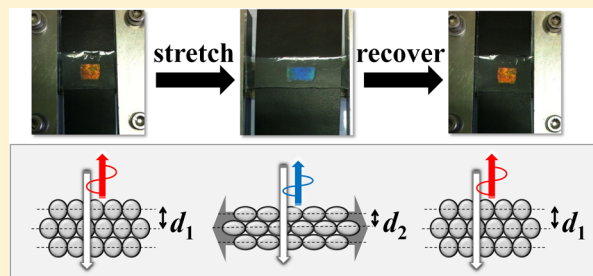


Strain-Responsive Structural Colored Elastomers by Fixing Colloidal Crystal Assembly

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ABSTRACT: Colloidal crystal assembly film was prepared by using monodispersed colloidal particles of cross-linked random copolymer of methyl methacrylate and ethyl acrylate prepared by soap-free emulsion polymerization. The colloidal crystal film exhibited structural color when swollen with ethyl acrylate monomer. The structural color was maintained even after polymerization of the swelling monomer and cross-linker, suggesting the colloidal crystalline order was successfully fixed and embedded in the matrix of poly(ethyl acrylate) elastomer. Stretching deformation of the structural colored elastomer induced a sensitive change to shorter wavelength color. Peak wavelength of the UV–vis absorption spectrum of the stretched elastomer revealed an excellent proportional relationship with film thickness. In the swollen colloidal crystal film, ethyl acrylate was absorbed in the colloidal particle; therefore, poly(ethyl acrylate) chain should be penetrating into the colloidal particle after the polymerization of the matrix elastomer. This interpenetrated polymer network structure was considered to be effective for the rubber-like elasticity and sensitive strain-responsive color-changing phenomena of the structural colored elastomer.



INTRODUCTION

Polymer colloidal particle with narrow size distribution is known to form colloidal crystal assembly with three-dimensional periodic structure. If the lattice spacing of the colloidal crystal is close to visible light wavelength, incident light is spectrally reflected and structural color with a specific wavelength can be visibly observed. Because the structural color depends on the lattice constant of the colloidal crystal, the color can be tuned by controlling the self-assembled structure of the colloidal particles.

In recent years, structural colored colloidal crystal assemblies have been attracting wide attention as application in sensing and optical materials, and various external stimuli such as mechanical deformation,^{1–13} chemical substance,^{14–20} temperature,^{21–24} and so on^{25,26} have been investigated in order to regulate the structural color. For these applications, hydrogel matrices were commonly used in order for fixing the colloidal crystal because the self-assembly of the colloidal particle was most widely investigated in aqueous solution. However, gel samples have some demerits for practical applications such as solvent evaporation and weak mechanical strength. Fudouzi et al.⁸ reported photonic rubber sheets without swelling solvent, which revealed tunable structural color by elastic stretching deformation. In their photonic rubber, closely packed colloidal crystal of polystyrene (PS) particles was embedded in poly(dimethylsiloxane) (PDMS) elastomer matrix. Stretching of the rubber resulted in reducing sheet thickness as well as the lattice spacing of the colloidal crystal in the perpendicular direction of the sheet; as a result, the reflected light shifted to shorter wavelength. Viel et al.¹⁰ and Wohlleben et al.¹¹ reported elastic colloidal crystal film from core–shell beads consisting of

rigid core and cross-linked soft elastomeric shell from diblock copolymer. Their structural colors were changed by mechanical deformation.

In these elastic colloidal crystal films, hard particles such as glassy PS were embedded in soft matrix. Therefore, as pointed out by Fudouzi et al.,⁸ the stretching of the film deformed the soft matrix but only shifted the position of the rigid colloidal particle. This local inhomogeneous deformation resulted in a smaller Poisson's ratio (0.22–0.28)^{8,10} than general soft elastomers (~0.5). As the result, deformation strain and wavelength of the structural color revealed a complicated relationship. Additionally, as usually observed in composite materials consisting of hard fillers, an exfoliation at the interface between the particle and matrix and a low durability will be concerned under large deformation. Considering these structural aspects, sensitive response of the structural color of elastomer consisting of hard colloidal particles against deformation seems to be difficult. Colloidal crystal film from soft particles, however, is pointed out to not reveal structural color because of a lack of optical contrast;¹⁸ i.e., it would be deformed during the drying process to polygon structure without voids between the particles.^{10,27} Duan et al.¹² fabricated mechanochromic colloidal crystal of soft polymeric particles by blending with nanosilica particles; however, it also revealed a small Poisson's ratio.

