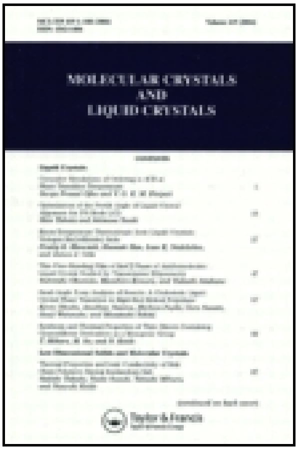

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Rubbed Polyimide Thin Films for Zigzag Free Surface Stabilized Ferroelectric Liquid Crystal

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We investigate the effects of rubbing on the surface free energies of polyimide thin films, and how the surface energetic properties influence the molecular alignment of ferroelectric liquid crystals and the formation of zigzag defects. Rubbing breaks the uniformity in free energy at the surface of polyimide thin film. By properly rubbing the polymer, a diminishment of the difference between the polar part of the surface energies along and against the rubbing direction, respectively, can be achieved, and will favour the formation of zigzag free ferroelectric liquid crystal layer.

Keywords: chevron structure; ferroelectric liquid crystal; liquid crystal alignment; rubbed polyimide; zigzag lines

INTRODUCTION

In order to realize ferroelectric switching, the molecules in the chiral smectic (SmC*) phase mesogen must be aligned to form a bookshelf structure and operate in the surface stabilized ferroelectric liquid crystal (SSFLC) model [1]. Rubbed polymer is the principal technique which is used for the molecular alignment of ferroelectric liquid crystals (FLCs). In this application, polyimide (PI) thin films coated on glass substrates are rubbed using a piece of nylon velvet. One of the knotty problems for the use of rubbed polyimide in the alignment of the FLC is the appearance of zigzag lines in the SSFLCs [2,3]. It is recognized that the zigzag lines are domain walls between the two

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different chevron, C1 and C2, structures which have their apex pointing in opposite directions. [4–6]. As these defects can seriously degrade the performance of FLC devices, to eliminate the zigzag lines and produce defect free SSFLC is crucial to high quality FLC displays. Since the chevrons, which originate from a competition between the pinning of the LC molecules on the substrate and the shrinkage of the smectic layers when the LC enters the SmC* phase, are natural structures of SSFLC, a practical way to obtain zigzag free SSFLC layers is to produce a monodomain, either C1 or C2, chevron over the entire cell. Over the years, a great deal of effort has been made to control and remove these undesired defects. However, a reliable technique which can produce zigzag free FLC has not been developed yet. One of the reasons for the unsuccessfulness is the lack of knowledge on the characteristics of rubbed polymer surfaces.

The most adopted way to date to approach the chevron issue is to consider the balance in thermal energy of the FLC and substrate system, and the formation of a particular type of chevron is explained in terms of elastic characteristics and bulk free energy of the FLC and the strength of the anchoring of the substrate to the LC molecules [7,8]. Based on this model, it was suggested that the C2 chevron can be sustained and zigzag free SSFLC with single domain C1 structure can be produced when the pretilt of FLC molecules at the substrate surface was large [9]. It was also predicted that single domain C1 structure with low molecular tilt can be obtained by lowering the anchoring strength of the substrate to the FLC [7]. However, this kind of model is found to be hardly put into practical applications as analytical results cannot be obtained until the SSFLC devices have been completed.

While more attention has been turned to the bulk of the SSFLC, the knowledge on the surface characteristics of the alignment layers, which play vital roles in the determination of molecular tilt and anchoring strength, is very little, and may be a missing link in the understanding of the formation of the chevron structures. In the present study, we focused on the studying the surface free energy of rubbed PI alignment layers. In this paper, we demonstrate that rubbing cause changes in surface free energy of PI thin films, and the surface energetic state of the alignment layer may be crucial for the formation of zigzag lines. Special attention has be focused on the effects of polar part of the surface free energy on the product of zigzag free SSFLC.

