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Hairy Particles Prepared by Living Radical Graft-Polymerization

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Summary: Novel particles having designed hairs were prepared by living radical graft-polymerization on core particles. The living radical species used in this study was a kind of photo-iniferter, N, N-diethyl-thiocarbamate. Main component of hair was poly(N-isopropylacrylamide) (PNIPAM) which was a representative thermo-sensitive polymer. The polymerization was carried out by UV irradiation at room temperature that was lower than the transition temperature of PNIPAM. Incorporation of a small amount of acrylic acid into the hair caused significant change in the properties of hairy particles. The mode of comonomer charge also enabled to design the hair structure on the particles.

Introduction

Hairy particles are a kind of core shell particles whose shell is composed of linear polymer chains having high affinity to the dispersion medium. They have no chemical crosslinks among chains.

When poly(N-isopropylacrylamide) (PNIPAM) hair-carrying particles are warmed up in water, the hairy layer shrinks at the transition temperature of 32 °C and the shrinkage causes hardening and hydrophobization of the shell layer (1). The transition takes place very quickly and reversibly (2).

There are several methods to prepare hairy particles (1- 6). If we start the hairy particle formation by use of existing core particles, there are two ways for this. One is binding linear polymer molecules onto core particles at the chain end, so called "grafting-on" (6). Hairs are hardly bound with high density and apt to be bound at any part along the chain. To overcome these disadvantage of "grafting-on", we adopted "grafting-from" which corresponds to graft polymerization from the particle surface. Grafting radical polymerization includes two methods, one of which is conventional radical graft-polymerization and the other is living radical graft-polymerization (7). In

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the former, the average chain length is kept constant but the density of hairs increases with increasing conversion. On the contrary, in the latter, the situation is inverse to that of conventional radical polymerization, that is, the density of hairs is unchanged but the length of hairs increases with increasing conversion. The more important feature of the living radical graft polymerization is the possible designing of hairs (7), for example, the formation of block polymer hairs. For these reasons we decided to create novel hairy particles using living radical graft polymerization.

Several types of living radical polymerizations have been proposed recently such as stable radical polymerization (SRP) mediated by nitroxide radicals (8), reversible atom transfer polymerization (RATP) (9), reversible addition fragmentation polymerization (RAFT) (10), etc. But when the history of living radical polymerization is searched, we notice "iniferter" is the first living radical polymerization reagent (11). The iniferter is a compound which serves as an initiator, a transfer reagent, and a terminater. Otsu developed a number of iniferters in early 80th (12). The "iniferter" is more convenient than other living radical polymerization agents because the polymerization needs no severe conditions. There are no studies on living radical graft-polymerization on particles under a mild condition in aqueous media. In this article, we report a new methodology on living radical polymerization using a photo-iniferter at room temperature. The low polymerization temperature is desirable for the polymerization of NIPAM because PNIPAM is obtained under highly swollen state. In this study, a kind of iniferters, sodium N, N-diethyldithiocarbamate (NaDC) was bound onto a core particle surface and used as an immobilized iniferter, and then polymerization was started by ultraviolet irradiation at room temperature. In order to give novel hairy structures to the particles, the composition of monomers and mode of monomer charge were controlled. The resulting hairy particles were characterized in terms of hydrodynamic size and electrophoretic mobility as functions of temperature.

Experimental Part

Materials

Styrene (St) and acrylic acid (AAc) were distilled under reduced pressure. Vinyl benzylchloride (VBC) was washed with 0.5% NaOH aqueous solution. NIPAM (Kojin

Co.) was re-crystallized from hexane/toluene (1/1. v/v) . Potassium persulfate (KPS) was re-crystallized from hot water (40 °C). Sodium N, N-diethylthiocarbamate was of extra pure grade and used as received. Water was ion-exchanged and distilled.

