ATR-IR Spectroscopy Study of NLC Orientation at the Plasma-Polymerized Layers Surface

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Abstract   The comparative analysis of ATR IR spectra of the CB molecules mixture aligned planar by a-C:H and homeotropic by PPO layers produced by CVD technique in plasma are done. The dichroic ratios of main absorption bands of the spectra have been calculated. The models of the intermolecular interaction mechanism of the CB with a-C:H and PPO layers in the absence of external field are discussed.

INTRODUCTION

The orientation of liquid crystal (LC) molecules on the solid surface is of great importance for design of devices on nematic and smectic LCs. Several theories have been proposed for the mechanism of LC alignment that is roughly classified into two categories: the geometric effect and the intermolecular interaction effect. Geometric effect implies that the elastic deformation energy of the LC caused by geometric surface structure of the alignment layer can be controlled by geometric modification of the alignment layer surface.[1-3] Intermolecular interaction effect may occur in case of polymer-like surfaces.[4] The molecular structure of plasma-polymerized layers influences on the alignment of LCs and can be systematically varied by preparation condition and plasma treatment after producing.[5] The amorphous hydrogenated carbon (a-C:H) layers prepared from hydrocarbon plasma ensure stable planer alignment of cyanobiphenyls (CB) without any treatment their surface[6] as distinct from the known plasma-polymerized alignment layers.[7-9] However, the nature of the distinction is not clear yet. IR spectroscopy Attenuated Total Reflection (ATR) is the highly sensitive technique in measuring molecular structure of thin layers[10] and a well suitable one to characterize the intermolecular solid surface - LCs interaction.

In this paper we present our recent measurements of IR spectra by polarized ATR technique of the CB mixture aligned at the plasma-polymerized layers surface. The determination of a dichroic ratio of main absorption bands are described. The influence

of the molecule structure of the alignment layers on the nematic orientation in the absence of external field are discussed

EXPERIMENTAL METHODS

Preparation of Alignment Layers

The alignment layers were produced from hydrocarbons by plasma-activated chemical vapors deposition (CVD) technique under the sliding angles to a substrate in glow discharge on direct current. The layers were deposited at a room temperature onto a surface of Ge prism, which was used as an optical guide for the IR beam. The prism was mounted on a substrate holder. The angle between the substrate surface and a normal to electrodes was 5^0. In case of a-C:H deposition the substrate holder was grounded. The positive ions are accelerated towards the substrate and take part in a layer formation together with neutral products of a hydrocarbon decomposition thereby the adsorption mechanism. The a-C:H layer used in this work was produced from benzene vapors under the pressure 0.4 mTorr and the discharge power was 1.6 W. Plasma-polymerized octane (PPO) layer was deposited, when the substrate holder was not grounded unlike a-C:H deposition. Therefore the condensation mechanism of PPO layer was different and the deposition rate was smaller. PPO layer was deposited under pressure 2 mTorr and the power 1.8-3 W.

ATR Technique

The polarized infrared ATR technique provides obtaining the dichroism of an anisotropic absorbing layers. To obtain the dichroic ratio two ATR spectra for s-polarization, when the electric vector of IR radiation polarized perpendicular to plane of incidence (R_S) and p-polarization for the case of parallel polarized IR radiation (R_P) should be obtained. In multiple ATR spectroscopy[11] the value of measured reflectance is equal to:

$$R = (1 - \alpha d_e)^N \qquad (1)$$

where N - number of reflection; α - absorption coefficient; d_e - effective thickness. We have calculated a dichroic ratio of infrared absorption bands of a vibration of bond in theLC molecular as the ratio of the absorption coefficient (α_S) in the case of s-polarization to the absorption coefficient (α_P) in the case of p-polarization of IR radiation.

Under an angle of incidence $\theta = 45^{0}$ $d_{eP} = 2$ d_{eS} and

$$\alpha_S \, \alpha_P = \frac{2(1 - \sqrt[N]{R}_s)}{(1 - \sqrt[N]{R}_P)} \tag{2}$$

The penetration depth of infrared radiation was calculated on formula:

$$d_P = \frac{\lambda_1}{2\pi \, (\sin^2\theta - n_{21}^2)^{1/2}} \tag{3}$$

where wavelength $\lambda_1 = \lambda / n_1$ and refractive index $n_{21} = n_2 / n_1$, n_1 - refractive index Ge, n_2 -refractive index LC ($n_1 = 4.0$ and $n_2 = 1.6$).

