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Novel Liquid Crystal Display on Polyaniline Modified Glass

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Novel liquid crystal (LC) cells were fabricated using polyaniline covalently attached onto ordinary glass surfaces. The latter fulfils three functions, namely, the substrate, the conducting medium and the template for the alignment of LC molecules. Both nematic and ferroelectric LC cells fabricated show perfect alignments and require comparatively low voltage for the switching of molecular orientations from one to another.

Keywords: Liquid crystal; nematic; ferroelectric; polyaniline; covalent attachment

1. INTRODUCTION

In our previous publication, we described the suitability of polyaniline as a template for the alignment of both nematic and ferroelectric liquid crystalline molecules in liquid crystal display devices (LCDs) [1, 2]. These devices were fabricated using electrochemically grown polyaniline films on indium doped tin oxide (ITO) conducting glass surfaces. The advantage of this polymer over the conventional polymers is that, since the former is a conducting polymer, its presence does not have an adverse effect on the conductivity of the glass plates while the conventional polymers that are generally insulators, do reduce the conductivity. Thus, with the former, a relatively low voltage is sufficient to operate the devices. However, these devices also required conducting glasses for polyaniline to electrodeposit on them. We have recently devised a method to covalently attach polyaniline onto

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ordinary glass surfaces by functionalising the glass surface with aniline [3,4]. When polyaniline is covalently bound to the glass surface in its conducting state the conductivity of such a surface was a few orders of magnitude greater than those of ITO glasses. In this publication we describe a novel method developed to fabricate LCDs on ordinary glass surfaces functionalised with polyaniline. The latter surface is a trifunctional surface that acts as the substrate, the conducting surface and the template, in these devices.

2. EXPERIMENTAL

All chemicals used were of Analar grade and used without further purification if not specified otherwise. The aniline used was distilled at 184°C under N_2 atmosphere and stored at 4°C. The water used was doubly distilled (DDW).

2.1. Surface Modification of Glass

Ordinary pre-cleaned glass surfaces were cut into 1 cm × 1 cm pieces and rinsed thoroughly with dust free DDW and dried in an oven at 110°C. The glass plates were heated on a hot plate to 400°C and thionyl chloride liquid was sprayed onto them in a fume cupboard for two minutes. This results in a replacement of surface hydroxyl groups of the glass surface by chloride groups as confirmed by reflectance FTIR measurements [3]. The SiCl groups are much more reactive than SiOH groups and hence Cl can be replaced by NHC_6H_5 by simply spraying distilled dry aniline onto these glass surfaces. This reaction was also followed by reflectance FTIR measurements [3]. The modified glass surfaces were placed in the vessel containing 0.1 mol dm^{-3} aniline and 0.05 mol dm^{-3} $K_2S_2O_8$ in 0.1 mol dm^{-3} HCl for 10 hours. In this mixture, aniline undergoes polymerisation in the acidic medium initiated by the oxidant $S_2O_8^{2-}$ and polyaniline is formed. It has been confirmed previously that the polyaniline formed on the aniline-modified glass surfaces has been initiated through the bound NHC_6H_5 group resulting in covalently attached polyaniline on the glass surface [3]. The glass plates containing covalently attached polyaniline were rinsed thoroughly with distilled water to remove any oxidant present on their surfaces. The as-prepared glass plates were green in colour indicating that the polymer exists mainly in the emaraldine salt form of polyaniline. The electrical neutrality is then obtained by the entrapment of anions within the polymer. The polymer layer on glass thus obtained has a conductivity of 0.028 S cm^{-1}

at room temperature and the polymer layer does not peel off even by mechanical rubbing. There were no appreciable change in the colour or the conductivity of the glass plates with aging (The observations were made for nearly one year.) indicating that there were no entrapped persulphate ions within the polymer matrix. The anion exchange studies with NO_3^- showed that Cl^- and SO_4^{2-} are present as the counter ions in the polymer.

2.2. Fabrication of Liquid Crystal Cells

The cells were prepared by separating two rubbed modified glass plates by 6 μm thick mylar spacers for thin cells and 25 μm thick mylar spacers for thick cells and sealing the two sides. Care was taken to ensure that the rubbed faces formed the inside of the cell with the directions of rubbing of the plates being parallel. Some cells were filled with the nematic liquid crystal, 4-cyano-4′-heptylbiphenyl (7CB) and others with the ferroelectric liquid crystal CS1013 (Chisso Petrochemical Corporation) in their isotropic phases. The nematic liquid crystal 7CB has the phase sequence of crystal 28.5°C, N 42.5°C isotropic and CS 1013 has Sm C* 63°C, Sm A 70°C, N* 80°C isotropic. Planer thin and thick nematic cells and surface stabilised ferroelectric liquid crystal cells prepared by polyaniline attached glass plates were observed under cross polarisers and polarising optical micrographs of both 7 CB and CS 1013 cells were taken using a polarising microscope.

