

Effects of Thermal Imidization and Annealing on Liquid Crystal Alignment over Rubbed Polyimide Layers: Change in the Pretilt Angle

Sang-Hyon Paek

Materials Research Center for Information Displays, Institute of Natural Sciences, Kyung Hee University,
Seochun-Ri 1, Yongin 449-701, Korea

Received June 29, 2001

Abstract : The fabrication of liquid crystal display (LCD) panels involves several thermal processes such as imidization of the alignment layer (AL) and annealing of the rubbed polyimide AL. The nature of these processes on the LC alignment, especially on the pretilt angle (Θ_p) has been systematically studied, employing various types of polyimide structures. The imidization effect depends on the nature of polyimide precursors; Θ_p increases with the degree of the imidization for the main-chain type of ALs, due to the decrease in the surface polarity, but this relation is not applicable to the alkylated ones in which the steric effect at the AL surface by the aliphatic side chains is dominant. Annealing of the rubbed polyimide AL deteriorates its rubbing-induced molecular orientation and subsequently the overlying LC alignment, resulting in the decrease in Θ_p . Especially, annealing of the LC cell affects the LC-AL interaction as well as the AL orientation and thus its effect on LC alignment depends sensitively on the nature of LC-polyimide interface; aromatic moiety in the polyimide structure gives better thermal stability of LC alignment while fluorinated polyimide ALs induce the less stable alignment.

Introduction

Twisted nematic (TN) liquid crystal displays (LCDs) with thin film transistors (TFTs) as switching elements are the leading products in the current flat panel display industry. In such systems, a polyimide (PI) alignment layer (AL) unidirectionally rubbed with a cloth is the most commonly employed to achieve uniform LC alignment, since it has good thermal stability and provides uniform LC alignment with strong anchoring energies.¹⁻⁴ The majority of nematic LCs in contact with a rubbed PI AL orient along the rubbing direction, resulting in the LC director at the surface in the rubbing direction with a certain pretilt. This LC surface monolayer induces the bulk alignment along its director. The pretilt angle (Θ_p), defined as the angle between the LC director and the AL surface plane, prevents generation of disclinations and also affects the electro-optical (EO) characteristics

of LCDs⁵⁻⁷ and thus, for defect-free LC alignment and desired LCD performances, an appropriate Θ_p , which depends on the LCD modes, and its stability are required. Understanding the factors to affect Θ_p is therefore of great practical importance to control Θ_p and thus to obtain the desired LC alignment.

Since LC and polymer molecules at the AL surface interact and the details of these interactions clearly affect Θ_p , it depends on the AL polymers⁷⁻¹¹ and the LC materials^{8,12-15} as well as the rubbing strength.^{8,10,15-22} The fabrication process of the LCDs includes several thermal treatments including the curing of AL films and the annealing of rubbed AL films or LC-filled cells. It was reported that Θ_p increases with imidization temperature of poly(amic acid) ALs.^{7,23-25} In this work, we study the nature of the effects of thermal treatments on LC alignment, focusing on the change in Θ_p ; employing various PI structures, the details of how Θ_p depends on curing temperature of the AL are first discussed and then the effects of annealing of the

*e-mail : shpaek@khu.ac.kr

rubbed ALs and LC-filled cells on LC alignment are investigated, which have not been well understood.

All designed experiments in this work are carried out at fixed rubbing conditions. Relatively high-force rubbing is employed, since it produces the fully oriented AL surface and the defect-free LC alignment with consistent Θ_p for a given AL.²⁶

Experimental

Materials. 11 different PIs, polystyrene (PS), and poly(methyl methacrylate) (PMMA) were employed as the ALs in this work. The poly(amic acid) precursor solutions of poly(pyromellitic dianhydrideoxydianiline) (PMDA-ODA), poly(3,3',4,4'-biphenyl-tetracarboxylic dianhydride-*p*-phenylene

diamine) (BPDA-PDA), poly(2,2'-bis-3,4-dicarboxyphenyl hexafluoropropane dianhydride-oxydianiline) (6FDA-ODA), and poly[2,2'-bis-3,4-dicarboxyphenyl hexafluoropropane dianhydride -2,2'-bis-(4-diaminophenyl) hexafluoropropane dianiline] (6FDA-HFDA) PIs and a pre-imidized solution of poly[2,2'-bis-3,4-dicarboxyphenyl hexafluoropropane dianhydride-(oxydianiline)_{0.7}-(diphenyl sulfone diamine)_{0.3}] (6FDA-ODA-DSDA) PI were purchased from Du Pont Electronics or HD Microsystems. A pre-imidized PI solution, Nissan RN1024TM, was obtained from Nissan Chemical Industries. Five other PIs, poly(cyclobutanetetracarboxylic dianhydride-oxydianiline) (CBDA-ODA) and poly(cyclobutanetetracarboxylic dianhydride -3,3'-dimethyl-4,4'-biphenyl diamine) (CBDA-

