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Chiral Molecular Recognition in Polymer Langmuir–Blodgett Films Containing Axially Chiral Binaphthyl Groups

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Abstract: Axially chiral binaphthalene chromophores (BN) can be incorporated into polymer Langmuir–Blodgett (LB) films as comonomers of *N*-alkylacrylamides which have an excellent ability to form stable monolayers and LB multilayers. The spreading behavior of the copolymers of (*S*)-2-methoxy-1,1′-binaphthalen-2′-yl methacrylate ((*S*)-MeBN) or (*S*)-2-hydroxy-1,1′-binaphthalen-2′-yl methacrylate ((*S*)-HOBM) with *N*-decyl- (DA), dodecyl- (DDA), or tetradecylacrylamide (TDA) was investigated by a measurement of the surface pressure–area isotherms. The isotherms show that the copolymers, especially DDA copolymers, form a stable condensed monolayer on pure water and the axially chiral binaphthalene chromophore is dispersed uniformly, having its own surface area on water when the mole fraction of BN is less than ca. 20 mol %. The copolymer monolayers could be transferred onto solid supports successively by the Langmuir–Blodgett technique (Y-type deposition). The strong CD (circular dichroism) spectra consisting of positive first and negative second Cotton effects were observed for the LB films, supporting the (*S*)-configuration of the chiral binaphthyl chromophore. The enantioselective response of the chiral copolymer LB films to optically active 1-phenylethylamine (PEA) was investigated by an electrochemical potentiometric method. The electrodes modified with the copolymer monolayers induced a very sensitive potential change on addition of PEA. The electrode with (*S*)-HOBN copolymer monolayers showed a large chiral discrimination to distinguish between (*R*)- and (*S*)-PEA, whereas the (*S*)-MeBN copolymers showed no discrimination. The mechanism for the chiral molecular recognition is discussed.

Introduction

Biological membranes perform specialized functions such as highly selective transport of solutes and highly sensitive and selective responses to external stimulation, where molecular recognition is an important factor.[1] Molecular recognition in ordered molecular assembly systems mimicking biomembranes has therefore been studied not only to elucidate biological processes but also to realize biomimetic functions in technologically useful devices such as chemical sensors or biosensors, various kinds of transducers, and ion-selective membranes.[2,3] Moreover, chiral recognition in organized molecular assemblies has received much attention recently.[4–6]

The Langmuir–Blodgett (LB) technique can provide organized molecular assemblies with well-defined molecular orientation and ordered layer structure similar to that of biological membranes.[7] The introduction of molecular recognition sites, especially chiral sites, into LB assemblies is desired from the standpoint of designing an organized molecular assembly system capable of discriminating chiral substrates or biomaterials. In spite of these interesting features, there has been no success in preparation of LB film showing chiral discrimination. First the difference in spreading behavior of chiral phospholipid monolayers on the air/water interface, which is monitored by surface pressure–area isotherms, was reported.[8,9] Arnett *et al.* have extensively studied chiral molecular recognition in monolayers of amino acid derivatives by surface pressure–area measurements and surface shear viscosities.[6,10–12] Vodyanoy *et al.* have elucidated the chiral recognition of enantiomeric molecules of an odorant carvone by phospholipid monolayers by monitoring the changes in the surface pressure–area isotherms.[13] No study on chiral molecular recognition by the monolayers transferred onto a solid substrate or Langmuir–Blodgett multilayers has been reported as yet.

Recently we have found that *N*-alkylacrylamide series have an excellent ability to form a stable condensed monolayer and LB multilayer in both the monomer and polymer forms.[14,15] Moreover, we have proposed a method to incorporate various functional groups into the polymer LB assemblies as a comonomer of *N*-dodecylacrylamide (DDA), which forms the most stable condensed monolayer.[16] In the previous preliminary study, an axially chiral binaphthyl group was incorporated into the DDA polymer monolayer by the copolymerization method, giving optically active polymer LB multilayers.[17] In the present study, various *N*-alkylacrylamide copolymers containing axially chiral binaphthyl groups (2-methoxy- or 2-hydroxy-substituted derivatives) (**1a–f** and **2a–f** in Scheme I) have been prepared to