Preparation of core particle

Core particles having benzyl chloride groups on the surface were obtained by soap-free emulsion copolymerization of St and VBC, referring to the reference (14). 2.85 g St, 0.15 g VBC and 75 g distilled water were put into a four-necked 200 ml flask equipped with a stirrer a condenser, a nitrogen inlet and a serum rubber. After purging oxygen with nitrogen, 0.1 g KPS in 10 g water was added to the solution at 70 °C. The soap-free emulsion polymerization thus started was continued for 24 hr under gentle stirring. The resulting particles were separated from the serum by centrifugation followed by decantation. The particles were redispersed in fresh water and the above-mentioned cleaning process was repeated three times. The yield of particles was measured by gravimetry.

Immobilization of Iniferter onto the core particle

Iniferter fragment was immobilized onto the core particle by the reaction of NaCl elimination between NaDC and benzylchloride group on the particle. 80 g of aqueous dispersion of 2.0 g core particles was charged into a three-necked 300 ml flask in a cold bath filled with ice. 20 g of aqueous solution of 0.74 g NaDC was drop-wisely added to the gently-agitated dispersion for 30 min. The reaction to immobilize dithiocarbamate onto the particle was continued at room temperature overnight. The resulting particles, coded as SV-DC particle, were cleaned by the procedure described above.

Living radical graft-polymerization to form hairy particles

2.16 g NIPAM was dissolved into an aqueous dispersion of 0.5 g SV-DC particle. The total amount of mixture was adjusted to be 200 g in a reaction vessel. The content was UV-irradiated using a 400W mercury lamp that emerges the UV of 312-577 nm (peak wave length: 365 nm). The PNIPAM hair-carrying particles thus obtained (SV-N) were cleaned by the same way described above.

The amount of monomer remaining was measured by gas chromatography to calculate the conversion as a function of time. A small aliquot of sample was drawn out of the polymerization vessel and centrifuged. 200μl of supernatant was diluted with 1700μl of ethanol and 100μl of 1wt% dioxane/ethanol. The solution was injected into a gas chromatography system GC353 (Gas Chromat. Ind. Co.) equipped with a capillary column of TC-5 (Toso Co.) at 270 °C. The carrier gas was N_2 of 400kPa and the composition in eluted gas was detected by a hydrogen ion detector.

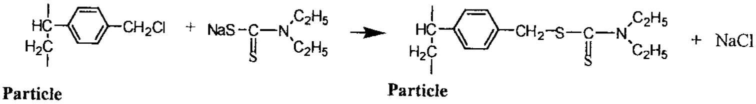
Characterization of particles

The size and shape of particles were observed by transmission electron microscopy using a JSM-5200 electron microscope (JEOL). The surface composition of particles was measured by X-ray photon spectroscopy using a JPS-900MX spectrometer (JEOL). The hydrodynamic size of particles was measured by dynamic light scattering/photon correlation spectroscopy with a PAR-III system (Ohtsuka Electron Co.)

Results and Discussion

1. Core particle formation

Among several particle-forming polymerizations, soap-free emulsion co-polymerization was selected to prepare St-VBC particles. It was because the soap-free emulsion co-polymerization gives clean, monodisperse particles. In this polymerization, VBC was used as a comonomer to offer binding sites of iniferter for the reaction shown in Scheme 1. St was a necessary component to prepare stably dispersing particles with smooth surfaces.



Scheme 1. Immobilization of DC to St-VBC particles.

The resulting particles had a diameter of 400 nm and were monodisperse as shown by the Dw/Dn ratio less than 1.01. In the co-polymerization of St with VBC, more hydrophilic monomer units, VBC, were supposed to locate more at the surface layer of particles although this was not measured quantitatively. Decomposition of benzyl chloride group during the polymerization at 70 °C for 24 hr made the determination more difficult.

