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Selective Crosslinking of Polyimide for Photonic Devices

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Vertically aligned nematic (VAN) liquid crystals (LC) are interesting for many photonics applications. The performance of VAN cells depends on different factors; the boundary interactions between the LC monolayer and the alignment layer surface are the most important ones. These interactions are determined by anchoring energy. A set of procedures have been developed to modify by crosslinking the alignment properties of a specific polyimide (PI) for VAN cells; this PI produces vertical alignment with a small pretilt. We used two diepoxides as crosslinking agent of PI. The cells show different switching voltages for crosslinked and not crosslinked areas in the device. A small variation of the voltage, such as 1–2 V, can be adequate to generate phase grating with vertically aligned cell.

Keywords: alignment layer; crosslinking; liquid crystals; polyimide

1. INTRODUCTION

Nematic liquid crystals are useful for a number of non-display applications. Specifically, vertically aligned nematic liquid crystals with negative dielectric anisotropy are interesting for many photonics applications, since they can provide phase-only devices with no modifications of the state of polarization (SOP) of the incoming light. The off state of perfectly homeotropic cells behaves as an isotropic

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medium at normal incidence; consequently, it looks dark between crossed polarizers independently of the cell orientation, LC thickness, birefringence and wavelength. The performance of VAN cells depends on several factors, including the interactions between the LC monolayer at the surface and the alignment layer. These interactions determine the LC pretilt and polar anchoring energy of the cell. Development of VAN liquid crystal cells with reliable control of pretilt and polar anchoring energy is of great importance for most applications. A technique based on chemical surface-induced alignment to control pretilt angle is proposed in this work.

The polar anchoring energy and pretilt affect crucial electro-optic properties such as threshold voltage and response time. This opens the possibility of creating diffractive patterns inside the cell having different electro-optic properties for the same driving waveform, thus avoiding the need of electrode-pixelation and multiplexing of the said cell.

We have studied the effect of crosslinking on polyimide alignment surfaces of VAN cells, looking for variations in electro-optic response that could be made useful for the fabrication of non-pixelated photonic devices.

2. EXPERIMENT

2.1. Sample Cells Preparation

A set of experiments have been performed modifying the alignment properties of commercial polyimide (PI) SE1211 (Nissan Chemicals Industries, Ltd), in order to stabilize the layer through crosslinking and change its alignment properties. SE1211 is specifically designed to induce vertical alignment in nematic LCs. The liquid crystal used for the VAN cells is MLC 6608 mixture from Merck with negative dielectric anisotropy.

Polyimides with long alkyl side chain, such as SE1211, are attractive for VAN applications, because of their potential interactions between similar alkyl chains of LC molecules and the PI. The long alkyl side chains of the PI are tilted along the rubbing direction giving a uniform pretilt in homeotropic alignments, which increases with rubbing strength [1–2].

The PI SE1211 is purchased as polyamic acid dissolved in organic solvent [2]. A thin layer of the PI was obtained through the conventional two-step method employing thermal imidization of the polyamic acid. The structure of PI is shown in Figure 1 [1]. The imidization is described in Figure 2.

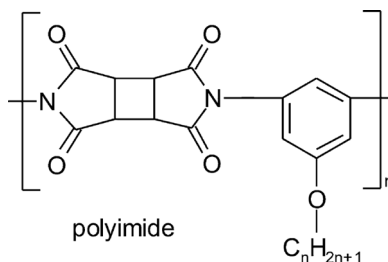


FIGURE 1 Structure of polyimide SE 1211. The alkyl chain length: $n = 18$.

Two different diepoxides, (Fig. 3), have been employed at varying concentrations as crosslinking agents for PI.

The difference between the two diepoxides is that one includes an aryl structure (DEX1) while the other one is aliphatic (DEX2). DEX1 structure contains phenyl rings rich in π electrons. Those phenyl rings in DEX1 structure contribute to π -electron elongated conjugation through the molecule and increase the polarizability along the molecular axis.

We have prepared four mixtures by adding different quantities of DEX1 or DEX2 into the PI solution at 1:2 w/w and 1:1 w/w ratio respectively. Five different kinds of cells without or with modified PI layer by DEX1 or DEX2 in different concentrations were prepared.

The bond angle of oxirane rings of the epoxy compounds is small, about 60° ; this results in poor electron density and increases reactivity of the epoxy compounds. The ring opening reaction is through an S_N2 mechanism in which the carbon oxygen bond is breaking and a $NH-C$ bond is forming. Both diepoxide structures (DEX1 and DEX2) contain two functional oxirane rings and react with polyamic acid forming a cross-linked polymer network. The creation of new crosslinked polymer net is shown on the reaction example between polyimide and DEX1 (Fig. 4).

