Importance of rubbing-induced inclination of polyimide backbone structures for determination of the pretilt angle of liquid crystals

R. Arafune,* K. Sakamoto, and S. Ushioda

Research Institute of Electrical Communication, Tohoku University, Sendai 980-8577, Japan

S. Tanioka and S. Murata

Chisso Petrochemical Corporation Specialty Chemicals Research Center, 5-1 Goikaigan, Ichihara 290-0058, Japan

By using polarized infrared absorption spectroscopy, we have determined the average inclination angle of the backbone structure of a series of polyimides with alkyl side chains induced by rubbing. We examined four polyimides. They have an identical backbone structure, but the number (n) of carbon atoms in the alkyl side chain is different: $n = 1, 3, 6,$ and 11. The inclination angle of the polyimide backbone structure increases with the number of carbon atoms in the alkyl side chain. To learn the behavior of the alkyl side chain under rubbing, we have also measured the contact angle of water on the film surface. For the rubbed films of polyimide with short alkyl side chains ($n = 1, 3,$ and 6), *almost all* the alkyl side chains at the film surface orient inward, toward the bulk of the film. On the other hand, the alkyl side chains that orient outward exist at the rubbed film surface for the polyimide with a long alkyl side chain ($n = 11$). The pretilt angle of liquid crystals (LC) is proportional to the inclination angle of the polyimide backbone structure independent of the orientation of the alkyl side chain. From these results we conclude that the rubbing-induced inclination of the polyimide backbone structure has the dominant effect in determining the pretilt angle of LC. [S1063-651X(98)04811-9]

I. INTRODUCTION

The alignment mechanism of liquid crystal (LC) molecules in contact with a rubbed polyimide film is a subject not only of scientific interest, but also of technological importance. Even though the LC alignment mechanism is not understood completely, rubbed polyimide films are widely used as an alignment film in practical applications. Two possible mechanisms were proposed to explain the alignment of LC molecules on rubbed polymer films. One is based on an elastic interaction between LC molecules and the microgrooves at the polymer film surface created by rubbing [1]. The other is based on an intermolecular interaction between LC molecules and polymer chains in the underlying film [2]. As a result of previous studies [3,4], now it is well recognized that for rubbed polyimide films the intermolecular interaction plays a more important role in LC alignment than the elastic interaction.

LC molecules in contact with a rubbed polyimide film are, on average, oriented along the rubbing direction with a certain tilt angle. This tilt angle measured from the substrate surface is called the ''pretilt angle.'' The pretilt angle is a parameter that characterizes surface-induced alignment of LC molecules and also an important variable in the fabrication of LC devices. Fukuro and Kobayashi [5] demonstrated that the pretilt angle can be controlled in a range from a few degrees up to 30° by using polyimides with alkyl side chains. The pretilt angle of LC increases with the length of the alkyl side chains of polyimide. However, the effect of the alkyl side chain on the pretilt angle is still not yet clear.

In our previous study on a polyimide without alkyl side chains, we found that in a rubbed film the backbone structure is oriented along the rubbing direction and inclined up from the film surface [6–8]. There is a positive correlation between the inclination angle of the backbone structure and the pretilt angle of LC [8]. Thus, we suggested that the pretilt angle is determined by the inclination of the polyimide backbone structure. For rubbed films of polyimides with alkyl side chains, the inclination of the backbone structures is also expected to play an important role in determining the pretilt angle of LC. Thus, the aim of the present study is to examine the role of alkyl side chains and polyimide backbone structures in determining the pretilt angle of LC. To avoid the effect of the difference in the backbone structure of polyimide on its inclination angle and the pretilt angle of LC, we used a series of polyimides with an identical backbone structure but with different lengths of alkyl side chains [9]. We examined four polyimides with 1, 3, 6, and 11 carbon atoms in the alkyl side chain.

