Development of Anisotropic Thermo-sensitive Hairy Particles Using Living Radical Graft Polymerization

Daisuke Suzuki, Sakiko Tsuji, and Haruma Kawaguchi*
Faculty of Science & Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223-8522

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Temperature-responsive anisotropic particles were developed. Au was sputtered onto one side of the particle and, thermo-sensirive polymer was grafted from the other side. Obtained particles were characterized by dynamic light scattering, electrophoresis, and electron microscopy. These particles showed thermo-sensitive behavior when they dispersed in water. They also showed anisotropic adsorption onto the substrate, and the particles were self-assembled into particle chains.

Recently there has been an increased interest in preparing anisotropic particles which have a large potential for applying to photonic devices, and diagnosis reagents, so that several methods were investigated, for example, by metal deposition onto the hemisphere of particles,[1] by use of Langmuir–Blodgett technique,[2,3] and by microcontact printing technique.[4] They provide amphiphilic particles which had an hydrophilic face on one side and an hydrophobic face on the other side, or dipolar particles whose surface charges segregated onto separate poles.

In this paper, we report temperature-responsive anisotropic particles. They would show anisotropy when the polymer swells, and they would show isotropy when the polymer shrinks. Thus, anisotropy would be controllable by changing the temperature. We tried to synthesize anisotropic hairy particles using the technique of living radical polymerization.[5] The hair was composed of poly(*N*-isopropylacrylamide) (PNIPAM) which was a representative thermo-sensitive polymer. Novel temperature-sensitive hairy particles which were previously reported[5] had advantages of sharp response and being controllable in polymer structure.

In this study, first, we prepared benzyl chloride group-carrying particles, and attached them a photo-initiator. Then Au was sputtered onto the hemisphere of particles. Next, we carried out living radical graft polymerization of NIPAM from only one hemisphere. Finally, we obtained comet-like particles which had Au film on one hemisphere and thermo-sensitive polymer hair on the opposite hemisphere. The scheme of this process and obtained particles are shown in Figure 1.

The preparation of iniferter[6] immobilized particles (SV–DC particles) was described in our previous report.[7] We obtained monodispersed SV–DC particles whose weight-average diameter measured by dynamic light scattering (DLS; PAR-III, Otsuka Electronic Co.) was 440 nm. Then SV–DC particles were arranged to a monolayer on a polystyrene substrate by a spin coater. Although it was difficult to prepare a hexagonally packed monolayer, spin cast has advantages in terms of easy and quick processing. After that, Au was sputtered onto the particle monolayer at a discharge current of 20 mA for 20 s. After the sputtering treatment, the particles were re-dispersed in an aqueous medium by sonication within 1 min. At this stage, they had Au film only on one side, and had exposed iniferter groups on the opposite side. There was no Au aggregates apart from particles in the medium. This meant that Au film deposited on particles or polystyrene substrate was not peeled off by sonication. Obtained particles (SV–DC–Au particles) were monodispersed in size, and diameter measured by DLS was almost the same as that of SV–DC particles. Iniferter-localized particles were successively dispersed in 1.0 wt % NIPAM solution, and living radical graft polymerization was carried out through UV irradiation with a 400-W mercury lamp from which UV radiation of 312–577 nm (peak wavelength, 365 nm) emerged for 1 h at 20 °C. After the polymerization, particles (SV–DC–Au–N particles) were purified by centrifugation, decantation of supernatant, and re-dispersed in fresh water. That was repeated four times.

Temperature response of SV–DC–Au–N in hydrodynamic diameter and electrophoretic mobility (EPM) were investigated. The apparent diameters of SV–DC and SV–DC–Au–N particles are shown in Figure 2. The apparent diameters were calculated from the diffusion coefficients of particles by using Einstein–Stokes equation which could be applied to spherical particles. Although it is difficult to decide the accurate diameter of aniso-

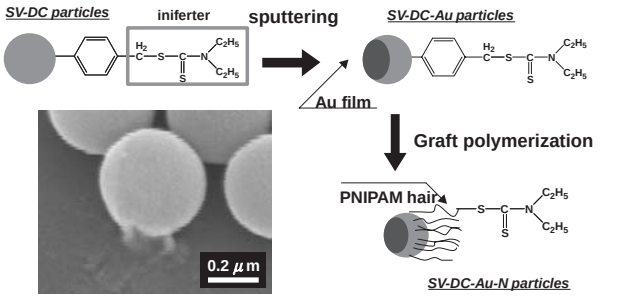

Figure 1. Thermo-sensitive anisotropic particles.