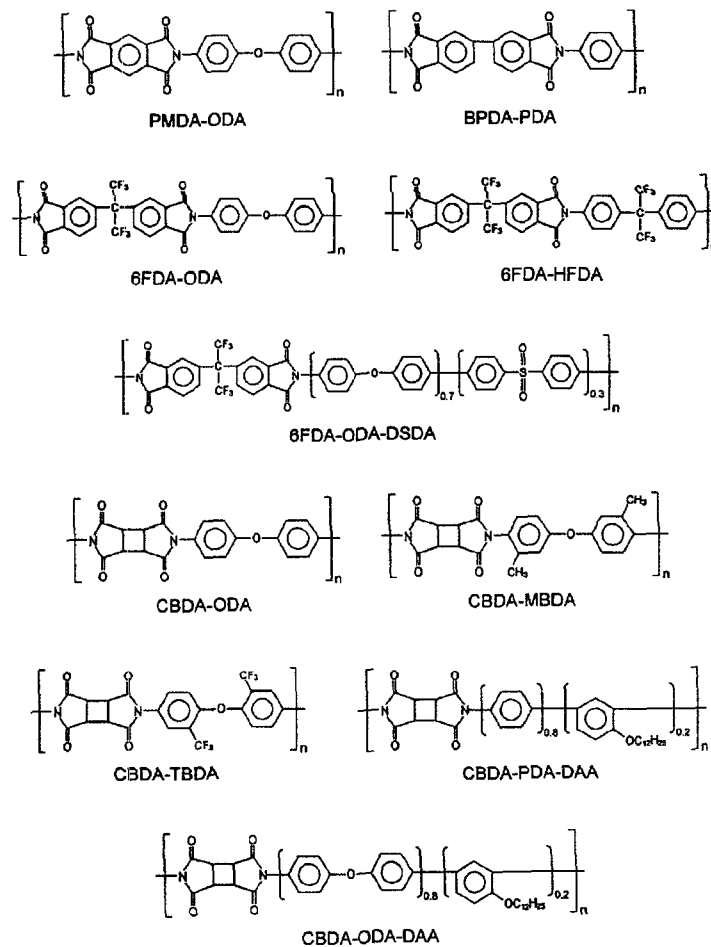


Figure 1. Chemical structures of polyimide repeating units.

MBDA), poly[cyclobutanetetracarboxylic dianhydride - 2,2'-bis(trifluoromethyl benzidine)] (CBDA-TBDA), poly[cyclobutanetetracarboxylic dianhydride-(oxydianiline)_{0.8}-(diaminododecanoxybenzene)_{0.2}] (CBDA-ODA-DAA), and poly[cyclobutanetetracarboxylic dianhydride-(phenylene diamine)_{0.8}-(diaminododecanoxybenzene)_{0.2}] (CBDA-PDA-DAA) were prepared as poly(amic acid) precursor solutions at the Nissan Chemical laboratories. The chemical structures of the repeating units of the final, fully imidized PIs are shown in Figure 1. They all were used without further purification and *N*-methyl-2-pyrrolidinone (NMP) and γ -butyrolactone were used as diluents for the PI precursors. Polydisperse polystyrene (PS) of M.W. = 280,000 and poly(methyl methacrylate) (PMMA) of M.W. = 395,000 were purchased from Scientific Polymer Products and were dissolved in cyclopentanone reagentgrade from Aldrich Chemical Co..

The PIs used here can be categorized broadly in two groups as "main-chain", meaning that the backbone has no side chains (or branches) (here, -CF₃ and -CH₃ are not considered as side chains), and "alkylated". The main-chain PIs can be also divided into three types: fully aromatic, alicyclic, and fluorinated. The fully aromatic main-chain PIs, PMDA-ODA and BPDA-PDA, have relatively rigid repeating units dominated by aromatic moieties. The alicyclic main-chain ones, CBDA-ODA and CBDA-MBDA, have cyclobutane moiety in the backbone. The fluorinated PIs, CBDA-TBDA, 6FDA-ODA, 6FDA-HFDA, and 6FDA-ODA-DSDA, contain -CF₃ moieties in the repeating unit. The alkylated PIs, CBDA-ODA-DAA, CBDA-PDA-DAA, and Nissan RN1024TM have long aliphatic side chains incorporated into the backbone.

