

Preparation of polymer latex particles carrying salt-responsive fluorescent graft chains



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ABSTRACT

We prepared the novel fluorescent polymer latex particles which can change their fluorescence intensity in response to the increasing NaCl concentration in water. Core polymer latex particles were synthesized by emulsifier-free emulsion polymerization of styrene and 2-(2-chloroisobutyroxy)ethyl methacrylate. Hydrophilic polymer chains containing epoxy groups were grafted from the core particles by surface-initiated atom transfer radical copolymerization of methoxy polyethyleneglycol methacrylate (MEO_xMA, $x = 4$ or 9) and glycidyl methacrylate in aqueous media. After azidation of epoxy groups in graft chains, a water-soluble fluorescent dansyl derivative was successfully coupled with the graft chains by copper-catalyzed azide-alkyne cycloaddition in aqueous media. The wavelength of maximum fluorescence intensity of polymer particles carrying graft chains with longer PEG side chains ($x = 9$) was slightly blue-shifted (7 nm) and the fluorescence intensity increased (1.35 times) with an increase in NaCl concentration as opposed to polymer particles with shorter PEG chains ($x = 4$).

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1. Introduction

Polymer particles with a precisely controlled size, shape and chemical structure have attracted much attention over the past decade as smart materials responding to applied external stimuli such as temperature [1–6], pH [3–6], sugar [5,7,8], protein [9–11], magnetic field [12–19] and so on. Fluorescent polymer particles have immense potentials in biochemical applications because of the high efficiency and selectivity of fluorescence emission. For instance, quantum dots-containing polymer particles have been widely studied as a useful emission probe for bio-imaging and sensor technology due to a high absorption coefficient, a high fluorescence quantum yield, and photo-stability. Feng et al. developed an imaging system by co-encapsulation quantum dots and iron oxides in poly(lactic acid)-D-alpha-tocopheryl polyethylene glycol 1000 succinate nanoparticles [20]. Organic fluorescent dye-embedded polymer particles have been also studied energetically for biomedical applications including intracellular delivery, optical imaging and sensors. Larpent et al. prepared dual fluorescent polymer nanoparticles with a sensitive fluorescein-based dye on

the surface and a reference dye entrapped within polystyrene-based core particles for ratiometric sensors [21].

For further functionalization of polymer particles, surface modification is quite effective because of a large specific surface area of nanoparticles compared to that of bulk materials. Surface modification techniques of solid substrates, such as grafting-from Refs. [10,22–26] or grafting-to method [26–28], layer-by-layer assembly [29–32], and click chemistry [31–35] have been actively developed. Grafting-from methods have been mainly conducted by surface-initiated controlled/living radical polymerization (CRP) like atom transfer radical polymerization (ATRP) [22–24,26], reversible addition fragmentation chain transfer (RAFT) polymerization [10,25], and initiator-transfer agent-terminator (iniferter) polymerization [27]. Among them, surface-initiated ATRP is regarded as the most useful technique for functionalization of particle surface because polymer chains can be grafted more densely than grafting-to technique. In addition to grafting-from methods, click chemistry including copper-catalyzed azide-alkyne cycloaddition (CuAAC) and thiol-ene reaction are also considered as a powerful technique for surface functionalization of various substrates because of their high efficiency, selectivity, and adaptability in aqueous media [36–40]. As functional molecules can be covalently attached to the surface of substrates, materials with precisely controlled chemical structure can be readily produced by click chemistry. Krueger et al.

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demonstrated that fluorescent dyes can be covalently attached on the surface of diamond nanoparticles by CuAAC [41].

Polymer particles carrying fluorescence dyes on their surface are expected to respond sensitively to the environmental changes like ion concentrations, pH, temperature, solvent polarity, etc. Kawaguchi et al. investigated dependence of fluorescence on temperature and solvent compositions for dansyl-labeled core-shell and core-hair type microspheres [42]. By far, fluorescent polymer particles are potent substrates for biochemical applications, fluorescent polymer particles with a controlled architecture that respond to external stimuli have been not reported enough.

In our previous works on preparation of functional core-shell particles, the graft chain length (or shell thickness) on core particles was found to have enormous influence on physicochemical property [43–48] as well as the colloidal characteristics. Therefore, the particular attentions have been paid to the grafting-from technique by ATRP for controlled polymerization on polymer latex particles. In addition, the biocompatible PEG-based polymer chains with reactive sites grafted on latex particles have been regarded as the potential dispersed materials for practical applications in biomedical fields. Few studies on transformation of PMEO_xMA graft chains carrying reactive sites on latex particles, however, have ever been reported in the literature to our knowledge. It would be of great interest to investigate the response of PMEO_xMA chains grafted on particles to external stimuli such as salt concentration, temperature, and so on.