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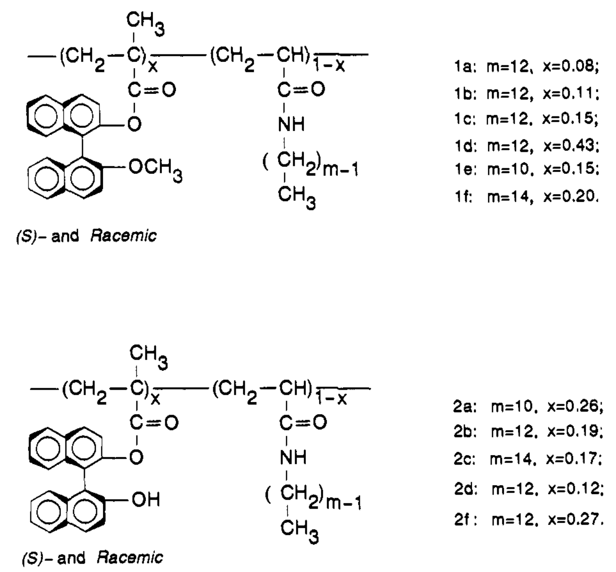
Scheme I



1a: m=12, x=0.08;
1b: m=12, x=0.11;
1c: m=12, x=0.15;
1d: m=12, x=0.43;
1e: m=10, x=0.15;
1f: m=14, x=0.20.

2a: m=10, x=0.26;
2b: m=12, x=0.19;
2c: m=14, x=0.17;
2d: m=12, x=0.12;
2f: m=12, x=0.27.

investigate the monolayer and Langmuir–Blodgett film formation of the optically active copolymers in detail. Moreover, enantioselective recognition by the copolymer monolayer containing the (*S*)-2-hydroxybinaphthalene group transferred onto a solid support (electrode) was realized for the first time as discrimination in the output potential response to optically active isomers.

Experimental Section

Materials. Homochiral (*S*)-1,1′-binaphthalene-2,2′-diol ((*S*)-OH) was purchased from Nakarai Chemicals Co., Ltd., and used as received. (*S*)-2-Hydroxy-1,1′-binaphthalen-2′-yl methacrylate ((*S*)-HOBN) was synthesized from the reaction of (*S*)-OH and methacryloyl chloride in the presence of Et_3N in dry CH_2Cl_2. The reaction mixture was washed with 2 N HCl, 2 N $NaHCO_3$ (aqueous), and distilled water and then dried with Na_2SO_4. The product was purified by column chromatography (eluent: chloroform). ^1H NMR ($CDCl_3$) $\delta = 1.6$ (s, 3H, CH_3), 5.17 (br, 1H, OH), 5.33 (m, 1H, C=CH), 5.7 (s, 1H, C=CH), and 7.05–8.10 (m, 12H, Ar-H); IR (KBr) 3430 (OH), 1724 cm^{-1} (C=O). The synthesis of (*S*)-2-methoxy-1,1′-binaphthalen-2′-yl methacrylate ((*S*)-MeBN) is described elsewhere.[18] The copolymers of (*S*)-HOBN or (*S*)-MeBN with *N*-alkylacrylamides were prepared by free-radical polymerization in benzene at 60 °C with 2,2′-azobis(isobutyronitrile) (AIBN) as a thermal initiator. The copolymers were purified by reprecipitation from filtered benzene solution into a large excess of acetonitrile and dried under vacuum at room temperature. The copolymer compositions were determined by ^1H NMR and UV spectroscopy. Optically active 1-phenylethylamines ((*S*)- and (*R*)-PEA) were purchased from Wako Pure Chemical Industries, Ltd.: (*R*)-PEA $[\alpha]^{20}_D = +38.0$ ($c = 2$, ethanol); (*S*)-PEA $[\alpha]^{20}_D = -38.0$ ($c = 2$, ethanol).

Spectroscopic Measurements. Optical rotations were obtained at ambient temperature (20–25 °C), using a Union Giken PM-101 polarimeter. CD spectra were measured at room temperature on a JUSCO J400X spectropolarimeter. IR spectra were measured on a Shimadzu IR-460 infrared spectrophotometer. UV absorption spectra were measured on a Shimadzu UV-160 spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC-250T instrument at 250 MHz. GPC measurements were carried out at 39 °C on a Tosoh HLC-802UR instrument equipped with TSK gel G5000H8, G4000H8, and G3000H8 columns using THF as an eluent.

