Preparation of the novel sensing system using structural color plate

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For the creation of novel sensing systems, we prepared light-transmitting structural color plates using polypeptide and glass. From Hansen's formulas, we found that the structure that consists of a polymer layer and silver layers on both sides of the polymer shows structural color. The spectra of the light pass through such structure were expected to show sharp peaks, which indicates that the color is brilliant. We actually prepared such structure on glass plates. The plates were showed different colors dependent on the number of polypeptide layers: the plate including 60 layers of poly(n-hexyl L-glutamate)(PHLG) showed blue, 90 layers showed yellow green, and 120 layers showed red. The transmission spectra of the plates showed sharper peaks than the reflection spectra of recent reflecting-type plates. The colors were changed by molecular absorption. For example, the color of the plate including 90 layers of PHLG changed to orange in a cell (50 ml) with 5 ml of 1,4-dioxane, and the color was changed to red using 1,2-dichloroethane instead of dioxane. The difference of color depends on absorbed solvent indicates the possibility of the novel sensor of various matters.
Key words: structural color, LB film, sensing system, polypeptide, solvent

1. INTRODUCTION

"Structural color" is a color derived not from pigments but from the fine structures of material surfaces, which can be seen on the wings of morpho butterflies, the bodies of tropical fish, and so on.[1-3] Light of a specific wavelength is reflected on their surfaces due to light interference. These structures can be made artificially and have been investigated for application to cosmetics, fibers, and so on.[4,5]

Light interference is also applied to optical filters. Many optical interference filters are made using multiple deposition of alternating high and low refractive index films.[6,7] The transmission spectrum of these filters shows a very sharp peak. These filters are usually made from inorganic materials because they are expected to be stable. Conversely, if they are made from materials whose optical character is unstable and dependent on the environment, they can change color as a result of environmental stimuli.

Various gas sensors that detect a specific element in the atmosphere have been developed as solid electrolyte types, semiconductor types, etc.[8] They transfer the adsorption of a material to electric signals by changing their electric character, and always need electric apparatus. If a sensor directly transfers the adsorption of a material to visual information, it is assumed to be more useful than conventional sensors in some situations.

We investigated stimuli-sensitive structural color plates consisting of polypeptide multilayers and a silicone substrate.[9] We controlled the thickness of the surface polymer layer by deposition of rod-like hydrophobic polypeptides using the LB method, and created plates that change color by light irradiation or molecular adsorption.[10]

The plate we prepared was the type that shows reflecting light color (the "reflecting-type"). Therefore, a special device to measure reflection spectra was necessary to estimate the color. In addition, the observed peaks shown in the spectra of reflecting-type plate were broad, causing low chroma (vividness).

In this study, we prepared "transmitting-type" structural color plates that show transmitting light colors. We assumed that a thin clear film whose thickness is the order of 100 nm, and both surfaces of which have efficient high reflectivity drive interference of light, and created structures of polypeptide thin films with silver layers whose thickness is the order of 10 nm on both surfaces.

We calculated the spectra of transmitting-type films using Hansen's formula,[11,12] and confirmed that the spectra were expected to show sharp peaks. Therefore, we built the former structures on glass plates using vacuum plating and Langmuir-Blodgett (LB) method. We estimated the colors of the plates by transmission UV-VIS spectroscopy. Moreover, color changing when the plates were left in the vapor-phase of an organic solvent was confirmed, and the relation between molecular absorption and color change was examined.

