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Preparation of a structural color forming system by polypeptide-based LB films

Takatoshi Kinoshita[a,*], Shujiro Hayashi[b], Yoshiyuki Yokogawa[b]

[a] *Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*
[b] *Ceramics Research Institute, National Institute of Advanced Industrial Science and Technology, Hirate-cho 1-1, Kita-ku, Nagoya 462-8510, Japan*

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Abstract

To prepare novel display systems like chameleon which change the color by stimuli, we prepared a structural color forming system by use of LB films consisting of polypeptide multilayers. We think this system change its color depending on the molecular structure like photochemical systems. Poly(γ-hexyl-L-glutamate) (PHeLG) was used as the multilayer component and silicon was used as the substrate for reflection of incident light. PHeLG monolayers were transferred onto substrates hydrophobized with octadecyl trimethoxy silane (OTS). LB films with various layer numbers up to 160 layers were prepared and they showed different colors depending on the thickness of polypeptide layer due to interference of light. The structures of LB films were estimated by using AFM and FT-IR spectroscopy. Interference colors were characterized by reflective visible spectra and compared with theoretical ones. Silicon wafer pre-colored by excessive oxidization was also used, and it was confirmed that only 10 or 20 layers of PHeLG could show the structural color. In this study, the base for preparation of chameleon-type display system was established. We will introduce photochemical moiety (azobenzene moiety, etc.) into this system and produce display systems which change their colors by optical stimuli.

Keywords: Structural color; LB film; Polypeptide; Silicon; Chameleon-type display

1. Introduction

Recently, the technology of flat panel displays has been advancing rapidly. Colored liquid crystal displays are penetrating in our lives, which are carried on many potable telephones or computer games. The other display systems, such as PDP (plasma display panel) or organic EL (electroluminescence), are also developed. On the other hand, novel display systems are expected from the view of problem of ecology, energy, human health, and so on.

Nature has unique display systems such as structural color of butterflies, beetles, and tropical fish [1–3]. Structural color is derived from interference and/or diffraction and/or scattering, etc. of light reflected from nano-scale structure of surface without pigment. For example, color by interference of light (interference color) is shown when a layer of whose thickness is of the order of 100 nm is on a flat and lustrous (having high reflectivity) surface. The incident light with certain incident angle (α) is emphasized or enfeebled at surface, depending on wavelengths (λ) of light. The λ values of emphasized or enfeebled lights are expressed by the following equations [4]:

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

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

where h is the thickness of the layer on the lustrous surface, n the refractive index of the layer, and m the natural number ($m = 1, 2, \ldots$). Thus, we could see the light having particular wavelength (particular color) from such surface.

As application of biomimetic science, various structural colored materials are investigated by many researchers and engineers. In the field of inorganic chemistry, many interference colored materials have been developed and published. They applied coating techniques for the metal or ceramic surface [5], or oxidized metals such as titanium. Also in the field of organic chemistry, various materials have been investigated, e.g. solution [6] and gel [7] for cosmetic application, and structural color fiber [8]. These materials cannot be used for display systems because they cannot change the color of themselves.

We have been trying to prepare display systems which change their colors by specific stimuli, like a chameleon

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[*] Corresponding author. Tel./fax: +81-52-735-5267.
E-mail address: kinosita@mse.nitech.ac.jp (T. Kinoshita).

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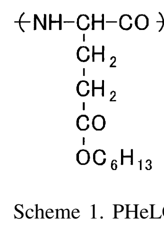
(chameleon-type display). We are using: (1) simple interference color and (2) hybrid system of organic layer and inorganic substrate. This system will change the color of reflecting light by changing the structure (thickness) or optical character (refractive index) of the organic layer. In this study, we will investigate the behavior of light depending on molecular structure, while researchers of general photochemistry investigate the behavior of molecules depending on the light.

