Fabrication of Colloidal Crystal Gel Film Using Poly(\(N\)-vinylcaprolactam)

Takaki Kaneda\(^1\), Yutaro Seki\(^2\), Naoto Iwata\(^1\), and Seiichi Furumi\(^{1,2,*}\)

\(^1\) Department of Applied Chemistry, Faculty of Science, 
\(^2\) Department of Chemistry, Graduate School of Science, 
Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan 

\(*\)furumi@rs.tus.ac.jp

In this report, we successfully fabricated the colloidal crystal (CC) gel films of silica microparticles combined with a temperature-responsive biocompatible hydrogel of poly(\(N\)-vinylcaprolactam) (VCL). When the CC VCL film was prepared by filling VCL precursor into the void space between silica particles of CC film, followed by the thermal polymerization, the Bragg reflection peak was red-shifted from 475 nm to 535 nm due to the change of refractive index contrast. Subsequently, immersion of the CC VCL film into an excess of water led to the formation of CC VCL gel film, wherein the VCL matrix swelled in water to form the hydrogel state. As elevating the temperature from 25 °C, this CC VCL gel film showed the reflection color changes from red to green, arising from the decrease of lattice constant induced by the shrinkage of VCL hydrogel. Moreover, the reflection color changes of CC VCL gel film were found to be fully reversible. In this way, we believe that such CC VCL gel films can be potentially applied to novel temperature sensors with biocompatibility.

**Keywords:** Colloidal crystal, Temperature response, Poly(\(N\)-vinylcaprolactam), Hydrogel, Silica particle, Bragg reflection

1. Introduction

Colloidal crystals (CCs) are three dimensionally ordered arrays composed of monodisperse colloidal particles with the submicrometer size [1-5]. The CCs are also regarded as one of the 3D photonic crystals, which show the photonic band gaps in the visible wavelength range due to the spatial periodicity of the refractive indices [6-9]. Therefore, the CCs can reflect visible light in accordance with the Bragg’s law [9,10]. The suspensions of uniform colloidal particles often show Bragg reflection after the deionization. However, the fluid suspensions with CCs would be impractical due to the difficulty in handling. To overcome this issue, the CC gel films, in which the CC structures are stabilized with polymer gels, have been developed for the application to intriguing photonic devices [11-15]. Many polymer gels can alter their volume in response to the changes in environmental conditions such as temperature, solvent, and pH [12-14,16]. Thus, CC gel films are attracting interests due to their ability to manipulate their Bragg reflection colors caused by the changes of lattice constant of CCs accompanied with the swelling or shrinking of gels [12-14]. Such CC gel films have been expected as sensors for detecting and monitoring the environmental fluctuations through its Bragg reflection color changes [12,15].

So far, there have been numerous reports on the temperature responsive CC gel films fabricated using poly(\(N\)-isopropylacrylamide) (NIPA) derivatives [12-15]. However, it is well known that acrylamide as the basic skeleton of NIPA has strong toxicity and harm for human health. This toxicity is an important concern from both practical and environmental perspectives.

Therefore, we focused on poly(\(N\)-vinylcaprolactam) (VCL) as a new temperature responsive hydrogel instead of NIPA. Although
VCL has attracted a great deal of attention for its biocompatibility in the field of biology [17-19], the report on CC gel films combined with VCL has not been made yet. Figure 1 shows the chemical structure of VCL. Because VCL has both hydrophilic and hydrophobic groups in a similar structure to NIPA, VCL hydrogel exhibits the temperature response of volume change [20-25].

In this study, we investigated the volume phase transition behavior of a pristine VCL hydrogel film by temperature. By combining the CC film of silica microparticles with VCL hydrogel, we successfully demonstrated the reflection color changes by temperature. The present report indicates that VCL is an alternative material of NIPA to produce the biocompatible CC gel films.

Fig. 1. Chemical structure of a temperature-responsive biocompatible hydrogel of poly(\(N\)-vinylcaprolactam) (VCL).

2. Experimental
2.1. Materials
As a monomer, \(N\)-vinylcaprolactam was purchased from Sigma-Aldrich Japan. After recrystallization from hexane and heating above the melting temperature of 38 °C, \(N\)-vinylcaprolactam was used to prepare the VCL precursor. We adopted 1,4-bis(acryloyloxy)butane (BAOB) as a crosslinking agent and 2,2’-azobis(isobutyronitrile) (AIBN) as a thermal radical initiator, which were obtained from Tokyo Chemical Industry Co., Ltd. The materials were used as received without any further purification. A 20 wt% aqueous suspension of silica microparticles with the diameter of ca. 220 nm was obtained from Nippon Shokubai Co., Ltd.

2.2. Fabrication of pristine VCL gel film
A mixture of \(N\)-vinylcaprolactam (2.0 g) and BAOB (50–200 μL) was degassed under nitrogen flow at 50 °C. In this time, \(N\)-vinylcaprolactam showed the supercooled liquid state which maintained the liquid state below its melting temperature. After 20 min, AIBN (6.0 mg) was added into the mixture at room temperature to prepare the VCL precursor. Successively, the VCL precursor was injected into a pair of two glass plates with a gap of 800 μm, and heated at 60 °C for 4 h. The VCL gel film was obtained after exfoliating from the glass plates, and subsequently immersing into an excess of water for swelling of VCL matrix.