In this study, we report a structural colored elastomer consisting of colloidal crystal assembly of cross-linked poly-

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Table 1. Preparation Recipes of P(EA–MMA) Colloidal Particles by Soap-Free Emulsion Polymerization and Their Hydrodynamic Diameter in Water (D_h) and EA Prepolymer Solution ($D_{h,EA}$)

sample	molar ratio					D_h (nm)	$D_{h,EA}$ (nm)	$D_{h,EA}/D_h$
	EA	MMA	NaPSS	EGDM	$K_2S_2O_8$			
CP(0.12)	100	100	1	0.25	0.3	170	350	2.06
CP(0.25)	100	100	1	0.50	0.3	171	312	1.82
CP(0.50)	100	100	1	1.0	0.3	165	285	1.73
CP(0.75)	100	100	1	1.5	0.3	154	234	1.52

(ethyl acrylate-*co*-methyl methacrylate), P(EA–MMA), colloidal particles immobilized by cross-linked poly(ethyl acrylate), PEA, elastomer with interpenetrated polymer network (IPN) structure. Colloidal crystal assembly films of P(EA–MMA) particles were prepared by solvent casting of the as-prepared suspension solution. By swelling the film in ethyl acrylate (EA) monomer, the film revealed brilliant structural color. By polymerization of EA with swollen state, the colloidal crystal of P(EA–MMA) particles was fixed as found that the structural color was maintained even after the polymerization. Thus, prepared P(EA–MMA) colloidal crystal embedded in the PEA elastomer revealed a unique deformation-sensitive structural colored phenomenon. Structure of the colloidal crystal elastomer and mechanism of its strain-responsive 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 ($K_2S_2O_8$), *p*-styrenesulfonic acid sodium salt (NaPSS), and α,α' -azobis(isobutyronitrile) (AIBN) were used as received.

P(EA–MMA) Colloidal Particle. P(EA–MMA) colloidal particles were synthesized using soap-free emulsion polymerization method reported by Tsukigase et al.²⁸ Typically, 0.055 g of KH_2PO_4 , 0.4 mL of KOH aqueous solution (1 mol/L), 10.63 mL of MMA, 10.87 mL of EA, and 0.0475 mL of EGDM 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. Into this solution, 0.081 g of $K_2S_2O_8$ and 0.206 g of NaPSS 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 Assembly Film. The obtained turbid suspension was cast on cellulose membrane with nominal cutoff molecular weight of 8000 and dried at room temperature to obtain colloidal crystal film of P(EA–MMA) particles.

Structural Colored Elastomer. Acrylic monomer EA, cross-linker EGDM, and initiator AIBN were mixed with the molar ratio of 100/0.25/0.15. In this prepolymer solution, the above obtained colloidal crystal film was immersed in a cell with 1 mm thickness, until the swollen film revealed visible structural color. After the color became almost unchanged, polymerization reaction was started by heating the cell at 60 °C for 24 h.

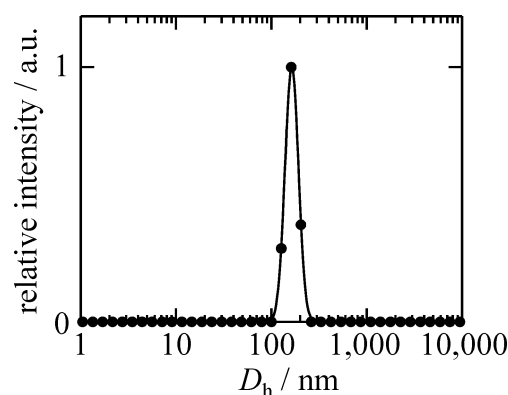
Measurements. The hydrodynamic diameter (D_h) of P(EA–MMA) colloidal particle was measured by a dynamic light scattering (DLS) apparatus equipped with an ALV/SO-SIPD detector and an ALV-7000 correlator using He–Ne laser (wavelength $\lambda_0 = 633$ nm) as light source. The turbid suspension after the colloidal particle preparation was diluted by excess amount of pure water or the EA prepolymer solution for DLS measurements. The obtained correlation functions were treated by cumulant and CONTIN analysis as described in the previous paper,^{29,30} and evaluated decay rate and Einstein–Stokes equation were used to calculate D_h . Viscosity and refractive index of EA were referred to literature values.³¹ Degree of swelling of the colloidal crystal assembly film was evaluated from the