For organic layer, we prepared α-helical polypeptide, which is rod-like and is the model molecules of proteins. We can fabricate molecular membranes with a well-defined molecular orientation on a substrate by LB method. Preparation and characterization of LB multilayer of α-helical polypeptides onto hydrophobized silicon wafer was investigated by Wegner's group [9–12] using hairy-rod polypeptides such as poly(γ-octadecyl-L-glutamate) which had long alkyl side chains. They evaluated molecular and supramoleculer structure [9], and estimated the property for optical waveguide [10,11], anisotropic reflectivity [11], and so on. However, they did not mention about structural color of the LB films in detail. In addition, they did not use preparative hairy-rod with shorter alkyl chains such as poly(*n*-hexyl-L-glutamate) (PHeLG).

In this paper, we report on preparation and characterization of LB films consisting of PHeLG on silicon substrate. We evaluated the structure of LB films by using AFM observation and FT-IR spectroscopy. Interference colors were estimated by reflective visible (VIS) spectra and compared with theoretical ones. Moreover, silicon wafer pre-colored by excessive oxidization was used, and we confirmed that the thickness of polymer layer expected for particular color was controllable. We will introduce photochemical moiety (azobenzene moiety, etc.) into this system and produce display systems which change their colors by optical stimuli. This study has established the base for preparation of such chameleon-type display systems.

2. Experimental

Poly(*n*-hexyl-L-glutamate) (PHeLG, Scheme 1) was synthesized by the ester interchange [13] of poly(γ-methyl-L-glutamate) which was obtained by the polymerization of the *N*-carboxy anhydride [14] of L-glutamic acid γ-methyl ester (MG–NCA) with benzylamine as an initiator. An average degree of polymerization of PHeLG moiety was estimated to be 114 by high-resolution ^{1}H NMR measurement (Varian XL-200 spectrometer) of the sample in trifluoroacetic acid (1 mg/ml). To be exact, this molecule contained 9% of γ-methyl-L-glutamate residues.



$$\left(NH-\underset{\underset{\underset{\underset{OC_6H_{13}}{|}}{\underset{CO}{|}}}{\underset{CH_2}{|}}}{\underset{CH_2}{|}}{CH}-CO \right)_n$$

Scheme 1. PHeLG.

Silicon wafers were purchased from Shin-Etsu Chemical. Silicon substrates were hydrophobized by use of octadecyl-trimethoxysilane (Tokyo Kasei Kogyo) transferred by LB method and fixed by heating at 110°C for 20 min [15,16].

Surface pressure–area (π–A) measurements and monolayer deposition by LB method were performed by use of an LB Film Deposition Apparatus NL-LB400NK-MWC (Nippon Laser and Electronics Lab.). AFM was performed by use of a Nanoscope III (Digital Instruments). Reflective VIS measurements were performed by use of an UV/VIS Spectrophotometer V-500 (JASCO) together with an attachment, ARV-474 (JASCO).

3. Results and discussion

Fig. 1 shows a π–A isotherm of a PHeLG monolayer at the air/water interface. Spreading solvent was benzene/DMF (7:3) and measured at 20°C. The limiting area was estimated to be ca. 0.23 nm^2/residue. Because the pitch of helix is 0.15 nm/residue, the diameter of the PHeLG helix was calculated to be ca. 1.5 nm.

We tried to transfer the PHeLG monolayer onto hydrophobic substrates. The depositing pressure was 15 mN/m. First step was down mode of substrate, the second was up mode, and after those both mode was repeated alternately. Fig. 2 shows the deposition ratio of PHeLG monolayers onto substrates. Each deposition ratio is ca. 1, which shows the monolayers were transferred onto substrates keeping their structures on the water surface in both modes.

The structure of PHeLG multilayer on the silicon substrate was characterized by the use of polarized FT-IR measurement (Fig. 3). The transmission FT-IR spectrum of 120-layer PHeLG LB film was measured using polarized IR spectroscopy with the polarization parallel or perpendicular to the dipping direction of deposition. Both spectra show four major peaks at 1738 cm^{-1} (C=O in side chain), 1656 cm^{-1}

