

Langmuir Monolayers and Multilayered Langmuir-Blodgett Films of Main Chain Liquid Crystal Polymers Containing 1,4-bisstyrylbenzene Groups

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Langmuir monolayers and multilayered Langmuir-Blodgett (LB) films of main chain liquid crystal polymers (MCLCPs) having 1,4-bisstyrylbenzene (BSB) groups and polyoxyethylene (POE) chains were prepared. The properties of monolayers at an air-water interface can be related to the characteristics of these polymers in the bulk LC phase. The multilayered structure of the LB film is consistent with that of the smectic LC phase. In the layer, the BSB groups form the H-aggregated structure and the POE chains form the hair-pin loops.

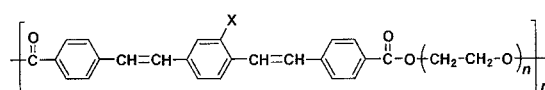
Key words: π -conjugated system, main chain liquid crystal polymer, Langmuir monolayer, multilayered Langmuir-Blodgett film, X-ray diffraction measurement

1. INTRODUCTION

Organic polymers having π -conjugated groups are attracting much interest as photonic and electronic materials^[1,2]. Organization of these π -conjugated groups into an ordered nano-structure leads to novel nano-devices^[3,4]. Langmuir-Blodgett (LB) technique has been used for the preparation of highly-ordered ultra thin films of the polymers having the π -conjugated functional groups^[5,6]. Stable monolayers at an air-water interface are usually obtained by the introduction of long alkyl chains into these polymers^[7]. In addition, nonfunctional co-surfactants often must be inserted between the functional π -conjugated groups for the fabrication of multilayered LB films^[8-11].

Amphiphilic liquid crystalline polymers (LCPs) usually have the π -conjugated groups as a mesogenic core and can form the LB films without co-surfactants. Extensive studies on the LB films of side chain LCPs have been carried out^[12,13]. However, the preparation of multilayered LB films using main chain LCPs is hardly reported because of the difficulty in forming well-packed stable monolayers.

Recently, we reported the fabrication of multilayered LB films by means of amphiphilic side chain LCPs which exhibit a smectic phase in the bulk state^[14]. The periodic multilayered structures of the LCPs can be formed through their specific amphiphilic interactions in not only 3-dimensional bulk state but also LB films. In this study, the Langmuir monolayers and the multilayered LB films of main chain LCPs having 1,4-bisstyrylbenzene (BSB) as hydrophobic rigid groups and polyoxyethylene (POE) chains as hydrophilic flexible segments were prepared. The stabilities and the packing states of the monolayers at the air-water interface were studied by the investigation of pressure-area (π -A) isotherms. Structural parameters of the LB film including the alignments of BSB groups and the layer spacings were estimated by the spectral analysis and the X-ray diffraction measurements.



POEBSBCI-3 : X = Cl
 $n = 3$

POEBSB-*n* : X = H
 $n = 5, 6, 8$

Fig. 1. Chemical structures of main chain LCPs used in this study.

2. EXPERIMENTAL

The structures of a repeat unit of main chain LCPs used in this study are shown in Figure 1. The synthesis and the LC properties of the polymers were reported previously^[15].

The π -A isotherms were obtained by using a FSD-300 film balance controller (USI). The subphase was deionized water, kept at 25 °C by means of a water circulating system equipped with a thermostat. The polymers were spread from the chloroform solutions (1.0 mg·ml⁻¹). After the solvent was evaporated, the films were compressed at a speed of 36 cm²·min⁻¹ to record the π -A isotherm. The preparations of LB films were carried out on a FSD-21 LB lift controller (USI). The monolayers were transferred by the vertical dipping method onto hydrophilic solid substrates with a dipping speed of 5 mm·min⁻¹.

The UV-visible absorption spectra were recorded on a U-1800 spectrophotometer (HITACHI). The X-ray diffraction patterns were obtained with a XRD-6100 diffractometer (SHIMADZU). All of these measurements were carried out at room temperature (23 °C).