A multi-component fluorinated LC, ZLI-5080TM, and a single-component LC, 4-pentyl-4'-cyanobiphenyl (5CB) were purchased from E. Merck Industries. Both LCs are nematic at room temperature. ZLI-5080TM LC molecules have -OCF₃, -CF₃, -CH₂F, and -CH₃ end groups, -F on some phenyl rings, and ester (-CO₂-) groups.

Preparation of Alignment Layer Films and LC Cells. The polymer films for ALs were fabricated by spin-coating the corresponding solutions on indium-tin-oxide(ITO)-coated glass substrates

with the dimension of 100 mm × 75 mm × 1.1 mm. The films were baked at 80°C for 30 min and cured for 60 min at an appropriate temperature; the curing temperature depended on polymers and experiments. The curing at 85°C was conducted on a hot plate and that at other temperatures was done in a convectional oven. CBDA-TBDA films for an IR study were spin-coated on KBr substrates with the 1-inch diameter and cured at 85-300°C.

The polymer-coated substrates were rubbed by a rubbing machine with a 15 cm-diameter rotating roller covered with a cotton velvet cloth having fiber length of about 2.5 mm and a stage moving the substrate under the roller (Figure 2). The rubbing conditions were set at roller speed of 200 rpm, speed of substrate stage of 144 cm/min, pile impression of 0.40 mm, and 2 rubbings. The rubbed substrate was N₂-purged to remove debris during the rubbing process. Some rubbed samples were annealed prior to filling of LCs to study the annealing effect.

The antiparallel cell with 5 μ m-cell spacing was assembled using a UV-curable adhesive; the cell spacing was achieved by placing polymer spacers on the rubbed AL by a dry sprayer. Then, the adhesive was UV-exposed while shielding the main area of the cell. ZLI-5080 or 5CB was introduced into the cell in a vacuum chamber under 350 Torr at room temperature. The LC-filled cell was finally sealed with the same UV-curable adhesive followed by UV-exposure.

Analysis of Alignment Layer Films. Contact

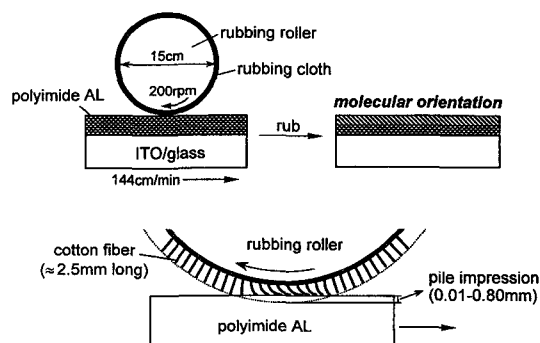


Figure 2. Schematic of rubbing process and the values of rubbing parameters used in the experiment.

Table I. Water Contact Angles and LC Pretilt Angles on the Main-chain Poly(amic acid) and Polyimide Films

Polymer	Curing Temperature (°C)	Water Contact Angles ^a (deg) (advancing/receding)	Pretilt Angle of ZLI-5080 (deg)
CBDA-ODA	85	58/7	1.0
	230	63/19	2.4
CBDA-MBDA	85	56/8	1.3
	230	65/25	3.8
CBDA-TBDA	85	66/19	1.8
	230	70/35	8.0

^afor the plain, unrubbed films.

--- 85 °C-curing was conducted on a hot plate while 230 °C-curing was done in a N₂-circulating, convectional oven. The thermal curing at 85 °C and 230 °C produces poly(amic acid) and polyimide, respectively.

Table II. Dependences of the Degree of Imidization, Water Contact Angles, and LC Pretilt Angles on Imidization Temperature of CBDA-TBDA

Curing ^a Temperature (°C)	Degree of Imidization ^b (%)	Receding Water Contact Angle (deg)		Pretilt Angle of ZLI-5080 (deg)
		[unrubbed]	[rubbed]	
85	2	19	12	1.8
180	30	16	11	2.7
200	72	23	14	4.5
230	98	35	23	8.0
300	100	45	33	12.0

^aThe film for 85 °C was cured on a hot plate while the other films was done in a N₂-circulating, convectional oven.

^bThe degree of imidization was determined on the basis of two peak absorbances at 795 cm⁻¹ corresponding to imide and 1530 cm⁻¹ due to amide in the unit of amic acid, using the following equation:

$$\text{the degree of imidization} = \frac{1}{2} \left[\frac{(A_{795})_T}{(A_{795})_{300}} + \left\{ 1 - \frac{(A_{1530})_T}{(A_{1530})_{85}} \right\} \right]$$

where (A₇₉₅)_T and (A₁₅₃₀)_T are the absorbances at 795 cm⁻¹ and 1530 cm⁻¹ for the curing temperature T, respectively. The degree of imidization for 300 °C-curing was taken as 100% as a normalization; (A₁₅₃₀)₃₀₀ was considered as zero.

angles on polymer films were measured using a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Deionized water was used as the probing fluid. Dynamic advancing and receding contact angles were determined by measuring the tangent at the intersection of the air/water/polymer surface while adding and withdrawing water to and from the drop, respectively. IR spectra of CBDA-TBDA films were obtained under N₂-purge using a Nicolet-510 FTIR spectrometer with 4 cm⁻¹ resolution.

