Orientation of merocyanine dye in Langmuir-Blodgett films of mixtures of poly(γ-benzyl L-glutamate)/poly(ethylene oxide)/ poly(γ-benzyl L-glutamate) block copolymer and dye

Chong-Su Cho[1,*] and Toshihiro Akaike[2]

[1]Department of Polymer Engineering, Chonnam National University, Kwangju, 500-757, Korea
[2]Kanagawa Academy of Science and Technology, Takatsuku, Kanagawa 213, Japan, and
Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology, Midoriku,
Yokohama 227, Japan

Summary

Merocyanine dye(MD) can be spread with poly(γ-benzyl L-glutamate)/poly(ethylene oxide)/poly(γ-benzyl L-glutamate)(PBLG/PEO/PBLG) onto the air-water interface from a solvent in which the copolymer assumes a helical conformation. The expanded isotherm of the copolymer changed into compressed one with mixing of MD in the copolymer monolayer. Langmuir-Blodgett(LB) assemblies can be built up from copolymer/MD mixture layer when the helical axes of the polypeptide chains are oriented in the compression direction. The dichroic absorption of the copolymer/MD mixtures indicates that dyes are located with a preferential orientation of their molecular axes with regard to the director axis of the polypeptide.

Introduction

Langmuir-Blodgett(LB) multilayers with incorporation of dye molecules have often been investigated for the systems such as energy transfer(1), photoelectric effects(2), optical communication(3,4), or other physicochemical studies. Combining suitable properties of dye compounds can be done by simply mixing the compound in the spreading solution, by attaching the active dye chemically to the polymers, or by making alternate layers of polymers and dye species.

Stroeve et al.(5) have mixed merocyanine dye(MD) with poly(methacrylate) on the water surface. They have found that the films showed no evidence of aggregate formation. Schoondorp et al.(6) have found that mixtures of dye with amylose acetate formed stable monolayers whereas dye did not form a stable one at 23°C at the air-water interface. Duda et al.(7) have reported that oleophilic dyes can be cospread with copoly(γ-n-alkyl L-glutamates) onto the air-water interface from a solvent in which the copolyglutamate assumes α–helical conformation.

We have recently reported(8) that monolayers of the triblock copolymers consisting of poly(γ-benzyl L-glutamate)(PBLG) as the hydrophobic group and polyether as the hydrophilic one could be formed. Moreover, we observed that the block copolymer films were formed as oriented state of the polymer chains by the LB technique and the orientation is dependent on the content of polyether in the block copolymers(9).

---

*Corresponding author

Fig. 3 shows the F-A isotherm curves of the PBLG/PEO-1 copolymer and copolymer/MD mixtures. It can be seen that the plateau regions disappeared in the block copolymer monolayer because the PEO component is in a liquid-like conformation and has a plasticizing effect on the block copolymer main chains(8), reappeared after mixing of MD with block copolymer. The apparent plateaus of the PBLG/PEO-1/MD mixture increases with an increase of MD mol per one mole of PBLG/PEO-1 in the mixture. The plateau regions for PBLG/PEO-1/MD-0.1(0.1 mol per one mole of PBLG/PEO-1 repeating unit), PBLG/PEO-1/MD-0.2(0.2 mol) and PBLG/PEO-1/MD-0.3(0.3 mol) are 10.8, 15.8 and 16.8 dyne/cm, respectively. It might be regarded that the expanded type of the pure copolymer changed into compressed type with mixing of MD into copolymer monolayer and the rigidity of the copolymer monolayer increased with an increase of MD content in the mixture.
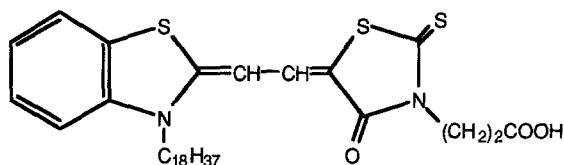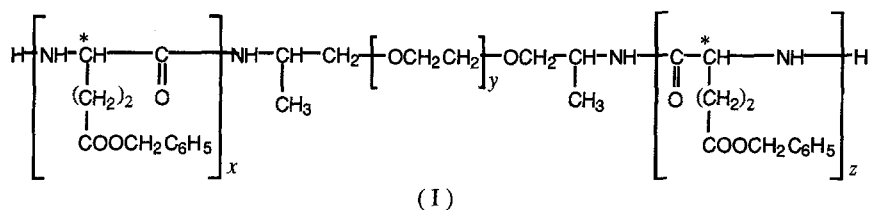

(I)

(II)

Fig. 1 Chemical structure of PBLG/PEO/PBLG copolymer(I) and MD(II).