EXPERIMENTAL

In the present study, PI thin films were produced by spin-coating a 5 wt% amide acid solution JASL-9800-R1, commercially available from

JSR (Japan), on to ITO glass substrates and then thermal curing the amide reagent to complete the imidization. The PI films coated on the substrates were then subjected to unidirectionally mechanical rubbing which was carried out using a house made rubbing machine that consists of a drum wrapped with a piece of standard rubbing velvet. The degree of rubbing was measured by rubbing strength (*RS*) that is evaluated using the following equation [10]

$$RS = N \cdot \Lambda\left(\frac{2\pi R\omega}{\nu} - 1\right), \tag{1}$$

where Λ is the pile impression of the velvet fibers, ω is the rotation speed of the drum, R is the radius of the drum, v is the lateral speed of the substrate, and N the number of rubbing cycles. In the present study we fixed ω at 135 rpm and v at 30 mm/min. Thus the RS, with a dimension of mm, was determined by Λ and N.

Surface characteristics, in particular the surface free energy, of rubbed PI films were evaluated using the sessile drop method, which was performed in a DSA100 surface tension meter (Krüss). The data of contact angles were collected for at least three probe liquids. In the present study, the probe liquid used were diiodomethane, glycerol, ethylene glycol, and deionized water. The surface energy of the rubbed PI was determined based on the Owens-Wendt model [11]. As rubbing generates a preferential direction at the surface of a rubbed PI thin film, the azimuthal behavior of surface characteristics against the rubbing direction must be taken into account. The details of the measurement of the surface characteristics of rubbed PI are given elsewhere [12].

The liquid crystal used was a FLC mixture CS1031 (Chisso). SSFLC samples were prepared by injecting CS1031 in cells constructed with two substrates in the anti-parallel configuration. The gap of the cells was 1.8 μm, determined by spacers fabricating in situ at the substrates by means of photolithography. The technique used for producing the spacers is described in a follow-up paper. The optical textures of the samples were examined using a polarizing microscope (Axioscop40, Zeiss). The sample temperature was controlled using a Linkam TMS93 temperature system (Linkam Scientific Instrument Ltd).

RESULTS AND DISCUSSIONS

The surface of the PI thin films was examined by means of atomic force microscopy (AFM), and appeared to be very flat, with an average roughness of 0.33 nm. We set the pile impression at 0.3 mm, and rubbed a sample up to 6 times. After each rubbing cycle completed,

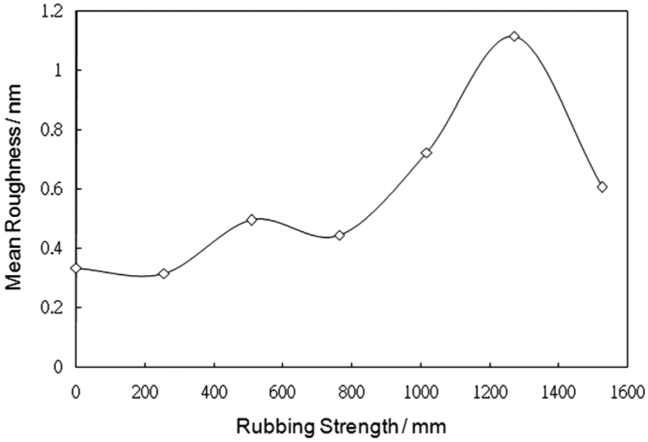

FIGURE 1 Surface roughness of polyimide thin films as a function of the rubbing strength. The pile impression of the rubbing velvet was set at 0.3 mm for the rubbing.

the surface topography of the sample was examined. AFM analysis revealed that rubbing produced grooves on the polymer surface. However, the surface of the PI thin film was rather flat. Figure 1 shows the variation of the surface roughness of the PI film with *RS*. The surface roughness increases with *RS*, however, is below 1.0 nm when *RS* is within the range up to 1600 mm. We notice that the variation of the surface roughness with *RS* is in an oscillated manner. The surface roughness drops when the third rubbing cycle completed, then increases as the number of rubbing accumulated, and then drops again after the sixth rubbing completed. This appears to be a normal phenomenon, and has been observed repeatedly in experiment. Although the grooved surface will lead to only a small variation in pile impression, and hence rubbing strength, across the surface, the peaks in the corrugated surface surfer higher abrasion rates than troughs leading to a reduction in surface roughness. Subsequent rubbings will cause more PI material to be excavated from the surface leading to a rougher surface. As the rubbing continuing, a new course of flatness is started.