Measurements of Surface Pressure–Area Isotherms. The measurement of surface pressure (π)–area (A) isotherms and the deposition of the monolayers were carried out with an automatic Langmuir trough (Kyowa Kaimen Kagaku HBM-AP using a Wilhelmy-type film balance). Distilled, deionized water was used as the subphase. The chloroform used for spreading monolayers on the water surface was of spectroscopic grade. The quartz slides, on which the LB multilayer was deposited, were cleaned in a boiling H_2SO_4–HNO_3 (2:1) solution and made hydrophobic with dichlorodimethylsilane. The deposition of monolayers was performed by means of the vertical dipping method. The monolayers were transferred onto solid substrates at a surface pressure of 20 mN/m and a deposition rate of 5 mm/min. The transfer ratios were unity (1.0 ± 0.1).

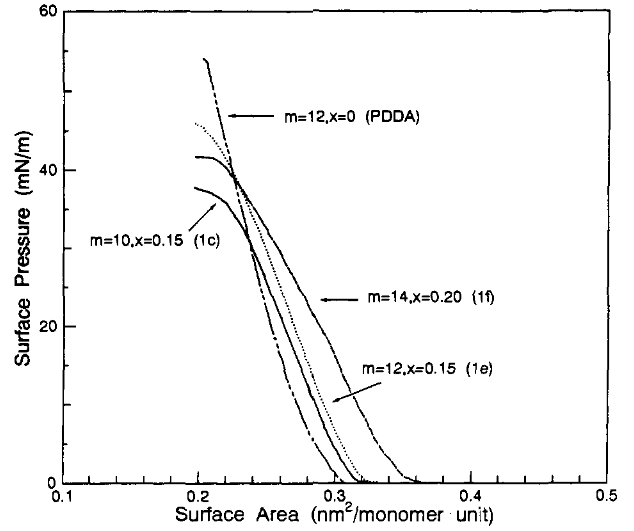


Figure 1. Surface pressure–area isotherms of **1c**, **1e**, **1f**, and PDDA homopolymer at 15 °C.

Electrode Modification and Potential Measurement. The electrodes were modified by deposition of one monolayer of **1a**, **1b**, or **1c** onto ITO electrodes (20 × 50 mm, CELEC K-LC, Daicel Ltd.). The potential of the modified electrodes against the SCE (saturated calomel electrode) reference electrode was monitored at room temperature on a HA-104 potentiostat electrometer (Hokuto Denko Ltd.). Aqueous Na_2SO_4 (0.10 M) was used as a supporting electrolyte. The solutions were deaerated by N_2 bubbling before measurement.

Results and Discussion

Monolayer and Multilayer Formation. Copolymers having various lengths of alkyl side chains and copolymer compositions were prepared, and the spreading behavior was examined by measuring surface pressure–area isotherms. Figure 1 shows the π–A isotherms for the copolymer monolayers of (*S*)-MeBN with *N*-decyl-, *N*-dodecyl-, or *N*-tetradecylacrylamide having similar copolymer compositions. The π–A isotherms indicate that all the copolymers form condensed monolayers with a steep rise in surface pressure and high collapse pressure. The most well-defined condensed monolayer was obtained with the copolymer of *N*-dodecylacrylamide (DDA). This result coincides with the properties of the corresponding homopolymer monolayers;[15] that is, in the hydrophobic–hydrophilic balance for the monolayers of preformed poly(*N*-alkylacrylamides) having alkyl chains from hexyl to octadecyl, the dodecyl chain is most preferred for condensed monolayer formation. The π–A isotherms for the DDA copolymers were measured also as a function of (*S*)-MeBN mole fraction (Figure 2). Apparently the isotherms change with the (*S*)-MeBN mole fraction: the slope for the rise in surface pressure becomes smaller, and the collapse pressure also decreases with the mole fraction. Due to the introduction of the (*S*)-MeBN comonomer, which is nonamphiphilic, into PDDA, the copolymer monolayers tend to be unstable. All copolymers, however, with mole fraction of (*S*)-MeBN less than 0.2 form stable monolayers which can be transferred onto solid substrates, giving Y-type LB multilayers.

The average limiting surface area per monomer unit is defined as the water surface area occupied by a monomer unit of the copolymer monolayer. It can be estimated from the isotherms by extrapolating the steeply rising parts of the surface pressure curves to zero surface pressure. The average limiting area obtained from Figure 2 was plotted against the (*S*)-MeBN mole

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[18] Tamai, Y.; Qian, P.; Matsunaga, K.; Miyano, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 817–823.

