# Modeling the Contact Region of Command Layer/Liquid Crystal Molecule by Langmuir-Blodgett Technique

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A molecularly homogeneous mixed monolayer composed of an azobenzene containing amphiphilic polymer and 4'-pentyl-4-cyanobiphenyl (5CB) was formed on a water surface. Photoirradiation onto the single LB layer from this mixed monolayer induced reversible orientational changes of 5CB molecule. Preparation of a reasonable model of command layer/liquid crystal molecular interface by LB method is proposed.

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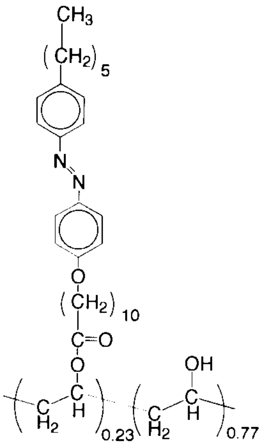
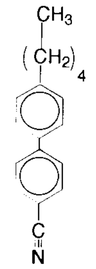
Monolayers of azobenzene (Az) containing derivatives on the solid substrate having a thickness of ca. 2 nm can induce alignment changes of nematic liquid crystal (LC) molecules having a thickness of several micrometers.[1-3] In this regards such layers can be referred to as command surfaces or command layers.[2] Understanding of the molecular contact region on the command layer is essential in these systems, and thus observation of the initial process taking place in molecular contacting interface of the command layer/LC is the subject of keen interest. However, extraction of molecular information from the interfacial region at a molecular level is severely difficult for a LC cell of several micrometers thickness. In this context, we constituted a research approach for modeling the hetero-molecular interface by Langmuir-Blodgett (LB) technique. In this letter, we will show that an amphiphilic Az side chain polymer (6Az10-PVA) mixed with an equimolar amount of LC molecules provides a reasonably good model for the above motivation. Xue and coworkers[4] have reported that a cyanobiphenyl type LC molecules form a uniform monolayer with the aid of the polar cyano group. It seemed hence appropriate to start with 4'-pentyl-4-cyanobiphenyl (5CB), a typical nematic LC material.



6Az10-PVA



5CB

Figure 1 indicates the surface pressure-area isotherms of spread monolayers of pure 5CB (a), pure 6Az10-PVA (b), and 1:1 molar mixture of the two materials spread from a mixed solution (co-spreading, c), and from the separate pure solutions (separate-spreading, d). The area axis is expressed as to show that per Az unit except for pure 5CB. For pure 5CB film the first pressure uprise was observed at 0.42 nm$^2$ per molecule and exhibited a collapse or phase transition at 0.33 nm$^2$. The plateau region at 5.0 mN m$^{-1}$ should correspond to the continuous collapse to multilayers.[4]

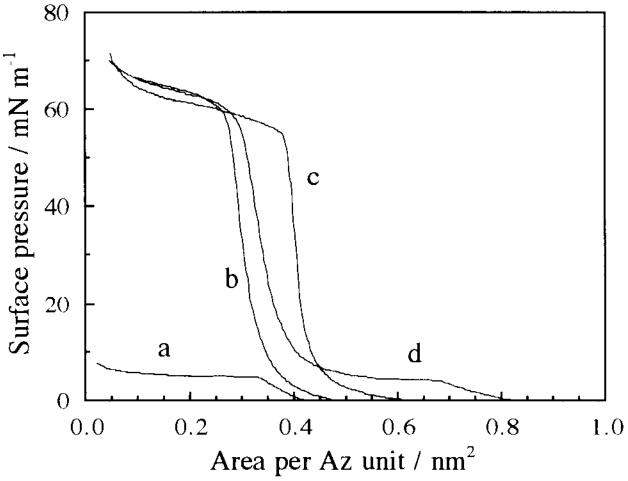


**Figure 1.** Surface pressure-area isotherms of pure 5CB (a), pure 6Az10-PVA (b), co-spread 5CB/6Az10-PVA (1:1 molar mixture, c), and separately spread 5CB/6Az10-PVA (1:1 molar mixture, d) on pure water at 20 °C.

The monolayer of separate-spreading (d) gave the π-A isotherm which can be regarded as the sum of pure 5CB and 6Az10-PVA monolayers showing the plateau region at low pressures and a high collapse pressure (ca. 60 mN m$^{-1}$). On the other hand, the co-spread monolayer (c) gave a different shape of isotherm which resembles that of pure 6Az10-PVA monolayer showing an expansion in the limiting area by 0.09 nm$^2$. The limiting area of monolayers of pure 6Az10-PVA and co-spread film were 0.33 and 0.42 nm$^2$, respectively. The increment of the occupying area is nevertheless considerably smaller than that expected for a 5CB molecule (ca. 0.3 nm$^2$, see curve a). The above facts shows that the co-spread monolayer is composed of the molecular mixture of 6Az10-PVA and 5CB, and that the separate-spreading gave phase separated heterogeneous film. This interpretation was further rationalized by Brewster angle microscopic (BAM) observation (data not shown).