We have investigated the correlation between the inclination angle of the backbone structure of polyimide and the pretilt angle of LC. Many techniques have been used to measure the molecular orientation in rubbed polyimide films [10–14]. We have chosen polarized infrared (IR) absorption spectroscopy because we have established a method for quantitative determination of the molecular orientation in the surface region (~ 125 Å) of a rubbed polyimide film [6–9,15,16]. To learn the orientation of the alkyl side chains, we have measured the contact angle of water on unrubbed and rubbed films of these polyimides. Since the contact angle of water is sensitive to the hydrophilicity of film surfaces, we can obtain qualitative information on the orientation of alkyl side chains by measuring whether the alkyl side chains orient inward (toward the bulk of the film) or outward [17,18]. In this paper we present the details of experimental results and discuss the role of alkyl side chains and the importance of

---

*Electronic address: arafune@ushioda.riec.tohoku.ac.jp

the inclination of the polyimide backbone structure in determining the pretilt angle of LC.

II. THEORY

The orientational distribution of the polarization of an IR-active vibration can be determined by measuring the incident angle dependence of the IR absorption and the IR dichroic ratio at normal incidence. The details of the theory that we use to determine the orientational distribution were presented elsewhere [7]. Thus, we will describe only the orientational distribution function of the polarization of an IR-active vibration that we assume in this study.

Before we present the orientational distribution function, we define two frames of reference with respect to a rubbed polyimide-coated substrate. 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 (x, y, and z) of the rubbed polyimide film. Since the molecular orientational distribution of the rubbed polyimide film has C_{1v} symmetry with the XZ plane as a mirror plane [7], the two dielectric axes (the x and z axes) lie in the XZ plane. Thus, the xyz coordinates are related to the XYZ coordinates by a single angle θ_{incl}. This is the inclination angle of the $+x$ axis from the film surface (the XY plane). A positive value of θ_{incl} represents a rotation of the $+x$ axis toward the $+Z$ axis around the Y (y) axis. We define the orientational distribution function $g^{\nu}(\theta,\phi)$ of the polarization of the νth IR-active vibration with respect to the dielectric principal axes (the xyz coordinates) by

$$g^{\nu}(\theta,\phi) = F \exp\left[-\frac{\left(\theta-\frac{\pi}{2}\right)^2}{2\sigma^2} \right](1+a_2\cos 2\phi), \quad (1)$$

where F is a normalization constant; θ and ϕ are the polar and azimuthal angles that specify the polarization direction with respect to the dielectric principal axes; σ is the standard deviation for variable θ; a_2 is the coefficient of the second order term of the Fourier cos series that expresses the azimuthal distribution. Although the Fourier cos series contains an infinite number of terms of $\cos n\phi$, the term that can be determined by IR absorption is only the $\cos 2\phi$ term. This is the case where the polar angle (θ) part of $g^{\nu}(\theta,\phi)$ is given by a Gaussian distribution with the center at $\theta = \pi/2$. The a_2 coefficient describes the orientational anisotropy of the polarization between the x and y axes. The standard deviation σ describes the sharpness of the polar angle distribution of the polarization with respect to the xy plane.

The parameters a_2 and σ describe the orientational distribution with respect to the dielectric principal axes. The dielectric principal axes are related to the laboratory frame by the inclination angle of the x axis, θ_{incl}, as described above. Thus, the orientational distribution of the polarization, with respect to the laboratory frame, is expressed by a parameter set a_2, σ, and θ_{incl}. When the a_2 coefficient is positive and s has a finite value, the average orientation direction is the x axis. In this case the inclination angle θ_{incl} corresponds to the average inclination angle of the polarization vector from the film surface.
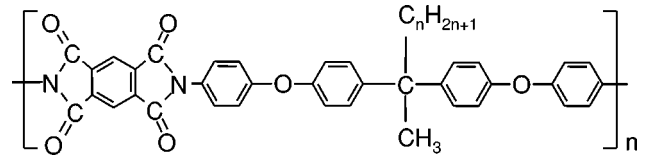

FIG. 1. Molecular structure of An-PI, where n is the number of carbon atoms in the alkyl side chain.

