

Solvent-responsive coloring behavior of colloidal crystal films consisting of cross-linked polymer nanoparticles

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Abstract

Cross-linked poly(ethyl acrylate-co-methyl methacrylate) (P(EA-MMA)) nanoparticles were prepared by soap-free emulsion polymerization. Size of the isolated nanoparticles in various organic solvents was largely swollen when the solubility parameter of the solvent was similar to that for P(EA-MMA). Well-ordered colloidal crystal assembly film of the P(EA-MMA) nanoparticle was prepared by drying the as-prepared aqueous suspension. The transparent and colorless film exhibited structural color when it was swollen in the organic solvent. Wavelength of the structural color revealed linear relationship with the size of the isolated nanoparticle in the same solvent. This solvent-responsive color changing behavior was explained that the solvent swelling of the nanoparticle increased the repeating distance of the

colloidal crystal and the wavelength of the reflected light from the ordered structure. These results suggest that the structural color of the swollen film can be tuned by the solvent quality for P(EA-MMA).

Keywords

Colloidal crystal / Structural color / Nanoparticles / Responsive systems / Swelling behavior

Introduction

Structural color can be commonly observed in nature, such as wing of butterfly, soap bubble, compact disc, and so on. It originates by selective reflection of light with specific wavelength from finely ordered nanostructure. In that sense, the structural color is stable against fading and can be easily tuned by controlling the nanostructure. Because of these advantages, structural colored materials have attracted wide attention for application to novel type display, color pigments, optical sensors, and so on [1–3].

In the research field of structural colored materials, colloidal crystal assemblies consisting of well-ordered array of monodispersed spherical particles have been widely investigated. In these materials, the structural color can be tuned by changing the layer spacing of colloidal crystal, which can be achieved by control of the particle size or the inter-particle distance [4–6]. The particle size can also be tuned by swelling of chemical substance, and the resulting structural color changing behaviors of the colloidal crystal have been reported [7–16]. Duan et al. [12] reported solvatochromic-responsive coloring phenomena of poly(styrene-butyl acrylate-acrylic acid) latex film in polar organic solvents.

In our previous study [17], strain responsive structural colored elastomer was fabricated. Monodispersed and cross-linked nanoparticles of copolymer of ethyl acrylate and methyl methacrylate (P(EA-MMA)) were prepared and assembled to form ordered colloidal crystal structure. The obtained colloidal crystal film was colorless and transparent, and revealed structural color after immersed in ethyl acrylate (EA), because the reflected light wavelength was increased to the visible light region by the swelling. The observed color was influenced by the cross-linking density of the nanoparticle, i.e., a densely cross-linked system revealed a color with shorter wavelength. After polymerization of the swelling solvent EA to poly(ethyl acrylate) (PEA) with adding a small amount of crosslinker, the structural color was successfully immobilized in the cross-linked PEA matrix. The obtained colloidal crystal

film sensitively changed its structural color by stretching or compressing deformation, which was explained by deformation of the nanoparticle by the macroscopic deformation and the accompanied change in the repeating distance of the colloidal crystal. These results suggest that the colloidal crystal films consisting of polymer nanoparticles can be used as visible sensing material which changes its structural color with responding to external stimuli such as swelling of chemical substances and mechanical deformation. It should be noted that the mechanical deformation of the colloidal crystal occurs in anisotropic manner and has a possibility to destroy the ordered structure, as pointed out by Viel et al. [18]. On the other hand, when the solvent swelling was used as the external stimulus, the colloidal crystal changes its size in isotropic manner, which should be an advantage for the sensing material because the destruction of the ordered structure can be avoided.

In this study, solvent-responsiveness of the colloidal crystal film of P(EA-MMA) nanoparticle has been investigated. As like the case of immersing in EA in the previous study [17], the originally colorless transparent film revealed structural color after swelling in some organic solvents. The color was found to depend on a quality of the swelling solvent to P(EA-MMA). In this sense, this colloidal crystal film is possible candidate as a sensing material for organic solvent. Relationship between the size of nanoparticle, solvent quality, and structural color will be discussed.

