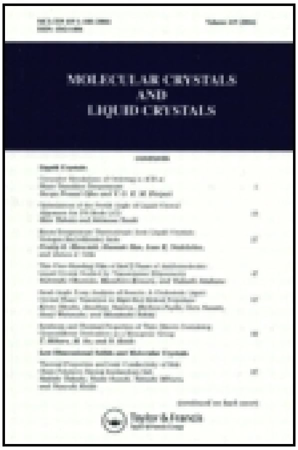

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Planar Orientation of Nematic Liquid Crystals by Chemisorbed Polyvinyl Alcohol Surface Layers

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Planar Orientation of Nematic Liquid Crystals by Chemisorbed Polyvinyl Alcohol Surface Layers

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Boundary surface films of monomolecular thickness of polyvinyl alcohol PVA deposited in a specific way onto transparent ITO or TAO electrodes induced parallel alignment of most available nematic liquid crystals having positive dielectric anisotropy. Chemisorption of PVA is improved by a previous ethyl silicate immersion bath. Stable surface layers are obtained by condensation reaction during curing at 180°C. Further, parallel orientation is achieved mechanically by unidirectional buffing of the PVA film. By changing the duration of solution adsorption, one can vary the tilt angle. From concentration measurements of PVA on ITO surfaces by means of a C^{14} marker technique it has been found that the molecules of PVA are lying not flat on the surface; those segments of the polymer chain which are not directly attached to the surface form loops. These polymer loops become asymmetric after buffing and curing and thus generate tilted profiles in the adjacent liquid crystal layer. The influence of these various treatments on the static and transient optical transmission characteristics of two particular liquid crystal mixtures is discussed. The change in sharpness of transition is correlatable to the anchoring characteristics of the PVA film through chemical interactions, while the rise and decay characteristics are more related to the mechanical orientation of the surfactant film. These silica-PVA surfactant films are very convenient for the mass production of durable, large-area liquid crystal displays.

Paper presented at the Ninth International Liquid Crystal Conference, Bangalore (India) December 9, 1982.

INTRODUCTION

The crucial demands in selecting a surfactant method of orientation of nematic liquid crystals for displays are reliability of perfect orientation, simplicity of application, low cost, extended life time, utility of producing large-area panels, and compatibility with the cell sealing technique. In our on-going efforts to develop multi-element thin-film-transistor-matrix-addressed twisted-nematic liquid crystal (TFT-TNLC) display panels,[1] we have evolved a method of LC orientation which satisfies the above requests[2] in every respect. The procedure involves the generation of boundary layers of PVA on the transparent indium-tin oxide (ITO) or tin-antimony oxide (TAO) electrodes on glass,[3] which, in turn, induce parallel, tilted molecular alignment in most of the commercially available nematic liquid crystal mixtures with positive dielectric anisotropy. Moreover, our method is also applicable to guest-host LC panels, for instance of the Heilmeier type. It is possible that the method is already in use elsewhere,[4] but to date, we are not aware of any publication enumerating the actual methodology and the probable mechanism.

The alignment of nematics in contact with solid substrates is influenced by chemical as well as mechanical interactions. The practically used orientation methods — exhaustively elucidated in no case — may involve both effects. Chemically adsorbed films of a large number of surface-active agents (surfactants) induce parallel alignment of the liquid crystal molecules. The classical method of directional rubbing a glass plate with a cotton swab is probably due to a directionally adsorbed film of fatty contaminants (Zocher, Chatelein[5,6]). Haller[7] as well as Proust *et al.*[8] obtained parallel LC alignment with monolayers of hexadecyl trimethyl ammonium bromide (HMAB). Kahn and co-workers[9,10] used organosilanes, $RSi(OCH_3)_3$, containing hydrolysable groups and organofunctional orientating groups (R) where R contains short carbon chains. With N-methyl-3 amino propyl trimethoxy silane (MAP), Kahn[10] obtained parallel alignment of mesomorphic molecules.

Surface coupling and polymerization during curing have been proposed to yield a two-dimensional cross-linked network of organosilanes.

Matsumoto *et al.*[11] employed a dicarboxylato chromium complex for planar alignment of nematics although this was not universally effective for various nematic liquid crystals.

In principle, planar LC alignment using chemical methods can be achieved using surfactants with two polarizable heads and also when the surface density of adsorbed molecules on the electrode is low.[7,8]

Nevertheless, a nondeteriorating parallel alignment is generally not easily achieved by purely chemical methods so that rubbing of the substrate after deposition of the surface-active agent, or of the surface before deposition, is required (mechanical action). The vacuum-deposition of thin solid films under oblique incidence (*e.g.* SiO_x) whereby a micro-landscape of directionally oriented hillocks is formed[12] yields planar directional LC alignment involving purely physical methods.

In most of the reports, the significance of the individual steps is largely unspecified such that these methods have little reliability, but systematic experiments on rubbed surfaces in a controlled way have shown that chemical and physical mechanisms play competitive roles in planar alignment.[13,14]

It must be mentioned that the surfactants quoted above are expensive complex chemicals often involving difficult synthesis steps; besides, they are often sensitive to minor comtaminants. Many of them are incompatible to most of the cell sealing techniques which involve curing at elevated temperature.

Obliquely deposited SiO_x films for purely physical LC orientation are cumbersome to produce.

In these aspects, our silica-PVA orientation layers described below have a decided edge over all the reported methods.

EXPERIMENTAL

All the chemicals used were of British Drug House (BDH), Hoffmann-LaRoche, E. Merck, or American Liquid Crystal Co. The transparent electrodes employed were mostly NESATRON glass from PPG Co., Pittsburgh. ITO and TAO electrodes were also prepared by ourselves by sputtering. For the electro optical measurements, a polarizing microscope (Leitz Orthoplan-Pol) equipped with a photodetection system was used.