In this study we are interested in the orientational distribution of the backbone structure of polyimide. If we analyze an IR absorption band polarized along the backbone structure, we can determine the orientational distribution of the backbone structure; to be exact, the orientational distribution of the specific chemical bond whose vibrational polarization produces the relevant IR absorption band.

III. EXPERIMENT

Figure 1 shows the molecular structure of polyimides with alkyl side chains used in this study. Since the polyimides have alkyl side chains that contain n carbon atoms, from now on we denote the polyimide by ''An-PI.'' Four polyimides, A1-PI, A3-PI, A6-PI, and A11-PI were examined in this study. An-PI films were made by spin-coating a solution of the polyamic acid in N-methyl-2-pyrrolidone onto CaF$_2$ plates (5 mm thick) for IR absorption measurements or quartz plates (1.1 mm thick) for water contact angle measurements. Baking the plates at 250 °C for an hour in a nitrogen atmosphere formed the films.

Rubbing treatments were performed by a homemade rubbing machine whose roller (with a diameter of 70 mm) is covered with 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; and the bending depth of the cloth fibers due to contact pressure [19] was 0.1 mm.

The IR absorption spectra of the An-PI films were measured by using a Fourier-transform IR spectrometer (Mattoson Galaxy 3020) with a mercury cadmium telluride detector. The spectral resolution was set at 4 cm^{-1}, and the spectra were obtained by integrating the result over 400 scans.

Figure 2 shows the experimental geometry for measuring the incident angle dependence of IR absorption. The IR light was incident from the An-PI film side and the absorption of p-polarized light was measured. The angle dependent absorption was measured by varying the angle of incidence in
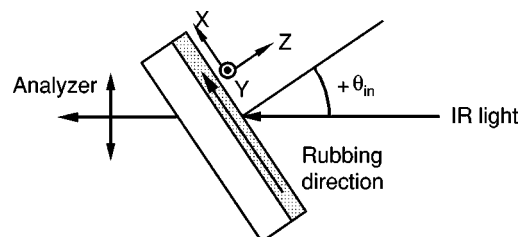

FIG. 2. Experimental geometry for the measurement of incident angle dependence of IR absorption. θ_{in} is the angle of incidence of IR light.
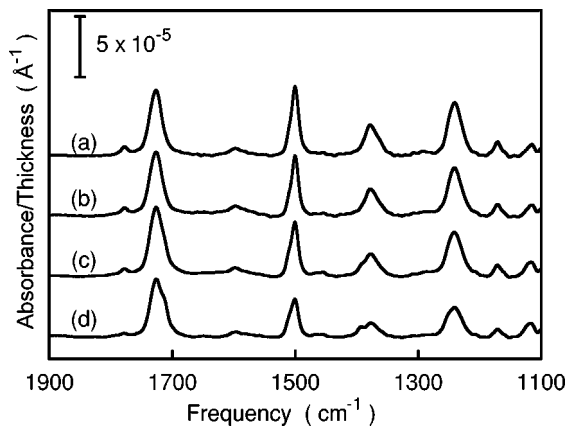
FIG. 3. IR absorption spectra of the unrubbed A1-PI (a), A3-PI (b), A6-PI (c), and A11-PI (d) films on the CaF$_2$ substrate.

the plane that contains the rubbing direction. At normal incidence we measured the absorption spectra, for light polarized both parallel and perpendicular to the rubbing direction, to obtain the IR dichroic ratio.

The contact angle of water on the An-PI film was measured by a face-contact angle meter (Kyowa Interface Science Co. ltd. CA-A type). Five water droplets were put on each sample. We measured four contact angles per droplet: both sides of the droplet along the rubbing direction and both sides perpendicular to the rubbing direction. Twenty contact angles were measured for each sample.