Experimental Section

Materials Commercially available methyl methacrylate (MMA), ethyl acrylate (EA), ethylene glycol dimethacrylate (EGDM), potassium dihydrogen phosphate (KH_2PO_4), potassium hydroxide (KOH), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), *p*-styrenesulfonic acid sodium salt (NaPSS), ethanol, acetone, *N,N*-dimethyl acetamide (DMAc), hexane, and toluene were used as received. Chloroform and tetrahydrofuran (THF) were purified by distillation before use.

Preparation of P(EA-MMA) nanoparticle [17] Cross-linked P(EA-MMA) nanoparticle was synthesized by soap-free emulsion polymerization method reported by Tsukigase et al. [4]. 0.055 g of KH_2PO_4 , 0.4 mL of KOH aqueous solution (1 mol/L), 10.63 mL of MMA (100 mmol), 10.87 mL of EA (100 mmol), and 190 μL of EGDM (1.0 mmol) were mixed with 72.8 mL of distilled water. The solution was purged with nitrogen gas and heated to 65 °C under stirring with 500 rpm for 30 minutes. Into this solution, 0.081 g of $\text{K}_2\text{S}_2\text{O}_8$ (0.3 mmol) and 0.206 g of NaPSS (1.0 mmol) dissolved in 6 mL of distilled water were added. The polymerization reaction was carried out with stirring at 65 °C for 5 h, and subsequently at 80 °C for 1 h. The reaction was terminated by cooling the solution to room temperature.

Colloidal Crystal Film The above obtained turbid aqueous suspension was cast on cellulose membrane with nominal cutoff molecular weight of 8,000 and dried at room temperature to obtain colloidal crystal film of P(EA-MMA) nanoparticles. The obtained films were swollen in various solvents such as ethanol, EA, THF, acetone, chloroform, DMAc, hexane and toluene. First, the film was immersed in each solvent encapsulated in vial bottle and warmed at around 60 °C, which was effective to avoid cracking of the film. Subsequently, the immersed solvent was gradually cooled to room temperature and kept for 5 h before the film was measured by UV-vis spectroscopy.

Measurements Hydrodynamic diameter (D_h) of P(EA-MMA) nanoparticle in water and various solvents was measured by a dynamic light scattering (DLS) apparatus equipped with an ALV/SO-SIPD detector and an ALV-7000 correlator using He-Ne laser (incident wavelength $\lambda_0 = 633 \text{ nm}$) as light source. The turbid suspension of the as-prepared nanoparticle was diluted by excess amount of pure water or organic solvent for DLS measurements. The obtained correlation functions were treated by cumulant and CONTIN analysis [19], and

evaluated decay rate Γ and Einstein-Stokes equation were used to calculate D_h . The polydispersity index of DLS, μ_2/Γ^2 , was evaluated by the second-order cumulant method. Viscosity and refractive index of various solvents were referred to literature values [20]. Because the amount of the diluted aqueous suspension in organic solvent was too small (less than 0.05 %), reported properties for pure solvents were used without considering the effect of water.

Transmission UV-vis absorption spectra were measured on a U-3310 spectrophotometer (Hitachi). The swollen film was put into a glass cell with 2 mm of optical path length, and the cell was set as the swollen film surface was normal to the incident light.

The surface of the colloidal crystal film was observed on an atomic force microscope (AFM, MultiMode 8, Bruker AXS K.K.) with Scan Asyst mode. The cross-section surface of the fractured colloidal crystal film was observed on a scanning electron microscope (SEM, JSM-6010LA, JELO) with using the dried P(EA-MMA) film fractured and subsequent gold deposition.

^1H NMR spectrum of the suspension after the polymerization was recorded on an Avance400 (Bruker).

