Microscopic Molecular Reorientation of Alignment Layer Polymer Surfaces Induced by Rubbing and Its Effects on LC Pretilt Angles

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ABSTRACT: The orientation of functional groups, side chains, and repeat units at the surface of a liquid crystal (LC) alignment layer (AL) polyimide was changed by rubbing with a cotton velvet cloth. It was discovered that rubbing induced polar functional groups and repeat units to reorient out-of-the-plane of the surface, and it made nonpolar aliphatic side chains partially reorient inward, toward the bulk of the film. The polar AL surface provided relatively small LC pretilt angles while polyimides with long alkyl side chains gave relatively large LC pretilt angles. The results suggest that LC pretilt angles are greatly affected by both electronic interaction and steric repulsion between LC molecules and an alignment layer polyimide surface.

Introduction

Langmuir[1] proposed the principle of independent surface action by which one would predict that a polymer surface organizes to have a lowest surface energy.[2] The surfaces of polymer blends,[3,4] solutions,[5] block copolymers,[6] and polymers with polar end groups[7−10] obey this principle and are seen to organize so that their surfaces have the lowest possible energies. For example, polar functional groups introduced at polymer surfaces (for example, by oxygen plasma) fold inward to lower the surface energy.[11−14] Koberstein et al.[7−10] demonstrated that high-energy end groups such as carboxyl, hydroxyl, and amine attached to poly(styrene) (PS), poly(methyl methacrylate) (PMMA), poly(dimethylsiloxane) (PDMS), or copolymers of these orient inward, toward the bulk when in contact with dry air, as shown in Figure 1b. Upon exposing these films to water vapor, the high-energy (polar) end groups reorient out-of-the-plane of the surface, as illustrated in Figure 1c.

Such phenomena often emerge in applications of polymer films in industry. For example, in multilevel thin-film packaging for multichip modules, the substrate polyimide layer is usually treated with O_2 or H_2O plasma to enhance adhesion. This treated surface is very polar (high energy), but it becomes less polar at ambient conditions over time as the system reorganizes to have a lower surface energy. Similar phenomena are of importance in connection with modern liquid-crystal-flat-panel displays. Typically, a polyimide (PI) is employed as a liquid crystal (LC) alignment layer (AL).[15,16] In order to obtain a good LC alignment, the PI film is rubbed with a roller covered with a cotton velvet cloth, causing the outer layer of the rubbed film to become oriented. The rubbing process and the structure of the cotton cloth are illustrated in Figure 2. The nature and stability of this orientation are critical to the functioning of flat panel displays and are the focus of this work.

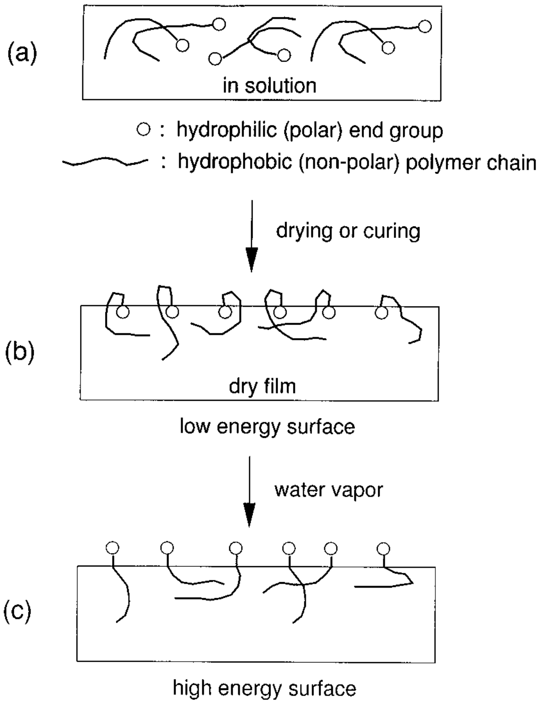

Figure 1. (a) Block copolymer with a nonpolar main chain and a polar end group as a homogeneous solution. (b) Dried film of the copolymer. (c) Reorientation due to a specific interaction between the end group and the water molecules.

