

Structural Color with Polypeptide LB Film

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A polypeptide, poly (γ -methyl L-glutamate), containing an azobenzene group in the side chain, azo-10-PMLG and azo-28-PMLG were prepared. The polypeptide monolayer on water was deposited on a silicon substrate at a surface pressure at 18 mN/m to produce its LB films. Then the structural color appeared in the LB films. Secondly the UV/VIS reflection spectra of the LB films were measured in the dark adaptation, irradiation UV and VIS light alternately. As the result of irradiation UV and VIS light, the maximum peak of reflection spectra of LB film showed a shift. This was explained in terms of the thickness changes resulting from the photoisomerization of azobenzene moiety in the LB films. In addition, the structural color was also changed by the solvent sorption. The change of color was caused by the solvent induced changes in the refractive index and thickness of the LB film-solvent system.

Key words: polypeptide, azobenzene, LB film, photoisomerization, structural color

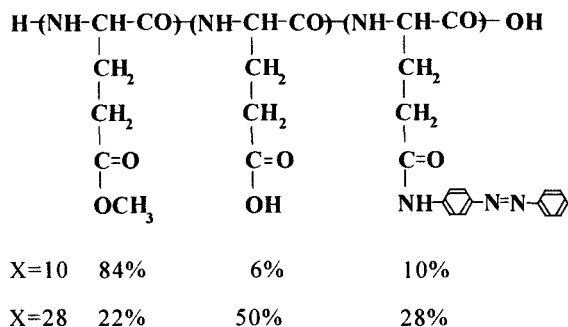
1. INTRODUCTION

Many colors in our environment generally originate in pigments. However, in nature, the color forming systems without pigment exist such as body color of insects or tropical fishes [1]. These color forming systems originate the interference of light according to the regular stratified structure where the refractive indices differ from each layer, and emphasis or enfeeblement of the intensity of the visible light determines the colors. These are called the structural colors. The artificial structural color formation has been already reported on surfactant solutions and fiber systems [2-4]. However, the 2-dimensional color formation system using rod-like polymers has not been examined. We have already reported a construction of color forming LB films composed of α -helical polypeptides on the silicon substrate [5]. The color of these LB films could be explained by the following equations of interference of light [6].

$$\lambda = \frac{2h}{m} \sqrt{n^2 - \sin^2 \alpha} \quad (\text{emphasized}) \quad (1)$$

$$\lambda = \frac{4h}{2m-1} \sqrt{n^2 - \sin^2 \alpha} \quad (\text{enfeebled}) \quad (2)$$

where, λ is wavelength of light, α is incident angle, h is thickness of the layer LB film on the lustrous surface, n is refractive index of the layer, and m is natural number ($m = 1, 2, \dots$). Thus, it was confirmed that the color of these LB films is based on the regular layered structure of the rod-like polymers.



Scheme 1. Chemical structure of azo-X-PMLG

In this study we prepared the polypeptides with azobenzene groups in the side chain as a photosensitive group and their LB films, and tried to photocontrol of structural color of these systems.

2. EXPERIMENT

The membrane of poly (γ -methyl L-glutamate) (PMLG) containing an azobenzene group in the side chain (azo-X-PMLG, X is the mole % of the azobenzene moiety) was prepared as follow [7].

PMLG ($M_w = 1.5 \times 10^5$) was hydrolyzed partly. Then it was dissolved in dimethylformamide (DMF) at 0°C. *p*-aminoazobenzene, 1-hydroxybenzotriazole and dicyclohexylcarbodiimide were added to the stirred DMF solution at 0°C. After 1h, the mixture was further

stirred at 25°C for 24h. The dicyclohexylcarbodiurea were filtered off, and the solution was poured into diethyl ether. The azobenzene content in the polymers was determined from absorbance at λ_{\max} (341 nm) of 2,2,2-trifluoroethanol (TFE) solution of azo-X-PMLG on the basis of the molar extinction coefficient of the model compound, *p*-aminoazobenzene, at 341 nm. The results of the modification of PMLG and azobenzene content, X, are shown in Scheme 1.

Silicon wafers (Nilaco) were used as substrates. The surface of silicon, SiO₂ thin layer, was modified with silane-coupling agent to produce the hydrophobic surface [8, 9]. First, substrates were cleaned by acetone and nitric acid, and then immersed in octadecyl-trimethoxysilan 1mM chloroform solution for 24h and heated at 110 °C for 20 min.

LB method was apply to build regular stratified structure of azo-X-PMLG on the substrates. Surface pressure-area (π -A) measurements and monolayer deposition by LB method were performed by use of LB film deposition apparatus NL-BIO40-MWCT (Nippon Laser & Electronics Lab.). Samples were spread from chloroform/TFE (20:1) solution on a Langmuir trough filled with pure water. The spectrum of FT-IR was recorded on a Spectrum 2000 (Perkin Elmer) equipped with an MCT (Mercury-Cadmium-Telluride) detector. Reflection spectrum measurements were performed by use of a UV/VIS spectrophotometer V-550 (JASCO) together with an attachment, ARV-474 (JASCO). Irradiation of the LB films was performed by a 500W super-high-pressure mercury lamp USH-500 (USHIO) equipped with UV-350 filter (Toshiba) (300 nm < λ < 400 nm) for ultraviolet (UV) light irradiation, or L-42 filter (Toshiba) (λ > 420 nm) for visible (VIS) light irradiation.