WAVETEC square wave or sine wave generators where the amplitude could be varied at fixed frequencies, or vice versa, supplied the driving voltages. Static optical transmission of the cells was plotted using an X-Y recorder, while the dynamic transmission was monitored with a TECTRONICS storage oscilloscope. The details of the C^{14} marker technique to determine the concentration of adsorbed PVA molecules by means of Langmuir isotherms will be published elsewhere. For the tilt angle measurements, a Varian magnet was used.

RESULTS AND DISCUSSION

Orientation

In our early experiments, the thoroughly cleaned NESATRON glass substrates were first dipped into very dilute aqueous silica-sol for a short while and then dried by blowing with filtered compressed air. Then these plates were dipped into dilute PVA solution for a specified time, dried at 120°C, and the surface was then unidirectionally rubbed with a cotton swab.

In our later unified method, one solution of the following composition is used: 0.02% PVA and 0.01% ethyl silicate, originally diluted in ethyl acetate, in deionized water. Ethyl silicate can be substituted by any of the commercially available immersion baths used to produce silicon dioxide coatings (*e.g.* No. 11 675 from E. Merck). The pH of the solution must be adjusted to ~4 with hydrochloric acid. The glass plates are typically kept in the solution for 1 h, blown with air to remove excess solution after withdrawing from the bath, and dried at 120°C for 20 min. Subsequently, the adsorbed PVA layer is mechanically treated with a motor-driven cylinder coated with a velvet made either of long-fiber cotton, or a ARAMIDE (supplied by Dr. Fergason, Internat. Liquid Xtal Co). The pressure of the buffing is maintained by keeping a controlled gap between the glass plate and the rotating cylindrical wheel. The number of buffing passes has an influence (see below). The buffed glass plates are further maintained at 180°C for 15 min for the final curing. Perfected alignment of nematic liquid crystals is observed when placed between two such treated glass plates with opposite buffing direction. The filling technique, and the novel spacers used, are described in Ref. 2.

TN LCs can be prepared when the glass plates are twisted 90° to each other with respect to the direction of the buffing, provided the LC mixture contains a trace of a chiralic compound to introduce a uniform direction of twist. Otherwise, the twist of the plates has to be slightly less than 90°, with some loss of optical contrast. Perfect orientation was observed when the plates were separated by spacers from 6 μm to 50 μm thick, over areas sized 90 × 120 mm. The oriented PVA surfactant film was stable up to 220°C, thus adequately compatible with the thermoplastic silk-screenable cell sealing pastes commercially available.

As proposed earlier[2] the sequence of the reactions taking place in the surfactant film is given in Figure 1. The chemisorbed silica molecules (possibly in the form of islands) adsorb PVA molecules which get anchored through hydrogen bonding. Mechanical orientation of the PVA chains takes place during the buffing step. The silica-PVA bonds undergo a condensation reaction during drying and curing at 120°C and 180°C respectively.

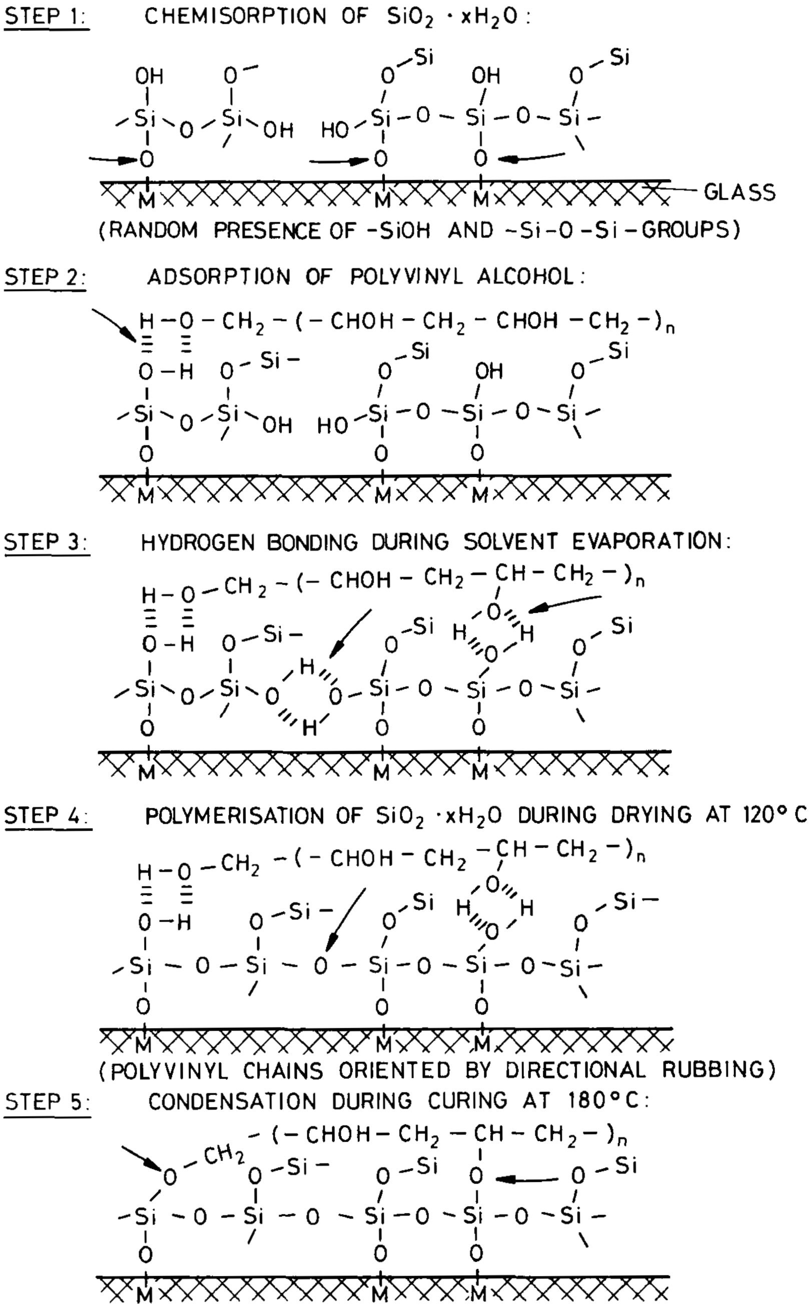


FIGURE 1 Possible sequence of reactions in the chemisorbed film.

