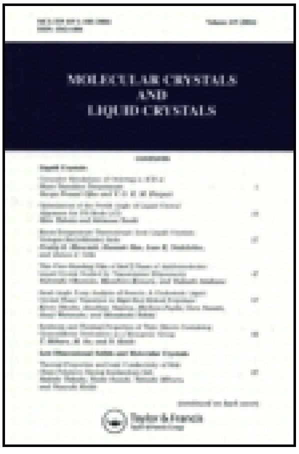

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A TECHNIQUE TO ALIGN LIQUID CRYSTALS BASED ON BULK-INDUCED PHOTO-POLYMERIZATION

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Abstract A technique based on bulk-induced alignment of liquid crystals by photo-polymerization to produce uniform planar and homeotropic orientation of liquid crystals is presented. The liquid crystal-photopolymer mixture is cured with linearly polarized UV-light in the isotropic phase. This technique obviates the need to give any special treatment to the bounding substrate and as such is independent of the nature of the substrate. This has given rise to possibilities of using liquid crystals for storing information with a high degree of spatial resolution of 10-20μm and has been used to generate patterned orientation of liquid crystals.

The homeotropic alignment in the smectic C phase has opened up new possibilities to make storage displays. The surface studies of the photopolymer aligned substrate with a Scanning Tunneling Microscope suggest that the surface modification dominates the alignment of liquid crystals.

INTRODUCTION

Uniform alignment of liquid crystals has been a subject of intensive research investigations during the last more than two decades. The subject is essential and interesting for both basic studies as well as for device applications. A variety of techniques have been developed and commercialized to produce uniform orientation of liquid crystals. Most of these techniques are based on surface modification of the substrate which can be produced by i) angular deposition of dielectric materials[1], ii) thermal polymerization followed by buffing[2], iii) organosilane coating[3], iv) lecithin coating, v) photo-polymerization[4-7] etc. All these techniques are based on complex anisotropic surface anchoring interactions. Recently reported new techniques based

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on photo-polymerization have stimulated considerable research interests due to their unique feature in providing the capability to control and vary the macroscopic orientation direction of liquid crystal molecules locally within a plane. This has opened up new possibilities to make complex hybrid liquid crystal displays for data storage with a high degree of spatial resolution. We wish to report below a new modified technique to promote uniform planar and homeotropic orientation of liquid crystals based on bulk-induced photo-polymerization. This technique has been used to record patterns with a high degree of spatial resolution on liquid crystal cell without resorting to etching of the electrode patterns on the bounding substrate.

The homeotropic aligned smectic C cell by this technique has been shown to exhibit storage capability by application of appropriate low frequency electric field and subsequent heating to smectic A phase. The imaging of liquid crystal molecules adsorbed on surface of a photo-polymer aligned substrate with a Scanning Tunneling Microscope has revealed interesting results and strongly suggests that the surface modification dominates the alignment of liquid crystal molecules even in the present case.

EXPERIMENTAL

Cleaned glass substrate without any previous surface treatment were used to make a liquid crystal cell. The cell thickness was controlled by glass/polymer spacers of a desired thickness(4-10μm). A number of liquid crystal mixtures exhibiting nematic, smectic and chiral tilted smectic phases were used. A small amount (0.1-1.0% by wt.) of the photopolymer, poly-vinyl-methoxy cinnamate (PVMC) was added to the liquid crystal mixture and a uniform solution was made in chloroform which was subsequently allowed to evaporate completely. The mixture was filled into the sandwich cell in its isotropic phase. The cell was cured with linearly polarized UV-light ($\lambda \sim 320$-420 nm) using a Xenon lamp or a metal halogen lamp . A Glan prism polarizer from Bernhard Halle, Berlin was used as a UV-linear polarizer. The light intensity was ~ 3-10 mW/cm^2 and the curing time was 5-30 minutes. The cell temperature was maintained at $> 10°C$ above the clearing temperature during curing by an Instec Hot Stage. A Leitz polarizing microscope along with a photomultiplier setup and a digital storage oscilloscope were used to study the alignment and electro-optical properties of the aligned cells. Electrical signals were generated using a function generator (Hewlett-Packard 3312A) coupled with an amplifier (Krohn-Hite 7500).

The STM studies were performed with a commercial Nanoscope II (Digital Instruments, Inc.). The STM was operated in the constant current mode. The tunneling conditions were typically 0.2-1.0 nA (tunneling current) and 200-1500 mV (tip negative bias).