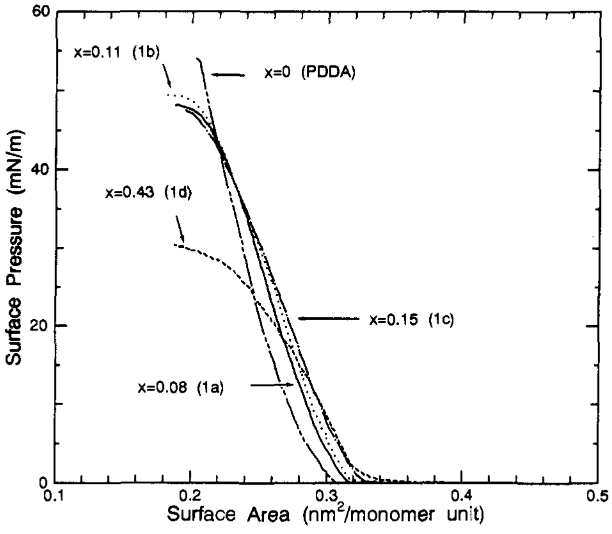

Figure 2. Surface pressure–area isotherms of DDA copolymers with (*S*)-MeBN having various copolymer compositions and PDDA homopolymer at 15 °C.

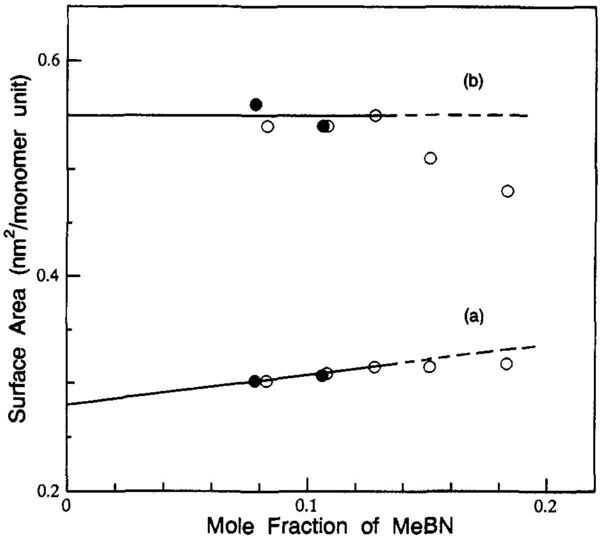

Figure 3. Average limiting surface area per monomer unit (a) and calculated surface area per MeBN monomer unit (b) for (*S*) (○) and racemic (●) copolymers.

fraction, giving a straight line up to ca. 0.2 (*S*)-MeBN mole fraction (Figure 3). Since the area for a DDA monomer unit is determined to be 0.28 nm²/monomer from the isotherm of PDDA homopolymer,[15] the area for (S)-MeBN can be estimated from the average values and the mole fractions. A constant surface area of ca. 0.55 nm²/monomer for (*S*)-MeBN was obtained for the copolymers with mole fraction less than 0.15 (Figure 3). The determined area (0.55 nm²) is consistent with the value estimated from a space-filling molecular (CPK) model shown in Figure 4, where the polymer main chain is laid horizontally on the water surface and the binaphthyl group tends to orient away from the water surface and toward air. A similar orientation of the copolymers has also been proposed for PDDA homopolymer,[15] the styrene/DDA copolymer,[16a] and the carbazole/DDA copolymer.[16b] The determined surface areas for DDA, styrene, and vinylcarbazole are 0.28, 0.16, and 0.34 nm²/monomer, respectively, which are consistent with the corresponding CPK molecular models. The results of π–A isotherms support that the (*S*)-MeBN monomer unit in the copolymer monolayer occupies a constant surface area on the water surface of the copolymers with MeBN mole fraction less than 0.15. If the copolymer chain has a folded or coiled form on the water surface, the area allotted to the (*S*)-MeBN monomer unit becomes smaller and changes

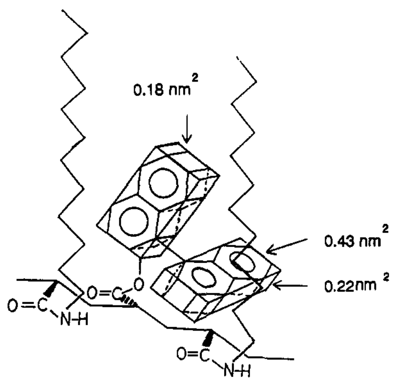

Figure 4. Most probable orientation of the binaphthyl group in the monolayer.