In this paper, we have represented that salt responsive fluorescent polymer latex particles with a novel architecture, the water-soluble fluorescent dansyl derivative was covalently attached to hydrophilic polymer chains grafted on the surface of polymer particles (Scheme 1).

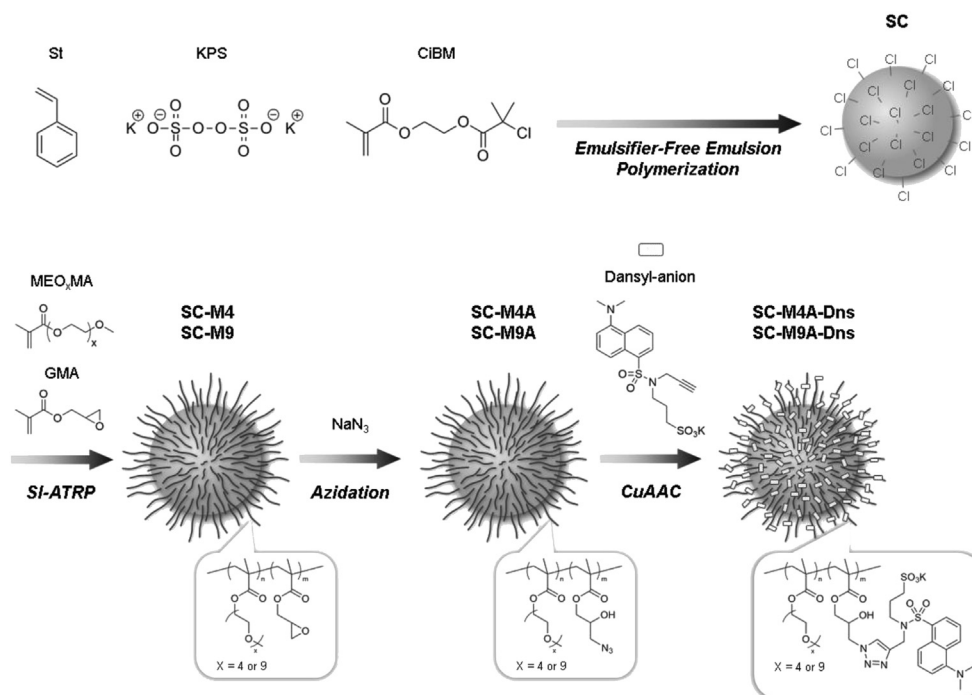
Core polymer particles containing ATRP initiators were prepared by emulsifier-free emulsion polymerization of styrene (St) and 2-(2-chloroisobutyroxyloxy)ethyl methacrylate (CiBM), and surface modification of the polymer particles was conducted by surface-initiated activator generated electron transfer atom

transfer radical copolymerization (SI AGET-ATRP) of methoxy oligoethylene glycol methacrylate (MEO_xMA, $x = 4$ or 9) and glycidyl methacrylate (GMA). The reactive epoxy side-chains of graft polymers were then converted to the azide groups by a reaction with NaN₃. The water-soluble fluorescent dye, potassium 3-((5-(dimethylamino)-*N*-(prop-2-yn-1-yl)naphthalene)-1-sulfonamido)propane-1-sulfonate (Dansyl-anion), which was newly synthesized, was coupled with azide groups by CuAAC in aqueous media. The dispersion stability of the obtained polymer particles was examined in terms of the critical coagulation concentrations (CCCs). The dependence of emission behavior on NaCl concentration in aqueous dispersion was investigated by fluorescence spectrum measurement.

2. Experimental

2.1. Materials

St was obtained from Kanto Chemical and dried over calcium hydride and distilled under reduced pressure. Glycidyl methacrylate purchased from Kanto Chemical and methoxy polyethyleneglycol 400 methacrylate (MEO₃MA) kindly provided by Shin-Nakamura Chemical were passed through a basic alumina column to remove a polymerization inhibitor. Tris(2-pyridylmethyl)amine (TPMA) [49] and 5-(dimethylamino)-*N*-(prop-2-yn-1-yl)naphthalene-1-sulfonamide (Dansyl-alkyne) [50] were synthesized according to the methods reported in previous literatures. Thionyl chloride, methacryloyl chloride, tetraethylethyleneglycol monomethyl ether, sodium azide, and pentamethyldiethylenetriamine (PMDETA) purchased from Wako Pure Chemical Industries were used as received. 2-Hydroxyisobutyric acid and potassium *tert*-butoxide were purchased from Tokyo Chemical Industry and used as received. 2-Hydroxyethyl methacrylate, triethylamine (TEA), 1,3-propanesultone, potassium persulfate (KPS), ethyleneglycol, copper sulfate pentahydrate, copper chloride dehydrate, L(+)-ascorbic acid (AsCA), sodium ascorbate



Scheme 1. Schematic protocol of preparation of salt-responsive polymer latex particles.

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