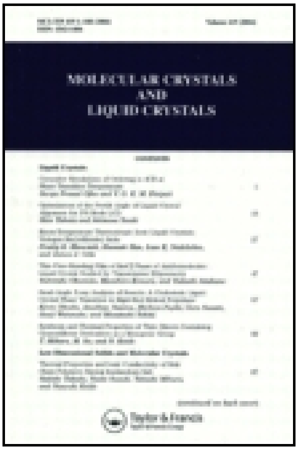

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Improvements in Fabrication Conditions of Liquid Crystal-Polymer Composite Cells

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Improvements in Fabrication Conditions of Liquid Crystal-Polymer Composite Cells

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For the development of reflective flat displays, polymer liquid crystal composite is a good potential challenger material. In order to reduce the driving voltage and to enhance the brightness of the back-scattered off-state, it is necessary to understand and optimise the composite formation. Based on a suitable liquid crystal and polymer couple, we describe a model for the fabrication of polymer dispersed liquid crystal. The influence of the main parameters on the composite production is studied. We choose the case of polymerization-induced phase separation, by means of ultra violet light polymerizing monomer. This study shows how the polymerization parameters control the droplet size and the remaining monomer content, both of which play a role in back-scattering and saturation voltage. We bring to light, the strong temperature sensitivity of PDLC formation and the necessary precautions to reach the optimum performance of the chosen liquid crystal-polymer couple. As this step is essential to exploit PDLC systems, it could also be systematically used to compare then under the best conditions.

Keywords: Liquid crystal, polymer, electro-optic properties, polymerization, polymer-dispersed liquid crystal.

1. INTRODUCTION

One of the most important challenges for flat panel displays is to lower their electrical consumption. Thus, for example, portable computers have only a small working autonomy, because they need a power hunger back light working with the twisted nematic active matrix (AM)[1]. For a few years now, new materials, such as liquid crystal polymer composites (LCPC) have been studied as substitutes for TN liquid crystal, to give purely reflective displays. These materials consist of submicrometer-size nematic droplets dispersed in a polymer matrix and their optical response is based on electrically controlled back-scattered light[2]. Without an electric field, the nematic directors of the droplets are randomly oriented in such a way that part of the light entering the LCPC cell is back-scattered towards the observer, thus, the display appears white. An electric field aligns the nematic droplets, and will thus yield a transparent state, because the ordinary refractive index ($n/_0$) of the LC is chosen to be close to the polymer one (n_p). As a result, the light passing through the LCPC is absorbed by a black sheet placed behind the cell, and the display is black.

The LPCP materials are called polymer-dispersed liquid crystal[3] or in some cases polymer network liquid crystal (PNLC)[4]. In the area of display studies, a lot of work nowadays is devoted to PDLC. The previous main works on PDLC were aimed at finding the most suitable liquid crystal and monomer molecules[5,6].

However PDLC performance does not thoroughly fulfil the display requirements, especially for some properties such as both saturation driving voltage and contrast ratio (CR). In this paper we demonstrate the influence of fabrication conditions which affect the critical characteristics such as driving voltage and brightness. From a description of the PDLC fabrication process, it is possible to get a better understanding of the influence of the parameters fabrication and hence to be able to improve PDLC performances. By using this optimised process, we have made a 10.4″ diagonal VGA alpha grahic direct view reflective display[7].

2. EXPERIMENTAL

2.1. Materials and Fabrication Method

There are only a few suitable liquid crystal-monomer couples for thin film transistor (TFT) PDLC devices, which are actually available. Active matrix-based TFT arrays for flat panel displays[8] need extremely low voltage drives (below 10 Volts), and require very high electrical qualities. The specific resistivity has to be higher than 10^{12} Ω.cm which allows high holding ratio values (98%) or long RC time constants (>2000 ms). Low driving voltage necessitates a thin PDLC film (around 10 μm) and therefore, a LCPC having a strong scattering efficiency in the electrical off-state.

