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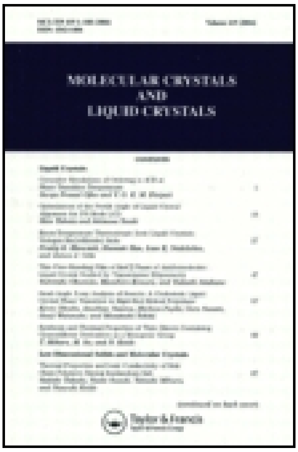

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Rubbing-Induced Molecular Alignment on a Rubbed Alkyl-Branched Polyimide Film

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Version of record first published: 24 Sep 2006.

To cite this article: J. Y. Huang , J. S. Li & S. H. Chen (1995): Rubbing-Induced Molecular Alignment on a Rubbed Alkyl-Branched Polyimide Film, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 270:1, 77-84

To link to this article: http://dx.doi.org/10.1080/10587259508031017

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Mol. Cryst. Liq. Cryst., 1995, Vol. 270, pp. 77–84
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(Received January 9, 1995; in final form March 14, 1995)

Rubbing-induced molecular alignment on an alkyl-branched polyimide film with varying unidirectional rubbing strength has been investigated with the use of optical phase retardation measurement, atomic force microscopy (AFM), and second-harmonic generation (SHG). Our AFM images suggest that the rubbing-induced micro-groove should play a minor role in aligning liquid crystal (LC) molecules. The polar angle of the polar head group of a LC monolayer on an alkyl-branched polyimide film was found to vary with the rubbing strength. The results obtained from various experimental techniques can be reconciled with a simple molecular model proposed in this paper.

Keywords: Liquid crystal, polyimide, alkyl-branched, phase retardation, pretilt angle, atomic force microscopy, optical second-harmonic generation.

In the fabrication of a liquid crystal device (LCD), a uniform, defect-free alignment of the liquid-crystal (LC) molecules is a prerequisite for an efficient performance of the LCD. In the past, this LC alignment was generally achieved by the use of an orienting layer of rubbed polymer.[1] It is found from optical second-harmonic generation (SHG) studies that information deduced for the LC monolayer on the surface of a rubbed polymeric film directly correlates to the bulk pretilt angle within a LC cell.[2] The polar ordering of the LC monolayer on a typical main-chain polymer film, however, was found to be irrelevant to the azimuthal in-plane ordering.[2]

The LC alignment on a rubbed polymer film generally results in a low bulk pretilt angle ($\theta_p < 5°$). For a high performance device with better electro-optical effects and wider viewing angles, a super twist nematic (STN) cell with twist angles from 180° to 270° is desired.[3] This configuration requires the LC bulk pretilt angles ranging from 5° to 20°. Recently, it has been discovered that alkyl-branched polyimide films are useful in generating a high pretilt angle.[4] The chemical structure of the polyimides generally comprises of two parts with one being an ordinary long polymer chain and the other being a chemically attached hydrocarbon branch.[5] The main polymer chain is considered to play a major role in aligning LC in a single direction introduced by the rubbing and the alkyl branch is responsible for producing a high pretilt angle.[5] The short-range intermolecular interactions between the LC and polymer molecules are believed to play an important role in the alignment of the LC on the rubbed polymeric surface;[6] however, the detailed mechanisms of the alignment are not yet sufficiently understood.

In this paper, evidence of the LC alignment by the intermolecular interaction on a rubbed alkyl-branched polyimide film is reported. Optical phase retardation measurements and atomic force microscopy (AFM) were used to investigate the rubbing-induced molecular anisotropy in the rubbed polymer film. The orientational distribution of a LC monolayer on the polymer surface rubbed with varying strength was then deduced from the experimental SHG results.

