

Note

Asymmetric Arrangement of Monolayer in the Multilayer Films of 2-Hydroxy-4,4'-dihexyloxy-azobenzene

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Multilayer films of 2-hydroxy-4,4'-dihexyloxy-azobenzene (HAB) on silicon substrates have been studied with atomic force microscopy, temperature-dependent FTIR, and X-Ray diffraction technique. The results show that the multilayer films are formed by stacking of HAB monolayers via π - π interactions and the adjacent two monolayers in the film are arranged in an asymmetric way in the multilayer films.

Keywords azobenzene, monolayers, asymmetry, stacking interactions

Introduction

Construction of functional molecular units into structurally well-defined supramolecular assemblies has attracted great attention due to their potential applications in complex electronic structures and molecular devices.¹⁻⁵ Among the various functional organic molecules, azobenzene derivatives have been widely studied because of their interesting photoresponsive behavior.⁶⁻¹¹ Extensive studies have shown that suitably designed azobenzene derivatives can form long range ordered arrangement of two- or three-dimensional molecular lattice at various surfaces and interfaces.^{7,12,13} For rational design of molecular devices based on azobenzene derivatives, it is interesting to explore the relation between their molecular structures and the resulting supramolecular architecture.

In this work, the multilayer films of 2-hydroxy-4,4'-dihexyloxy-azobenzene (HAB) (Fig. 1), in which a hydroxyl

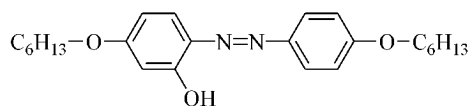


Fig. 1 Structure of HAB.

group is introduced in 2 position of 4,4'-dihexyloxy-azobenzene, were studied. It is expected that the introduction of the hydroxyl group can allow the formation of inter-

molecular hydrogen bonds between the molecules and make the structure of the molecule asymmetric. The results show that the multilayer films are composed of monolayers of HAB and these monolayers are arranged in an asymmetric way in the film.

Experimental

The synthesis of HAB has been reported elsewhere.¹⁴ HAB is identified to be a kind of nematic liquid crystal and its phase transition is determined to be Cr 78 °C CN 120 °C I. To prepare the HAB multilayer films, the HAB powder was dissolved in chloroform with a concentration of 5×10^{-4} mol/L and then kept in dark for two days to allow all HAB molecules exist in *trans* form. A drop of the solution was spread onto Si(111) substrates and the multilayer films were obtained after solvent evaporation.

Atomic force microscopy (AFM) measurements were performed by using a Digital Nanoscope II scanning probe microscope. A triangular shaped Si_3N_4 cantilever was used to acquire images in the non-contact mode. Temperature-dependent infrared spectra were recorded with a Bio-Rad FTS 3000 instrument equipped with a hot stage at a heating rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ from 40 °C to 130 °C. X-Ray diffraction patterns were obtained on a Rigaku D/max γA X-Ray diffractometer. All experiments were conducted at room temperature.

Results and discussion

The AFM image and the corresponding phase image of the HAB film are shown in Fig. 2. The observed surface exhibits ordered layer-by-layer stacked sheets with flat defect-free terraces. The phase image also shows that the surface of every terrace is flat and uniform. The sheet height is determined to be 0.42 nm by measuring the average height change between adjacent sheets in the AFM image. It is shown that every sheet is composed of one HAB

