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## Chemical Structural Effects of Polyimides on the Alignment and Electro-optical Properties of Liquid Crystal Cells

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**Abstract:** The nature of the nematic liquid crystal (LC) alignment induced by the rubbed polyimide (PI) alignment layers (ALs) and the electro-optical (EO) properties of the LC cells are expected to depend on the chemical and physical features of the PI. By employing five pyromellitic dianhydride (PMDA)-type PIs having different functionalities, we have studied the effects of the PI's structure and chemistry on the alignment characteristics and the cell's EO properties. Increasing the flexibility of the PI increases the pretilt angle and tends to improve the alignment stability. On the other hand, the rigid, fluorinated PI displays poor stability for LCs and induces a less stable/uniform LC alignment and, subsequently, a small pretilt angle. It also transpired that fluorination of the PI deteriorated the voltage-transmittance characteristics and the voltage holding ratio; increasing the flexibility of the PI structure improves these EO properties. The finding that the qualitative trends for the PI's functionalities are similar for both the alignment and EO properties suggests that the EO properties are closely related to the alignment characteristics, which are determined by short-range interactions between LC and PI molecules.

**Keywords:** polyimide, rubbing, liquid crystal alignment, stability, electro-optical properties.

### Introduction

In the current liquid crystal display (LCD) industry, a polyimide (PI) alignment layer (AL) unidirectionally rubbed with a cloth (typically rayon or cotton) is employed to achieve uniform liquid crystal (LC) alignment, since it has excellent thermal and mechanical properties and provides stable LC alignment.<sup>1,2</sup> Rubbing changes the topography of the AL surface<sup>3-5</sup> and induces the anisotropic orientation of PI molecules along the rubbing direction.<sup>5-8</sup> The nematic LC molecules in contact with the AL surface orient preferentially along the rubbing direction, resulting in

the LC director at the surface in the rubbing direction with a pretilt. Then, the bulk LCs are epitaxially aligned along the surface LC director.<sup>6</sup> That is, LC alignment is a result of interactions between LCs and PI molecules at the AL surface. Also, operation (or driving) of LCDs is based on the uniform alignment and its change. Therefore, the nature of LC alignment and the electro-optical (EO) properties of LCDs depend on the chemical and physical features of the AL. There have been the studies showing that the PI ALs affect the LC pretilt angle and the EO properties such as voltage holding ratio (VHR), residual DC voltage and so on.<sup>9-14</sup> However, most of these studies were limited to the specific type of PI or the specific properties of LC alignment or LCDs. Thus, we still lack a detailed connection between the PI structure and the properties of LC alignment

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and LCDs.

There are many possible interactions between LC and PI molecules at the AL surface, including dipole-dipole interaction, dispersion force, hydrogen bonding, and steric interaction. The details of these short-ranged, molecular-level interactions affect the properties of LC alignment and further LCDs. Considering the chemical viewpoint of these interactions, we have comprehensively investigated how the properties and stability of both LC alignment and LC cells are affected by the PI structure/chemistry, employing the 5 PIs (PMDA-ODA and its 4 derivatives). Based on the results of this study, potential relations between the properties of the AL, the LC alignment and the LC cell have been discussed.

## Experimental

**Materials.** To give systematic AL structures, the poly(amic acid) precursor solutions for 5 PIs, poly(pyromellitic dianhydride-4,4'-oxydianiline or -4,4'-diaminophenyl ether) (PMDA-ODA; "PI1"), poly[pyromellitic dianhydride-2,2'-bis(4-aminophenyl) hexafluoropropane] (PMDA-HFDA; "PI2"), poly[pyromellitic dianhydride-2,2'-bis{4-(4-aminophenoxy)phenyl} propane] (PMDA-BAPP; "PI3"), poly[pyromellitic dianhydride-2,2'-bis{4-(4-aminophenoxy)phenyl} hexafluoropropane] (PMDA-HFBAPP; "PI4"), and poly[pyromellitic dianhydride-(4,4'-methylenedianiline)<sub>0.95</sub>-(3,5-diamino-*n*-hexadecyl benzoate)<sub>0.05</sub>] (PMDA-MDA-DAHDB; "PI5"), were made, using *N*-methyl-2-pyrrolidinone as a solvent, and then optimized for spin-coating with  $\gamma$ -butyrolactone and 2-butoxyethanol. The chemical structures of the repeating units of the final, fully imidized PIs are shown in Figure 1.