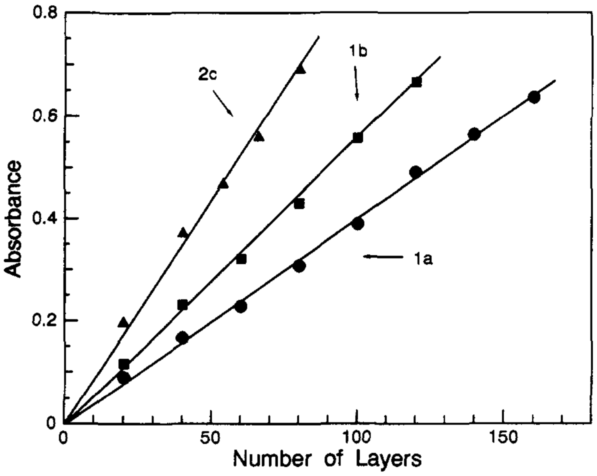

Figure 5. Linear relationships between the absorbance and the number of layers in **1a** ($m = 12, X = 0.08$), **1b** ($m = 12, X = 0.11$), and **2c** ($m = 14, X = 0.17$) LB films.

with the copolymer compositions. The surface area for the copolymer with (*S*)-MeBN mole fraction more than 0.15 deviates from 0.55 nm² to a smaller value. This means that the copolymers begin to have a slightly coiled form in the monolayers. The copolymer of DDA with styrene forms a stable monolayer up to the 0.6 mole fraction of styrene, giving a constant surface area for styrene (0.16 nm²). The (*S*)-MeBN monomer is larger than styrene, disturbing the more stable monolayer formation of PDDA. Similar results for the copolymers with (*S*)-HOBN were obtained, except that the surface area for the binaphthyl group was 0.44 nm². The (*S*)-HOBN copolymers also exhibit well-defined behavior toward the monolayers with 0.2 mole fraction of binaphthalene.

The properties of the monolayers formed from the copolymers with *rac*-binaphthalenyl methacrylate were also investigated. The π–A isotherms for the racemic copolymers were completely identical with those of the copolymers of the (*S*)-isomer (Figure 3). Physical properties of the copolymer monolayers appear not to be influenced by the stereochemical configuration.

Absorption and CD Spectra of the Copolymer LB Films. The condensed copolymer (**1** and **2**) monolayers can be transferred onto quartz slides with a transfer ratio of 1.0, yielding Y-type LB films. The electronic absorption spectra show typical absorption bands (^1B_b, ^1L_a, and ^1L_b) due to the binaphthyl group at 228, 285, and 325 nm, respectively. A linear relationship between the absorbance at 228 nm and the number of transferred layers for the LB films was observed (Figure 5), indicating that regular and homogeneous deposition of the monolayer takes place. The slopes of the linear relationship for **1a** ($m = 12, X = 0.08$), **1b** ($m = 12$, $X = 0.11$), and **2c** ($m = 14, X = 0.17$) copolymer LB films give 4.01×10^{-3}, 5.6×10^{-3}, and 9.32×10^{-3} absorbance per layer,

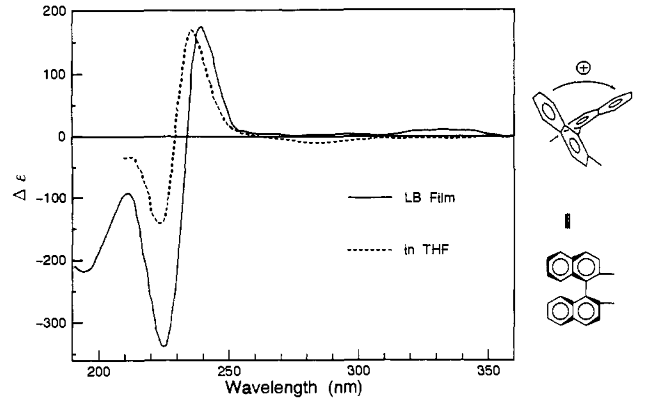

Figure 6. CD spectra of **2c** copolymer in THF (- - -) and LB film (—).

