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Immobilization of colloidal crystals, formed by polymer-grafted silica in organic solvent, in physical gels

Received: 13 August 2005
Accepted: 12 October 2005
Published online: 1 February 2006
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Abstract Immobilization of colloidal crystals by gelation of polymer-grafted silica suspension in acetonitrile with alkyl amides derived from amino acids was investigated. Addition of *N*-benzyloxycarbonyl-L-isoleucylaminooctadecane (Z-Ile-C18) and 1,12-bis(*N*-benzyloxycarbonyl-L-valylamino)dodecane [Bis(Z-Val)-C12] to poly(maleic anhydride-*co*-styrene)-grafted silica suspension in acetonitrile resulted in formation of physical gels preserved colloidal crystal structure. From the reflection spectra, intersphere distance and size of crystallite in the gel formed with Bis(Z-Val)-C12 were confirmed to be mostly same as those of colloidal crystals in suspension.

Keywords Colloidal crystals · Physical gel · Gelling agent · Immobilization · Polymer-grafted silica

Introduction

In recent years, periodic particle-arrayed materials have received great attention due to their potential application to optical-electric devices. For an aqueous or alcoholic colloidal suspension, it is well known that spherical colloidal particles form three-dimensional periodic ordering in a limited range of volume fractions [1–4]. 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 electric double layer. We have previously reported that monodisperse polymer-grafted silica forms the colloidal crystals in organic solvent, which is a polar and good solvent for the grafted polymer [5, 6]. If it was possible to incorporate the particle array formed by colloidal crystallization into a polymer matrix, the particle-arrayed composite led to new functional materials. For example, nanoscale periodic particle array, i.e., photonic crystal, is a potential application to optical devices, such as dielectric mirror, or photofilter. In this respect, there are recent reports concerning immobilization of colloidal crystals

by radical polymerization into hydrogels [7–15]. We have also successively immobilized the colloidal crystals from polymer-modified silica by radical polymerization into poly(methyl methacrylate) gels [16, 17]. In these cases, however, the radical polymerization usually involves contraction in volume so that the immobilization sometimes causes destruction or distortion of the crystal structure.

On the other hand, it has also been reported that the gelation in organic solvents takes place by the addition of alkyl amides derived from amino acid [18–20]. The gelling is confirmed to make physical organogel by the formation of cross-linked fibers assembled through hydrogen bond without volume contraction. Thus, immobilization of the colloidal crystals in physical gels in organic solvent by addition of a gelling agent without volume contraction is practically a challenging subject for fabrication of photonic crystals. In this paper, the immobilization of colloidal crystals, formed from poly(maleic anhydride-*co*-styrene)-modified silica [P(MA-ST)/SiO₂] in acetonitrile, in physical gels by the addition of alkyl amide derivatives of L-amino acid was described.

Experimental

Materials

Monodisperse colloidal silica ethanolic suspension, containing 20 wt% SiO₂ of 136 nm in diameter with polydispersity of 0.01, was kindly presented by Catalysts & Chemicals Co. Ltd., Japan. Amino acids, L-isoleucine and L-valine were purchased from Wako Chemicals Ltd., Japan. Trimethoxysilyl-terminated poly(maleic anhydride-*co*-styrene) [P(MA-ST)-Si(OCH₃)₃] of number average molecular weight of 4,700 was synthesized by the method reported previously [21]. Other reagents were used without further purification.

Measurements

The reflection spectra were recorded on a photonic multi-channel spectral analyzer of Hamamatsu Photonics PMA-111 with a 150-W halogen lamp on Hayashi LA-150UX. In this work, the spectra were taken at a middle position of a vial containing colloidal crystals. Colloidal crystallization was recognized by the observation by naked eyes or Bragg reflection on the spectrum. The amount of grafted polymer on the silica was determined by weight loss during the temperature elevation from 100 to 800°C on a thermal gravimetric analyzer, Shimadzu TA-50 H.

Polymer grafting on colloidal silica

The modification of colloidal silica with polymer was carried out by the reaction of colloidal silica with P(MA-ST)-Si(OCH₃)₃ under refluxing for 4 h in 1,2-dimethoxyethane, as reported previously [21]. Unreacted polymer silane was removed by a centrifugal washing five times with 10 cm³ acetone.

