPLGA $_n$ was grafted. Dependences of particle size and surface density on several conditions of initial concentration of the mPLGA_n, chain length of the mPLGA_n, medium composition, styrene concentration, and initiator concentration were investigated and compared with the theoretical exponents. Finally, we try to discuss the relation between polymerization kinetics and formation mechanism based on compositions of the surface-functional particles.

2. Experimental section

2.1. Materials

N,N-Dimethylformamide (DMF; Nacalai Tesque, Kyoto, Japan, 99%) was dried over calcium hydride and distilled before use. Styrene (Nacalai Tesque, 98%) was washed with 5 wt% aqueous sodium hydroxide, dried over magnesium sulfate then calcium hydride, and distilled before use. 2,2'-Azoisobutyronitrile (AIBN; Nacalai Tesque, 98%), benzylalcohol (Wako Pure Chemical Industries, Osaka, Japan, 99%), tert-buthylamine (Tokyo Chemical Industry, Tokyo, Japan, 98%), p-tert-butylcatechol (Nacalai Tesque, 98%), 4-chloromethylstyrene (Tokyo Chemical Industry, 90%), diethyl ether (Wako Pure Chemical Industries, 99%), ethanol (Wako Pure Chemical Industries, 99%), L-glutamic acid (Wako Pure Chemical Industries, 99%), hydrazine monohydrate (Nacalai Tesque, 80%), 25% hydrogen bromide-acetic acid solution (Wako Pure Chemical Industries), lithium chloride (Nacalai Tesque, 98%), methanol (Wako Pure Chemical Industries, 99%), phthalimide potassium salt (Nacalai Tesque, 98%), sodium hydroxide (Nacalai Tesque, 97%), trifluoroacetic acid (Nacalai Tesque, 99%), triphosgene (Tokyo Chemical Industry, 98%), and urea (Nacalai Tesque, 99%) 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, Rheinstein, Germany). The ¹H NMR measurements were taken in 20% trifluoroacetic acid—chloroform-*d* mixture, dimethylsulfoxide*d*₆, or 20% sodium hydroxide—D₂O solution. Helix content (*f*_{H,NMR}) was determined from the ratio of signal intensities assigned to C^αH protons of residues in a helix at 4.1 p.p.m. to those in the other conformation in 4.4–4.2 p.p.m [39].

Gel-permeation-chromatography (GPC) measurements were carried out by a Jasco-Borwin system (version 1.50; Jasco, Tokyo, Japan) equipped with Waters styragel HR4 THF and HR2 THF Download English Version:

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