In order to achieve uniform tilt over the entire area without having to remember the sign of the unidirectional buffing for both plates for proper assembly, the two electrodes of a cell have to be treated differently. One of the electrodes is dipped for 1 h into the dilute silica bath and dried. It is then immersed into the PVA solution for 5 min. This will give the plate increased tilt. The other electrode is treated as described above.

The PVA method works well on electrodes with oxidic surfaces, but it fails on metallic surfaces such as the transparent metal electrodes which are also present on our thin-film transistor matrix display electrode.[1] However, when the entire matrix electrode is covered with an evaporated oxide layer (*e.g.* 100 Å alumino-silicate[1]), the PVA surfactant layer is found to be uniform.

Chemical nature and stereoregularity of PVA

In order to understand the molecular mechanism of orientation, it is necessary to know the chemical nature of the PVA used in these experiments. PVA can have varying stereoregularity and bulk crystallinity and these factors are important in the orientation process. Since, strictly speaking, PVA is a copolymer of vinyl alcohol and vinyl acetate, the influence of the acetate groups has to be verified. This is due to the fact that PVA is prepared by hydrolysis of polyvinyl acetate. In the present experiments, PVA with different degrees of hydrolysis was used (99.8%, 99%, 97.5%, and 96%). The analytical tests were carried out according to the methods given by Finch.[15] The presence of carbonyl groups is indicated from the infrared absorption band around 1710 cm^{-1} (Figure 2). The best orientation results are obtained with PVA hydrolyzed 99%, indicating that some amount of polyvinyl acetate is desirable. Considering PVA as a random copolymer of polyvinyl-alcohol (X), and polyvinyl acetate (Y), the latter can have two functions: (i) effective interaction with the electrode and further anchoring of X, or (ii) Y may provide end terminal groups for the X-chains and hence prevent cross-linking of X on the electrode surface as well as with neighbors.

If the former reasoning is valid, the stability of the adsorbed layer should increase with increasing Y, i.e. with lower degree of hydrolysis. Since this is not true and the stability of the adsorbed layer has some sort of maximum with respect to the acetate content, the second explanation is probably more valid.

The stereoregularity of PVA has been tested by infrared abdorption and NMR spectra, following the method of Murahashi *et al.*[16] and Toyoshima.[17] There are three forms of stereoregularity for PVA (Figure 3). It has been found that the tacticity of PVA is not very critical for obtaining molecular

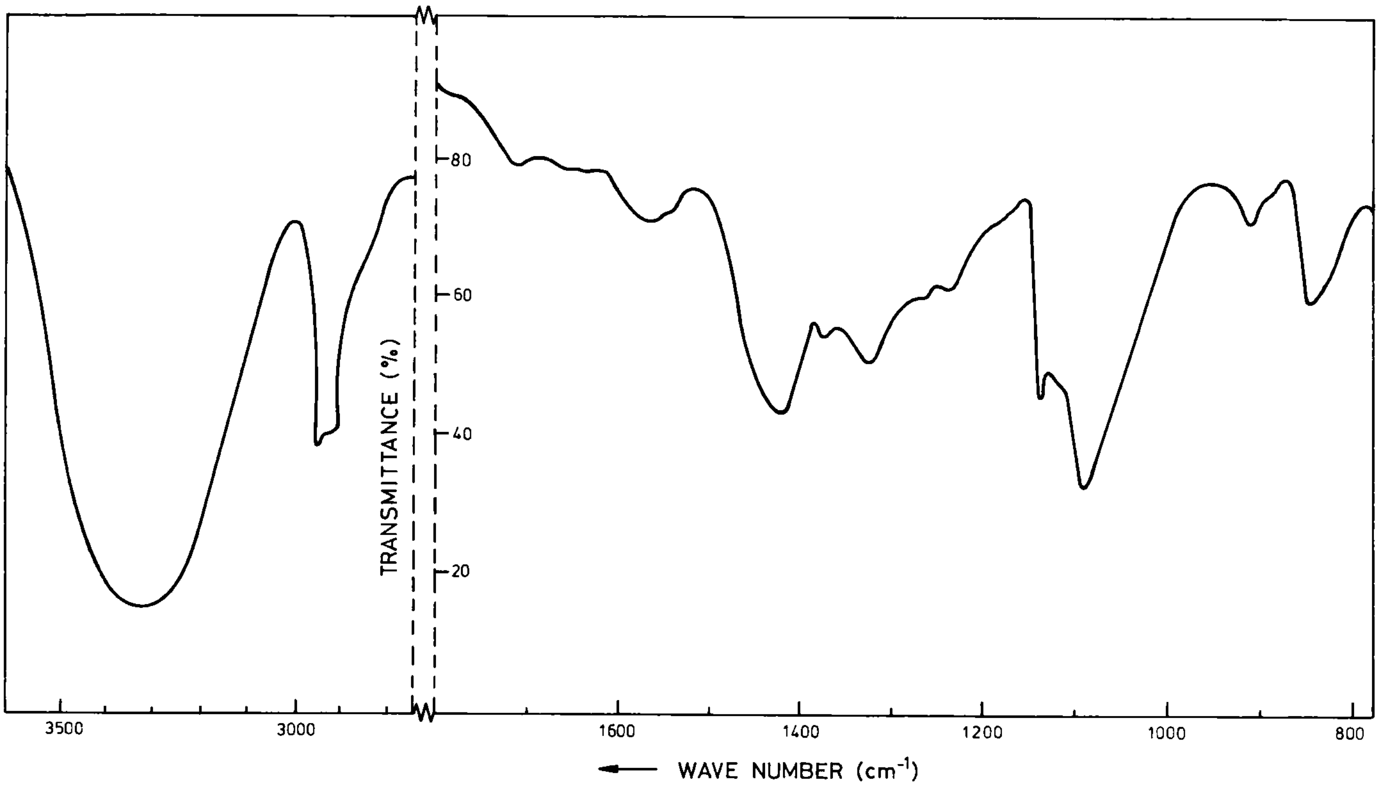
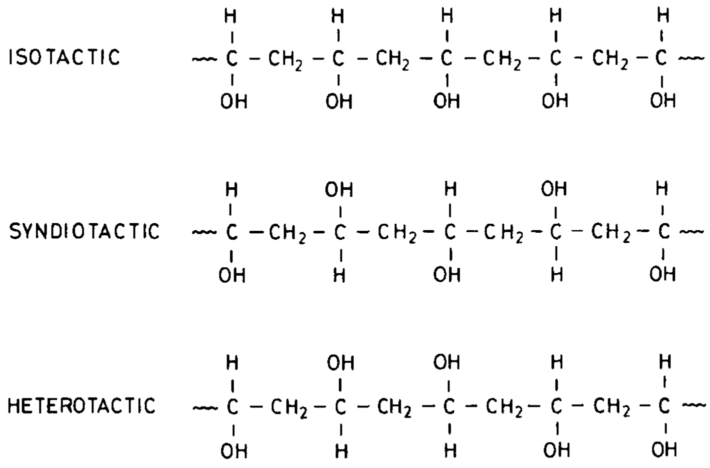