size of the film before and after the swelling in the prepolymer solution. Absorption UV–vis spectra were measured with the incident light normal to the plane of the film on a U-3310 spectrophotometer (Hitachi). Morphology of the colloidal crystal film was observed on a scanning electron microscope (SEM, JSM-6010LA, JEOL) with using the dried P(EA–MMA) film fractured in liquid nitrogen and subsequent gold deposition. T_g of the colloidal crystal film and the structural colored elastomer were measured on a DSC-8230 (Rigaku).

RESULTS

P(EA–MMA) Colloidal Particles. The prepared P(EA–MMA) colloidal particles are summarized in Table 1. The molar ratio of EA/MMA/ionic monomer NaPSS/initiator $K_2S_2O_8$ was kept constant at 100/100/1/0.3, and the molar ratio of cross-linker EGDM was varied as shown in Table 1. Each sample was designated as CP(*x*), where *x* is the mol % of EGDM. After the polymerization of P(EA–MMA) particles, the reaction suspension was milky white in color.

DLS measurements of the diluted suspension in excess pure water were performed in order to evaluate the particle size, D_h , and the results are listed in Table 1. The obtained D_h distribution curve of CP(0.50) from CONTIN analysis (Figure 1) showed narrow peak, and the width of the diameter

**Figure 1.** Distribution of hydrodynamic diameter D_h of as-prepared CP(0.50) in aqueous dilute solution evaluated by DLS measurement with CONTIN analysis.

distribution evaluated from cumulant analysis was ca. 30 nm. This suggests the formation of monodispersed colloidal particle. The size of the particle became slightly smaller with the increase in cross-linker content. The colloidal particle suspension diluted with the prepolymer solution of EA/EGDM/AIBN was also measured to evaluate the diameter in the prepolymer solution, $D_{h,EA}$. As shown in Table 1, $D_{h,EA}$ in the prepolymer solution became larger than that in water because of the better solubility of EA for P(EA–MMA) than water. In Table 1, the swelling ratio of the particle, $D_{h,EA}/D_h$, is also indicated. Values of $D_{h,EA}/D_h$ were decreased with the cross-linking density, as expected from the Flory–Rehner

equation,³² which suggests that the size of the colloidal particle can be controlled by changing the cross-linker content in the polymerization reaction.

Morphology of the Colloid Crystal Assembly. A transparent film of P(EA-MMA) was obtained by casting the as-prepared turbid suspension of P(EA-MMA) colloidal particle. A typical SEM image of the fractured surface of the colloidal crystal film is shown in Figure 2. The image indicates

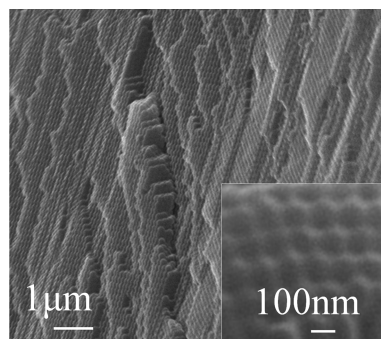


Figure 2. SEM image of fractured surface of the colloidal crystal film obliquely gazed from the film surface direction.

that the monodispersed colloidal particles with size of more than 100 nm are forming ordered array and the layers are stacked parallel to the film surface. Figure 2 suggests that the colloidal crystal assembly film of the P(EA-MMA) particles prepared by soap-free emulsion polymerization can be fabricated by the simple solvent casting method.

In Figure 3, DSC curve for CP(0.12) film is indicated. The shift of the baseline suggests that the T_g of the film is around 35

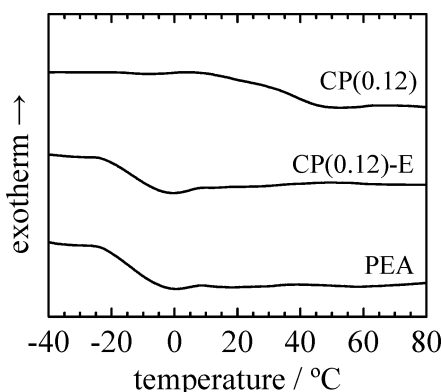


Figure 3. DSC thermograms measured at heating rate of 10 °C/min for solvent casted colloidal crystal film (CP(0.12)), composite colloidal crystal elastomer consisting of CP(0.12) in PEA matrix (CP(0.12)-E), and cross-linked PEA film.