3. RESULTS

The nematic phase of the 7CB cell shows a perfect alignment when observed under cross polarisers. Figure 1 shows the texture of the nematic phase of the 7CB liquid crystal cell of 6 μm thickness (thin cell) taken at 28°C. The extinction direction appeared along the direction of rubbing (Fig. 1a) and this when rotated by 23° results in the bright appearence as shown in Figure 1b. The same ones with the thick cell (cell of 25 μm thickness) are shown in Figures 2a and 2b respectively. High quality planer alignment was observed for CS 1013 cells. The textures of cholestric, smectic A and smectic C* phases of CS 1013 cell are shown in Figure 3. In the cholestric phase, various colours were observed with the change of temperature due to selective reflection of light by helix formed by liquid crystalline molecules. The maroon colour which appeared in

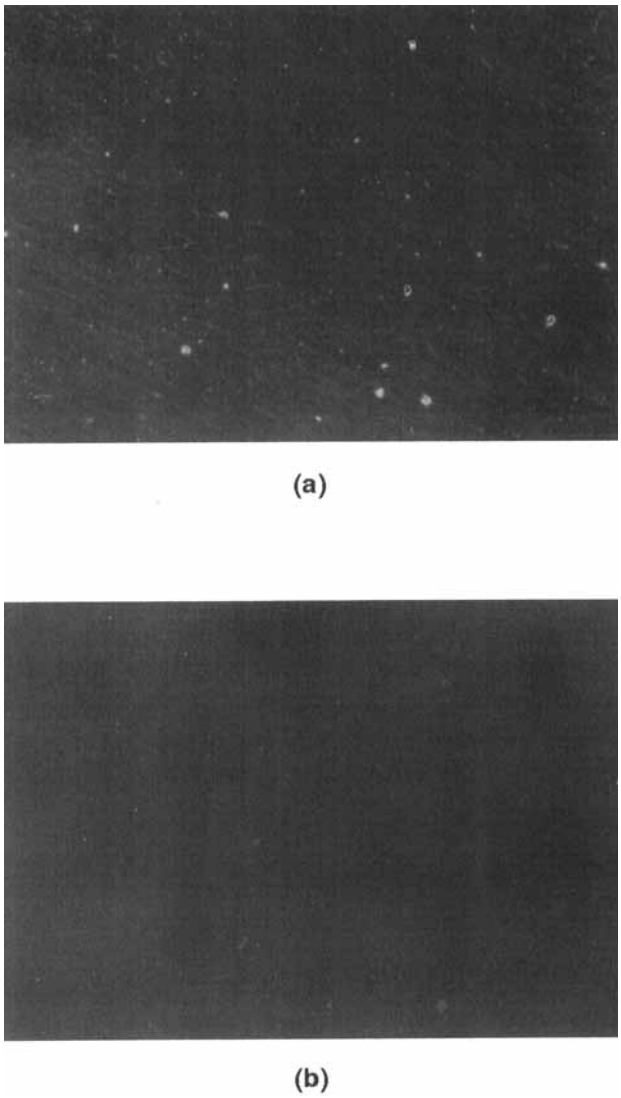
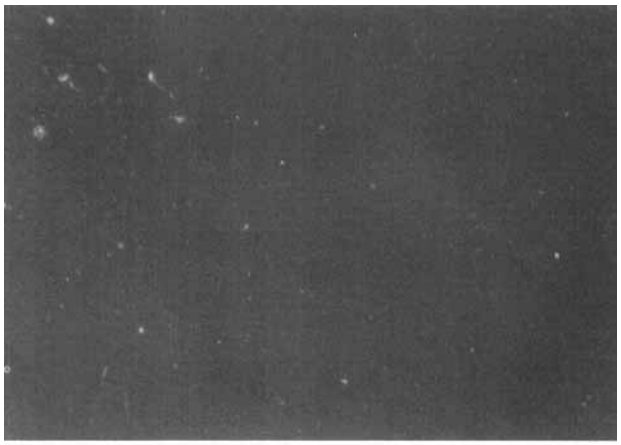
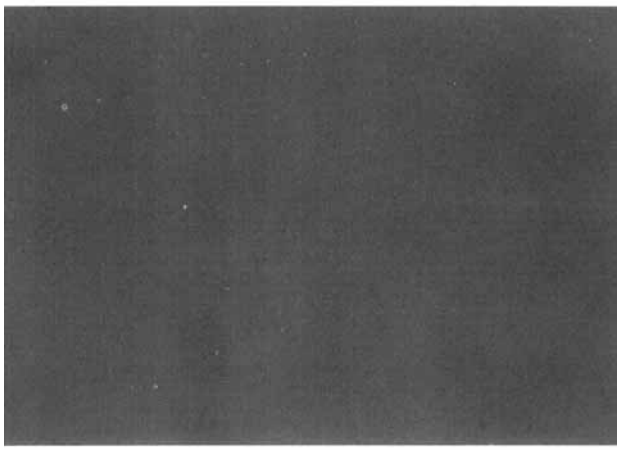