With other parameter of the rubbing machine fixed, both the pile impression and the number of rubbing cycle, according to Eq. (1), can determine *RS*. Figure 2 shows the variation of surface free energy of the PI films with *RS* for different pile impressions. It can be seen that the variation of the surface free energy is also oscillated. In general, the surface free energy decreases with an increase in *RS*.

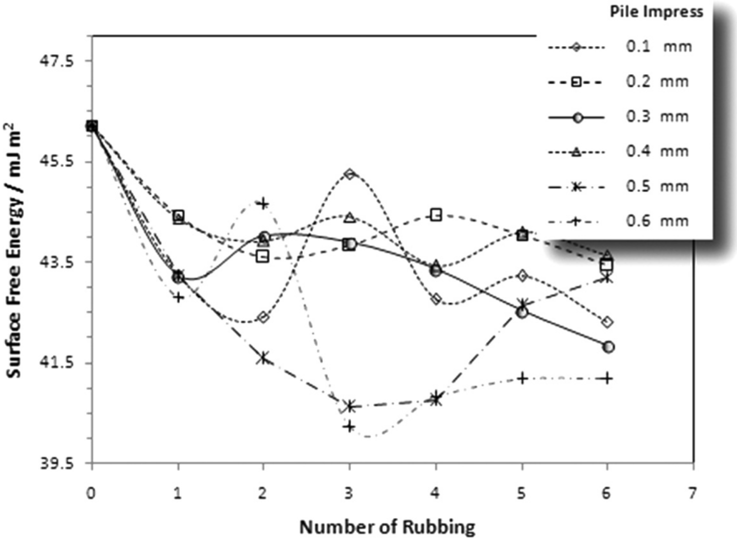

FIGURE 2 The surface free energy of polyimide thin films against the number of rubbing cycles for different pile impression of the rubbing velvet.

It appears that the pile impression had stronger impact on the surface characteristics of the rubbed PI. From Figure 2, it can be seen that the variation of the surface free energy of the PI rubbed with the velvet of 0.3 mm pile impression, appears to be gentler. This phenomenon can be explained in mechanical point of view as follows. With a smaller pile impression, the pressure that the rubbing velvet produces would be too small to impose a sufficient modification to the surface, whereas a larger pile impression will impose a large pressure on the surface and can easily cause serious damage to the PI surface. Thus we fixed the pile impression at 0.3 mm for the rubbing process.

The rubbing produces grooves on the PI surface. The formation of the grooved surface indicates that the uniformity in the surface topography of the PI film is broken, and a form anisotropy, which is defined as topographical difference in two orthogonal directions on a surface, is created. Such form anisotropy had once been thought to be the main driver for the molecular alignment of liquid crystals, and a model, based on the thermal balance in the LC and surface, had been proposes to support the argument [13]. The changes in the surface topography must induce changes in surface characteristics. In other words, the form anisotropy should be reflected by some surface characteristics. In the present study, we concentrated on the

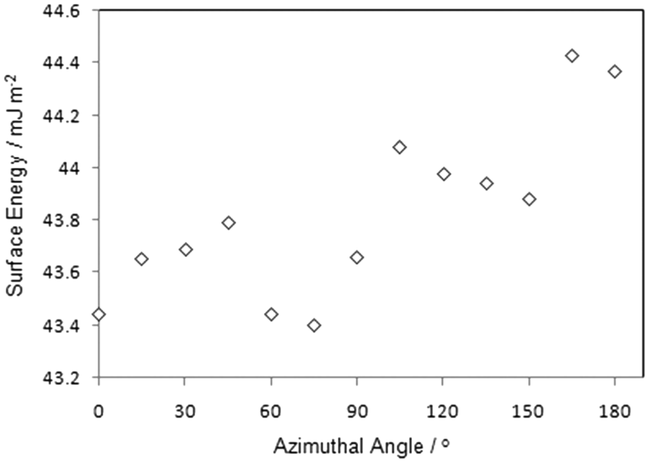

FIGURE 3 Azimuthal variation of the surface free energy of rubbed polyimide against rubbing direction. The polymer was rubbed by rubbing textile with a pile impression of 0.3 mm.