°C for all the prepared samples. Therefore, in the solvent casting and drying process, the colloidal particles should be in glassy state below T_g .

Swollen Colloidal Crystals Films. Photo images in Figure 4 show the colloidal crystal assembly film of P(EA-MMA), with various cross-linking density, after swollen with the prepolymer solution of EA. Here, the swollen films are designated as CP(x)-S. The length of side of the rectangular film before (l_0) and after (l) the swelling was measured, and the swelling ratios l/l_0 are shown in Table 2. Although the dried film was colorless and transparent, all the films exhibited

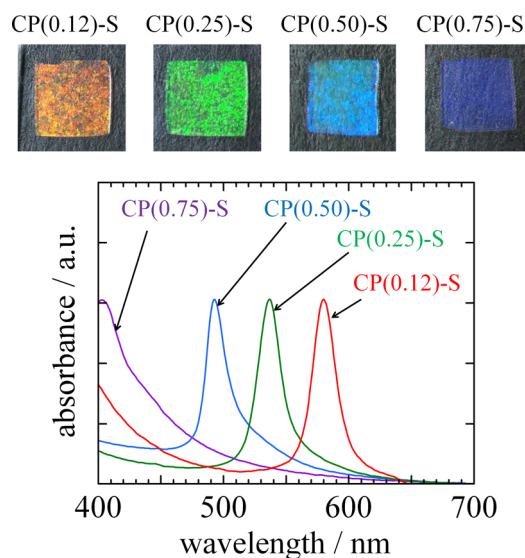


Figure 4. Photo images of CP(x)-S films swollen by EA prepolymer solution (upper) and their UV-vis absorption spectra (lower). In the UV-vis measurements, the films were placed normal to the incident light. In these spectra, the baseline and peak height were adjusted in order to show the peak clearly.

Table 2. Swelling Ratio (l/l_0), UV-vis Absorbance Peak Wavelength (λ_{\max}), and Evaluated Particle Size (D) of the Swollen Colloidal Crystal Film CP(x)-S and the Colloidal Crystal Elastomer CP(x)-E

sample	l/l_0	λ_{\max} (nm)	D (nm)
CP(0.12)-S	1.81	580	252
CP(0.25)-S	1.64	537	233
CP(0.50)-S	1.57	493	213
CP(0.75)-S	1.50	402	174
CP(0.12)-E		593	247
CP(0.25)-E		538	224
CP(0.50)-E		490	204
CP(0.75)-E		442	184

opalescent color after swelling. The film containing the lowest cross-linking density particle, CP(0.12)-S, was red in color, and the color changed to shorter wavelength such as green, blue, and purple with increasing the cross-linker concentration. In Figure 4, the absorption spectra of the swollen films are indicated. The peak position, λ_{\max} , shifted to the shorter wavelength region with the cross-linking density, which is consistent with the visible observations. The observed color was changed when the film was inclined, which is consistent with general structural colored materials. These results strongly suggest that the ordered colloidal crystal was maintained even after the swelling with the prepolymer solution, and the swollen film selectively reflected visible light corresponding to the repeating distance of the colloidal crystal.

As mentioned above, the size of the colloidal particle in EA dilute solution was decreased with the cross-linker content. As shown by the closed symbols in Figure 5, the peak wavelength λ_{\max} of the absorption spectrum has a good relationship with the particle diameter $D_{h,EA}$. This result suggests a possibility to tune the structural color of the swollen colloidal crystal film by the cross-linker content.