Merck Ltd are developing a new class of materials such as the liquid crystal TL205 ($\Delta n = 0.217$, $\Delta\varepsilon = 5.01$), and the monomer mixture PN393, which achieve both a high birefringence and good electrical properties[9]. This monomer mixture has a large content range of compatibility with liquid crystals and both displays fast curing and full LC phase separation after polymerization.

In our process, we use control of the polymerization parameters to adapt the PDLC structure in order to achieve the best characteristics for AM/TFT display. Our phenomenon interpretation of the UV-PIPS process is developed in Figure 1.

First of all, monomer[10] PN393, and liquid crystal TL 205 (20 to 23% and 80 to 73% respectively), are mixed homogeneously by a mechanical mixer at room temperature[11]. This clear and homogeneous solution is used to fill a standard cell. Secondly, at t = to, U.V. irradiation starts. From "to", the monomer begins to polymerize. After a time "tb", phase separation occurs between the growing polymer phase and nematic phase. Thus the cell bleaches. "tb" takes some seconds. Phase separation goes on and shapes the polymer matrix until time "ts", when the PDLC structure is thoroughly fixed. Time "ts" is around 100 to 200 seconds. In the following, we will show that UV irradiation must be help up to time "tf" for complete monomer consumption. In this way any short monomer molecules cannot pollute the liquid nematic phase. In the same way as "tb" and "ts", depends on U.V. power, and is reached when the energy level needed for the complete polymerization has been attained[12].

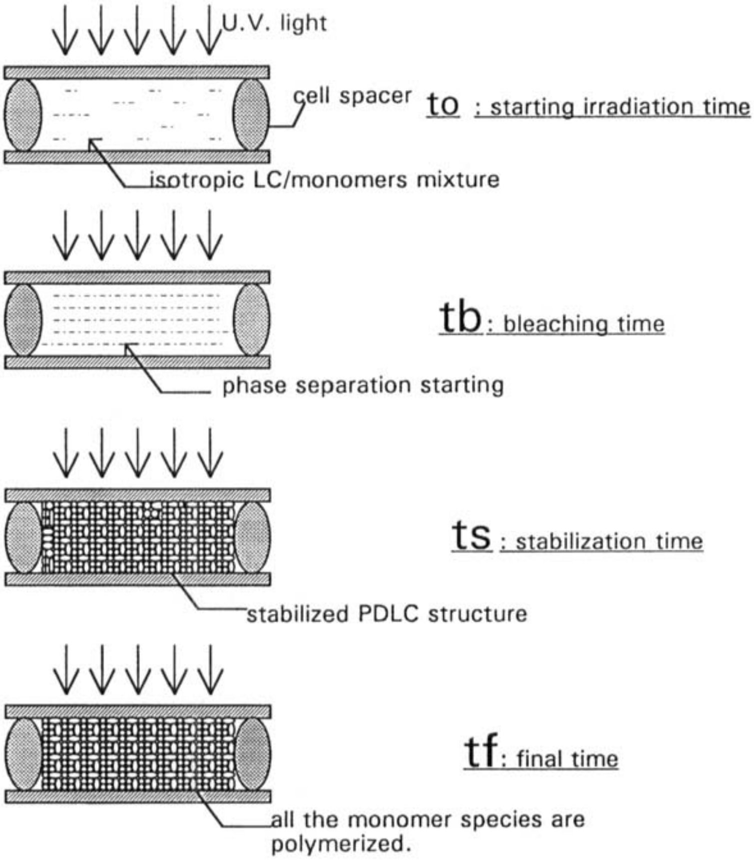

FIGURE 1 Process schema for PDLC formation by UV-PIPS.

2.2. Implementation and Measurements

The standard cells are composed of two indium-tin oxide (ITO) coated glass substrates with spherical polymer spacers. Spacer diameter is chosen between 6 to 14 μm[13]. Cells are filled by vacuum pumping at the outlet while monomer liquid crystal solution feeds the cell inlet. After filling and before polymerization, the cell is pressed (400 Torr) to obtain a correct and uniform thickness[14].