2.3. Fabrication of CC films of silica microparticles stabilized with VCL and VCL hydrogel gel
A CC film was formed on a glass substrate by dropping an aqueous suspension of silica microparticles with the diameter of ca. 220 nm on a hydrophilic glass substrate and heating at 90 °C for 40 h. Then, another glass plate was covered on the CC film with a gap of 500 μm, and the VCL precursor was injected into the pair of two glass plates. The CC film stabilized with VCL (CC VCL film) was obtained after heating at 60 °C for 4 h for the thermal polymerization of VCL precursor. Finally, after immersing the CC VCL film in water, we obtained the CC film stabilized with VCL hydrogel (CC VCL gel film).

2.4. Measurement of the volume phase transition temperature of pristine VCL gel film
After the pristine VCL gel film was cut into a disk shape with a diameter of 10 mm, its diameter was measured in the temperature range of 25 °C to 50 °C.

2.5. Measurement of the reflection spectra
The reflection spectra of CC films were measured using a compact CCD spectrometer of Ocean Optics, Inc. equipped with both halogen light source and optical fiber with reflection probe. The reference was taken as the distance between reflection probe and total reflection mirror was set at 2 mm. Then, the reflection spectra of CC film, CC VCL film, and CC VCL gel film were measured at the same distance for the quantitative comparison of spectral shapes and their light intensities. As the white light was irradiated from the surface normal of film, the reflection spectra were measured in the direction of regular reflection.

3. Results and discussion
3.1. Diameter changes of VCL hydrogel film
Figure 2 (A) shows the changes in diameter of a VCL hydrogel film in the temperature range from 25 °C to 50 °C. The diameter of VCL hydrogel film decreased in a sigmoidal way with elevating the
temperature, suggesting the thermally induced shrinkage of VCL gel film. Especially, the VCL hydrogel film shrank drastically in the range from 30 °C to 34 °C. Therefore, it found that the volumetric phase transition of VCL hydrogel film occurs at around 32 °C. Moreover, the VCL hydrogel film shrank by 33% at 50 °C from initial state at 25 °C, as shown in Fig. 2 (B). The shrinkage of VCL hydrogel film upon increasing the temperature can be explained by the interaction between the hydrophilic groups and hydrophobic groups in the chemical structure of VCL [24]. The VCL hydrogel was hydrophilic and swollen state below approximately 32 °C. However, as heating, the VCL hydrogel changed gradually from hydrophilic to hydrophobic because hydrophobic interactions became dominant [24]. As a result, hydrophobic interactions led to the aggregation of polymer chains and shrinkage of VCL hydrogel. Furthermore, it turned out that the volumetric phase transition temperature of VCL hydrogel is nearly equal to that of NIPA gel with the temperature of 32–34 °C [14,15,22]. Thus, we considered that the VCL gel would be applied in the biological realm such as drug delivery system from its volumetric phase transition temperature which is close to human body temperature.

3.2. Fabrication and reflection properties of CC films of silica microparticles stabilized with VCL and VCL hydrogel

As mentioned in the Experimental Section, we fabricated three kinds of films: CC film, CC VCL film, and CC VCL gel film.

Figure 3 shows the reflection spectra of their films. As the CC film of silica microparticles with the diameter of ca. 220 nm, the reflection peak of CC films appeared at 475 nm and the reflectance reached around 60%, which suggests the relatively high uniformity of CC structure. After that, the void space between the silica microparticles in the CC film was filled with VCL precursor, followed by heated at 60 °C for 4 h for the thermal polymerization. In other words, the background medium of CC film was exchanged from air to VCL matrix. At this stage, the reflection peak of CC VCL film appeared at 535 nm and the reflectance was around 20%. The decrease in reflectance can be ascribed to the slight disorder of silica microparticles in the CC structure by immersing the VCL precursor. Finally, after the CC VCL film was immersed into an excess of water to form the CC VCL gel film, the reflection peak was shifted from 535 nm to 640 nm. From the experimental results, we presumed that the reflection wavelength is red-shifted due to the changes of refractive index contrast caused by filling the background of silica microparticles in CC film with air, VCL, and VCL hydrogel.

