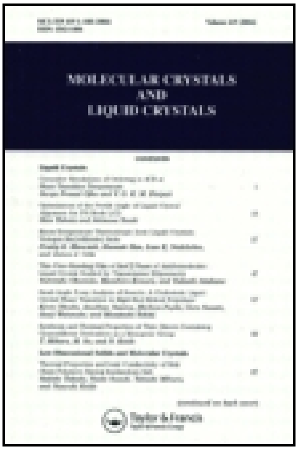

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Effect of a Cleaning Treatment on the Orientational Distribution of Polyimide Backbone Structures in Rubbed Films and on the Pretilt Angle of Liquid Crystals

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Version of record first published: 24 Sep 2006

To cite this article: Ryuichi Arafune, Kenji Sakamoto & Sukekatsu Ushioda (2001): Effect of a Cleaning Treatment on the Orientational Distribution of Polyimide Backbone Structures in Rubbed Films and on the Pretilt Angle of Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 368:1, 633-641

To link to this article: http://dx.doi.org/10.1080/10587250108029996

Mol. Cryst. and Liq. Cryst., 2001, Vol. 368, pp. 633-641
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Effect of a Cleaning Treatment on the Orientational Distribution of Polyimide Backbone Structures in Rubbed Films and on the Pretilt Angle of Liquid Crystals

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We have investigated the effect of a cleaning treatment on the orientational distribution of polyimide backbone structures in rubbed films and on the pretilt angle of liquid crystals (LCs). The rubbed polyimide films were washed in isopropyl alcohol with an ultrasonic cleaner for 5 min, and then in pure water in the same manner. The orientational distributions of the backbone structures in the unwashed and the washed polyimide films were determined by using infrared absorption spectroscopy. The orientational distribution of the polyimide backbone structures in the washed films was broader than that in the unwashed films, but the average inclination angle was the same for both films. The pretilt angle of LC was not changed by the cleaning treatment. We found that the cleaning treatment affect neither the average inclination angle of polyimide backbone structure nor the pretilt angle of LC, although it induces the relaxation of the orientational distribution of the polyimide backbone structures.

Keywords: rubbed polyimide film; cleaning treatment; pretilt angle; inclination angle of the polyimide backbone structure

INTRODUCTION

The alignment control of liquid crystal (LC) molecules by the substrate surface is one of the key technologies for the fabrication of LC displays.

Currently rubbing of polyimide films is widely used as a technique to obtain homogeneous alignment of LC molecules. The LC molecules in contact with a rubbed polyimide film align along the rubbing direction with a certain vertical tilt angle.[1,2] This angle is called the "pretilt angle". The control of the pretilt angle is an important factor in realizing defect-free LC displays.[3,4] From previous studies,[1,2,5–16] it is known that the molecular orientation of rubbed polyimide films plays an important role in the determination of the orientation of LC molecules. Recently we reported that the pretilt angle of LC is proportional to but not equal to the inclination angle of the polyimide backbone structure in the underlying film.[17–20]

To remove the dust particles created by mechanical rubbing, the rubbed films must be cleaned before LC cells are assembled. Recently Hirosawa et al.[21] reported the change of the molecular orientation of rubbed polyimide films caused by a cleaning treatment. However, they did not measure the change of the pretilt angle of LC. We have investigated the effect of a cleaning treatment both on the molecular orientation of rubbed polyimide films and on the pretilt angle of LC. In this study the orientational distribution of the polyimide backbone structures in rubbed films was determined by infrared (IR) absorption spectroscopy. The pretilt angle of LC was measured by the improved crystal rotation method.[22] Since the method for the pretilt angle measurement is already well established,[22,23] we will mainly describe the measurement of the orientational distribution of the polyimide backbone structures. Then we will discuss the effect of the cleaning treatment on the orientational distribution of polyimide backbone structures and on the pretilt angle of LC.

THEORY

The orientational distribution of the polarization of an IR active vibration can be determined by measuring the dichroic ratio at normal incidence and the incident angle dependence of the IR absorption. When we focus on an IR absorption band polarized parallel to the polyimide backbone structure, its orientational distribution can be determined. The detail of the theoretical treatment that is used in this study was already described elsewhere.[24,25] Thus we will present only the orientational distribution function of the polarization (parallel to the polyimide backbone structure) that was assumed here.