After U.V. curing, the cell is sealed with U.V. epoxy glue. The U.V. light is provided by a medium pressure mercury lamp supplied by Epotecny Co. (ELC 4000 type), and already implemented with an U.V. filter to avoid short wavelengths ($<$ 300 nm). This is fitted to the absorption spectrum (365 nm, 382, and 390 nm) of the electronic vibration bands. In the following, we show the great importance of process temperature, implying that all steps have to be rigorously thermally controlled, and therefore, we also added to the UV source device, a laboratory-made infrared filter to prevent uncontrolled cell heating.

Using the above techniques we produced a large number of cells which were found to have, after measurement, a very good uniformity for driving voltage (better than 0.1 Volt) and off-state transmission (better than 0.1%) over a cell surface of about 20 cm^2.

In the transmissive mode, the electro-optic measurements are made with a Varian spectrophotometer (CARY 2300 model). The transmittance ($100 \times I_T/Io$, where I_T is the transmitted light intensity through the sample, and Io the incident light intensity) is recorded for green light (550 nm). The applied voltge is provided by a Wavetek function generator. Signal shape is an equal mark/space ratio square wave signal at 50 Hz.

Results obtained in the transmission mode allow cell comparison in order to adjust the process parameters to reach the best characteristics. These characteristics are both transmission in the off-state (Toff) and driving voltages V10 and V90 (voltages in Vrms needed to reach 10 and 90% respectively of the total transmitted light of the on-state) which must be as low as possible. After assessment of Toff V10 and V90, we use an integrating sphere device to determine reflective mode characteristics such as the contrast ratio and off-state brightness (luminance of the sample in candela/m^2 divided by the luminance of the $BaSO_4$ standard material). The set-up is shown in Figure 2.

Droplet size was determined by polarized light microscopy using applied voltage to make for easier droplet diameter evaluation. After polymerization it is important to know the amount of monomer remaining in order to determine the polymerization time needed to ensure that the cell properties will be stable. To do this, a cell is opened and the PDLC film is immersed in diethyl ether solvent which solubilizes all free molecules having a molecular weight below 7000 g/mole approximately. After removing the solvent, the free molecules are partly mixed with KBr powder (~ 2 mg for 100 mg). Tablets are cast to record their infrared spectra. By comparing the acrylic carbonyl band (1725 cm^{-1}), it is possible to know all monomer-oligomer species because the known liquid crystal content is taken as an internal standard. Then tablets undergo a vacuum pumping (10^{-2} mbar) during 12 h in order to remove the remaining

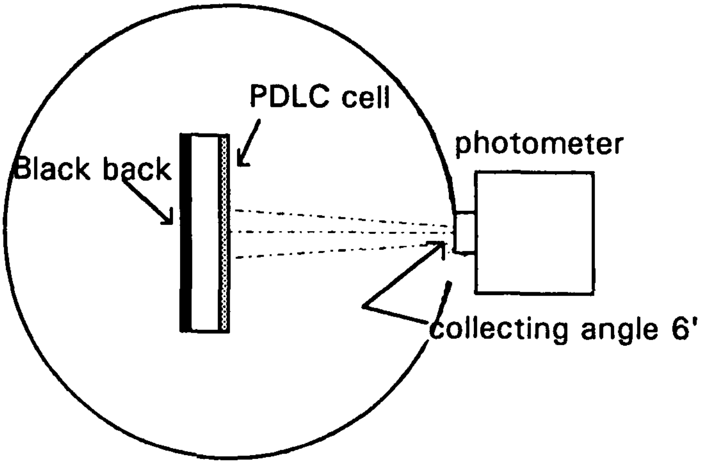

FIGURE 2 Normalised integrated sphere with uniform light radiance for reflective brightness measurements.

monomer and the depletion of the acrylic band provides the monomer content in the PDLC sample.