IV. RESULTS AND DISCUSSIONS

Figure 3 shows the IR-absorption spectra of unrubbed An-PI films on CaF$_2$ plates at normal incidence. The vertical axis is normalized by the film thickness. The main features of the spectra for all An-PI films are the same, except for the absorption intensity. Three absorption bands polarized along the polyimide backbone structure are observed at 1244 cm^{-1}, 1377 cm^{-1}, and 1500 cm^{-1}. 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 [20]. Since the backbone structure of An-PI is not straight, the polarization directions of the three absorption bands are not parallel to each other. Thus, the orientational distributions of the polarizations of the three absorption bands are different in general. However, the difference between them is small, and the average inclination angle of the polarization, which is the most important parameter in this study, is the same for the three absorption bands [16]. In this study we focus only on the strongest and narrowest band at 1500 cm^{-1}, and determine the orientational distribution of its polarization. We refer to this orientational distribution as that of the backbone structure of An-PI.

Figure 4 shows the incident angle dependence of IR absorption for the rubbed An-PI films. The vertical axis of Fig. 4 is the IR absorbance normalized by the film thickness. Solid circles, triangles, squares, and diamonds are the data points for the rubbed A1-PI, A3-PI, A6-PI, and A11-PI films, respectively. The maximum absorption occurs on the positive side of the incident angle for all rubbed An-PI films. The dichroic ratios (A$_\parallel$/A$_\perp$) at normal incidence are 1.19, 1.15, 1.12, and 1.12 for the rubbed A1-PI, A3-PI, A6-PI, and
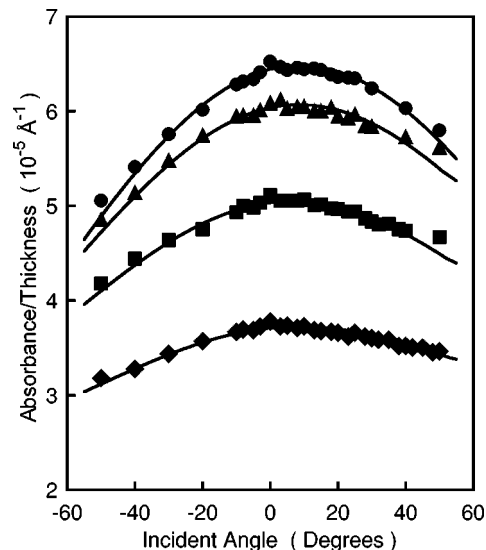

FIG. 4. Incident angle dependence of IR absorption of the rubbed An-PI films. The IR absorbance of the 1500 cm^{-1} band is plotted. The vertical axis is normalized by the film thickness. The solid circles, triangles, squares, and diamonds are the data points for rubbed A1-PI, A3-PI, A6-PI, and A11-PI films, respectively. The solid curves are the best-fit calculated results.

A11-PI films, respectively, where A$_\parallel$ and A$_\perp$ are the IR absorbance for light polarized both parallel and perpendicular to the rubbing direction. From this simple observation alone one can deduce that the polyimide backbone structure is oriented, on average, along the rubbing direction and inclined up from the surface plane; i.e., $a_2 > 0$ and $\theta_{incl} > 0°$.

To determine the orientational distribution of the polyimide backbone structure (a_2, σ, and θ_{incl}) by a fitting process, it is necessary to know the depth of the region oriented by rubbing. The depth can be estimated by measuring the IR dichroic difference A$_\parallel$-A$_\perp$ as a function of the film thickness [7]. We performed the measurement, and the depth was estimated to be ~ 125 Å for all An-PI films. The film thickness of all samples used in this study was below 125 Å. Thus, in determining a_2, σ, and θ_{incl}, we can assume that the rubbed An-PI films have a uniform orientational distribution of the backbone structure across the entire film thickness [7].