Results and Discussion

P(EA-MMA) Nanoparticle After the polymerization of P(EA-MMA) nanoparticle, the reaction suspension was milky white in color. The suspension was dissolved in dimethylsulfoxide- d_6 and measured by ^1H NMR, and in the obtained spectrum, ^1H peaks assigned to $\text{CH}_2=\text{C}$ for unreacted monomers and cross-linkers could not be detected. Therefore, the reaction time and temperature was enough to complete the polymerization reaction, and molar ratio of each monomer for P(EA-MMA) copolymer in the obtained nanoparticles and degree of cross-linking can be evaluated from the used amount of reagents

for the polymerization: EA/MMA/NaPSS/EGDM = 100/100/1.0/1.0. D_h distribution curve obtained from CONTIN analysis of DLS measurement of the diluted suspension in excess pure water indicated that the obtained nanoparticle was monodispersed, which was also supported by small polydispersity index $\mu_2/I^2 = 0.03$. The particle diameter in water evaluated from cumulant analysis was 165 nm. In the soap-free emulsion polymerization method adopted in this study, addition of soap or surfactant was not necessary. Instead, a small amount of ionic NaPSS as co-monomer was copolymerized with EA and MMA during the polymerization, and its electrostatic charge was effective for stable dispersion of monomer droplet without coagulation [4]. Even after the polymerization reaction was completed, the nanoparticles were also stably dispersed since the particle surface was negatively charged by the copolymerized NaPSS.

The particle diameter swollen in organic solvents became larger than in water. The evaluated D_h values was influenced by the swelling solvent and ranged from 255 nm to 356 nm, as listed in Table 1. Even though the increase in D_h , its narrow distribution was maintained after the swelling in organic solvent. The particle diameter in hexane and toluene could not be measured because the aqueous P(EA-MMA) suspension was difficult to be mixed in these hydrophobic solvents.

Table 1 Particle diameter D_h , peak wavelength of absorption spectrum λ_{\max} , and solubility parameter δ_1 for each solvent

Solvent	D_h / nm	λ_{\max} / nm	δ_1 / (MPa) ^{1/2}
water	165	—	47.9
ethanol	255	407	26.0
EA	274	497	17.6
THF	279	518	18.6
acetone	294	529	20.3
chloroform	300	583	19.0
DMAc	356	—	22.1
hexane	—	—	14.9
toluene	—	—	18.2

The swelling ratio of cross-linked polymer particle is expected to be evaluated from the following Flory-Rehner equation, which is theoretically proposed for swelling behavior of cross-linked polymer gel [21].

$$-\ln(1-v_s)-v_s-\chi v_s^2 = v_1 V_1 \left(v_s^{1/3} - \frac{v_s}{2} \right) \quad (1)$$

$$v_s = \frac{V_p}{V_s} \quad (2)$$

$$v_1 = \frac{\rho}{M_c} \quad (3)$$

$$\chi = \frac{V}{RT} (\delta_1 - \delta_2)^2 \quad (4)$$

Here, V_1 the molar volume of solvent, v_s the inverse of swelling ratio, v_1 the network density of cross-linked polymer, V_p and V_s the volume of cross-linked polymer before and after swelling, M_c the molecular weight of the bridging chain between cross-linking points, and ρ the density

of polymer. The Flory χ parameter depends on the solubility parameters of solvent (δ_1) and polymer (δ_2), and V the reference volume (100 cm^3), R the gas constant, and T the absolute temperature.

Reported values of the solubility parameter of solvent (δ_1) [20] are listed in Table 1, and relationship between δ_1 and D_h is shown in Fig. 1. In this figure, the measured values of D_h in various solvents by DLS are indicated by closed circles, and the theoretically calculated results from eqs (1)–(4) are indicated by the solid line. In the calculation, volume of the non-swollen particle was evaluated from D_h in water, and the molecular weight for the bridging chain, M_c , was estimated from the used amount of monomer (EA, MMA, and NaPSS) and cross-linker (EGDM) for the polymerization reaction. With using these values, solubility parameter of the polymer (δ_2) was adjusted in order to fit the theoretically calculated D_h with the experimental one. The theoretical line reasonably reproduced the experimental δ_1 dependence of D_h , suggesting that the particle diameter in the swelling solvent can be estimated by its solubility parameter. The P(EA-MMA) nanoparticle was most highly swollen in DMAc ($D_h = 356 \text{ nm}$). From this result, the solubility parameter of P(EA-MMA) (δ_2) can be evaluated to be around $22 \text{ (MPa)}^{1/2}$, which is a little larger than the value expected from reported δ values of PEA and PMMA ($19.1 \text{ (MPa)}^{1/2}$) [20].

