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ORIENTATION OF THE BACKBONE STRUCTURE OF POLYIMIDE WITH ALKYL SIDE-CHAINS: DETERMINATION BY INFRARED ABSORPTION SPECTROSCOPY

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Abstract By infrared absorption spectroscopy we have determined the orientation of the backbone structure of polyimide with alkyl side-chains in the rubbed film. The backbone orientation was determined from the dichroic ratio at normal incidence and the incident angle dependence of absorption by the IR active vibrations polarized along the backbone structure. We found that the backbone structure is oriented along the rubbing direction and tilted up on average by 23° from the surface. The pretilt angle of bulk liquid crystal (LC) in contact with this rubbed film is 9.6°. The average inclination angle of the backbone structure and the pretilt angle are much higher than those for the polyimide without a side-chain reported in our previous papers. This result indicates that the high inclination angle of the backbone structure of polyimide with alkyl side-chains plays an important role in causing a high pretilt angle in bulk LC.

INTRODUCTION

Rubbed polyimide films coated on substrates are widely used to align bulk liquid crystal (LC) along the rubbing direction with a certain vertical tilt angle. This angle is called the "pretilt angle." The control of the pretilt angle is of critical importance in the fabrication of LC devices. For example, the pretilt angle greater than 5° is required for a super-twisted nematic display to prevent the generation of disclination loops.[1] To generate such a high pretilt angle, polyimides with alkyl side-chains[2] are commonly used as alignment layer materials. For pretilt angles of a few degrees, polyimides without a side-chain are used. These choices are made empirically, and the mechanism that determines the pretilt angle is not yet understood in spite of the efforts by many researchers.[3-7]

To understand the mechanism, we recently measured the pretilt angles of bulk LC in contact with rubbed polyimide films with different inclination angles of the polyimide backbone structure. For a polyimide without a side-chain, we found that the pretilt angle

has a positive correlation with the inclination angle of the polyimide backbone structure.[8] If the pretilt angle is mainly determined by the inclination of the polyimide backbone structure, one expects that the inclination angle of the backbone structure of polyimide with alkyl side-chains should be higher than that of polyimide without a side-chain. Thus in the present study, we have measured the orientation of the backbone structure of polyimide with alkyl side-chains in rubbed films by polarized infrared (IR) absorption. This study is a first step toward understanding the mechanism of the generation of high pretilt angles by polyimide films with alkyl side-chains.

THEORY

The calculation procedure of the IR absorption spectra of a polyimide film on a substrate was previously described in detail.[9] In this section we only present the form of the distribution function for the polarization direction of an IR active vibration.[10]

We define two frames of reference with respect to the sample. One is the laboratory frame labeled by X, Y, and Z-axes, where the Z-axis is normal to the surface and the +X-direction is the rubbing direction. The other is the frame defined by the principal dielectric axes of the rubbed polyimide film. We denote this coordinate system by x, y, and z. Since the rubbed film has a mirror symmetry with respect to the XZ-plane, the two principal dielectric axes (x- and z-axes) lie in the XZ-plane. Thus, the xyz-coordinates are related to the XYZ-coordinates by a single parameter, the inclination angle θ_{incl} of the x-axis from the XY-plane. The rotation of the +x-axis toward the +Z-axis around the Y-axis is represented by a positive value of θ_{incl}.

The distribution function $g^{\nu}(\theta,\phi)$ of the polarization direction of the ν th IR active vibration is defined with respect to the principal dielectric axes, and is assumed to have the following form:

$$g^{\nu}(\theta,\phi) = F\exp\left[\frac{(\theta-\pi/2)^2}{2\sigma^2}\right]\cdot\left(1+\sum_{n=1}^{\infty} a_n \cos n\phi\right) \tag{1}$$

where F is a normalization constant, the angles, θ and ϕ are the polar and the azimuthal angles that specify the polarization direction of the corresponding vibration, respectively, and σ is the standard deviation for variable θ. Although we express the azimuthal distribution by a Fourier cosine series in Eq. (1), the only term that contributes to the linear dielectric tensor is the cos 2ϕ term. The a_2 coefficient describes the orientational anisotropy of the polarization between the x- and y-axes. The positive value of a_2 means that the polarization is oriented on average along the x-axis. Under the distribution function of Eq. (1) the average inclination angle of the polarization from the