Mixtures of PBLG or PBLG/PEO-1 with MD at different concentrations could be transferred by the LB technique onto quartz substrate whereas mixtures of PBLG/PEO-2(PEO: 35.6 mol-%) or PBLG/PEO-3(PEO: 73.8 mol-%) with MD could not be transferred at 10 dyne/cm. In previous study(13), circular dichroism(CD) spectra of LB films for the PBLG and PBLG/PEO-1 changed radically both in shape and in magnitude in response to the rotation of sample whereas CD spectra of LB films for the PBLG/PEO-2 and PBLG/PEO-3 did not change both in shape and magnitude as the films were rotated. These results indicated that there were close relationship between orientation of α-helical structure of PBLG in the LB films and transferring onto the substrate.

UV spectra of LB layers consisting of MD and PBLG/PEO-1 with polarized light parallel and perpendicular to the compression direction is shown in Fig.4. We observed a shift of wavelength of the maximum λ(max) of the absorption band from 520 nm to 504 for light polarized parallel and to 508 nm for light polarized

In this study, we wish to clarify orientation of MD in the mixtures of copolymer/dye LB layers. Cyanine dyes known to form different types of aggregates(10) are nonlinear optical dyes. Therefore, the mixtures of copolymer/dye LB film can be considered as applied optics. Also, such a material provided by the copolymer can be used as a solvent matrix for oleophilic molecules.

Experimental

The PBLG homopolymer was obtained by polymerization of γ-benzyl L-glutamate N-carboxyanhydride(γ-BLG NCA) initiated by triethylamine in 1,4-dioxane in a mole ratio of 25/1.

PBLG/PEO/PBLG block copolymers(I) were prepared by polymerization of γ-BLG NCA initiated with amine-terminated PEO in methylene dichloride by the same method as that described previously(11).

MD(II) was kindly supplied by Nippon Kankoh Shikiso Kenkyusho, Okayama, Japan.

The copolymer and the dye were codissolved in chloroform. The concentration of the dye was adjusted between 0 and 0.3 moles per mole of repeating unit of the polymer.

Surface pressure was measured by the Wilhelmy hanging plate method and the sensor plate was placed on the end position at 3 cm from the wall of trough. The compression of the monolayer was made by a moving barrier by the same procedure as that described previously(12). The monolayers were spread from chloroform solutions on the surface of double-distilled water. Isotherms were measured using a barrier speed of 15 mm/min after 10 min at 20°C. A stable pressure was observed when a constant area was maintained.

Monolayers on the water surface were transferred onto quartz plate by the horizontal lifting method, with some alternations to that reported previously(12), at surface pressure of 10 dyne/cm. Monolayers were transferred only when the quartz plate was lowered in solution, i.e., the X-type deposition. The transfer ratios were found to be reproducible and 1.2 and 0.99 for PBLG/MD and PBLG/PEO-1/MD(PEO: 22.4 mol-%), respectively. A constant pressure of 10 dyne/cm was maintained during transferring to the plate.

UV spectra were obtained from multilayers on quartz plate with polarized light parallel and perpendicular to the compression direction.