FIGURE 2 Infrared absorption spectrum of a PVA film (600 nm thick); 99% hydrolyzed; $\overline{m}_w$ (weight-average mol. wt.) 1.7 × 10^5.



ISOTACTIC $$-\underset{OH}{\overset{H}{C}}-CH_2-\underset{OH}{\overset{H}{C}}-CH_2-\underset{OH}{\overset{H}{C}}-CH_2-\underset{OH}{\overset{H}{C}}-CH_2-\underset{OH}{\overset{H}{C}}-$$

SYNDIOTACTIC $$-\underset{OH}{\overset{H}{C}}-CH_2-\underset{H}{\overset{OH}{C}}-CH_2-\underset{OH}{\overset{H}{C}}-CH_2-\underset{H}{\overset{OH}{C}}-CH_2-\underset{OH}{\overset{H}{C}}-$$

HETEROTACTIC $$-\underset{OH}{\overset{H}{C}}-CH_2-\underset{H}{\overset{OH}{C}}-CH_2-\underset{H}{\overset{OH}{C}}-CH_2-\underset{OH}{\overset{H}{C}}-CH_2-\underset{OH}{\overset{H}{C}}-$$

FIGURE 3 Tacticity of PVA.

orientation. 99% hydrolyzed PVA which showed the best results has the following percentages of tacticity, as per the infrared absorption D_{916}/D_{849} ratio: isotactic 25.8%, syndiotactic 32.3%, heterotactic 41.9%. NMR data (100 MHz in $CDCl_3$), with the dominant peak at $\tau = 8.00$, also indicate the dominance of the heterotactic form. Qualitative observations indicate that isotactic PVA leads to a less perfect orientation. The higher intensity of the infrared absorption band around 1146 cm^{-1} indicates higher crystallinity for the 99% hydrolyzed sample used, possibly owing to higher concentration of microcrystalline regions.

Effect of the silica immersion bath

From the quality of orientation of nematic LC cells made with the chemisorbed PVA film with or without the addition of ethyl silicate it has been shown that the latter has a tremendous influence for the adsorption of the PVA molecules to the electrode surface. The silica treatment builds up a hydrous oxide surface film containing hydroxyl groups, which in turn can exhibit amphoteric behavior dependning upon the pH of the solution:

$$\underset{\text{decreasing pH}}{\underleftarrow{M - OH_2^+}} \rightleftharpoons \underset{\text{neutral}}{M - OH} \rightleftharpoons \underset{\text{increasing pH}}{\underrightarrow{M - O^- + H^+}}$$

The significance of this equilibrium process is indicated from a study of the effect of pH on the stability of the adsorption layer. Better adsorption is observed as the pH is lowered. This is in agreement with the report of Tadros[18] that PVA adsorption on SiO_2 particles increases as one moves toward the isoelectronic point of silica (pH = 2.65), i.e. the pH for zero mobility of the oxide particles under an electric field which carries the counterions as the ions get displaced in the solution. However, the PVA adsorption on an electrode surface is more complicated since it involves not only polymer-surface interactions but also surface-solvent interactions. These are modified by the initially adsorbed hydrated silica as it provides OH groups to the oxide surface otherwise devoid of OH, by forming M—O—Si— bonds. Interaction of OH groups leads to stable PVA adsorption. The adsorbed PVA film may then block the surface from other diffusing species present in the solution.