RESULTS AND DISCUSSION

Well aligned planar cells could be obtained by curing the liquid crystal-photopolymer mixture with linearly polarized light well above its clearing point (>10°C). The quality of the alignment was checked by rotating the cell between crossed polarizers and under a polarizing microscope. The preferred macroscopic orientation of the liquid crystal molecules in the nematic phase was determined by tilting the cell under a polarizing microscope between crossed polarizers. The tilting of the planar oriented cell results in birefringence, unless the director is aligned parallel to one of the polarizers and parallel to the tilting axis. The macroscopic orientation direction of the liquid crystal molecules is perpendicular to the polarization direction of the UV-light. The orientation direction is more easily identifiable in planar oriented smectic phases by the direction of the fan shaped texture. We could produce by this technique, uniformly aligned planar oriented cells using different liquid crystal mixtures exhibiting nematic, smectic and chiral smectic phases. The cell could be easily switched by appropriate voltage pulses in the nematic and chiral smectic C phases. The switching characteristics of the nematic cells prepared by photo-polymerization and prepared by the conventional rubbing technique were quite similar. However, there was a lowering of the nematic-isotropic transition temperature by a few degrees by doping with photo-polymer. The electro-optical response of the LC cells in chiral tilted smectic phase (S_C^*) prepared in this manner and in conventional manner were qualitatively identical. Figure 1(a,b) show the variation of the spontaneous polarization as a function of temperature and switching times as a function of voltage, respectively, of two cells containing ZLI-3654 mixture (K →<-30°C → S_C^* →62°C S_A →76°C Ch →86°C Iso) prepared by

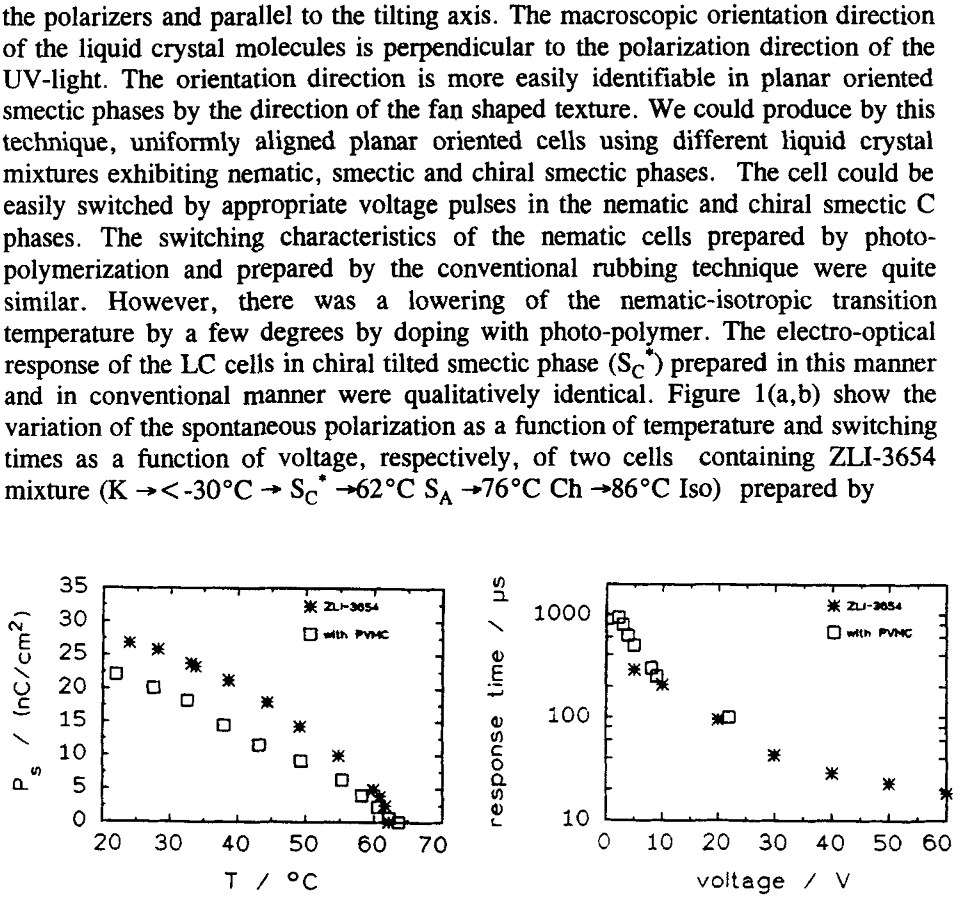

Figure 1(a) Variation of spontaneous polarization with temperature and (b) variation of switching time with applied voltage.

conventional surface alignment technique using a rubbed polyimide layer and by bulk-induced alignment using PVMC (0.8% by weight). The spontaneous polarization and the switching times are nearly identical in the two cases. Figures