A thin layer of alkyl-branched AL-3046 polyimide, developed by Japan Synthetic Rubber Co. for high pretilt LC bulk alignment,[7] was applied on a glass substrate by spin coating. The polymer-coated substrate was followed by a pre-baking step at 80°C for 15 min to evaporate the solvent remainder. The sample was then cured by baking at 200°C for 1 h. The resulting film, which typically has a thickness of 1000 Å, was then successively rubbed along one direction by a rotating velvet-wrapped cylinder to achieve the desired rubbing strength. The rubbing strength exerted on the polymer film is characterized by $R_s = N\gamma f$, where N is the cumulative number of rubbings, γ is the total length of cloth in contact with a given point on the glass substrate, and f is a characteristic coefficient of the interface between the rubbing cloth and the substrate.[8,9] In this experiment, γ is estimated to be about 13.6 cm. Since f is not a well-defined quantity, we cannot determine absolute values for the rubbing strengths, but we can accurately control the relative rubbing strengths by varying N. After each rubbing, we measure the optical phase retardation and atomic force microscopic image to characterize the rubbed polymer film. A LC monolayer of 4-n-octyl-4′-cyanobiphenyl (8CB) was thermally evaporated onto the surface of the rubbed polymer film.[9] The optical second-harmonic signal at 0.266 μm reflected from the LC monolayer was then detected to reflect the rubbing-induced orientational distribution of the LC monolayer.

In Figure 1, we first present the measured pretilt angle (see the filled symbols) of 4-n-pentyl-4′-cyanobiphenyl (5CB) liquid crystal sandwiched between two antiparallel

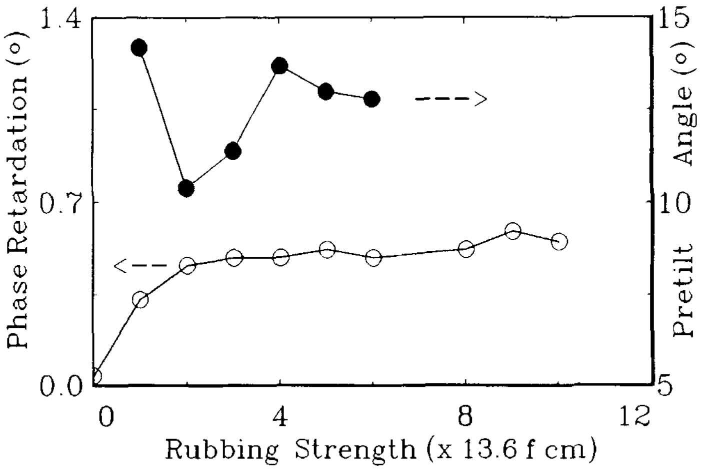

FIGURE 1 Pretilt angle (see the filled circles) of 4-n-pentyl-4′-cyanobiphenyl liquid crystal sandwiched between two anti-parallel rubbed AL-3046 polyimide coated glass substrates, and the rubbing-induced phase retardation (open symbols) introduced into the AL-3046 polyimide films are plotted as functions of rubbing strength. The rubbing strength indicated along the x-axis is in the unit of 1 γf = 13.6f·cm.

rubbed AL-3046 polyimide-coated glass substrates with varying rubbing strength. The substrates of the LC cell are separated at a distance of 75 μm. The rubbing-induced phase retardation from the polymeric layers was also shown in Figure 1 by open circles for comparison. It is clearly observed that the molecular anisotropy introduced in the rubbed AL-3046 is almost saturated with $R_s > 27f\cdot\text{cm}$. All these LC cells exhibit a uniform bulk alignment with a high pretilt under the examination of a conoscope. The pretilt angle in the LC bulk achieves 14.2° with the first time rubbing (i.e., $R_s = 1\,\gamma f = 13.6f\cdot\text{cm}$) and it then decreases to a minimum of 10.4° at a rubbing strength of $2\gamma f$. The LC bulk pretilt increases again to a local maximum of 13.7° at $4\gamma f = 54f\cdot\text{cm}$ and then levels off at higher rubbings. The more complicated dependence of the LC bulk pretilt on rubbing strength than the phase retardation from the rubbed polymer film suggests that two interactions may compete for the LC bulk alignment.

In Figure 2(a), a topographic image of a rubbed AL-3046 film with $R_s = 13.6f\cdot\text{cm}$ is presented. The surface of the rubbed AL-3046 film does not exhibit any observable rubbing scars. However, simultaneous lateral force microscopic (LFM)[10] scan over the same area (see Fig. 2(b)) clearly shows an anisotropic distribution of friction force. The period of the friction-force distribution is about 5.6 μm. Note that from Figure 1 this rubbed polymer film is shown to exhibit significant rubbing-induced phase ratardation and a capability of aligning a LC medium. The AFM image in Figure 2(a) supports the theory that the rubbing-induced micro-groove plays a minor role in LC alignment. This result agrees with a previous study which indicates that the measured azimuthal surface anchoring strength of a LC on a rubbed polymer is about two orders of magnitude larger than the theoretical prediction from the micro-groove.[11] The observed anisotropic friction-force distribution most likely originates from plastic deformation which is introduced into the polymer film by unidirectional rubbing.[6]