Tilt angle measurements

Accurate tilt angle measurements were carried out by the magneto-capacitive method (Odawara *et al.*[19]). The LC cell is mounted on a turntable positioned between the magnetic poles and oriented in such a way that the center of the cell lies on the pole axis. A VARIAN electromagnet which gives a field up to 6 K Oe at 70 mm gap was used (Figure 4). Capacitance measurements were carried out with a Wayne-Kerr universal autobalance bridge. In the measurement range of 10 000 pF the measuring voltage was 55 mV. The cell thickness was 10 μm and the measured area 5 × 5 cm. The LC cell is turned around the axis perpendicular to the figure. The position is read accurate to 0.05°. As the magnetic field strength is scanned, the capacitance of the cell shows a variation as in Figure 5a. The field strength at which the deviation occurs varies with the angular position of

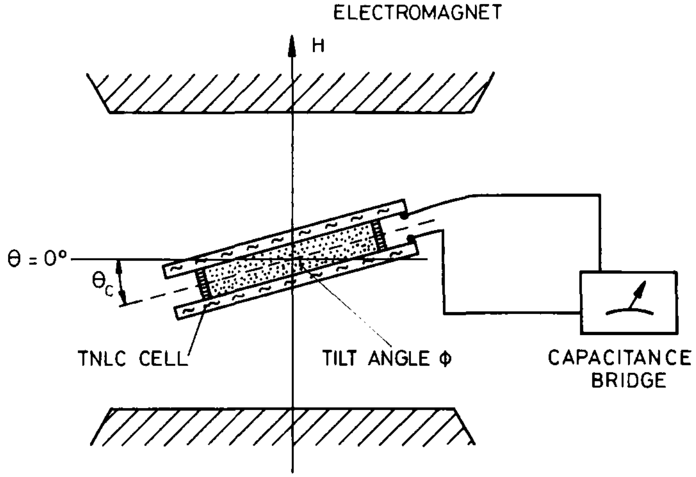
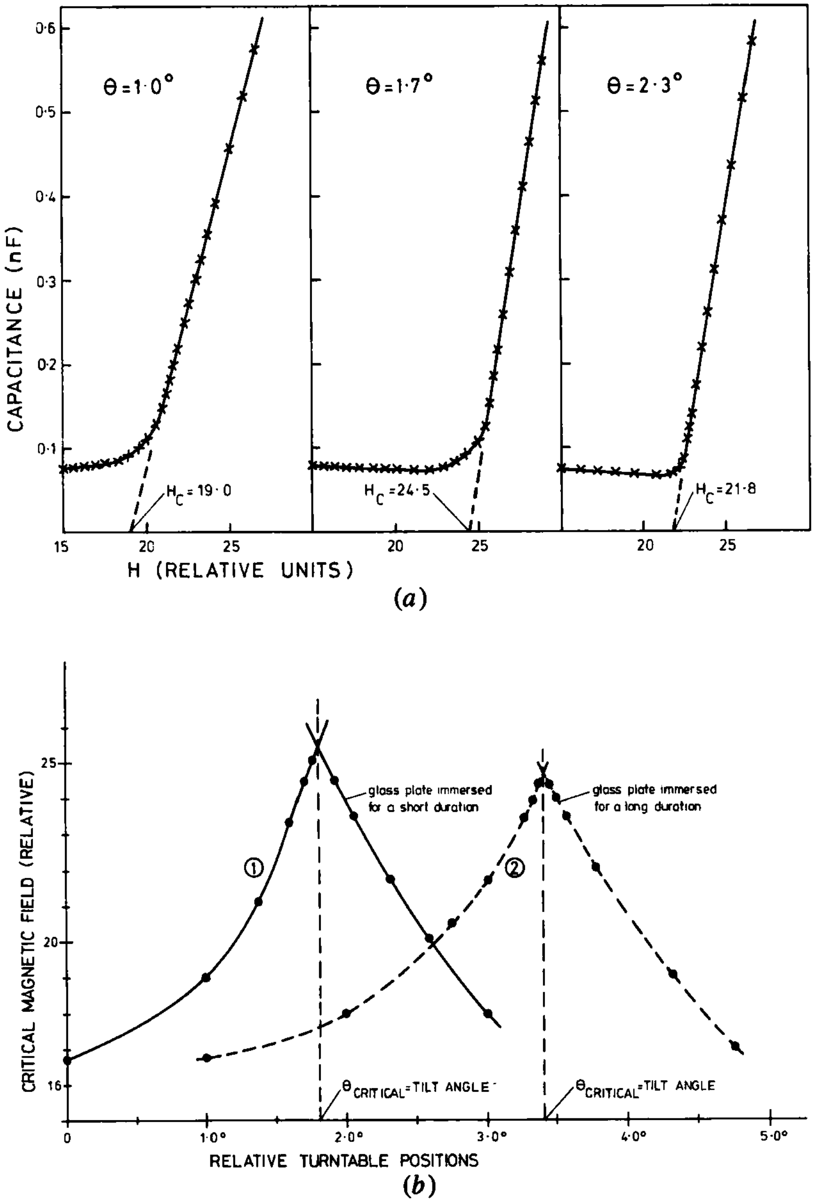


FIGURE 4 Experimental setup for measuring the tilt angle.



(*a*)

(*b*)

FIGURE 5 (a) Capacitance vs magnetic field; typical curves for three different turntable positions. (b) Threshold magnetic field vs turntable position for NESATRON glass plates treated for different duration. LC used is a mixture of cyanobiphenyls with aryl esters.

the cell. The threshold field (H_t) is obtained for various angles and yields a maximum (Figure 5b) called the critical threshold field H_c. The corresponding critical angle is the tilt angle of the liquid crystal molecules.

It was found that the tilt angle is variable with different modes of the PVA treatment. In Figure 5b, curve 1 shows a tilt angle of 1.8° for substrates treated with the SiO_2 immersion bath followed by immersion in the PVA layers, but not unidirectionally buffed, show a textured alignment (Figure 6a). With the mechanical treatment, the textured features change to are directionally buffed in the same way. The glass plates were treated before identically. Top and bottom plates are buffed in opposite directions. The difference in tilt angle can be explained on the basis of the film density of the chemisorbed PVA layer or on the basis of a difference in the molecular conformation of the adsorbed PVA polymer.