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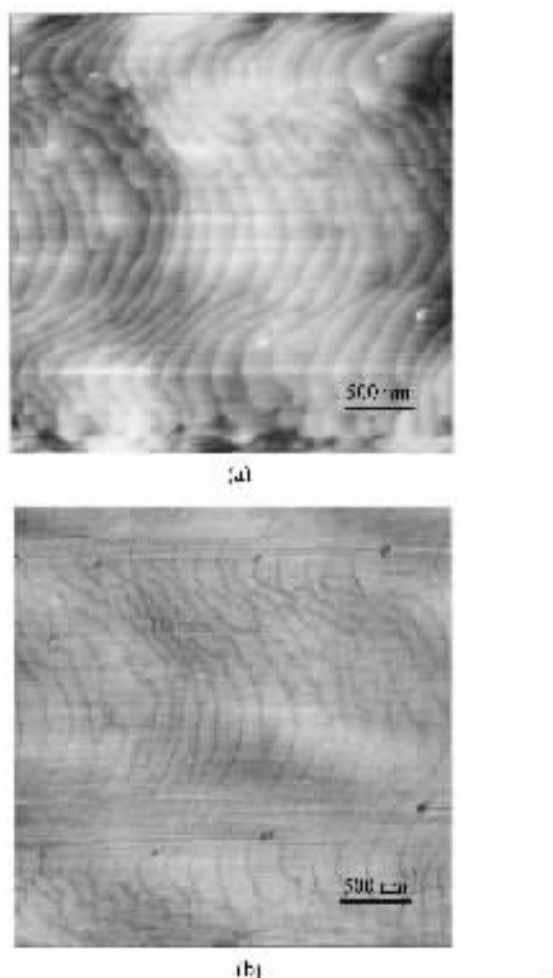


Fig. 2 (a) AFM image ($4\ \mu\text{m} \times 4\ \mu\text{m}$) and (b) corresponding phase image of the HAB multilayer films.

monolayer and the monolayers are parallel to each other. Introduction of the hydroxyl group allows the formation of two kinds of *trans* configuration taking the position of hydroxyl group into account, configurations I and II as shown in Fig. 3. Generally, configuration I is prior to form intermolecular hydrogen bond, and configuration II is readily to form intramolecular hydrogen bond. Hartree Fock (HF) calculation method was used to evaluate the stable energy of the two configurations. To simplify the calculation, the methyl group was used to replace the hexyl group. Hartree Fock (HF) was calculated to be -866.85 and -866.82 respectively for configurations I and II. This means that configuration I is more stable than II and the difference of their stable energy is $75.2\ \text{kJ/mol}$. So in our system, the HAB molecules should adopt configuration I and tend to form lateral intermolecular hydrogen bonds between neighboring molecules. This means that all molecules in each monolayer should be connected by intermolecular hydrogen bond network. Therefore it can be expected that in every sheet layer, the HAB molecules are connected by intermolecular hydrogen bonds to form organized monolayers with the large-scale and planar sheet structure.

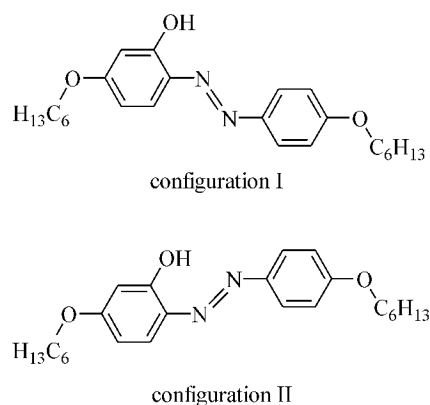


Fig. 3 Two possible configurations of the *trans* HAB molecule.

As for azobenzene molecules, the conjugated planar structure of azobenzene part will be favorable for stacking of the monolayers into the multilayer films. The existence of π - π interaction coming from azobenzene planes has been suggested by temperature-dependent FTIR spectra, as shown in Fig. 4. At lower temperature, HAB shows a relatively narrow and sharp band at $845\ \text{cm}^{-1}$. This band is assigned to C—H out-of-plane deformation $\gamma(\text{CH})$ of the phenyl ring. It indicates the existence of ordered arrangements of the phenyl rings in HAB molecule due to the strong interactions between the conjugated planes of the azobenzene derivatives.¹⁵ When the temperature was raised to the temperature of liquid crystal (LC) transition ($80\ ^\circ\text{C}$), the band at $845\ \text{cm}^{-1}$ undergoes a shift to lower wavenumber ($837\ \text{cm}^{-1}$). This means that the interactions between the conjugated parts of HAB are weakened and the molecules become mobile when the molecules experience the transition from the crystalline state to the LC phase.