2. CALCULATIONS

The reflectivity, R, and the transmissivity, T, of the incident light irradiated with incident angle, θ_1, to a thin multilayer system as in Fig.1A consists of N layers (the first and Nth layers are outside the multilayer) are represented by the following equations[11,12]:

$$R = \left| \frac{\left(m_{11} + m_{12}q_N\right)q_1 - \left(m_{21} + m_{22}q_N\right)}{\left(m_{11} + m_{12}q_N\right)q_1 + \left(m_{21} + m_{22}q_N\right)} \right|^2$$

$$T = \frac{\mathrm{Re}(\cos\theta_N / \hat{n}_N)}{\cos\theta_1 / n_1} \left| \frac{2q_1}{\left(m_{11} + m_{12}q_N\right)q_1 + \left(m_{21} + m_{22}q_N\right)} \right|^2$$

where, for jth layer, $q_j = \cos\theta_j / \hat{n}_j$, $\hat{n}_j(= n_j + ik_j)$ is the complex refractive index, θ_j is the incident and refraction angle, and m_{kl} is given by the following matrix:

$$\begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = M_2 M_3 \cdots M_{N-1}$$

$$M_j = \begin{bmatrix} \cos\beta_j & -(i/q_j)\sin\beta_j \\ -iq_j \sin\beta_j & \cos\beta_j \end{bmatrix}$$

where $\beta_j = (2\pi h_j \hat{n}_j / \lambda)\cos\theta_j$, h_j is the thickness of jth layer, and λ is wavelength of light.

The spectrum of visible light (400 ~ 750 nm) transmitted vertically through the multilayer like Fig.1B which consists of the first silver layer ($h_2 = 20$ nm), polymer layer($n_3 = 1.5$, $k_3 = 0.01$), and the second silver layer($h_4 = 20$ nm) in air ($n_1 = n_5 = 1$, $k_1 = k_5 = 0$) was calculated by the former equations with increasing of the thickness of polymer layer (h_3). The refractive index of silver was quoted from ref. 13 and the data at unwritten wavelength were interpolated by smoothing of written data. The peak in the spectrum did not appear until h_3 was less than 70 nm. If h_3 was more than 70 nm, there was a sharp peak in the spectrum (Fig.2A). The peak shifted to a longer wavelength with an increase in h_3. When h_3 exceeded 200 nm, one more peak appeared from the lower side of wavelength (Fig.2B). The second peak also shifted with the increase in h_3, and more peaks appeared. When h_3 increased sufficiently, many peaks appeared, but the intensities of the peaks decreased. Thus, it is expected that the thin triple layer structure of
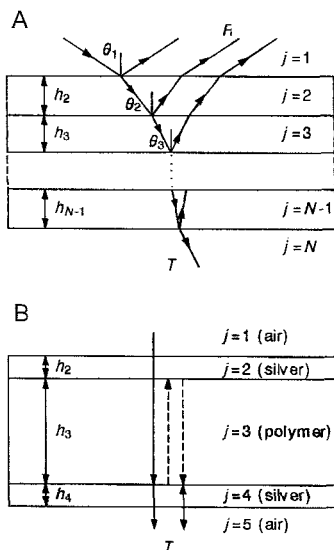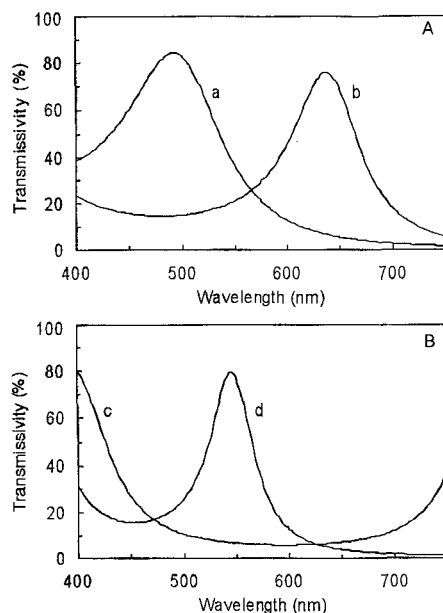

