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Structural characterization of BDN-SOH LB films using small angle XRD and Fourier transform IR spectroscopy

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We investigated the structure of BDN(bis(4-diethylaminodithiobenzil) Nickel)-SOH(Stearyl alcohol) Langmuir-Blodgett films using small angle X-ray diffraction and polarized FTIR spectroscopy. The results show that the microcrystal domains formed on the surface of LB film resemble a well-laminated periodic structure with a molecular spacing of 2.56 nm. Meanwhile, the tilted angles of the molecules of SOH and BDN are about 30°, referring to the normal direction of the sample surface, as determined by our XRD and FTIR studies.

1. Introduction

Recently, considerable attention has been focused on the Langmuir-Blodgett technique due to its promising applications in gas sensor, nonlinear optic and ultrahigh density information storage [1–4]. Many studies show that the macro properties of LB films are to great extent influenced by its microstructure, such as organized, crystal, molecular arrangement etc. [5–10]. Therefore, investigations on organic molecular structure using Infrared and UV-Visible spectrometric methods were carried out extensively. Infrared (IR) spectroscopy is now a very important tool for the study of molecular packing and orientation in ultrathin organic films [11–16]. There are several FTIR spectroscopy modes including attenuated total reflection (ATR), grazing angle (GA), polarized transmission (PT) and surface enhanced infrared spectroscopy (SEIRS) which have their particular advantages on different aspects.

BDN-SOH LB film is an ideal candidate for the N_2H_4 gas detector due to its high sensitivity to N_2H_4 and rapid response and recovery time [17, 18]. Meanwhile BDN diothiolene complexes show a potential application in nonlinear optics [19–21]. In this paper, FTIR, UV-Visible spectroscopy and small angle XRD were employed to investigate the structural properties of the BDN-SOH LB films.

2. Experimental

BDN was purchased from Kodak (Assay by UV/V is 98% min TLC no detectable impurities). Surface pressure vs. area isotherm and film deposition were carried out at 20 °C using an LB film trough (Face Surface Science Co., Japan). Milli-Q water with a resistance of >15 MΩ cm was used as the subphase solution. Solutions of BDN and of BDN-SOH 1 : 1 mole ratio were prepared in chloroform, typically 1 mmol/l in BDN-SOH. The LB films were transferred by Y-type deposition at a constant speed of 0.25 mm/s and 30 mN/m surface pressure, with the monolayer being coated and allowed to dry in air for 6 min after each down-up cycle. The transfer ratio was nearly unity. The π-A isotherm of BDN-SOH LB film(see Fig. 1) shows that the pressure between molecules increased with decreasing of the mean cross-sectional area of molecule and the collapse pressure reached at 33.4 mN/m while the value of average area per molecule is about 0.15 nm^2, which is in good agreement with data reported in reference [17].

The FTIR spectra of BDN powder in KBr pellets and BDN-SOH LB film were recorded with a Perkin-Elmer system 2000 FTIR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The spectra were collected at a resolution of 4 cm^{-1}.

Small angle XRD patterns were measured using a computer-interfaced diffractermeter (Regaku D/Max 2000, Japan).

3. Results and discussion

3.1. Consistency of transfer and uniform of the LB Films

As shown in Fig. 1, we see that the predominately linear π-A dependence, apparently corresponding to the first stable configuration of the molecular arrangement in the

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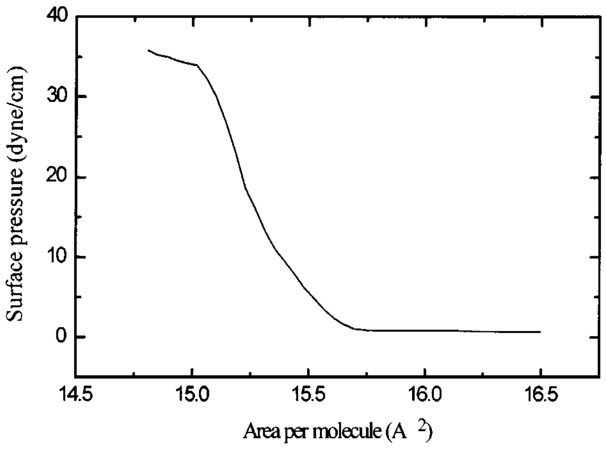

Figure 1 The π-A isotherm of BDN-SOH LB film.