Structural Colored Elastomer. The colloidal crystal film swollen with the prepolymer solution was heated for polymer-

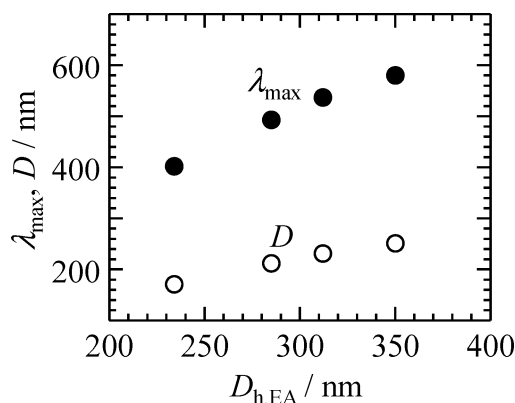


Figure 5. Plots of absorption peak position (λ_{max} , ●) and size of the colloidal particle evaluated from λ_{max} (D , ○) for the swollen colloidal crystal CP(x)-S against the hydrodynamic diameter of the as-prepared colloidal particle in dilute prepolymer solution, $D_{h,EA}$.

ization, and the composite film consisting of the colloidal crystal assembly in the cross-linked PEA matrix was prepared. The obtained elastomer after the polymerization of CP(x)-S is designated as CP(x)-E. It should be noted that the structural color of the swollen colloidal crystal film with the prepolymer solution was successfully fixed even after the polymerization, as shown by photos in Figure 6, although the color of the

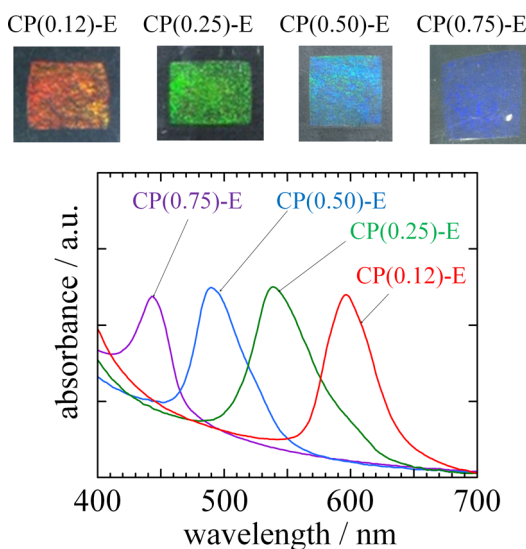


Figure 6. Photo images of the colloidal crystal elastomer CP(x)-E (upper) and their UV-vis absorption spectra (lower). See legend to Figure 4.

elastomer was less distinct than the swollen film. In the lower part of Figure 6, the absorption spectra of the structural colored elastomer are indicated, which can be compared with those for CP(x)-S's in Figure 4. The peak width of the elastomer was obviously larger than that of the swollen film, and the absorption spectrum varied within a range of several nanometers depending on the incident light position. These results suggest that the colloidal crystalline order became worse after the polymerization of the matrix. Even though the broadening of the peak, the averaged peak position was almost identical before and after the polymerization, as shown in Table 2.

As shown in DSC curves in Figure 3, T_g of PEA and CP(0.12)-E was lower than room temperature (-10 °C), and

T_g for the original CP(0.12) (~ 35 °C) was not recognized in the curve for CP(0.12)-E. As a result, the obtained composite film was rubber-like elastomer and can be deformed largely with weak force and recovered to the original size after unloading.

Strain-Responsive Behavior of the Structural Colored Elastomer. The original length of the colloidal crystal film of CP(0.12)-E embedded in the elastomer, L_0 , was stretched to L by tensile deformation, and the accompanying change of the elastomer film thickness from T_0 to T was measured. Evaluated true strain for tensile and thickness directions, $\epsilon_L = \ln(L/L_0)$ and $\epsilon_T = \ln(T/T_0)$, respectively, are plotted in Figure 7. From this

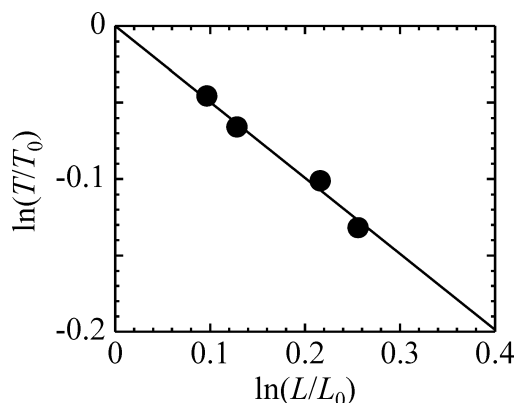


Figure 7. Relationship of the true strain for tensile and thickness direction of the uniaxially stretched film.

plot, Poisson's ratio $\nu = -\epsilon_T/\epsilon_L$ was obtained to be 0.497. This value is close to that for an incompressible material, suggesting that the obtained elastomer deforms like a usual rubbery elastic material.

