Surface Free Energy and Pretilt Angle on Rubbed Polyimide Surfaces

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ABSTRACT: To investigate surface free energy of rubbed polyimide surfaces as a function of the rubbing strength, we measured the contact angle of distilled water and methylene iodide on the polyimide surfaces. For this purpose, a main-chain-type and two side-chain-type polyimides were used. The dispersion force (γ^d) and the polar force (γ^p) of the rubbed polyimide surfaces was measured. The rubbing induced polarity on the polyimide surfaces. Also, polar forces contributed to form a pretilt angle of liquid crystals on the rubbed polyimide surfaces. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 267–271, 1999

Key words: surface free energy; pretilt angle; optical-phase retardation; liquid crystal display

INTRODUCTION

Liquid crystal displays (LCDs) are widely used in devices because of their portability, flatness, low voltage requirements, and low power consumption. For optimal electrooptic performance of LCD, it is essential to obtain a uniform alignment of the liquid crystal (LC) molecules. Various technologies for LC alignment, such as oblique evaporating,¹ rubbing,^{2,3} and nonrubbing methods,⁴ have been reported for many years. Rubbing is widely used in LCD production because of its high productivity. In the nematic phase, the LC molecules are aligned parallel to the rubbing direction, while making a pretilt angle with the alignment layer surface. The pretilt angle (θ) is the angle that the optical axis of a nematic LC makes at a boundary surface of the cell (see Fig. 1). The

pretilt angle strongly influences the performance of LCD devices. Twist nematic displays, for example, prepared with a low pretilt angle, may show undesirable light-scattering effects because of the formation of inversion walls in the nematic layer when the device is turned on. Displays with a large pretilt angle, on the other hand, often show disturbing interference colors and have a reduced multiplexing capacity. Also, the pretilt angle affects the electrooptic properties in an LCD (i.e., threshold voltage, contrast, response time, and so on). Therefore, to optimize the display performance, it is important to control the pretilt angle.

In general, the pretilt angle depends on the properties of the LC and the molecular structure and surface properties of the orienting polymer. Although many theoretical and experimental studies on LC alignment have been performed, the actual alignment mechanism on the rubbed films is still not fully understood.¹⁻⁴ A few publications indicate that the molecular orientation and surface polarity of a polymer surface plays a key role in the alignment of LC molecules at the surface.⁵⁻⁷

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To study the surface properties and pretilt angle on rubbed polyimides, first of all, we chose a main-chain-type and two side-chain-type polyimides and investigated the contact angles of distilled water and methylene iodide on the rubbed polyimide surfaces as a function of rubbing strengths. The surface free energy was calculated. The relationship between the surface free energy and the pretilt angle was investigated.

EXPERIMENTAL

We used three types of polyimides from the JSR Co: AL-1051 as a main-chain-type polyimide (MCPI), and AL-8044 and JALS-246 as sidechain-type polyimides (SCPI1, SCPI2). The polyimides were coated onto an indium-tin-oxide (ITO) glass substrate (800 Å thick) by a spincoating method and were cured at 80°C for 30 min and at 180°C for 1 h. The cured polyimide surfaces were rubbed with nylon velvet (fiber diameter: 2 μ m; length: 1.8 mm). The rubbing strength (RS) was calculated using the expression⁸

$$\mathbf{RS} = \gamma \times L \tag{1}$$

where γ is a characteristic of the rubbing process that includes the rubbing pressure, the fiber density in the rubbing material, the coefficient of friction, etc. *L* is the total rubbing length of the rubbing fiber in contact with a certain point of the substrate and is expressed by

$$L = N \times l(1 + 2\pi rn/60v) \tag{2}$$



Figure 1 Cross section of an LC cell showing the pretilt angle (θ) , angle of light incidence (Ψ) , and thickness of the LC (d).



Figure 2 Systematic diagram of rubbing. *V*: roller moving speed; *n*: rpm of the roller; *d*: rubbing depths; *l*: contact length (i.e., $2 \times$); *r*: roller radius + cloth thickness.

where *N* is a cumulative number of rubbings (i.e., rubbing times); *l*, is the contact length (m) of the rubbing fiber; *n*, the number of revolutions per minute (rpm); *r*, the radius (m) of the roller; and v, the velocity (m/s) of the substrate stage (Fig. 2).

The rubbing parameters used were as follows: (1) rubbing depth (d) (0.05, 0.1, 0.3, 0.5, and 0.7 mm), and (2) rubbing times (one, two, four, six, and eight), which are the cumulative number of rubbings. Contact angles were measured by the sessile drop method⁹ using a contact anglemeter (ERMA, goniometer type) using highly pure distilled water and methylene iodide (Junsei Co.). The surface free energy was calculated by Owens's formula.⁹ Pretilt angles of nematic LL (MLC-6012: Merck Co.) were measured with a TBA101 (Autronic Co.) by application of the crystal rotation method.¹⁰

RESULTS AND DISCUSSION

Figure 3 shows the contact angles of distilled water and methylene iodide as a function of rubbing depth and the cumulative number of rubbings. The contact angles of liquid on rubbed polyimide surfaces at a fixed rubbing depth of 0.03 mm does not change even with increase of the rubbing times from one to eight $[\blacksquare, \bullet, \text{ and } \blacktriangle$ line in Fig. 3(a)]. On the other hand, these angles obviously decreased with increasing rubbing depth $[\blacksquare, \bullet, \text{ and } \bigstar$ line in Fig. 3(b)]. In the case of AL-1051, the contact angle of distilled water was