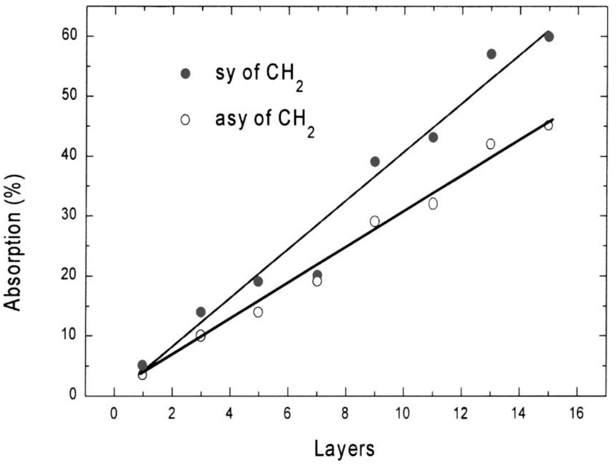

Figure 3 The relationship between the infrared absorption intensity and the layer number of LB film.

monolayer. We also found that the collapse pressure of the monolayer is dependent on the BDN : SOH ratio. Previous report showed the collapse pressure of different BDN : SOH molar ratios [26]. Fig. 2 is infrared absorption of BDN-SOH LB films deposited on CaF_2 substrate. The relation of infrared absorption of symmetric and asymmetric stretching vibration mode vs. the thickness of LB film (shown as layer number) is presented in Fig. 3. Fig. 3 shows that a good linear relationship between the infrared absorption intensity and the layer number of LB film which indicates an excellent repeatability of the density in each layer. The UV-Vis.-NIR analysis results are presented in Figs 4 and 5. As shown by the obtained spectra, there are two absorption peak located at 321 and 1165 nm, corresponding to σ-π and π-π^* transition respectively [22–24]. A good linear correlation between the transmission and the thickness of LB film also can be seen from Fig. 5 (for 1165 nm peak). While same kind of result can be found with the transmission of the absorption peak at 321 nm (the figure was omitted here). All above suggested that the amount of material on the substrate is linearly proportional to the number of LB layers, confirming the practical use of the LB technique for the reproducible deposition of very thin films of this material.

3.2. XRD results

Fig. 6 shows the small angle X-ray diffraction data obtained from 25-layer BDN-SOH LB film deposited on quartz substrate with Al interdigital electrodes (which are used for the measurements of the electrical properties of the LB films). Details of that were described elsewhere [25]). The detection of fifth-order Bragg peak indicates a well-ordered layer structure of the LB film. According to the position of the first diffraction peak, the bilayer spacing *d* value of 5.12 nm was determined. Therefore, the thickness of monolayer of LB film is 2.56 nm. The orientation of SOH molecular can also be estimated by the thickness measurement of LB film. Generally, the length of CH_2 is about 0.15 nm [21] and a stearyl chain should be 2.85 nm approximately which equals to 0.15 times 19. Thus, the tilted angle of SOH molecule is about 26.07°, quite close to 30°.

