

# Fabrication of Particle-arrayed Poly(methyl methacrylate) Films from Colloidal Crystals formed in Organic Solvent

K. Yoshinaga<sup>a</sup>, Emiko Mouri<sup>a</sup>

<sup>a</sup> Department of Applied Chemistry, Kyushu Institute of Technology, 1-1 Sensui, Tobata, Kitakyushu 804-8550, Japan

## Abstract

Colloidal crystallization of polymer-modified silica in organic solvent and incorporation of the colloid crystals into polymer matrix were investigated. Colloidal crystallization of Polymer-grafted silica, of 136 nm diameter, was observed in organic solvents, which were polar and good ones for modified polymer. The crystallization was confirmed to occur due to the electrostatic repulsion between the modified silica in the suspension. Neighboring inter-particle distances in the colloidal crystals were fairly longer than length of grafted polymer chains. Colloidal crystals formed by polymer-grafted silica particles were immobilized by a step-wise procedure consisting of gelation by radical copolymerization followed by solidification by further polymerization. In the first step, the poly(methyl methacrylate)-grafted silica colloidal crystal suspension was successfully incorporated into the gel by copolymerization of methyl methacrylate (MMA) and 1,2-dimethylacryloyloxyethane (DME). The second radical polymerization of MMA or trifluoroethyl methacrylate (TFEMA) was performed after substituting the solvent with each monomer. By this two-step procedure, the silica particle array of colloidal crystals was immobilized to make into durable material.

**Keywords:** Colloidal crystals, Immobilization, Particle arrayed structure, PMMA film, Polymer grafting

## 1. Introduction

For an aqueous or alcoholic colloidal suspension, it is well known that monodisperse and spherical colloidal particles periodically array in a limited range of volume fractions [1,2]. The three dimensional particle array, so called “colloidal crystals,” is based on an electrostatic repulsive interaction among the particles, arising from spreading of the electric double layer [1]. If it were possible to incorporate the colloidal crystal structure into polymer matrix, the polymer led to a noble functional material. For examples, the periodic particles array, i.e. photonic crystal, is recently receiving much attention for application to optical devices, such as dielectric mirror or photonic filters [3,4]. Concerning application of colloidal crystals into photonic crystals, the immobilization of the crystals into polymer film or sheet is one of essential processes. In this respect, some researchers have so far reported the immobilization of colloidal crystals into polymer hydrogels by a radical polymerization [5]. However, the gel is generally too soft to utilize the devices. In this sense, the colloidal crystals, formed in organic solvent, have advantages for the solidification, because it is possible to choose various organic reactions or polymerizations in organic media to solidify. As reported previously [6,7], we found out that polymer-grafted silica formed colloidal crystals in organic solvents. In order to immobilize colloidal crystals of polymer-modified silica into polymer matrix, the incorporating should be carried out via two step polymerization, first gelation and successive solidification, because a radical polymerization of vinyl compound in the suspension containing colloidal crystals usually led to phase separation between silica and polymer. In this paper, we report that two-step immobilization of colloidal

crystals, first gelation and solidification via radical polymerization, to prepare silica particle array film (Figure 1).

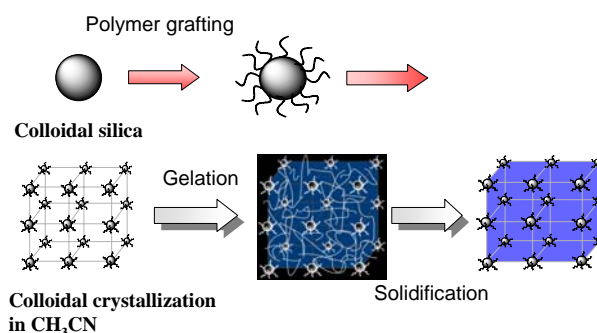


Figure 1. Schematic representation of immobilization of colloidal crystals of polymer-grafted silica.

## 2. Experimental

### 2.1 Materials

Monodisperse colloidal silica, containing 20 % SiO<sub>2</sub> of 78 and 135nm diameter suspended in ethanol was kindly offered by Catalysts & Chemicals Ind. Co, Japan. Trimethoxysilyl-terminated poly(methyl methacrylate) (PMMA-Si(OMe)<sub>3</sub>) of number average molecular weight 8100 was synthesized by the method reported previously [8]. The particles of PMMA/SiO<sub>2</sub> were prepared by the reaction of the colloidal silica with PMMA-Si(OMe)<sub>3</sub> in acetone [9].

**2.2 Measurements**  
Amount of grafted polymer was estimated from the weight loss during temperature elevation from 100 °C to 800 °C, after

keeping at 100 °C for 1 h to remove moisture. The critical volume fraction ( $\phi_c$ ) of PMMA/SiO<sub>2</sub> in the colloidal crystallization was determined by a naked eyes or a digital camera. Reflection spectra of colloidal crystals were recorded on a photonic multi-channel spectral analyzer, Hamamatsu Photonics PMA-111, employing a 150-W halogen lamp on Hayashi LA-150UX. Scanning electron micrographs were recorded on JEOL JSM-6320F.