Synthesis of gelator

A typical synthesis was as follows [19]. A mixture of 0.5 g *N*-benzyloxycarbonyl-L-isoleucine and 0.42 g *N,N'*-dicyclohexylcarbodiimide and 4 cm³ ethyl acetate was stirred at 4°C for 30 min, and then 0.50 g octadecylamine was added to the mixture. The solution was stirred at 4°C for 1 h and at 45°C for 10 h, and successively at 60°C for 4 h. The hot solution was filtered and then cooled down to room temperature. Cooled solution made the gel of ethyl acetate, and then drying resulting in gel under reduced pressure yielded 0.56 g of *N*-benzyloxycarbonyl-L-isoleucylaminooctadecane (Z-Ile-C18). Other gelators, *N*-benzyloxycarbonyl-L-isoleucylaminooctane (Z-Ile-C8), *N*-benzyloxycarbonyl-L-isoleucylaminododecane (Z-Ile-C12), and *N*-benzyloxycarbonyl-L-isoleucylaminohexadecane (Z-Ile-C16) were prepared by the same procedure as that of Z-Ile-C18. Bola-form type gelling agents,

1,12-bis(*N*-ethyloxycarbonyl-L-isoleucylamino)dodecane (Bis-(Et-Ile)-C12), 1,12-bis(*N*-benzyloxycarbonyl-L-isoleucylamino)dodecane (Bis-(Z-Ile)-C12), and 1,12-bis(*N*-benzyloxycarbonyl-L-valylamino)dodecane [Bis-(Z-Val)-C12] were also made using corresponding diamines by a similar manner to that of Z-Ile-C18.

Gelation of colloidal crystals

A typical run is as follows. To suspension of 21.1 mg P(MA-ST)/SiO₂ [volume fraction (ϕ), 0.141] in 1.0 cm³ acetonitrile was added 4.0 mg Z-Ile-C18 (0.55 wt%). The mixture was heated up to 65°C and then cooled down to room temperature. Colloidal crystals incorporated into gel were confirmed by naked eyes or reflection spectrum. A neighboring intersphere space (D_{obs}) was estimated by the following equation, assuming face-center close-packing or hexagonal close-packing [22]:

$$D_{obs} = \sqrt{\frac{3}{8}} \frac{\lambda_p}{n_p}$$

where n_p and λ_p are the refractive index and wave number of the peak top. The refractive index, n_p , was estimated by the following equation:

$$n_p = 1.50\phi + n_s(1 - \phi)$$

where ϕ and n_s are the volume fraction of polymer-grafted silica and the refractive index of solvent (1.344 for acetonitrile at 293 K); the value of 1.50 is the refractive index of

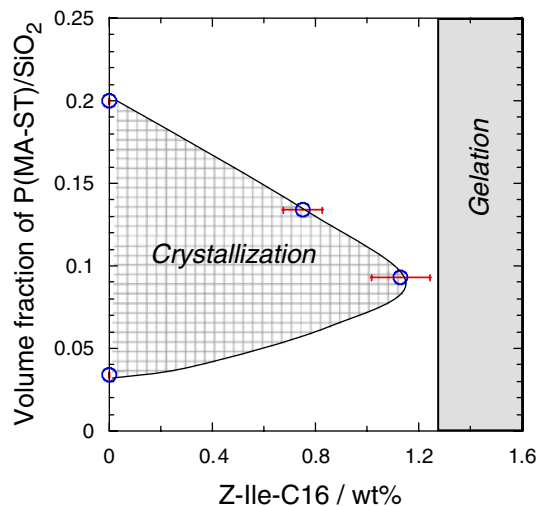


Fig. 1 Phase diagram in colloidal crystallization and gelation of poly(maleic anhydride-*co*-styrene)-modified silica [P(MA-ST)/SiO₂] acetonitrile suspension with *N*-benzyloxycarbonyl-L-isoleucylaminohexadecane (Z-Ile-C16)

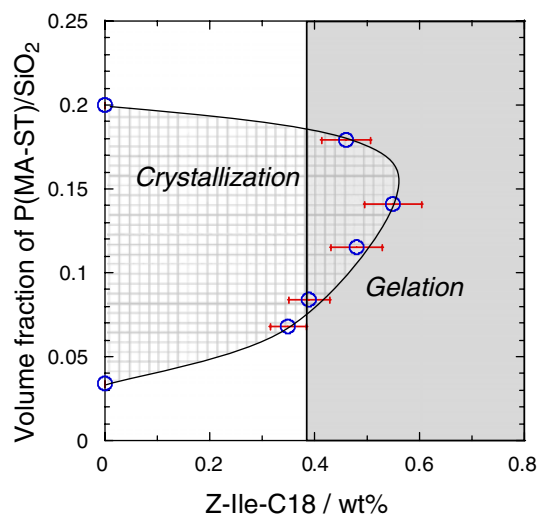


Fig. 2 Phase diagram in colloidal crystallization and gelation of P(MA-ST)/SiO₂ acetonitrile suspension with *N*-benzyloxycarbonyl-L-isoleucylaminooctadecane (Z-Ile-C18)

silica. The estimation of size of crystallite (L) was carried out by Scherrer's equation [23, 24],

$$L = 1/(S_1 - S_0)$$

where $S_x = 2\sin\theta/\lambda_x$, λ_1 is the larger wavelength at half-maximum, and λ_0 is the smaller wavelength at half-maximum. θ is the incident angle.