3. RESULTS AND DISCUSSION

Figure 1 shows the (π -A) isotherms of azo-10-PMLG (a) and azo-28-PMLG (b). The limiting area was estimated to be 0.18 nm²/residue and 0.16 nm²/residue, respectively. This shows that azo-10-PMLG and azo-28-PMLG monolayers are almost laying on the air-water interface since the area/residue of PMLG was calculated to be 0.18 nm²/residue.

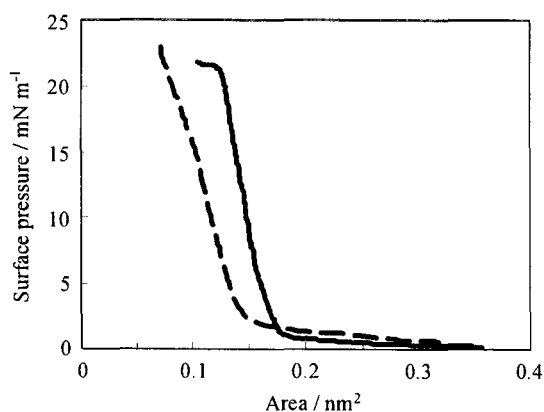


Figure 1. Surface pressure-area isotherms of azo-10-PMLG (solid line) and azo-28-PMLG (dotted line) monolayer at 20 °C.

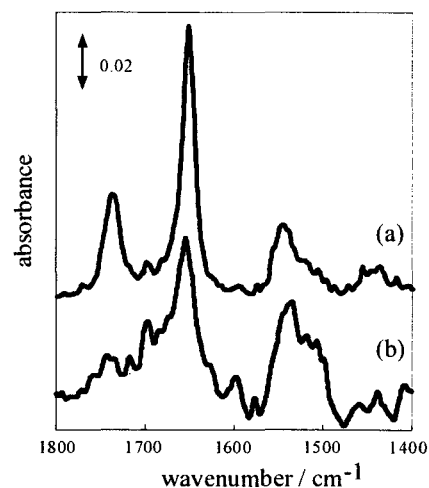


Figure 2. FT-IR spectra of 100 layers of azo-10-PMLG (a) and 30 layers of azo-28-PMLG (b) LB films.

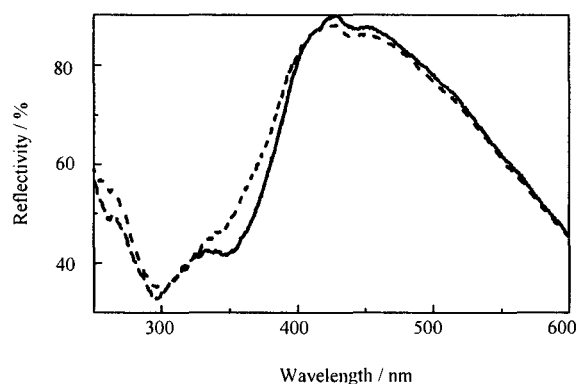


Figure 3. Reflective UV-VIS spectra of 100 layers of azo-10-PMLG LB film at dark adaptation (solid line) and after irradiation UV light (dotted line).

We tried to transfer the monolayer onto the silicon substrates. The depositing pressure was 18 mN / m and compression speed was 5 mm / min for all samples. The structure of azo-10-PMLG and azo-28-PMLG multilayer on silicon substrate was characterized by FT-IR measurements (Figure 2). The transmission FT-IR spectra of 100 layers of azo-10-PMLG LB film and 30 layers of azo-28-PMLG LB film show major peaks at 1655 cm⁻¹ (amide I in α -helical structure) and at 1550 cm⁻¹ (amide II in α -helical structure) [10]. This suggests that azo-10-PMLG and azo-28-PMLG form α -helical structure in LB films. The LB films with azo-10-PMLG and azo-28-PMLG showed interference colors depending on the number of depositions. The colors can be evaluated using reflection spectrum of LB film. Figure 3 shows reflective UV-VIS spectra of 100 layers of azo-10-PMLG LB film at an incident angle of 10°. The minimum of reflectivity based on the π - π^* transition band of azobenzene group in the samples was observed around 350 nm for all spectra. But the