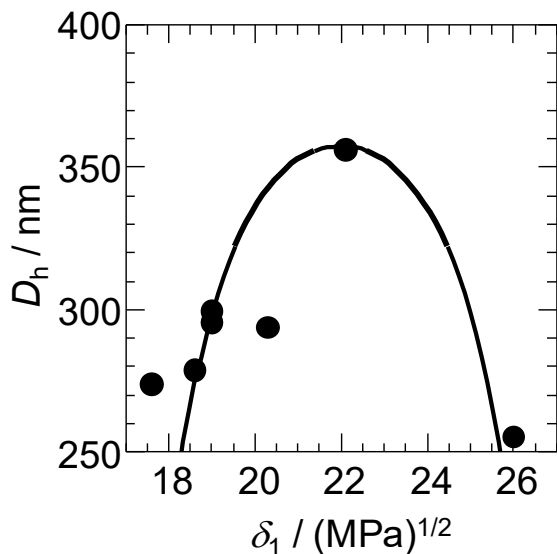


Fig. 1 Hydrodynamic diameter D_h of nanoparticle in various swelling solvents are plotted against the solubility parameter δ_1 of the solvent (circle). Theoretical calculation by Flory-Rhener equation is indicated by the solid line.

Morphology of the Colloidal Crystal Film After casting of aqueous suspension of P(EA-MMA) nanoparticle, a transparent film was obtained. AFM image of the film surface is shown in Fig. 2. The mono-dispersed particles with size of more than 100 nm are forming an array with closely packed hexagonal structure for wide range. As shown in our previous study [17], SEM image of the fractured surface indicated that the nanoparticle-arrayed layers were regularly stacked parallel to the film surface (the image is not shown in this paper). Therefore, the P(EA-MMA) nanoparticles formed self-assembled colloidal crystal structure in the simply solvent-casted film.

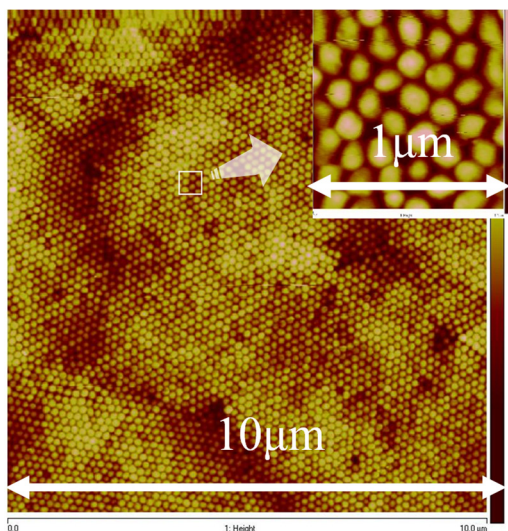


Fig. 2 AFM image for the film surface of P(EA-MMA) cast film.

Coloring Phenomena of Colloidal Crystal Films Swollen in Various Solvents After the obtained colloidal crystal film was swollen in various organic solvents, the transparent film exhibited opalescent brilliant color as shown in Fig. 3. The observed color was changed when the film was inclined, which is commonly observed in general structural colored materials. The color was changed variously with depending on the swelling solvents. It should be noted that the color with longer wavelength was observed in the solvent which swelled the isolated P(EA-MMA) nanoparticle largely; i.e., the film was red in chloroform ($D_h = 300$ nm) and green in THF ($D_h = 279$ nm). Wavelength of the observed color was numerically evaluated from UV-vis spectroscopy in Fig. 4, and the wavelength at the peak maximum (λ_{\max}) was plotted in Fig. 5 by filled circle against the particle diameter D_h measured by DLS for the dilute solution. This figure shows good relationship between the observed wavelength of the structural color and the size of the swollen particle.