A choice between these two possibilities can be made only through the surface adsorption studies given in the next section.

Influence of chemical and mechanical forces

Nematic liquid crystals placed between glass plates carrying chemisorbed PVA layers, but not unidirectionally buffed, show a textured alignment (Figure 6a). With the mechanical treatment, the textured features change to more perfect planar alignment (Figure 6b). As the directional perfection is bettered by the buffing treatment, the domains with ϕ-type surface disclination[20] become smaller and finally vanish (Figure 6c). These observations indicate that mechanical orientation plays a definite role. If the PVA films are buffed after curing at 200°C, θ-type defects are present (Figure 6d). Since curing brings about a condensation reaction and rigid anchoring of the polymer chains, buffing cannot orient them any more.

The physicochemical interactions during nematic alignment are evident from the variation of tilt angle with different surface density of the adsorbed molecules or with differences in their molecular conformation. In order to get clarity, we have collected data on adsorption isotherms of PVA on ITO electrodes. The surface concentrations were measured using C^{14} marked PVA molecules. Details of Langmuir isotherms, and the conclusions drawn thereupon, will be published elsewhere. The results indicate that PVA chains are not adsorbed as a monolayer through end-on anchoring, nor are the molecules lying flat. The amount of PVA molecules adsorbed per unit area would correspond to ca. 3-molecular thickness if all the OH groups of PVA (one OH group per monomer segment) were attached to the surface. This would not be stable during buffing.

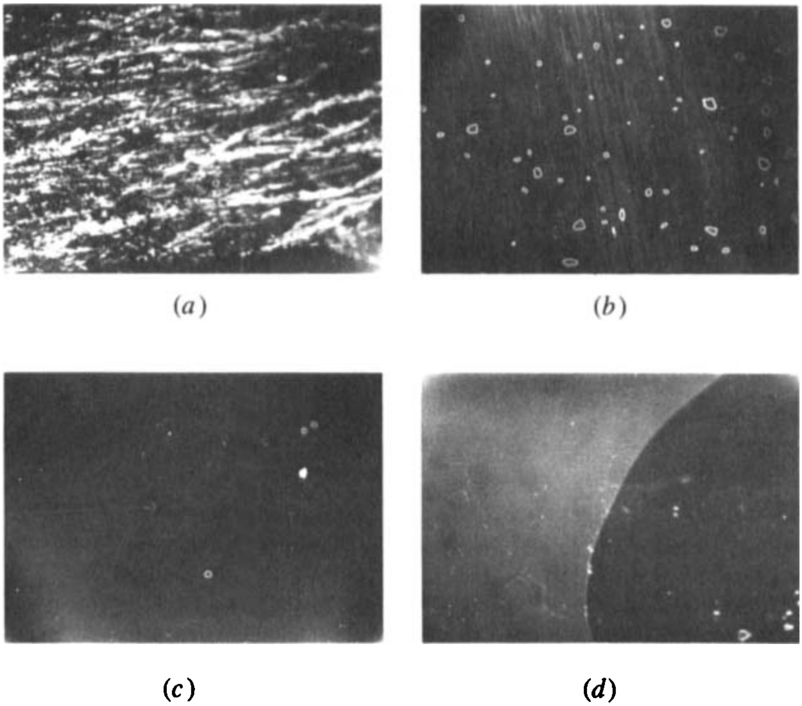
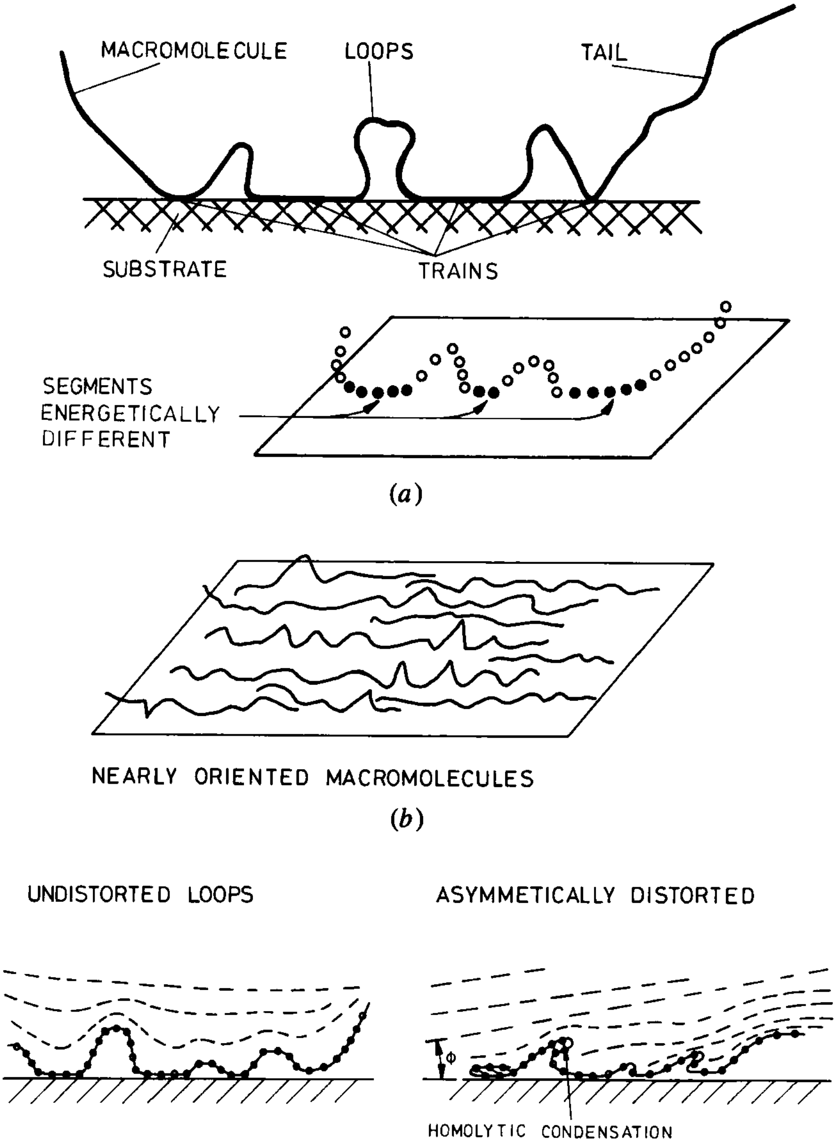