In Figure 8, photo images of the stretched colloidal crystal elastomer CP(0.12)-E with various draw ratios are indicated. The nonstretched film exhibited red color, and by stretching,

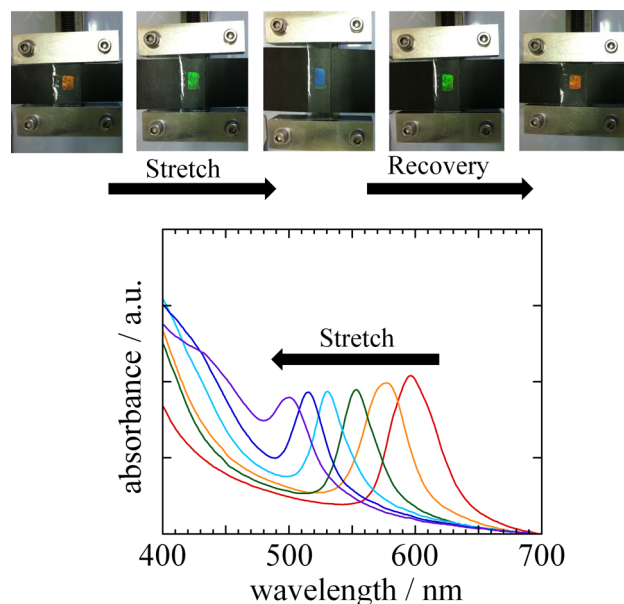


Figure 8. Photo images of the stretched colloidal crystal elastomer CP(0.12)-E (upper) and their UV-vis absorption spectra (lower). See legend to Figure 4.

the color changed to green and blue, i.e., the color with shorter wavelength. When the sample strain was recovered to the original state, the red color was also recovered. A similar color change by deformation was also observed in other elastomers, for example, the green colored CP(0.25)-E changed to light violet by stretching, i.e., a shift to shorter wavelength. The peak shift of the absorption spectra with stretching shown in Figure 8 was consistent with the visual observation. Plots of the absorption peak wavelength (λ_{\max}) against the film thickness are shown in Figure 9. This graph clearly indicates an excellent

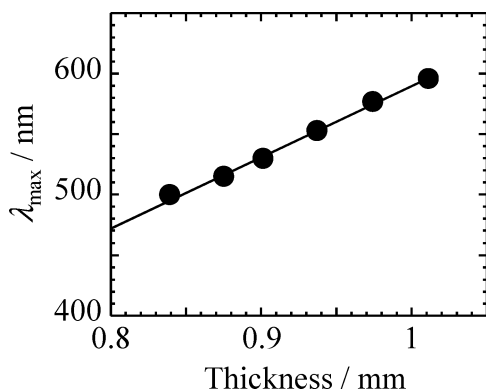


Figure 9. Plots of the absorption peak position, λ_{\max} , of the stretched film against the film thickness. The straight line is connecting the plot of the nonstretched sample and the origin.

linear relationship between the structural color and the film thickness. It should be noted that the solid straight line in Figure 9 connects between the plot of the nonstretched sample (1.011 mm, 596 nm) and the origin (0 mm, 0 nm) and reproduces the experimental data satisfactorily. This film-thickness dependence of the structural color indicates that repeating distance of the colloidal crystal changes proportionally with thinning of the film.

The change of the structural color was also confirmed by a local compressive deformation. In Figure 10, the film was

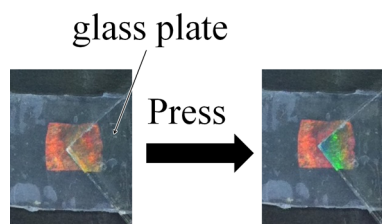


Figure 10. Photo images of the colloidal crystal elastomer CP(0.12)-E under compressional deformation.

partially compressed with using a rectangular glass plate. The original red color changed to green under the glass plate, which corresponds to the shift of the structural color to shorter wavelength with thinning of the film.