PI2 and PI4 are "fluorinated", i.e., they contain -CF<sub>3</sub> moieties in the repeating unit and have structural similarity to PI1 and PI3, respectively. PI1 and PI2 have relatively rigid repeating units while PI3 and PI4 have more flexible structures. The "alkylated" PI, PI5 has long aliphatic side chains incorporated into the backbone.

E7, a mixture of LCs with a cyano terminal, and MLC-6628, a mixture of fluorinated LCs, were obtained from Merck Industries. Their physical properties are listed in Table I.

**Preparation of Alignment Layers and LC Cells.** The polymer films for ALs were fabricated by spin-coating the corresponding solutions on indium-tin-oxide (ITO)-coated glass substrates; the patterned ITO/glass ones were used for LC cells whose EO properties are to be measured. Prior to coating, the substrates were edge-beveled and cleaned with a soap solution followed by deionized water. The films were then baked at 85°C for 30 min and cured for 1 hr on a 250°C hot plate; the films for an IR study were spin-coated on KBr substrates with the 1-inch diameter and cured at 85-300°C. The thicknesses of the final, cured PI films were in the range of 60 ± 2 nm. The PI-coated substrates were

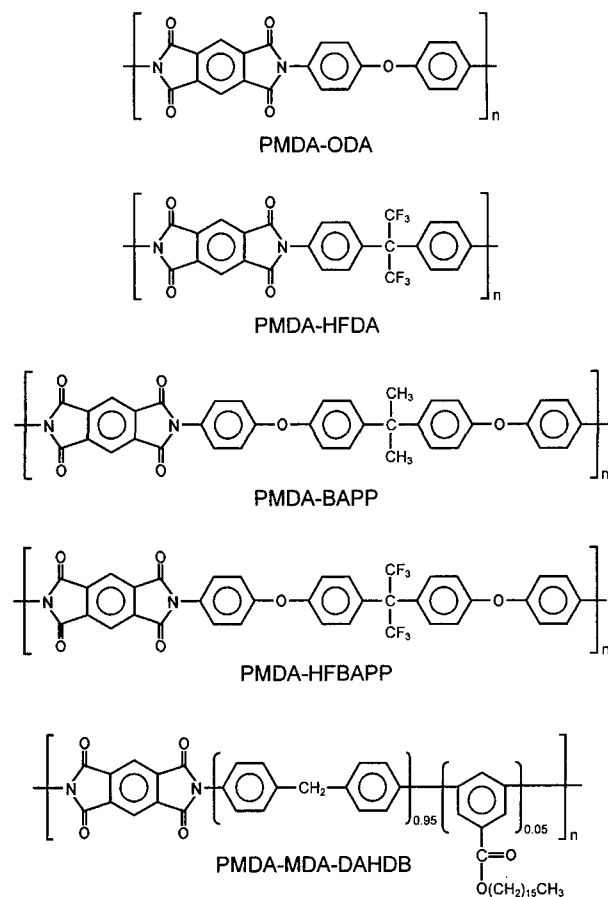


Figure 1. Chemical structures of polyimides used in this study.

Table I. The Physical Properties of E7 and MLC-6628

	$\epsilon_{  }$	$\epsilon_{\perp}$	$n_e$	$n_o$	Nematic range
E7	19.6	5.1	1.7500	1.5231	-10 ~ 60°C
MLC-6628	10.8	3.4	1.5646	1.4766	-40 ~ 88°C

rubbed by an automatic rubbing machine (from Shindo Eng. Ltd.) with a 10 cm-diameter rotating roller covered with a rayon velvet cloth (YA-20-R, Yoshikawa Co.) and a stage moving the substrate under the roller. The rubbing conditions were set at roller speed of 500 rpm, speed of substrate stage of 100 cm/min, pile impression of 0.30 mm and 1 rubbing.