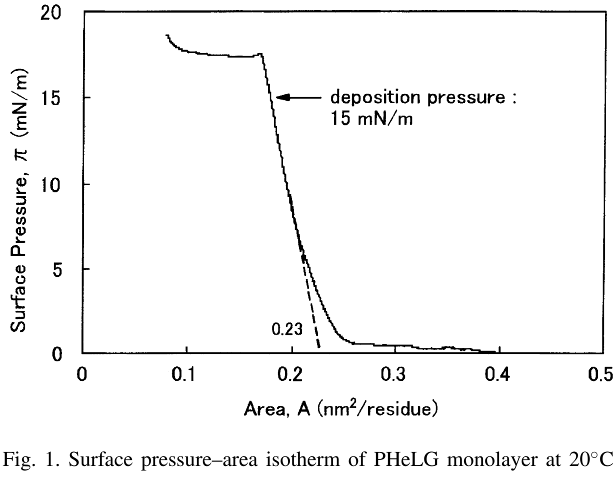


Fig. 1. Surface pressure–area isotherm of PHeLG monolayer at 20°C.

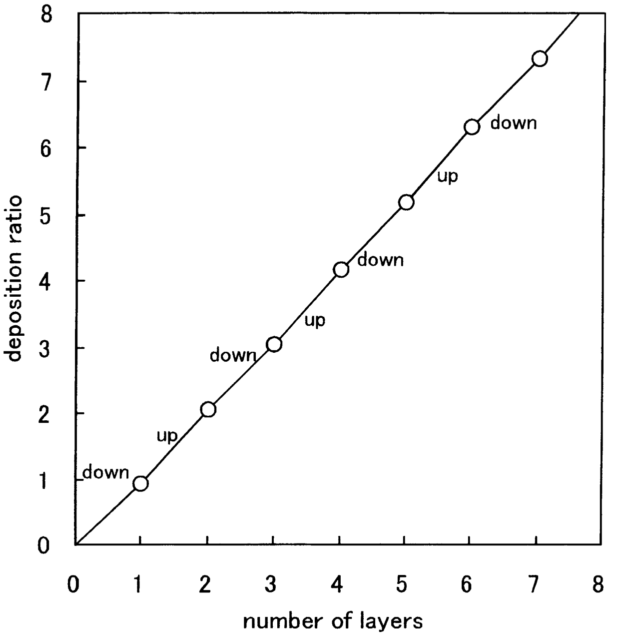


Fig. 2. Deposition ratio of PHeLG monolayer onto hydrophobic substrate as a function of number of layers.

(amide I in α-helical structure), 1626 cm^{-1} (amide I in β structure), and 1551 cm^{-1} (amide II in α-helical structure) in 1500–1800 cm^{-1} [17]. The peak at 1656 cm^{-1} is much larger than the peak at 1626 cm^{-1}, which indicates PHeLG molecules keep α-helical structure also in the LB film.

The peak at 1656 cm^{-1} (amide I) is also larger than the peak at 1551 cm^{-1} (amide II). It is known that the transition moment of vibrations of amides I and II of α-helix is oriented at 39° and 75° with respect to helical axis, respectively [18]. The transmission FT-IR emphasizes transition moment parallel to the film plane. Therefore, the small amide II peak indicates that the transition moment of amide II is oriented almost perpendicular to the surface and that the helixes lay parallel to the surface. The two polarized IR spectra are similar to each other, while the case of poly(γ-octadecyl-L-glutamate) showed difference [9]. This indicates that within the two-dimensional plane the orientation of PHeLG helix rod in the LB film is totally homogeneous.

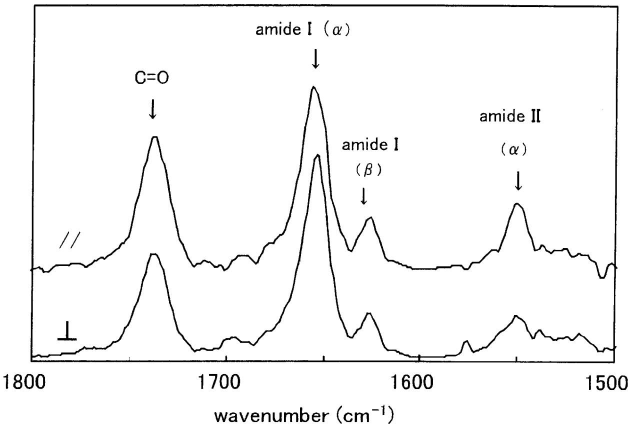


Fig. 3. The transmission FT-IR spectrum of 120-layer PHeLG LB film measured using polarized IR spectroscopy with the polarization parallel (upper, indicated by the sign of ||) or perpendicular (lower, indicated by ⊥) with respect to the dipping direction of deposition.