The orientational distribution of a LC monolayer on rubbed polymer films can be effectively probed by SHG. Rubbing reduces the surface symmetry of a LC monolayer from $C_{\alpha v}$ to C_{1v}.[9] The nonvanishing components of the surface-effective second-harmonic susceptibility tensor from a C_{lv}-symmetric monolayer on xy plane are $\chi^{(2)}_{zzz}$, $\chi^{(2)}_{xxx}$, $\chi^{(2)}_{zyy} = \chi^{(2)}_{yzy} = \chi^{(2)}_{yyz}$, $\chi^{(2)}_{zxx} = \chi^{(2)}_{xzx} = \chi^{(2)}_{xxz}$, $\chi^{(2)}_{zxz} = \chi^{(2)}_{zzx} = \chi^{(2)}_{xzz}$, and $\chi^{(2)}_{xyy} = \chi^{(2)}_{yxy} = \chi^{(2)}_{yyx}$.[9] These components can be determined experimentally from the azimuthal SH intensity patterns obtained with various polarization combinations of the excitation and SH beams. Assuming a rodlike LC molecule, the measured SH susceptibility, $\chi^{(2)}_{ijk}$, is related to the single dominant component of the second-order moleclar polarizability $\alpha^{(2)}_{\xi\xi\xi}$ by[12]

$$\chi^{(2)}_{ijk} = N_s \sum_{\xi} \langle (\hat{\imath}\cdot\hat{\xi})(\hat{\jmath}\cdot\hat{\xi}) \rangle \alpha^{(2)}_{\xi\xi\xi}. \tag{1}$$

Here $\langle\,\rangle$ denotes the orientation averaging, which can be calculated with a proper assumption of the orientation distribution[9]

$$\begin{aligned}\langle A(\theta,\varphi)\rangle &= \int A(\theta,\varphi)\,g_1(\theta)\,g_2(\varphi)\,d\Omega \\ &= \int A(\theta,\varphi)\exp[-(\theta-\theta_o)^2/(2\sigma^2)]\left(\frac{1}{2} + \sum_{n=1}^{3} a_n \cos n\varphi\right)d\Omega \end{aligned} \tag{2}$$

