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INFLUENCE OF CHARGE TRANSFER COMPLEX DOPING OF POLYAMIDE ALIGNMENT FILM ON SSFLC CELL PERFORMANCE

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Abstract New alignment films for surface stabilized ferroelectric liquid crystals displays (SSFLCD's) have been produced by doping standard polyamide alignment films with an organic conducting charge transfer complex. The doping process exploits absorption equilibrium between a solution of the dopant and the polymeric solid phase. Dopant concentration in the solid state has been evaluated by spectrophotometric analysis in the UV-visible range. Test displays with ITO electrodes and doped alignment layers have been fabricated and their performance evaluated with new techniques.

It has been found that optical response is a function of dopant concentration in the alignment layer and that display performances can improve at an optimum concentration. In fact addressing hysteresis is reduced at low dopant concentration, but increases at higher concentrations.

INTRODUCTION

Organic charge transfer complexes (CTC) are crystalline complexes formed by partial or total charge transfer from a donor to an acceptor molecule.[1,2,3] The particular arrangement of molecules in the crystals, with donor and acceptor molecules forming stacks of opposite charge, confer high electrical conductivity to these species, which are currently used as conductive filler to dope a variety of polymer matrixes, both amorphous and semicrystalline.[4,5]

A positive influence of doping alignment films with CTC's on the performance of surface stabilized ferroelectric liquid crystals displays (SSFLCD) has been already

pointed out. With rubbed polyimide improved switching amplitude was found[6], with obliquely evaporated SIO_x reduced response time was reported for mixtures with high spontaneous polarization[7,8].

The present work is focused on the development of new FLC polymeric alignment layers with improved performances by doping standard polyamide films with an organic charge-tranfer complex. Poly ε-caprolactam (nylon 6) alignment films produced by mean of spinning techniques have been doped with the ion-radical complex between tetrathiafulvalene and 7,7,8,8-tetracyanoquinodimethane, in the attempt to improve SSFLCD electrooptical response. New sensitive diagnostic techniques have been used to evaluate the results.

EXPERIMENTALS

Preparation of polyamide films

Standard FLC alignment films have been deposited by spinning from a solution of nylon 6 in 2,2,2-trichloroethanol. Then the nylon films were gold shaded, scratched with a razor blade and observed by scanning electron microscopy in order to measure their thickness.

A thickness of about 75 nm was measured for a film obtained by using a 0,5 % weight/volume solution spinned at 4000 rpm.

FIGURE 1 Scanning electron microscope of a nylon film deposited by spinning. The film section appears dark, due to lack of gold.

After spinning the films are amorphous, therefore rubbing is necessary to get aligning capabilities. Rubbing was performed at room temperature, afterwards the film

was annealed at 160 °C in air, cooled, and rubbed again.[9] A rubbing machine equipped with a cylinder covered by a velvet cloth has been employed in order to control pressure during rubbing. This process slightly reduces nylon thickness, down to 40 nm after rubbing and annealing, as Figure 1 shows.

The final standard polyamide films have been taken as reference films.

Doping process

Equilibrium absorption between a solid phase and a liquid one has been exploited in order to dope polyamide films. The polyamide films have been swollen in a distilled dimethylformamide (DMF) solution of the complex, at constant temperature (100 °C), until absorption equilibrium was reached. Then the films were cleaned by means of fresh DMF and dryed in vacuum at 100 °C to allow complex recrystallization. After drying a third rubbing was performed to restore full aligning capabilities.

A set of solutions with different initial CTC concentrations was employed in order to vary the CTC concentration in the solid phase at equilibrium. The actual concentration in the solid state was determined by means of spectrophotometric techniques in the visible spectrum. The bands used are centred at 750 and 840 nm, typical of tetracyanoquinodimethane salts with partial charge transfer[10]. An attempt to evaluate CTC concentration by mean of light absorption in the IR spectrum failed due to excessive light scattering on the doped polyamide film surface.