The solid curves in Fig. 4 are the results of best-fit calculations. The theoretical curves reproduce the experimental result extremely well. The parameters for the best-fit calculation are summarized in Table I. The a_2 coefficient is almost constant for all rubbed An-PI films. σ and θ_{incl} increase with the number of carbon atoms in the alkyl side chain. Since the backbone structure of An-PI is identical, from this result we can see that the alkyl side chains affect

TABLE I. Best-fit parameters obtained from fitting the data of Fig. 4.

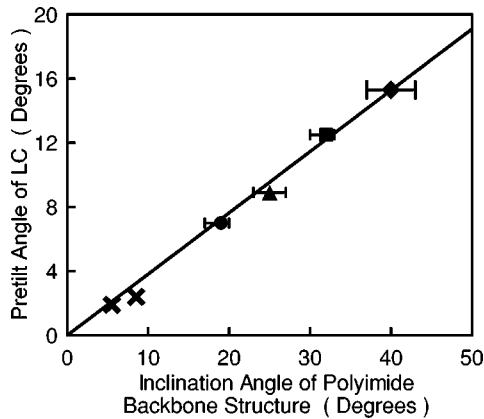|	A1-PI	A3-PI	A6-PI	A11-PI
a_2	0.21 ± 0.05	0.20 ± 0.02	0.20 ± 0.01	0.18 ± 0.05
σ	$56 \pm 10°$	$65 \pm 4°$	$113 \pm 6°$	$136 \pm 10°$
θ_{incl}	$19°$	$25°$	$32°$	$40°$

FIG. 5. Relation between the pretilt angle of LC and the inclination angle of the polyimide backbone structure. The symbols are the same as in Fig. 4. The experimental uncertainty in the pretilt angle is smaller than the size of the plotted symbols. The crosses are the data for the rubbed PMDA-ODA films from our previous work (Ref. [8]).

the polar angle distribution (σ and θ_{incl}) of the polyimide backbone structure in the rubbed films.

Figure 5 shows the relation between the inclination angle of the polyimide backbone structure (θ_{incl}) and the pretilt angle of LC in contact with the rubbed film. The pretilt angle of 4-n-pentyl-4'-cyanobiphenyl (5CB) was measured by an improved crystal rotation method [21]. Figure 5 shows that the relation between the inclination angle of the backbone structure and the pretilt angle of LC is linear. We also plotted the data for the rubbed PMDA-ODA films [8] in Fig. 5. PMDA-ODA has a similar backbone structure but no alkyl side chain (the molecular structure of PMDA-ODA was illustrated in Fig. 2 of Ref. [7]). The linear relation holds for the data for PMDA-ODA as well; e.g., the linear relation holds independent of the presence or absence, and the length of the alkyl side chain. This linear relation strongly suggests that the inclination angle of the polyimide backbone structure determines the pretilt angle of LC, and also that the alkyl side chains do not directly affect the pretilt angle of LC.

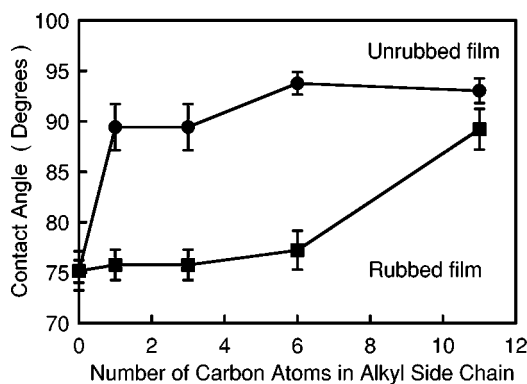Figure 6 shows the experimental results for the contact

FIG. 6. The contact angle of water on the An-PI and the PMDA-ODA films. The horizontal axis is the number (n) of carbon atoms in the alkyl side chain. The data at $n=0$ are for the PMDA-ODA films. The solid circles and squares are the data points for the unrubbed and rubbed films, respectively.

angle of water on An-PI and PMDA-ODA films on quartz plates. The horizontal axis is the number (n) of carbon atoms in alkyl side chains. Since PMDA-ODA has no alkyl side chain, the data for PMDA-ODA films are shown at $n=0$. The solid circles and squares are the contact angles of water on the unrubbed and rubbed films, respectively. As described in the experimental section, we measured the contact angles along the four directions every 90° with respect to the rubbing direction. Since the measured contact angle shows no directional dependence within our experimental uncertainty, the average of the contact angles along the four directions is plotted in Fig. 6.