### 2.3 Gelation

Cross-linker, DME (4~7wt%) and MMA monomer (ca.2mol/l) acetonitrile solution was added to the PMMA-grafted silica colloidal suspension ( $\phi = 0.08\sim 0.15$ ). The solution was poured into a Pyrex® glass cell with 1mm~10mm width. AIBN (0.05~0.1mol/l) was added to the solution as an initiator. Radical polymerization of DME and MMA was carried out by UV irradiation (high pressure Hg lamp, 500W) to give the gelation of the suspension.<sup>10</sup> DMAAm monomer was also used in copolymerization instead of MMA. The condition of colloidal crystals was investigated by reflection spectroscopy, TEM and LSM.

### 2.4 Solidification

The above gel was put into the cell again. The cell was immersed into vinylidene-1,3-dioxolane, MMA or TFEMA at a room temperature for 24 h to exchange CH<sub>3</sub>CN with MMA in the gel by freeze-drying and solvent exchange. The polymerization was carried out in monomer vapor-saturated cell by UV light irradiation, as described above.

## 3. Results and discussion

### 3.1 Colloidal crystallization in organic solvents

When the composite particles of PMMA/SiO<sub>2</sub> were dispersed in organic solvents, such as acetonitrile, it was observed that the particles began to appear the iridescent colour due to the Bragg reflection in a few minutes. The particle array, i.e. colloidal crystallization, took place so quickly, as compared with those of unmodified silica in aqueous solution. The minimal volume fraction ( $\phi_c$ ) for the crystallization was 0.023, 0.053 and 0.055 in acetonitrile, acetone and acrylonitrile, respectively [6]. Thus, the crystallization was observed in polar and good solvent for grafted polymer, such as acetonitrile and acetone. In these cases, it was observed that there was matching or mismatching combination between grafted polymers and solvents for colloidal crystallization. The reason why there are the combination in the crystallisation is not still unclear.

Table 1. Inter-space distance (Dobs) of colloidal crystals before and after gelation

Cell [mm]	DME [mol/L]	AIBN [mol/L]	Dobs [nm]			
			Before gelation	Fron <sup>a)</sup>	rear <sup>b)</sup>	
10	0.2	0.2	0.05	230	220	210
10	0.1	0.3	0.06	280	270	280
2	0.1	0.3	0.04	260	250	250
2	0.1	0.3	0.006	270	280	270

a) Front side of cell. B) Rear side of cell.

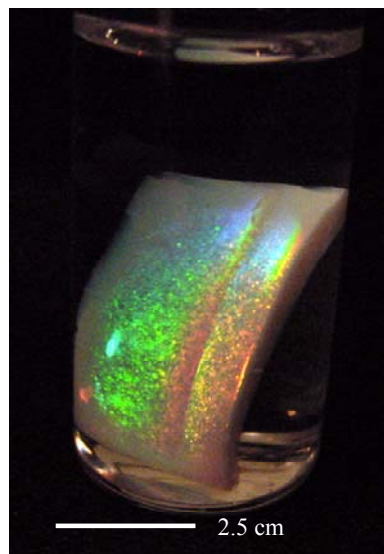


Figure 2. Iridescence from the colloidal crystal gel immersed in CH<sub>3</sub>CN [10].

### 3.2 Gelation by radical polymerization

For gelation of colloidal crystals by polymerization, it is required to keep particle array during polymerization. We first studied effects of monomer addition on the colloidal crystallization of PMMA/SiO<sub>2</sub> in acetonitrile, because the addition of organic compounds to colloidal suspension sometimes disturbs the crystallization. We investigated dependence of  $\phi_c$  on MMA and DME concentrations were shown. The  $\phi_c$  is the minimal volume fraction at which colloidal crystals can be formed. Thus, the small value of  $\phi_c$  indicates the high stability of colloidal crystals. The monomer that shows a low  $\phi_c$  in the wide range of monomer concentration should be recognized as a suitable monomer for the gelation process. These monomers showed a  $\phi_c$  of less than 0.1, throughout the wide range of monomer concentrations. We next searched for the optimal condition for polymer gelation without colloidal crystals. The gelation was preceded by copolymerization of the divinyl monomer, DME, and MMA initiated by AIBN with UV irradiation. Gelation condition with MMA was investigated in detail: The concentration of DME was varied from 2wt% to 8wt% while the MMA concentration was kept 50wt%. DME of 3wt% was found to be threshold value for the gelation. On the other hand, the MMA concentration was varied from 10wt% to 50wt% while the DME concentration was kept at 5wt%. The threshold value for gelation was found to be 20wt% of MMA. The optimal condition for obtaining the gel is concluded to be DEM >5 wt% and MMA of 20~30 wt%. The gelation of colloidal crystals was carried out by copolymerization of DME and MMA [7]. The degree of gel swelling in acetonitrile, i.e., the ratio of swelling gel weight to dry gel weight, was calculated to be 180-210%. Iridescence was observed in the MMA and EDM copolymerization, which indicated that the particle array of PMMA/SiO<sub>2</sub> colloidal crystals was maintained throughout the gelation process as shown in Figure 2. The detailed structure of colloidal crystals was investigated by the reflection spectra. The representative experimental condition and the result of reflection spectra are summarized in Table 1. The inter-particle distance and size of single crystals were ca. 230nm-270nm and 1-20 nm, respectively. The reflection spectra of the colloidal crystal gel obtained using a 10mm cell showed extreme low Bragg reflection