3. RESULTS AND DISCUSSION

3.1 Monolayer properties and LB film deposition

The π -A compression isotherms for the polymers are shown in Figure 2. There are extremely steep region where the surface pressure increases rapidly with compression. This indicates the formation of a liquid-condensed Langmuir monolayer. The collapse pressure (π_c) and the limiting area per repeat unit (A_0) of monolayers are listed in Table I. The A_0 was estimated by extrapolating the sharp rising part of the π -A curves to zero surface pressure. The π_c was determined by the inflection point after the sharp rising part of the curves.

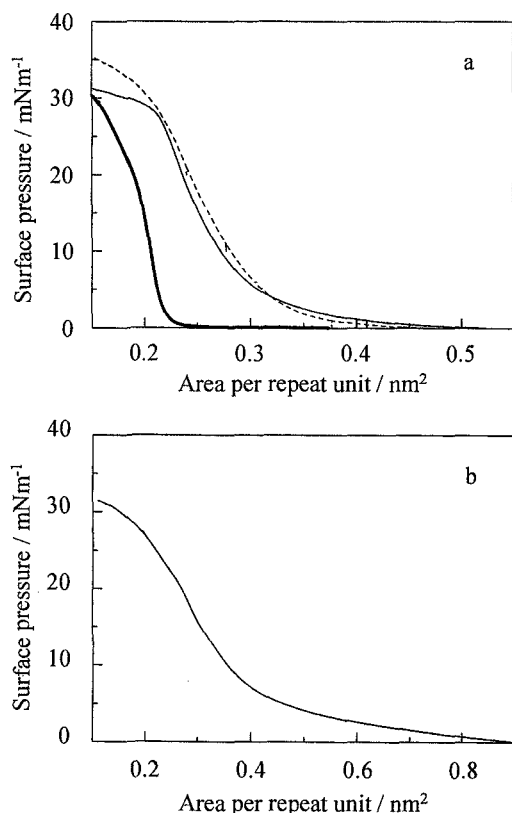


Fig. 2. π -A isotherms on a pure water subphase at 25 °C: (a) **POEBSBCI-3** (bold line), **POEBSB-5** (dashed line), **POEBSB-6** (solid line), (b) **POEBSB-8**.

Table I. Collapse pressure (π_c) and limiting area (A_0) of the monolayers.

| polymer | π_c / mNm^{-1} | A_0 / nm^2 |
|-------------------|---------------------------|---------------------|
| POEBSBCI-3 | 16.1 | 0.22 |
| POEBSB-5 | 26.3 | 0.31 |
| POEBSB-6 | 27.2 | 0.29 |
| POEBSB-8 | 26.0 | 0.42 |

Watakabe *et al.* reported that the π_c of low-molecular-weight BSB derivatives was 25 ~ 29 mNm^{-1} [16]. The π_c values of the polymers used in this study (except **POEBSBCI-3**) were in the same range of those for the low-molecular-weight BSB derivatives. This result indicates that the BSB polymers can form stable monolayers as the low-molecular-weight derivatives. This is due to the suitable hydrophile-lipophile balance of the polymers and the anisotropic interaction between the BSB groups preferring to stack the BSB groups.

The length of POE chains mainly influenced the molecular packings in the monolayers. It is reported that the A_0 of well-packed low-molecular-weight BSB derivatives was 0.25 ~ 0.27 nm^2 [16]. In these monolayers, the long molecular axis of BSB groups aligned parallel to the normal of water surface. As shown in Table I, the A_0 values of the monolayers for **POEBSB-5** and **POEBSB-6** are 0.31 and 0.29 nm^2 , respectively. These A_0 values support a structure of monolayer with a zig-zag folding as shown in Figure 3. It is a well-known fact that 18-crown-6 ether has a stable cyclic structure, therefore the formation of hair-pin loops of POE chains in these polymers is considered reasonable. In the case of **POEBSBCI-3** having shorter POE chains, the isotherm exhibits the smallest A_0 (0.22 nm^2) and the lowest π_c (16.1 mNm^{-1}). From this, **POEBSBCI-3** in the monolayer was found to be tightly packed, but the monolayer was unstable. The formation of the tight packing is due to the smallness of the free volume of polymer segments arising the shortness of flexible POE chains. The lack of stability is probably due to the steric effect originated from a chlorine substituent in the BSB groups. In contrast, **POEBSB-8** formed an extremely expanded monolayer above a surface area of about 0.5 nm^2 because of a long oxyethylene chain (Figure 2b). This is ascribed to the fact that the free volume in the monolayer of **POEBSB-8** are too large to pack the BSB groups tightly. Moreover, since the surface pressure increased immediately after the compression was started at 0.9 nm^2 , it was suggested that the monolayer of **POEBSB-8** must have a large surface area more than 0.9 nm^2 . Further work is underway to clarify the monolayer property of **POEBSB-8**.