The experimental set-up used in this work is shown in Fig.1a. It was the cell consisted of a high refractive index Ge prism served as the total reflection element and an ordinary glass plate. The cell thickness was adjusted to ~10 μm with spacers. The cells were filled with the nematic liquid crystal at room temperature. We used the commercial nematic mixture on base of CB molecules (NIIOPiK LC-1282) with positive dielectric anisotropy. The cell was assembled such that the preference director of light orientation axis of LC molecules was parallel to the Y axis in the case of planar alignment and parallel to the Z axis in the case of homeotropic alignment of the CB mixture. Schemes shown in Fig.1b illustrate the orientation of CB molecules at the alignment surface. Registration of the reflectance ATR spectra in the range of 4000-900cm^{-1} were made using PE-621 IR spectrometer.

RESULTS AND DISCUSSION

Figure 2 shows the polarization ATR IR spectra (R_S and. R_P) of the CB mixture aligned by a-C:H (a) and PPO (b) layers. The assignment bands observed in the IR spectra of the CB mixture are given in Table1. We calculated the dichroic ratio and the penetration depth for each absorption band for $\theta = 45^{0}$ and N=12 in accordance with equations (2) and (3). Its values are also given in the Table 1. The dichroic ratios of absorption bands of the CB mixture aligned by means of careful rubbing of the Ge prism surface in the single direction (along Y axis in Fig.1) prefer to introduction of LCs are given in the able for comparison. The higher value of the dichroic ratio should be observed for bonds, which vibrate along the direction of the electric vector of incident IR radiation.
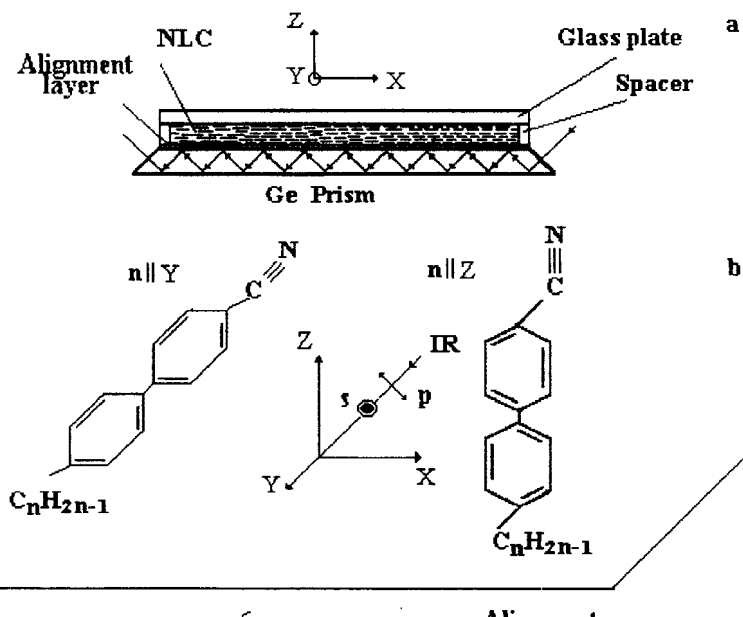
FIGURE 1   Experimental set-up (a) and schemes of planar (n∥Y) and homeotropic (n∥Z) alignment of CB molecules at the surface (b).
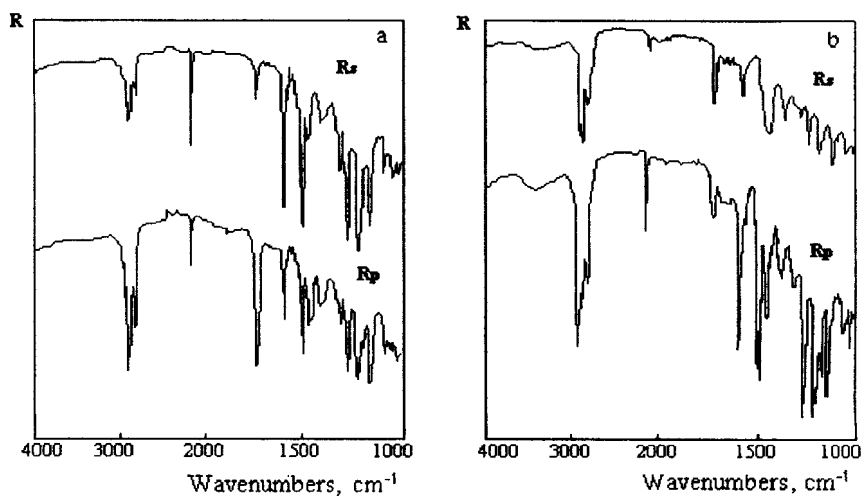