FIGURE 6 Photomicrographs showing: (a) textured alignment of nematic LC on chemisorbed PVA layer without directional buffing, (b) planar alignment with ϕ-type surface disclination domains in twisted cell; note the barely visible textured features after two directional buffing passes, (c) twisted planar cell with minimum ϕ-type defect lines after multiple buffing passes; no textured features visible, (d) θ-type boundary with PVA layer buffed after curing at 200°C.

On the other hand, this situation is similar to the polyacrylate adsorption on silica and glass powders reported by Jenkel and Rumbach[21] who proposed that not all the segments of the polymer chain are attached to the surface. Further approaches to this problem developed by Frisch *et al.*,[22] Simha and others,[23] as well as by Silberberg[24,25] indicate that those segments of the polymer chain which are in contact with the surface ("trains") are energetically different from the segments which are folded ("loops"), and from the free ends ("tails") (Figure 7a). It has been shown by the above authors that there is increased train configuration at lower surface concentration of the molecules, while the number of loops increases at higher surface concentrations of the chain molecules.



(*a*)

(*b*)

(*c*)

FIGURE 7 Schematic representation of the adsorbed macromolecules on the substrate: (a) "trains" are energetically different from the rest of the segments, (b) alignment of the polymer after directional buffing, (c) asymmetric tilting of the "loops" after multiple buffing passes and curing.

Since the number of C^{14}-tagged PVA molecules per unit area of the ITO glass plate was found to be much higher than that for the nonsilica-treated surface, it is safe to assume that the number of loops must be much larger in the former case than in the latter, which further increases as the concentration of PVA in the solution increases and as the duration of exposure to the solution increases (until saturation).

These polymer loops can be used to explain the observed change in bias tilt of the nematic LC cells with short or long duration of immersion (see above). The loops can also explain why the tilt angle for PVA surfactants is larger than that observed for other surfactants like HMAB (usually less than 1°[8,20]). In the following, a model for the orientation of nematic LCs by a chemisorbed PVA film is proposed: when the PVA layer is buffed unidirectionally before curing, the polymer chains orient themselves along the direction of buffing (particulary if this was preceded by a buffing step with a fine abrasive, leaving directional scratches). Moreover, the looped segments of the PVA chains get tilted in the buffing direction, as shown in Figure 7b. These tilted loops become fixed during curing by means of homolytic condensation. The fixed, oriented polymer molecules with their humps create undulating steric, dipolar and dispersive effects. Their influence on the adjacent nematic molecules is similar to that of obliquely evaporated SiO_x where the nematics align parallel to the ridges and valleys,[12] only at a much finer scale. Similarly like Meyerhofer[26] who assumes that behind each SiO_x asymmetric hillock an LC molecule is anchored, pointing upward, which explains the strong tilt that is observed with these obliquely evaporated inorganic layers, we conclude that the director of the LC molecules is tilted upward by these molecular, asymmetric loops, as shown in Figure 7c. Since the PVA layer that is produced by longer immersion has a higher number of loops per unit area than that produced by brief immersion, the corresponding tilt angle can be expected to be higher, in agreement with observation, because the neighboring asymmetric loops point up steeper due to mutual crowding.

Electrooptical performance

For a given orientation technique, the electrooptical characteristics of a cell depend upon the LC materials used. We have tested most of the commercially available nematic mixtures with positive dielectric anisotropy (as such and doped with low amounts of chiarlic additives[2]) comprising alkyl cyano Schiff bases, alkyl cyanoesters, aryl cyano esters, alkyl and alkoxy cyanobiphenyls as well as cyanobiphenylcyclohexanes and cyclohexyl bi-