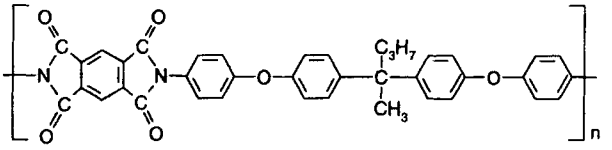

FIGURE 1 Molecular structure of the polyimide with alkyl side-chains (A3-PI).

surface is represented by θ_{incl}. Thus the orientational distribution with respect to the laboratory frame is expressed by a_2, σ and θ_{incl}.

EXPERIMENTAL

The molecular structure of polyimide used in this study is illustrated in Figure 1. Since the number of carbon atoms in the alkyl side-chain is three, hereafter we denote this polyimide by "A3-PI". The A3-PI film was spin-coated on a clean Si (0.5 mm thick) substrate. The film was cured at 250°C for an hour in a nitrogen atmosphere. The film thickness measured by ellipsometry (Shimadzu AEP-100) was 115 Å. Rubbing was done under the same condition as used in our previous studies.[9,11]

The IR absorption measurements were previously described in detail.[9] The IR absorption spectra were measured for the p-polarized light as a function of the incident angle. The experimental geometry is shown in the inset of Figure 2. The rubbing direction is in the plane of incidence of the IR light. To obtain the IR dichroic ratio, at normal incidence we measured the IR absorption spectra for the light polarized parallel and perpendicular to the rubbing direction. We determined the orientation of the backbone structure of A3-PI by fitting the incident angle dependence and the dichroic ratio at normal incidence with a theoretical calculation.

RESULTS

A3-PI has three strong IR active vibrations at 1240, 1375, and 1500 cm^{-1} that are polarized along the backbone structure. They are assigned to the C-O-C asymmetric stretching vibration, the C-N stretching vibration of the $(CO)_2NC$ bond, and the phenyl C-C stretching vibration, respectively. We used these three vibrations to determine the orientation of the backbone structure of A3-PI.

The dichroic ratio is defined by $A_{//} / A_{\perp}$, where $A_{//}$ and $A_{\perp}$ are the absorbance for the IR light polarized parallel and perpendicular to the rubbing direction, respectively. For rubbed A3-PI film, the dichroic ratios of the 1240, the 1375, and the 1500 cm^{-1} bands were 1.78, 1.75, and 1.58, respectively. These dichroic ratios indicate that the backbone

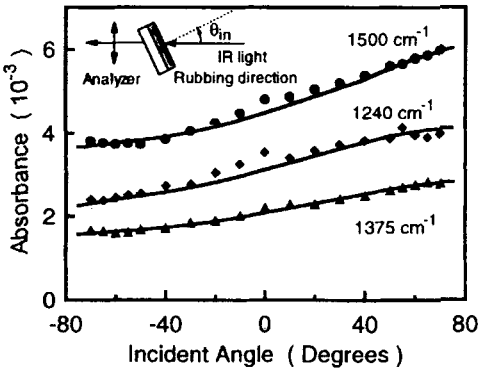

FIGURE 2 Incident angle dependence of the IR absorption of the rubbed A3-PI film on a Si substrate. The filled diamonds, triangles, and circles are the data points for the 1240, 1375, and 1500 cm^{-1} bands, respectively. The solid curves represent the best fit calculated results. The inset shows the experimental geometry and the definition of the sign of the incident angle.

structure in the rubbed film is on average aligned along the rubbing direction.

Figure 2 shows the experimental results on the incident angle dependence of the IR absorption of the three bands. The absorption intensity of all three bands increases as the incident angle increases. The sign of the incident angle is defined in the inset of Figure 2. This angle dependence indicates that the backbone structures of A3-PI are aligned on average along the rubbing direction and tilted up from the film plane; i. e. $\theta_{incl} > 0$.