The long alkyl side chains extending in the direction perpendicular to the substrate induce homeotropic alignment and support the pretilt of LC molecules, see Figure 5. An increase of diepoxide concentration

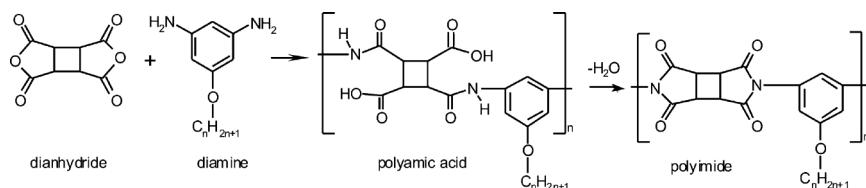


FIGURE 2 The reaction scheme of the polyimide formation.

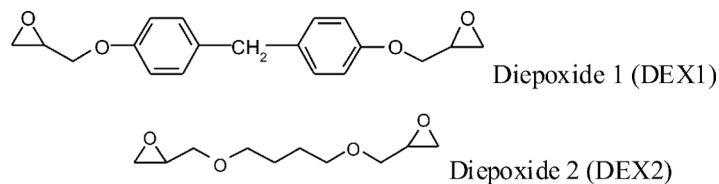


FIGURE 3 Diepoxides structures used for PI as crosslinking agents: DEX1-bis(4-glycidyloxyphenyl)methane and DEX2-1,4-butandiol diglycidylether.

would form, in principle, a less dense polymer network, yielding a weaker anchoring force, which modifies the LC pretilt on the substrate surface.

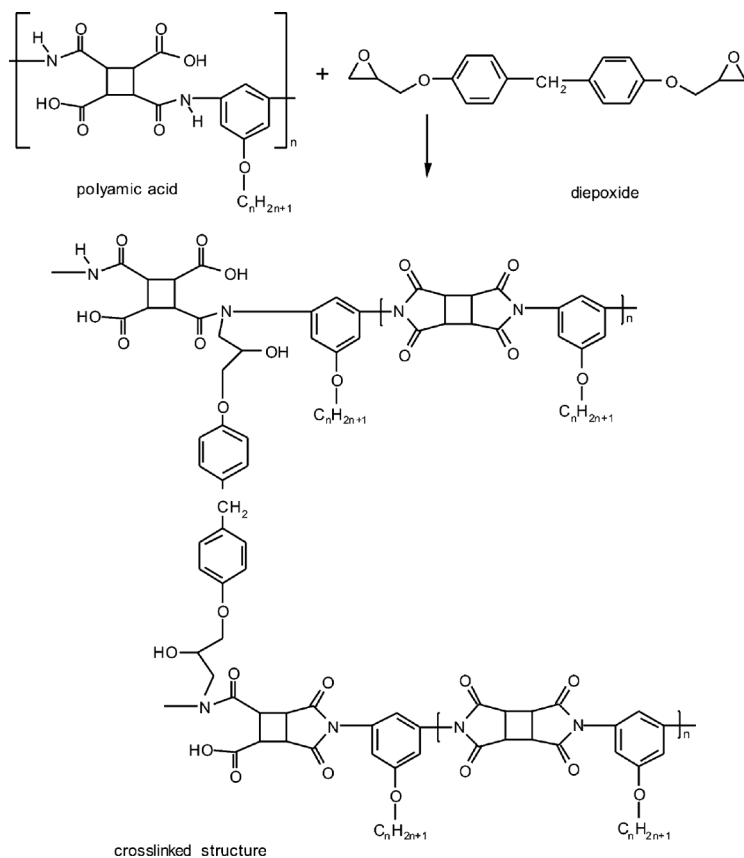


FIGURE 4 Crosslinking reaction between PI and DEX1.