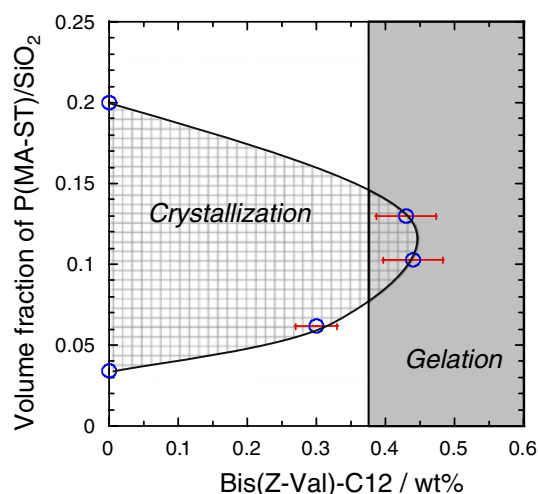


Fig. 3 Phase diagram in colloidal crystallization and gelation of P(MA-ST)/SiO₂ acetonitrile suspension with 1,12-bis(*N*-benzyloxycarbonyl-L-valylamino)dodecane [Bis(Z-Val)-C12]

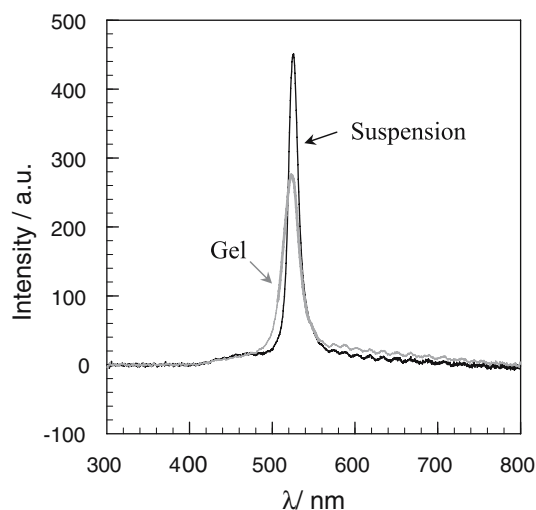


Fig. 4 Reflection spectra of colloidal crystals in P(MA-ST)/SiO₂ acetonitrile suspension and in gel formed with Z-Ile-C18

Results and discussion

As reported in our previous paper [5, 6], colloidal crystallization of P(MA-ST)/SiO₂ efficiently took place in acetonitrile. However, the colloidal crystallization of polymer-grafted silica in organic solvents is sometimes disturbed by addition of organic compounds in the suspension system [16]. Therefore, in the present system, gelling agents should be required to exhibit high gelation capability, which was usually evaluated by minimum gelling concentration (MGC). According to Hanabusa et al.'s paper [19], L-isoleucine derivatives with alkyl amide showed relatively low MGC values for gelling in acetonitrile. Hence, we first investigated the gelation capability of alkyl amides derived from L-

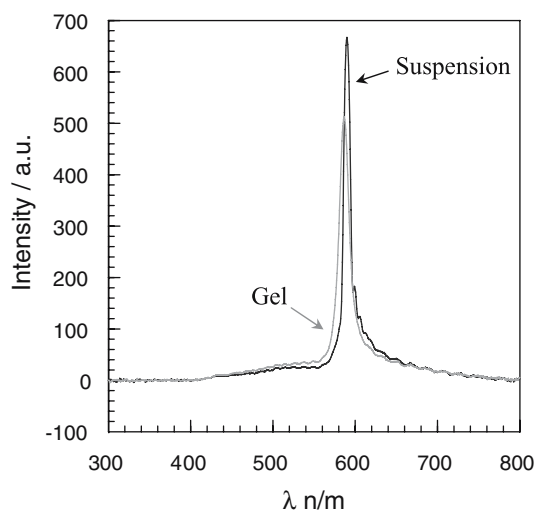


Fig. 5 Reflection spectra of colloidal crystals in P(MA-ST)/SiO₂ acetonitrile suspension and in gel formed with Bis(Z-Val)-C12