The thickness of PHeLG layer on the substrate was measured by the use of AFM. Fig. 4 shows an AFM image of a boundary region between 20 layers of PHeLG and the bare surface of the substrate. The height difference of the two planes is ca. 32 nm. Therefore, the thickness of one layer is calculated to be 1.6 nm. This value is almost similar to the diameter (1.5 nm) of PHeLG calculated from the limiting area.

We succeeded in fabricating the LB film with 160 layers of PHeLG in maximum as far as we examined. Substrates showed various interference colors depending on the number of polypeptide layers; brown at 40–50 layers, dark blue at 60–70 layers, light blue at 80–100 layers, yellow at ∼120 layers, and red-purple at ∼160 layers (Fig. 5).

The colors can be related with reflective VIS spectra of LB films. Fig. 6 shows VIS spectra of LB films consisting of

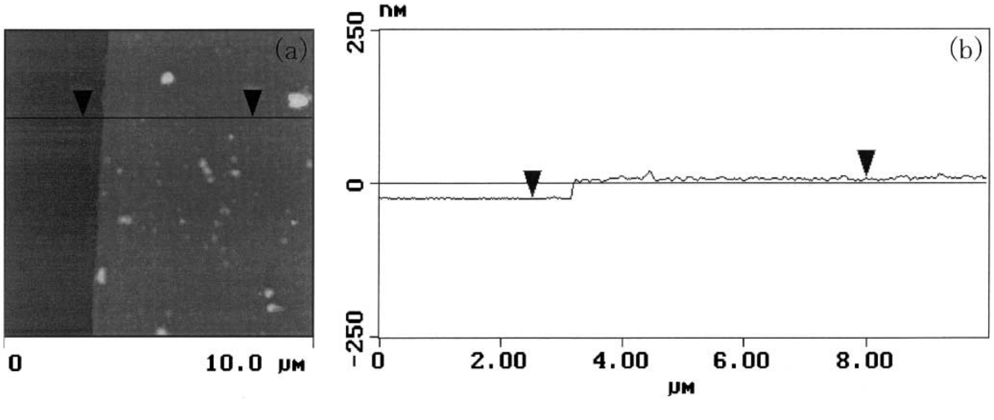


Fig. 4. (a) AFM image of PHeLG LB film in a boundary region between 20 layers of PHeLG and the bare surface of the substrate; (b) section of the line in (a). The height difference of the two planes is ca. 32 nm.

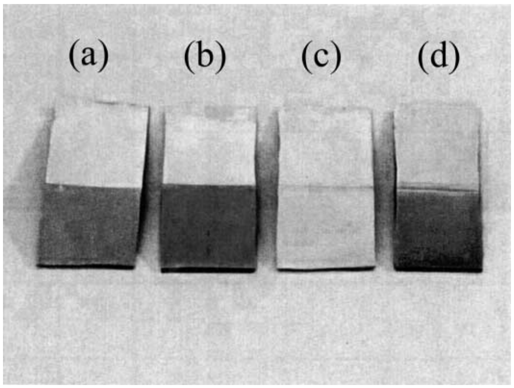


Fig. 5. Photographs of LB films of PHeLG of 40 (a), 80 (b), 120 (c), and 160 (d) layers.

40, 80, and 120 layers of PHeLG at an incident angle of 10°. The spectrum of the 80-layer film shows a peak at 418 nm at which the light looks blue. Oppositely, the 40-layer film shows a minimum at 456 nm. Therefore, the 40-layer film looks brown (dark orange) which is a complementary color to blue. The 120-layer film shows a peak at 619 nm and a minimum at 409 nm. The light at 619 nm looks yellow which is emphasized by decreasing of the light at 409 nm. We compared the peak positions to the calculated values from Eqs. (1) and (2). Fig. 7 shows peak positions of VIS spectra and calculated values as a function of number of layers. The calculated values fit measured ones.