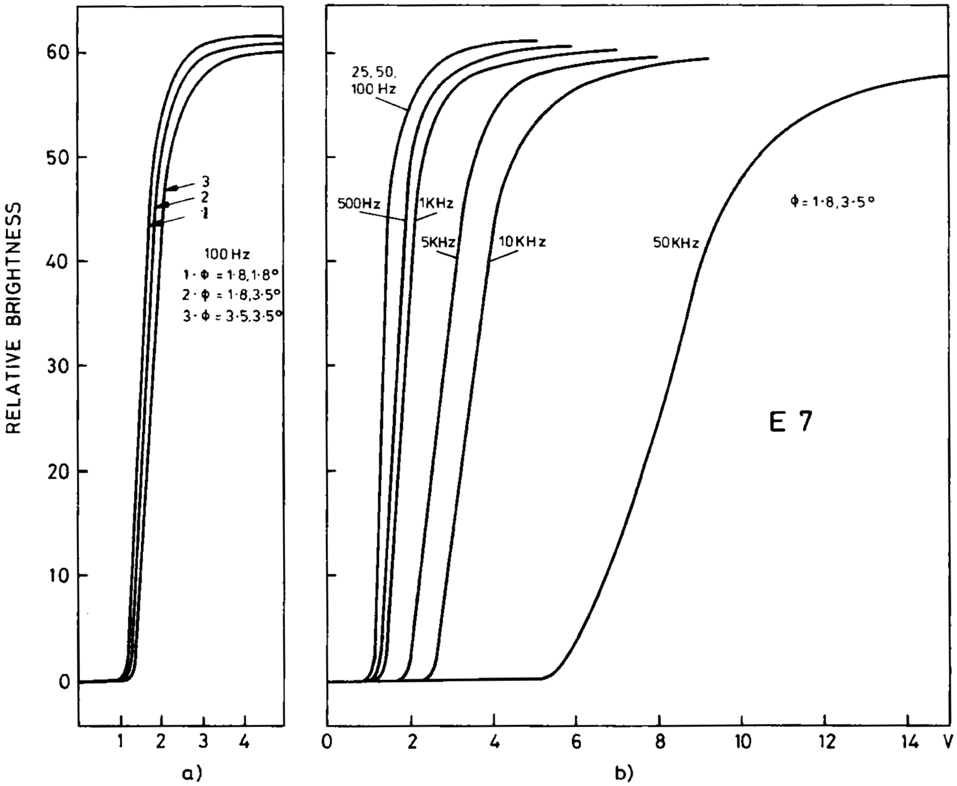


FIGURE 8 Static transmission vs voltage characteristics of TN-LCD using E7: (a) effect of tilt angle variation, (b) effect of frequency of applied voltage.

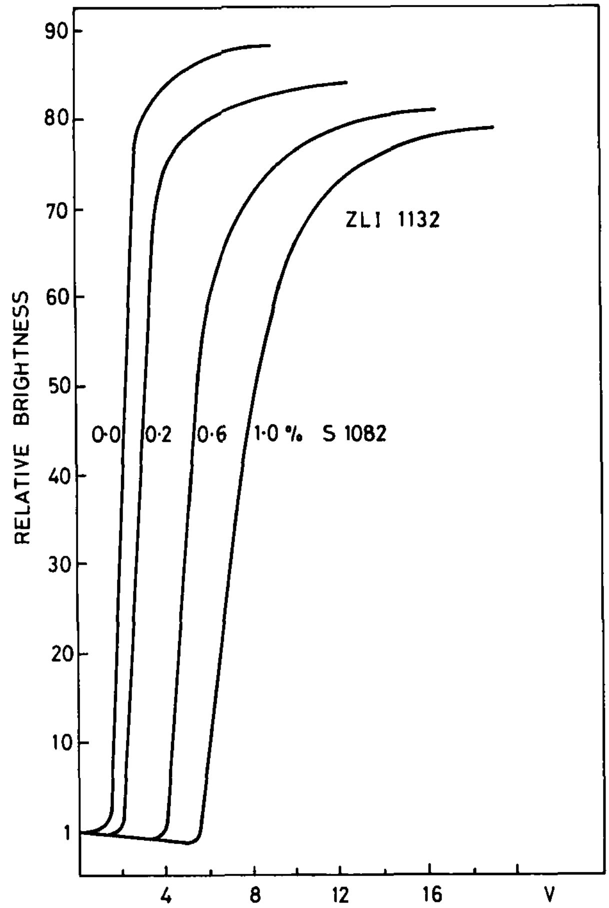


FIGURE 9 Static transmission vs voltage characteristics of TN-LCD using ZLI 1132, and effect of addition of the optically active chiralic compound S1082.

phenyls. Alkyl cyano-pyrimidines have not been tried. Good planar directional orientation could be attained in all cases.

It is not intended to present here the electrooptical performance of each of these mixtures, we chose only the data for E 7 (BDH) and ZLI 1132 (E. Merck).

Figures 8 and 9 show the static optical transmission curves when mounted in 10 μm thick cells of identical tilt on both glass plates (ϕ_1 = 1,8°; ϕ_2 = 1,8°), or different tilts on both plates (ϕ_1 = 1,8°; ϕ_2 = 3.5°) where the first value indicates the tilt angle at the incident electrode surface.

TABLE I

Response characteristics of positive dielectric nematic LC mixtures (10 μm thick twisted cells; sweep time 400 ms; pulse frequency 100 Hz)

Number of buffing passes	E7			ZLI 1132		
	t_{on}(ms)	t_{off}(ms)	V_{10}	t_{on}(ms)	t_{off}(ms)	V_{10}
1	115	156	1.59	130	160	1.62
2	110	135	1.56	123	144	1.63
3	103	120	1.57	116	126	1.60
4	98	112	1.55	108	118	1.58
5	95	107	1.55	102	113	1.56
6	96	105	1.56	102	110	1.57
7	95	105	1.55	102	110	1.57

There is only a slight shift in the threshold voltage when shifting from the first to the second combination. Lower tilt angles bring about higher contrast. ZLI 1132 is reported to have a less sharp voltage threshold than E7 using SiO_x orientation.[27,28] This is not the case with our PVA technique. Figure 9 shows that the threshold characteristics of ZLI 1132 are comparable to that of E7.

The addition of a chiralic dopant, or increase of the working frequency, will shift the threshold voltage upward considerably.[2]

Table I gives data on the electrooptical transient characteristics of TN LCDs prepared by the PVA technique, differing in the number of passes under the buffing wheel. The rise and decay times reach minimum values after a few passes. The threshold voltage shows little variation. There is a more pronounced decrease in the t_{off} values. We conclude that repeated buffing renders the loops to be more asymmetrically inclined in the direction of buffing (Figure 7c). This induces tilted alignment of the LC molecular azimuth in accordance with the surface profile of the macromolecules. This is sufficient to influence the rheological processes during turn-on and turn-off of the TN LCD.

Acknowledgments

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