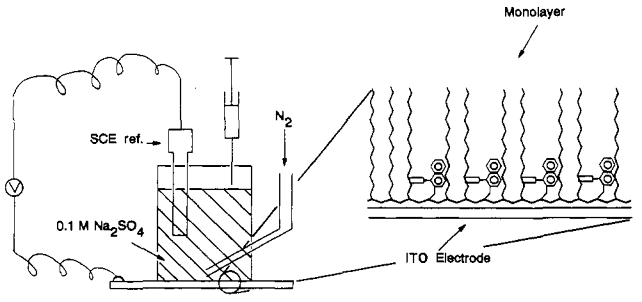

Figure 7. Setup for electrochemical potential measurement of monolayer-modified electrode.

respectively. The molar extinction coefficient (ε) can be calculated from the slope to be $8.53 \pm 0.27 \times 10^4\ M^{-1}\ cm^{-1}$ using the following two-dimensional Lambert–Beer's equation

$$\mathrm{OD} = \epsilon n/N = (1.66 \times 10^{-21})\epsilon n$$

where OD, n, and N are absorbance per layer, two-dimensional density of molecule (cm^{-2}), and Avogadro's number, respectively. The ε values were consistent with those taken in solution. This means that the binaphthyl group is uniformly dispersed in LB films.

A strong CD (circular dichroism) spectrum consisting of positive first and negative second Cotton effects due to coupling of the ^1B_b transition (228 nm) was observed for the LB films (Figure 6). The Cotton effect supports the (*S*)-configuration of the chiral binaphthyl chromophore with a dihedral angle of around 90°.[19] The CD spectra are consistent with that taken in tetrahydrofuran solution and that for the starting binaphthol compound, (*S*)-1,1′-binaphthalene-2,2′-diol, confirming that an axially chiral binaphthyl group can be safely introduced into the polymer LB films. Well-defined and highly ordered ultrathin polymer films having a potential chiral molecular recognition site were prepared conclusively. In the following section, the chiral recognition response of the chiral LB films to optically active isomers is investigated.

Chiral Discrimination Response of the Copolymer LB Films. The enantioselective response of the chiral copolymer LB films to optically active isomers was measured by means of an electrochemical potentiometric method. Figure 7 shows the setup for the electrochemical measurement. One layer of the (*S*)-HOBN copolymer monolayer (**2f**) is transferred from the hydrophilic surface onto an ITO electrode. The monolayer electrode is contacted with an electrolyte aqueous solution (0.1 M Na_2SO_4), the potential being monitored against the SCE reference electrode. The potentials of the monolayer-modified electrode are changed by the interaction between the monolayer and added species on the electrode surface in an anodic or cathodic direction, depending on the nature of the charged species. When optically active 1-phenylethylamine (PEA) is added to the electrolyte solution, the electrode potential vs SCE reference is shifted to the cathodic direction and the potential reaches a constant level after a few minutes (Figure 8). The cathodic shift of the potentials indicates that the monolayer electrode is charged negatively against the SCE reference in the presence of PEA. Even in dilute solutions (≈10^{-7} M), the monolayer electrode induces a marked potential change, showing a high sensitivity of the electrode to PEA (Figure 8). The potential changes of the electrode modified with the DDA and TDA copolymer monolayers are plotted as a function of the concentration of 1-phenylethylamine in Figures 9 and 10, respectively. Apparently the potentiometric responses are discriminated by (*R*)- and (*S*)-isomers in low concentration; that is, the potential changes caused by addition of (*R*)-PEA are larger than those for (*S*)-PEA. This means that (*R*)-PEA is able to interact (bind) more strongly with the chiral monolayer having an (*S*)-configurational binaphthyl group on the electrode surface. Moreover, the monolayer of copolymer (TDA) having a longer alkyl side chain showed larger

