Photocontrol of ζ-Potential of Poly(styrene) Microspheres Prepared by Soap-free Emulsion Copolymerization

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Exposure to UV light at wavelengths of ≥254 nm caused poly(styrene) microspheres in deionized water to exhibit a negatively shifted ζ-potential value by generation of carboxyl groups due to photooxidation. Their ζ-potential value could be tuned simply by an exposure dose without a change in their average diameter.

Polymer microspheres prepared by soap-free emulsion copolymerization[1,2] have attracted much attention due to distinctive advantages of their monodispersity and clean surface without emulsifier surfactants. Their surface charge density and ζ-potential can be controlled by a choice of the sort of a hydrophilic radical polymerization initiator and/or a hydrophilic monomer copolymerized with a hydrophobic monomer. Their average diameter can be tuned by a change in a feed ratio of a hydrophobic monomer to a hydrophilic monomer and/or initiator. When the surface charge property is changed by the feed ratio, the average diameter varies simultaneously.[3] In this communication, we report a facile method for controlling ζ-potential of poly(styrene) microspheres in an aqueous solution by UV-light exposure causing photooxidation without a change in their average particle size. Although there are several reports[2,4] on oxidation of a microsphere surface by treatment with oxidant chemical reagents, our method by irradiation technique has a distinctive advantage of no emission of chemical wastes from a viewpoint of green sustainable chemistry.

Three kinds of monodisperse poly(styrene) microspheres **1**–**3** were prepared by similar methods described in previous papers.[3,5,6] Cationic microsphere **1**[3] exhibiting a ζ-potential value (ζ) of 58 ± 5 mV and having an average diameter (*d*) of 196 nm with a coefficient of variation of particle distribution (*Cv*) of 4.7%, zwitterionic microsphere **2**[5] showing $\zeta = 17 \pm 5$ mV, $d = 375$ nm, and $Cv = 2.4\%$, and anionic microsphere **3**[6] showing $\zeta = -35 \pm 2$ mV, $d = 370$ nm, and $Cv = 2.0\%$ were obtained.[7] Deionized water (30 mL) containing 0.025 wt % microsphere was poured into a stainless petri dish ($\phi = 70$ mm, $h = 10$ mm) placed on a cooling stirrer, and a temperature of the dispersion was maintained at 10 ± 0.5 °C. The gently stirred dispersion was exposed to UV light at wavelengths of ≥254 nm emitting from a 200-W He-Xe lamp (San-ei, Supercure 202S). A ζ-potential of microsphere was measured in a 10 mmol dm^{-3} NaCl aqueous solution.

Figure 1a shows ζ-potential values of the microspheres **1**–**3** as a function of exposure dose measured at 254 nm, with results for changes in their average diameters indicated in Figure 1b. ζ-Potential values exhibited by all microspheres **1**–**3** were shifted negatively upon an increase of the exposure dose, while their average diameters measured by a dynamic light scattering method were unchanged. As seen in Figure 2 indicating scanning electron microscope (SEM) images of the cationic microsphere **1** before and after the UV-exposure, its sphere-shape morphology was not transformed even after the UV-exposure. No significant change in morphology was also observed for the zwitterionic and anionic microspheres **2** and **3**.

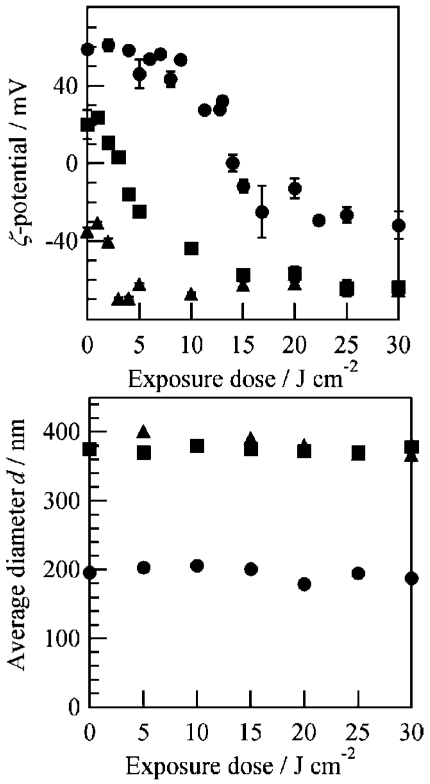

Figure 1. Changes of (a) ζ-potential values and (b) average diameters of poly(styrene) microspheres **1**–**3** as a function of exposure dose at 254 nm. (●) Cationic microsphere **1**, (■) zwitterionic microsphere **2**, and (▲) anionic microsphere **3**.