investigation of surface free energy of the rubbed PI. Figure 3 shows the azimuthal variation of surface free energy against the rubbing direction. The surface free energy of the rubbed PI film is not uniform: the surface free energy along the rubbing direction (i.e., azimuthal angle = 0°) is lower than that against the rubbing direction (with azimuthal angle = 180°). We define the difference between surface energies measured along and against the rubbing direction, respectively, as the in-line anisotropy of surface free energy to distinguish it from the common anisotropy defined as the difference of a physical quantity in two orthogonal directions. The appearance of the in-line anisotropy in the surface free energy of the rubbed PI can be attributed to an oriented polymer chains at the outmost PI layer [12], and the anisotropic energetic characteristics of the alignment layer is thought to provide the driving force for the LC alignment.

FLC samples were prepared by injecting CS1031 into cells constructed in parallel configuration using substrates with their inner surfaces coated with PI thin films which were rubbed with certain *RS*. In this study, we fixed the pile impression of the rubbing textile at 0.3 mm thus the RS was determined by the number of rubbing. Microscopic examination of the samples revealed that FLC in all cells showed good FLC alignment in terms of the orientation of the molecules. Figure 4 shows photomicrographs of the FLC in cells consisted of substrates rubbed with different *RS*. As can be seen, in the cell

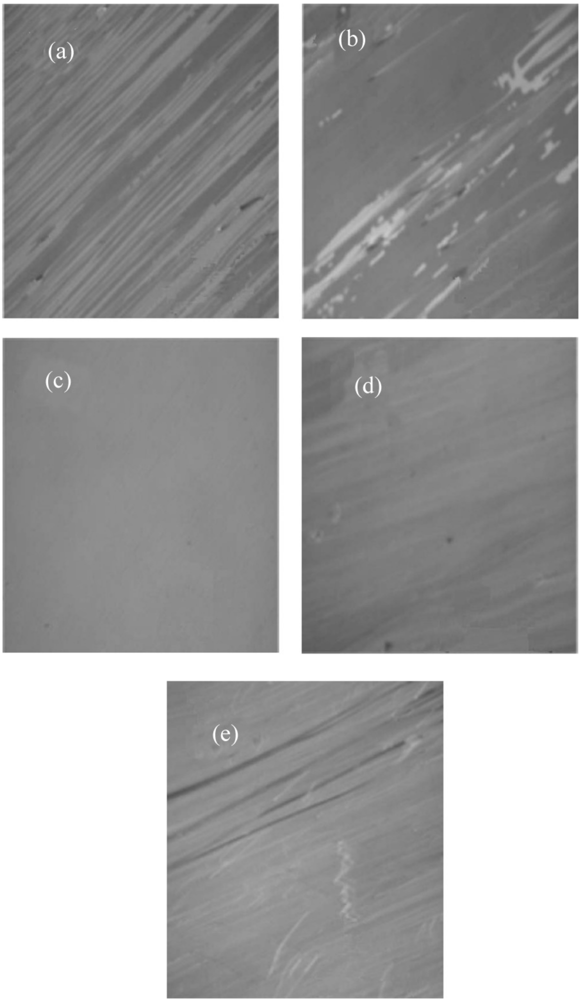

FIGURE 4 Photomicrographs show the variation of the optical textures of SSFLC samples made using substrates coated with polyimide thin films which were rubbed by (a) one time, (b) two times, (c) three times, (d) four times, and (e) five times, respectively. For all rubbing process, the pile impression of the velvet on the polyimide surface was set at 0.3 mm.

made using PI films rubbed three times the FLC layer shows no evidence of zigzag lines, whereas the zigzag lines appear in those cells constructed with substrates that have been rubbed with a weaker or a stronger *RS*. Although the type of chevron in the cell has not been identified yet, it can be affirmed that a single chevron, either C1 or C2, structure forms in the cell. Several factors, which were thought to be responsible for the single chevron structure, can be excluded here. Surface roughness of the substrates is not considered as it is too small ($<1.0\,\text{nm}$) to have significant effect on the surface characteristics of the alignment layer. The rubbed PI used in the present study can only generate a moderate pretilt of 6° [14]. Such a pretilt angle is not large enough to sustain the development of C2 structure in the cell. There is also not enough evidence to prove that the strength of molecular anchoring of the PI rubbed three times is lowest as the PI rubbed with weaker RS may have lower anchoring strength.