To define the orientational distribution function, we introduce two

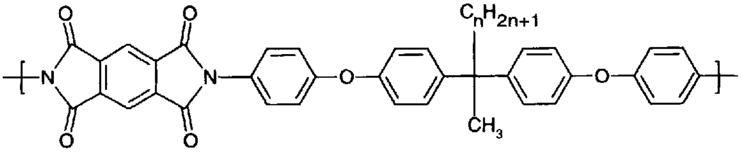

FIGURE 1 Molecular structure of An-PI, where n is the number of carbon atoms in the alkyl side-chain.

frames. One is the laboratory frame labeled by XYZ, where the Z-axis is normal to the surface, and the $+X$ direction is the rubbing direction. The other is the coordinates defined by the dielectric principal axes of a rubbed polyimide film (labeled by xyz). Since the molecular orientation in a rubbed film has C_{1v} symmetry with the XZ plane as a mirror plane, the Y-axis coincides with the y-axis. Thus these two frames are related to each other by a single angle (θ_{incl}) between the X-axis and the x-axis. (The rotation of the $+x$-axis toward the $+Z$-axis around the $Y(y)$-axis is represented by a positive sign of θ_{incl}.)

We define the orientational distribution function of the polarization of the νth IR-active vibration with respect to the dielectric principal axes by:

$$g^{\nu}(\theta,\phi) = F\exp\left[-\frac{\left(\theta-\frac{\pi}{2}\right)^{2}}{2\sigma^{2}}\right]\left(1+a_{2}\cos 2\phi\right), \qquad (1)$$

where F is a normalization constant; θ and ϕ are the polar and azimuthal angles that specify the polarization direction; σ is the standard deviation in θ. For the azimuthal distribution, we have written only the Fourier expansion term that can be determined by IR absorption measurements. When the a_2 coefficient is positive and σ has a finite value, the average orientation direction of the polarization is the x-axis. In this case, θ_{incl} means the average inclination angle from the film surface. The larger a_2 and the small σ mean the narrower orientational distribution around the x-axis.

EXPERIMENT

Figure 1 shows the molecular structure of the polyimides used in this study. We denote the polyimides by "An-PI", where n is the number of carbon atoms in the alkyl side-chain. To investigate the influence of the

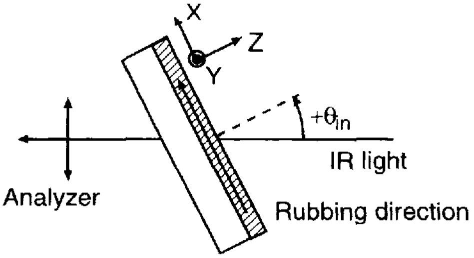

FIGURE 2 Experimental geometry for the measuring the incident angle dependence of IR absorption. θ_{in} is the angle of incidence of IR light. *XYZ* indicates the laboratory flame.

alkyl side-chain length on the orientational distribution of the polyimide backbone structures and the pretilt angle of LC by a cleaning treatment, we examined four polyimides: A1-PI, A3-PI, A6-PI, and A11-PI. The An-PI films were made by spin-coating a solution of the polyamic acid in N-methyl-2-pyrrolidone onto CaF_2 plates for IR absorption measurements or onto quartz plates for the pretilt angle measurements. To form the films the samples were baked at 250 °C for 1 hour in a nitrogen atmosphere. The film thickness was controlled in the range of 115 ± 10 Å.

The samples were rubbed by a home-made rubbing machine whose roller (diameter 70 mm) is covered by a rayon cloth (Yoshikawa Chemical Co., YA-18-R). The rubbing condition was as follows: the rotation speed of the roller was 400 rpm; the sample was passed once under the roller at a feeding speed of the sample stage of 10 mm/sec; the bending depth of the cloth fibers due to contact pressure[26] was 0.1 mm. After rubbing, the rubbed samples were washed in isopropyl alcohol with an ultrasonic cleaner for 5 min, and then in pure water in the same manner.