FIGURE 1 Optical micrographs of 7CB thin cell (6 μm thick) taken at 28°C under cross nicols. (a) Extinction position, (b) Bright position at 23° from extinction. (See Color Plate I).

this phase at 75°C is shown in Figure 3a. The smectic A was a smooth phase with extinction along the layer normal. The optical micrograph shown in Figure 3b was taken at 64°C in the smectic A phase at an angle of 23° from the layer normal. The black and pink regions in Figure 3c



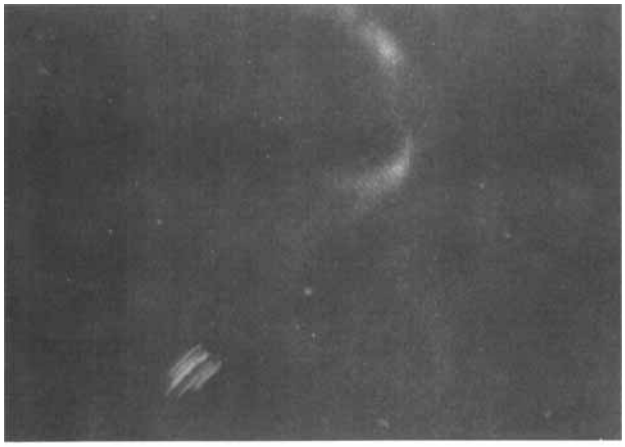
(a)



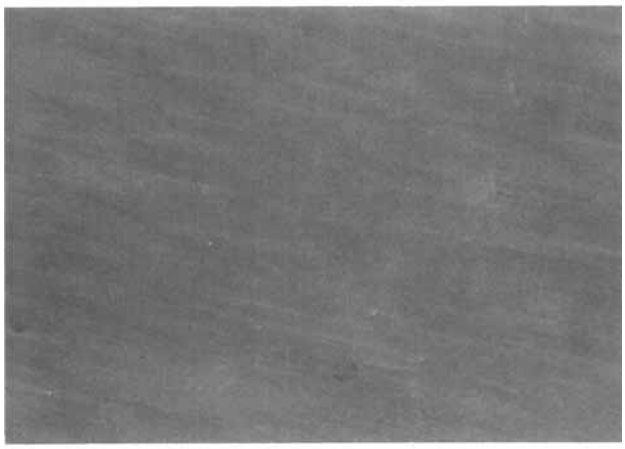
(b)

FIGURE 2 Optical micrographs of 7CB thick cell (25 μm thick) taken at 28°C under cross nicols. (a) Extinction position, (b) Bright position at 23° from extinction. (See Color Plate II).

are the two uniform states observed in the smectic C* phase at 28°C. These two states alternate their colours when the cell is rotated by the cone angle 2θ as in Figure 3d. These optical micrographs clearly illustrate the perfect alignment of liquid crystalline molecules in the cholestric,



(a)

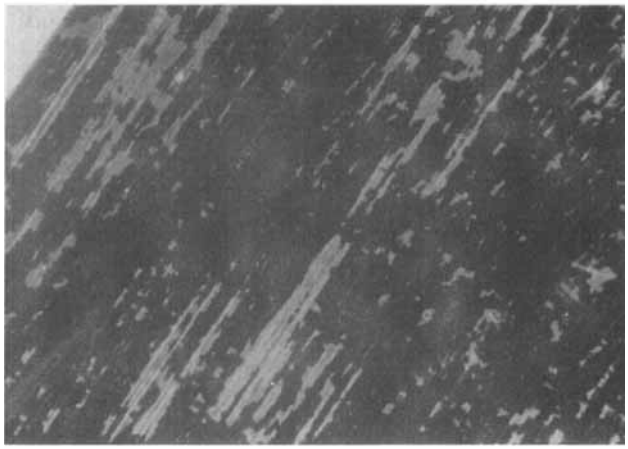


(b)