A simple equation was applied to equilibrium absorption :

$$n_0 = n_s + n_l \tag{1}$$

where n_0 is the number of CTC moles in the initial solution used for doping, n_s and n_l are respectively the number of CTC moles in the solid and liquid phase at equilibrium. Equation (1) may be written in terms of concentrations, instead of moles:

$$c_0 V_l = c_s V_s + c_l V_l \tag{2}$$

being V_s and V_l the volumes of the solid phase and the liquid phase respectively, and c_0, c_s, c_l are the complex concentrations in the initial solution, in the solid and liquid phase at equilibrium respectively. Rearranging:

$$\frac{1}{c_s} = \frac{1}{c_0}\left(\frac{V_s}{V_l} + \frac{c_l}{c_s}\right) \tag{3}$$

In our case it is $\frac{V_s}{V_l} << \frac{c_l}{c_s} = K_{100}$ which represents the partition constant at 100 °C, therefore Equation (3) may be rewritten:

$$\frac{1}{c_s} \cong K_{100} \cdot \frac{1}{c_0} \tag{4}$$

This equation has been used to fit experimental data and calculate the value of the partition function:

$$\frac{1}{c_s} = 11.22 + 8.50 \cdot \frac{1}{c_0} \tag{5}$$

with c_s and c_0 expressed in moles/l (molarity, M). By introducing the molecular weight of the complex, and the density of nylon 6 one finds: c(weight percent) = 34 c(moles/l). The experimental results and the related fitting curve are plotted in Figure 2.

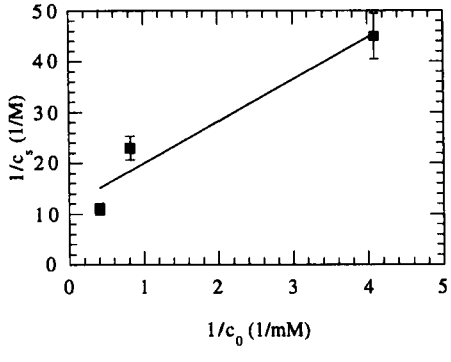

FIGURE 2 Plot used for the calculation of the partition function at 100 °C.

FLC cells fabrication

Test cells were assembled to evaluate the performance of alignment films.

Figure 3 sketches the cross section of a standard test cell. ITO transparent electrodes were patterned on both glass substrates, 1,4 μm thick polyimide spacers and doped nylon 6 alignment layers were used. After assembling, the cells were sealed and filled under vacuum with the ferroelectric liquid crystal mixture Merck ZLI-4851-025.

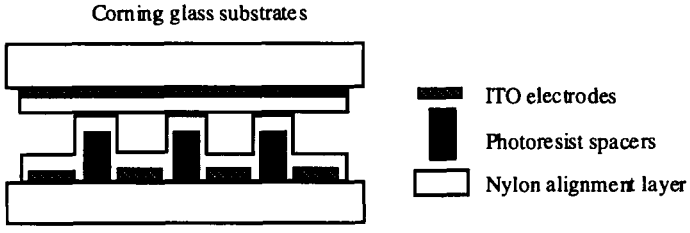

FIGURE 3 Cross section of a test cell. Spacers are photoresist stripes patterned by photolitographic process.

MEASUREMENTS AND RESULTS

The evaluation of the optical response was carried out by using addressing tests designed by Maltese et al.[11] The selection waveform was the $4_{1/2}$:3:1 type (numbers refers to time slots) which is shown in Figure 4. The data waveforms consisted of pulses modulated in position: eight different positions (marked conventionally from 0 to 8) are set corresponding to the white state, six different levels of grey, and the black state. During a single cycle data are repeated eight times at position 0, sixteen times at position 8 and other eigth times at position 0.