2 & 3 show the variation of contrast ratio as a function of applied voltage and

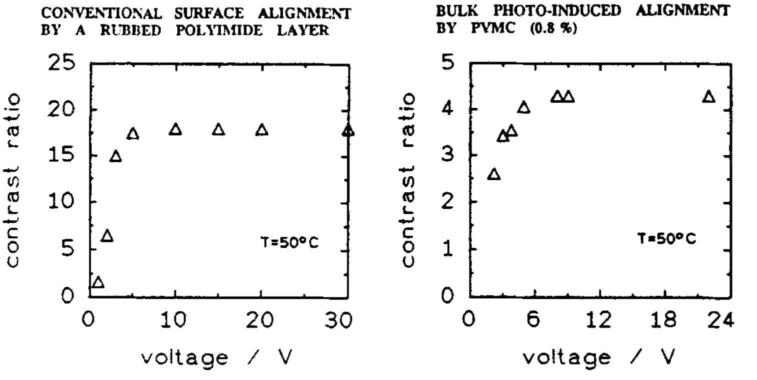

Figure 2 Variation of contrast ratio of polyimide rubbed cell and photo-polymer aligned cell containing ZLI-3654 mixture as a function of the applied voltage.

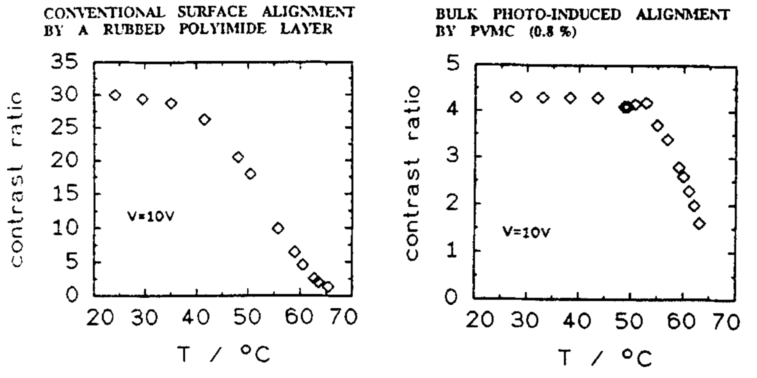

Figure 3 Variation of the contrast ratio of polyimide rubbed cell and photo-polymer aligned cell containing ZLI-3654 mixture as a function of temperature.

temperature for the above two cells. The contrast ratio is much lower in the cell prepared by photo-polymerization than the one prepared by conventional rubbing.

Pattern Storage By Bulk-induced Photopolymerization

This alignment technique has been used to store patterns optically on a liquid crystal cell. The pattern to be stored is made on a photomask. The nematic liquid crystal-polymer cell was exposed with linearly polarized UV-light through the photomask till the polymerization is complete. Subsequently, the polarizing prism was rotated through an angle of ±45° and the cell was exposed with polarized UV-light through a complementary mask. The two portions of the cell have different macroscopic orientation direction of the liquid crystal molecules. The liquid crystals being birefringent, they produce optical contrast when viewed between appropriately oriented polarizers. Figure 4 shows one such pattern recorded by this technique. The

Figure 4 Photograph of a pattern stored optically on a liquid crystal cell by bulk-induced photopolmerization. See Color Plate IV.

spatial resolution could be as high as (10-30μm) and the stored pattern has a long memory. Recorded patterns have not shown any visible decay for more than a year under ambient conditions. Memory test under extended UV-exposure has not been carried out so far. The pattern could also be recorded in a planar oriented liquid crystal cell filled with liquid crystal-polymer mixture by curing the cell with polarized light with its polarizing axis rotated through an angle of ±45° with respect to the planar orientation direction.

HOMEOTROPIC ALIGNMENT

Uniformly aligned homeotropic cells could also be produced by bulk-induced photopolymerization. The homeotropic alignment was produced when the liquid crystal-photopolymer mixture was cured just a few degrees above the isotropic transition temperature of the nematic. The homeotropic cell appears dark between crossed polarizers and do not show any variation in transmission under rotation between them. The homeotropic alignment was also checked by rotating the cell under a polarizing microscope and with conoscopic investigations. Figure 4 shows the micrographs of a homeotropically aligned cell containing liquid crystal mixture [ZLI-2711(PYP-709)80% + A-7(racemate)20%] and 0.5% PVMC with the following phase transition (K→43°C→S_C54°C→S_A→58°C N→66°C I) at 53°C.