On fabricating a sample cell, the desired cell gap ( $\approx 4.8 \mu\text{m}$ ) was achieved by placing polymer spacers on the rubbed AL surface by a wet sprayer. Using a thermally curable adhesive, the 90°-twisted cell, whose bottom and top substrates have 90°-crossed rubbing directions, was assembled and then hot-pressed at 150°C and 2 bar to cure the adhesive. For measurement of the pretilt angle, the antiparallel cell with the about 70  $\mu\text{m}$  cell gap was assembled using a double-

side adhesive tape. Then, the capillary introduction of a nematic LC into the assembled cell was conducted at room temperature. The LC-filled cell was finally sealed with an epoxy adhesive.

**Analysis of Alignment Layers.** Contact angles on the cured PI films were measured using a contact angle/surface tension analyzer (Phoenix 300, S.E.O. Ltd). Deionized water and diiodomethane were used as the probing fluid. IR spectra were obtained in transmission using a FTIR spectrometer (System 200, Perkin-Elmer Co.) with  $4\text{cm}^{-1}$  resolution. The hardness and modulus of the PI films were determined by a nano-indenter (Model XP, MTS) with a diamond tip.

**Characterization of LC Alignment.** Uniformity of LC alignment was determined by visual observation of the LC texture for defects, with the naked eye and a polarizing microscope. The pretilt angles at three different spots in the area showing a uniform LC texture of each antiparallel cell were measured at room temperature by the crystal rotation method<sup>15</sup>; the average value is reported.

**Characterization of Electro-optical Properties of LC Cells.** For the  $90^\circ$ -TN cell with the patterned ITO/glass substrates, the change in transmittance with the applied voltage, i.e. the voltage-transmittance (V-T) characteristic curve was evaluated, in a normally white (NW) mode, with increasing the voltage stepwise from 0V to 5V. The contrast ratio (CR) and the threshold voltage ( $V_{th}$ ), defined here as the ratio of transmission at 0 V to that at 5 V and as the voltage corresponding to 90% of transmission, respectively, were determined from the obtained V-T characteristic. The voltage holding ratio (VHR) of the  $90^\circ$ -TN cell was estimated by a VHR measurement system (VHRM-105 from Autronic-Melchers), repeatedly applying the pulse of 1 V with the width of 64  $\mu\text{s}$  and the field-off time of 16.67 ms.

## Results and Discussion

**Properties of Alignment Layers.** Poly(amic acid) is the most common precursor of PI. Normally, it is imidized *in-situ* at an elevated temperature, which increases the degree of imidization.<sup>16,17</sup> Table II shows the degree of imidization

for PI1-PI5 with imidization temperature. The degree of imidization was determined on the basis of relative absorbance of two peaks at  $1380\text{cm}^{-1}$  of imide (imide  $\nu_{C-N}$ ) and  $1540\text{cm}^{-1}$  of amide (amide  $\nu_{C-N}$ ) contained in amic acid,<sup>17,18</sup> taking that the PI precursor film was 100% imidized when it was treated at  $300^\circ\text{C}$  for 60 min. In the cases of the more flexible PIs, PI3 and PI4, the higher degree of imidization was obtained, compared to PI1, for relatively low-temperature curing;  $230^\circ\text{C}$ - and  $250^\circ\text{C}$ -curing induced 96% and 100% imidization, respectively. On the other hand, the opposite trend in imidization of the rigid, fluorinated PI, PI2 was shown. For all PIs except PI1, the absorbances of all peaks in IR spectra obtained after  $300^\circ\text{C}$ -curing under air decreased, indicating degradation of the PIs. Based on the foregoing results, the imidization in the following study has been conducted at  $250^\circ\text{C}/1\text{ hr}$  under air which gives the high degree of imidization without the degradation.<sup>19</sup>