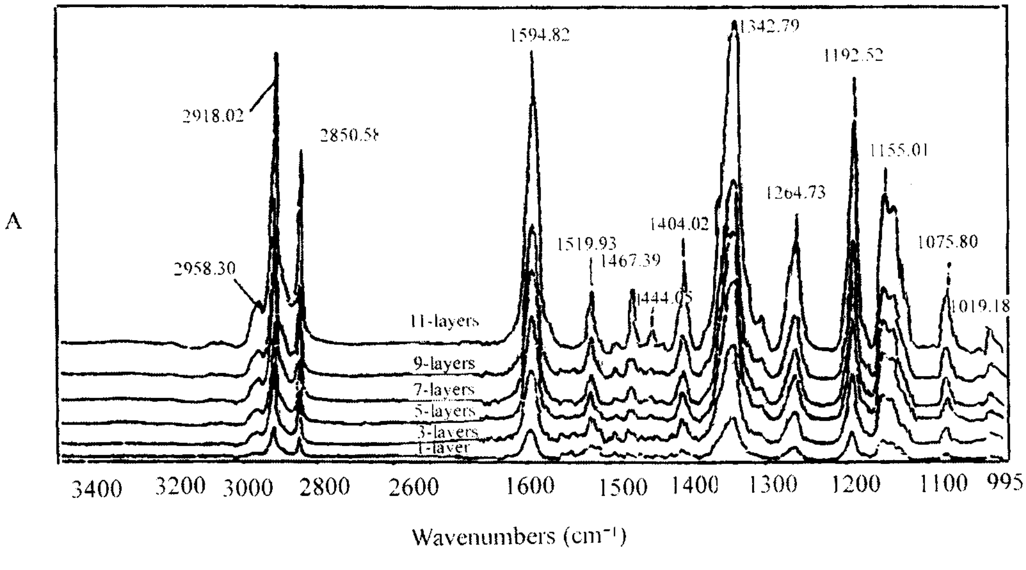

Figure 2 The infrared absorption spectra of BDN-SOH LB films deposited on CaF_2 substrate.

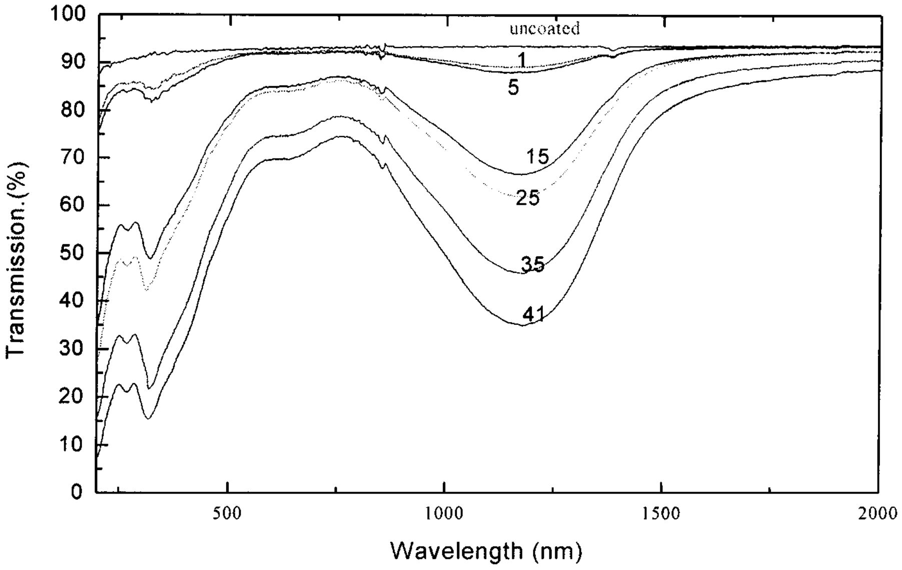

Figure 4 The UV-Vis.-NIR spectra of BDN-SOH LB film with different thickness deposited on quartz substrate.