DISCUSSION

The structural colored elastomer was prepared by fixing the colloidal crystal film swollen with the EA prepolymer solution and subsequent polymerization of EA. After the swelling, the glassy P(EA-MMA) film at room temperature became soft, so the segmental motion of P(EA-MMA) was possible during the polymerization of EA, which lowers the regularity of the closely

packed colloidal crystal. This might be the reason why the structural color of the elastomer was less distinct after the polymerization as shown in Figure 6. The polymerization of EA may occur not only in the cavity between the colloidal particles but also inside of the particle, so the prepared composite elastomer can be regarded as an interpenetrated polymer network (IPN) consisting of the cross-linked P(EA-MMA) particle and the cross-linked PEA matrix. The present result reveals that, although the regularity was lowered, the colloidal crystal assembly could be fixed successfully by the IPN structure even after the stretching. Application of the IPN method for immobilization of the colloidal crystal for hydrogel system can be found in the literature;^{22,23} however, that for bulk system has not been reported to our knowledge.

If the swollen P(EA-MMA) and PEA formed fully IPN structure with homogeneous mixing, volume fraction of P(EA-MMA) in the particle can be calculated by using the swelling ratio l/l_0 of CP(*x*)-S and expected volume change from EA to PEA (density $\rho = 0.92$ and 1.12 g/cm³, respectively³³) by polymerization and evaluated to be 0.21–0.36. These low values suggest that the P(EA-MMA) particles may be softened at room temperature by mixing with PEA having low T_g , which means that all of the colloidal crystal elastomer is in the rubbery state. Because of the liquid-like IPN structure, the colloidal particles as well as the crystalline lattice can be deformed with obeying the affine deformation, as depicted schematically in Figure 11. This structure change decreases the repeating

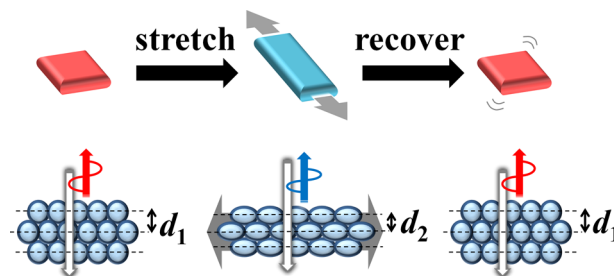


Figure 11. Schematic illustration of the structure change of the colloidal crystal elastomer by the stretching deformation.

distance of the colloidal crystal perpendicular to the film from d_1 to d_2 , resulting in the decrease of λ_{\max} as shown in Figure 9. As mentioned in the Introduction, reported colloidal crystal elastomers in the literature^{8,10} contained rigid colloidal particles in soft elastomeric matrix; the former could not be deformed by mechanical deformation of the elastomer. As a result, they exhibited a smaller Poisson's ratio ($\nu = 0.22$ – 0.28) than the present CP(*x*)-E samples, $\nu \approx 0.5$ (see Figure 7), which is typical value for rubbery soft material. This large Poisson's ratio of CP(*x*)-E is effective for the sensitive structural color change because the film thinning as well as the decrease of the colloidal crystal repeating distance can be achieved sensitively by stretching deformation. It should be pointed out that these unique structural coloring behaviors in the present system are based on the IPN structure consisting of the soft colloidal particle in the soft matrix.

According to Bragg's law, the diffraction light wavelength against the normal incident light, λ_{\max} , can be calculated by eq 1

$$\lambda_{\max} = 2n_{\text{eff}}d \quad (1)$$

where d is the lattice spacing of the colloidal crystal and n_{eff} is effective refractive index of the film represented by eq 2.

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

In the swollen CP(*x*)-S film, n_i and ϕ_i are refractive index and particle volume fraction, and suffixes “p” and “s” represent the swollen P(EA–MMA) particle and swelling solvent EA, respectively. Because of the good solubility of P(EA–MMA) in EA, the swelling solvent can exist not only in the void around the colloidal particle but also in the particle. n_p can be evaluated from the swelling ratio of the colloidal crystal film with assuming additive rule.

