Communication

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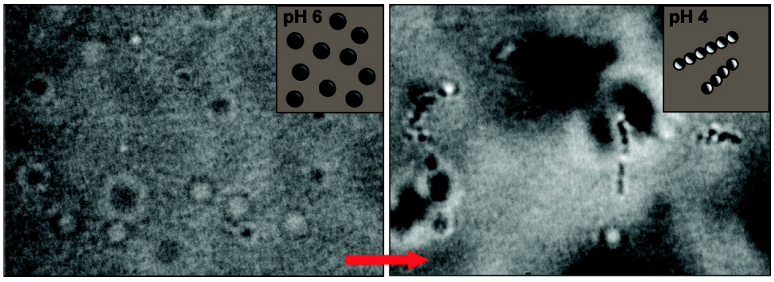
J. Am. Chem. Soc., **2007**, 129 (26), 8088-8089• DOI: 10.1021/ja072258w • Publication Date (Web): 07 June 2007



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Published on Web 06/07/2007

Janus Microgels Prepared by Surfactant-Free Pickering Emulsion-Based Modification and Their Self-Assembly

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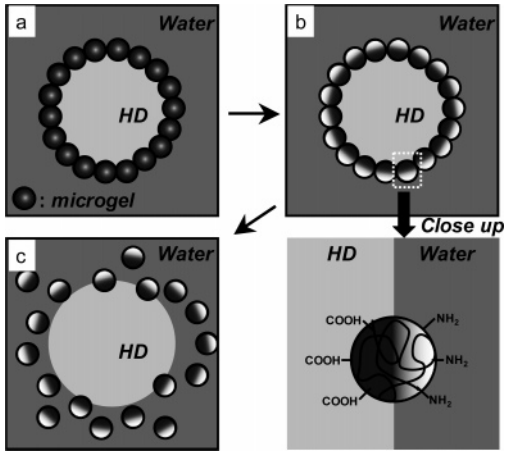
Polymer microgels, which are cross-linked particles having a network structure that swells in a suitable solvent, have attracted much attention in material science due to their "softness".[1] Particularly, stimuli-responsive microgels have found many applications. One of the most studied stimuli-responsive microgels[2] is composed of poly(*N*-isopropylacrylamide) (pNIPAm), which is a representative thermo-responsive polymer exhibiting a lower critical solution temperature (LCST) at ~31 °C.[3] As well, pNIPAm microgels can be made pH-responsive by ionic monomer copolymerization.[4] Many researchers have functionalized pNIPAm-based microgels by constructing core/shell structures,[5] making composites with inorganic nanoparticles[6] for application in more complex biotechnologies and nanotechnologies (e.g., drug delivery,[7] chemical/biological separation,[8] and photonic crystals[9]).

Particles in which the surfaces of both hemispheres are different from a chemical point of view are called "Janus particles".[10] Compared to chemically homogeneous particles, Janus particles may particularly undergo directed assembly in a pre-programmed fashion in the manner of proteins. For instance, amphiphilic Janus particles could be produced to face the same side spontaneously in an air/water interface,[10a] and dipolar Janus particles could be rotated in an electric field.[11] Basically, these "hard" Janus particles are unstable in water since they have neither electrostatic nor steric stabilization effects. This is one of the problems associated with Janus particles when they are assembled into well-defined complex supra-particular structures. Therefore, we designed Janus particles that possess a tunable function. A "Janus microgel", whose colloidal stability can be tuned by stimuli, may assemble into supra-particular structures in a controlled manner. Herein, we report the introduction of a hemispherical distribution of functional groups into preformed microgels using Pickering emulsion, which is an emulsion stabilized by a colloidal suspension of finely divided solids.[12] PNIPAm microgel is known to be adsorbed onto oil/water interfaces and to form stable Pickering emulsions.[12c] Using an oil/water interface of Pickering emulsions allows the introduction of a distributed functional group into the microgels if the functionalization occurs on only one side (the side immersed in oil or the water phase) of the microgels (Scheme 1). This methodology does not require an expensive apparatus (such as sputtering[11] or the Langmuir−Blodgett apparatus[13]) and might be applied to the large-scale production of Janus particles.[14]

We synthesized pH- and thermo-responsive poly[*N*-isopropylacrylamide-*co*-(acrylic acid)] (pNA) microgels (~2.8 μm at pH 6, ~1.5 μm at pH 4, both measured at 25 °C) with uniform size distribution via precipitation polymerization. Acrylic acid (AAc) was chosen as a co-monomer to introduce functional groups into the microgel hemisphere by means of a simple carbodiimide coupling reaction. Using pNA microgels as stabilizers, Pickering emulsion was formed by stirring hexadecane (HD) and water with pNA microgel (pH 6) at 25 °C (Scheme 1a). In this case, an oil-in-water type emulsion was formed, which was confirmed by

Scheme 1. (a) Preparation of Pickering Emulsion Stabilized by Microgels, (b) Hemispherical Modification of Amino Groups into Microgels Attached at the Oil/Water Interface, and (c) Microgel Collection by Destabilizing Emulsion



conductivity measurement (162 μS/cm). As can be seen from Figure 1b, each emulsion was stabilized by pNA microgels. After removing microgels unattached at the oil/water interface, amino groups were introduced by a carbodiimide coupling reaction using ethylenediamine (ED) and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), which is soluble only in water at 25 °C (Scheme 1b). After 2 h reaction and purification of the emulsion, the microgels were collected by destabilizing the emulsion (Scheme 1c). The emulsion was destabilized by freezing the HD (T_m = 16−19 °C) at 4 °C and then melting it. Approximately 80% of the emulsion was destabilized by this freezing/melting process, and the modified microgels (pNA-EDh microgels) were separated into the aqueous phase.