The macroscopic orientation of rubbed polymer surfaces has been reported.[17−20] Optical retardation, X-ray diffraction, grazing angle X-ray scattering, birefringence, atomic force microscopy, and IR dichroism were the analytical techniques employed for determining the macroscopic scale structures of rubbed polymers. A few recent publications[21−24] indicate that molecular scale orientation at a polymer surface plays a key role in aligning LC molecules at the surface and that macroscopic scale "microgrooves"[25] are not important. For example, Toney, et al.[21] reported that rubbing a BPDA−PDA [poly(3,3′,4,4′-biphenyltetracarboxylic dianhydride−*p*-phenylenediamine)] polyimide caused near-surface (10-nm outerlayer) alignment of the polyimide molecules, and Murata et al.[22] showed that the orientation

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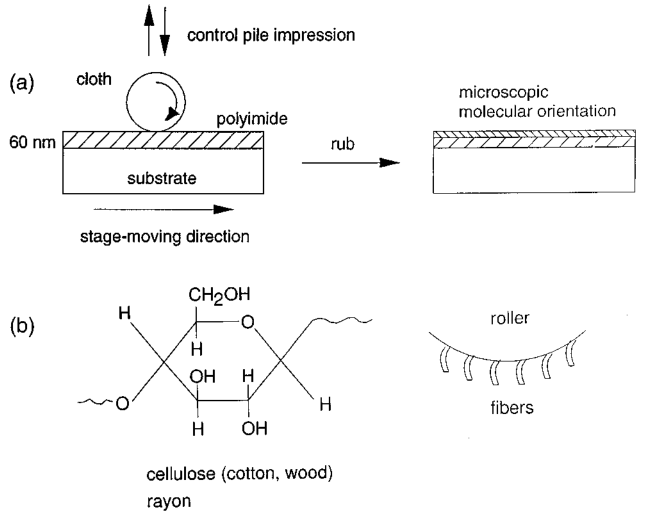

Figure 2. (a) Illustration of the rubbing process; roller speed = 200 rpm, speed of the substrate stage = 24 mm/s. (b) Rubbing cotton cloth structures. The average fiber length is 2.5 mm.

of the polymer molecules at an alignment film surface determined the alignment of LCs.

In this work, we study the changes in microscopic molecular surface structures[26] induced by rubbing and the effects of such changes on the LC pretilt angle,[27] a key parameter affecting the electro-optical properties of LCDs. The investigation shows that both electronic interaction and steric repulsion between LC molecules and the AL surface affect the LC pretilt angle and that these are influenced strongly by rubbing via changes in microscopic molecular surface structures. Several new polyimides were designed and synthesized for this study.

Experiments

Materials. Commercially available polymers SE7210, SE7792, RN1024 (Nissan Chemical), AL1054 (Japan Synthetic Rubber Co.), PI5878 (PMDA–ODA), PI2611 (BPDA–PDA), PI2590 (6FDA–ODA–DSDA), and PI2566 (6FDA–ODA) (DuPont) were purchased. CBDA–MBDA, CBDA–TBDA, CBDA–ODA, CBDA–ODA–DAA2, CBDA–ODA–DAA3, and CBDA–PDA–DAA2 were prepared using the procedure described below. The available repeat unit structures for the final imidized polymers are shown in Figure 3. 1-Methylpyrrolidinone (NMP) and γ-butyrolactone used as solvents for preparation of polymers and alignment layers were purchased from Aldrich and used as received. Liquid crystal ZLI-5080 was purchased from E. Merck Industries and used as received. ZLI-5080 is a mixture of several compounds which contain various functional groups such as CF_3, OCF_3, CH_2F, F, ester, and aromatic mesogens. It is in a nematic state at room temperature and its isotropic transition temperature is 103 °C.