3. RESULTS AND DISCUSSION

3.1. U.V. Power Influence on Brightness and Transmission

One goal of this study consists of making high brightness or low transmission PDLC cells in the electrical off-state. These characteristics are closely related to droplet size, insofar as submicronic diameters yield poor transmission in the off-state. According to the process fabrication model, it seems that competition between polymerisation and phase seperation phenomena controls droplet diameter. Therefore, the polymerisation kinetics can be adapted to reach the most suitable droplet morphology. The U.V. power level, with which the PDLC material is made, has a determining influence for acting on the polymerisation rate, and thereby the droplet growth rate. To elucidate this, we made PDLC cells using different U.V. power levels ranging from 0.08 to 20 mW/cm^2 everything else being the same. Figure 3 presents the average droplet radius versus UV power. It is remarkable that below 4 mW/cm^2 the droplet size increases as the power decreases, but above this level, the same size remains constant at around

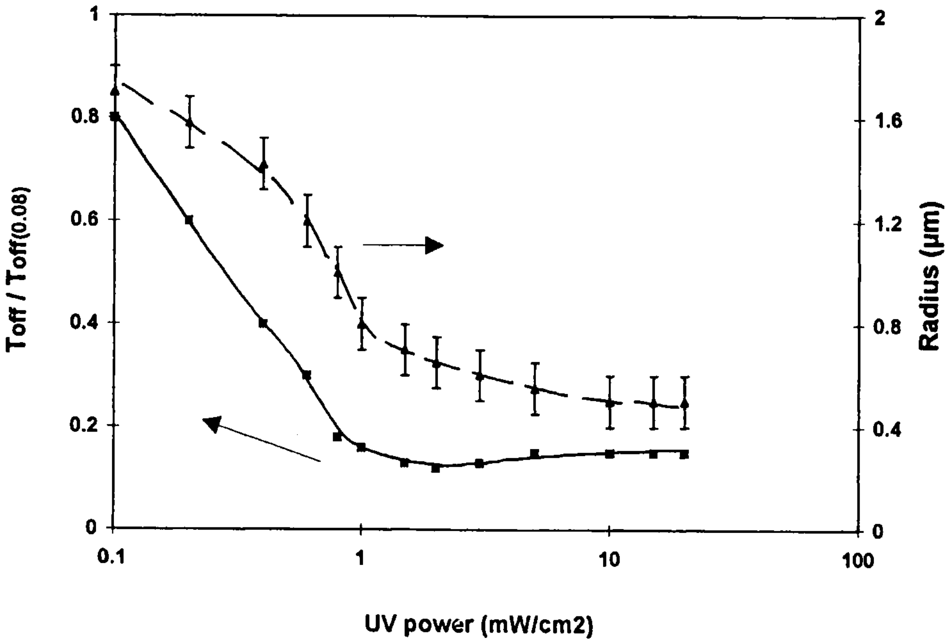

FIGURE 3 Droplet radius and relative transmission in the off-state to TOFF when PUV is 0.08 mW/cm^2, versus UV power.

0.5 μm. For larger sizes, bleaching time can reach a few minutes whereas it is less than one second when the power level is high (i.e. when the droplet size is small).

It appears that, when the polymerisation rate is low, the droplet can grow because the gel point occurs later. For the higher rate, the growth is stopped very early. As a result, the transmission in the off-state is rather low when the power is high and it reaches its lowest value from 4 mW/cm^2 upward.

These results show the strong influence of polymerisation kinetics and indicate that it is necessary to choose a sufficiently high power in order to benefit from strong back-scattering. However, for TFT (or thin film diode) active matrix appplications, we have to take care to fix a power level below the damaged threshold. An acceptabled value is 20 mW/cm^2.

3.2. Total Energy Stabilizing Driving Voltages

In cell fabrication, the total UV energy is often a neglected parameter. It determines the end of the formation process, and it ensures that any monomer traces do not remain in the liquid phase. For example, with the TL205/PN393 couple, after around one min under 15 mW/cm^2 UV light power, a low V90 incited us to stop the irradiation step. However, after a few weeks, this saturation voltage increased noticeably. This effect led us to record V90 during PDLC formation. Figure 4 shows V90 versus time or UV energy measured when the bleaching time has been reached. V90 is seen to decrease until about 2 J/cm^2 (for 20 mW/cm^2, UV power), and during this time, Toff also