It was reported that the surface polarity of the substrate could induce significant action on the FLC molecules [15,16]. In the present study, we evaluate the surface polarity of the substrate using the polar part of the surface free energy. Figure 5 illustrates the variation of the polar part of the surface free energy of the PI against the rubbing cycles. The polar surface energy of unrubbed PI, with a measured value of $1.1\,\text{mJ/m}^2$, is rather small. After the first rubbing, it increases drastically. As the rubbing continues, the polar energy reduces. The in-line anisotropy in the polar surface free energy is obvious, and varies with *RS*. It is noticed that when the PI is rubbed three

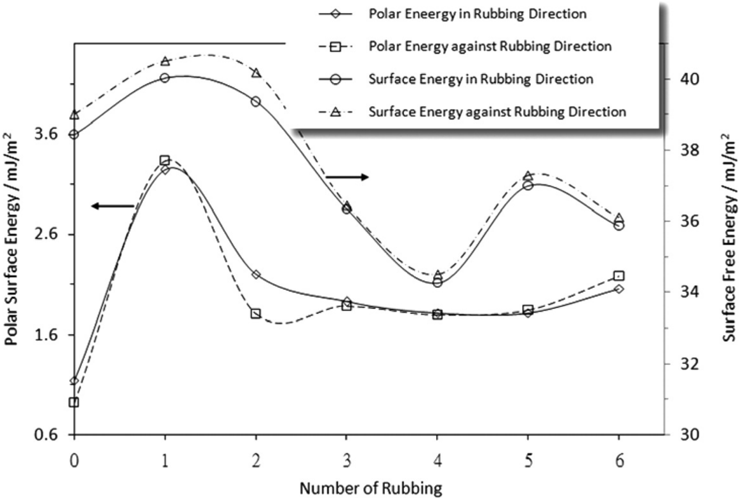

FIGURE 5 The polar part of surface free energy of polyimide thin films as a function of rubbing strength. In rubbing process for all substrated, the pile impression of the rubbing velvet on the polymer surface was set at 0.3 mm. The total surface free energy is drawn as a reference.

times the in-line anisotropy in polar surface free energy is vanished or minimized, and also the anisotropy in total surface free energy becomes minimum. This reduction in the anisotropy in the polar surface free energy may play an important role in the elimination of zigzag lines.

The function of the surface energetic anisotropy of the substrate for the formation of the chevron structure is still not understood. It is thought that the existence of the in-line anisotropy in the surface free energy of the substrates may drive the smectic layers in the Sc* phase to form different types of chevron in a cell leading to the formation of zigzag defects. The diminishment of the in-line anisotropy in the surface free energy of the substrates will favour to form a single domain chevron structure and this would be helpful for the elimination or the reduction of the zigzag lines. It must be pointed out that the arguments presented here are some preliminary results. The correlations between molecular behaviours and surface characteristics are not revealed yet.

CONCLUSIONS

We have investigated the SSFLCs aligned by rubbed PI thin films. The surface energetic characteristics of the rubbed PI have significant effects on the formation of the chevron structure that is the origin the zigzag defects. The rubbed PI alignment layers exhibit an anisotropic surface energetic state, and an anisotropic surface free energy is necessary for the achievement of a unidirectional molecular alignment for LCs. However, in the case of the Sc* phase, a difference in the surface free energy of the substrates along and against the alignment direction, i.e., the rubbing direction, may drive the smectic layers to form a chevron structure that consists of both C1 and C2 domains leading to the appearance of zigzag lines. Our preliminary results show that a reduction in the difference between the polar surface free energies of the PI alignment layer measured along and against the rubbing direction, respectively, is in favour of the formation of zigzag free FLC layer in a cell.

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