Thermosensitive Spherical Organosilicate Hybrid Particles with a Multilayered Structure

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OTS spherical particles   60 ºC   Room temperature

REPRINTED FROM

Chemistry Letters

The Chemical Society of Japan

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A simple one-pot synthesis of thermosensitive spherical organosilicate hybrid particles is described. These organosilicate hybrid particles exhibit solid–liquid transition behaviors whose temperature can be changed by the modification of interdigitated arrays of long alkyl chains.

The self-organization of amphiphilic molecules has recently emerged as an efficient way to prepare hybrid materials possessing highly ordered structures in a wide variety of compositions.[1,2] It is well known that the controlled hydrolysis and condensation of long alkyl chain alkoxy silanes can lead to spontaneous organization, producing a new class of materials consisting of two-dimensional (2D) organic arrays, and inorganic networks linked by covalent Si–C bonds.[3,4] In early studies, alkyl trichloride silanes and alkyl trialkoxy silanes were widely used to construct closely packed, highly oriented 2D self-assembled structures. These structures were assembled on a solid surface or at a liquid/air interface using Langmuir–Blodgett (LB) and self-assembled monolayer (SAM) techniques.[4–6] Huo et al. were the first to discover that a lamellar structure could be prepared by the hydrolysis and condensation of hexadecyltriethoxysilane under acidic conditions.[7] Later, Parikh et al. found that hydrolytic polycondensation of octadecyltrichlorosilane in water could lead to the spontaneous formation of layered crystals in the form of multiple head-to-head ordered bilayers.[4] Kuroda et al. have also investigated the formation of two- and three-dimensional multilayered hybrid films using various types of alkyltrifunctional silanes with or without tetrafunctional silanes.[8–10] Recently, Bourlinos et al. reported the synthesis of layered organosilicate nanoparticles that exhibited a reversible solid–liquid transition at $55\,°C$.[11] In their study, they mentioned that the nonaqueous sol–gel reaction of octadecyltrichlorosilane in toluene, with a small amount of water, produced more condensed silica networks in hybrid nanoparticles. These condensed networks prevent further condensation reactions between silanol groups, thus forming reversibly meltable products.

In this paper, we describe the synthesis of thermosensitive spherical organosilicate hybrid particles using a modified sol–gel process. The controlled hydrolysis and condensation of octadecyltrimethoxysilane (OTS) or a mixture of OTS with vinyltrimethoxysilane (VTMS) in an aqueous alcohol solution produced monodisperse, spherical particles in 70% yield. These organosilicate hybrid particles have a multilayer structure, and they exhibit solid–liquid transition temperatures of $58\,°C$ for OTS and $48\,°C$ for the OTS/VTMS mixture.

Figure 1 shows optical microscopy (OM) images of OTS-based emulsion droplets in H_2O and ethanol. The emulsion droplets exhibited a mesoporous structure in H_2O, while those in ethanol had a linear polymeric structure. The hydrophobicity
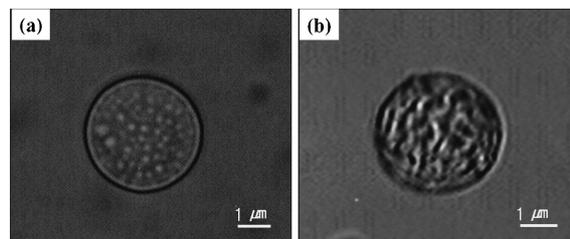

Figure 1. Optical microscopy images of OTS-based emulsion droplet in (a) H_2O and (b) EtOH.

of the long alkyl chains made OTS molecules immiscible with the H_2O phase, producing O/W/O emulsion droplets when the OTS was introduced into H_2O. In contrast, O/W emulsion droplets formed in ethanol produced lamellar multilayer structures from the OTS molecules.

Upon isolation, the morphology of the OTS particles prepared in H_2O collapsed, leaving a gel-like material. The immiscibility between OTS and water prevented the hydrolysis and condensation reactions of OTS, thereby preventing the networking of the OTS molecules. The shape of the W/O/W emulsion droplets was destroyed during isolation, as the filtration and drying disrupted the condensation between the OTS molecules. The eventual product was a gel-like material. Spherical OTS particles, however, could be prepared in a solid form when ethanol was used as a solvent. The miscibility of ethanol with both H_2O and OTS facilitated the hydrolysis and condensation of OTS, resulting in the networking of OTS molecules inside the emulsion droplets. While the use of ethanol was vital to the synthesis of the spherical particles, the amount of water used also played an important role in determining the morphology of the final product. The R value, which is defined as $[H_2O]/[silane]$, is known to be one of the critical parameters in the sol–gel process.[12] For monodisperse, spherical OTS particles, the optimum R value was found to be 22.4, while the optimum R value for the OTS/VTMS composite particles was 18.7. Scanning electron microscopy (SEM) images of OTS and the composite particles are shown in Figure 2. As can be seen in Figure 2, both OTS and composite particles appear to be layered like an onion, although VTMS/OTS composite particles exhibit less uniformity in their size compared to OTS particles.