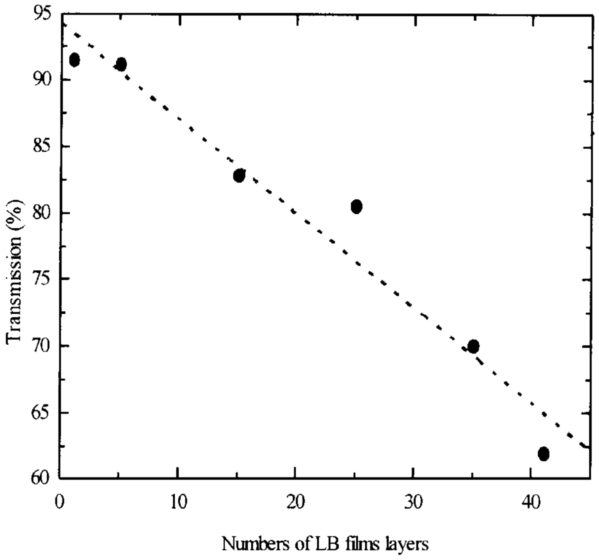

Figure 5 The relation between the transmission of 1165 nm absorption peak and the thickness of BDN-SOH LB films on quartz slide substrate.

3.3. IR spectra

In order to get a comprehensive understanding of the mixed LB films, two kinds of experiments were employed. The grazing-angle reflecting IR spectra were obtained from the LB films on slide glass coated with Au, and the polarized transmission IR spectra of the LB film on CaF_2 substrate were also recorded. Fig. 7 is the grazing-angle reflecting and transmission IR spectra of 8-layer BDN-SOH LB film. The IR spectra of BDN power on KBr pellet were given in Fig. 8 for comparison.

It is known that the reflection-absorption (RA) or grazing-angle IR spectrum of monolayers deposited in a metal substrate is measured most efficiently at high angles of incidence, and that only the component of incident light that is parallel to the plane of incidence gives measurable absorption. In the RA spectrum the broad band at 3275 cm^{-1} corresponding to the OH stretching vibration disappeared in the transmission spectrum. The ratio of symmetric and asymmetric stretching

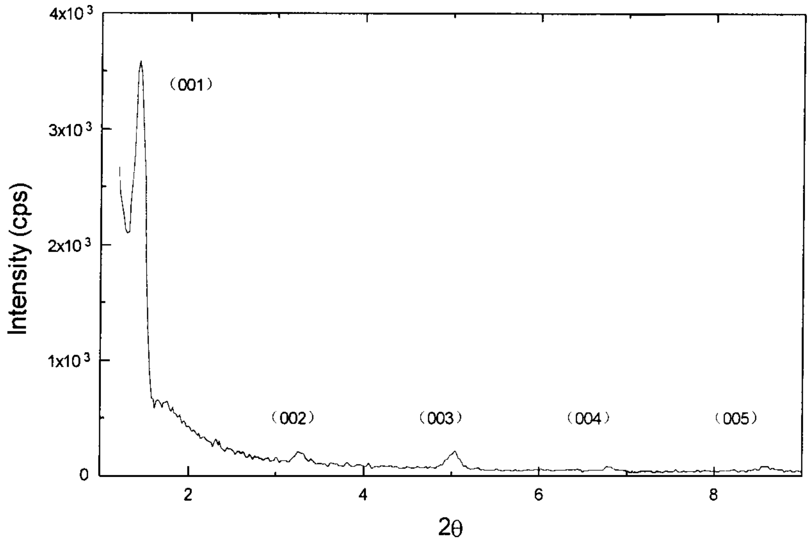

Figure 6 Small angle X-ray diffraction pattern of 25-layer BDN-SOH LB film deposited on quartz substrate with Al interdigital electrodes.

