Immobilization of Colloidal Crystals, Formed from Polymer-modified Silica in Organic Solvent, in Polymer Gel with Radical Polymerization

Kohji Yoshinaga,* Kumiko Fujiwara, Yasuyuki Tanaka, Mikiko Nakanishi,[†] and Masafumi Takesue[†]
Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Sensui-cho, Tobata, Kitakyushu 804-8550
[†]*Technical Development Department, Research & Developing Center, Bando Chemical Industries, Co., Ashihara-dori, Kobe 652-0882*

Radical copolymerization of methyl methacrylate and 1,2-di-methacryloyloxyethane in acetonitrile solution containing colloidal crystals of poly(methyl methacrylate)-grafted silica afforded polymer gels involving the particle arrays.

The size-controlled and ultrafine particles are much attractive in a field of materials chemistry. For an aqueous or alcoholic colloidal suspension, it is well known that spherical colloidal particles periodically array in a limited range of volume fractions.[1] The ordering of the colloidal particles, so called "colloidal crystals," is based on a strong electrostatic repulsive interaction among the particles, arising from spreading of the electric double layer.[1c,2] We have previously reported that monodisperse polymer-modified silica forms the colloidal crystals in organic solvent, which is a polar and good solvent for the grafted polymer.[3] If it is possible to incorporate the colloidal crystal structure into a polymer matrix, the particle-arrayed polymer leads to new functional materials. For example, nanoscale periodic particles array, i.e., photonic crystal, is promising to application to optical devices, such as dielectric mirror, or photofilter.[4] In this paper, we describe the immobilization of colloidal crystals of polymer-modified silica into polymer gels by radical polymerization in organic solvent.

Monodisperse colloidal silica, of 136 nm in diameter, was kindly presented by Catalysts & Chemicals Co. ltd., Japan. The modification of colloidal silica with polymer was carried out by the reaction of colloidal silica with trimethoxysilyl-terminated poly(methyl methacrylate) (PMMA) of number average molecular weight 6600 in 1,2-dimethoxyethane.[5] The amount of grafted polymer on silica particles was 92 mg/g-SiO_2. Unreacted polymer coupling agent was removed from the suspension by centrifugal washing with acetone five times. The critical volume fraction (ϕ_0) in the colloidal crystallization was determined by naked eyes or a digital camera. The reflection spectra were recorded on a photonic multichannel spectral analyzer of Hamamatsu Photonics PMA-111 employing a 150-W halogen lamp on Hayashi LA-150UX.

As we have reported previously, colloidal crystallization of polymer-modified silica takes place in organic solvent, which is a good solvent for grafted polymer, and ϕ_0 varies with the combination of grafted polymer and solvent. The PMMA-modified silica (PMMA/SiO_2) was formed the crystal structure in acetonitrile, acetone, and acrylonitrile. Although the colloidal crystallization of PMMA/SiO_2 takes place in acrylonitrile, the radical polymerization seems to lead to destruction of particle array, because excluded volume effects of resulting polymer chains on the electrostatic repulsive interaction among the particles are strong enough to break the crystal structure to give rise to a phase separation between the particles and polymer. In fact, the photo-initiated radical polymerization of acrylonitrile suspension containing PMMA/SiO_2 colloidal crystals led to complete phase separation. If it is possible to surround the colloidal crystals with loosely cross-linked

