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## Dipping and Photo-Induced Liquid Crystal Alignments Using Silane Surfactants

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Dipping and photo-induced liquid crystal (LC) alignments were demonstrated using new silanes as surface coupling agents. In the dipping method, both homogeneous and homeotropic alignments can be achieved depending on the alkyl chain length of the silane employed. The 110°C post curing temperature makes the dipping method especially attractive for low temperature processing of active matrix displays. In the UV-induced LC alignment, homogeneous cells are obtained and the LC directors are perpendicular to the impinging UV polarization. The pretilt angle of both methods is found to be  $\sim 0.5^\circ$ .

KEYWORDS: liquid crystal display, dipping, photo-alignment, silane surfactants

### 1. Introduction

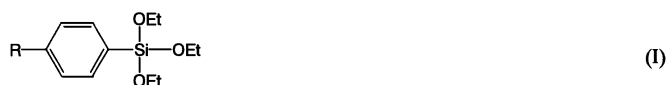
Unidirectional buffing of spin-coated polyimide (PI) film produces sufficient anchoring energy for aligning nematic liquid crystals.<sup>1)</sup> This process is so simple that it has been commonly utilized for fabricating large-sized liquid crystal display (LCD) panels. However, three problems are encountered: 1. The mechanical rubbing process may damage, contaminate or cause static charges to the thin-film-transistors (TFTs). As a result, the production yield is reduced. 2. The post-curing temperature of a commercial-grade PI is around 200–300°C. This curing temperature is too high for some displays, such as low-temperature poly-silicon TFT-LCD.<sup>2)</sup> 3. The thickness of a spin-coated PI layer over a large substrate may not be sufficiently uniform. The different PI thickness could result in non-uniform voltage drop across the film. There is urgent need to develop low temperature and non-rubbing alignment process for LCD industry.

The dipping-induced alignment using various surfactants has been studied extensively.<sup>3–6)</sup> Kahn<sup>4)</sup> demonstrated that trialkoxy-silanes can self-assemble to glass, indium tin oxide (ITO), CdS, CdZnS and Al surfaces and produce LC alignment. Two other well-known surfactants are: DMOAP (N,N-Dimethyl-N-Octadecyl-3-Aminopropyl trimethoxy silyl chloride) for homeotropic and MAP (N-Methyl-3-Aminopropyl-trimethoxysilane) for homogeneous alignment. A major problem of such dipping-induced LC alignment is thermal stability. As the temperature increases, the pretilt angle also increases significantly. Since the electro-optic behavior of a LCD is strongly dependent on the pretilt angle, practical application of such dipping-induced alignment is therefore limited.

In this paper, we report on the dipping and photo-induced alignment methods for aligning LC molecules. The curing temperature of the dipping method is as low as 110°C. It is attractive for low temperature TFT-LCD applications. Our new silane surfactants can produce homeotropic or homogeneous alignment by simply varying the alkyl chain length. A further step was taken to modify these silanes to be suitable for UV-induced LC alignment.

### 2. Dipping-Induced Alignment

The molecular structures of the trialkoxy-silane compounds we synthesized for dipping-induced LC alignment are shown below:



Here, R can be an alkyl ( $C_nH_{2n+1}$ ) or an alkoxy ( $OC_nH_{2n+1}$ ) group, and Et is the ethyl ( $C_2H_5$ ) group. We have prepared seven silane compounds with  $R=H$ ,  $C_5H_{11}$ ,  $C_7H_{15}$ ,  $C_{10}H_{21}$ ,  $OC_7H_{15}$ ,  $OC_{10}H_{21}$ , and  $OC_{10}H_{21}$  in the meta position. Since trialkoxy-silanes are sensitive to moistures, all the reactions involved were performed under dry nitrogen environment.

These trialkoxy-silane compounds do not adsorb to glass directly. Thus, we dissolved 0.5% of each surfactant in the ethanol and water solution. We then dipped the glass substrate in the solution and stirred it with ultrasound. Due to the energy transfer, the trialkoxy is converted to a more energetic triol group and then adsorbed to the immersed ITO-glass substrate through either hydrogen or oxane bonding.<sup>7)</sup> Afterwards, the glass substrate was baked at 110°C for one hour to form polysiloxane film. These polysiloxane monolayers are cross-linked on the ITO-glass surface, as illustrated in Fig. 1. Using an ellipsometer, we measured the  $OC_{10}H_{21}$  polysiloxane ( $OC_{10}PSi$ ) mono-layer thickness to be 2.012 nm. This is close to the computer-simulated result of 1.724 nm.