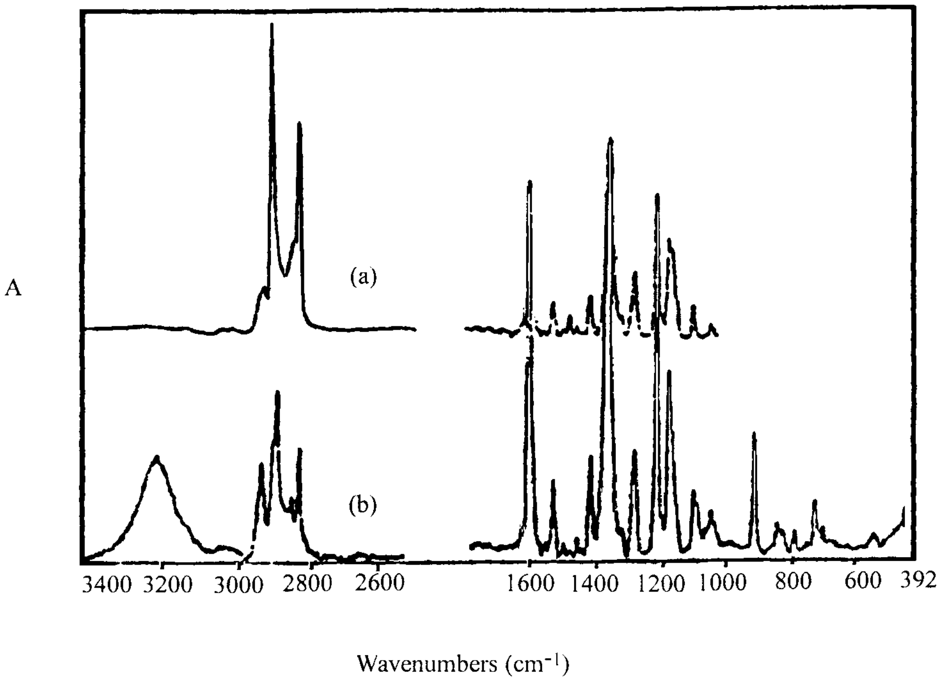

Figure 7 The grazing-angle (a) and transmission IR (b) spectra of 8-layer BDN-SOH LB film.

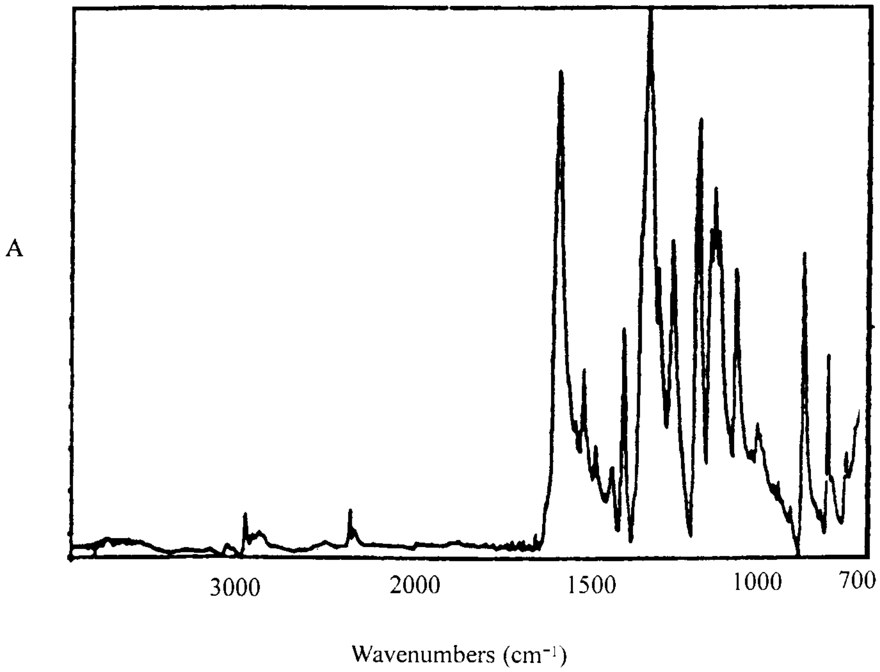

Figure 8 The IR spectra of BDN powder in KBr pellet.