Synthesis of Polyimides. Precursor polymers for CBDA–ODA, CBDA–ODA–DAA2, CBDA–ODA–DAA3, CBDA–PDA–DAA2, CBDA–MBDA, and CBDA–TBDA were pre-

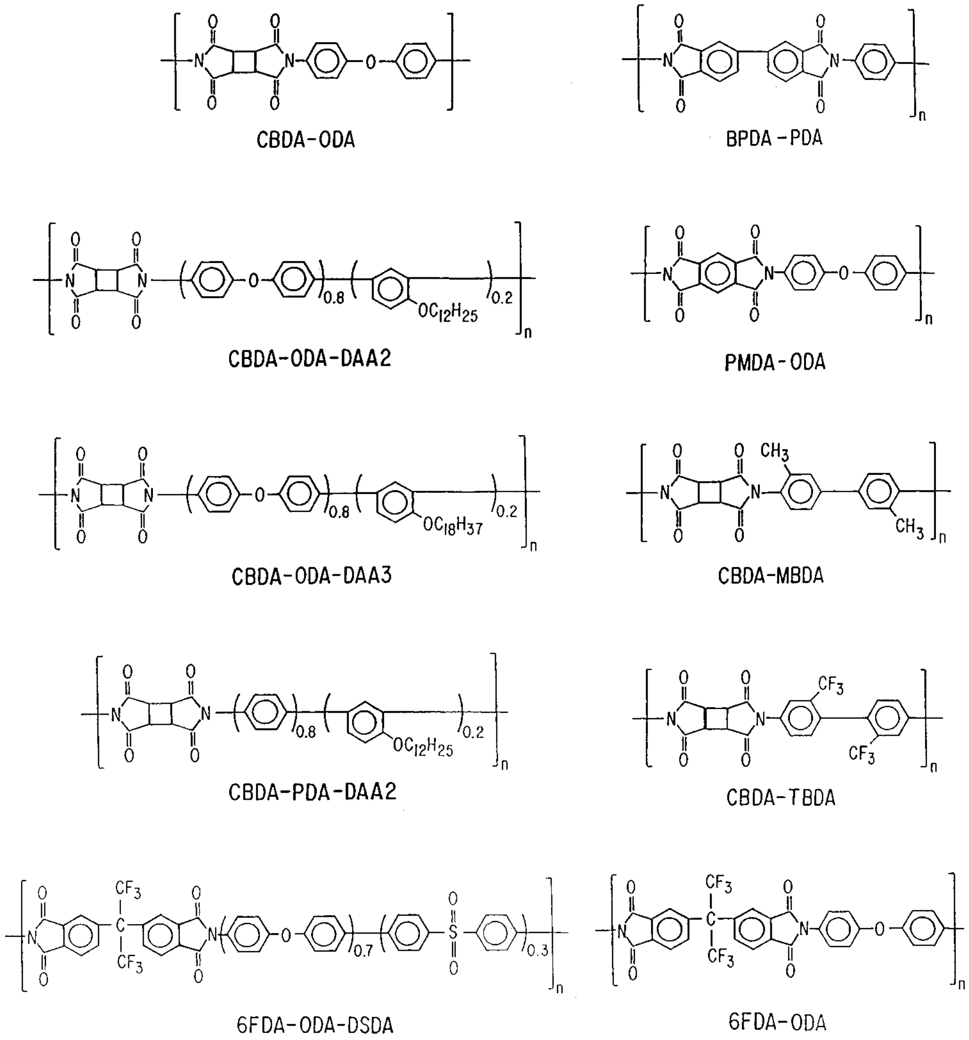
CBDA-ODA
BPDA-PDA
CBDA-ODA-DAA2
PMDA-ODA
CBDA-ODA-DAA3
CBDA-MBDA
CBDA-PDA-DAA2
CBDA-TBDA
6FDA-ODA-DSDA
6FDA-ODA