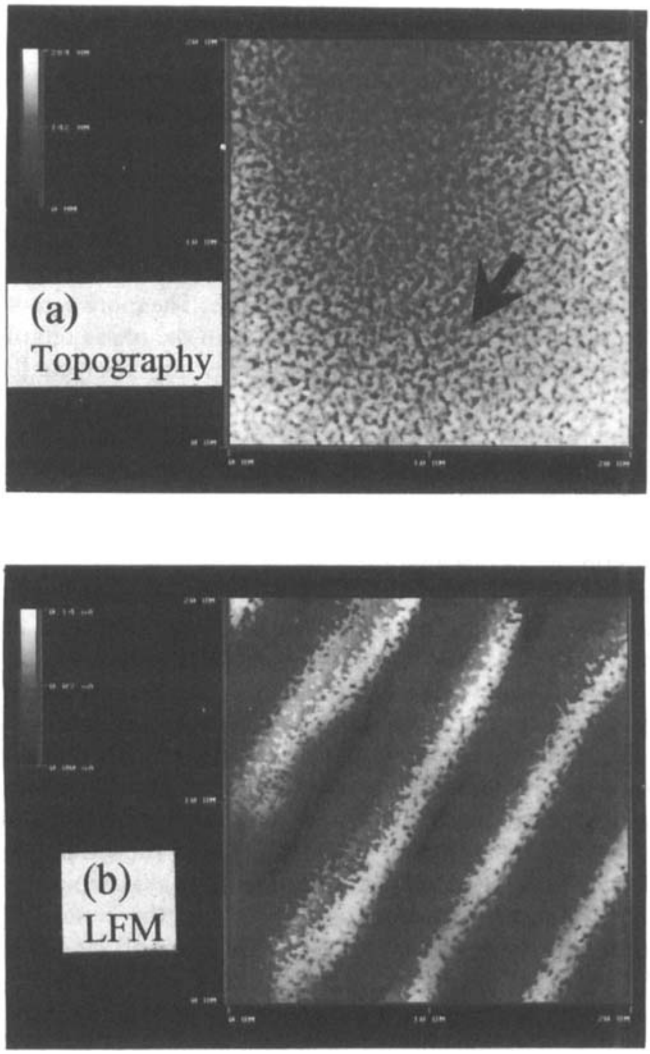

FIGURE 2 (a) Topographic image, and (b) lateral force microscopic (LFM) image of an AL-3046 film rubbed with a strength of 1 $\gamma f = 13.6 f$-cm. The overall scan area is 20 μm × 20 μm. The arrow in Fig. 2(a) indicates the rubbing direction. See Color Plate VI.

Thus with the six experimentally determined values of $\chi^{(2)}_{ijk}$, Eqs. (1) and (2) form simultaneous equations which can be used to deduce the related orientational distribution parameters: θ_o, σ, and a_i (with $i = 1, 3$). The yielded in-plane azimuthal distribution $g_2(\varphi)$ of a 8CB monolayer on rubbed AL-3046 films is depicted in Figure 3. The rubbing direction is along the x-axis. In this Figure, the inner solid circle represents the result of $g_2(\varphi)$ on an unrubbed polymer film, while the dashed (and dotted) curve depicts the azimuthal distribution of 8CB on a rubbed AL-3046 layer with a rubbing

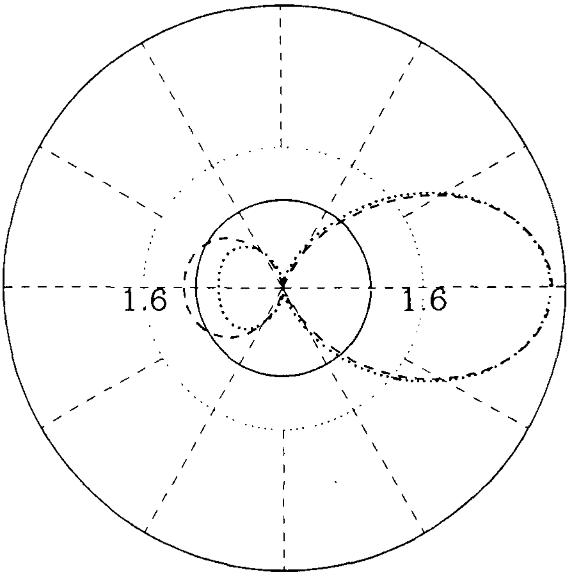

FIGURE 3 In-plane azimuthal distribution of an 8CB liquid crystal monolayer is deduced experimentally from second-harmonic generation measurements. The LC monolayer is deposited on an AL-3046 polyimide film without rubbing (solid curve) and with a rubbing strength of 1 γf (dashed curve) and 10γf (dotted curve).

strength of 1 γf (and 10γf). It is clearly seen that undirectional rubbing of an AL-3046 film gradually orients the LC molecules along the rubbing direction.

More quantitative information about the in-plane azimuthal distribution of the 8CB monolayer on rubbed AL-3046 can be presented with an in-plane order parameter Q and an in-plane anisotropy A. These parameters are defined as[13]

$$Q = \frac{1}{2} a_2 = \frac{1}{2} \frac{\chi^{(2)}_{zxx}}{\chi^{(2)}_{zxx} + \chi^{(2)}_{zyy}},$$

$$A = \frac{\langle \cos^2 \varphi \rangle - \langle \sin^2 \varphi \rangle}{\langle \cos^2 \varphi \rangle} = \frac{\chi^{(2)}_{zxx} - \chi^{(2)}_{zyy}}{\chi^{(2)}_{zxx}}. \tag{3}$$

Note that the value of A varies between zero for a completely in-plane isotropic surface to one for complete alignment, while Q describes the surface anisotropy between x and y-axis. We can also use A, Q, and a_1 to describe the in-plane distribution of the LC monolayer. The measured results of a_1, A, Q and the averaged polar angle θ_0 of an 8CB monolayer on AL-3046 are presented in Figure 4. It is interesting to note that all these parameters exhibit a significant change at $R_s = 13.6 f \cdot \mathrm{cm}$. As $R_s > 13.6 f \cdot \mathrm{cm}$, both A and Q first decrease and then level off, while a_1 continues to increase but with a smaller slope. We note from Figure 3 that a small portion of the LC molecules which are initially aligned along $-x$ axis under weak rubbing are oriented towards the y-axis