polymer network containing solvent, i.e. gel, the excluded volume effects of the polymer chains on the electrostatic interaction between the particles per unit volume of the suspension are considerably small enough to maintain the crystal structure. Thus, we tried to incorporate the particle arrays into cross-linked organogel formed by the radical copolymerization of methyl methacrylate (MMA) and macromonomer **1**, prepared by the reaction of poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) with acryloyl choloride, or 1,2-dimethacryloyloxyethane (EDM). In Figure 1, effects of the cross-linker addition on ϕ_0 for the colloidal crystallization in PMMA-silica suspension in CH_3CN are shown. Interestingly, it was observed that the addition of EDM gave a two-step increase of ϕ_0, but the reason for the phenomenon was still unclear. In both cases, however, ϕ_0 increased with addition of cross-linker. These results showed that the gelation by copolymerization should be carried out in the concentration less than 20 and 80 wt % for the macromonomer and EDM, respectively. Thus, the polymerization was carried out in the PMMA/SiO_2 suspension in the range from volume fraction (ϕ) = 0.087 to ϕ = 0.152, 2.02–2.31 mol L^{-1} MMA, 4.2–7.1 wt % cross-linker and 0.051–0.100 mol L^{-1} AIBN in acetonitrile in a 10×10 mm quartz cell at 25 °C by ultraviolet light irradiation using a high-pressure Hg lamp (500 W).

Copolymerization of MMA and macromonomer **1** containing colloidal crystals of PMMA/SiO_2 in CH_3CN gave polymer gels, but brought about destruction of the crystal structure. On the other hand, the copolymerization of MMA and EDM in the suspension containing colloidal crystals of PMMA/SiO_2 resulted in the formation of the gel included crystal structure of PMMA/SiO_2, and the brilliance based on Bragg reflection was observed on the cross section of the gel. The observation indicated that the crystal struc-
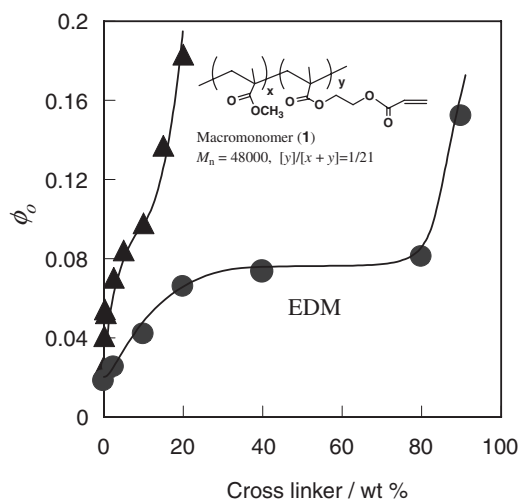

Figure 1. Effects of cross-linker addition on the critical volume fraction in colloidal crystallization of PMMA/SiO_2 in acetonitrile.
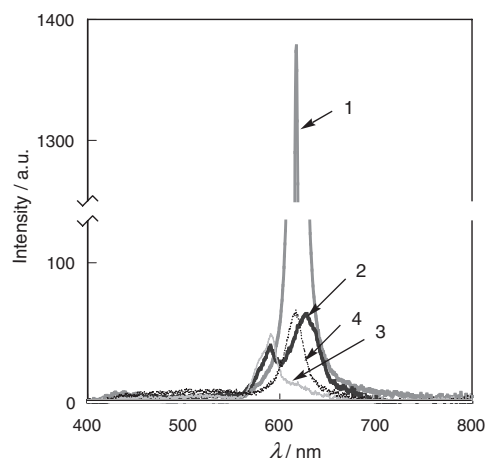
Figure 2. Reflection spectra of immobilized colloidal crystals of PMMA/SiO$_2$ in acetonitrile (**1**) and in the front side (**2**), cross section (**3**) and rear side (**4**) of the gel formed by the polymerization of MMA and EDM in a 10-mm cell.

Figure 3. Reflection spectra of immobilized colloidal crystals of PMMA/SiO$_2$ in acetonitrile (**1**) and in front side (**2**) and rear side (**3**) of PMMA gel formed by the polymerization of MMA and EDM in a 2-mm cell.