Figure 3. Chemical structures of liquid crystal alignment layer polyimides.

pared by solution polymerization. The reactions were carried out in a four-necked flask equipped with a thermometer, a stirrer, a reflux condenser and an inlet for nitrogen. As a typical example, CBDA−ODA−DAA2 was prepared by introducing 4.634 g of a diamine (ODA) and 1.692 g of another diamine (DAA2) to dissolve in 100 mL of NMP as the solvent. Then, the flask was dipped in a water bath between 0 and 30 °C to control the heat generation, and then 5.62 g of CBDA was introduced. After the CBDA dissolved, the water bath was removed, and the reaction was continued at room temperature for 10 h to obtain a highly viscous solution. Analogous procedures were used for the other polymers.

Preparation of Alignment Layer and Cell. Alignment layer precursor films were fabricated, by spin-coating solutions at 3000 rpm for 1 min, on indium−tin−oxide (ITO)-coated glass substrates, with the dimension of 100 mm × 75 mm × 1.1 mm. Prior to PI coating, the substrates were edge-beveled and cleaned with a soap, 0.3% Micro (Cole-Palmer Instrument Co) solution, by a plate-cleaning machine. The precursor films were baked at 80 °C and then cured at an appropriate temperature (180−300 °C) for 60 min. Thicknesses of cured PI films were in the range 60−90 nm. The variation in polymer thicknesses on a substrate was within ±3 nm.

The PI-coated substrate was rubbed twice by a rubbing machine (Fujioka Manufacturing Co.) with a 6-in.-diameter roller covered with a cotton velvet cloth from Agehara-Velvet Ltd. The fiber length is 2.5 mm. The rubbing conditions were as follows: roller speed = 200 rpm, speed of substrate stage = 24 mm/s, and pile impression = 0.40 mm (the pile impression can be controlled within ±0.01 mm with this rubbing machine). The polymer spacers for a desired cell gap (5 μm) were placed on the PI surface by spraying. Using a UV-curable adhesive, the cells (or panels) were assembled with rubbing of the opposing glass plates aligned in antiparallel directions. A typical size of an assembled cell was 75 mm × 75 mm × 0.005 mm.

The cell was then filled with the nematic liquid crystal, ZLI-5080, in a vacuum chamber at room temperature. Finally, the cells were sealed with the same adhesive used for assembly. In some experiments, the LC-filled cells were annealed at 45−120 °C for 5−60 min depending on the thermal treatment desired.

Measurement of Pretilt Angles. The pretilt angle of a uniform area in an antiparallel cell was measured by the crystal rotation method.[28] The optical setup was arranged in the following sequence: a light source, a filter, a focusing lens, a diffuser, an entrance polarizer, the sample (rotated by a motion controller), an exit polarizer, and a photometer. The filter transmits a monochromatic light with a 560-nm wavelength and 10-nm band width. The transmission axis of the entrance polarizer was adjusted so as to make a 45° angle with respect to the projection of the LC director onto the substrate plane. The axis of the exit polarizer was perpendicular to that of the entrance polarizer. Transmission at a certain incidence angle formed by rotation of the sample was recorded on the photometer. A symmetry offset angle, which is related to the pretilt angle,[28] was determined from a plot of transmission versus incidence angle.

Polyimide Film Analysis. Contact angle measurements were made using a Ramé-Hart telescopic goniometer and Gilmont syringe with a 25-gauge flat-tipped needle. Distilled water was used as the probe fluid. Dynamic advancing and receding contact angles were determined by measuring the tangent at the intersection of the air/drop/surface while adding (advancing) and withdrawing (receding) water to and from the drop. XPS spectra were taken on a Perkin-Elmer Phi 5500 system with Mg Kα excitation. The electron take-off angles were 45° and 15° from the sample surface. Transmittance infrared spectra were obtained under nitrogen using a Nicolet-510P FTIR spectrometer.