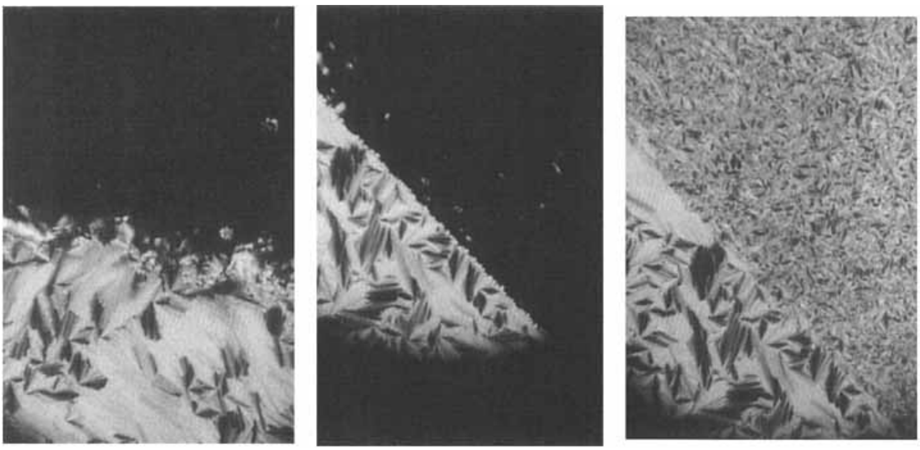

Figure 5 Micrographs of a homeotropically aligned cell in S_C phase: ϕ=(a) 0°, (b) 45°, and (c) scattering state with electrical voltage (20V,100 Hz). See Color Plate V.

Storage Effect

On application of a low frequency voltage signal in the S_C phase, the cell goes into a scattering state (Fig.5c) and on voltage removal the scattering state persists. The scattering state returns to homeotropic state on heating into S_A phase and persists on cooling into S_C phase (Fig5b). This principle can be used to selectively energize the selected areas in to scattering state which persists even on field removal and the original state can be regained by heating the cell into the S_A phase. The detail experiments are underway.

ALIGNMENT MECHANISM

It was thought that the uniform alignment in the photo-polymerization based cell could arise due to formation of an anisotropic polymer net work in the bulk/ or by surface modification of the substrate by the photopolymer as reported by Schadt et al.[4] In order to elucidate on this, a planar oriented cell obtained by bulk-induced photo-polymerization was opened up and the glass substrate were cleaned carefully with a mild solvent while ensuring that their molecular structure was not disturbed or modified by cleaning. On re-assembling the cell with such a pair of glass plates and filling it with a pure liquid crystal mixture, produced uniformly aligned planar cell, which was identical to the bulk-induced planar cell. This procedure could be repeated several times. It is obvious, that the alignment in subsequently cleaned cells is caused by the surfaces of the substrates as the filled liquid crystal mixture does not contain any photopolymer. The formation of the anisotropic polymer network in the bulk in the subsequent cell is ruled out. It was reasonable to conclude that an ultra thin layer of the anisotropic polymer network gets deposited on the glass substrate during photo-polymerization. To check on this hypothesis, the Scanning Tunneling Microscope studies were carried out.[8] A small amount of liquid crystal PCH-5 was transferred on one such conducting optically flat glass plate and was heated to isotropic transition temperature (55°C) for five minutes and then slowly cooled down to room temperature. A Pt-Ir tip was brought close to the liquid crystal and carefully driven into the tunneling range. The STM was operated in constant current mode.

The adsorbed liquid crystal molecules on the glass substrate were observed to form ordered arrays of molecules over large areas (Fig.6). The liquid crystal

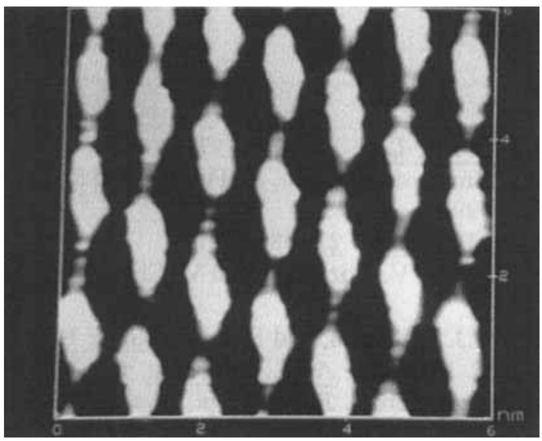

Figure 6 A 6*6 nm STM image of PCH-5 molecules on indium oxide coated glass substrate with a ultra thin layer of PVMC deposited by bulk-induced photo-polymerization. See Color Plate VI.

molecules exhibit in addition to a long range orientational order, a high degree of positional order which is absent in the bulk.

The ordering of the liquid crystal molecules on the conducting glass substrate can be caused only by the anisotropic polymer net work on the glass surface. These studies lend support to the hypothesis that the surface modification of the substrate during photo-polymerization leads to the alignment of liquid crystal molecules.

CONCLUSIONS

A new technique based on bulk-induced photopolymerization to produce planar and homeotropic alignment has been developed. The planar orientation technique has been used to store patterns optically with a high degree of spatial resolution. The homeotropically aligned cell in the S_C phase could give rise to new type of storage displays. The subsequent planar cells obtained after cleaning the glass substrate and STM studies on them strongly suggest that even in the bulk-induced photo-polymerization technique, the surface modifications dominate the alignment mechanism.

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