Measurement of LC Pretilt Angles. The pretilt angles at three different spots in the area

showing a uniform texture of each antiparallel LC cell were measured at room temperature by the crystal rotation method²⁷; the average value was reported.

Results and Discussion

Effect of Imidization of Alignment Layers.

We here discuss how imidization of the ALs from poly(amic acid) precursors affects Θ_p . To investigate its genuine effect, the values of Θ_p reported in this section are for the samples without any annealing of the rubbed AL or the LC cell.

Poly(amic acid) is the most common precursor of PI. A poly(amic acid) film has much more polar surface than the corresponding PI, due to presence of polar carboxylic acid (-COOH) and amide (-CONH-) groups. Normally, poly(amic acid) is imidized *in-situ* by thermal treatment at elevated temperatures. The degree of imidization increases with the imidization temperature.²⁸ Table I shows Θ_s of ZLI-5080 LC and dynamic water contact angles for the films of the "main-chain" polymers thermally cured for 1 hr at 85°C and 230°C. The contact angle data indicate that the film cured at 85°C, corresponding to poly(amic acid), has more polar surface than that cured at 230°C, corresponding to PI. Θ_p is smaller on the more polar surface than on the other, which is presumably due to the increased strength of attractive interaction between the LC and polymer molecules at the AL surface.

To study more systematically the correlation between the degree of imidization, surface polarity, and Θ_p , CBDA-TBDA was chosen because its non-polar-CF₃ group can produce a wide range of Θ_p without causing the steric effect. The degree of imidization and the surface polarity were manipulated by various curing temperatures (85-300°C) for a fixed curing time (1 hr) and determined by IR spectra and the receding water contact angles, respectively. Both the degree of imidization of CBDA-TBDA and the receding water contact angle on the films increase with the imidization temperature, as given in Table II. This reflects a decrease in the surface polarity due to conversion of the polar poly(amic acid) to the less polar PI with increasing imidization temperature. As antici-

pated, Θ_p increases with the degree of imidization, i.e. imidization temperature, since attraction between the LC and CBDA-TBDA molecules at the surface falls due to the decrease in the polarity.

The degrees of imidization at 230°C and 300°C were here determined as 98% and 100%, respectively, but the water contact angles and Θ_s showed significant difference. This is probably because the small amount of poly(amic acid) left unimidized by curing at 230°C, which cannot be easily detected by IR, is relatively enriched at the surface by rubbing; polar carboxylic acid and amide groups of poly(amic acid) near the surface are expected to be exposed to the surface by rubbing.²⁹ This results in a smaller receding contact angle, more attraction between LC-AL, and consequently a smaller Θ_p for 230°C-curing.

The same result, that Θ_p increases with imidization temperature, was observed in several other studies,^{7,18,24,25} and it was proposed^{15,22} that this increase is due to increase in crystallinity (or ordering) of the unrubbed PI prior to rubbing treatment, which is different from our viewpoint based on the change in the surface polarity of ALs.

The changes noted above are generic to the "main-chain" polymers from poly(amic acid) precursors. In the case of "alkylated" polymers, such a relation is not clearly observed. For both CBDA-ODA-DAA and CBDA-PDA-DAA, although there is considerable difference in the surface polarity between 85°C and 230°C curing, Θ_p is nearly independent of the imidization temperature, as shown in Table III; the difference in Θ_p is quite

Table III. Water Contact Angles and LC Pretilt Angles on the Alkylated Poly(amic acid) and Polyimide Films

Polymer	Curing Temp. (°C)	Water Contact Angles ^a (deg)		Pretilt Angle (deg)	
		(Advancing/Receding)		ZLI-5080	(5CB)
CBDA-ODA-DAA	85	78/8		5.7	12.5
	230	86/34		6.2	11.4
CBDA-PDA-DAA	85	77/8		5.6	
	230	84/29		5.3	

^afor the plain, unrubbed films.

--- 85°C-curing was conducted for 1 hr on a hot plate while 230°C-curing was done in a N₂-circulating, convectional oven. The thermal curing at 85°C and 230°C produces poly(amic acid) and polyimide, respectively.