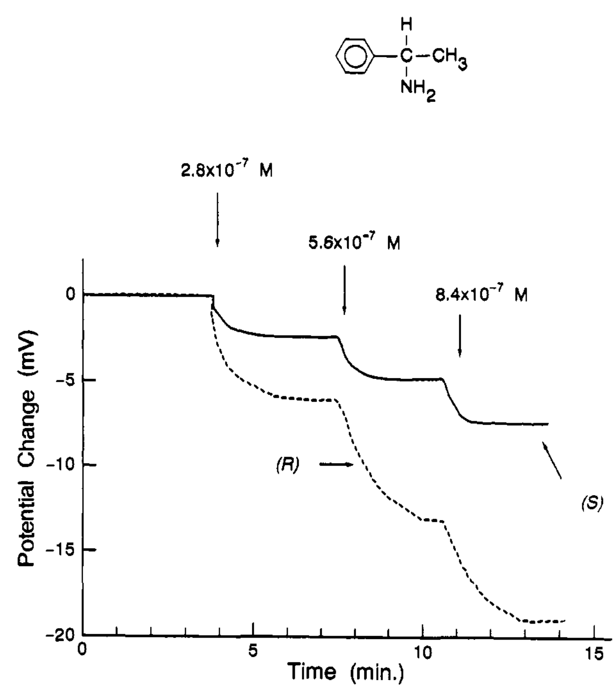

Figure 8. Potential change by addition of (*S*)- and (*R*)-PEA.

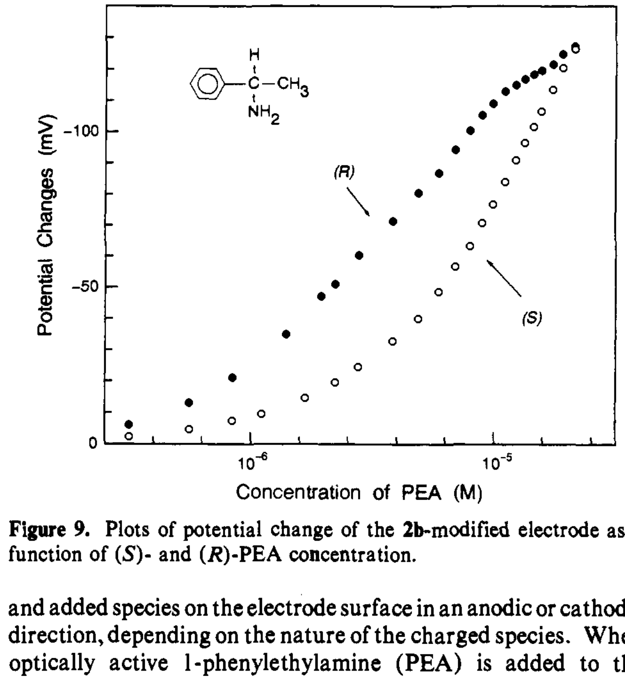

Figure 9. Plots of potential change of the **2b**-modified electrode as a function of (*S*)- and (*R*)-PEA concentration.

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[19] Harada, N.; Nakanishi, K. *Circular Dichroic Spectrsocopy—Extion Coupling in Organic Stereochemistry*; University Science Books: Oxford, 1983.

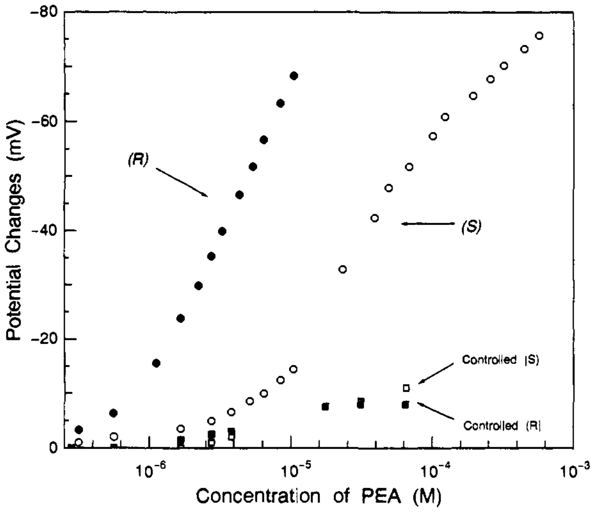

Figure 10. Plots of potential change of the **2c**-modified electrode and an unmodified electrode (control) as a function of (*S*)- and (*R*)-PEA concentration.