The characteristics of LC alignment depend on the surface energy.<sup>2</sup> To determine the surface energy of the PIs, the static contact angles of both deionized water and diiodomethane droplets on each PI film cured at  $250^\circ\text{C}$  were measured. It was determined by the two contact angles using the geometric mean method<sup>20</sup> (Table III). The fluorination of PI reduces the surface energy; PI2 has a lower surface energy than PI1, and so does PI4 than PI3. This is due to the trifluoromethyl ( $-\text{CF}_3$ ) moieties. The (critical) surface energy of trifluoromethyl is known to be about 6 mN/m, which is much smaller than that of methyl (about 22 mN/m) or phenyl (about 35 mN/m).<sup>21</sup> On the other hand, PI3 has a lower surface energy than PI1, and so does PI4 than PI2, which relates to (i) the longer diamine structure, i.e. the longer repeating unit and (ii) the higher degree of imidization of PI3 and PI4. It is the imide group that is the most polar part in the repeating units of PI1-PI5 and thus contributes to increase in the surface energy most. All PIs have two imides in the repeating unit. As the length of the repeating unit increases, the proportion of the polar imide moieties decreases, which results in the decrease in the surface energy. On the other hand, a poly(amic acid) film generates much more polar surface than the corresponding PI, due to presence of polar carboxylic acid

**Table II. The Degree of Imidization of Poly(amic acids) with respect to Imidization Temperature**

Curing condition	PI1	PI2	PI3	PI4	PI5
$150^\circ\text{C}/1\text{hr}$	19.6%	17.3%	40.4%	40.0%	35.5%
$180^\circ\text{C}/1\text{hr}$	53.6%	47.3%	74.8%	64.6%	69.1%
$210^\circ\text{C}/1\text{hr}$	81.4%	70.9%	92.3%	94.0%	89.3%
$230^\circ\text{C}/1\text{hr}$	89.5%	81.5%	96.6%	97.7%	92.2%
$250^\circ\text{C}/1\text{hr}$	94.0%	90.8%	100%	100%	95.7%
$300^\circ\text{C}/1\text{hr}$	100%	100%	100%	100%	100%

**Table III. The Static Contact Angles on the Surface of Polyimides Imidized at  $250^\circ\text{C}/1\text{ h}$  and their Surface Energy**

	Static contact angle (deg.)				Surface energy (mN/m)
	water	diiodomethane	E7	MLC-6628	
PI1	63.8	16.2	< 5	< 5	52.8
PI2	70.3	33.9	< 5	~6	45.7
PI3	69.6	24.7	< 5	< 5	48.8
PI4	73.5	48.1	38.5	35.6	39.3
PI5	65.9	27.8	< 5	< 5	49.1

(-COOH) and amide (-CONH-) groups in the former. Therefore, the surface polarity decreases with the degree of imidization, due to conversion of the polar poly(amic acid) to the less polar PI; i.e. the higher degree of imidization, the lower surface energy of PI. PI4 has all the factors to decrease the surface energy (trifluoromethyl moiety, the longer repeating unit, and the higher degree of imidization) and thus shows the lowest surface energy.

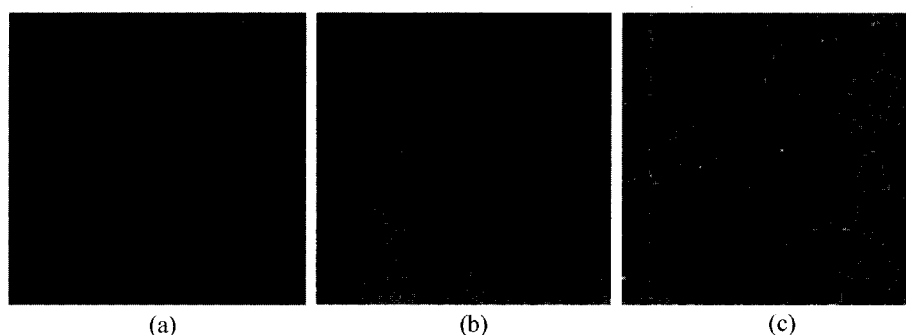
**Characteristics of LC Alignment.** LC alignment is characterized by the alignment uniformity (or homogeneity), the pretilt angle, and the anchoring energies. In the fabrication process of LCDs, the LC-filled cell is stabilized with annealing at a higher temperature than the LC's nematic-isotropic transition temperature. Good image and optimal EO performance of LCDs require uniform, homogeneous LC alignment throughout the cell (panel) even after this annealing. The uniformity and stability of LC alignment were investigated by observing the LC texture of 90°-TN cells after both LC-filling and annealing at various temperatures (Table IV). After LC-filling, all the cells showed the defect-free, uniform LC texture (Figure 2(a)), regardless of LCs and PIs. For all the cells of relatively flexible PIs such