Fig.2 Expected transmission spectra of the plates including silver layers whose thickness is 20 nm and whose polymer layer has a thickness of 100 nm (a), 150 nm (b), 200 nm (c), 300 nm (d), calculated using Hansen's formula
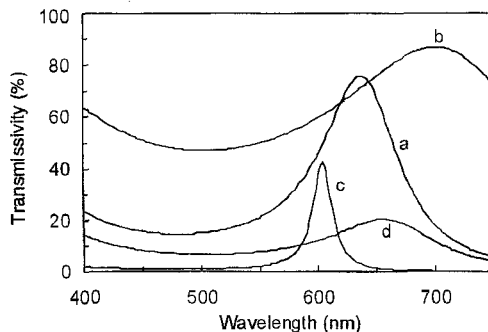

Fig.3 Expected transmission spectra of the plates including silver layers whose thickness is 20 nm (a), 10 nm (b), 40 nm (c), and where one layer is 10 nm and the other is 40 nm (d). The thickness of the polymer layer is 150 nm.

the metal-polymer-metal transmitted the light of a particular wavelength and represented brilliant color, which was controlled by changing the polymer thickness.

Silver was used because its reflectivity is close to 100% in all regions of the wavelength of visible light, and is assumed to cause efficient interference. The silver thickness of 20 nm was expected to be the most suitable for this system. Too thick a silver layer would not transmit light, and too thin a layer would cause a low contrast of color. The spectra of the system with $h_2 = h_4$ = 10 nm or 40 nm were calculated and compared when $h_2 = h_4 = 20$ nm (Fig.3). The peak was broader at $h_2 = h_4$ = 10 nm, and the peak intensity was lower at $h_2 = h_4 =$ 40 nm. Moreover, the peak in the spectrum calculated using $h_2 = 10$ nm and $h_4 = 40$ nm was broad and weak.

Fig.1 Schematic pictures of cross-sections of multilayers (A: N-2 layers, B: 3 layers consists of silver-polymer-silver) and transmitting and reflecting light

3. PREPARATION OF SAMPLES

The silver-polymer-silver structure was built on a glass plate. First, a silver layer was deposited on a glass plate by vacuum plating. After this, a polypeptide multilayer was deposited using the LB method, and a silver layer was again deposited on the polymer surface. The glass plate (S-1111, Matsunami Glass, Osaka) was washed with acetone and Milli-Q water, dipped in concentrated nitric acid for 3 days and washed by Milli-Q water before use.

The silver was deposited using a vacuum deposition device (SK-TM15K, Shinku, Nagoya), while the thickness of the deposited layer was monitored and controlled using a quartz oscillator (XTM/2, Anelva, Tokyo). The thickness was also confirmed by atomic force microscopy after deposition. Silver pellets were purchased from Koch Chemicals (particle size 1~3 mm).

A polymer multilayer was deposited onto the plate by LB method using the L-B film deposition system NL-LB400NK-MWC (Nippon Laser & Electronics Lab., Nagoya). Poly (*n*-hexyl L-glutamate) (PHLG) was used as the polymer. In previous report, the synthesis and confirmation of deposition onto the hydrophobic surface of PHLG were represented. [9] In this study, PHLG was deposited onto a silver surface hydrophobized by dipping in an ethanol solution of stearylmercaptan (Tokyo Kasei Kogyo) for 1 day and dried after washing with ethanol. 60, 90, and 120 layers of PHLG were deposited on the plates. Their thicknesses were calculated as 96, 144, and 192 nm, respectively, from the thickness of one layer of PHLG measured to be 1.6 nm in a previous report.

After polymer deposition, the silver layer was again deposited onto the plate using the above method, while cold water was passed through the supporting board for the plate to keep the temperature of the plate down, so as not to make the polypeptide unfold. The IR spectroscopy of the PHLG deposited onto a CaF_2 plate showed that unfolding by heating did not occur.