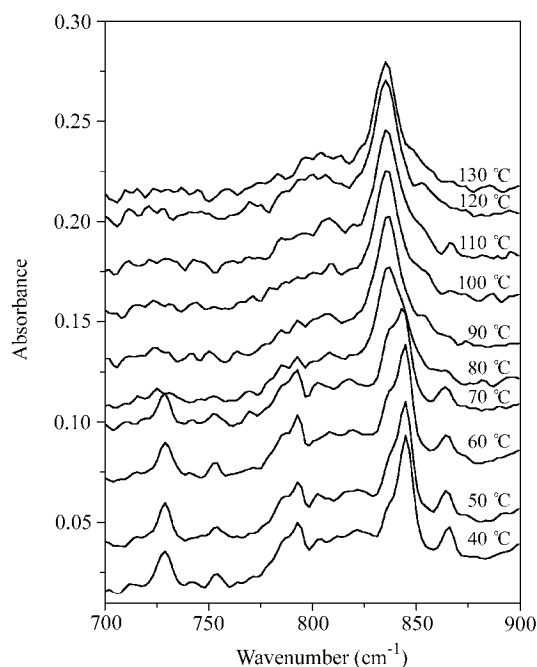


Fig. 4 Temperature-dependent FTIR spectra of the HAB film in the region of $700\text{--}900\ \text{cm}^{-1}$.

From the above discussion, the possible structures of the multilayer films are proposed as shown in Fig. 5.¹⁶ In the monolayer, the HAB molecules are connected by intermolecular hydrogen bonds to form a two-dimensional lattice, and these monolayers are held together via π - π interactions to form the multilayer films. Due to the asymmetric feature of the HAB molecule, there are two possible types of arrangement of adjacent monolayers. In type I, the hydroxyl groups in adjacent monolayers are at one side. It is suggested that the monolayers are arranged in a symmetric way. In type II, the hydroxyl groups in adjacent monolayers are not at one side but interlaced. It means that, the monolayers are arranged in an asymmetric way. The two types of arrangement should exhibit different periodical d -spacing. The symmetric arrangements of type I should bear a periodical d -spacing with the distance of about 0.42 nm as measured by AFM. While the asymmetric arrangements of type II should bear a periodical d -spacing whose distance is 0.84 nm, double of that of the symmetric arrangement.

The molecular arrangement for the multilayer structure was further determined by XRD measurement. Fig. 6 shows the XRD pattern of the multilayer films. Three orders of Bragg diffraction peaks located at $2\theta = 10.10^\circ$ are

observed, corresponding to a periodical d -spacing of 0.87 nm. This indicates that the arrangement of two adjacent monolayers is in an asymmetric way. Whitesides *et al.*^{17,18} studied widely the self-assembly of molecular components with different substituent groups and they concluded that the conformation of the resulting supramolecular tapes was determined by the steric repulsion between the adjacent substituent groups. In type II, the hydroxyl groups between the adjacent monolayers are kept as far as possible while keeping the intermolecular π - π interactions of HAB molecules in case of the asymmetric interlaced arrangements. Such an arrangement can reduce the steric repulsion between the hydroxyl groups between adjacent monolayers. This means that the introduction of the hydroxyl group can affect the stacking of the monolayer in the multilayer films. From the view of geometry, as for HAB molecules, the introduction of the hydroxyl group makes the structure of HAB molecule asymmetry, and this asymmetric information can be expressed in the stacking of the monolayers into the multilayer films. From this study it is suggested that the construction of supramolecular assemblies with desired structure should be engineered by appropriate design of the molecular structures.