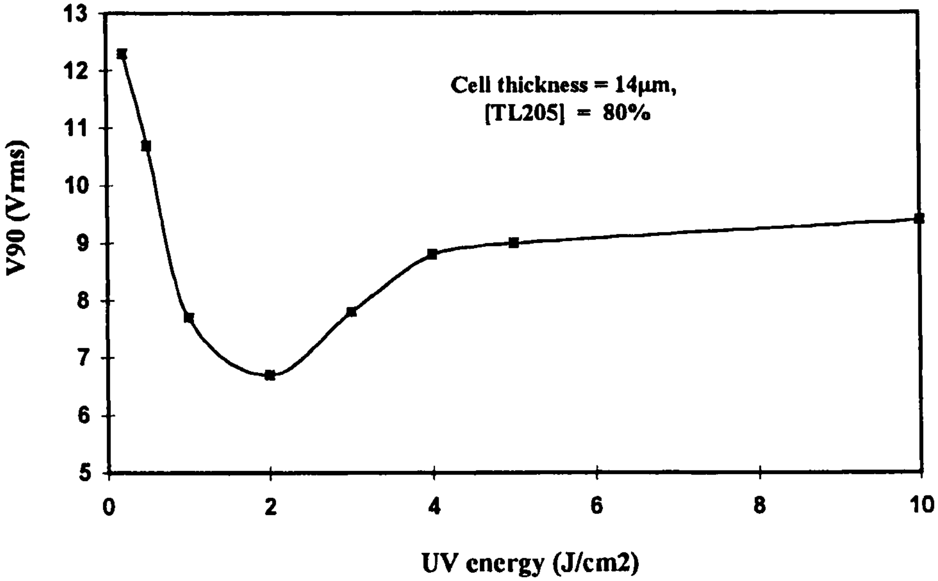

FIGURE 4 Example of saturarion voltage change with energy under 20 mW/cm^2 U.V. irradiation.

decreases. At this point, the layerstructure is stabilised, meaning that the optical properties do not change with time (i.e. "ts" is reached). Beyond this energy level, V90 increases until total energy reaches a few J/cm^2, whereupon the V90 level stabilises. We have verified that all electro-optical properties do not change between 10 and 90 J/cm^2. We did notice that the position of the minimum depends slightly on the UV power.

It is difficult to explain this "V" shaped curve, which is probably due to several causes. Nonetheless it is true that more than 20% monomer content remains in PDLC layer at 2 J/cm^2 while less than 2% is present at the end (10 J/cm^2). A possible reason for the increase in V90 above 2 J/cm^2 could be that the oligomer content increases too. It is well known that free radical type polymerization provides more and more low molecular weights at the end of the polymerisation. As a result, very short length polymer molecules are solubilized in the LC phase, and could thereby raise the saturation voltage.

3.3. Fabrication Temperature Influence on Electro-optical Properties

Fabrication temperature is the third main parameter which acts on polymerisation, and thereby, on the control of PDLC structure. Its influence can be great when process temperature is not far from the phase seperation temperature[15]. For the TL205/PN393 couple we report in Figure 5 cell electro-optic curves for different fabrication temperatures, chosen close to room temperature.

In this case, we observe that when this temperature is lowered by ten degrees, the driving voltages, V10 & V90, are halved. This strong temperature sensitivity shows the