4. RESULTS AND DISCUSSION

4.1 Appearance of the colors on the plates

The plates which consisted of 20 nm thickness of two silver layers and 60, 90, or 120 layers of PHLG were prepared. The plates showed vivid colors; the 60 layers showed blue, the 90 layers showed yellow green, and the 120 layers showed red. The colors of the plates were estimated by transmission spectroscopy. The spectrum of PHLG films are shown in Fig.4, with a reflection spectrum of the former reflecting-type plate (the incident angle is 10°). The peaks in the spectra of the transmitting-type were sharper than the peak of the reflecting-type, which indicates vivid color of the transmitting-type.

The wavelength at the peak top shifted to high wavelength as the PHLG thickness increased; 430 nm for 60 layers, 563 nm for 90 layers, and 622 nm for 120 layers. The calculated peak top values were 464 nm for 60 layers, 596 nm for 90 layers, and 732 nm for 120 layers. The peak position of the measured spectrum is almost equal to the calculation, which proves that light interference caused the colors.
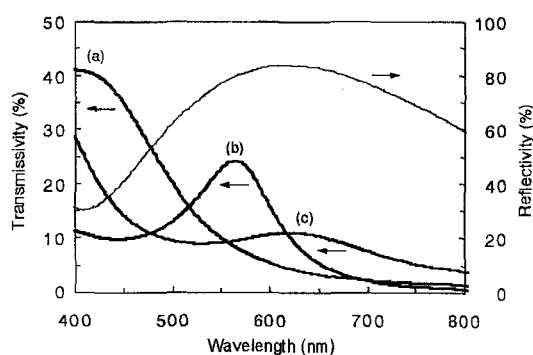
The measured peak shifted to lower wavelength and

Fig.4 Transmission spectrum of the structural color plate including 60 (a), 90 (b), and 120 layers (c) of PHLG prepared in this report (solid lines) with the reflection spectrum of the former reflecting-type of the structural color plate including 120 layers of PHLG (thin line).

had lower intensity than the calculated peak. This is assumed to be caused by the actual optical character of the deposited silver, which disagrees with the literature. [13] Calculation of spectrum was tried using refractive index (n_2 and n_4) of silver that was 7 times that in the literature for a system consisting of a polymer layer ($h_3 = 144$ nm) and silver layers ($h_2 = h_4 = 20$ nm). The calculated peak resembled the measured peak. This indicates that the refractive index was main cause of the smaller peak at the lower wavelength compared with the theoretical one.

4.2 Color changing due to molecular absorption

To estimate color changing by molecular absorption, transmitting-type plates were introduced into a cell filled with the vapor of an organic solvent (Fig.5), and the color change was observed. Plates with a thickness of 20 nm for both silver layers, and 60, 90, or 120 layers of PHLG were set in glass cell (60 ml) with 5 ml of ethanol in a vial. The plate was placed on the vial and did not directly touch the solvent liquid.

Soon after setting, color changing of the plate occurred. About 2 hours later, the color of the 90 layers changed from yellow-green to orange, and the color of the 120 layers changed from red to purple. In the case of 60 layers, the blue color became lighter. The spectra of the plates after setting in the cell were measured. From the spectra, color changing was also confirmed as a peak shift (Fig.6). The peak position increased 34 nm, 66 nm, and 87 nm in the case of the 60, 90, and 120 layers, respectively. The shift value increased with the increase
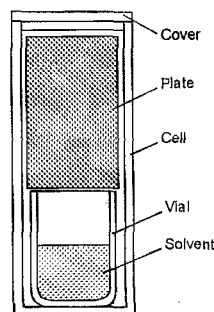

Fig.5 Schematic picture of a structural color plate in a glass cell with solvent
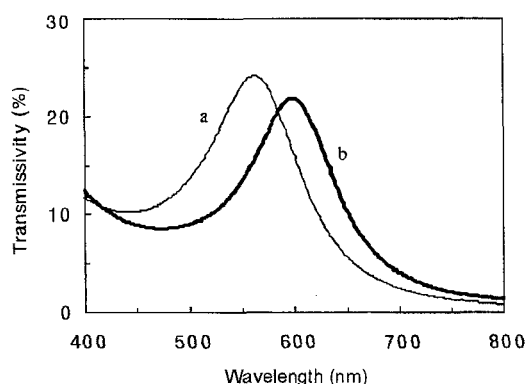
Fig.6 The transmission spectra of the structural color plate including 90 layers of PHLG in air (a) and that set in a glass cell with 5 ml of ethanol in a vial for 2 hours

in the number of layers, which supports the origin of color changing that is assumed to be increase in the thickness of the polymer layer.