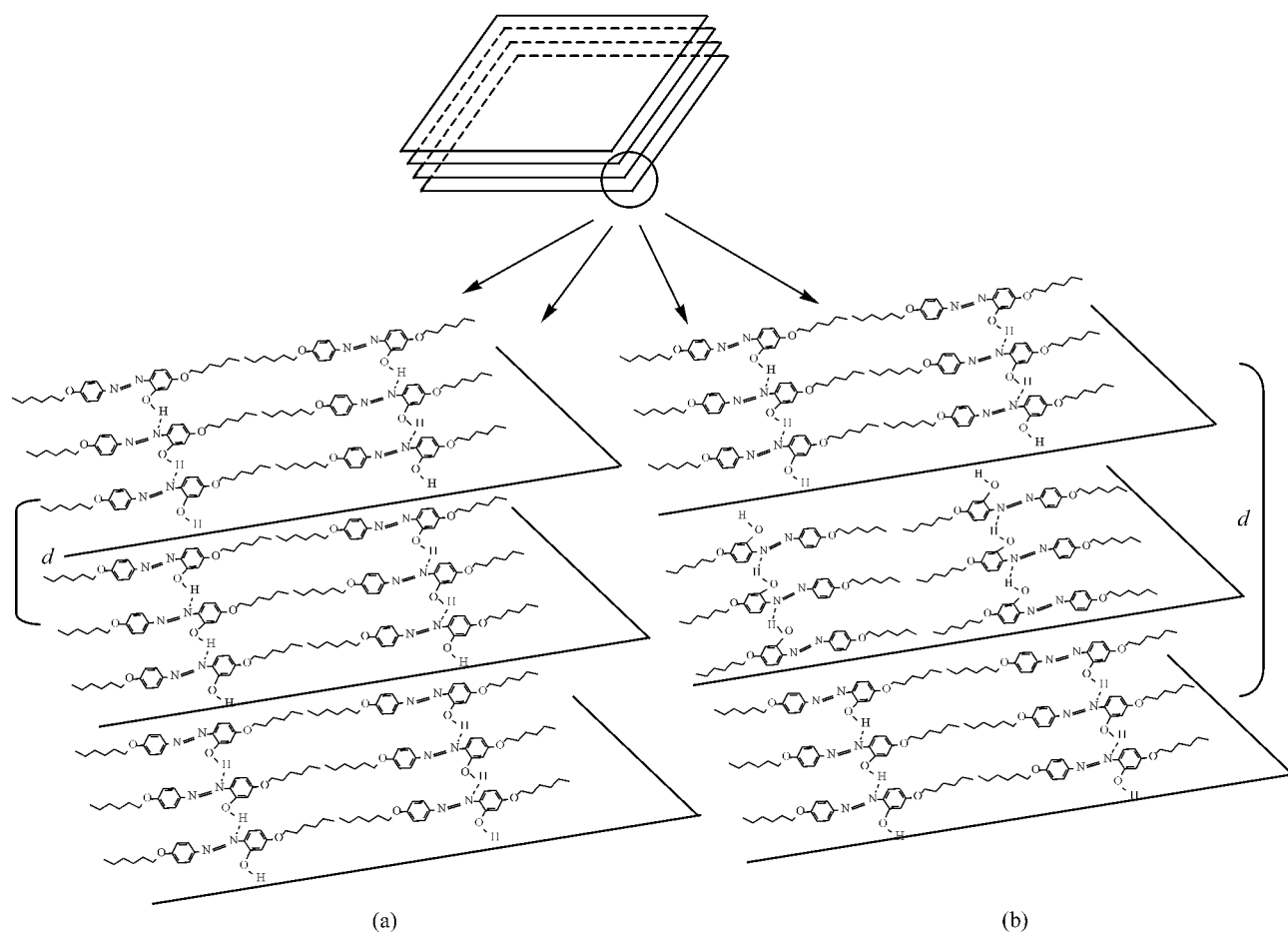


Fig. 5 Proposed models for (a) symmetric arrangement of HAB monolayers in the multilayer structure (type I) and (b) asymmetric arrangement of HAB monolayers in the multilayer structure (type II).

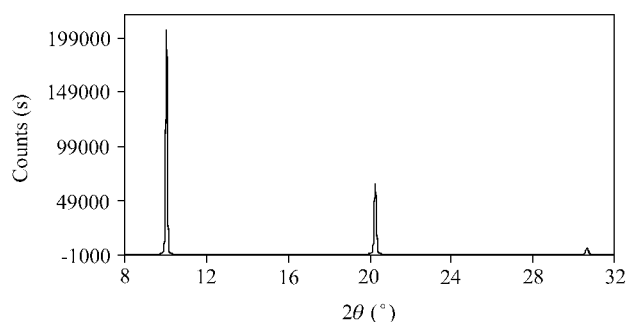


Fig. 6 X-Ray diffraction pattern of the HAB multilayer films.

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