as PI3-PI5, the same uniform texture also appeared even after 180°C/1 hr-annealing. In the cases of the E7/PI1 cell annealed at 180°C and the MLC-6628/PI2 one annealed at 120°C or higher temperatures, these showed the texture with reversely twisted domains (Figure 2(b)), which may be resulted from a small pretilt angle. On the other hand, the annealed cell of E7/PI2 showed the LC texture with tiny domains having various local LC directors (Figure 2(c)), which indicates the non-uniform, random alignment. This multi-domain texture became more severe as the annealing temperature increased. In summary, the rigid, fluorinated PI induces the LC alignment with poor stability/uniformity, while the increased flexibility of PI improves the alignment stability. This poor stability of LC alignment has been also observed for other rigid, fluorinated PIs.<sup>22</sup>

The similar situation is seen in deterioration of orientation of the rubbed PI films by soaking in organic solvents<sup>23</sup>; 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 weak molecular interac-

**Table IV. The LC Alignment and Texture of TN Cells before and after Thermal Annealing**

		After LC filling (no annealing)	After annealing of LC cell at 120°C/1 hr	After annealing of LC cell at 180°C/1 hr
E7	PI1	uniform, no defects	uniform, no defects	reverse-twist domains
	PI2	uniform, no defects	non-uniform, multi-domains	non-uniform, multi-domains
	PI3	uniform, no defects	uniform, no defects	uniform, no defects
	PI4	uniform, no defects	uniform, no defects	uniform, no defects
	PI5	uniform, no defects	uniform, no defects	uniform, no defects
MLC-6628	PI1	uniform, no defects	uniform, no defects	uniform, no defects
	PI2	uniform, no defects	reverse-twist domains	reverse-twist domains
	PI3	uniform, no defects	uniform, no defects	uniform, no defects
	PI4	uniform, no defects	uniform, no defects	uniform, no defects
	PI5	uniform, no defects	uniform, no defects	uniform, no defects



**Figure 2.** LC textures of TN cells observed by a polarizing microscope: (a) uniform texture, (b) reverse-twist domain texture, and (c) multi-domain texture.

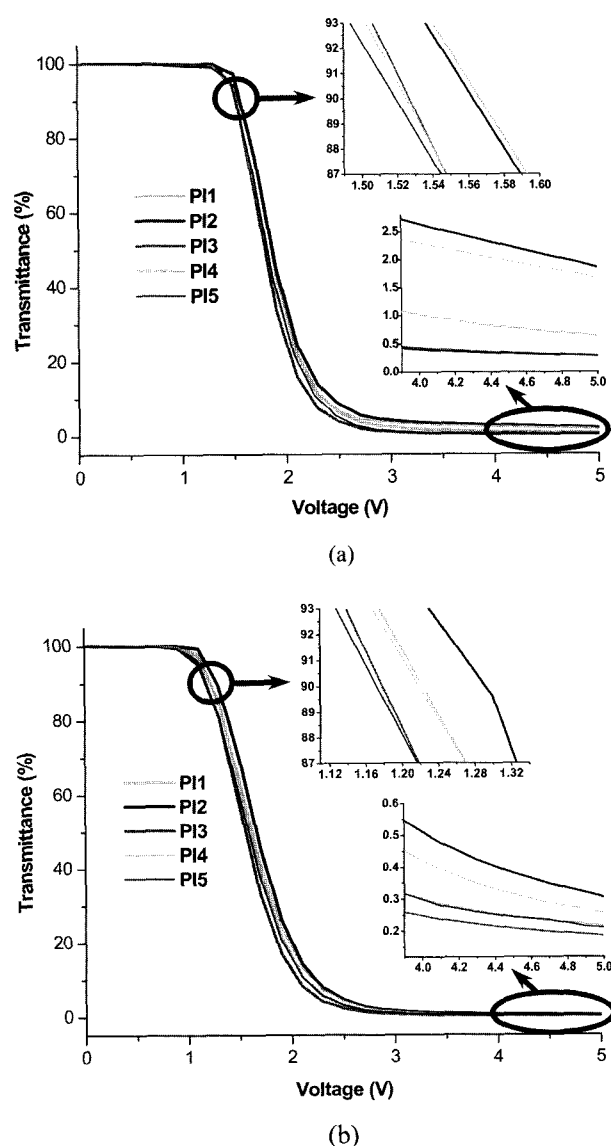
**Table V. Pretilt Angles of E7 and MLC-6628**