In experiment, we prepared LC cells using these polysiloxane films as alignment layers. We first compared the electro-

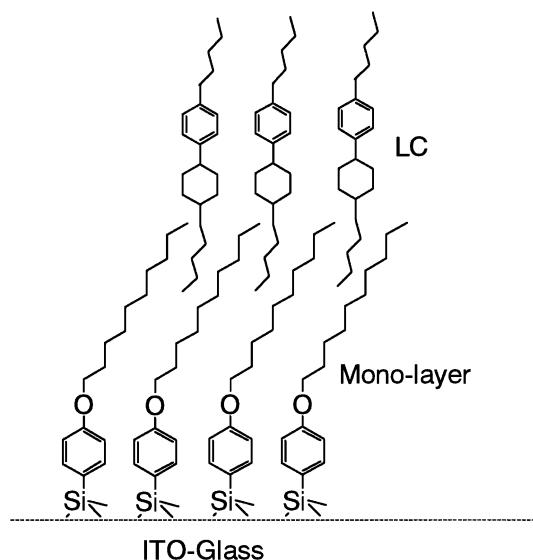


Fig. 1. Schematic illustration of monolayer para  $OC_{10}PSi$  induced LC alignment.

optic behaviors of rubbed and non-rubbed substrates using OC<sub>10</sub>PSi as surfactant. For the rubbed cell, the buffing direction on each substrate is anti-parallel. Both cells were then filled with Merck ZLI-2806 LC mixture ( $\Delta\epsilon = -4.8$ ,  $\Delta n = 0.043$  and clearing point  $T_c = 100.5^\circ\text{C}$ ). Although the non-buffed cell exhibits a reasonably good dark state between crossed polarizers, its voltage-on state transmission varies by  $\sim 10\%$  across the cell aperture and disclination lines appear. This implies that the non-rubbed cell lacks pretilt angle. On the other hand, the rubbed cell shows a uniform domain. Thus, in the dipping method buffing is still needed in order to generate uniform domain.

The alignment quality is strongly affected by the solution used. For each silane surfactant, we tried 4-5 solutions as listed in Table I. For example, if we dissolve the C<sub>10</sub> phenyl trialkoxy-silane compound (C<sub>10</sub>PSi) in a pure ethanol (sample A1) or pure water (A5), homeotropic alignment with good dark state is observed. However, when the applied voltage exceeds the threshold, disclination lines appear indicating that the LC directors are not pre-tilted to the same direction. If we mixed the ethanol with water at 9 : 1 ratio, sample A3 shows an excellent homeotropic alignment without disclination lines. Similar results are found in sample E2.

From Table I, the short-chain phenyl trialkoxy-silane (D1

and D2) produces homogeneous alignment. As the side chain length increases (both alkyl and alkoxy), a homeotropic alignment is obtained. A longer chain results in a better homeotropic alignment. This phenomenon is similar to the tilted perpendicular cells using evaporated long chain alcohol on SiO<sub>2</sub> surface.<sup>8)</sup>

To examine the thermal stability of the induced LC alignment, we used the E2 cell (Table I) and filled with Merck ZLI-2806 mixture. The cell gap was controlled at  $d \sim 9\ \mu\text{m}$  so that the total phase retardation is about  $\delta = 1.2\pi$  at  $\lambda = 633\ \text{nm}$ . The cell was heated at  $T = 50, 100$  and  $140^\circ\text{C}$  for 20 min, respectively, and cooled down to room temperature ( $T = 25^\circ\text{C}$ ) for measuring the voltage-dependent light transmittance. Results are shown in Fig. 2. From Fig. 2, the data at  $T = 140, 100, 50^\circ\text{C}$  overlap closely with those at  $T = 25^\circ\text{C}$ . This indicates that the OC<sub>10</sub>PSi coupling agent has a superb thermal stability.

The pretilt angle of the E2 cell was measured by the crystal rotation method<sup>9)</sup> (Autronic DMS-101) to be  $\sim 0.5^\circ$  tilted from surface normal. Such a small pretilt angle maybe attributed to the relatively linear OC<sub>10</sub>PSi structure. To enlarge the pretilt angle, we purposely synthesized the alkoxy chain at the meta position (mOC<sub>10</sub>PSi). Through this chemical structure change, we anticipated to get a larger pretilt angle. To

Table I. The LC alignments of various silane compounds in solution. In the quality column,  $\otimes$  = excellent alignment, O = uniform alignment but has disclination lines when activated,  $\Delta$  = poor alignment, and X = no alignment.