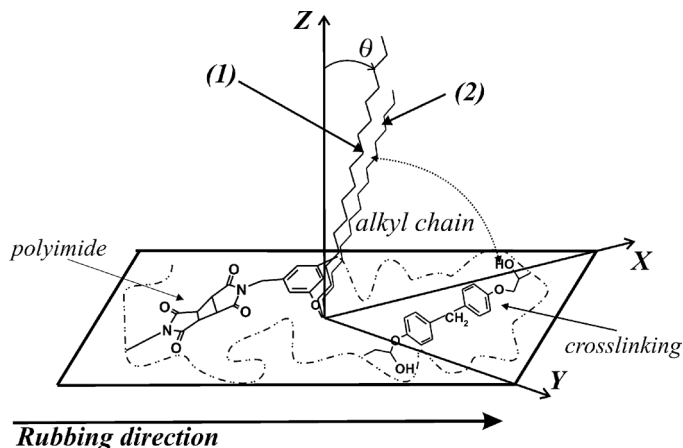


FIGURE 5 Surface of crosslinked polymer network: (1) – position of alkyl side chain before crosslinking; (2) – position of alkyl side chain after crosslinking.

The main chains of the polyimide align in the direction of rubbing and the phenyl rings of the crosslinked agent orient in orthogonal direction with respect to the main chain. This determines the major axis of the optical indicatrix that is attributable to the polarization of the π electrons in phenyl rings. In the new crosslinking polymer net appear polar $-\text{OH}$ groups which promote planar anchoring and higher tilt angle [3].

2.2. Electrooptical and Pretilt Angle Measurements

Electrooptical properties have been measured in cells made with indium-tin-oxide (ITO) coated glass plates covered by a rubbed alignment layer and filled with the MLC 6608 mixture. The alignment layer was deposited by spin coating, and cell thickness was kept to $4\text{ }\mu\text{m}$. This thickness is enough for the material to induce π retardation between the fast and the slow polarization of light in transmission mode.

To study the induced pretilt, optical characterization of cells has been performed by variable angle spectroscopic ellipsometry [4]. Normal to the surface is used as reference for pretilt angles, i.e., null pretilt would correspond to perfectly homeotropic alignment.

2.3. Polar Anchoring Energy Measurements

Various techniques for measuring the polar anchoring strength between the LC and the alignment layers have been developed. These can be divided into two categories: field-on or field-off techniques [5–9].

We have used a “high electric field” method (a field-on technique) for the determination of the LC polar anchoring energy (W) of the cell using the approach based on the optical retardation (R) and electric capacitance measurements as a function of applied voltage (V). The technique is summarized below. Full details can be found in [5–9].

The polar anchoring energy has been measured for the five kinds of cells at 25°C. A 1 kHz sinusoidal external field was applied in the direction parallel to the homotropically aligned LC molecules. At strong field conditions (above 4 times the threshold voltage) the bulk was fully oriented in direction perpendicular to the field; however at the boundary surfaces the reorientation was not complete due to the surface anchoring energy. The simultaneous measurements of the capacitance and the phase retardation of the cell, allowed for the calculation of the anchoring energy. In our experiment the modification of alignment layer resulted in a weaker anchoring, which decreased the corresponding threshold voltage and an improved response time.

The normalized optical retardation (R/R_0) can be cast as a function of a proportionality constant which depends on the bulk parameters of the LC (I_0), the capacitance of the cell (C), the applied voltage (V_{rms}), the thickness of the cell (d) and the so-called extrapolation length (d_e) [9]:

$$\frac{R}{R_0} = \frac{I_0}{CV_{rms}} - \frac{2d_e}{d}, \quad V_{rms} \geq 4V_{th}$$

The value of d_e can hence be determined by extrapolation of a plot of (R/R_0) against $1/CV_{rms}$.

The polar anchoring energy (W) for vertically aligned liquid crystals cells can be calculated from the following relationship:

$$W = \text{modulus} \frac{2K_{33}}{2d_e - d} \text{ modulus}$$

where K_{33} is the bend elastic constants.

3. RESULT AND DISCUSSION

The experiments have verified that the PI alignment modified by diepoxides can align the LC molecules well with a control of pretilt angle. It has been found that the induced pretilt is about 1° in the case of non-modified PI and change to 5.5° for a 1:2 w/w ratio of DEX1 added to PI. The pretilt increased up to 14° with double concentration (1:1 w/w ratio) of DEX1. However in the case of the aliphatic DEX2 the induced pretilt saturate at about 5° independently on the concentration.