Cationic microsphere **1** dispersed in water after the UV-exposure under an air atmosphere was collected by centrifugation at 12,000 rpm, freeze-dried and subjected to FT-IR and CHNO elemental analysis measurements. The measurements allowed us to confirm that the negative shift of ζ-potential was caused by photooxidation of a microsphere surface rather than Norrish type II photochemical reaction to which acrylic and methacrylic acid esters were susceptible.[8]

Figure 3 shows FT-IR spectra of freeze-dried cationic mi-

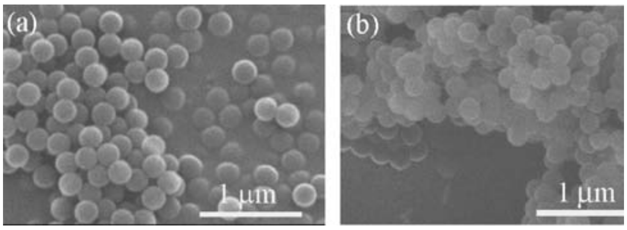

Figure 2. SEM images of cationic poly(styrene) microsphere **1** (a) before and (b) after UV-exposure at $20\,\mathrm{J\,cm^{-2}}$.

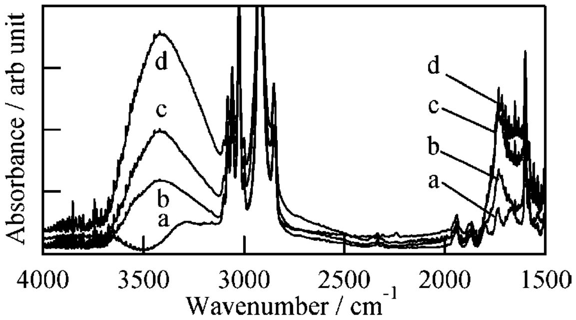

Figure 3. FT-IR spectra of freeze-dried microsphere **1** after UV-exposure at (a) 0, (b) 10, (c) 20, and (d) $30\,\mathrm{J\,cm^{-2}}$.

crosphere **1** exposed to UV light every $10\,\mathrm{J\,cm^{-2}}$ in an exposure dose range of $0–30\,\mathrm{J\,cm^{-2}}$. To compare these FT-IR spectra, the intensity of an absorption band at $2860\,\mathrm{cm^{-1}}$ attributable to a methylene C–H symmetrical stretching vibration band was chosen as an internal standard under an assumption that the majority of poly(styrene) in the microsphere was hardly affected by surface photooxidation. As the exposure dose was increased, an O–H stretching vibration band around $3400\,\mathrm{cm^{-1}}$ and a C=O vibration band at about $1700\,\mathrm{cm^{-1}}$ were significantly increased. The spectral changes suggested that hydroxy, formyl, and carboxyl groups were generated by the UV exposure. 0.30% nitrogen before UV-exposure was decreased to 0.13% after UV-exposure at $30\,\mathrm{J\,cm^{-2}}$, while 0.64% oxygen was increased significantly up to 7.37% in the elemental analyses. If Norrish type II reaction from carboxylic acid ester to carboxylic acid took place, a percentage of oxygen would not increase dramatically. These results strongly suggested that oxidant species such as activated oxygen atom and molecule and ozone caused photooxidation[9,10] of organic moieties collocated at an outermost layer of the microsphere.

Generation of carboxyl groups at an outermost layer of the microspheres was supported in pH-dependent ζ-potential measurements. The pH values of microsphere aqueous dispersions with a constant ionic strength were varied by addition of HCl or NaOH in the manner we described previously.[11] The cationic microsphere **1** without UV-exposure exhibited a constant ζ-potential value of $57 \pm 2\,\mathrm{mV}$ irrespective of the pH value. In contrast, the ζ-potential value of $-42 \pm 7\,\mathrm{mV}$ at pH 7 was gradually increased up to $-7 \pm 1\,\mathrm{mV}$ at pH 3, as the pH value was decreased in the case of the cationic microsphere **1** exposed to UV light at an exposure dose of $30\,\mathrm{J\,cm^{-2}}$. Such pH dependence of ζ-potential is observed identically for carboxy-modified poly(styrene) microspheres.[11] This means that a lot of photogenerated carboxyl groups as a weak acid were formed by the UV-exposure.

In conclusion, we displayed that a ζ-potential value exhibited by monodisperse poly(styrene) microspheres in their aqueous dispersions could be tuned simply by UV-exposure causing photooxidation. Charge-controlled microspheres will be useful in studying on microsphere monolayers of regular arrangement with a controlled periodicity on a solid substrate surface.[3] Carboxy-modified polymer microspheres will be also available to metal electroless deposition and biomolecule modification.

References and Notes

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7 The ζ-potential value (ζ) and average diameter (d) were measured in a $10\,\mathrm{mmol\,dm^{-3}}$ NaCl aqueous solution of pH 7 at 25 ± 1 °C with an Otsuka Electronics ELS-8000 electrophoretic light scattering spectrophotometer. The *Cv* value was determined with a Hitachi S-3000N SEM.
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