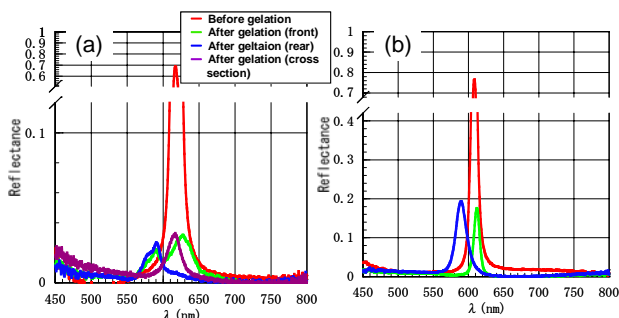


Figure 3. Reflection spectra of colloidal crystals gel prepared by a 10mm (a) and 2mm (b) cell [10].

after gelation (Figure 3(a)). This result suggests that low and broad reflection may be attributable to destruction of particle array due to inhomogeneous progress of polymerization. Thus, we next carried out the gelation using a 2mm cell, and then we found that the particle array in the colloidal crystals was preserved by reducing the amount of initiator to 1/10 amount with a 2mm-width cell. Excellent reflection spectra were obtained as in Figure 3(b). Because of the slow polymerization, the particle array was not disturbed by loose cross-linking.

### 3.3 Polymethacrylate films of colloidal crystals

The exchange of acetonitrile with MMA or TFEMA in colloidal crystals gel, prepared from colloidal silica of 135nm in diameter, by solvent exchange and successive UV light irradiation in a 1 or 2 mm cell gave a durable film showing slight iridescent colour due to Bragg reflection. In this case, the refractive index of PMMA is 1.490 [11], being very close to that of silica, and therefore the resulting PMMA or poly(trifluoroethyl methacrylate) (PTFEMA) film was translucent [12]. In Figure 4, photographs of PMA and PTFEMA film containing PMMA/SiO<sub>2</sub> was shown. a SEM photograph of the cross-section of PMMA and PTFEMA film containing PMMA/SiO<sub>2</sub> was shown. In Figure 5, typical SEM photographs of the cross-section of PMMA film containing PMMA/SiO<sub>2</sub> at volume fraction of  $\phi=0.17$  was shown. The micrograph showed the silica particles periodically arrayed in the cross section. We also investigated changes of inter-sphere distance between particles in PMMA matrix with volume fraction through colloidal crystallization in solution, gelation and solidification in the range from  $\phi=0.07$  to 0.25. At  $\phi=0.07$  and 0.25, colloidal crystallization in acetonitrile solution containing vinyl monomers was not observed. In cases of  $\phi=0.11$  to 0.17, Bragg reflections due to periodic silica particle array of colloidal crystals were recognized in the suspension and gel. In Table 2, inter-sphere distances between neighboring particles in the suspension, gel and PMMA film are listed. In the case of solidification of colloidal crystal gel formed at  $\phi=0.17$ , a standard deviation of the inter-particle distance of 240 nm was 19 nm, less than 10% of the distance. These results suggested that particle array structure in colloidal crystals of PMMA-grafted silica formed in acetonitrile was preserved in less distortion at relatively high volume fraction. In this sense, the procedure of the particles array structure immobilization in polymer gel and solidification would be applicable to preparation of new materials.

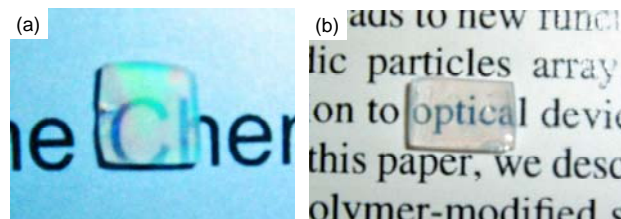


Figure 4. Photographs of PMMA (a) and PTFEMA (b) films prepared by solidification of colloidal crystals.

Table 2. Changes of inter-sphere distance of colloidal crystals in suspension, gel and film

	Dobs [nm]		
	Suspension	Gel	Film <sup>a)</sup>
0.11	260	260	290 [38]
0.14	230	240	250 [32]
0.18	220	230	210 [19]

a) Figures in parentheses signify standard deviation.

## 4. Conclusions

Colloidal crystals from polymer-modified silica could be immobilized by a step-wise procedure. In the first step, the colloidal crystals formed in organic solvent were incorporated into the gel by copolymerization of a divinyl monomer and MMA. Further photo-irradiation to the gel, which was thoroughly swelled with MMA or TFEMA, gave a durable film preserved particle array structure. Particle array structure in PMMA film via gelation of colloidal crystallization in acetonitrile was preserved in relatively less distortion at higher volume fraction,  $\phi=0.17$ .

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