Results and Discussion

Microscopic Molecular Reorientation of Polymer Surfaces Induced by Rubbing. The polymer films were rubbed with a cotton velvet cloth, which is widely used in applications since it generates a relatively low static charge on the polymer film.[29] The cotton velvet is not deposited significantly onto the polymer surface, as indicated by the contact angles discussed below as well as by the published work.[30] The polarity change of an alignment layer (AL) surface induced by rubbing was measured with dynamic water contact angles. The atomic composition of the AL's outer layer was also determined before and after rubbing by X-ray photoelectron spectroscopy (XPS). It turned out that reorientation of surface functional groups depended on the polyimide (PI) type. Two classes of PI, commonly used as a liquid crystal (LC) AL in modern liquid crystal displays (LCD), were investigated. One type contains large nonpolar side groups [e.g., aliphatic chains (≥12 carbons)] while the other does not contain such side chains (methyl and ethyl groups are not large enough to give the same effects).

Table 1. Water Contact Angles on LC Alignment Layers

alignment layer polymer	rubbing status	contact angles, deg advancing/receding
CBDA−ODA	unrubbed[a]	65/22
	rubbed[b]	66/20
PMDA−ODA	unrubbed	79/39
	rubbed	77/38
CBDA−ODA−DAA2	unrubbed	82/34
	rubbed	82/20
RN1024	unrubbed	86/42
	rubbed	83/24
SE7210	unrubbed	91/55
	rubbed	84/41
SE7792	unrubbed	88/47
	rubbed	84/28
BPDA−PDA[c]	unrubbed	74/35
	rubbed	74/17
6FDA−ODA	unrubbed	86/56
	rubbed	89/53
PI2590	unrubbed	85/62
	rubbed	80/52

[a] The polymer was spin-coated and cured between 180−300 °C. [b] Rubbing conditions: roller speed = 200 rpm, speed of substrate stage = 24 mm/s, pile impression = 0.40 mm, and rubbed twice in the same direction. [c] Only 95% of BPDA−PDA poly(amic acid) was imidized to polyimide. Thus this polymer molecule contains approximately 95% imide and 5% amic acid repeat units.

The surface polarity of fully imidized PIs without a large nonpolar side group was not significantly changed by rubbing, while the surface polarity of PIs with a large nonpolar side group definitely increased (Table 1). For example, poly(cyclobutanetetracarboxylic dianhydride−oxydianiline) (CBDA−ODA), which does not include a large side group in the repeat unit (Figure 3), was fully imidized at 300 °C for 1 h followed by rubbing. The water contact angles on the rubbed film were almost the same as those on the unrubbed film. Similar results were obtained with poly(pyromellitic dianhydride−oxydianiline) (PMDA−ODA), JSR AL1054, and 6FDA−ODA (Table 1). On the other hand, rubbing of CBDA−$(ODA)_{0.8}$−$(DDA2)_{0.2}$ [poly(cyclobutanetetracarboxylic dianhydride−oxydianiline−diaminododecanoxybenzene)], which includes C_{12} side chains in the DAA2 diamine repeat unit (ODA/DAA2 = 80/20 mole ratio), resulted in decreased receding water contact angles. Interestingly, in both cases, the XPS atomic compositions of the outer 1.0−1.5-nm layer were not altered by rubbing. These results indicate that the nonpolar C_{12} chains are reoriented inward (partially hidden underneath the surface) while the polyimide backbones align