In this study, the outer silver layer was deposited onto a polymer surface by vacuum plating. Such layer is expected to be a polycrystal which has defects between crystals. The molecules of solvent was supposed to pass through such fine defects in the silver layer and swell the polymer layer.

Color changes using of 1,4-dioxane instead of ethanol were also observed. In this case, the color of the 60 layers changed to green, that of the 90 layers changed to red-purple, and that of the 120 layers changed to blue-green. These results are different from the case using ethanol. The peak shift in the spectra of the 60 and 90 layer plate was 82 and 248 nm, respectively (the shift value in the case of the 120 layer plate was supposed to be also more than 200 nm but could not be determined exactly because the value was too great to measure). These values are much larger than the case using ethanol. These results are assumed to relate to the difference in the affinity of ethanol and 1,4-dioxane to PHLG.

Similar experiments have been performed using various solvents, and the shift values were estimated (Fig.7). The shift was small when the affinity of the solvent to PHLG was low, such as alcohol. Conversely, the shift was large when the affinity of the solvent to PHLG was high, such as hydrocarbon or alkyl halide.
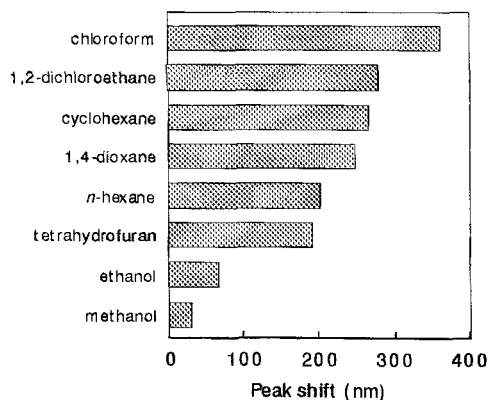

Fig.7 The shift values of the structural color plate including 90 layers of PHLG set in a glass cell with various solvents

Solvents having high affinity to polymer are expected to significantly swell the polymer layer and efficiently increase the thickness of polymer layer. The character of the solvent was transformed to the thickness of polymer layer and the color of the plate.

5. CONCLUSION

For upgrade of vividness and convenient use of stimuli sensitive structural color plate, we prepared "transmitting-type" of structural color plate using polypeptide and silver. The deposition of two thin silver layers onto both sides of thin polypeptide layer realized both transmission and reflection of light at polypeptide surface and interference of transmitting light. The vivid color of this structure was expected by calculations of spectra using Hansen's formula, which was also useful for solution of the origin of colors. Actually, prepared plates showed vivid colors as expected and changed their colors by absorption of solvent. Appeared color was dependent on solvent, which leads to development of the novel sensor.

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SYMBOLS

h_j : thickness of jth layer

i : imaginary unit

k_j : absorption coefficient

M_j : matrix consists of β_j and q_j

m_{kl} : element of matrix $M_2 M_3 \cdots M_{N-1}$

N : the number of layers in multilayer structure including two phases of outside the multilayer

n_j : refractive index of jth layer

$\hat{n}_j$: complex refractive index of jth layer ($= n_j + ik_j$)

q_j : $\cos\theta_j / \hat{n}_j$

R : reflectivity

T : transmissivity

β_j : $(2\pi h_j \hat{n}_j / \lambda)\cos\theta_j$

θ_j : incident and refraction angle at jth layer

λ : wavelength of light