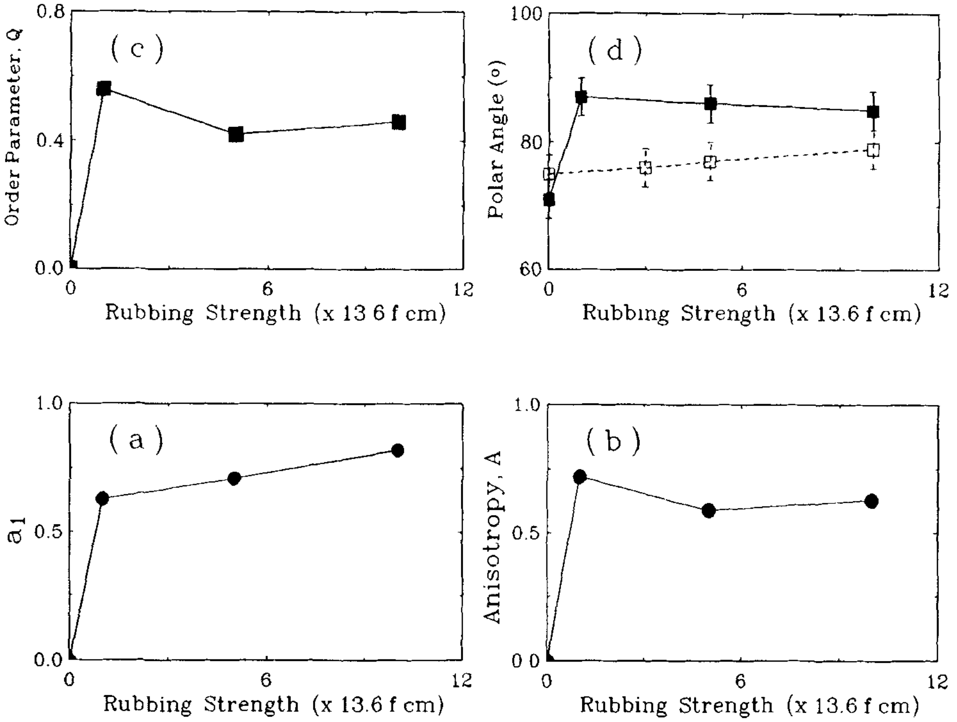

FIGURE 4(a) The coefficient a_1 in the Fourier series of the azimuthal distribution function, (b) in-plane anisotropic parameter A, (c) in-plane order parameter Q, and (d) polar angle of an 8CB liquid crystal monolayer on AL-3046 *(the filled symbols) are plotted as functions of rubbing strength. The open squares in* 4(d) indicate the polar angle of 8 CB molecules on an alkyl branchless main-chain AL-1051 polyimide, which are included for comparison.

instead of $+x$ with strong rubbing. This can originate from the imperfect unidirectional rubbing procedure utilized in this study. Indeed a topographic image (not shown here) of a AL-3046 film with a rubbing strength of $10\gamma f$ clearly exhibits some unparallel rubbing streaks. This type of rubbing imperfection cannot reduce a_1 since a_1 reflects the asymmetry along the x and $-x$ axes only.

It is important to point out that the averaged polar angle of 8CB monolayer (θ_0) on rubbed AL-3046 polyimide films (see filled squares in Fig. 4(d)) changes with rubbing strength. This result is different from that observed by using an alkyl branchless main-chain OPTMER® AL-1051 polyimide film[7,14] available from Japan Synthetic Rubber Co., Ltd. (see open symbols in Fig. 4(d)). Clearly, the alkyl branches play an important role in aligning the polar orientation of the LC molecules. The rubbing may create slanted hydrocarbon chains off the surface[15] on AL-3046 that then affect the polar orientation of the LC monolayer through the chain-chain steric interaction[16] between the LC molecules and AL-3046 polymer (see Fig. 5). Thus, in addition to the strong polar interaction between the cyano biphenyl head groups of 8CB molecules and the polar sites on the polymer surface, the chain-chain steric interaction should be taken into account in determining the polar angle of the first LC monolayer on