Interference light is affected by the angle of incident light. Therefore, we measured reflective VIS spectra with incident light at various angles. Fig. 8 shows observed and calculated peak positions as a function of number of layers. The observed peak positions are consistent with the calculated ones at all observed angles. These confirmed that the colors of these films are interference colors.

Actually, it is hard to perform the deposition of more than 100 layers and polypeptides are often expensive. So, we try to save the polypeptide by use of pre-colored silicon wafer. Silicon can be oxidized by heating, and show the interference color by the oxidized surface (SiO_2) layer. First, the silicon wafer was heated at 950°C for 3 h, which became brown. After hydrophobizing, LB films of PHeLG of 10 or 20 layers were deposited. They showed dark red-purple or blue, respectively. Fig. 9 shows reflective VIS spectra of the LB films and the bare pre-colored substrate at an incident angle of 10°. The spectrum of the bare pre-colored substrate

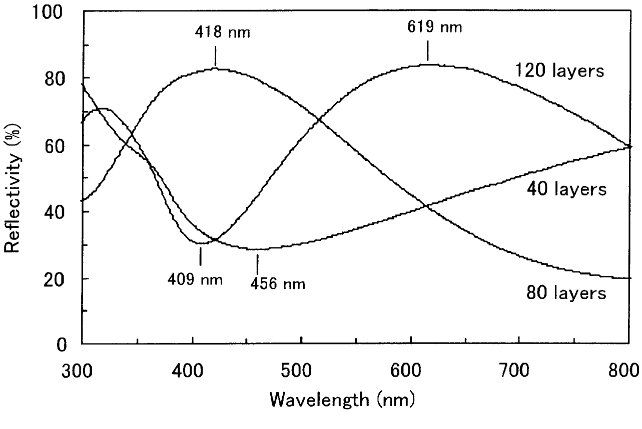


Fig. 6. Reflective VIS spectra of 40, 80, and 120 layers of PHeLG LB films. Incident angle was 10°.

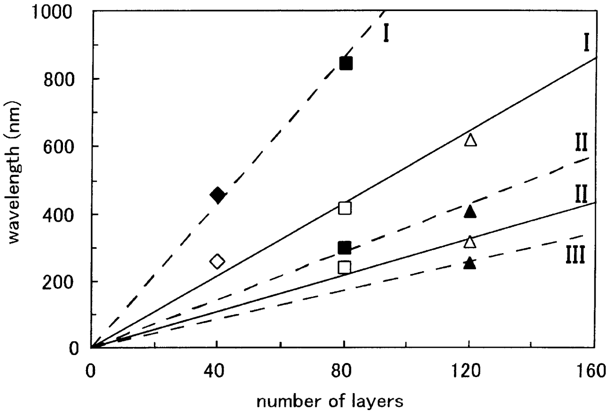


Fig. 7. Measured and calculated positions of maxima and minima in the reflection spectra as a function of the number of layers. Dots show the maxima (open) and minima (closed) of the measured spectra of 40-layer (triangles), 80-layer (squares), and 120-layer LB films. Lines were calculated from Eq. (1) (straight lines) and Eq. (2) (dashed lines) with $t = 1.7$ nm and $n = 1.6$ and $h = t$ (thickness of one layer) $\times\ l$ (number of layers). Roman numerals show orders of interference (the m value in Eqs. (1) and (2)).