To quantitatively determine the distribution function of the polarization direction, we need to know the depth of the region oriented by rubbing. The depth can be estimated by measuring the dichroic difference of the 1500 cm^{-1} band as a function of the film thickness.[9] We performed the measurement, and the depth was estimated to be ~125Å. Since the thickness of the film used in the present study was 115 Å, the rubbed A3-PI film can be assumed to have a uniform molecular orientation across the entire film thickness. We use this assumption when the IR absorption spectra are calculated.

The solid curves in Figure 2 show the best fit calculated results. The calculated angle dependence reproduces the experimental data extremely well. The dichroic ratios of the three bands are also reproduced by the calculation. The parameters of the distribution function for the best fit calculations are summarized in Table I. In the present study we determined the distribution function for each absorption band independently.

From Table I, the backbone structure of A3-PI in the rubbed film is found to be oriented along the rubbing direction and to be tilted up on average by 23° from the surface. The values for a_2 and σ differ somewhat for the three bands. This difference is

Table I Parameters of the distribution function for the best fit calculations.

ω_ν	a_2	σ	θ_{incl}
1240 cm^{-1}	0.655 ± 0.005	40 ± 2°	23 ± 1°
1375 cm^{-1}	0.625 ± 0.005	42 ± 2°	23 ± 1°
1500 cm^{-1}	0.530 ± 0.005	48 ± 2°	23 ± 1°

understandable, because the polarization directions of the three bands are not parallel to each other.

To measure the pretilt angle of bulk LC in contact with rubbed A3-PI films, anti-parallel rubbed cells with the cell gap of 50 μm were made. They were filled with 4-n-pentyl-4'-cyanobiphenyl (5CB). The pretilt angle measured by an improved crystal rotation method[12] was 9.6° at 25°C.

DISCUSSION

Let us concentrate our attention on the relation between the pretilt angle θ_{LC} of bulk LC and the inclination angle θ_{incl} of the backbone structure of polyimide. Previously we measured the pretilt angle θ_{LC} of bulk LC in contact with the rubbed poly [4, 4'-oxydiphenylene-pyromellitimide] (PMDA-ODA) film with different inclination angles θ_{incl} of the backbone structure. The PMDA-ODA has no side-chain. The measured pretilt angles θ_{LC} were 1.9° and 2.4° for θ_{incl} = 5.5° and 8.5°, respectively.[8] There is a positive correlation between these angles, θ_{LC} and θ_{incl}. In the present study the angles, θ_{LC} and θ_{incl} for polyimide with alkyl side-chains (A3-PI) were measured, and they were 9.6° and 23°, respectively. Both angles, θ_{LC} and θ_{incl} for A3-PI are much higher than those for PMDA-ODA. These results indicate that the high inclination of the backbone structure of polyimide with alkyl side-chains plays an important role in causing the high pretilt angle of bulk LC.

Sugiyama et al.[4] has suggested that the high pretilt angle of bulk LC is caused by the orientation of the side-chains. In the present study we found that the backbone structure of the side-chained polyimide is inclined at a lager angle than that of the polyimide without side-chains. Further the pretilt angle for the two kinds of polyimide is correlated with the value of the inclination angle. Thus we suggest that the high pretilt angle is caused not by the interaction between the LC molecule and the alkyl side-chain but by the interaction between the LC molecule and the inclined backbone structure. The alkyl side-chains affect the pretilt angle indirectly through the increase in the inclination angle of the backbone structure.

To confirm our suggestion we are now measuring the inclination angle of the backbone structure of rubbed polyimide with different length of the alkyl side-chains.

The pretilt angle of bulk LC in contact with the rubbed film is known to increase as the length of the alkyl side-chain increases.[2]

CONCLUSION

We have determined the orientation of the backbone structure of polyimide with alkyl side-chains in rubbed films by polarized IR absorption spectroscopy. We found that the backbone structures are oriented along the rubbing direction with the inclination angle of 23° from the surface. The pretilt angle of bulk LC in contact with this rubbed film was 9.6°. These two angles are much higher than those for the polyimide without a side-chain. We suggest that the high inclination of the backbone structure of polyimide with alkyl side-chains plays an important role in causing the high pretilt angle of bulk LC.

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