2. Introduction of dithiocarbamate groups onto SV particles

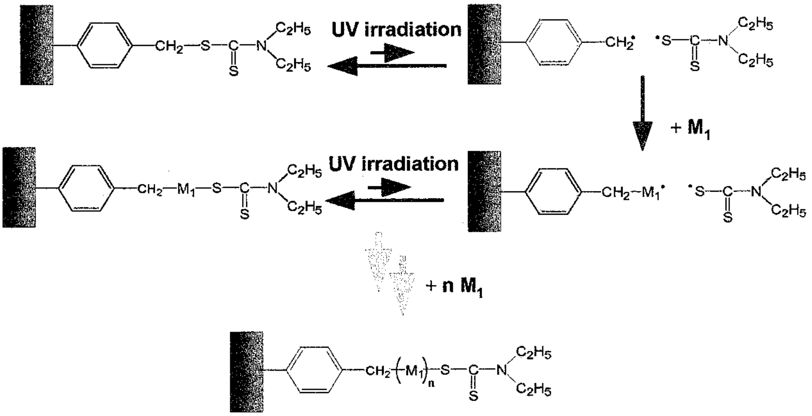
NaDC was chosen as a living radical species immobilized on particles because of two reasons; 1. it is water-soluble and can be immobilized onto particles in an aqueous medium, and 2. it enables to carry out living radical polymerization under a mild condition. In terms of the latter, it would be emphasized that the polymerization temperature was kept below the transition temperature of PNIPAM so that the chains could propagate under a hydrated state.

NaDC was immobilized on SV particles at room temperature. The successful immobilization was confirmed, by XPS, with an appreciable increase in S/C and decrease in Cl/C values for dithiocarbamate-immobilized SV particles (SV-DC particles) compared with those of SV particles.

3. Living radical graft-polymerization of N-isopropylacrylamide

The expected reaction scheme is shown below (Scheme 2) for living radical polymerization by dithiocarbamate on UV irradiation.

The availability of this system for NIPAM polymerization on polymer particles in an aqueous dispersion has not been examined so far although graft polymerization of hydrophilic monomer on flat polymer surfaces was carried out by Matsuda to obtain a novel biomaterial (14). In the present study, surface graft-polymerization of NIPAM was done on SV-DC particles under several conditions to form highly thermo-sensitive hairs and multi-functional hairs on the particles. The superiority of surface grafting on particles to that on flat surfaces is that a large amount of grafting can be done at once and the extent of grafting is easily determined by measuring the hydrodynamic size by dynamic light scattering.



Scheme 2. Living radical graft-polymerization onto SV-DCparticles.

3.1. Effects of monomer concentration and polymerization time on hair formation

The polymerization was carried out using 0.5 g core particles and 2.16, 1.08, or 0.65 g NIPAM. As the number of active site was kept constant in these systems, the amount of monomer charged affects the chain length of hairs or the thickness of grafted layers.

The polymerization was stopped at scheduled times and the hydrodynamic size of hairy particles was measured as a function of polymerization time. The result is shown in Figure 1. As illustrated, the conversion and hydrodynamic diameter both increased till the conversion reached 70%. This implies the polymerization took place in a living radical polymerization process. However, the conversion and hydrodynamic size were leveled off above 70% conversion. This was attributed to the formation of free soluble polymer dissolving in the aqueous medium. The fact means the iniferter used was not ideal living radical species but some radical fragment escaped into the aqueous phase to form water soluble polymers. Such polymers accumulated with increasing conversion.

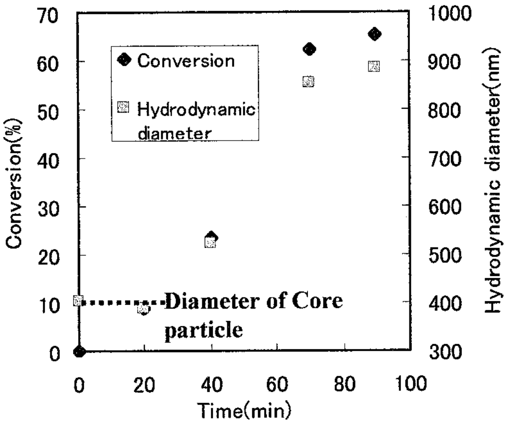


Figure 1. Time dependence of conversion and hydrodynamic size for living radical graft-polymerization of NIPAM onto SN-DC.