Table IV. Effects of Annealing of Rubbed Nissan RN1024 Polyimide Alignment Layer on Water Contact Angles, LC Alignment, and LC Pretilt Angles

Film Treatment before Filling of Liquid Crystals	Water Contact Angles (deg) (Advancing/Receding)	Alignment Defects	Pretilt Angle of ZLI-5080 (deg)
none	86/42		N.A.
rubbing	82/24 ^a	none	11.5
rubbing + 1-hr annealing at 80 °C	85/29	none	10.2
rubbing + 1-hr annealing at 120 °C	85/34	none	8.8
rubbing + 1-hr annealing at 180 °C	86/36	none	6.7
rubbing + 2-hr annealing at 180 °C		none	5.9
rubbing + 4-hr annealing at 180 °C		many	5.2

^aRubbing of polymer films with a cotton cloth induces microscopic molecular reorientation of the surface, occurring within the very top layer (< 1.5 nm), such that polar groups like carboxylic acid, hydroxyl, and amide orient out-of-the-plane of the surface while non-polar alkyl side chains fold toward the bulk. This effect results in the more polar AL surface, i.e. the decrease in receding water contact angle.

--- The films were cured (dried) for 1 hr in an air-circulating, convectional oven at 180 °C.

small compared with that for a typical, imidizable "main-chain" material, CBDA-TBDA. This result reflects that in the case of "alkylated" polymers the steric effect by long alkyl side chains, which are enriched at the surface,³⁰ is dominant in determining Θ_p . The degree of imidization thus doesn't affect Θ_p for this type of polymer.

Effect of Thermal Annealing of the Rubbed Alignment Layer. After rubbing, the AL-coated substrate is normally cleaned with water or a soap solution to remove the rubbing debris followed by thermal annealing for removal of water and stabilization of the AL. Table IV shows the effect of this annealing on Θ_p of ZLI-5080 for an alkylated PI, Nissan RN1024TM. The receding water contact angle on the rubbed surface increases, i.e. the surface polarity decreases with the annealing, and the bigger change occurs for a higher temperature. On the other hand, Θ_p decreases with the thermal treatment; the extent of the decrease becomes greater as the temperature or the time increases, but the major decrease is caused by the first 1 hr annealing.

Rubbing of polymer films with a cotton cloth induces microscopic molecular reorientation of the surface such that polar groups in the repeating unit reorient toward the surface while non-polar alkyl side chains fold toward the bulk.³¹ As a result, the polymer surface becomes more polar, resulting in the decrease in receding water contact angle. However, thermal annealing of the rubbed

films causes relaxation of polymer molecules (or chains) and subsequently brings some deterioration of the rubbing-induced molecular orientation, leading to the increases in receding water contact angle, i.e. the decrease in the surface polarity. The deterioration of the AL orientation worsens in-plane orientation of the LCs anchoring at the AL surface (i.e. surface alignment of the LCs) and thus causes a decrease in Θ_p . On the other hand, the result in the previous section shows that Θ_p for alkylated polymer ALs is not nearly affected by their surface polarity (see Table III), so that the decrease in the surface polarity due to the annealing doesn't seem to increase Θ_p for an alkylated PI, RN1024TM. Therefore, the result shown in Table IV suggests that the decrease in Θ_p caused by the annealing is related to loss in molecular orientation of the AL surface. It is noteworthy that the LC cell with the rubbed films annealed for 2 hrs at 180 °C shows some alignment defects and the defects become more severe for the 4-hr annealing, giving smaller Θ_s . This supports that Θ_p is affected by uniformity of LC alignment and its decrease is due to the deterioration of the AL orientation. The decrease would be greater when the annealing temperature is higher, as indicated by the result shown in Table IV.

The molecular chain relaxation caused by thermal annealing would depend on the polymer properties such as its glass transition temperature

Table V. Effects of Annealing of Rubbed Alignment Layer on Liquid Crystal Alignment and Pretilt Angles

Polymer	Film Treatment before Filling of Liquid Crystals	Liquid Crystal Alignment	Pretilt Angle of ZLI-5080 (deg)
CBDA-MBDA ^a PI	rubbing	uniform	3.8
	rubbing + 1-hour annealing at 180 °C	uniform	2.7
PMMA ^b	rubbing	uniform	3.7
	rubbing + 1-hour annealing at 75 °C	uniform	1.8
	rubbing + 5-min annealing at 120 °C	random	N.A.
PS ^b	rubbing	uniform	0°
	rubbing + 5-min annealing at 120 °C	random	N.A.

^aThe film was imidized for 1 hr in a convectional oven at 230 °C.

^bThe films were dried at 130 °C for 1 hr in a convectional oven.

^cThe direction of LC alignment is perpendicular to the rubbing direction. As a result, the pretilt angle measured by the crystal rotation method is zero due to degeneracy.