Compound	LC Cell	Solution (EtOH:H <sub>2</sub> O)	Quality	Alignment
C <sub>10</sub> PSi	A1	100 : 0	O	Homeotropic
	A2	95 : 5	$\otimes$	Homeotropic
	A3	90 : 10	$\otimes$	Homeotropic
	A4	80 : 20	O	Homeotropic
	A5	0 : 100	O	Homeotropic
C <sub>7</sub> PSi	B1	100 : 0	X	—
	B2	90 : 10	O	Homeotropic
	B3	80 : 20	O	Homeotropic
	B4	0 : 100	O	Homeotropic
C <sub>5</sub> PSi	C1	100 : 0	$\Delta$	Homeotropic
	C2	90 : 10	$\Delta$	Homeotropic
	C3	80 : 20	$\Delta$	Homeotropic
	C4	0 : 100	X	—
PSi	D1	100 : 0	O	Homogeneous
	D2	90 : 10	O	Homogeneous
	D3	80 : 20	X	—
	D4	0 : 100	X	—
OC <sub>10</sub> PSi	E1	100 : 0	O	Homeotropic
	E2	90 : 10	$\otimes$	Homeotropic
	E3	80 : 20	O	Homeotropic
	E4	0 : 100	O	Homeotropic
OC <sub>7</sub> PSi	F1	100 : 0	X	—
	F2	90 : 10	X	—
	F3	80 : 20	X	—
	F4	0 : 100	X	—
mOC <sub>10</sub> PSi	G1	100 : 0	$\Delta$	Amorphous
	G2	90 : 10	$\Delta$	Amorphous
	G3	80 : 20	$\Delta$	Amorphous
	G4	0 : 100	X	—

our surprise, this meta silane does not produce a single domain, as indicated in the bottom row of Table I. A possible explanation is that the tails of the meta silanes are not pointing to the same direction, as illustrated in Fig. 3. During post curing, the polymerization process could simultaneously take place everywhere on the substrate surface. Thus, some silane molecules may be oriented at different direction so that the amorphous domains are formed. Amorphous domains<sup>10)</sup> are helpful in widening the viewing angle, but the domain-induced light scattering would degrade the image contrast ratio and brightness. In principle, some amorphous domains should also be present in the para-silanes (E2 cell) shown in Fig. 1. However, the para-silane molecules are more closely packed and the inter-molecular spacing is much shorter. If it would form amorphous domains, the domain sizes could remain tiny so that their impact to alignment is not too noticeable.

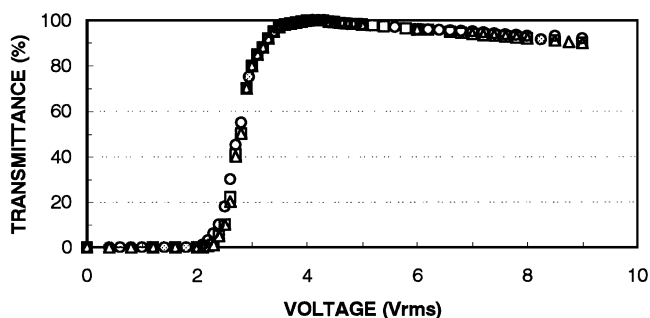


Fig. 2. The voltage-dependent light transmittance of a homeotropic LC cell. LC=ZLI-2806,  $d \sim 9 \mu\text{m}$ , alignment surfactant is  $\text{OC}_{10}\text{PSi}$  and  $\lambda = 633 \text{ nm}$ . The data for  $T = 25, 50, 100$  and  $140^\circ\text{C}$  are represented by dots, squares, triangles, and open circles, respectively.

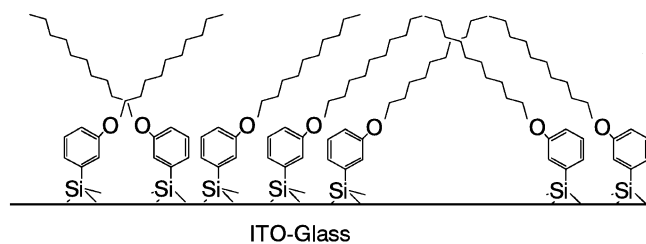
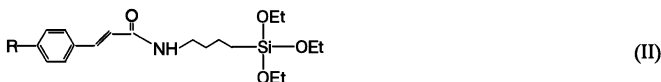


Fig. 3. Schematic illustration of monolayer meta  $\text{OC}_{10}\text{PSi}$  induced amorphous domains.