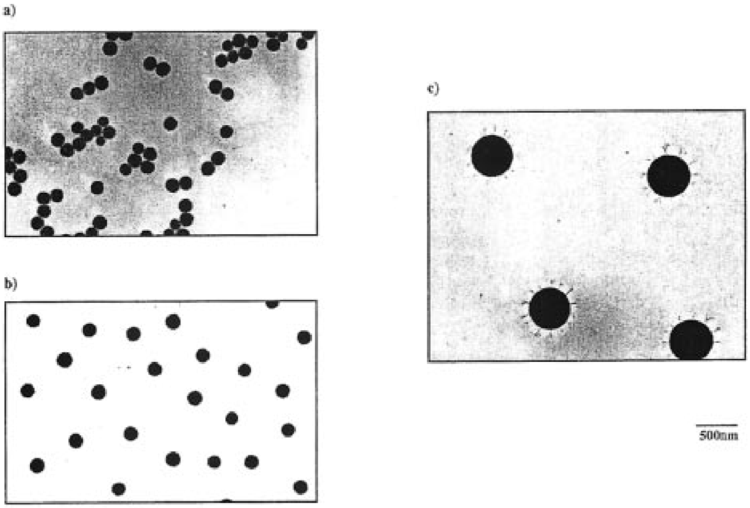


Figure 2. TEM views of a) SV-DC, b) SV-N, and c) SV-N zoomed-up.

Figure 2 shows TEM views of core particles (SV particles) and PNIPAM hair-carrying particles. There is a significant difference between two views. Most SV particles contacted each other but hairy particles kept a certain inter-particle distance. The individual appearance of hairy particles is believed to have resulted from the fixation of swollen, hairy particles onto a corrosion membrane followed by dehydration/shrinkage of hydrated hairy layer. Namely steric exclusion effect between adjusent particles kept the dried particles to be separated. The close-up of the TEM view of the latter shows some strings around the particles that are considered to be bundles of shrunken PNIPAM hairs.

3.2. Preparation of particles with ionic groups-containing PNIPAm hairs

We previously prepared particles with acrylic acid (AAc) unit-containing PNIPAM hairs by general radical graft polymerization (1, 2). The polymerization was initiated by CH_2OH group (on the particle)-ceric ion (in the aqueous medium) redox system. As the polymerization was carried out for NIPAM and a small amount of AAc fed simultaneously into the polymerization system, the resulting copolymer hairs exhibited a sharp transition in a very narrow temperature range around 32 °C. This was attributed to the AAc units evenly distributed in the hairy layers that reduced the entanglement of PNIPAM hairs and promoted the sharp conformational change of PNIPAM.

The particles with AAc unit-containing PNIPAM hairs (SV-NAx particles where x is AAc wt% in NIPAM. $x = 0 - 0.5$) were prepared by living radical graft-polymerization in this study. The hydrodynamic diameter of the hairy particles was measured as a function of temperature and is shown in Figure 3. The diameter of swollen particles having AAc-containing PNIPAM hairs below the transition temperature increased with increasing amount of AAc.

Another characteristic point for AAc-containing hair-carrying particles was the shift of transition temperature dependent on the amount of AAc. This is because the incorporation of AAc in the hair increased the hydrophilicity of the hair. The shift of transition temperature was confirmed by the change of inflection points on the hydrodynamic diameter vs. temperature curves in Figure 3.