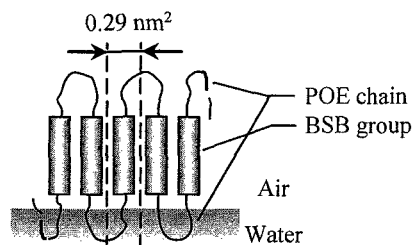


Fig. 3. Plausible packing state of monolayers of **POEBSB-6**.

The above-mentioned properties of monolayers at the air-water interface seem to be related to the behaviors in the bulk LC phases of these four polymers [15]. **POEBSBCI-3** forms a nematic phase above a smectic phase and exhibits a nematic-isotropic phase transition temperature over 300 °C. On the other hand, **POEBSB-5**

and **POEBSB-6** only form smectic phases. The isotropization temperatures of **POEBSB-5** and **POEBSB-6** are 274.0 and 258.7 °C, respectively. **POEBSB-8** also forms the smectic phase, however the isotropization temperature is about 70 °C lower than that of **POEBSB-6**. The free volume of polymer segments will affect their isotropization temperatures in the bulk LC state as well as their A_0 in the monolayer state. In the case of **POEBSB-3**, there may be some correlations between the formation of the nematic phase and the instability of the monolayer.

The monolayers of **POEBSB-5** and **POEBSB-6** were deposited onto quartz plates (for spectroscopic measurements) or glass slides (for X-ray diffraction measurements) at 15 mNm⁻¹. The multilayer depositions proceeded solely during the upstroke motions with transfer ratio approximately 0.7 (for **POEBSB-6**). In the case of **POEBSB-5**, the deposited monolayer was partially peeled off during the downstroke motions, therefore the transfer ratio was not evaluated. The deposition of the monolayer of **POEBSB-3** was tried at 7 mNm⁻¹, but it aborted. The monolayer collapsed when the glass slide was inserted to the water subphase. This is due to the instability of the monolayer.

3.2 Structural characterization of multilayered LB films

Figure 4 shows the UV-vis absorption spectra of the 20 layered LB films of **POEBSB-5** and **POEBSB-6**. The spectra exhibit two peaks around 310 and 250 nm. The peaks around 310 nm, which are blue-shifted from that of monomeric states (358 nm in chloroform solution) are attributed to the π - π^* transition of longitudinal molecular axis of H-aggregated BSB groups. The peaks around 250 nm correspond to the absorption of the π - π^* transition of short axis [16]. The H-aggregation in the LB films indicates the strong interaction and the parallel stacking between the BSB groups.

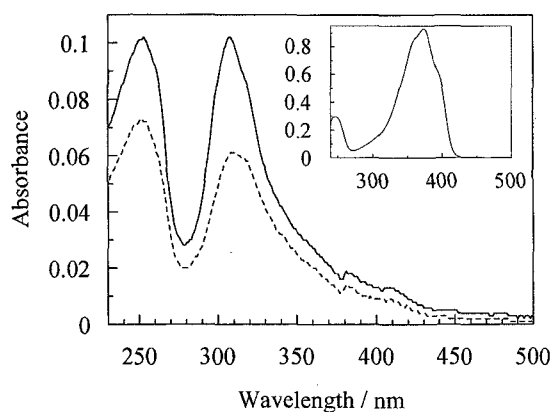


Fig. 4. UV-vis spectra of 20 layered LB films on quartz plates and of 10 mgL⁻¹ chloroform solution (inset): **POEBSB-5** (dashed line), **POEBSB-6** (solid line).