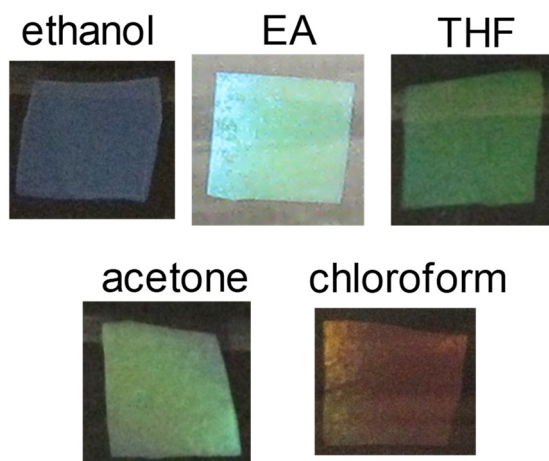


Fig. 3 Photo images of the colloidal crystal films swollen in various solvents.

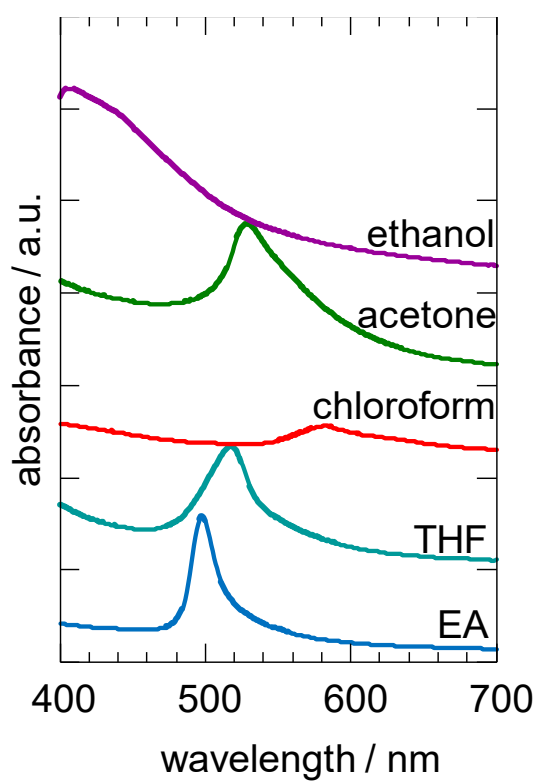


Fig. 4 Transmittance spectra of colloidal crystal films swollen in various solvents. The spectra were shifted along the vertical axis in order to avoid overlapping.

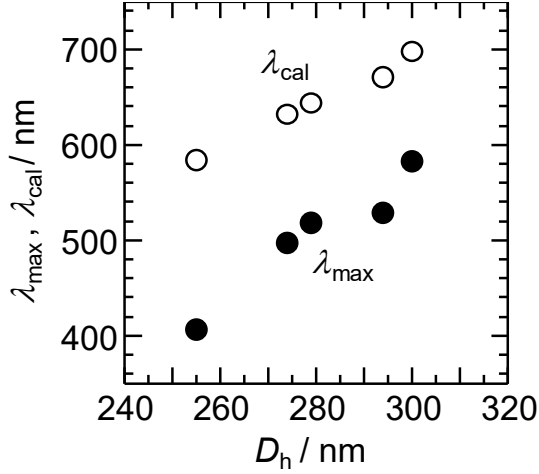


Fig. 5 Filled circle: relationship between the nanoparticle diameter (D_h) and peak wavelength of the structural color (λ_{max}) for each swelling solvent. Open circle: relationship between D_h and the calculated structural color (λ_{cal}) from eqs (5)-(7).