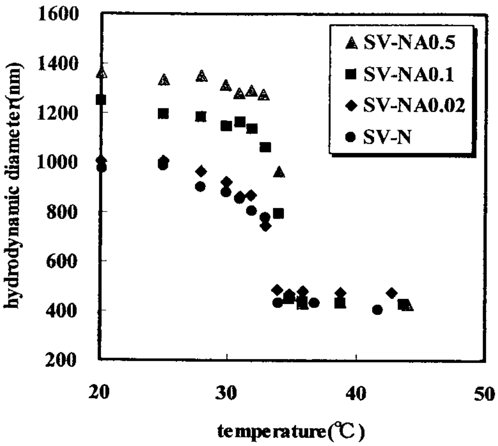


Figure 3. Hydrodynamic diameter of SV-NA particles containing different amounts of AAc in hairs, as afunction temperature.

Another evidence for the shift of transition temperature was presented by temperature dependent electrophoretic mobility of the particles (data not shown). Swollen particles exhibited little electrophoretic mobility due to buried ionic groups in the hairy layer but did high electrophoretic mobility above the transition temperature due to exposed and concentrated ionic groups that effectively attributed to the electrophoretic mobility.

We have no detailed data on the distribution of AAc units in PNIPAM hairs but expect that AAc units are distributed evenly in the hairs when the monomers were added simultaneously at the beginning of the polymerization. The pH control for polymerization system is supposed to regulate the distribution of AAc units in the hairs. But, in this study no pH control was done. Instead, reference hairy particles were prepared to confirm the effect of AAc distribution in hairs. Namely AAc was fed in the polymerization system after PNIPAM hairs were grown up to a certain length to prepare the PNIPAM hairs having AAc sequence at the chain ends.

3.3 Preparation of PNIPAM hair particles having PAAc at the hair ends

Whole amount of NIPAM was first grafted by living radical polymerization and the particles were once separated from the dispersant. Then the particles were re-dispersed in a fresh water containing a certain amount of AAc. Living radical polymerization was re-started by UV irradiation at 25 °C. These polymerizations should result in the formation of hairy particles having hairs in which AAc sequences exist only at the chain end portion (SV-N-Ax where x is AAc wt% in NIPAM. x = 0 – 2.0). The hydrodynamic diameter and electrophoretic mobility of these hairy particles are shown in Figure 4 as functions of temperature. Although the ratio of AAc to NIPAM in this two-step method was kept in the same range with that for one-shot co-polymerization, the thermo-sensitivity of hydrodynamic size and electrophoresis was quietly different from those of the one-shot co-polymerization. Namely, as shown by the curves in Figure 4, no shift of transition temperature was observed among the curves, that is, the length of AAc blocks at the PNIPAM chain end did not affect the thermo-sensitivity of PNIPAM hairs up to 2% AAc. The significant difference in thermo-sensitivity between the hairs obtained by one-shot and two-step polymerizations shows us how living radical polymerization is useful in designing hairs.

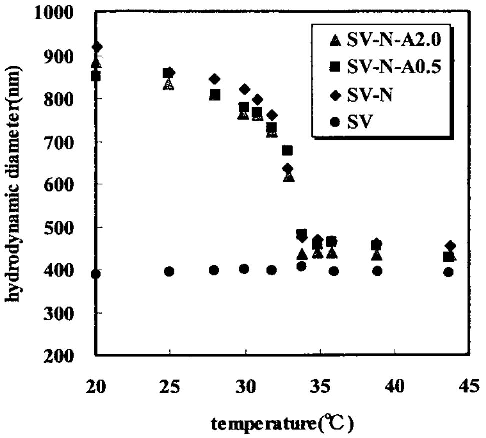


Figure 4. Hydrodynamic diameter of SV-N-A particles containing different amount of AAc.

3.4 pH dependence of hairy particles obtained by one- or two-step living radical polymerizations

Incorporation of AAc units in PNIPAM hairs made the hairy particles pH-sensitive. The hydrodynamic diameter of hairy particles by one-shot polymerization fairly depended on pH at the swollen state as shown in Figure 5. The transition temperature also depended on pH. That is, the hairs having highly dissociated carboxyl groups have stronger inter-and intra-hair repulsive force and became more hydrophilic, keeping the hydrated state till the higher temperature.