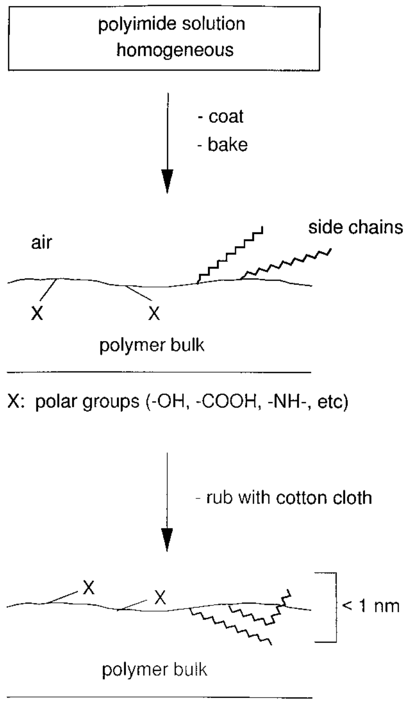

Figure 4. Illustration of microscopic molecular reorientation of a polymer surface induced by rubbing.

outward at the surface. The side groups are enriched at the outermost layer before rubbing, but the backbone functional groups are dominant at the surface after rubbing. This mechanism is illustrated in Figure 4.

Water contact angles on the commercial Nissan SE7210, SE7792, and RN1024 also showed a significant change with rubbing. These polymers are known to have long alkyl chains, but the detailed repeat unit structures are proprietary. The advancing/receding angles on the cured unrubbed SE7210, SE7792, and RN1024 films were 91°/55°, 88°/47°, and 86°/42°, respectively, which are larger than those for typical aromatic polyimides [e.g., poly(biphenyltetracarboxylic dianhydride–*p*-phenylenediamine) (BPDA–PDA) gave 77°/38° water contact angles]. XPS analyses of these film surfaces indicate no F content but a relatively large concentrations of carbon at the surface, which suggests that the surface has an aliphatic character relative to the typical aromatic polyimide. Rubbing reduced the contact angles from 86°/42° to 83°/24° for RN1024, from 19°/55° to 84°/41° for SE7210, and from 88°/47° to 84°/28° for SE7792. However, the XPS atomic compositions remained unchanged by rubbing even with a grazing takeoff angle, with which the sampling depth is only 1.0–1.5 nm. The decreased receding contact angles induced by rubbing gradually increased over a time scale of 3–4 months during storage at ambient conditions. These results indicate again that the PI surface becomes more polar by rubbing. Interestingly, the resulting polar surface ages at ambient conditions, back to a less polar surface.

A copolymer of polar and nonpolar repeat units was prepared. BPDA–PDA poly(amic acid) is relatively polar while BPDA–PDA polyimide is relatively nonpolar. The water contact angles of BPDA–PDA poly(amic acid) and polyimide were 64°/8° and 77°/38°, respectively. 95% of BPDA–PDA poly(amic acid) was thermally imidized to polyimide, producing a copolymer molecule containing approximately 95% imide and 5% amic acid (amide–carboxylic acid) repeat units. The water contact angles were 74°/35° on the 95%-imidized BPDA–PDA film and 74°/17° on the subsequently rubbed film. A significant decrease of the receding contact angle (from 35 to 17°) indicates that the rubbed film surface becomes more polar. The receding contact angle (17°) of the rubbed film is between 38° for polyimide and 8° for poly(amic acid). The intermediate value indicates that the carboxylic acid and amide groups were preferentially oriented out-of-the-plane of the surface by rubbing and thus the rubbed film surface contains more of these polar functional groups than of the unrubbed one. Another copolymer, 6FDA–ODA–DSDA [poly(2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride–(oxydianiline)$_{0.7}$–(diphenyl sulfone diamine)$_{0.3}$), DuPont PI2590], containing both polar groups (DSDA) and nonpolar groups (6FDA–ODA) showed behavior similar to that of BPDA–PDA poly(amic acid–imide) copolymer. The receding contact angle decreased from 62 to 52° by rubbing. On the other hand, the contact angles on 6FDA–ODA (DuPont PI2566) did not significantly change, probably since the polymer does not contain a polar repeat unit and the 6F group is not reorienting due to its geometrical constraint.