	PI1	PI2	PI3	PI4	PI5
E7	1.5°	0.4°	2.6°	5.0°	3.9°
MLC-6628	1.0°	0.3°	2.6°	4.2°	3.3°

tion and steric hindrance caused by  $-\text{C}(\text{CF}_3)_2-$  groups, and greater gas permeability than non-fluorinated ones.<sup>24,25</sup> LCs may be considered as kind of a (poor) organic solvent. It thus appears that LCs can more easily diffuse into or swell fluorinated PIs, which may result in more deterioration of the rubbing-induced orientation of the PI. In the case of PI2, its relatively low degree of imidization could accelerate this action.

The pretilt angle, defined as the angle between the LC director and the AL surface plane, prevents generation of disclinations and also affects the EO characteristics of LCDs.<sup>1,26,27</sup> Thus, for defect-free LC alignment and desired LCD performances, an appropriate pretilt is required. Table V shows the pretilt angles of E7 and MLC-6628 for PIs cured at 250°C/1 hr. PI3 and PI4, having the relatively flexible structure, and PI5 with the long branch induced a relatively high pretilt angle. For a LC molecule with a polar terminal like cyano group, it appears that the cyano terminal anchors on the PI surface and the other terminal heads for the LC bulk with a tilt angle from the surface plane. The tilt angle is expected to become higher when there exists the steric hindrance (or effect) to prevent the terminal stretching out into the LC bulk from lying down toward the PI surface. This steric effect can be caused by a bulky group (here,  $-\text{C}(\text{CH}_3)_2-$  or  $-\text{C}(\text{CF}_3)_2-$ ) or a (long) side chain. It seems to be a major factor to induce the higher pretilt angles for PI3-PI5, compared with PI1. Especially, PI4 induced the higher pretilt angle than PI3, which resulted from trifluoromethyl moieties. Introduction of trifluoromethyl moieties decreases the surface energy of the AL and increases the contact angles of LCs (refer to Table III); the static contact angles of both E7 and MLC-6628 for PI4 and PI3 are greater than 35°, while the angles for PI3 are smaller than 5°. It indicates that LC molecules anchor more tilted up from the surface of PI4 and consequently the higher pretilt angle is generated. This result is in accordance with the previous other works<sup>9-11</sup> suggesting that the pretilt angle increases as the surface energy of the AL decreases. However, the contrary result was observed for PI2; despite of existence of trifluoromethyl moieties, the smaller pretilt angle was induced. This is due to the poor stability of PI2 to LCs as discussed previously. The poor stability causes severe destruction of the rubbing-induced orientation of the AL and subsequently decrease in the alignment uniformity, which leads to generation of a small pretilt angle. It turned out in the literature<sup>11,28,29</sup> that the pretilt angle decreases as the alignment uniformity (or the LC order parameter) reduces.

**Electro-optical Properties of LC Cell.** The V-T characteristics, including the CR and the  $V_{th}$ , and the VHR were measured for all PIs to investigate the effect of the AL structure on the EO properties of the LC cells. The V-T characteristic curve of a 90°-TN cell was obtained in a NW mode, taking the transmittance at 0 V, i.e. in field-off state as 100% as a normalization. Figure 3 shows that the V-T curves for E7 are rather steeper than those for MLC-6628, which is due to a larger birefringence of E7, while the steepness is not affected much by the PI structure. The fluorinated PIs, PI2 and PI4 showed higher transmittance at high applied voltages for both LC materials, leading to lower CRs as shown in Table VI. The higher transmittance is the result of more leakage of light in the field-on state. It



**Figure 3.** The V-T characteristics of TN cells; (a) E7 cells and (b) MLC-6628 cells.

could be due to less uniformity of LC alignment in the AL surface region. On the other hand, the results in Figure 3 (or Table VII) and Table V show that the  $V_{th}$  relates to the pretilt angle; for both LCs, it tends to decrease as the pretilt increases.