vibration in transmission spectrum is much larger than that in grazing-angle IR spectrum. The above results indicate that the stearyl alcohol chain is inclined to the normal direction of the LB film and its head group-OH is parallel to the normal direction of the film (see Fig. 9), which has been proved also by the investigation on the bending vibration of CH_3 and CH_2. It should be noticed that two kinds of substrate, CaF_2 and KBr pellet respectively, were used for comparison here. Generally, the peak position shifting of symmetric and asymmetric stretching vibration of CH_2 can be used to investigate the existence status (total reflection conformation or liquid phase) of the alkyl chains in isotropic ordered thin films. The peak position on CaF_2 substrate should be same as or close to that on KBr pellet if the alkyl chains exist in total reflection configuration; and when the alkyl chains exist in liquid phase, the peak position on CaF_2 substrate will shift to higher wavenumber about 4–8 cm^{-1}. In our experiment, the alkyl chains exist in total reflection configuration, therefore, the peak positions of symmetric (2850 cm^{-1}) or asymmetric(2918 cm^{-1}) stretching vibration on two substrates are same for two substrates which was shown in the reflectionabsorption and transmission spectra.

Most of vibration features of BDN molecular, such as at 1598 cm^{-1} (breathing vibration of benzene ring), 1353 cm^{-1} (breathing vibration of benzene ring),

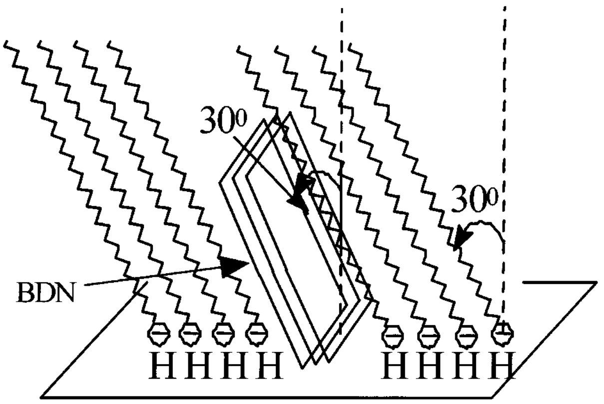

Figure 9 Schematic graph of possible arrangement of BDN-SOH LB film.

1265 cm^{-1} (benzene-carbon stretching vibration), 1195 cm^{-1} (benzene-nitrogen stretching vibration), 1157 cm^{-1} (benzene-nitrogen stretching vibration) and 1057 cm^{-1}(benzene ring bending vibration) can be found at refection-absorption and transmission spectra. The out-plane bending vibration of benzene-H (883 cm^{-1}) is very obvious. The above facts reveal that the planar BDN molecule is inclined at a certain angle to the normal direction of the substrate surface.

It can also be drawn from the IR spectra that domain-like structure exists in the film owing to the following reasons:

(a) Firstly, if there is no domain structure in the film, which means BDN molecule should be among the alkyl chains, the distance between the alkyl chains would be increased, consequently the asymmetric and symmetric vibration of CH_2 should shift to the higher wavenumber. As mentioned above, the alkyl chains exist in total reflection configuration in the film and the asymmetric and symmetric vibration of CH_2 located at 2850 and 2918 cm^{-1} respectively, suggesting no wavenumber shifting;

(b) The UV-Vis. spectra shows that the absorption of BDN in solution located at 319 nm and shifted to 321.5 nm in the LB films which suggests that the BDN molecule aggregated in the LB films. The domain structure in BDN-SOH LB film was confirmed by our atomic force microscopy (AFM) studies [25, 26].

In our measurements the polarized transmission IR spectra were employed to investigate the molecular orientation on CaF_2 substrate. Fig. 10 illustrates the polarized transmission spectra of 7-layer BDN-SOH LB films, in which the sample plates are parallel to P (and perpendicular to S). The incident polarized beam with electric vector oscillating in the plane that contains the dipping direction. P-0 was obtained as the angle between the incident beam and the normal direction of film surface equals 0°, while S-0, S-30 and S-45 were collected by varying the incident angle, 0°, 30° and 45° respectively. By calculating the intensity of some selected bands in transmission spectra with different incidence angle, the angle between the molecular vibration direction and the surface normal can be obtained using the following equation:

$$\frac{A_{i1}}{A_{i2}} = \frac{n_s(1+n_s)}{\cos(\gamma)+n_s\cos(i)}\left[\frac{2\sin^2(i)}{(tg^2\varphi)n_f^4}+\frac{\cos(i)\cos(\gamma)}{n_s}\right] \tag{1}$$

where A is the absorption coefficient, n_s is the index of refraction of substrate and n_f is the index of refraction