It appears to be ubiquitous that at a PI film surface, reorganization is induced by rubbing with a cotton cloth such that polar groups orient out-of-the-plane of the surface and nonpolar groups fold inward, toward the bulk of the film, as illustrated in Figure 4. The polar groups examined here include carboxylic acid, carbonyl, hydroxyl, amide, and sulfone while the nonpolar groups include alkyl and CF_3. The driving force of this reorientation is probably the electronic attraction between the polar cotton cloth (Figure 2b) and the polar groups of an alignment layer polymer and the repulsion between the polar cotton cloth and the nonpolar groups of a polymer alignment layer. Rubbing with a nonpolar polymer such as poly(tetrafluoroethylene) did not give the decreased water contact angles on CBDA–ODA–DAA2 or Nissan SE7792.

In order to further understand the molecular reorientation, a wide range of rubbing force from 0.03-mm to 0.8-mm pile impressions was applied onto the 6FDA–ODA–DSDA and CBDA–PDA–DAA2 films, and the resulting water contact angles were measured. The 0.03-mm pile impression corresponds to a very weak rubbing while the 0.8-mm pile impression is the maximum force that the rubbing machine can apply. Van Aerle et al.[19] reported the relative rubbing forces corresponding to the 0.03-0.5-mm pile impressions. The 0.5-mm pile impression force is approximately 20 times greater than the force corresponding to the 0.03-mm pile impression. Thus the 0.8-mm pile impression force is expected to be even greater.

As shown in Table 2, a weak rubbing still changed the water contact angles and a strong rubbing gave the smallest contact angles. On another word, the greater the pile impression, the smaller the receding water contact angle. The receding water contact angles also decreased with the amount of rubbing. These results suggest that the surface area on which the molecules are reoriented increases as the rubbing force or density increases. This new finding is different from a previous proposal[19] which states "the top layer of the rubbed polyimide is almost instantaneously oriented to a certain maximum value—increasing the rubbing pressure or the rubbing density results in an increase of the penetration depth of the molecular orientation within

Table 2. Dependence of Receding Dynamic Water Contact Angles on Rubbing Conditions[a]

pile impression (mm)	no. of rubbing	receding water contact angles, deg		
		PI2590[b]	PI-4[c]	PI-4[c]
no rubbing		62	29	
0.03	2	56	24	
0.1	2	52	19	
0.4	2	52	11	
0.8	2	48	9	
no rubbing				29
0.1	1			21
0.1	2			19
0.1	5			16
0.1	20			15
0.1	90			14

[a] The polymer was spin-coated and cured at 230 °C. Rubbing conditions: roller speed = 200 rpm, speed of substrate stage = 24 mm/s. [b] DuPont PI2590 is 6FDA−ODA−DSDA. [c] PI-4: CBDA−PDA−DAA2.

the orienting layer, from 10 nm to 60 nm or greater". It is noteworthy that in the previous work[19−21] a surface (outermost layer) sensitive analytical technique was not employed. The combined results in this work and in the literature[19−21] strongly indicate that molecular reorientation induced by rubbing with a cloth increases in both depth and area as the rubbing force or density increases.

Electronic and Steric Effects on an LC Pretilt Angle. A thin layer (60−90 nm) of a polyimide was spin-coated onto indium−tin−oxide (ITO)-coated substrate, and cured between 180 and 300 °C depending on the polyimide and the investigation purpose. The cured polymer film was then rubbed twice in the same direction to enhance the LC alignment uniformity. Then a cell was prepared with the rubbing directions of the two substrates antiparallel. The Merck ZLI-5080 nematic LC mixture (refer to the experimental section) was introduced into the cell. The LC pretilt angles, θ_p, were measured by the crystal rotation method.[28] Neither cleaning nor heating after rubbing the polymer film was applied except where specified.[31]