### 3. Photo-Induced Alignment

Another non-rubbing method we tried is photo-induced LC alignment. We modified the silane compound (structure I) by adding a photo-sensitive amide group as shown below:



Two compounds with  $\text{R}=\text{H}$  and  $\text{OC}_{10}\text{H}_{21}$  were synthesized.<sup>7)</sup> For simplicity, they are abbreviated as  $\text{PCiSi}$  and  $\text{OC}_{10}\text{PCiSi}$ . To make a LC cell, the ITO glass was dipped in the 9 : 1 ethanol/water solution stirred with ultrasound. The substrate was then exposed to a linearly polarized UV light (Rayonet Model RPR-100;  $\lambda \sim 350 \text{ nm}$ ). The output intensity after passing through a polarizer is  $0.27 \text{ mW/cm}^2$ . A  $5\text{-}\mu\text{m}$  ZLI-4792 ( $\Delta\epsilon = +5.2$ ,  $\Delta n = 0.097$ ) LC cell was prepared for measurements.

To characterize the alignment quality under different UV fluence, we measured the polar angle dependent light transmittance ( $T_{\perp}$ ) of the cell at  $\lambda = 633 \text{ nm}$  through crossed polarizers. Table II shows the measured  $T_{\perp}$  at eight UV exposure levels. Without UV irradiation,  $T_{\perp}$  does not vary too noticeably as the cell rotates. This indicates that the cell has no preferred alignment direction. As the UV fluence reaches  $1 \text{ J/cm}^2$ , an alternating bright ( $T_{\text{max}}$ ) and dark ( $T_{\text{min}}$ ) state appears and the  $T_{\text{max}}/T_{\text{min}}$  ratio exceeds 300 : 1. This is an evidence of a good homogeneous cell.<sup>11)</sup> As the UV fluence further increases, the  $T_{\text{max}}/T_{\text{min}}$  ratio gradually decreases. At  $12 \text{ J/cm}^2$ , decomposition on the  $\text{OC}_{10}\text{PCiSi}$  layer could have occurred and a poor alignment results.

We also performed the same measurements using  $\text{PCiSi}$  as photo-alignment agent. Similar results as shown in Table II were obtained. However, the alignment quality of this short chain silane is inferior to that of the long chain  $\text{OC}_{10}\text{PCiSi}$ .

To inspect the alignment direction induced by the UV exposure, we doped 1% of a dichroic azobenzene dye ( $\lambda_{\text{max}} = 417 \text{ nm}$ ) to ZLI-4792. The major absorption axis of the dye molecules was found to be orthogonal to the polarization of the incoming UV light. Thus, the LC alignment direction is perpendicular to the electric field of the linearly polarized UV light.

Pretilt angle is a critical issue for photo-alignment cells.<sup>12-14)</sup> The LC cells we used for measurements shown in Table II have too small pretilt angle. Thus, disclination lines occur in the  $V > V_{\text{th}}$  regime. Methods for controlling LC alignment by photo-reaction of monolayers have been demon-

Table II. The polar angle dependent light transmittance of LC cells under different UV exposures. Alignment agent:  $\text{OC}_{10}\text{PCiSi}$ , LC = ZLI-4792,  $\lambda = 633 \text{ nm}$ .

Cell	UV Exposure ( $\text{J/cm}^2$ )	$T_{\perp}$ (%)							
		$0^\circ$	$45^\circ$	$90^\circ$	$135^\circ$	$180^\circ$	$225^\circ$	$270^\circ$	$315^\circ$
P1	0	33	70	56	60	60	50	50	69
P2	0.015	5	43	11	46	12	43	4	43
P3	0.08	1.5	58	1.1	50	1.5	58	1	63
P4	0.5	0.7	70	0.6	70	0.6	70	0.7	70
P5	1	0.2	77	0.3	77	0.2	77	0.3	77
P6	1.5	0.5	58	0.6	58	0.4	58	0.5	58
P7	6	0.5	58	0.6	58	0.5	58	0.5	50
P8	12	44	80	88	80	72	80	57	88

strated by Ichimura *et al.* a decade ago.<sup>15)</sup> Here, we used the second exposure method<sup>16)</sup> for enhancing the pretilt angle. At the second exposure, the cell was inclined at 45° with respect to the axis of the employed UV polarizer. At 0.15 J/cm<sup>2</sup> of UV fluence, the measured pretilt angle is ~0.5° and disclination lines disappear. Further increase in UV exposure results in degraded image contrast ratio of the LC cell.

#### 4. Conclusion

We have developed several new silane compounds for dipping and photo-induced LC alignments. In the dipping-induced molecular self-assembly method, homogeneous or homeotropic alignment can be obtained depending on the alkyl chain length of the silane employed. Since the post curing temperature is only 110°C, useful applications for low temperature TFT-LCDs are foreseeable. In the UV-induced LC alignment, so far only homogeneous cells were obtained. The LC alignment direction is perpendicular to the impinging UV polarization. Both alignment methods produce about 0.5° pretilt angle.

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