Results and discussion

Fig.2 shows the F-A isotherm curves of the pure PBLG homopolymer and PBLG/MD mixtures spread on the water surface from chloroform solution. The trend of the curves of PBLG/MD mixtures is almost similar to that of PBLG. But the apparent plateaus of PBLG which are regions of very high compressibility increases with an increase of MD mol per one mole of PBLG in the mixture. The plateau regions for PBLG, PBLG/MD-0.1(0.1 mol per one mol of PBLG repeating unit), PBLG/MD-0.2(0.2 mol) and PBLG/MD-0.3(0.3 mol) are 7.5, 11.5, 14.0 and 14.8 dyne/cm, respectively. These results may be attributed to the increased stability of PBLG monolayer with mixing of MD. It may be expected that the limiting areas for the PBLG/MD mixtures become larger than for pure PBLG. But the limiting areas for PBLG/MD mixtures decreased with an increase of MD in the mixture except PBLG/MD-0.1.
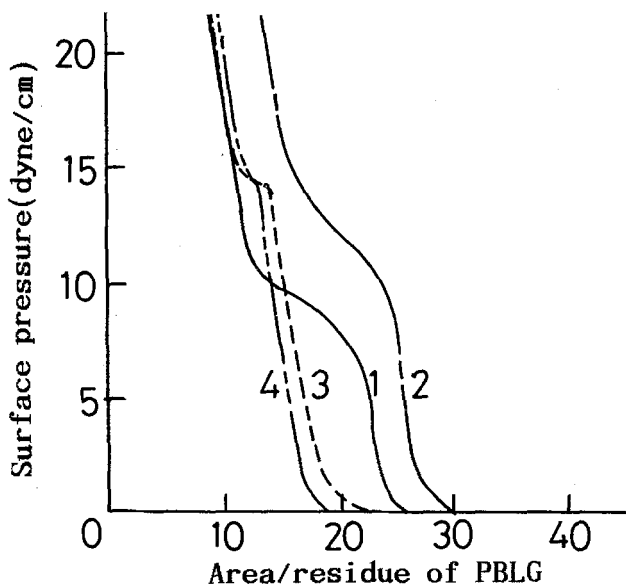
Fig. 2 Surface pressure-area isotherms of PBLG and PBLG/MD(1: PBLG, 2: PBLG/MD-0.1, 3: PBLG/MD-0.2 and 4: PBLG/MD-0.3).
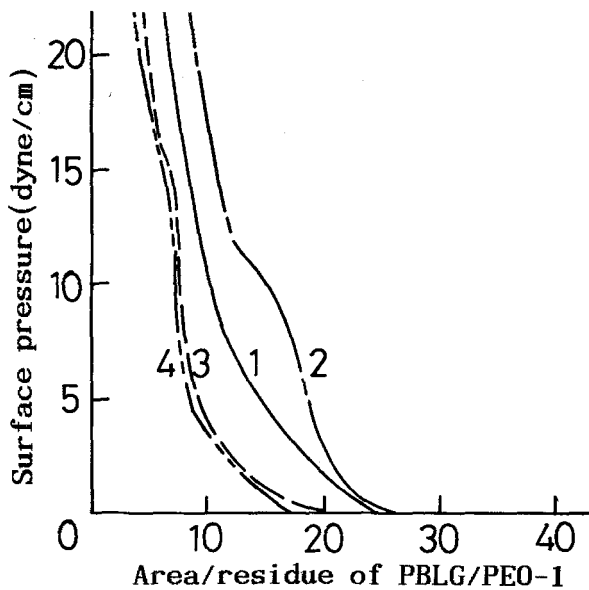

Fig. 3 Surface pressure-area isotherms of PBLG/PEO-1 and PBLG/PEO-1/MD(1: PBLG/PEO-1, 2: PBLG/PEO-1/MD-0.1, 3: PBLG/PEO-1/MD-0.2 and 4: PBLG/PEO-1/MD-0.3).
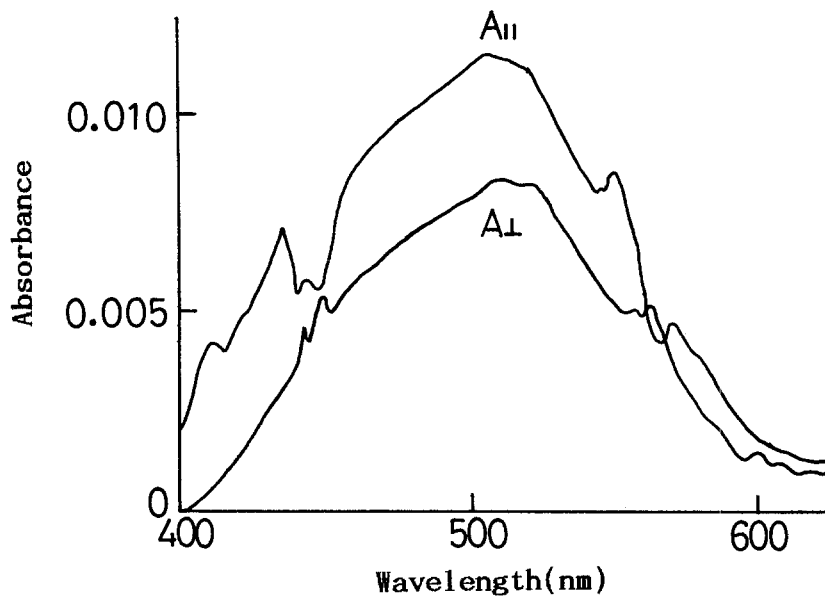
Fig. 4 UV spectra of PBLG/PEO-1/MD LB layers.
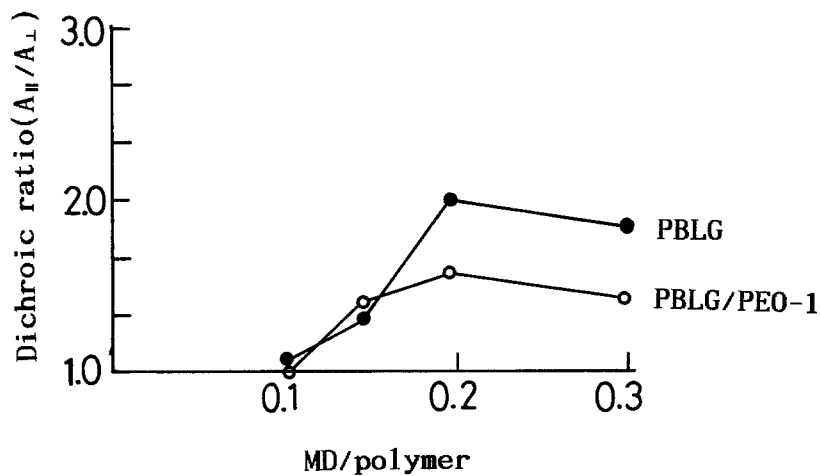(transferred onto the quartz at 10 dyne/cm, 20 mol-% MD and 20 layers)