A factor affecting θ_p is the strength of electronic interactions between LC molecules and their alignment layer surface.[32] In order to compare θ_p on polar and nonpolar polymer surfaces, the θ_p on a few poly(amic acid)s and their corresponding polyimide were measured. As shown in Table 3, the θ_p on CBDA−MBDA and CBDA−TBDA poly(amic acid)s are 1.3 and 1.8°, respectively, while those on CBDA−MBDA and CBDA−TBDA polyimides are 3.8 and 12.0°, respectively. In another experiment, we measured θ_p before and after the surface of the CBDA−ODA−DAA3 was modified with O_2 plasma. The water contact angles, measured after rubbing, showed this modification reduced the values from 86°/30° (advancing/receding) to 64°/7°, indicating that the surface became much more polar. θ_p was reduced from 13.3 to 2.6°. The polar surface gave a smaller θ_p than the nonpolar surface probably due to the stronger electronic interaction between LC molecules and the polymer surface. These interactions likely include hydrogen bonding and dipole−dipole interaction.

If the polymer backbones are different, θ_p cannot be correlated solely with the AL surface polarity. The rubbed surfaces of both 6FDA−ODA and 6FDA−ODA−DSDA polyimides are less polar than that of CBDA−ODA−DAA3, but θ_p's are much smaller. In order to study the steric factor,[32] three different polyimides were designed and synthesized (refer to the experimental section). They are CBDA−ODA (no side chain), CBDA−ODA−DAA2 (diaminododecanoxybenzene; C_{12} side chain), and CBDA−ODA−DAA3 (diaminooctadecanoxy benzene; C_{18} side chain). The chemical structures are shown in Figure 2. CBDA−ODA gave a small θ_p (2.4°), CBDA−ODA−DAA2 provided a greater θ_p (6.2°), and CBDA−ODA−DAA3 rendered the greatest θ_p (13.3°). A short side chain such as CH_3 and C_2H_5 did not affect the θ_p. These results indicate that a part of the long side chains pushes the LC molecules upward so that a relatively large θ_p is obtained.

Table 3. Fluorinated LC Pretilt (θ_p) and Water Contact Angles on Various PI's[a]

alignment layer polymer	θ_p, deg	water contact angle on rubbed polymer, deg
CBDA−MBDA[b] poly(amic acid)[c]	1.3	60/8
CBDA−MBDA polyimide	3.8	65/11
CBDA−TBDA poly(amic acid)	1.8	68/12
CBDA−TBDA polyimide	12.0	73/33
CBDA−ODA−DAA3 O_2 plasma	2.6	64/7
CBDA−ODA−DAA3	13.3	86/30
6FDA−ODA	3.3	89/53
6FDA−ODA−DSDA	3.6	80/52
CBDA−ODA	2.4	66/20
CBDA−ODA−DAA2	6.2	82/30
CBDA−ODA−DAA3	13.3	86/30

[a] The rubbed polymer films were neither cleaned with solvent nor thermally treated. A nematic liquid crystal, ZLI-5080, from Merck Industries, was used to make antiparallel cells for pretilt angle measurements. [b] CBDA−MBDA: poly(cyclobutanetetracarboxylic dianhydride−3,3′-dimethyl-4,4′-biphenyldiamine). [c] Poly(amic acid)s were baked at 80 °C for 60 min. Polyimides were cured between 180−300 °C.

Conclusion

Polar functional groups of an alignment layer polymer are reoriented out-of-the-plane of the surface by rubbing with a cotton velvet cloth while large, nonpolar groups fold inward, toward the bulk of the polymer film. The driving force is the electronic attraction and (or) repulsion between LC and AL molecules. The molecular reorientation increases in both depth and area as the rubbing force or density increases. An LC pretilt angle which is critical to electro-optical properties of an LCD is affected by both electronic interaction and steric repulsion between LC molecules and the alignment layer polymer surface. The stronger the electronic interaction, the smaller the LC pretilt angle. The greater the steric repulsion, the larger the LC pretilt angle.

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(26) A microscopic molecular structure means a chemical structure of a polymer repeat unit or specific functional groups such as hydroxy (OH), carboxylic acid (COOH), CF_3, aliphatic side chains, etc.

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