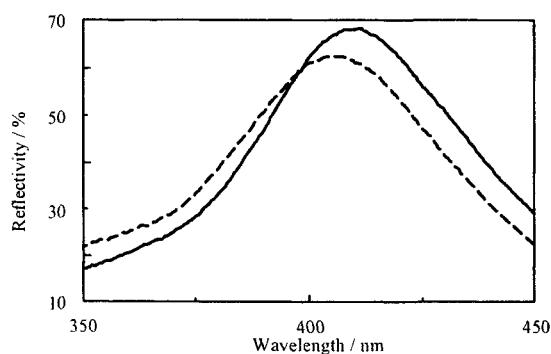


Figure 4. Reflective UV/VIS spectra of 30 layers of azo-28-PMLG LB film in dark adaptation (solid line) and after irradiation (dotted line).

maximum of reflectivity was appeared different position. The spectra of 100 and 140 layers of azo-10-PMLG showed a peak at 415 nm and 521 nm which corresponded to blue and yellow in color, respectively. The azo-28-PMLG LB film (30 layers) showed a peak at 413 nm corresponding to blue. These spectra show blue-shifts with increasing the incident angle (α) and showed good agreement between the peaks calculated by equation (1) and measured values. It is confirmed, therefore, that the colors of these films are interference colors.

After the irradiation of UV light for azo-10-PMLG and azo-28-PMLG LB films, the refraction spectra of both films were changed. The larger peak shift was obtained with azo-28-PMLG LB film, i.e., the peak moved from 413 nm to 403 nm (Figure 4). This range of wavelength has no relation with the absorption band of azobenzene. In addition, the spectrum was recovered the original one by the irradiation of VIS light or heat adaptation. We supposed that the trans-to-cis photoisomerization of azobenzene groups induced the thickness change of LB films.

Figure 5 shows the methanol induced changes in the reflective spectra of azo-10-PMLG LB film (140 layers). The LB film recovered the original color after the evaporation of methanol. It can be explained that the refractive index of the LB film system was decreased by

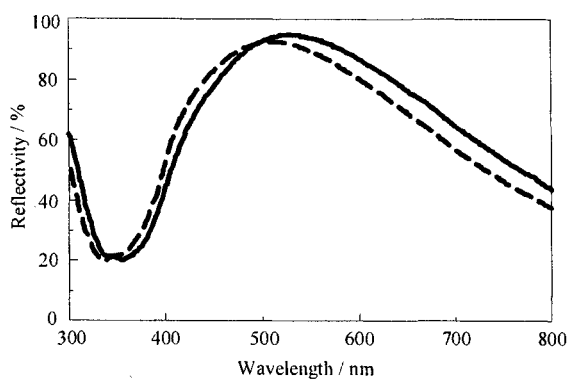


Figure 5. Reflective UV/VIS spectra of 140 layers of azo-10-PMLG LB film (solid line) with methanol (dotted line).

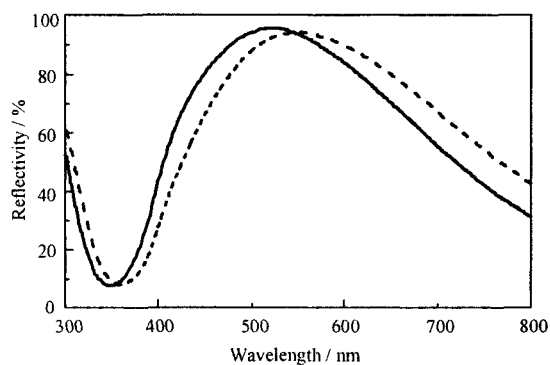


Figure 6. Reflective UV/VIS spectra of 140 layers of azo-10-PMLG LB film (solid line) with 1,4-dioxane (dotted line).

the sorption of methanol, which has lower reflective index ($n = 1.33$) than the polypeptide ($n = 1.6$). Equation (1) also supported that the sorption of molecules with lower reflective index can induce blue-shift of the maximum peak in the refraction spectrum. While the sorption of 1,4-dioxane into the azo-10-PMLG LB film (140 layers) induced the red-shift of the peak from 521 nm to 551 nm at 20 °C (Figure 6). This opposite shift may be explained as follows. 1,4-dioxane, a good solvent for the polypeptide, can induce the larger of swelling azo-10-PMLG LB film. The red-shift may be occurred based on this increase in the layer thickness in spite of the lower refractive index of 1,4-dioxane ($n = 1.42$). Thus, the opposite peak shift induced by the two solvents indicated that the color of the polypeptide LB film can be changed depending on the reflective index and sorption amount of the respective solvent.

4. CONCLUSION

In this study, we succeeded in building regular stratified structure with α -helical polypeptide containing azobenzene groups, on the silicon substrate. It showed various interference colors depending on the number of layers. The color could be changed by irradiation of UV light resulting from the thickness changes caused by the trans-to-cis photoisomerization of azobenzene side chains. In addition, the sorption of solvent could also induce the color change. It was found that methanol induced the peak of reflection spectrum to shorter wavelength, while 1,4-dioxane moved the peak to a higher wavelength. These facts can be explained in terms of the changes in the refractive index and/or thickness of the solvent swelling LB film systems. The results obtained in this study may be applicable to the construction of novel display or gas sensing systems.

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