The 1:1 co-spread monolayer was then transferred onto the both side of a hydrophilic clean quartz plate at 10 mN m$^{-1}$ and a lifting speed of 0.5 cm min$^{-1}$. The changes in the UV-visible absorption spectra of the transferred monolayer induced by the photoirradiation[6] taken in normal incidence were shown in Figure 2. The absorption peaks around 440 nm, 350 nm, and 280 nm are assigned to bands corresponding to the n-π* of Az unit, π-π* of Az (long axis), and π-π* of cyanobiphenyl (long axis) group, respectively.

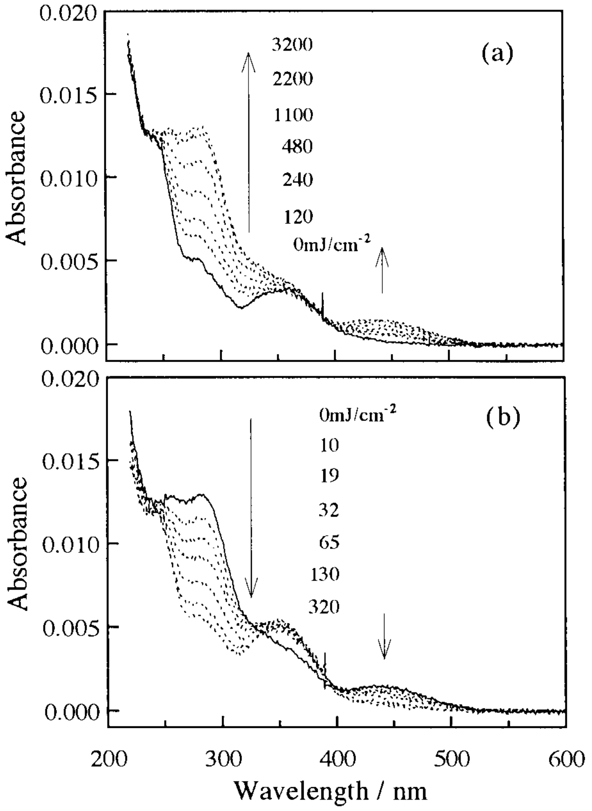


**Figure 2.** UV-visible spectral changes of a 5CB/6Az10-PVA (1:1) single layered mixed film on a quartz plate upon exposure to UV (365 nm, a) and visible (436 nm, b) light.

In the initial trans state of Az unit, the band intensities of the long axis π-π* bands for both Az and cyanobiphenyl chromophors was notably small (solid line in Figure 2a) taking into account their molar extinction coefficient ($\varepsilon_{280} = 2.7 \times 10^4$, and $\varepsilon_{350} = 3.0 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$, for cyanobiphenyl and Az, respectively). This should imply that the Az side chain of 6Az10-PVA and 5CB molecules are highly oriented perpendicular to the substrate plane as the consequence of a cooperative effect of the molecular mixing. It is also worth mentioning that the π-π* band peak of Az unit positioned at ca. 350 nm which shows that the Az unit exists in the monomeric state. In the pure 6Az10-PVA monolayer the Az units in the side chain form H-type aggregates that is characterized by a large hypsochromic shift to ca. 320 nm. This further justifies the interpretation that molecular mixing is fulfilled in the co-spread monolayer.

UV light (365 nm) illumination induced large absorption enhancement in the absorbing region of 5CB molecule around 280 nm (Figure 2a). Since the present experiment was carried out in the normal incidence, these spectral changes can be ascribed to induction of the orientational change of 5CB molecule from the perpendicular to parallel mode with respect to the substrate plane. The enhancement of absorption band at 280 nm was clearly consorted with that of the n-π* band of Az unit (440 nm), indicating that the orientational change of 5CB is induced by the photoisomerization of the Az side chain. The reverse process could also be performed (Figure 2b). The enhanced absorption band at 280 nm was almost reverted to the original level upon irradiation of visible light (436 nm). Essentially the same reversible process was observed for a 1:2 molar mixed film. The structural reversibility observed in the present system is worthwhile to be noted. In general, the photoirradiation induces significant and irreversible structural changes in LB multilayered films composed of Az side chain type polymers.[7-9] The good reversibility observed here may be attributed either to a reduced viscosity in the film due to involvement of low-molecular-mass material or to a particular case in the monolayer system. Therefore, evaluation of photoresponsive properties in built-up multilayers is a subject of urgent investigation.

We conclude that the mixed monolayer of co-spread 6Az10-PVA and 5CB provides a satisfactory interfacial model of command surface systems in the homeotropic/planar switching mode. This can be rationalized in terms of (i) the homogeneous molecular mixing with high orientation attained in a cooperative way, and (ii) the achievement of good *reversible* orientational changes of the LC molecule associated with the Az photoisomerization. Detailed results in the model system including BAM observation and FT-IR analysis will be reported in due course.

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## References

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5 Synthesis of 6Az10-PVA was described previously.[3] 5CB was kindly supplied by Rodic Co. and used without further purification. The spreading behavior of monolayers was evaluated using a Lauda FW1 film balance.[3]

6 Light irradiation was performed by a 200W Xe-Hg lamp (San-ei Supercure-203S) passed through optical filters (Toshiba, UV-35 and UV-D36A, Y-44 and V-42 for 365 and 436 nm, respectively). UV-visible absorption measurements were carried out on a JASCO MAC-1.

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