CP-MAS ^{29}Si NMR spectra of particles exhibited absorption peaks corresponding to T^2 ($-58.5\,ppm$) and T^3 ($-67.0\,ppm$) units for the OTS particles, while an additional peak of T^3 ($-80.5\,ppm$) from VTMS was observed for the composite particles.[13] Also, the relative intensity of T^2 as compared to T^3 from OTS was significantly reduced in the case of the composite particles.[13] This indicates that the heterocondensation between OTS and the comonomer had proceeded almost completely, resulting
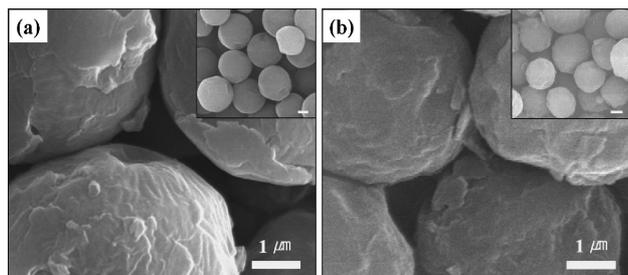
Figure 2. SEM images of (a) OTS and (b) OTS/VTMS composite particles.
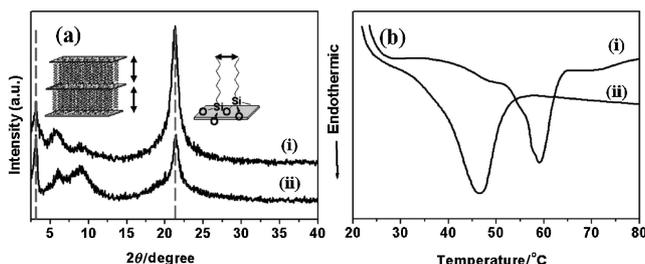

Figure 3. (a) XRD and (b) DSC curves for (i) OTS and (ii) OTS/VTMS composite particles.

in the alteration of the multilayer structures due to alkyl chain interactions.

X-ray diffraction (XRD) patterns of OTS and the composite particles are shown in Figure 3a. For OTS and OTS/VTMS composite particles, the XRD pattern shows a sharp peak at $2\theta = 21.5°$, which corresponds to a d spacing of 4.15 Å. This value is quite close to the lateral interchain spacing observed for densely packed alkyl chains.[9] In addition, a small peak around $2\theta = 3–4°$, corresponding to a d spacing of 28.3 Å, was observed for both organosilica particles. Parikh and Kuroda et al. reported that 28.3 Å is the length of a fully extended $C_{18}H_{32}SiO_x$ unit. It is possible that the structure of the OTS and composite particles could consist of interdigitated $RSiO_x$ layers with alternating up and down alkyl chains.[4,8,10] In contrast, the intensity of the peak at $2\theta = 21.5°$ relative to the intensity of the peak around $2\theta = 3–4°$ was significantly reduced in the composite particles as compared to the OTS particles. This could imply that the interactions between densely packed alkyl chains in the OTS particles were partly disrupted by the insertion of vinyl groups from VTMS, resulting in a less ordered multilayer structure. These changes in the interactions between the alkyl chains of the multilayer structures in the particles could result in the variation of the solid–liquid transition temperatures.

Differential scanning calorimetry (DSC) results of the OTS and composite particles are shown in Figure 3b. The DSC profile of the OTS particles exhibits a solid–liquid transition temperature around 58 °C due to the change in the octadecyl–alkyl chain interaction. This value is close to the one reported by Bourlinos et al.[11] For the composite particles, the solid–liquid transition temperature shifted to 48 °C, suggesting the disruption of chain–chain interactions between the OTS molecules. The insertion of vinyl groups from VTMS into the multilayers of alkyl chains would weaken the alkyl chain interactions by increasing the distance between interdigitated multilayers, eventually causing multilayered structures to be easily destroyed at low temper-

ature. Thermogravimetric analysis (TGA) of OTS particles showed that weight loss due to the decomposition of alkyl groups started at 350 °C.[13] The residual weight % was about 20%, which is in agreement with the theoretical organic/inorganic content ratio of 80 to 20%. For the composite particles, TGA curves exhibited similar decomposition patterns with slightly higher residual weights. When heated above the solid–liquid transition temperature, the OTS and composite particles became transparent liquids. Both transparent liquids solidified upon cooling, and these melting–solidification transitions were reversible.[13] The composite particles yielded a transparent solid upon cooling, while the OTS particles resulted in a rather opaque solid. The VTMS molecules might prevent the formation of ordered multilayers upon cooling, which would result in a rather amorphous structure. Raman spectra of the OTS particles showed that there were no discernible changes in the position and intensity of the Raman peaks before and after heat treatment, indicating that the layers of densely packed alkyl chains were sustained after reversible heating and cooling cycles.[13]

In summary, thermosensitive organosilicate hybrid particles were synthesized using a modified sol–gel process. Monodisperse, spherical particles were obtained by the controlled hydrolysis and condensation of OTS and a mixture of OTS/VTMS in an aqueous alcohol solvent. These particles have a multilayered structure and exhibit unique solid–liquid transition temperatures around 58 °C for OTS and 48 °C for OTS/VTMS particles. These transition temperatures indicate that the multilayered structure of the OTS particles could be partially disrupted by the insertion of VTMS molecules into interdigitated arrays. The OTS particles and the composite particles exhibit a high thermal stability and could be potentially used in applications for thermosensors, lubricants, and thermoplastic materials.

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13　Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.