$$n_p = n_{\text{P(EA-MMA)}}(l/l_0)^{-3} + n_s\{1 - (l/l_0)^{-3}\} \quad (3)$$

By assuming that the colloidal crystal lattice was in face-centered cubic (fcc) structure, ϕ_s and ϕ_p are 0.26 and 0.74, respectively. The refractive index value of $n_{\text{P(EA-MMA)}}$ = 1.48 was evaluated as an averaged value of those for PMMA and PEA,³⁴ and n_s = 1.40 was taken from ref 31. In the fcc structure, the lattice spacing d of 111 plane and the particle diameter D have the following relationship:

$$d = (2/3)^{1/2} D \quad (4)$$

The D value, corresponding to the particles diameter, can be evaluated from the experimentally obtained λ_{max} and eqs 1–4, as listed in Table 2, and plotted against the hydrodynamic diameter in EA by open symbols in Figure 5. The good linearity of the plots indicates the strong correlation between the size of the swollen colloidal particle in dilute solution and that in the swollen film, which was already pointed out in the previous section. However, as found in Figure 5, there was a large difference between $D_{\text{h,EA}}$ and D ; $D_{\text{h,EA}}$ values were 1.3–1.4 times larger than D . This result suggests that the as-prepared colloidal particle was swollen largely to $D_{\text{h,EA}}$, but after forming the colloidal crystal and drying to obtain the film, the swollen size of the particle was suppressed to a limited size. This result seems reasonable because the polymer chains in the outer region of the colloidal particle should be overlapped and entangled with each other in the drying process, which prevents a larger swelling.

The above evaluation of D was also performed for the CP(*x*)-E elastomer. Increase of the refractive index of the swelling media (n_s) and decrease of the swelling ratio (l/l_0) by the change of density after the polymerization of EA to PEA were considered, and the evaluated values of D from the experimental λ_{max} of CP(*x*)-E are listed in Table 2. The small decrease in D after the change from CP(*x*)-S to CP(*x*)-E corresponds to the increase on n_s and the volume contraction by the polymerization from EA to PEA was found to have a negligible effect on the particle size D . This result seems strange when considering the large difference between the density of EA (0.92 g/cm³) and PEA (1.12 g/cm³). One possible explanation of this apparent small decrease in D may be a contraction of the particle to a nonspherical shape after the polymerization.

In this report, the structural coloring phenomenon of P(EA–MMA) colloidal crystal swollen with EA was described. Solvent-responsive structural color induced by the refractive index contrast has been reported in the literature.^{18,35} In our preliminary experiments, we found that the structural color of the swollen P(EA–MMA) colloidal crystal varied sensitively by changing the swelling solvent. Details of the solvent-responsive behavior of the structural colored colloidal crystal film will be reported in a future paper.

CONCLUSIONS

Monodispersed colloidal particles of P(EA–MMA) were prepared by soap-free emulsion polymerization. By simple solvent-casting on cellulose membrane, a regularly ordered colloidal crystal assembly film was obtained. The colloidal crystal film, swollen in the prepolymer solution of EA monomer, revealed opalescence structural color. The observed color can be tuned by the size of the colloidal particle. After the polymerization of the prepolymer solution, the composite elastomer consisting of embedded P(EA–MMA) colloidal crystal and PEA matrix was obtained, and the structural color was successfully fixed in the elastomer. By stretching the structural colored elastomer, the color was sensitively changed to that with shorter wavelength with exhibiting excellent proportional relationship with the film thickness. By unloading and recovery to the original length, the structural color was recovered to the original one. In the elastomer, P(EA–MMA) particle and PEA matrix should be forming IPN structure, which possibly maintained the colloidal crystal stably even after the polymerization and stretching. The penetration of PEA chain into the P(EA–MMA) also lowered T_g of the particle than room temperature. The soft particle made it possible to show the sensitive structural color change, which was difficult to be realized in the elastomer from hard colloidal particle.

Wide-range structural color change by mechanical deformation of bilayer hydrogel was recently reported by Haque et al., which was prepared by applying double network principle.³⁶ In our present colloidal crystal elastomer system, a relatively simple fabrication method with using conventional acrylic polymers was applied, and by changing the colloidal particle size, the color changing phenomena would be achieved over entirely visible light wavelength. Such strain-responsive structural colored elastomer has a potential for application to high-performance polymeric materials with stimuli responsiveness. Further investigations for the color changing behavior of the colloidal crystal elastomer with various network structures are in progress.

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Notes

The authors declare no competing financial interest.

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