Fig. 5 Dichroic ratio $A_{II}/A_{\perp}$ at 500nm.

perpendicularly to the compression direction. The value 520 nm refers to λ(max) of the UV spectra with non-polarized light(14). This indicates that MD is oriented preferentially with the longest axis normal to the PBLG α-helical axis. But it is not clear that the oriented MD in the PBLG α-helical axis adopts helical structure although the helical conformation of PBLG obtained by CD measurement(not shown in the Fig.) in the PBLG/MD or PBLG/PEO-1/MD mixtures was not changed. Also, J-band(around 600 nm) due to the aggregate of MD(14) which appeared in the lipid/MD mixed monolayers was not observed in this LB films although the dimer form of MD as shown in around 445 nm(15) was observed as shoulder.

The dichroic ratio $A_{||}/A_{\perp}$ was at 500 nm versus mole ratio of MD per polymer repeating unit for the mixtures of MD/polymer in the form of LB layers are shown in Fig.5. The highest dichroic ratio $A_{||}/A_{\perp}$ was achieved when the concentration of MD was 20 mol-%. This value is equivalent to approximately one molecule of the dye per two turns of the helix because there are 3.6 repeating units per pitch of the α-helix. The higher dichroic ratio was obtained for the PBLG than PBLG/PEO-1.

References

1. H.Kuhn, D.Mobius, H.Bucker, in: "Physical Methods of Organic Chemistry", edited by A.Weissberger, vol.1, part 3B, Wiley-Interscience, New York 1972
2. M.Saito, M.Sugi, T.Fukui, S.Iizima, *Thin Solid Films*, **100**, 107(1983)
3. L.M.Hayden, S.T.Kowel, M.P.Srinivasan, *Opt.Commun.* **61**, 351(1987)
4. D.S.Chemla, J.Zyss, Eds., Nonlinear Optical Properties of Organic Molecules and Crystals; Academic Press:New York, 1987; Vols.1 and 2.
5. P.Stoeve, M.P.Srinivasan, B.G.Higgins, S.T.Kowel, *Thin Solid Films*, **146,** 209(1987)
6. M.A.Schoondorp, A.J.Schouten, J.B.E.Hulshof, B.L.Feringa, G.T.Oostergetel, *Langmuir*, **8**, 1817(1992)
7. G.Duda, G.Wegner, Makromol.Chem., *Rapid Commun.* **9**, 495(1988)
8. C.S.Cho, R.Nagata, A.Yagawa, S.Takahashi, M.Kunou, T.Akaike, J.Polym.Sci.:*Polymer Letters*, **28**, 89(1990)
9. C.S.Cho, S.C.Song, M.Kunou, T.Akaike, *J.Colloid and Interface Sci.*, **137**, 292(1990)
10.D.M.Sturner, in: "The Chemistry of Heterocyclic Compounds", edited by A.Weissberger and E.C.Tayer, vol.30, Wiley, New York, 1977, p 441.
11. C.S.Cho, S.W.Kim, T.Komoto, *Makromol.Chem.*, **191**, 981(1990)
12. T.Fururo, H.Sasabe, R.Nagata, T.Akaike, *Thin Solid Films*, **133**, 141(1985)
13. C.S.Cho, T.Akaike, Thin Solid Films, To Be Submitted
14. H.Nakahara, H.Uchimi, K.Fukuda, N.Tamai, I.Yamazaki, *Thin Solid Films*, **178**, 549(1989)
15.H.Bucher, K.H.Fleck, M.Kuhn, D.Mobius, F.P.Schafer, J.Sondermann, W.Sperling, P.Tillman and J.Wiegand, *Molec.Crystals*, **2**, 199(1967)