FIGURE 3 Optical micrographs of surface-stabilised ferroelectric cell CS1013 (6 μm thick) taken under cross nicols. (a) Cholestric phase at 75 C. (b) Smectic A phase at 17° from layer normal at 64 C. (c) Two uniform states in the Smectic C* phase at 28 C. (d) Colour alternation of bistable states of (c) above by rotating the configuration of c by 16 . (See Color Plate III).

smectic A and smectic C* phases of a SSFLC cell fabricated with polyaniline attached onto glass surfaces. Another striking feature observed in these SSFLC cells is the lower voltage required for switching molecules from one

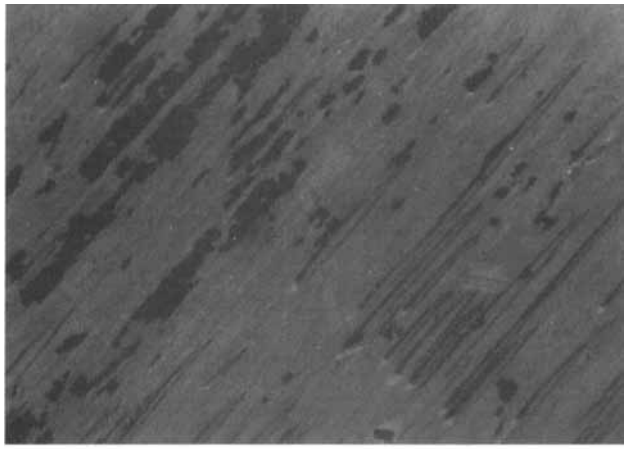
(c)



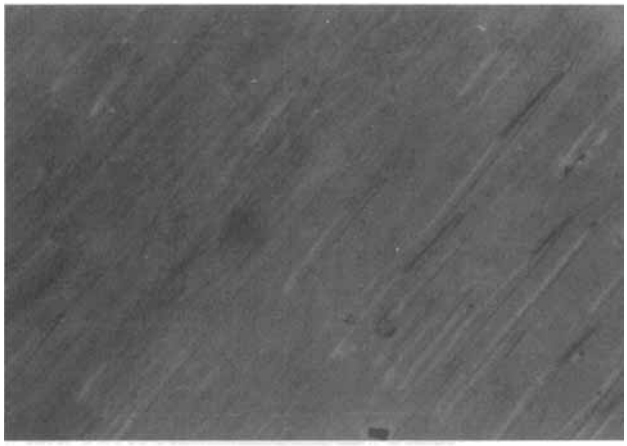
(d)

FIGURE 3 (Continued). (See Color Plate IV).

uniform state to another in the smectic C* phase as compared to that of convectional cells. This voltage is 1 V μm^{-1} at 28°C. Optical micrographs taken under cross polarisers for SSFLC cell at 28°C without applying an electric field and at the influence of 10 V are shown in Figures 4a and 4b respectively. The dark regions in Figure 4a indicate the alignment of LC



(a)



(b)

FIGURE 4 Optical micrographs of surface-stabilised ferroelectric cell CS1013 (6 μm thick) taken under cross nicols at 28°C. (a) in the absence of an applied electric field (b) under the influence of an applied voltage of 10 V. (See Color Plate V).

molecules in one of their uniform states. The other uniform state generated by switching these molecules under the influence of the applied voltage is shown in Figure 4b.

For comparison, a twisted (SSFLC) nematic cell of 7 CB (6 μm) was fabricated in the same manner and it was found that the complete rewinding of molecules can be effected by 1 V μm^{-1} at 28°C. This voltage is comparable with those prepared on polyaniline electrodeposited onto conducting glass surfaces [1]. Further, it was found that the alignment of molecules in each phase of all above cells is permanent and is unaffected by the repetitive transformations between phases and also by heating to the isotropic state followed by cooling to the respective phase.

4. DISCUSSION

The devices described in this publication are improved versions of the previous one [1,2] where both the conducting layer and the template polymer used in the previous devices have been replaced with just the conducting polymer. The polymer functions both as the conducting medium and the template for the alignment of the LC molecules. As the polymer does not adhere properly on an ordinary smooth glass surface we have devised a method to covalently attach the polymer onto the glass surface. This procedure ensures the longer life-time of the device. The polymer will not peel off from the glass surface with aging. In addition to the bi-functionality of the polymer this modification has overcome several other disadvantages associated with LCDs based on ITO-conducting glass surfaces. In the first instance, the life-time of the LCDs based on ITO-conducting glass surfaces is limited by the existence of the ITO layer on the glass surface. This layer can be damaged by acids and alkali. Secondly, as the ITO particles scatter light the performance of the device could be difficult to observe in some directions. The novel device is free from these obstacles and could be used in technological applications in its present form.

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