These experimental results suggest that the observed structural color was caused by the finely ordered colloidal crystal structure consisting of hexagonally arrayed nanoparticle layers stacked parallel to the film surface, which was maintained even after the swelling of the solvent. The swollen film selectively reflected visible light according to the repeating distance of the swollen colloidal crystal, which has the linear relationship with the swollen size of the isolated nanoparticle dispersed in the solvent. In the non-swollen dried film, the reflected light wavelength expected from the particle size should be shorter than the visible light, which may be the reason why the dried film before the swelling was non-colored state and transparent. It should be noted that this solvent-responsive coloring behavior was reversibly observed, i.e., the swollen colored film became non-colored state again after the solvent was evacuated in vacuum. This result also suggests that the colloidal crystal structure is maintained even after the solvent-swelling state and the assembled nanoparticles are stably bonded with each other. It seems reasonable that the polymer chains at the surface of the nanoparticle are entangled around the inter-particle area during solvent-evaporation process.

This physical interaction should be effective against the isolation of the nanoparticle in the immersed solvent.

From the Bragg's equation, the selectively reflected light wavelength from the incident light vertical to the surface (λ_{cal}) from the ordered layer with repeating distance d was derived by the next equation.

$$\lambda_{\text{cal}} = 2n_{\text{eff}}d \quad (5)$$

where n_{eff} the effective refractive index of the film represented by eq (6).

$$n_{\text{eff}} = \left(\phi_p n_p^2 + \phi_s n_s^2 \right)^{1/2} \quad (6)$$

In the swollen film, n_i and ϕ_i are refractive index and particle volume fraction, respectively, and the suffixes “p” and “s” respectively represent the swollen P(EA-MMA) particle and swelling solvent. If the colloidal crystal lattice is assumed to be in face-centered cubic (fcc) structure, following relationship between the lattice spacing d of 111 plane and the particle diameter D can be derived.

$$d = (2/3)^{1/2} D \quad (7)$$

With assuming that the swollen P(EA-MMA) particle in the film has the same diameter with that in the dilute solution (D_h), λ_{cal} in the various solvent can be calculated from eqs (5) - (7). Refractive index for the swollen particle, n_p , depends on D_h and calculated with considering the volume fraction of P(EA-MMA) and solvent in the swollen state. Values of ϕ_p and ϕ_s for the fcc packing are 0.74 and 0.26, respectively. In Fig. 5, λ_{cal} is plotted against D_h by open circles for the solvents of ethanol, EA, THF, acetone, and chloroform. λ_{cal} shows almost linear increase against D_h , suggesting that the effect of refractive index difference on the structural color is negligible and the color is substantially determined by the size of the particle. It should be noted that experimental structural color wavelength λ_{max} was found to be smaller than the calculated λ_{cal} , which means the particle size in the swollen colloidal crystal film was smaller than the swollen isolated particle in dilute solution. Before the immersing in solvent,

the colloidal crystal film was dried in vacuum after the solvent casting. As mentioned in the previous paragraph, it is reasonable that the polymer chains around the surface of the nanoparticle tend to highly segregated or entangled around the inter-particle area during the drying process, and the similar chain segregation will also occur within the nanoparticle, which makes it difficult to be solubilized in solvent. Probably because of the limited solubility of the used solvents for P(EA-MMA), the swelling ability of the once dried nanoparticle might be fairly restricted than the as-prepared nanoparticle.

These structural colors were stably observed in the above solvents for more than one month. On the other hand, in the case that the solvent was DMAc, the film color was changed from red to turbid white with elapsing the swelling time. Finally, the film was collapsed after swelling for one day, and the collapsed fragments were precipitated as show in Fig. 6. The particle size plotted in Fig. 1 suggests that the solubility parameter of P(EA-MMA) was very close to that of DMAc ($22.1 \text{ (MPa)}^{1/2}$) and the isolated nanoparticle was most largely swollen in DMAc. Because of the good solubility, the well-ordered colloidal crystal structure could not be maintained in DMAc because the above-mentioned inter-particle bonding by the physical entanglement between the nanoparticles was dissolved, as the result, the film was destructed by extremely high swelling. Additionally, DMAc is a polar solvent, which has an ability to weaken the electrostatic interaction between polar groups. The P(EA-MMA) nanoparticle contains ionic NaPSS unit as co-monomer, and the electrostatic interaction between the nanoparticles may be effective for the formation of highly ordered colloidal crystal during solvent evaporation. Immersing in polar DMAc will weaken the inter-particle interaction, which also tends to destroy the colloidal crystal structure. From these results, it can be pointed out that the solvent which revealed clear structural color in Fig. 3 should be a marginal and weakly polar solvent rather than a good and highly polar solvent. These solvents can be absorbed by the nanoparticle to some extent without weaken the inter-particle interaction to destruct the colloidal crystal.