![Fig. 2. (A) Changes in diameter of the pristine VCL gel film as a function of temperature from 25 °C to 50 °C. The film thickness was maintained at 800 μm using PTFE spacers during the measurement. (B) Snapshot images of the pristine VCL gel film at 25 °C (left) and 50 °C (right). The scale bars represent 5 mm.](image)

![Fig. 3. Reflection spectra of three kinds of CC films of silica microparticles such as CC film (a), CC VCL film (b), and CC VCL gel film (c).](image)
viewpoint. In general, the reflection peak of CC film stems from the light reflection from the (111) plane of face-centered cubic lattice of microparticles. Taking the geometric structure of CC in account, the lattice spacing along the (111) plane \((d_{111})\) is theoretically expressed as the following equation.

\[
d_{111} = \frac{a}{\sqrt{3}}
\]  

(1)

where \(a\) corresponds to the lattice constant of microparticles. Therefore, the reflection peak wavelength \((\lambda)\) of CCs can be calculated by the following equation.

\[
\lambda = \frac{2a(0.74n_P + 0.26n_B)}{\sqrt{3}}
\]  

(2)

where \(n_P\) is the refractive index of silica microparticles, \(n_B\) is the refractive index of background medium.

In this study, we used silica microparticles. So, \(n_P\) is assumed to be 1.43 according to the experimental data given from Nippon Shokubai Co., Ltd. In the case of CC film, \(n_B\) is 1.00 because the background medium of CC film is air. According to the equation (2) combined with \(n_P = 1.43\) and \(n_B = 1.00\), the Bragg reflection peak wavelength of CC film was calculated to be 474 nm, which is almost identical to that of measured spectrum \((\lambda = 475\) nm). In the case of CC VCL film, \(n_B\) is 1.55 because the background medium is VCL. Therefore, theoretical reflection wavelength is theoretically calculated to be 526 nm, which is also well-agreed with that of measured spectrum \((\lambda = 535\) nm). However, the theoretical reflection wavelength of CC VCL gel film was not consistent with the measured value. The Bragg reflection peak of VCL gel film appeared at 640 nm, which is much longer than the one calculated by the equation (2) \((\lambda = 505\) nm). From this result, we considered that the reflection wavelength shift of CC VCL gel film before and after immersion in water happens probably from not only the change of refractive index contrast, but also the increase of lattice constant of CCs. In fact, the ratio of the Bragg reflection peak between measured value \((\lambda = 640\) nm) and theoretically value \((\lambda = 505\) nm) regarding CC VCL gel film was 127%. This value is comparable to the swelling degree of CC VCL film before and after immersing into water. In the preliminary experiment, after the CC VCL film was immersed into an excess of water to form the CC VCL gel film, we observed that the CC VCL gel film swells by 135% rather than the state of CC VCL film without water. Therefore, we considered that the ratio of the Bragg reflection peak in CC VCL gel film is caused by changing the volume of CC VCL film before and after immersing into water. This is because the volume change rate was nearly equal to the difference rate of Bragg reflection peak in CC VCL gel film.

3.3. Temperature response of reflection properties of CC films of silica microparticles stabilized with VCL hydrogel

Furthermore, we pursued the changes of reflection spectra of the CC VCL gel film upon stepwise heating from 25 °C. Figure 4 (A) shows the changes in reflection spectrum of CC VCL gel film in the temperature range between 25 °C and 40 °C at the intervals of 5 °C. From this result, it was found that reflection wavelength is blue-shifted by heating from 25 °C to 35 °C. Such a shift of the
Bragg reflection peak can be ascribed to the decrease of lattice constant of CCs arisen from the shrinkage of VCL hydrogel triggered by heating. This is supported by the fact that the Bragg reflection wavelength is continuously blue-shifted exactly in the same manner to the monotonous reductions in diameter of CC VCL gel film, as shown in Fig. 4 (B).

However, the reflection peak thoroughly disappeared as heating above 40 °C because the CC VCL gel film became whitely-turbid. This behavior might be caused by the aggregation of polymer chains due to the shrinkage of VCL hydrogel. On the other hand, this CC VCL gel film showed the revival and red-shift of reflection peak upon cooling process from 40 °C. Moreover, we observed that the reflection peak wavelength observed on cooling process is consistent with the that of observed on heating process at the same temperature. In this way, this CC VCL gel film can be utilized as a temperature sensor with biocompatibility to quantitatively visualize the temperature through the reflection colors because the reflection peak wavelength is reversibly shifted on heating or cooling process.

4. Conclusion

In this report, we successfully fabricated the temperature-responsive CC film of silica microparticles with VCL hydrogel by filling the void space of CC film with VCL precursor. After exchanging from air to VCL hydrogel in the void space, the Bragg reflection peak was red-shifted from 475 nm to 640 nm by changes in the refractive index contrast as well as increase of lattice constant, as supported by the theoretical calculation combined with swelling degree of VCL hydrogel.

Furthermore, we demonstrated the changes in reflection color of CC VCL gel film between red and green induced by temperature. The reflection color change from red to green happened from the decrease of lattice spacing of colloidal particles in CC simultaneously with shrinking behavior of VCL hydrogel film. As the future outlook, we will attempt the fabrication of VCL gel films with the drastic changes of reflection peak in the wide visible wavelength range. The present report provides promising clues to fabricate the CC films with the temperature-responsive biocompatible hydrogel of VCL from the environmental viewpoint. Moreover, as the light-emitting dyes are embedded in the CC VCL gel films, we anticipate that the low threshold laser action is generated by optical excitation, arising from the effect of photonic band gaps of CC structures [26-28].

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