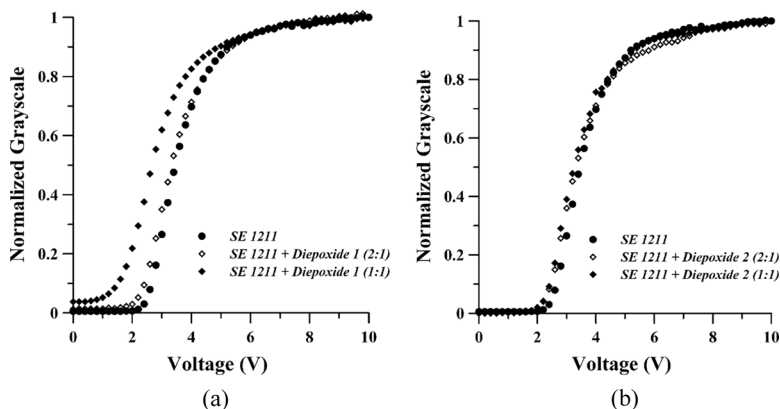


FIGURE 6 Comparison of switching voltage of cells without and with cross-linked alignment surface by two diepoxides: DEX1 (a) and DEX2 (b).

The cell with non modified layer exhibits a very good contrast between crossed polarizers at low voltage; in this case no phase retardation occurs consequently no light is transmitted through the analyzer. As the voltage increases, the LC molecules are oriented by the field and consequently phase retardation occurs resulting in light leakage through the analyzer. When the diepoxide is added to the polyimide a tilt of the director with respect of the normal of the boundary walls is introduced. This pretilt angle varies by increasing the diepoxide concentration, consequently the threshold voltage (V_{th}) is reduced (Fig. 6).

Voltage dependent transmitted light intensities of a 4 μm thick liquid crystal cell are shown in Figure 6. It was found that crosslinking of the PI alignment using DEX1 does vary the anchoring strength. The electrooptical measurements showed different switching voltages for crosslinked and no crosslinked areas in the device. Variations of the threshold voltage up to 1.5 V have been registered for the cells with PI crosslinked by DEX1, see Figure 6. Such variations are sufficient for making phase gratings with VAN cells applying a single driving voltage.

However, the V_{th} shifts observed in the case of cells made by PI crosslinked by DEX2 are too small for such a purpose.

Figure 7 plots present the rise and fall time measured in 4 μm vertically aligned cells with and without PI modifications. The cells with no modified PI exhibit low pretilt which lead to slower rise time, however in cells made with modified PI, a higher pretilt is obtained which leads to faster rise time. Fall time measured in

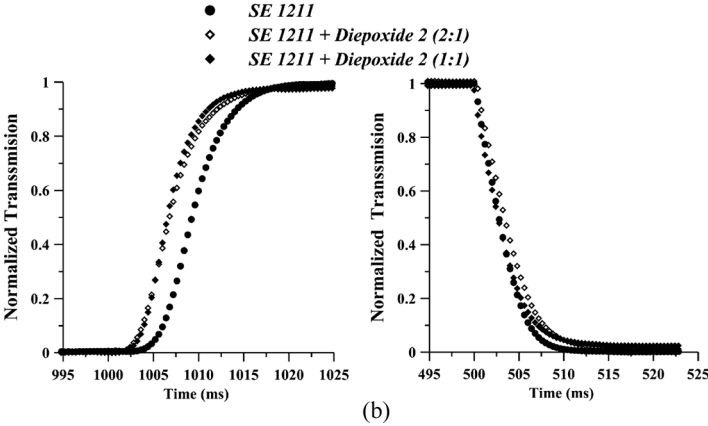
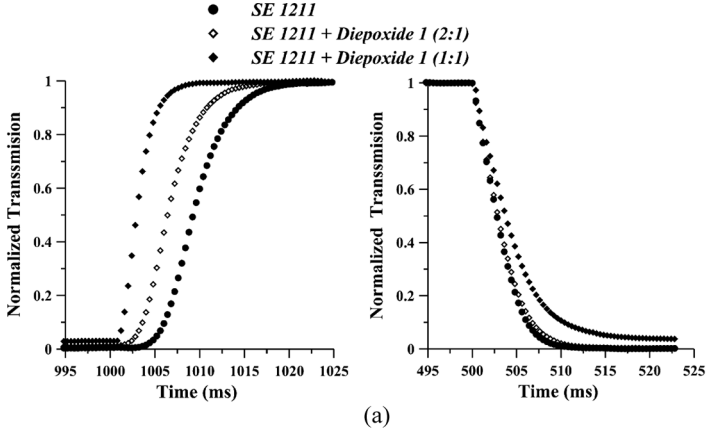


FIGURE 7 Comparison of rise time and fall time of cells without and with crosslinked alignment surface by two diepoxides: DEX1 (a) and DEX2 (b).

cells with crosslinked PI is longer than fall time measured in cells with no crosslinking corresponding to a reduced anchoring force – Figure 7.