Table VI. Effects of Annealing of LC-filled Cell on the Pretilt Angle

Polymer	Pretilt Angle (deg)						
	(none)	ZLI-5080			5CB		
		[annealing at 120 °C]	[no annealing]	[15-min annealing]	[15-min annealing]	[15-min annealing]	[15-min annealing]
		(5 min)	(15 min)	(60 min)	(at 45 °C)	(at 120 °C)	(at 120 °C)
BPDA-PDA PI	1.1		1.0		2.1	2.0	1.7
PMDA-ODA PI	1.8	1.8	1.8		2.3	2.5	2.3
CBDA-ODA PI	2.4		2.0				
CBDA-MBDA PI	3.8	2.8	2.6	2.5	5.1	4.8	2.3
CBDA-TBDA PI	8.0		4.8		13.6	12.3	6.6
6FDA-ODA PI	3.3	1.5	0.6		0.7	0.5	--- ^b
6FDA-HFDA PI	10.9 ^c	2.0	0.6				
6FDA-ODA-DSDA PI	3.6	2.6	2.3		1.0	0.7	--- ^b
CBDA-ODA-DAA PI	6.2	4.9	4.7		7.7	7.4	3.4
Nissan RN1024 TM PI	11.5	8.4	8.1	7.6			
		[no annealing]	[5-min annealing]				
PMMA		3.7	(at 75 °C)	(at 120 °C)			
			0.3	---			

^aLiquid crystal alignment showed the flow effect and many defects.

^bRandom liquid crystal alignment.

--- All films for polyimide ALs were cured for 1 hr in a convectional oven; the BPDA-PDA, PMDA-ODA, 6FDA-ODA, and 6FDA-HFDA films were imidized at 250 °C/N₂, the pre-imidized Nissan RN1024 one was cured (dried) at 180 °C/air, and the others were cured at 230 °C/N₂.

--- PMMA film was dried at 130 °C/air for 1 hr.

(T_g) and flexibility. We can expect that when a polymer has a low T_g or high flexibility, the relaxation can easily occur at even a relatively low

temperature, which will cause severe deterioration of the molecular orientation and a big decrease in Θ_p . T_g of PMMA is much lower (105 °C) than those

of typical PIs. Θ_p is significantly decreased when the rubbed PMMA AL is annealed at 75°C, as expected. The decrease is relatively greater than those for annealing of PIs, for example 80°C-annealing of RN1024 PI and 180°C-annealing of CBDA-MBDA PI (see Tables IV and V), even though the temperature is lower.

Since uniform LC alignment is generated by molecular orientation of the AL surface, it is expected that if the orientation is destroyed, the alignment would be lost. The results shown in Table V verify this argument. The polymer orientation can be destroyed by heating at a temperature higher than its T_g . Both rubbed PMMA and PS films induce uniform LC alignment. However, when these films are heated for only 5 min at 120°C, greater than their T_g s (105°C and 100°C for PMMA and PS, respectively), prior to filling of LCs, uniform LC alignment is not obtained; the LC cells show locally random alignment (Table V). We encounter the same situation when a LC-filled cell is heated at a temperature higher than the polymer's T_g ; for example, uniform LC alignment formed over the rubbed PMMA films is totally destroyed when the corresponding LC cell is heated at 120°C for just 5 min (Table VI).

Effect of Thermal Annealing of the LC-filled Cell. To improve the uniformity and stability of LC alignment, LC cells are annealed at a temperature higher than the nematic-isotropic transition temperature (T_{NI}) of the LC material. This annealing could affect not only the molecular orientation of the polymer AL but the interaction of LCs with the polymer molecules, so that the details of these effects would appear complicated. The proper thermal treatment of LC cells removes alignment defects and improves the alignment uniformity, but there is usually a concomitant decrease in Θ_h as shown in Table VI. The annealing is believed to improve in-plane orientation of LCs in the bulk and subsequently increase Θ_h . On the contrary, it deteriorates the molecular orientation of the AL surface and consequently decreases Θ_h as discussed previously. The deterioration of the surface orientation could be accelerated if plasticization of the polymer AL by LCs or diffusion of LCs into the AL occurs at the AL-LC interface and heating promotes both actions. Consequently, the anneal-

ing of LC cells has the contradictory effects on Θ_h . The results shown in Table VI, that Θ_p is decreased in most cases, suggest that the latter effect (i.e. deterioration of the AL orientation) is major and becomes greater as annealing temperature increases or polymer's T_g decreases, which causes more random orientations.⁵