The water contact angles for the unrubbed An-PI films are significantly larger than that for the rubbed PMDA-ODA films. Water contact angle depends on the hydrophilicity of the underlying film surface. A larger contact angle corresponds to a more hydrophobic surface. Since the alkyl side chain is more hydrophobic than the polyimide backbone [17], this result for the rubbed films means that a rubbing treatment reduces the number of alkyl side chains exposed on the film surface.

For PMDA-ODA films the contact angle does not change by a rubbing treatment. This means that the hydrophilicity of the PMDA-ODA film surfaces is not influenced by the orientational change of the backbone structures induced by rubbing. Since PMDA-ODA has no alkyl side chains, the hydrophilicity of the film surface is determined by that of the backbone structure independent of the orientational distribution of the backbone structures. Thus, the contact angles should be equal for the unrubbed and rubbed PMDA-ODA films. The measured results in Fig. 6 show that this reasoning is valid.

In contrast to the PMDA-ODA films, the water contact angles for the A1-PI, A3-PI, and A6-PI films decreased significantly after rubbing treatment. The contact angles for these rubbed films are equal to that for the PMDA-ODA films within experimental uncertainty. Since the polyimide backbone structure of An-PIs is similar to that of PMDA-ODA, the polarity of the An-PI backbone structure is expected to be equal to that of the PMDA-ODA backbone structure. These results indicate that for the rubbed A1-PI, A3-PI, and A6-PI films, almost all of the alkyl side chains at the film surfaces orient inward and they are not exposed on the surface. Since the LC molecules interact with the polyimide molecules at the interface, the alkyl side chains that orient inward should not contribute to the alignment of LC molecules. Thus, this result suggests that the alkyl side chains of A1-PI, A3-PI, and A6-PI do not directly affect the pretilt angle of LC.

For the A11-PI films the decrease of the contact angle by rubbing is only about 3°, while it is about 13° for the other An-PI films ($n=1$, 3, and 6). The contact angle for the rubbed A11-PI films is significantly larger than that for the PMDA-ODA films. These results indicate that the alkyl side chains that are exposed on the surface still exist at the rubbed A11-PI film surfaces. Although we have no direct experimental evidence, we can imagine the orientational picture of the alkyl side chains at the surface as follows; the alkyl side chain of A11-PI is so long that it cannot be buried by a rubbing treatment completely; the long alkyl side chain is probably bent halfway; the backbone side of the alkyl side

chain orients inward, but the end of the alkyl side chain orients outward (the reverse is also possible.).

Here, we should note that the alkyl side chain that orients outward at the film surface can interact with LC molecules at the interface. If the alkyl side chain has a significant effect on the determination of the LC pretilt angle, the linear relation between the inclination angle of the polyimide backbone structure and the pretilt angle of LC should not hold for A11-PI. This is because almost all of the alkyl side chains of An-PI ($n=1$, 3, and 6) orient inward at the rubbed film surface as described above. However, the linear relation holds for all An-PIs independent of the orientation of the alkyl side chains at the rubbed film surface, inward or outward. Thus, the results of the contact angle measurement for the An-PI films support the suggestion derived from the linear relation between the inclination angle of the polyimide backbone structure and the pretilt angle of LC; i.e., the alkyl side chains do not directly affect the pretilt angle of LC, independent of the length ($n \leqslant 11$) of the alkyl side chain.