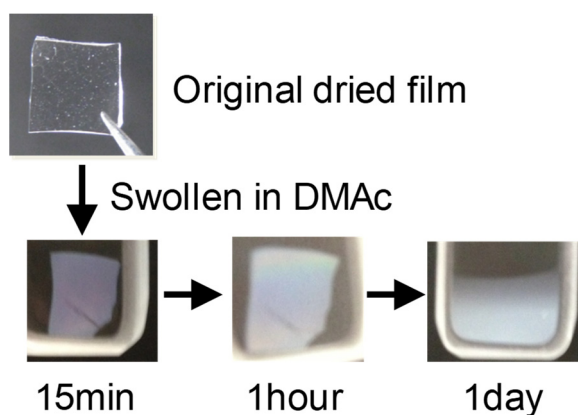


Fig. 6 Photo images of the colloidal crystal film swollen in DMAc.

It should be noted that the colloidal crystal films in hexane and toluene did not reveal any distinguished color but kept transparent non-color state. In case of hexane, the solubility parameter is reported to be 14.9, which is far from that for P(EA-MMA), therefore, the film was not able to be swollen to reflect visible light. On the other hand, the solubility parameter of toluene is close to chloroform, so the swollen colloidal crystal was expected to show red color, but the film was non-color even after swelling. This result may be explained with considering refractive index (RI) contrast. If RI of polymer and solvent is similar, RI of the swollen sample becomes almost homogeneous. In this case, the reflected light intensity becomes too weak to be recognized as structural color. The RI values of P(EA-MMA) and toluene are evaluated to be 1.48 and 1.49 [20], respectively, and the small difference between these RI values should be the reason why the structural color was not observed in the toluene-swollen film.

Conclusion

In this study, swelling behavior of the cross-linked P(EA-MMA) nanoparticle and the structural coloring phenomena of its colloidal crystal film swollen in various organic solvents have been

investigated. Diameter of the isolated nanoparticle in dilute solution was varied by changing the swelling solvent, and its size was reasonably described with considering the solubility parameter and cross-linking density. The nanoparticles formed well-ordered colloidal crystal assembly by simply casting the aqueous suspension. After immersing the obtained colloidal crystal film in organic solvents, the swollen film revealed clear structural color. The wavelength of the film color showed good relationship with the swollen size of the isolated nanoparticle in dilute solution. In DMAc, which is polar and has good solubility for P(EA-MMA), the sample film became highly swollen and could not maintain its shape. Therefore, low polarity and marginal solvent quality for the nanoparticle was important to reveal the solvent-responsive visible structural color.

In our previous study [17], the colloidal crystal film swollen in monomer such as EA was polymerized to immobilize the structural color. The color could be tuned by applying mechanical deformation because the macroscopic strain caused the microscopic deformation of the colloidal crystal structure, and this phenomenon should be potentially applicable as strain-responsive elastomer. In this study, the structural color was varied with solvent-responsive manner because the size of the particle depends on the solubility of the solvent, and this solvent-responsiveness of the colloidal crystal film is expected to be applied as visual sensor for chemical environment. Because the size and/or packing manner of the nanoparticle can be easily controlled, the structural colored colloidal crystal materials consisting of polymer nanoparticle are possible candidate for visible sensing materials against various external stimuli.

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Conflict of interest

The authors declare that they have no conflict of interest.

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