isoleucine for gelling in acetonitrile without colloidal crystals. MCGs of Z-Ileu-C16 and Z-Ile-C18 for gelling in acetonitrile were observed to be 0.65 and 0.32 wt%, respectively, while gelation with Z-Ile-C8 and Z-Ile-C12 never occurred up to more than 1.30 wt% due to relatively high solubility. Thus, we examined the gelation of P(MA-ST)/SiO₂ colloidal crystals in acetonitrile suspension employing gelling agents, Z-Ile-C16 and Z-Ile-C18. Figures 1 and 2 show phase diagrams in colloidal crystallization and gelation of P(MA-ST)/SiO₂ acetonitrile suspension as a function of Z-Ile-C16 or Z-Ile-C18 concentration. In these diagrams, overlapped areas exhibit formation of gel along with simultaneous colloidal crystallization. Here, the gelation was referred to as the formation of hard gel not to flow down when the gels in a vial were put upside down, and the preservation of colloidal crystals in gels was confirmed by appearance of Bragg reflection (Figs. 4 and 5). In the case of Z-Ile-C16 addition, the gelation took place over the concentration of 1.34 wt%, but colloidal crystals never came up in the range from $\phi=0.035$ to 0.14. Thus, Z-Ile-C16 formed gels at fairly higher concentration in the suspension than MCG, which possibly made colloidal crystallization disturbed. At the same time, Z-Ile-C18 presented excellent capability in gelation of colloidal crystals, as illustrated by overlapped area in Fig. 2. These results also implied that the colloidal crystallization of P(MA-ST)/SiO₂ in acetonitrile took place relatively much faster than gelation.

On the other hand, it was also reported that bola-form type amides derived from L-isoleucine and L-valine exhibited high gelation capability in organic solvents [18]. We next synthesized three gelators, Bis-(Et-Ile)-C12, Bis(Z-Ile)-C12, and Bis(Z-Val)-C12, and then examined gelation with these gelators in acetonitrile without colloidal crystals. MCG of Bis(Z-Val)-C12 was 0.32 wt%, while those of Bis-(Et-Ile)-C12 and Bis(Z-Ile)-C12 were, respectively, 0.43 wt%. Thus, we examined the gelation with Bis(Z-Val)-C12 in P(MA-ST)/SiO₂ acetonitrile suspension. In Fig. 3, the phase diagram of colloidal crystallization and gelation of P(MA-ST)/SiO₂ acetonitrile suspension with Bis(Z-Val)-C12 was shown. Although Bis(Z-Val)-C12 showed higher capability for gelation than Z-Ile-C18, the overlapped area in gelation

and colloidal crystallization with Bis(Z-Val)-C12 is more narrow than that with Z-Ile-C18. According to these diagrams, it was recognized that Z-Ile-C18 gave stable physical gels including colloidal crystals, as compared with Bis(Z-Val)-C12.

In Fig. 4, a typical reflection spectrum of colloidal crystals in the gel obtained by Z-Ileu-C18 at $\phi=0.141$ was shown along with that in the suspension before gelation. The reflection peak of colloidal crystals in the gel was scarcely sifted from that in acetonitrile suspension but became slightly broad. From these spectra, the intersphere space and the size of crystallite in gel were estimated to be 234 nm and 5.5 μm , respectively, while those in the suspension were 235 nm and 10.0 μm . This result suggested that gelling took place relatively homogeneously, in spite of making colloidal crystal size small. In the case of Bis(Z-Val)-C12 system at $\phi=0.103$, Bragg reflection peak also appeared at mostly same wave number, 590 nm, as that of the suspension, but slightly broadening the peak (Fig. 5). In this case, the intersphere space and the size of crystallite of colloidal crystals in the gel were estimated to be 264 nm and 11.5 μm , respectively, being comparable those of the suspension, 265 nm and 18.5 μm . Therefore, it was found out that a gelator exhibiting high gelation capability could preserve colloidal crystal structure in formed gel. The reason for property difference between Z-Ile-C18 and Bis(Z-Val)-C12 presumably comes from difference between mono- and di-binding site for formation of fiber-like network via hydrogen bonding among molecules. A gelator to Z-Ile-C18, however, was also recognized to be an effective one in terms of gelation ability of colloidal crystals in wide range of P(MA-ST)/SiO₂ volume fraction.

In conclusion, the addition of alkyl amide derivatives having L-isoleucine or L-valine moiety to polymer-grafted silica suspension in acetonitrile gave gels preserved colloidal crystal structure. A gelator exhibiting high capability for gelation, such as Bis(Z-Val)-C12, allowed the gel to preserve its colloidal crystal structure without distortion and much destruction during gelling process. Gels obtained here were not too hard enough to apply to optical materials, and further investigation on solidification of the gel is now in progress.

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