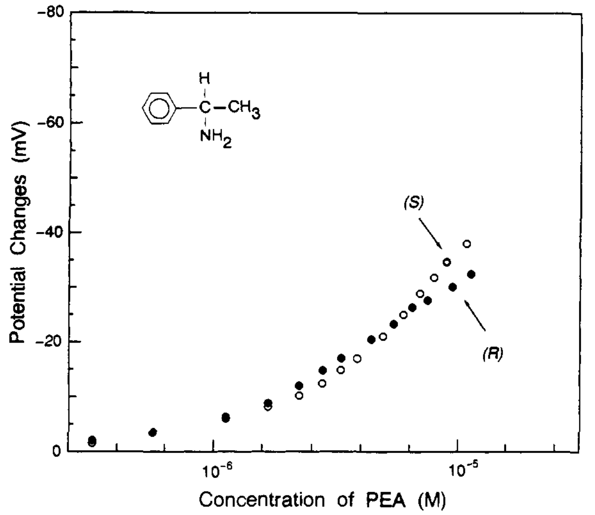

Figure 11. Plots of potential change of the **1b**-modified electrode as a function of (*S*)- and (*R*)-PEA concentration.

chiral discrimination between (*R*)- and (*S*)-isomers, compared with the DDA copolymer monolayer electrode (Figures 9 and 10). On the other hand, the electrodes covered with (*S*)-MeBN copolymer monolayers instead of (*S*)-HOBN copolymers showed no discrimination response toward (*R*)- and (*S*)-PEA (Figure 11). (*S*)-HOBN has an acidic hydroxy substituent on the 2-position of the binaphthalene ring, whereas (*S*)-MeBN has a methoxy group instead of the OH. This means that electrostatic interaction between PEA and the acidic hydroxy group is important for chiral molecular recognition of the monolayers. As a control experiment, the potential response of an unmodified electrode was measured. However, a stable potential response was not obtained; that is, on addition of PEA, the potential of the electrode is first shifted to a cathodic direction and then decreases, gradually approaching a constant potential. The potential after about 15 min was plotted in Figure 10.

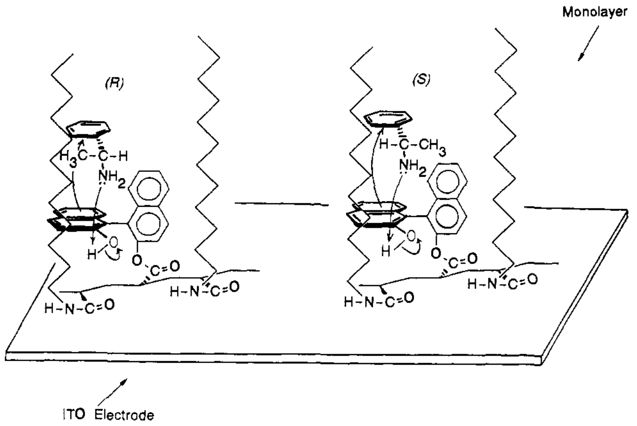

Figure 12. Schematic illustration for mechanism of chiral molecular recognition.

As the mechanism for the chiral molecular recognition, we have considered the scheme shown in Figure 12. Approach of the PEA molecule to the chiral monolayer on the electrode surface would be restricted by highly oriented hydrophobic alkyl chains. The PEA molecule appears to interact with the monolayer at two recognition sites. One is an electrostatic interaction between the amino group and acidic hydroxy group, causing cathodic (negative) potential shift; the other is a π–π electron interaction between the naphthyl ring and phenyl ring of PEA. Under the interaction, it can be understood easily that the steric hindrance of (*R*)-PEA is smaller than that of the (*S*)-isomer, because the methyl group in the (*R*)-isomer is apart from the other naphthyl group. (*R*)-PEA can bind strongly to the monolayer electrode, yielding larger electrochemical potential change. By increasing the alky chain length of the monolayers from dodecyl to tetradecyl, the approach of the PEA molecule to the monolayer may be restricted more tightly. The larger chiral discrimination by the TDA copolymers can be explained by the restriction.

Although the electrodes modified by the (*S*)-MeBN copolymer monolayers showed a potentiometric response to the addition of PEA, no chiral discrimination against the optical isomers was observed. This is due to the lack of an electrostatic interaction site in (*S*)-MeBN, where the acidic hydroxy group is replaced by a neutral methoxy group. The chiral recognition interaction shown in Figure 12 is impossible in (*S*)-MeBN copolymers.

In conclusion, chiral molecular recognition by the monolayers containing axially chiral binaphthyl groups can be realized by electrochemical potentiometric measurement. Application of this system to various chemical and biosensor devices is expected. Measurement of chiral recognition for other optically active species is currently under way.

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