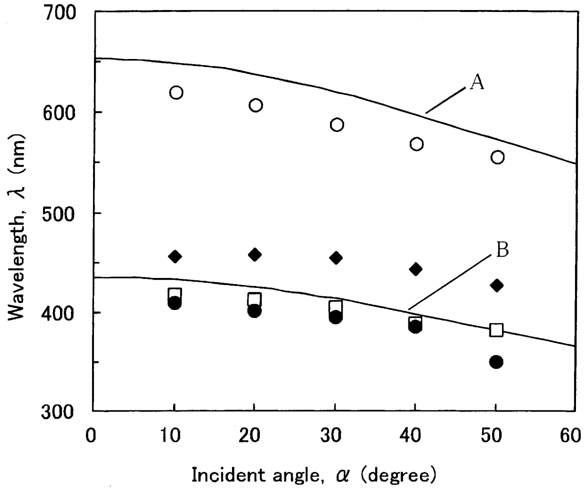


Fig. 8. Measured and calculated positions of maxima and minima in the reflection spectra as a function of incident angle. Measured ones are shown by dots; minima of the spectra of 40-layers LB films (◆), maxima of the spectra of 80-layer LB films (□), maxima of the spectra of 120-layer LB films (○), and minima of the spectra of 120-layer LB films (●). Line A was calculated by Eq. (1) with $l = 120$ and $m = 1$. Line B was calculated by Eq. (1) with $l = 80$ and $m = 1$ or Eq. (2) with $l = 40$ and $m = 1$, or Eq. (2) with $l = 120$ and $m = 2$ (these three curves are completely overlapping with each other). Both lines were calculated with $t = 1.7$ nm, $h = t \times l$ and $n = 1.6$.

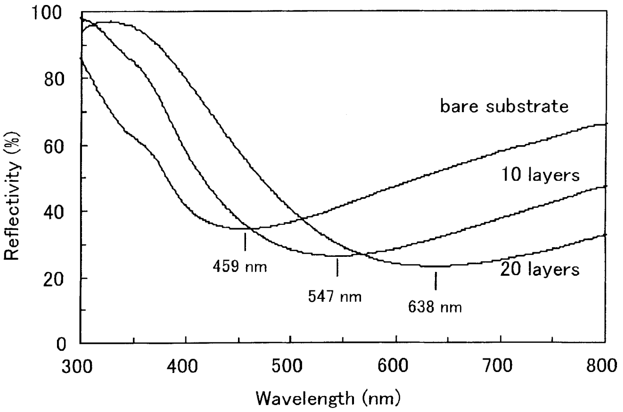


Fig. 9. Reflective VIS spectra of bare pre-colored substrate and 10- and 20-layer PHeLG LB films on the pre-colored substrate. Incident angle was 10°.

shows a minimum at 459 nm, which is brown, complementary color of blue. The LB films of 10 and 20 layers show minima at 547 and 638 nm. Therefore, their colors were red-purple or blue as complementary colors of green and orange. Because the refractive indices of PHeLG and SiO_2 are similar to each other ($\sim$1.5), SiO_2 layer can be regarded as polymer LB films in terms of interference of light.

4. Conclusion

In this study, we confirmed the ability of artificial polypeptide as a material for the color display system. PHeLG layers could be deposited on a hydrophobic substrate by LB method, and showed various interference colors depending on the number of layers. It is also confirmed that the required number of layers can be controlled by use of pre-oxidized substrate when a particular color is needed. Thus, the base for preparation of chameleon-type display system was established.

We are trying to prepare the polypeptide layer that changes its molecular orientation by stimuli. We have already succeeded in orienting α-helical polypeptide not only in the parallel direction but also in the perpendicular direction with respect to the surface of the substrate. Next, we will introduce functional moieties that can be transformed by stimuli (light, etc.) into this system. This will enable us to control the molecular orientation using stimuli (Fig. 10), which may change the thickness or refractive index of the film. Several examples of the polymer thin layers including azobenzene moiety were reported [12,19]. They could change their refractive index [12] or morphology [19] of surface. Therefore, the novel display system may be created in such a way with the knowledge obtained in this study.

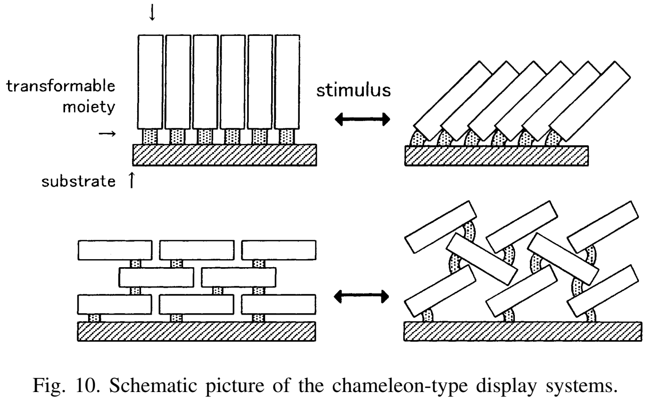


Fig. 10. Schematic picture of the chameleon-type display systems.