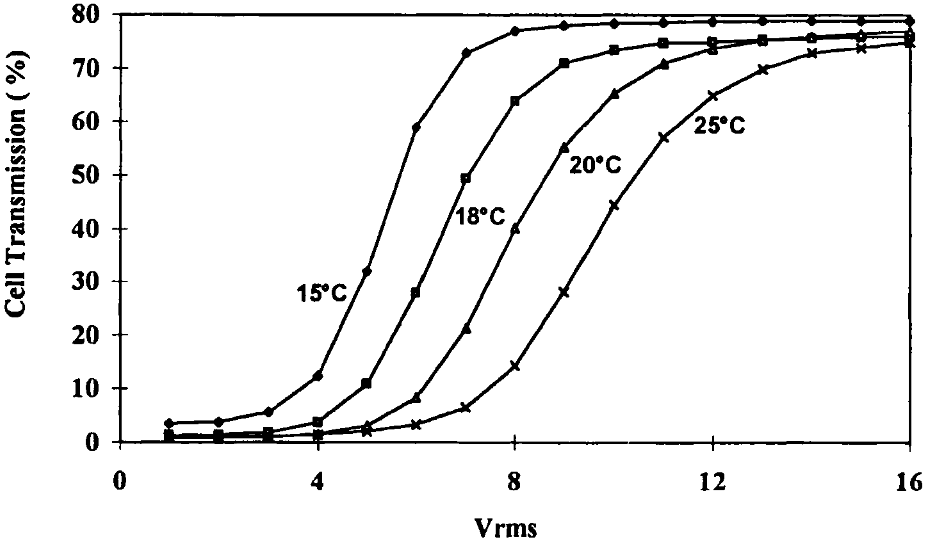

FIGURE 5 Transmission curves at several temperatures. Cell thickness 8 µm, CL(TL205) content: 77%, UV power 20 mW/cm^2.

importance of thermal control. However, to choose the process temperature we have also to consider its effects on cell transmission in the off-state. Figure 6 gives Toff versus the process temperature.

Low temperatures close to phase seperation temperature are not suitable because the transmision in the off state increases sharply. For example, the best compromise between Toff-V90 is around 20°C for a 77/23 TL205 /PN393 mixture.

A possible explanation for this temperature can be found with the process formation model described above. Thus, if the process temperature is brought "ts" and "tb" increases slightly. Therefore the phase seperation duration is increased. As a result, the droplets are larger and the off-state transmission increases too. Up to 25°C, network PDLC structure is insensitive to process temperature and the Toff remains constant.

3.4. Final Optimisation for Active Matrix Display

In order to make reflective flat displays, we applied this methodology to make cells which performed well. In addition to the polymerisation parameters, we have adjusted the others, such as cell thickness and liquid crystal mixture concentration. This last adjustment is made in the reflective mode. Figure 7 represents the electro-optic curves measured on test cells in an integrated sphere (as in set up of Fig. 2).

These curves show a strong enhancement of the brightness for a 14 μm cell thickness, but that saturation voltage also increases. If we want brightness in the off-state to be as high as possible and the driving to be very low, the best compromise is a cell thickness between 7 and 11 μm. Figure 8 shows that the 23% PN393 concentration is the best proportion for a high CR at 10 Volts (these 10 Volts can be reached by using 5 Volts

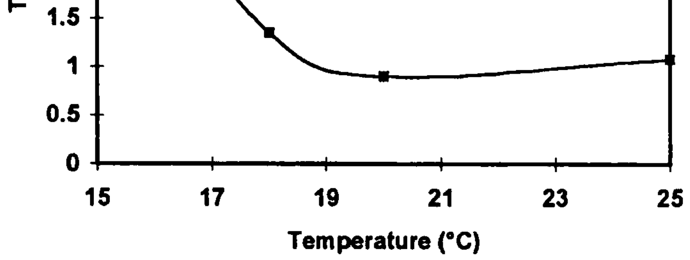

FIGURE 6 Transmission in the off-state versus process temperature for the same cells as in Figure 5.