The decrease in Θ_p with annealing of LC cells, of which the bulk occurred in the first 5 min, depends on the polymer and LC materials as well as the annealing temperature. The variation in the decrease with the temperature shows the same trend with that seen in annealing of the rubbed polymer ALs; the extent of the decrease becomes dominant as the annealing temperature increases. The data in Table VI also show that the extent of the relative decrease in Θ_p varies with the nature of PIs. The decrease for the "alicyclic" main-chain PIs (CBDA-ODA and CBDA-MBDA) is greater than that for the fully "aromatic" main-chain ones (PMDA-ODA and BPDA-ODA). Especially, in the case of the fluorinated PIs (CBDA-TBDA, 6FDA-ODA, 6FDA-HFDA and 6FDA-ODA-DSDA) not only the decrease in Θ_p is severe but uniform LC alignment is destroyed, in some cases, by 15-min annealing at 120°C. The bigger decrease in Θ_p or the alignment destruction corresponds to less stable LC alignment. The foregoing results indicate that the rigid aromatic moiety in the PI structure enhances the stability of LC alignment, as expected, while fluorination of PIs decreases its stability. The similar situation is seen in deterioration of orientation of the rubbed PI films by soaking in organic solvents³²; soaking of the rubbed PI in acetone or alcohols deteriorates its rubbing-induced orientation and the degree of deterioration increases in order of aromatic < aliphatic < fluorinated and aliphatic PIs. Fluorinated PIs are known to have larger free volume, which may be due to both weak molecular interaction and steric hindrance caused by $-\text{C}(\text{CF}_3)_2-$ groups, and greater gas permeability than typical, non-fluorinated ones.^{33,34} It thus appears that organic solvents can more easily diffuse into or swell fluorinated PIs, resulting in more deterioration of orientation of the rubbed films. This is also applicable to nematic LCs, as they may be considered as kind of a (poor) organic solvent, and seems to be the reason that thermal

treatment of the LC cell with fluorinated PI ALs causes the severe decrease in Θ_p and the alignment destruction.

Conclusions

How thermal imidization of the AL and annealing of the rubbed AL or the LC cell affect the rubbing-induced LC alignment, especially its pretilt angle (Θ_p) has been systematically investigated, employing various types of PIs, and the nature of these effects has been figured out. Θ_p increases with the degree of imidization of the "main-chain" poly(amic acid) ALs, i.e. with the imidization temperature since attractive interaction between the AL and LC molecules falls due to a decrease in the surface polarity by conversion of polar poly(amic acid) to less polar PI. But, it is hardly affected by the degree of imidization for the "alkylated" ALs in which the steric effect at the AL surface caused by the aliphatic groups in its side chains is dominant. Thermal annealing of the rubbed PI ALs, prior to filling of LCs, deteriorates the molecular orientation of the AL surface and subsequently the overlying LC alignment, which results in a decrease in Θ_p and even destruction of uniform LC alignment itself for the long annealing at a high temperature. On the other hand, annealing of the LC-filled cell affects both the orientation of the rubbed PI AL and the LC-PI interaction at the AL. The deterioration of the AL orientation usually dominates over the improvement of in-plane orientation of LCs in the bulk, so that there is a concomitant decrease in Θ_p . The degree of the relative decrease in Θ_p , which is a measure of instability of LC alignment, varies with the nature of both PIs and LCs, which reflects the importance of LC-PI interaction in the LC alignment. Rigid aromatic units in the PI structure are favored in terms of thermal stability of LC alignment, while fluorinated PI ALs induce less stable LC alignment such that the LC-cell annealing causes a big decrease in Θ_p or destroys uniform LC alignment itself.

Acknowledgement. This work was supported by a Korea Research Foundation Grant (KRF-2001-005-D00003).