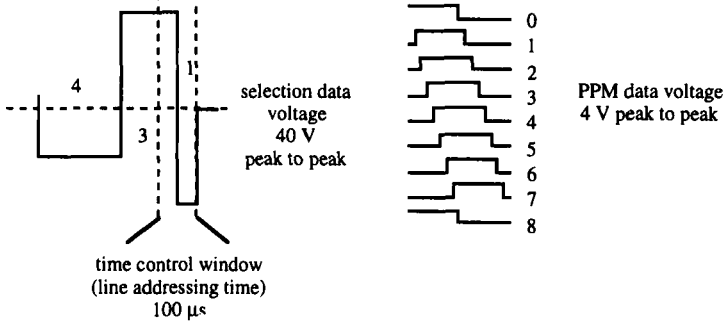

FIGURE 4 Waveforms employed to address the liquid crystals: the position of data pulses is modulated within the control window.

Mixed microdomains are produced for intermediate data and the space and time averaged electrooptical response shows hysteresis, as expected, both for cells using pure nylon (left hand plot of Figure 5) and for those ones using doped nylon (right hand plot of Figure 5).

Measurements were performed at constant selection to data voltages ratio: the

selection voltage was 40 V peak to peak and the data voltage was 4 V peak to peak, with a control window width of about 100 μs adjusted for the best operation of each cell. No significant dependence on CTC doping was found for this time. The high selection to data voltage ratio used is very unfavorable and was adopted to have larger hysteresis and magnify any positive effect due to CTC doping.

The integrated optical transmission was normalized and plotted against data pulse position obtaining hysteresis loops, then Fermi distribution like functions[11] were used to fit both the ascending and descending part of each loop, as shown in Figure 5.

The shape of the fitting curves is a function of some parameters which have been used to compare the electrooptical behaviour of cells with pure nylon and cells with doped nylon. Switching amplitude is the percentage difference between the highest and lowest optical transmission and is directly correlated to optical contrast. Shift is the difference between the x-coord of the ascending and descending curves at the flex point: this is a measure of optical hysteresis. The inclination of the curve respect to the x axis is particularly relevant for the generation of grey shades. The inclination parameter is the slope, which is defined in such a way that the higher the slope, the lower the inclination: therefore a high slope means a high possible number of grey levels.

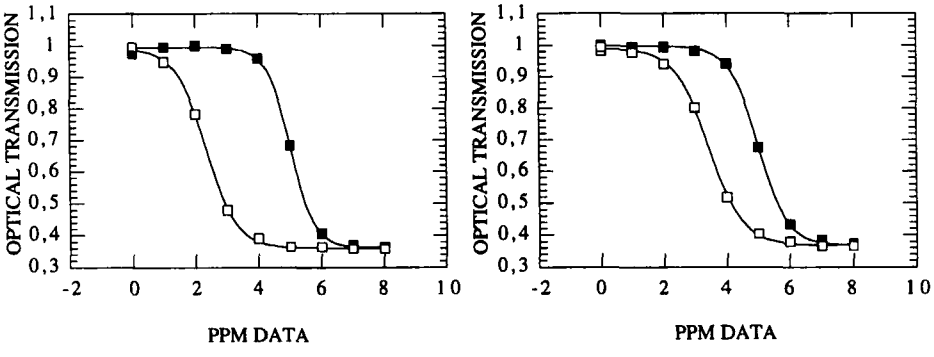

FIGURE 5 Examples of hysteresis loops obtained addressing cells with pure nylon (left plot) and doped nylon (right plot) alignment layers. CTC concentration in doped nylon is 55 mM. The white squares refer to the first half of the cycle from 0 to 8, the black ones to the second half from 8 to 0.

The electrooptical response is a function of dopant concentration in the alignment film. The reference undoped films corresponding to the zero value on the x axis were not solvent treated. It must be pointed out that all measurements were performed also on pure solvent treated polyamide films, and they were found equivalent in all respects. The

left hand plot of Figure 6 reports measured amplitude values versus complex concentration in nylon. This plot shows that switching amplitude has a random behaviour which seems to be due to defects in the measured pixel rather than to the presence of dopant.