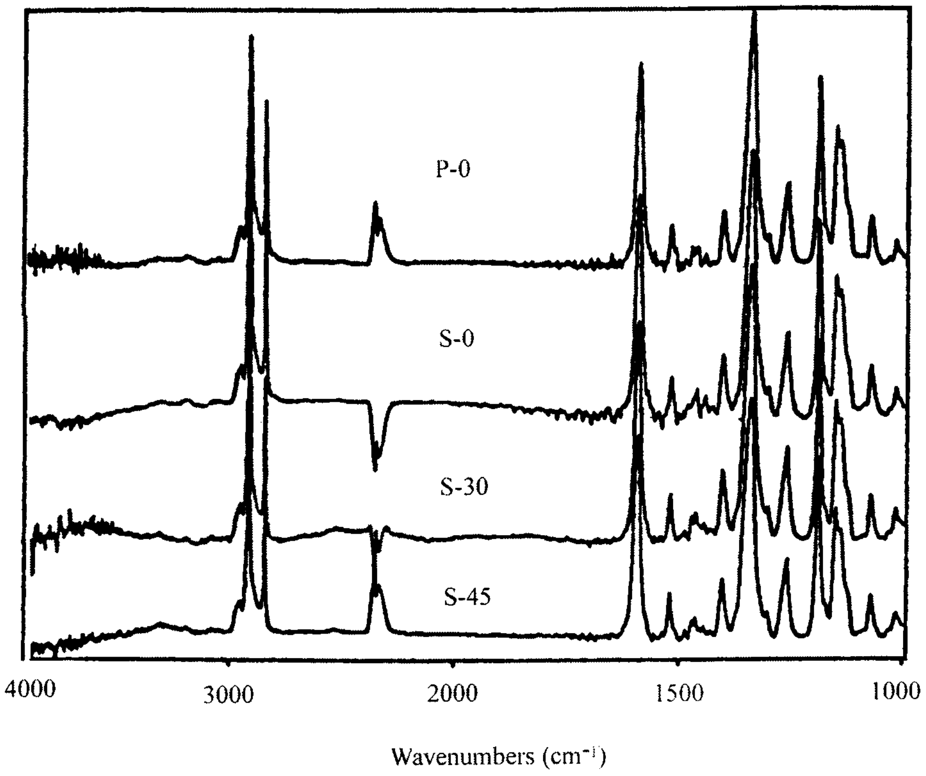

Figure 10 The Polarized transmission IR spectra of 7-layer BDN-SOH LB films.

of film (typically $n_f = 1.5$ for fat acid). i is the angel between incident light and surface normal. γ is the angle of refraction and here, $\sin(\gamma) = \frac{\sin(i)}{n_s}$. φ is angel between vibration direction and surface normal. The values are listed in Table I.

It can be seen from Table I, that the benzene ring in BDN molecular is inclined to the surface normal close to 30°, so the planar BDN molecular inclination can be regarded the same as the benzene ring. Meanwhile the angle between the symmetric and asymmetric stretching vibration and normal direction of substrate surface, α and β respectively, were also obtained. If we assumed the angle between carbon chain and substrate surface normal is assumed as γ, the equation below is given

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1 \qquad (2)$$

The angle between stearyl alcohol molecule and surface normal direction is around 30°, which was confirmed by our XRD results. So the molecular structure can be schematically shown in Fig. 9.

4. Conclusion

The grazing angle FT-IR and small angle X-ray diffraction studies of BDN-SOH LB films reveal that the domain-like structures formed in LB film resemble a well-laminated periodic structure with a molecular spacing of 2.56 nm. Meanwhile, the tilted angle between the SOH or BDN molecular and the surface normal direction is about 30°.

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