FIGURE 2   The polarization ATR IR spectra of the CB mixture aligned by a-C:H (a) and PPO (b) layers at an angle of incidence of IR radiation $\theta = 45^0$ and N=12.

TABLE 1   Dichroic ratio of absorption bands in spectra of the aligned CB mixture and penetration depth of IR radiation

Wave-number, cm^{-1}	Assignment bands in IR spectra of NLC	Penetration depth, d_P, μm	Dichroic ratio α_S/α_P		
			Rubbed surface	a-C:H surface	PPO surface
3400	OH	0.21	-	-	1.0
2920	C-H stretching of alkyl. chain	0.25	0,9	1.0	1.1
2220	C≡N	0.32	5,3	5.0	0.38
1770	C=O	0.40	0.45	0.45	1.4
1600	phenyl C-C stretching	0.45	5,0	4.5	0.4
1500	-"-	0.48	5,0	5.3	0.38
1450	CH deformation of alkyl. chain	0.49	1.0	1.0	1.0
1380	-"-	0.52	2,0	2.0	0.8
1240	C–C stretching of biphenyl ring	0.58	4,3	4.8	0.4
1200	phenyl C-H deformation	0.60	4,2	4.3	0.4
1120	C-O-C stretching	0.64	2,9	3.2	0.6

For the case of a-C:H the higher dichroic ratio of absorption bands in the spectra of CB there were the C≡N stretching (2220 cm^{-1}), the phenyl C-C stretching (1610cm^{-1} and 1500cm^{-1}) and the C-C stretching of biphenyl ring (1240 cm^{-1}). The dichroic ratios were equal to 4.3-5.3 and conformed with the data for the case of rubbing of the Ge surface. The directions of the vibration of these molecular bonds are parallel to the director (n) of CB molecular (Fig.1b). In the case of PPO layer α_S/α_P of the same bands were less than one. These results indicate the existence of the distinction between interaction of CB with a-C:H and PPO layers. We can conclude that a-C:H layer and the rubbing technique cause planar alignment of the CB molecules unlike PPO layer, which aligns the same molecules homeotropic.

In accordance with our investigation the planar alignment of the CB by a-C:H layers is associated with the dispersion interaction.[12] We have studied the molecular structure of a-C:H and PPO alignment layers by ATR IR spectroscopy eleare.[13] a-C:H layers differ from PPO by the smaller content of hydrogen and the presence of the greater polycyclic groups oriented parallel to substrate surface. We assume that the planar alignment is associated with strong dispersion interaction between polycyclic

groups of a-C:H layer surface and biphenyl rings of the CB. The homeotropic alignment of the molecules   by PPO may be associated with the dispersion interaction between hydrocarbon groups of layer and the tail-group molecule of CB.

CONCLUSION

Molecular orientation in the thin CB layers near the surface of a-C:H and PPO has been characterized by polarization ATR IR spectroscopy in the range of 4000-1000cm^{-1}. For the case of the a-C:H layer the higher value of dichroic ratios were obtained for C≡N stretching at 2220 cm^{-1}, the phenyl C-C stretching at 1600-1500 cm^{-1} and the C-C stretching of biphenyl ring at 1240 cm^{-1}. In the case of PPO layer dichroic ratios of the same absorption bands were less than one. These results corroborated to different mechanisms of interaction of the CB with a-C:H and PPO layers, which are caused by the peculiarities of molecular structure of the alignment layers.

ACKNOWLEDGMENTS

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