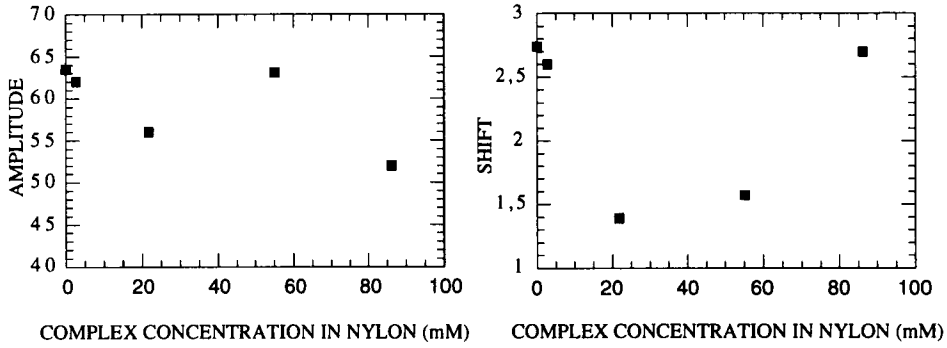

FIGURE 6 Results of switching amplitude (left hand plot) and shift measurements (right hand plot).

The positive effect of CTC on switching amplitude which is claimed in the literature[6] is not evident in our case. It is worth here pointing out that this is the first time to our knowledge that the actual concentration of CTC dopant in the alignment layer has been measured. Moreover, to avoid thermal degradation of the doping agent[7] all subsequent processing steps were performed in our case below 140 °C.

It was observed that doping positively influences hysteresis shift which is reduced by a small amount of dopant, but increases at higher CTC concentration, with an optimum concentration of about 20 mM as one can read from the right hand plot of Figure 6. This behaviour may be due to the low solubility of the complex employed in the liquid crystal mixture used to fill the cell: at high CTC concentrations charges might accumulate in the liquid crystal destroying any positive effect due to doping.

The values of the measured slope are reported in the left hand of Figure 7: no effect of CTC doping was observed at the optimum concentration of about 20 mM.

Finally, a different data pulse sequence was applied to evaluate image sticking: 81 data pulses corresponding to white state were appplied to the cells followed by 81 data pulses corresponding to black state. Sticking was defined as the change in the integrated optical transmission corresponding to the same state, in ratio to the total change[11]. Image sticking of both white and black states (S_W and S_b) is reported in the right side of Figure 7 versus CTC concentration. It may be seen that there is an influence of CTC

concentration on both slope and sticking. A decrease of both black and white state sticking is significatively observed at about the same concentration which assures the lowest value of addressing hysteresis.

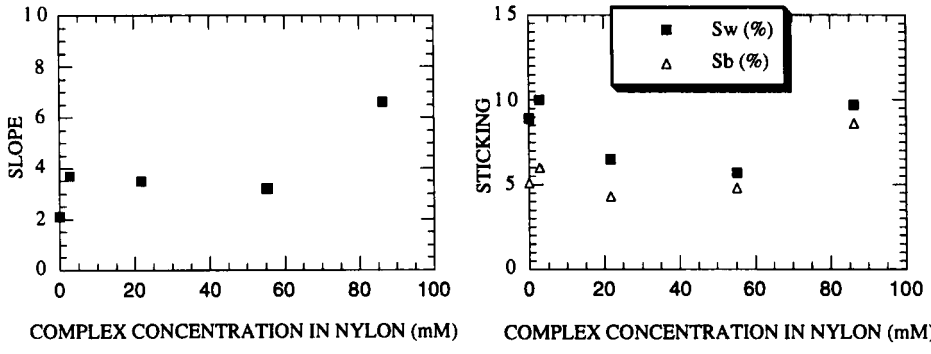

FIGURE 7 Results of slope (left hand plot) and image sticking (right hand plot) measurements.

CONCLUSIONS

CTC doped alignment layers for ferroelectric liquid crystals displays have been prepared by a new doping technique from polyamide films. Doped layers are equivalent to undoped ones in all respects except for addressing hysteresis: a reduction of both shift and sticking is observed for dopant concentration of about 20 mM. Other positive influences of CTC doping as reported in the literature[6,7,8] were not observed in our case.

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