Hemispherical distribution of the amino groups was confirmed using the Au nanoparticle (AuNP) labeling technique.[15] Figure 2 shows TEM images of AuNP-conjugated pNA-EDh microgels in a dried state. AuNPs can be seen only in a particular area of one microgel. We previously found that AuNPs could be synthesized in situ where amino groups exist when pNIPAm-based microgels were used as templates.[15] Therefore, TEM images revealed that Janus microgels can be prepared successfully by means of the Pickering emulsion-based technique.

Interestingly, pNA-EDh microgels are self-assembled into string structures at pH 4, where most carboxyl groups are protonated (pK_a of AAc = 4.25)[16] (Figure 3b), whereas they are individually dispersed at pH 6, where all carboxyl groups are deprotonated (Figure 3a). At pH 6, pNA-EDh microgels dispersed stably due to both electrostatic repulsion and steric hindrance among them. In this case, the positive charge from the amino groups can be negated due to small amount introduced.[17] On the other hand, at pH 4, the dispersion of pNA-EDh microgels was unstable because they

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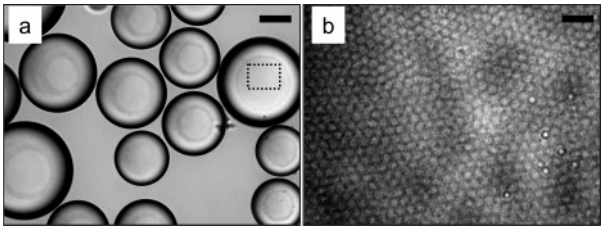

Figure 1. Optical microscope images of oil in water emulsion stabilized by pNA microgels at pH 6 at 25 °C. The photograph shown in b is a close-up image of the dot rectangle area in image a. The scale bars are 50 μm (a) and 5 μm (b).

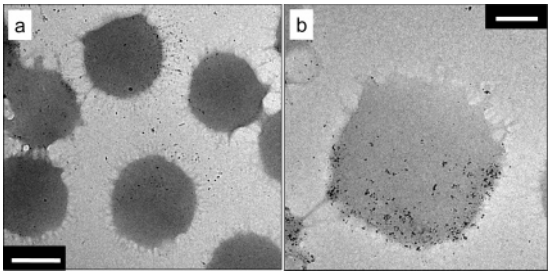

Figure 2. Field emission TEM images of AuNP-conjugated pNA-EDh microgels on a carbon-coated copper grid dried at 25 °C. The scale bars are 500 nm (a) and 200 nm (b). See the enlarged images in the Supporting Information.

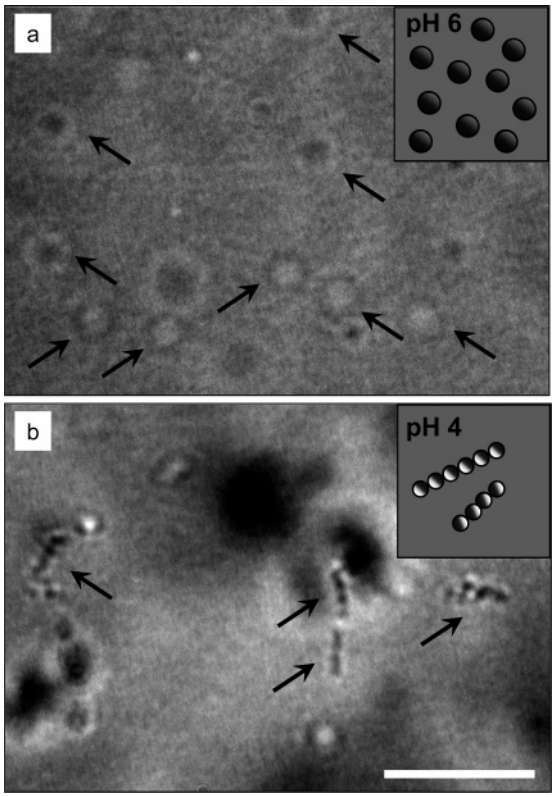

Figure 3. Optical microscope images of pNA-EDh microgels dispersed in a pH 6 (a) and a pH 4 aqueous solution (b). The microgels indicated by the arrows are in almost the same focus. The scale bar is 10 μm.

possessed differently charged surfaces whose charges alternated from one to the other in the manner of large dipoles. The positive charge on one hemisphere became effective, while another hemisphere should have a negative charge originating from the small amount of deprotonated AAc and initiator, resulting in self-assembling into strings. This self-assembly is further evidence that the modification was successful.

In conclusion, we have used a Pickering emulsion-based method to prepare a new type of Janus particle composed of stimuli-sensitive microgels. The microgels demonstrated pH-responsive assembly into string structures and might potentially express thermo-responsive behaviors. Such stimuli-responsive string structures may be of potential use as micro-actuators.

Acknowledgment. D.S., S.T., and H.K. are grateful to the research fellowships of the Japan Society for the Promotion of Science for Young Scientists. This work was supported by a Grant-in-Aid for the 21st Century COE program "KEIO Life-Conjugated Chemistry" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available: Experimental details, photographs of emulsion, enlarged TEM images, and optical microscope images of microgel string structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Since the reaction efficiency of the coupling is <100%, some portion of AAc groups is expected to remain.

JA072258W