Figure 4. A TEM image of immobilized colloidal crystals of PMMA/SiO$_2$ in PMMA gel.

ture was maintained on the inside of the gel. The reflection spectra of the front and rear sides of the gel containing the composite particles at $\phi = 0.087$ showed that the reflection intensities decreased to less than one tenth of that before gelation and that the peaks became broad, as shown in Figure 2. In the reflection spectrum, broadening of the peaks or appearance of bimodal peaks come from the distortion or heterogeneity of the crystal structure, respectively. These results therefore indicated that the crystal structure was partially distorted or destroyed. The space between neighboring particles in the gel at the front side in the gel, calculated by Bragg's equation, was 275 nm, which was slightly smaller than that, 280 nm, before the polymerization. However, the immobilization in the gel resulted in lowering of single crystal size, calculated by the reflection peak width,[2b] from 12.5 μm before the polymerization to 1.1 μm, which was corresponding to 5 particle layers. One reason for the distortion or destroy of the crystal structure probably come from the heterogeneity of the copolymerization in a 10 × 10 mm cell.

Thus, we tried the immobilization of the colloidal crystals with gelation employing a 2-mm-thickness cell. The polymerization was carried out in a suspension containing PMMA/SiO$_2$ in the range from $\phi = 0.090$ to $\phi = 0.112$, 2.12–2.27 mol L^{-1} MMA, 0.28–0.32 mol L^{-1} EDM and 0.006–0.044 mol L^{-1} AIBN in CH$_3$CN at 25 °C. The brilliance based on Bragg reflection was observed in the resulting gel. The reflection spectra of the resulting gel at $\phi = 0.090$ were shown in Figure 3. In this case, reduction of AIBN and the volume fraction of PMMA/SiO$_2$ in the polymerization made the reflection peak sharp and high. The spaces between neighboring particles in a front and rear side of the gel were 273 and 274 nm, respectively, which were mostly the same as that, 274 nm, before the polymerization. Also, the average size of single crystals was 11.0 and 3.8 μm in the gel at the front and rear side respectively, which were smaller than that of 15.2 μm before the polymerization. Therefore, this result suggests that slow polymerization employing a 2-mm cell is favorable for maintaining particle array. However, the size of immobilized crystals in the gel seemed to be relatively small to apply to the photonic crystals. On the other hand, employment of a 1-mm-thickness cell resulted in the formation of the gel more distorted crystals than those formed using the 2-mm cell. Probably, the destruction of the structure arises from the contraction in volume in the polymerization system, cannot be compensated in small volume of the 1-mm cell.

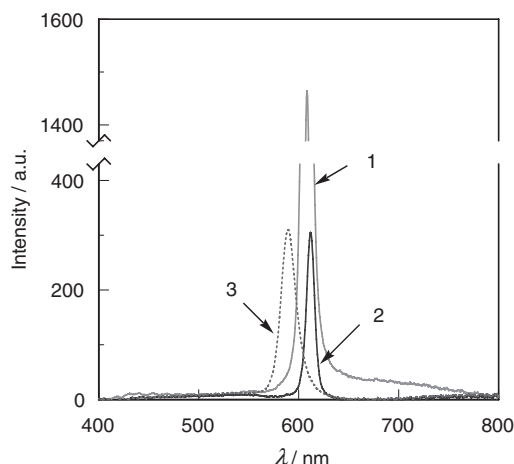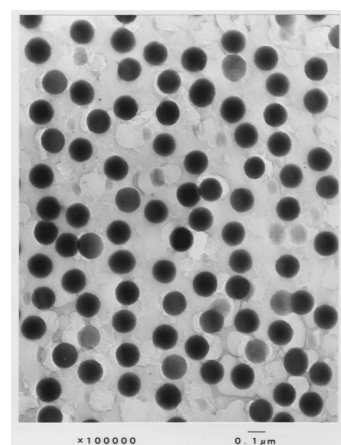In Figure 4, a TEM image of dried gel containing the particle was shown. The image exhibited the cross linking during the copolymerization takes place along with the penetration into the space among the particles.

In conclusion, the immobilization of particle array in organogels was achieved by the copolymerization of MMA and EDM in acetonitrile suspension containing colloidal crystals of PMMA/SiO$_2$. Studies of formation of large colloidal crystals in organic solvent and immobilization in polymer gel are now in progress.

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