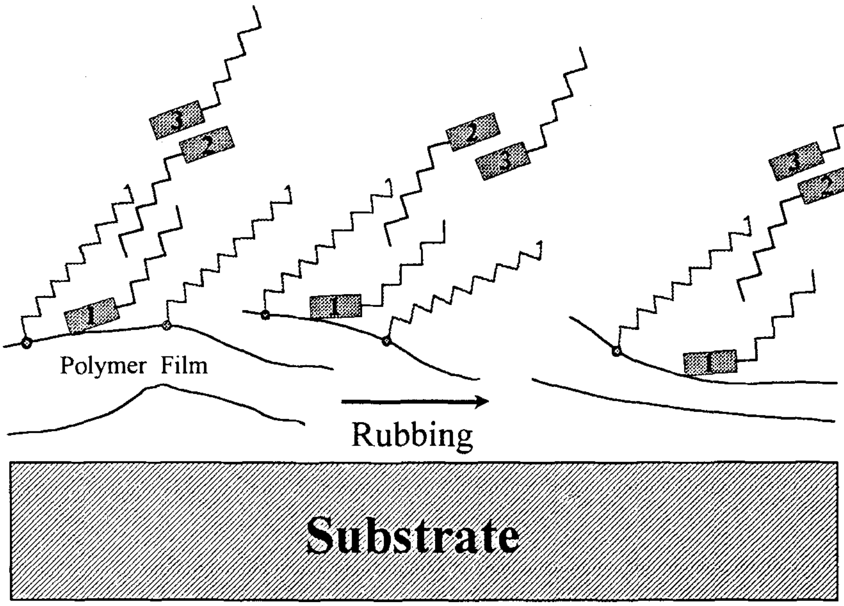

FIGURE 5 Schematic diagram which depicts the molecular aligning process of liquid crystal molecules for the first three molecular layes on a rubbed alkyl-branched polymer film. The rectangular boxes represent the polar head groups of the LC molecules, the numerical labels inside the rectangular boxes indicate the deposition order of the LC molecular layers.

AL-3046. According to a previously published result,[16] the chain-chain steric interaction may also straighten up the long alkyl chains of AL-3046 by reducing their trans-cis defects. The increased chain density in all-trans configuration after the first LC monolayer is deposited onto the polymeric surface yields a highly hydrophobic surface with a reduced surface energy.[7] Since the interaction between hydrophobic groups is stronger than that appearing between hydrophobic and hydrophilic groups,[17] it thus encourages the second LC monolayer to have their hydrocarbon tails encounter the surface (see Fig. 5). The strong polar interaction between the cyano biphenyl head groups of the second and third 8CB monolayers leads to the formation of an anti-parallel 8CB molecular pair.

The detailed molecular orienting process from the polar angle of the first monolayer to the LC bulk pretilt angle is not clear at this moment. However, it is believed that the effect of the slanted alkyl branches of rubbed AK-3046 polyimide films on the polar angle of the first 8CB monolayer can propagate into the LC bulk through a mechanism similar to an epitaxial layer-by-layer growth process (see Fig. 5 for the schematic). The LC bulk pretilt thus can be affected via complicated intermolecular interactions. The orientational transition region involves several LC molecular layers. The averaged properties of this region, which is typically reflected in surface anchoring energy, have been shown to vary with the rubbing strength.[14]

In summary, optical phase retardation measurement and atomic force microscopy have been applied to investigate the rubbing-induced anisotropy in an alkyl-branched

AL-3046 polyimide. Our AFM measurements give the first image data which clearly supports the theory that the rubbing-induced micro-groove plays a minor role in aligning LC molecules. We characterize the orientational distribution of the first LC monolayer on a rubbed polymeric surface by use of the optical second-harmonic generation technique. The polar angle of the polar head groups of a LC monolayer is found to be affected by the alkyl branches on the rubbed polymer film. Our results support the notion that the main polymer chain is responsible in aligning LC in a single direction due to unidirectional rubbing and the alkyl branch is responsible for producing a high pretilt angle in the LC bulk.

Acknowledgments

This work was supported by the National Science Council of the R.O.C. under contract No. NSC84-2112-M-009-016.

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