Acknowledgements

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References

[1] H. Ghiradella, Light and color on the wing: structural colors in butterflies and moths, Appl. Opt. 30 (1991) 3492–3500.

[2] B.D. Heilman, I.N. Miaoulis, Insect thin films as solar collectors, Appl. Opt. 33 (1994) 6642–6647.

[3] H. Tabata, K. Kumazawa, M. Funakawa, J. Takimoto, M. Akimoto, Microstructures and optical properties of scales of butterfly wings, Opt. Rev. 3 (1996) 139–145.

[4] E. Hecht, A. Zajac, Optics, Addison-Wesley, Reading, MA, 1974.

[5] S. Sakka, K. Kamiya, T. Yoko, Sol–gel preparation and properties of fibers and coating films, ACS Symposium Series 360, Inorganic and Organometallic Polymers, American Chemical Society, Washington, DC, 1988, pp. 345–353.

[6] K. Naitoh, Y. Ishii, K. Tsujii, Iridescent phenomena and polymerization behavior of amphiphilic monomers in lamellar liquid crystalline phase, J. Phys. Chem. 95 (1991) 7908–7915.

[7] M. Hayakawa, T. Onda, T. Tanaka, K. Tsijii, Hydrogels containing immobilized bilayer membranes, Langmuir 13 (1991) 3595–3597.

[8] H. Tabata, M. Asano, S. Shimizu, Structural color of a living things — dream fiber woven by light, Kobunshi 47 (1998) 738–741.

[9] G. Duda, A.J. Schouten, T. Arndt, G. Lieser, G.F. Schmidt, C. Bubeck, G. Wegner, Preparation and characterization of monolayers and multilayers of preformed polymers, Thin Solid Films 159 (1988) 221–230.

[10] W. Hickel, G. Duda, M. Jurich, T. Kröhl, K. Rochford, G.I. Stegeman, J.D. Swalen, G. Wegner, W. Knoll, Optical waveguides from novel polymeric Langmuir–Blodgett multilayer assemblies, Langmuir 6 (1990) 1403–1407.

[11] A. Mathy, K. Mathauer, G. Wegner, C. Bubeck, Preparation and waveguide properties of polyglutamate Langmuir–Blodgett films, Thin Solid Films 215 (1992) 98–102.

[12] M. Büchel, Z. Sekkat, S. Paul, B. Weichart, H. Menzel, W. Knoll, Langmuir–Blodgett–Kuhn multilayers of polyglutamates with azobenzene moieties: investigations of photoinduced changes in the optical properties and structure of the films, Langmuir 11 (1995) 4460–4466.

[13] H. Tanaka, T. Endo, M. Okawara, Transesterification of poly(γ-methyl-L-glutamate), Nippon Kagaku Kaishi (1973) 1770–1775.

[14] C.H. Bamford, A. Elliott, W.E. Handy, Synthetic Polypeptides, Academic Press, New York, 1959.

[15] S. Ge, A. Takahara, T. Kajiyama, Aggregation structure and surface properties of immobilized organosilane monolayers prepared by

the upward drawing method, J. Vac. Sci. Technol. A 12 (1994) 2530–2536.

[16] M. Ejaz, S. Yamamoto, K. Ohno, Y. Tsujii, T. Fukuda, Controlled graft polymerization of methyl methacrylate on silicon substrate by the combined use of the Langmuir–Blodgett and atom transfer radical polymerization techniques, Macromolecules 31 (1998) 5934–5936.

[17] T. Miyazawa, E.R. Blout, The infrared spectra of polypeptides in various conformations: amide I and II bands, J. Chem. Phys. 83 (1961) 712–719.

[18] M. Tsuboi, Infrared dichroism and molecular conformation of α-form poly-γ-benzyl-L-glutamate, J. Polym. Sci. 59 (1962) 139.

[19] T. Seki, J. Kojima, K. Ichimura, Light-driven dot films consisting of single polymer chain, J. Phys. Chem. B 103 (1999) 10338–10340.