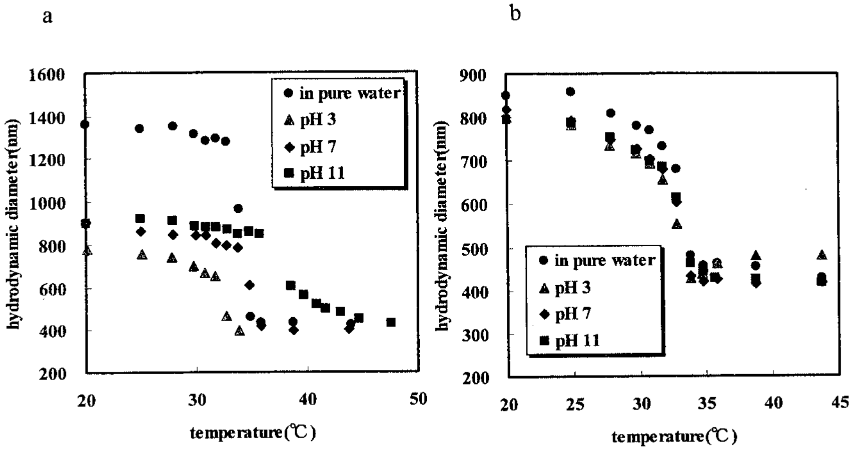


Figure 5. pH dependence of drodynamic diameter of SV-NA0.5 (a) and SV-N-A0.5 (b) particles.

It would be worth mentioning that the hydrodynamic size of the particles SV-NA0.5 (NIPAM and AAc were simultaneously charged) in alkaline solution was smaller than that in pure water. This was attributed to a significant effect of osmotic pressure caused by counter ions immersed into hairy layer. The influence of ionic strength to hydrodynamic size was quite smaller for the particles SV-N-A0.5 (NIPAM and AAc were sequentially polymerized). In this particle, osmotic pressure caused by counter ions in the hairy layer little contribute to the hydrodynamic size because they located only in the outermost layer.

3.5 Creation of particles exhibiting two step response to temperature

The most interesting feature of living radical graft-polymerization on polymer particles is designing novel particles with multi-functional hairs. In this study, two-step polymerization was carried out by feeding different monomer composition in each step. In the first step, pure PNIPAM hairs were formed and, in the second step, the hair was extended with NIPAM/AAc copolymer blocks. The hydrodynamic diameter of the particle is shown in Figure 6. The two transitions, one at around 32 °C and the other at 36 °C were assigned to those for PNIPAM and NIPAM-AAc copolymer, respectively.

Conclusions

Novel hairy particles with designed hairs were prepared by living radical graft-polymerization. The temperature- and pH-sensitive hydrodynamic size and transition temperature of NIPAM-AAc copolymer hair particles were controlled by the content and distribution of AAc in PNIPAM hairs.

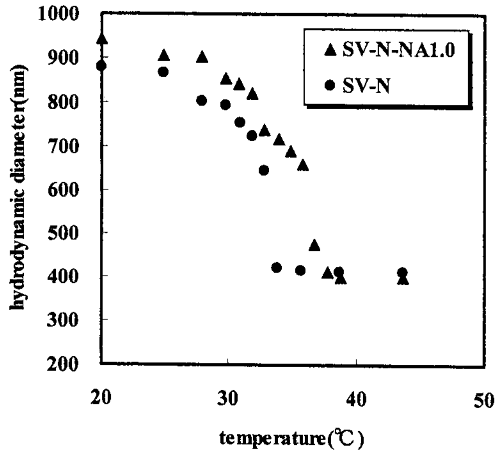


Figure 6. Hydrodynamic diameter of SV-N and SV-N-NA1.0 particles as a function of temperature.

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