Highly organized Langmuir–Blodgett (LB) films have been attracting much attention during last decades because of their prospective applications in fabricating molecular electronic devices.1–6 Many efforts have been made up to now on expanding the LB film family by attaching different functional groups and on correlating the film structure with its functionalities.7–12 One has recognized by these studies that it is very important to introduce specific interactions for stabilizing the highly ordered film structures.13–17 Generally speaking, intermolecular interactions within LB films mainly include hydrophobic interactions between alkyl chains, aromatic interactions between π-conjugation systems, and hydrogen bonding between specific groups. Hydrogen bonding is the strongest one among them, which has a direction-specific property.

In this paper, we report our studies on LB monolayers of a novel azobenzene compound with two alkyl chains attached to the aromatic ring through one amide group (Chart 1). We expect that the strong aromatic, hydrogen-bonding, and hydrophobic interactions between alkyl chains may greatly improve the ordered film structure and its stability. To evaluate the structure of LB monolayers, we employed a polarized Fourier transform infrared (FTIR) spectroscopic technique, which is known to be powerful in determining the orientation of functional groups and the local environments surrounding them.17–19 Our experimental results showed that a unique two-dimensional hydrogen-bonded structure has been formed in the LB films.

The azobenzene monolayers were deposited onto CaF2 substrates using a commercialized Langmuir–Blodgett trough (FACE Co. Ltd., Japan). Milli-Q water with a resistance of >17 MΩ cm was used as the subphase solution. The azobenzene compound was dissolved in chloroform and spread onto the air/water interface with a microsyringe. The CaF2 plate was cleaned by heating in a drying oven at 150°C. All the LB films were prepared at a constant surface pressure of 20 mN/m, and the subphase temperature was kept at 20°C. At the experimental conditions, the molecules formed Z-type multilayer films, and the transferring ratio was nearly unity. Figure 1 shows the surface pressure–molecular area isotherm of the monolayer on water at 20°C, in which three main characteristics can be seen obviously: (1) this π–A curve does not bear the three-stage feature like most other monolayers; (2) the slope of the curve is rather large (∼−46 mN/(mnm⁻²)); (3) the adsorption pressure of the monolayer is very high (∼46 mN/m). All these features indicate the existence of strong interaction between the azobenzene molecules inside the monolayer on the air/water interface. One may expect a highly ordered structure in the LB films transferred to the solid substrate.

The FTIR spectra were measured with a Perkin-Elmer System 2000 FTIR spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector. The resolution of the system was set to be 4 cm⁻¹, and 500 interferograms were collected to achieve a good signal to noise ratio. The infrared probe radiation was normally incident on the films.
Obviously, the C=O groups in the LB monolayers were all in the hydrogen-bonded states, but the bonding strength with the adjacent OH groups was not the same: the C=O group with its projection on the substrate surface being along the dipping direction was in a stronger hydrogen-bonded state than that along the direction perpendicular to dipping. A similar conclusion can also be drawn by analyzing the in-plane bending vibration of the hydroxyl group (δ(OH, ip)) involved in the carboxyl group. This vibration mode is also greatly influenced by the inter-molecular interactions. In contradiction to the C=O group, the δ(OH, ip) vibration shifts to higher frequency when the OH group is hydrogen-bonded. The stronger the hydrogen bond is, the higher the frequency the δ(OH, ip) mode has. It is seen from Figure 2 that the frequency of the δ(OH, ip) was 1407 cm$^{-1}$ for parallel polarization, and 1412 cm$^{-1}$ for perpendicular polarization, showing similar dichroism behavior. The former corresponds to the OH groups weakly hydrogen bonded to the adjacent C=O groups and the latter to the OH groups strongly hydrogen bonded to the neighbor C=O groups. Combining the C=O and OH spectral data, we can imagine that in such monolayers, the C=O and OH of the carboxyl group are all in the hydrogen-bonded states: the C=O group parallel to the dipping direction forms a strong hydrogen bond with the OH group perpendicular to the dipping direction; whereas the OH group parallel to the dipping direction forms a weak hydrogen bond with the C=O group perpendicular to the dipping direction.

To obtain more experimental evidence, the polarization angle dependence of the FTIR spectra was studied using the same LB film, where the polarization of the incident radiation was changed from −30° to 110° at a step of 10°, referring to the dipping direction. Figure 3a shows the spectra obtained in the range of 1650–1750 cm$^{-1}$, and the absorption intensities of $\nu$(C=O) at 1694 and 1708 cm$^{-1}$ versus the polarization angle are sketched in Figure 3b. It can be seen that the intensity at 1694 cm$^{-1}$ has its maximum around 0° and reaches its minimum around 90°, while the intensity at 1708 cm$^{-1}$ has its maximum around 0° and gets to its maximum around 90°. With these spectral data, numerical simulation was performed, based on a model of two transition dipole moments of the $\nu$(C=O) mode in two directions (see the solid and dashed curves in Figure 3b). The orientation angles of the $\nu$(C=O) transition dipoles at 1694 and 1708 cm$^{-1}$ were found to be −2° and 87°, respectively, referring to the dipping direction. This indicates that two differently hydrogen bonded C=O groups are oriented nearly perpendicularly to each other.