IR absorption measurements were performed by a Fourier-transform IR spectrometer (Mattoson Galaxy 3020). The spectral resolution was set at 4 cm^{-1}, and the spectra were obtained by integrating the results over 400 scans. Figure 2 shows the experimental geometry for measuring the incident angle dependence of IR absorption. The sample was oriented in such a way that incident plane contained the rubbing direction. The IR light was incident from the film side, and the p-polarized IR light was detected. To obtain the dichroic ratio ($A_{\parallel}/A_{\perp}$) we measured the IR ab-

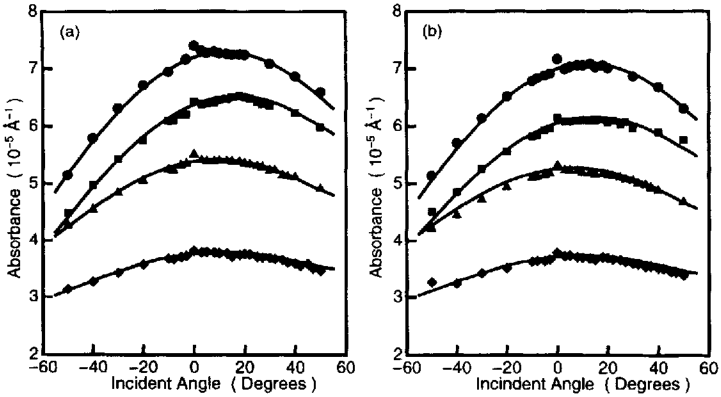

FIGURE 3 Incident angle dependence of IR absorption of the (a) unwashed and (b) washed An-PI films. The absorbance of the 1500 cm^{-1} band divided by the film thickness was plotted. The solid circles, squares, triangles, and diamonds are the data points for A1-PI, A3-PI, A6-PI, and A11-PI films, respectively. The solid curves are the best-fit calculated results.

sorption spectra at normal incidence for the light polarized parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the rubbing direction. The IR absorption measurements were carried out before and after the cleaning treatment; i. e. for each sample the orientational distribution of the polyimide backbone structures was determined before and after the cleaning treatment.

To investigate the effect of the cleaning treatment on the pretilt angle of LC, we fabricated LC cells with two unwashed (or washed) films. The rubbing directions of the two films were set antiparallel to each other. The cell gap was 50 μm. The 4-n-pentyl-4'-cyanobiphenyl (5CB) was poured into the cells in the isotropic phase. The pretilt angle of LC was measured by the improved crystal rotation method.[22]

RESULTS AND DISCUSSION

To determine the orientational distribution of the polyimide backbone structures, we used the absorption band at 1500 cm^{-1}. This band is assigned to the phenyl C-C stretching vibration, which is polarized along the polyimide backbone structure. Figure 3(a) shows the incident angle

TABLE I Best fit parameters obtained from fitting the data of Fig. 3. The uncertainty for a_2 is ±0.005.

	Unwashed film			Washed film		
Polyimide	a_2	σ	θ_{incl}	a_2	σ	θ_{incl}
A1-PI	0.46	43±5°	19±2°	0.39	43±5°	19±2°
A3-PI	0.51	40±5°	22±2°	0.42	46±5°	22±2°
A6-PI	0.29	90±10°	32±2°	0.23	130±10°	32±2°
A11-PI	0.27	130±10°	40±3°	0.25	160±20°	43±3°

dependence of the 1500 cm^{-1} band for the unwashed films. For all the An-PI films, the maximum absorption occurs on the positive side of the incident angle (the sign of the incident angle is defined in Fig. 2.). The IR dichroic ratios ($A_{\parallel}/A_{\perp}$) at normal incidence were 1.49, 1.57, 1.24, and 1.23 for the A1-PI, A3-PI, A6-PI, and A11-PI films, respectively. From these results, we can deduce that the polyimide backbone structures in the films are oriented along the rubbing direction and inclined from the film surface on average; i. e. $a_2 > 0$ and $\theta_{incl} > 0°$.