The VHR is an important performance parameter of active matrix addressed LCDs. It is defined as the ratio of transient voltage (i.e. voltage remaining over the LC cell in a field-off period) to applied voltage in pulse driving. A high value of VHR is required for high-quality images. Table VIII shows the values of VHR for empty and LC-filled cells. The VHRs of all empty cells were estimated as about 99.65%.<sup>30</sup> This high value of VHR and no difference between PIs indicate that there is no effect of the AL bulk itself on VHR. On the other hand, the VHR of LC cells showed diverse values depending on PI, LC and temperature. The fluorinated LC, MLC-6628 gave a higher value of VHR than the cyano LC, E7; it is known that a fluorinated LC has higher resistivity<sup>31</sup> and thus produces higher VHR.<sup>14,32</sup> The VHR of LC cells remarkably decreased at an elevated temperature. As temperature increases, the mobility of ion impurities in LCs increases while the resistivity of LCs decreases, which deteriorates the voltage holding characteristic. Table VIII also shows the dependence of the VHR on the chemical structure of PI ALs; the fluorinated PIs, PI2 and PI4 gave a lower VHR while the alkylated PI5 showed a higher one than PI1. That the VHR depends on the PI chemistry but not on the PI bulk suggests that the voltage holding characteristics are determined by interactions of LCs with PI molecules as well as intrinsic properties of the LC material.

**Table VI. Contrast Ratios of TN Cells**

	PI1	PI2	PI3	PI4	PI5
E7	156	54	345	60	337
MLC-6628	475	343	548	407	481

**Table VII. Threshold Voltages of TN Cells**

	PI1	PI2	PI3	PI4	PI5
E7	1.567V	1.563V	1.528V	1.525V	1.519V
MLC-6628	1.223V	1.292V	1.179V	1.219V	1.172V

**Table VIII. Voltage Holding Ratios of TN Cells**

	Empty cell at 20°C	E7 cell		MLC-6628 cell	
		at 20°C	at 50°C	at 20°C	at 60°C
PI1	99.64%	64.74%	31.75%	82.81%	64.37%
PI2	99.63%	44.05%	17.67%	76.76%	53.48%
PI3	99.62%	66.49%	36.60%	90.09%	70.13%
PI4	99.64%	56.29%	26.94%	79.24%	59.71%
PI5	99.66%	66.36%	32.89%	95.55%	88.38%

## Conclusions

Introduction of functionalities, such as fluorination and flexibility, into the PI structure not only changes its chemical features but greatly affects the characteristics of LC alignment and the EO properties of LC cells. The increased flexibility in the structure of the PI precursor spurs the imidization at low temperatures, while the imidization is relatively less progressed for the rigid, fluorinated structure. Both the fluorination and the more flexibility lower the PI's surface energy and thus affect the anchoring of LCs to the PI surface. The rigid, fluorinated PI induces the LC alignment with lack of stability/uniformity. It seems to be due to severe destruction of the rubbing-induced orientation of the PI surface by the contacting LCs, i.e. the PI's poor stability for LCs, which is also responsible for generation of a small LC pretilt angle. On the other hand, the increased flexibility increases the pretilt angle (by the steric hindrance and the reduced surface energy), and thus tends to improve the alignment stability. Evaluation of the cell's EO properties shows that the fluorination induces the inferior V-T characteristics and the lower VHR, while the more flexibility improves these properties. The alignment characteristics and the EO properties have shown the qualitatively similar trends for the PI structure (functionality), indicating that the short-ranged interactions between LC and PI molecules determine the alignment characteristics and also influence the EO properties.

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- (19) In actual TFT-LCD fabrication, the PI precursor is cured in air at a temperature lower than 230 °C, to protect the color filter components from thermal degradation, and thus 100% imidization is not achieved; such a curing gives, in general, about 90% imidization. To imidize a typical poly(amic acid) fully, the curing is normally conducted under N<sub>2</sub> at a temperature higher than 300 °C. However, this curing condition is not practical in the actual LCD process. Since one of aims this work pursues is to relate/apply the results in this work to the actual LCD process, the fixed curing condition, rather than the condition giving 100% imidization, was employed in this work and the different degree of imidization itself was considered as one of PI's characteristics. The different imidization characteristics could thus affect the properties of the LC cell as well as the surface energy/polarity of the AL.
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