Figure 3 Contact angle of liquid on surfaces of the rubbed polyimide as a function of the rubbing strength: (a) according to rubbing times at a constant 0.3-mm rubbing depth; (b) according to rubbing depth.

about 71.6° to the nonrubbing surface and changed from about 68.9° to 65.5° [Ine in Fig. 3(b)] when the rubbing depth increased from 0.05 to 0.7 mm. The contact angle of the test liquid on the rubbed polyimide surfaces with variation of the rubbing strength decreased as follows: AL-1051 < AL-8044 < JALS-246. It is well known that decreasing of the liquid contact angle on rubbed polyimide surfaces is due to increasing polarity on the surface. Also, the distilled water contact angle increases with the degree of the imidization, considering that the surface polarity was decreased during the polar polyamic acid conversion into nonpolar polyimide.⁷

It is important to understand the intermolecular forces at the rubbed polyimide surfaces when we discuss the alignment mechanism of LCs. In Figure 4(a), the dispersion force and polar forces do not change with increase of the rubbing times for the three polyimide surfaces at a constant rubbing depth 0.3 mm. However, polar forces vary significantly depending on the kind of polyimide (i.e., about 9.2 ergs/cm² to AL-1051, 5.1 erg/cm² to AL-8044, and 2.7 ergs/cm² to JALS-246 at a rubbing depth of 0.3 mm) as shown in Figure 4(b). Dispersion forces were about 40 ergs/cm² and remained nearly constant with increasing rubbing



Figure 4 Surface free energy (γ_s) of the rubbed polyimide surfaces as a function of the rubbing strength: (a) according to rubbing times at constant 0.3-mm rubbing depth; (b) according to rubbing depth. γ^d : dispersion force; γ^a : polar force.





Figure 5 Pretilt angle as a function of rubbing strength: (a) according to rubbing times at constant 0.3-mm rubbing depth; (b) according to rubbing depth.

depth regardless of the types of polyimide. The polar force for AL-1051 was increased and saturated to 9 ergs/cm² with change of the rubbing depth. In the case of AL-8044 and JALS-246, the polar forces were monotonically increased with increase of the rubbing depth. The increase in the polarity by rubbing followed the order AL-1051 < AL-8044 < JALS-246. Also, the polar forces of AL-1051 were greater than those of AL-8044 and JALS-246 in a constant rubbing condition. This was due to the alkyl side-chain effect masking the polar imide group in the polyimide molecule.

As shown in Figure 5(a), the pretilt angle was

slightly decreased by increase of the rubbing times and then reached a certain saturated value even with increased rubbing times. Also, the pretilt angle decreased in the order of AL-1051 < Al-8044 < JALS-246, as was expected due to the side-chain effect. In the case of AL-1051 [Im line in Fig. 5(b)], the pretilt angle decreased lower than about 2° as the rubbing depth increased from 0.05 to 0.7 mm. In the case of AL-8044 [O line in Fig. 5(b)], the pretilt angle rapidly decreased about 8° as the rubbing depth increased, even when the rubbing strength was small. This trend was more apparent with JALS-246 [V line in Fig. 5(b)].

The correlation between the pretilt angle and surface tension is plotted in Figure 6. It can be seen that the dispersion forces changed little with increase of the pretilt angle, but the polar force can greatly contribute to the pretilt angle. The change ratio of polar force to the pretilt angle followed the order AL-1051 > AL-8044 > JALS-246.

The relation between the retardation and the polar force of rubbed polyimide is shown in Figure 7. Increasing the rubbing depth can increase the polar force of the polyimide surfaces by an anisotropic alignment of the polymer chain to the rubbing direction. In the case of AL-1051, the polar force of the rubbed polyimide surfaces was initially increased and saturated with increasing retardation of the polymer. However, in the cases of AL-8044 and JALS-246, the polar force of the rubbed polyimide surfaces was monotonically in-



Figure 6 Relation between surface free energy of the polyimide surfaces according to rubbing and pretilt angles on the rubbed polyimide surfaces. γ_s : surface free energy, γ^d : dispersion force; γ^a : polar force.



Figure 7 Relation between polar force and optical phase retardation of rubbed polyimides. γ^{α} : polar force.

creased. Also, the polar force of the rubbed polyimide surfaces was larger in the order AL-1051 > Al-8044 > JALS-246 at constant retardation. This was due to the masking effect of the side chain.

CONCLUSIONS

The polar force of the rubbed polyimide surfaces was slightly increased with increase of the rubbing depth but hardly changed with increase of the rubbing times, indicating that increasing the rubbing strength by a change of the rubbing depth can increase the polar force of the polyimide surfaces by an anisotropic alignment of the polymer chain to the rubbing direction.

The polar force of each alignment material was clearly shown in the order AL-1051 > AL-8044

> JALS-246, which was due to the alkyl sidechain effect masking the polarity of imide groups in the polyimide molecule. The polar force of the rubbed polyimide surfaces contributed to form the pretilt angle of LCs on the rubbed polyimide surfaces.

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