The X-ray diffraction pattern of **POEBSB-6** LB film is composed of a small-angle sharp Bragg reflection and a broad reflection in the wide-angle region (Figure 5). The peak at the small-angle corresponds to the d -spacing of the multilayer structure in the LB film. The broad

reflection in the wide-angle region is due to a short range orientational order within the layer. The diffraction pattern resembles that of a typical liquid crystalline smectic phase. Note that **POEBSB-6** forms the smectic phase as described above, therefore a periodic multilayered structure of **POEBSB-6** can be formed through its specific amphiphilic interactions in not only the 3-dimensional bulk state but also the LB film. On the other hand, the d -spacing of LB film of **POEBSB-5** was not determined because the reflection around $2\theta = 1.5$ was too weak and broad to detect the peak position.

The results of X-ray diffraction measurements for **POEBSB-5** and **POEBSB-6** are summarized in Table II. In **POEBSB-6**, the d_f was shorter than the d_b [15]. This is due to the formation of the different orientational structures. The multilayered structure of the **POEBSB-6** LB film is schematically illustrated in Figure 6. In the **POEBSB-6** LB film, a folding structure are formed. In the layer, the BSB groups exhibit the H-aggregated structure, and the POE chains form the hair-pin loops. In the smectic LC phase, **POEBSB-6** forms the smectic layered structure that the polymer chains with the BSB groups and the POE chains are aligned along the director.

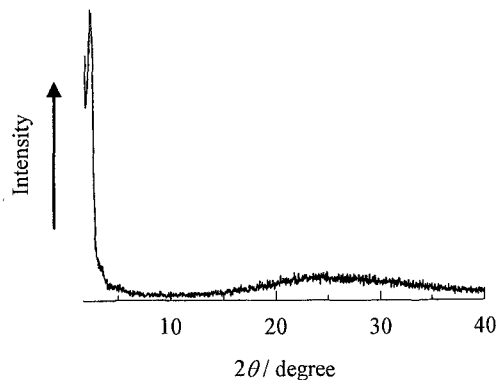


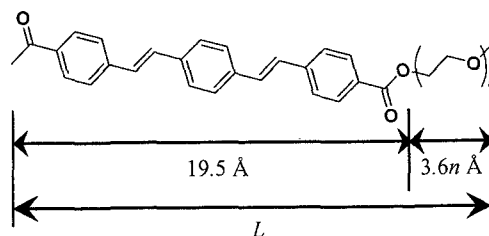
Fig. 5. X-Ray diffraction pattern of 20 layered **POEBSB-6** LB film.

Table II. Spacings of polymers determined by X-ray diffraction in bulk phase (d_b) and in LB films (d_f)

| polymer | n | $L^{(1)}$ / Å | d_b / Å | d_f / Å |
|-----------------|-----|---------------|-----------------|-----------------|
| POEBSB-5 | 5 | 37.5 | — ²⁾ | — ²⁾ |
| POEBSB-6 | 6 | 41.1 | 40.1 | 37.1 |

1) Calculated by molecular models (see below).

2) Not detected.



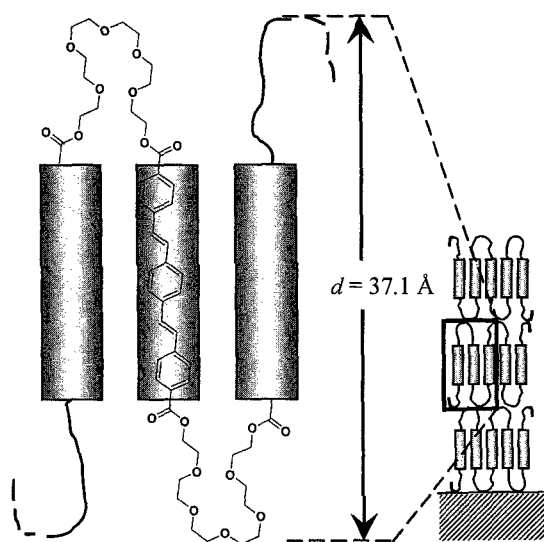


Fig. 6. A schematic illustration for multilayer structure of POEBSB-6 LB film.

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4. CONCLUSION

The Langmuir monolayers and the multilayered LB films of main chain LCPs, which have the mesogenic groups and the polyoxyethylene chains, were prepared. The characteristics of the mesogenic groups in the monolayers at the air-water interface can be related to the properties in the bulk LC phase of these polymers. In the layer of the LB films, the mesogenic groups form the H-aggregated structure, and the polyoxyethylene chains form the hair-pin loops.

5. REFERENCES

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