Figure 3(b) shows the incident angle dependence of the 1500 cm^{-1} band intensity for the washed films. The IR dichroic ratios at normal incidence were 1.39, 1.42, 1.21, and 1.20 for the A1-PI, A3-PI, A6-PI, and A11-PI films, respectively. For all the An-PI films, the IR dichroic ratio was reduced by the cleaning treatment. This reduction indicates the relaxation of the azimuthal angle distribution of the polyimide backbone structures. To obtain further information on the orientational distribution change induced by the cleaning treatment, we need to perform a theoretical fitting procedure. Before presenting the fitting results, we should note here that there is no difference in the IR absorption spectra before and after the cleaning treatment, except for the change of the absorbance due to the molecular orientation change (see below). This result indicates that no chemical reaction occurs during the cleaning treatment.

The solid curves in Fig. 3 are the best fit calculated results. Since the thickness of the films used in this study is less than the depth of the region affected by rubbing (~ 125 Å),[24,25] we assumed in the calculation that the orientational distribution is uniform across the entire film thickness. One can see that the calculated results reproduce the experimental data extremely well. We summarized the sets of parameters (a_2, σ, and θ_{incl}) for the best fit calculation in Table I. We also used the film thickness as a fitting parameter but it was the same for both the unwashed and

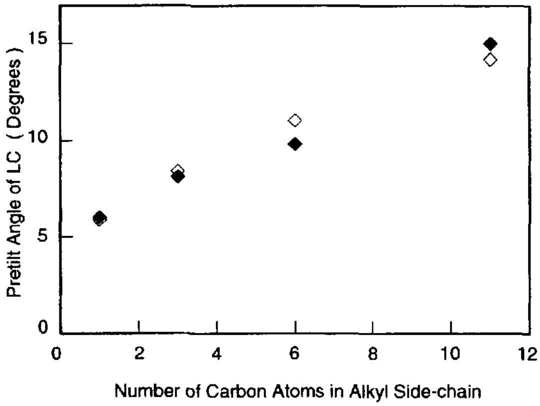

FIGURE 4 The pretilt angle of LC in contact with the rubbed An-PI films. The horizontal axis is the number of carbon atoms in the alkyl side-chain. The open diamonds and solid diamonds are the data points for the unwashed and washed An-PI films, respectively

washed films. This result means that the change of the incident angle dependence and the dichroic ratio of the 1500 cm^{-1} band is due to the change in the molecular orientation of the polyimide film caused by the cleaning treatment. For all An-PIs, the values of a_2 are smaller for the washed films than for the unwashed films. On the other hand the values of σ for the two kinds of films have the opposite relation. This result shows that the cleaning treatment relaxes the orientational distribution of the polyimide backbone structures in both the polar and azimuthal angle directions. On the other hand, the average inclination angle (θ_{incl}) did not change within the experimental error. Thus we found that the cleaning treatment does not affect the average orientation direction of the polyimide backbone structures. In addition, we also found from Table I that the orientational change of polyimide backbone structure does not depend on the length of the alkyl side-chain.

Figure 4 shows the result of the pretilt angle measurements. The pretilt angle of LC in contact with the washed An-PI film was almost the same as that for the unwashed An-PI film. Previously we reported a linear relation between the pretilt angle of LC and the average inclination angle of the An-PI backbone structures in the underlying rubbed films.[19,20] According to this relation, the pretilt angle of LC should be the same for both unwashed and washed films, because the cleaning treatment induces no change of the average inclination angle (see Table I). Thus this is the reason why the pretilt angle did not change after the cleaning treatment.

CONCLUSION

We have investigated the change of the orientational distribution of the polyimide backbone structures in rubbed films and the pretilt angle of LC by a cleaning treatment. We found that the cleaning treatment only causes the relaxation of the orientational order of the polyimide backbone structures, independent of the length of the alkyl side-chain. The average inclination angle of the polyimide backbone structure and the pretilt angle of LC are not affected by the cleaning treatment.

Acknowledgements

We would like to thank S. Murata of Chisso Co. Ltd. for supplying the chemical samples used in this work.

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