The above dichroism phenomenon of the C=O and OH


Figure 1. $\pi$-A isotherm of the monolayer on water at 20 °C.

Figure 2. Polarized FTIR transmission spectra of a nine-monolayer azo LB film: (a) polarization parallel to the dipping direction; (b) polarization perpendicular to the dipping direction.

Figure 3. Polarized FTIR spectra of a nine-monolayer LB film on CaF$_2$ substrate, which were taken with an incident radiation polarized parallel to (a) and perpendicular to (b) the dipping direction, respectively. Attention was paid on the two absorption bands of the carboxyl group, located in the frequency ranges of 1690–1710 and 1405–1415 cm$^{-1}$, which correspond to the stretching vibration mode of its carboxyl group ($\nu$(C=O)) and the in-plane bending vibrating mode of its hydroxyl group (δ(OH, ip)), respectively. The peak position of $\nu$(C=O) for parallel polarization was 1694 cm$^{-1}$, while for perpendicular polarization, it was 1708 cm$^{-1}$. This dichroism implies that the carboxyl groups were located in different microenvironments, or say, two different types of carboxyl groups were existing in the LB film. Generally, the frequency of $\nu$(C=O) in free carboxyl group falls into a range of 1735–1760 cm$^{-1}$. When the carboxyl group is in a hydrogen-bonded environment, the $\nu$(C=O) vibration shifts to lower frequency, and the stronger the hydrogen bond is, the lower frequency the $\nu$(C=O) peak has. 22-24
vibrations of the carboxyl group was also observed in LB films having different monolayers. As an example, Figure 4 gives the FTIR results of three, six, and nine monolayers in the frequency range of $\nu(C=O)$ mode.

From the spectra shown in Figure 2, additional information can be obtained. The first feature is the dichroism of the in-plane vibration mode of the aromatic ring, located at 1606, 1581, 1515, and 1481 cm$^{-1}$. The absorbances of these modes have larger values in the parallel polarization case than in the perpendicular case. A polarization dependence of the ring breathing mode at 1606 cm$^{-1}$ is shown in Figure 5, which indicates the parallel orientation of the aromatic rings is parallel to the dipping direction. Secondly, regarding the symmetric and asymmetric stretching mode of the CH$_2$ group, located at 2921 and 2851 cm$^{-1}$, both $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes have larger absorbance in the perpendicular polarization. As we know, the directions of the transition dipole moments of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ are perpendicular to each other, and therefore, to achieve the above spectroscopic feature of CH$_2$ group, two kinds of alkyl chains with different orientation would be required. It could be suggested that one kind of the alkyl chain have its C=C=C plane orientating along the dipping direction and the chain tilt in this plane. The other kind would have its C=C=C plane perpendicular to that of the alkyl chain described above and its C=C=C plane also have a tilting angle with respect to the substrate surface. We suggest that the two alkyl chains of one molecule have their C=C=C planes perpendicular to each other. Similar suggestion can be found in ref 24.

Apart from the FTIR data, UV-vis spectra of the molecules in LB monolayer and in solution were also measured, in which a ~40 nm blue shift of the absorption peak around 380 nm was observed for the LB monolayer compared with that for solution, which indicated the
existence of H-aggregated state of the molecules in monolayers.

The above observation demonstrates in-plane dichroism in IR absorption and, more importantly, the in-plane anisotropy in molecular orientation. It is noted that in-plane dichroism in other LB systems has previously been reported, for example, in IR absorption\(^\text{17}\) and UV–vis spectroscopy,\(^\text{27,28}\) and the in-plane anisotropic molecular orientation has been studied indirectly by other methods (e.g., X-ray technique).\(^\text{29}\)

Figure 6 illustrates the possible structural model of the LB film, where (a) represents the steric conformation of three carboxyl groups which create two hydrogen bonds and (b) is the projection of the two-dimensional hydrogen-bonded carboxyl group on the substrate surface. For simplicity, the molecular backbone was omitted from the structural model. In this model, each carboxyl group links two other carboxyl groups of different molecules via hydrogen bonds and the adjacent hydrogen-bonded carboxyl groups are perpendicular to each other in projection, leading to a zig zag structure. As can be seen from this model, the parallel orientating aromatic rings form H-aggregates in the LB monolayer. The larger absorption intensity of \(\nu(C=O)\) in perpendicular polarization suggests a closer molecular packing distance in the direction parallel to dipping, which results in the stronger hydrogen bonding between the C=O group along the dipping and the OH group perpendicular to dipping. On the other hand, the weaker H-bonds between the perpendicular C=O and the parallel OH is originated from the less close packing in the perpendicular direction. Such a structural model gives a satisfactory explanation of our FTIR results. A more detailed study on this two-dimensional hydrogen-bonded structure is in process.

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