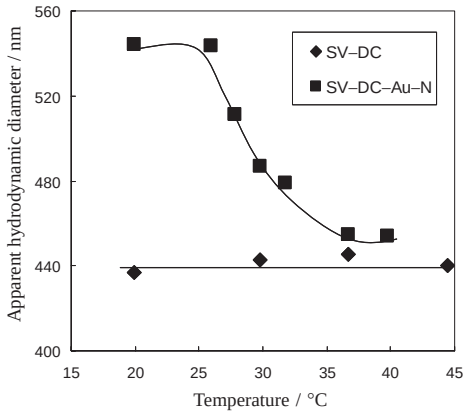

Figure 2. Apparent weight-average hydrodynamic diameter of SV–DC, SV–DC–Au–N particles as a function of temperature measured by dynamic light scattering.

tropic particles such as SV–DC–Au–N ones, we could see their changes in dynamic behavior by determining these data. The apparent diameter of SV–DC–Au–N particles changed before 30 °C, which coincided with the temperature of PNIPAM collapse,[5] while SV–DC core particles didn't change. These data suggested that SV–Au–N particles showed volume transition of PNIPAM. Then we conducted further investigation of electrophoresis (Figure 3). All measurements were performed in 0.001 M KCl solutions at different temperatures (Zeecom, Microtec Co., Ltd.) The EPM of SV–DC particles and SV–DC–Au particles changed monotonously in the range from 25 to 40 °C, while the EPM of SV–DC–Au–N particles dropped around 30 °C. The temperature range where the EPM changed almost coincided with the temperature ranges in which the hydrodynamic diameter changed significantly. The EPM change of thermo-sensitive particles was reported theoretically by Ohshima et al.[8] SV–DC–Au–N particles at swollen state had larger negative EPM than PNIPAM fully-covered particles as previously reported.[5,8] This indicates that PNIPAM hairs locally exist.

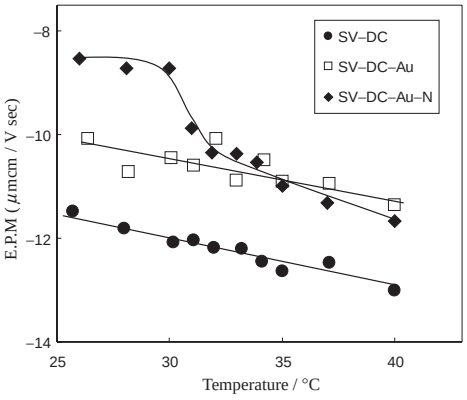

Figure 3. Electrophoretic mobility of SV–DC, SV–DC–Au, and SV–DC–Au–N particles measured as a function of the temperature in 0.001 M KCl.

To confirm anisotropic character of the particles, iniferter groups at the end of PNIPAM hairs were converted to thiol groups (SV–DC–Au–N–SH particles) so that site selective adsorption took place. Scheme is shown in Figure 4. Iniferter groups were reduced in 10 mM sodium borohydrate. After dispersion was stirred for a week, 10 μL of it was dropped on a polystyrene substrate and dried. We could find that particles were connected with each other, and ordered spontaneously in almost one-dimension (1-D) as shown in Figures 5a and 5b. These particles had an ability to combine with each other through spontaneous Au–SH reactions because SV–DC–Au–N–SH particles have Au film on one side, and thiol groups at the end of hairs on the other side. To confirm selective adsorption of SV–DC–Au–N–SH particles to Au film, a polystyrene/Au pattern substrate was prepared and immersed into dispersion of SV–DC–Au–N–SH particles, and observed by SEM (Figure 5c). The figure clearly shows that almost all particles were attached selectively on Au region that was the left half of image. Thus, anisotropic adsorption was done successfully by thiol groups at the end of hairs.

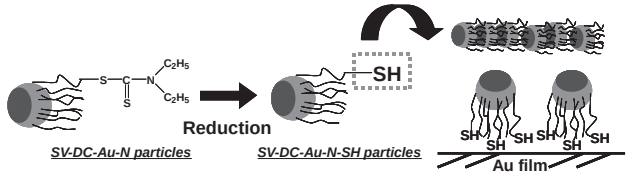

Figure 4. Scheme of site selective adsorption of anisotropic particles by using thiol groups converted from iniferter.

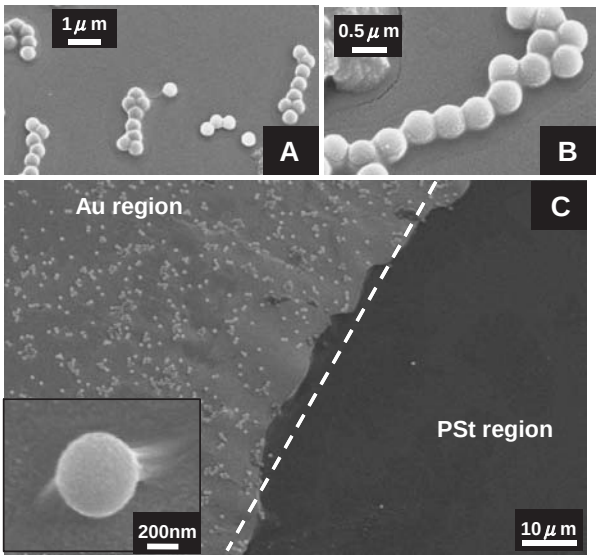

Figure 5. FE-SEM observation of SV–DC–Au–N–SH particles. (A) and (B): particle chain composed of SV–DC–Au–N–SH particles. (C): left half of image is Au-deposited substrate, and right half one is PS substrate. Inset is a close up image of the particle on Au-deposited substrate.

We concluded that thermo-sensitive anisotropic particles were prepared successfully. They had Au film on one side and PNIPAM hairs on the other side. They were self-assembled into 1-D with each other through Au and thiol group reaction to form particle chains. DLS and electrophoresis measurements revealed that the particles could also change their morphology depending on temperature. These particles will be able to be a building block of photonic or electronic device, and a model structure for particle semiconductor laser.

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