References

- (1) T. Scheffer and J. Nehring, in *Liquid Crystals: Applications and Uses*, B. Bahadur, Ed., World Scientific, Singapore, 1990. Vol. 1, pp 232-274.
- (2) N. A. J. M. van Aerle, *J. SID*, **2**, 41 (1994).
- (3) B. H. Ahn, D. W. Lee, J. K. Lee, S. S. Hong, and G. D. Lee, *Korea Polym. J.*, **8**, 19 (2000).
- (4) M. Ree, T. J. Shin, Y. H. Park, H. Lee, and T. Chang, *Korea Polym. J.*, **7**, 370 (1999).
- (5) A. Lien, R. A. John, M. Angelopoulos, K.-W. Lee, H. Takano, and A. Takenaka, *Appl. Phys. Lett.*, **67**, 3108 (1995).
- (6) Y. Koike, T. Yamada, K. Okamoto, M. Ohashi, I. Tomita, and M. Okabe, *SID 92 Digest*, **23**, 798 (1992).
- (7) C. Nozaki, N. Imamura, and Y. Sano, *Jpn. J. Appl. Phys.*, **32**, 4352 (1993).
- (8) M. Niskikawa, T. Miyamoto, S. Kawamura, Y. Tsuda, and N. Bessho, *Proc. Japan Display 1992*, 819 (1992).
- (9) B. O. Myrvold, H. Yokokura, Y. Iwakabe, K. Kondo, and S. Oh-hara, *Proc. Japan Display 1992*, 827 (1992).
- (10) D.-S. Seo, K. Araya, N. Yoshida, M. Nishikawa, Y. Yabe, and S. Kobayashi, *Jpn. J. Appl. Phys.*, **34**, L503 (1995).
- (11) D. H. Choi, J. H. Kim, and K. J. Cho, *Korea Polym. J.*, **8**, 172 (2000).
- (12) B. O. Myrvold and K. Kondo, *Liq. Cryst.*, **18**, 271 (1995).
- (13) V. N. Raja, D. S. S. Rao, S. W. Kang, J. C. Lee, S. S. Lee, and A. H. Jin, *Liq. Cryst.*, **20**, 41 (1996).
- (14) D.-S. Seo, N. Yoshida, S. Kobayashi, M. Nishikawa, and Y. Yabe, *Jpn. J. Appl. Phys.*, **33**, L1174 (1994).
- (15) K. Shirota, M. Yaginuma, T. Sakai, K. Ishigawa, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, **35**, 2275 (1996).
- (16) M. Barentlo, R. W. J. Hollering, and N. A. J. M. van Aerle, *Phys. Rev.*, **A46**, R4490 (1992).
- (17) X. Zhuang, L. Marrucci, and Y. R. Shen, *Phys. Rev. Lett.*, **73**, 1513 (1994).
- (18) M. E. Becker, R. A. Kilian, B. B. Kosmowski, and D. A. Mlynski, *Mol. Cryst. Liq. Cryst.*, **132**, 167 (1986).
- (19) D.-S. Seo, S. Kobayashi, M. Nishikawa, and Y. Yabe, *Liq. Cryst.*, **19**, 289 (1995).
- (20) D.-S. Seo, S. Kobayashi, and A. Mochizuki, *Appl. Phys. Lett.*, **61**, 2392 (1992).
- (21) K.-Y. Han and T. Uchida, *J. SID*, **3**, 15 (1995).
- (22) N. A. J. M. van Aerle, M. Barentlo, and R. J. W. Hollering, *Proc. EuroDisplay 93*, 5 (1993).
- (23) A. Mosley, B. M. Niclolas, and P. A. Gass, *Displays*, 17 (1987).

- (24) P. A. Gass, A. Mosley, B. M. Nicholas, J. T. Brown, C. P. Edwards, and D. G. McDonnell, *SID 87 Digest*, **18**, 376 (1987).
- (25) D.-S. Seo, S. Kobayashi, M. Nishikawa, and Y. Yabe, *Liq. Cryst.*, **19**, 289 (1995).
- (26) In the region of weak rubbing, the pretilt angle (Θ_p) quickly increases with the rubbing strength, due to increase of the area fraction of the AL surface modified by rubbing. But, LC alignment induced by weak rubbing has poor thermal stability and/or alignment defects. In applications, strong rubbing, especially high-force rubbing is thus applied on the AL to produce thermally stable, defect-free alignment. In this rubbing regime, Θ_p only changes slightly with rubbing strength and consistent Θ_p is thus generated for a given AL.
- (27) T. J. Scheffer and J. Nehring, *J. Appl. Phys.*, **48**, 1783 (1977).
- (28) F. W. Harris, in *Polyimides*, D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., Blackie, New York, 1990, pp 1-37.
- (29) K.-W. Lee, S.-H. Paek, A. Lien, C. J. Durning, and H. Fukuro, *SID 96 Digest*, **27**, 273 (1996).
- (30) K.-W. Lee, A. Lien, J. H. Stathis, and S.-H. Paek, *Jpn. J. Appl. Phys.*, **36**, 3591 (1997).
- (31) K.-W. Lee, S.-H. Paek, A. Lien, C. J. Durning, and H. Fukuro, *Macromolecules*, **29**, 8894 (1996).
- (32) I. Hirose, T. Matsushita, H. Miyairi, and S. Saito, *Jpn. J. Appl. Phys.*, **38**, 2851 (1999).
- (33) K. Okamoto, N. Tanihara, H. Watanabe, K. Tanaka, H. Kita, A. Nakamura, Y. Kusuki, and K. Nakagawa, *J. Polym. Sci.: Polym. Phys. Ed.*, **30**, 1223 (1992).
- (34) M. Langsam, in *Polyimides: Fundamentals and Applications*, M. K. Ghosh and K. L. Mittal, Eds., Marcel Dekker, New York, 1996, pp 697-741.