V. CONCLUSION

We have measured the average inclination angle of polyimide backbone structure in rubbed An-PI films. The average inclination angle of the polyimide backbone structure increases monotonically with the length of the alkyl side chain. We have also measured the contact angle of water on the unrubbed and rubbed An-PI films. We found that almost all of the alkyl side chains of A1, A3, and A6-PI orient inward at the rubbed film surfaces, while at the rubbed A11-PI film surface the alkyl side chains that orient outward exist. The pretilt angle of LC in contact with the rubbed An-PI films is proportional to the inclination angle of polyimide backbone structure, independent of the orientation of alkyl side chains at the rubbed film surface. From these results we conclude that the rubbing-induced inclination of the polyimide backbone structure has the dominant effect on the pretilt angle of LC. The alkyl side chain affects the inclination angle of the backbone structures induced by rubbing, but they do not directly determine the pretilt angle of LC. The effect, due to the alkyl side chain, is only indirect.

ACKNOWLEDGMENTS

[1] D. W. Berreman, Phys. Rev. Lett. **28**, 1683 (1972).

[2] J. M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Pastel, J. Appl. Phys. **62**, 4100 (1987).

[3] A. J. Pidduck, G. P. Bryan-Brown, S. Haslam, R. Bannister, I. Kitely, T. J. McMaster, and L. Boogaard, J. Vac. Sci. Technol. A **14**, 1723 (1996).

[4] E.-S. Lee, Y. Saito, and T. Uchida, Jpn. J. Appl. Phys., Part 2 **32**, L1822 (1992).

[5] H. Fukuro and S. Kobayashi, Mol. Cryst. Liq. Cryst. **163**, 157 (1988).

[6] K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suzuki, and S. Morokawa, Jpn. J. Appl. Phys., Part 2 **33**, L1323 (1994).

[7] K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suzuki, and S. Morokawa, J. Appl. Phys. **80**, 431 (1996).

[8] R. Arafune, K. Sakamoto, D. Yamakawa, and S. Ushioda, Surf. Sci. **368**, 208 (1996).

[9] R. Arafune, K. Sakamoto, and S. Ushioda, Appl. Phys. Lett. **71**, 2755 (1997).

[10] Y. Ouchi, I. Mori, M. Sei, E. Ito, T. Araki, H. Ishii, K. Seki, and K. Kondo, Physica B **208/209**, 407 (1996).

[11] I. Mori, T. Araki, H. Ishii, Y. Ouchi, K. Seki, and K. Kondo, J. Electron Spectrosc. Relat. Phenom. **78**, 371 (1996).

[12] M. F. Toney, T. P. Russel, J. A. Logan, H. Kikuchi, J. M. Sands, and S. K. Kumar, Nature (London) **374**, 709 (1995).

[13] K. Shirota, K. Ishikawa, H. Takazoe, A. Fukuda, and T. Shiibashi, Jpn. J. Appl. Phys., Part 2 **34**, L316 (1995).

[14] I. Hirosawa, Jpn. J. Appl. Phys., Part 1 **35**, 5873 (1996).

[15] K. Sakamoto, R. Arafune, and S. Ushioda, Appl. Spectrosc. **51**, 541 (1997).

[16] K. Sakamoto, N. Abe, R. Arafune, and S. Ushioda, Mol. Cryst. Liq. Cryst. **299**, 169 (1997).

[17] K.-W. Lee, S.-H. Peak, A. Lien, C. Durning, and H. Fukuro, Macromolecules **29**, 8894 (1996).

[18] K.-W. Lee, A. Lien, J. H. Stathis, and S.-H. Peak, Jpn. J. Appl. Phys., Part 1 **36**, 3591 (1997).

[19] D.-S. Seo, K. Muroi, and S. Kobayashi, Mol. Cryst. Liq. Cryst. **213**, 223 (1992).

[20] H. Ishida, S. T. Wellinghoff, E. Baer, and J. L. Koenig, Macromolecules **13**, 826 (1980).

[21] K. Y. Han, T. Miyashita, and T. Uchida, Mol. Cryst. Liq. Cryst. **241**, 147 (1994).