Polar anchoring measurements have been performed in the same cells used for the electro-optical study. From the plots of Figure 8, we can determine the anchoring energy which is related to the extrapolation length d_e (the intersection with the y-axis). The polar anchoring energy measured in the cells with a conventional PI show stronger anchoring than modified surfaces of PI and $W = 1.8 \cdot 10^{-3} \text{ J/m}^2$, see Figure 8(a). Intermediate anchoring energy ($W = 3.3 \cdot 10^{-4} \text{ J/m}^2$) was obtained by adding DEX1 into PI solution at 1:2 w/w (DEX1/ PI)

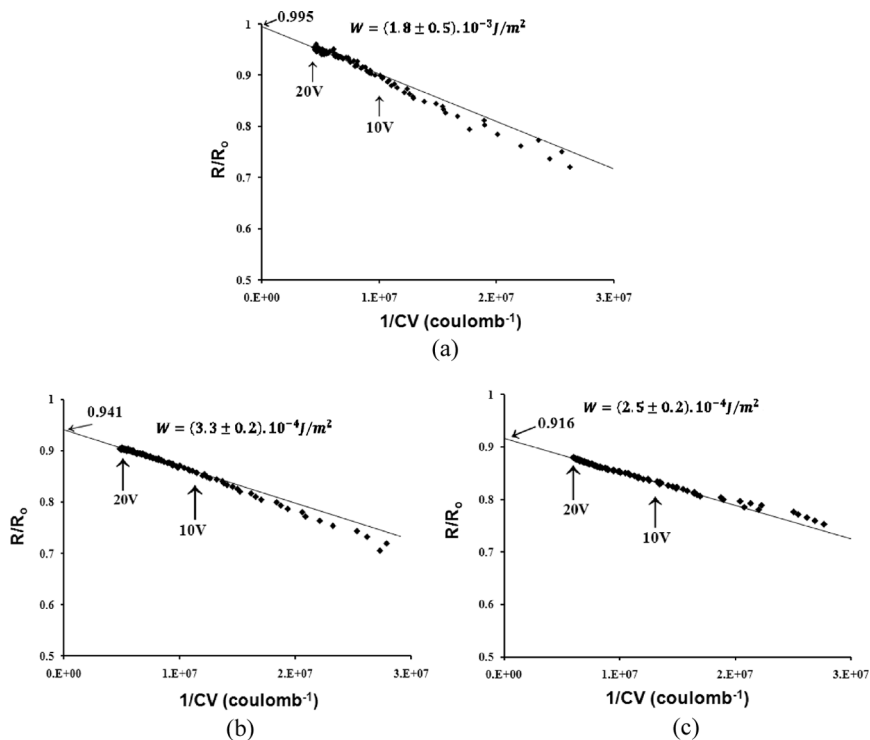


FIGURE 8 Plot of the extrapolation method. A linear fitting is obtained in the $V > 4V_{th}$ region of: (a) – cells without crosslinked alignment surface, (b) – cells with crosslinked alignment surface by DEX1 (1:2 DEX1/PI w/w ratio) and (c) – cells with DEX1 (1:1 DEX1/PI w/w ratio). The bulk parameter I_0 varies 20% between a) and the other two samples. This artifact is due to the zero pretilt in the a) sample, which results in micro domains, which in turn makes affect the accuracy of these measurements.

ratio – Figure 8(b), and weakest anchoring energy ($W = 2.5 \cdot 10^{-4} \text{ J/m}$) was obtained by 1:1 w/w ratio of DEX1 – Figure 8(c).

DEX2 show less influence on the strength of polar anchoring. The anchoring energy results obtained for DEX2 were the following: $W = 9.3 \cdot 10^{-4} \text{ J/m}^2$ (1:2 w/w DEX2/PI ratio) and $W = 6.4 \cdot 10^{-4} \text{ J/m}^2$ (1:1 w/w DEX2/PI ratio).

4. CONCLUSIONS

The alignment properties of PI in VAN cells are considerably modified by crosslinking with diepoxides. Anchoring strength is reduced and

voltage threshold is reduced accordingly. Crosslinking also induces a significant increase in pretilt angle from normal. Rise and fall times in the dynamic response are altered as well. All these effects are enhanced when the concentration of the crosslinking agent is increased. The aromatic diepoxide employed in this work shows variations significantly higher than the aliphatic diepoxide. The variation in threshold voltage is enough for delimiting specific switched and unswitched areas with an unpixelated cell, merely employing patterns of crosslinked and non-crosslinked areas in the aligning surfaces.

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