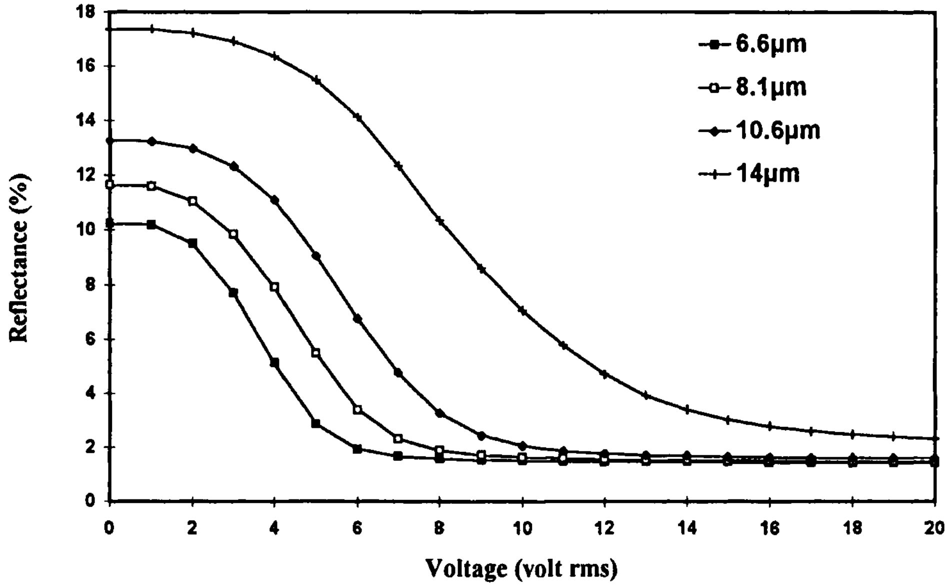

FIGURE 7 Electro-optic curves at various thickness in reflective mode for a 77/23 TL205/PN393 mixture.

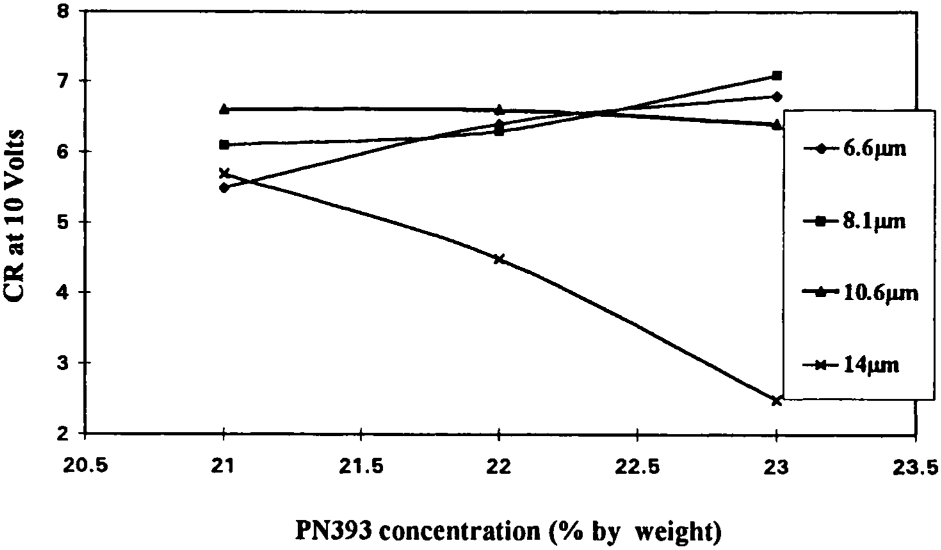

FIGURE 8 Contrast at 10 Volts in reflective mode versus monomer concentration.

electric drivers and alternating the counter electrode voltage at the line frequency of the active matrix)

Therefore, for AM reflective display applications we have chosen an 8 μm cell thickness and a 23% PN393 content. All these conditions enable us to achieve a contrast ratio as high as 7 in the reflective mode with our standard test cell. The electrical requirements for the working of our active matrix display forces this compromise between cell thickness and liquid crystal. It limits the brightness in the off-state at around 12%. This brightness stays lower than the of TN liquid crystal cells. Nevertheless, in the reflective mode, contrast ratio of PDLC cells is higher with benefit of large symmetrical viewing angles compared with TN-LC cells[16].

4. CONCLUSIONS

A formation model of U.V. PIPS LCPC enables us to optimise precisely the conditions to make PDLC cells. This study shows the strong influence of polymerisation control on the electro-optic properties. It leads us to find the best conditions to lower both the driving voltage and cell transmission in the off-state. Based on these results we can now carry out the fabrication of various purely reflective flat panels with good electro-optic properties,[7] e.g. 10.4″ diagonal data graphic active matrix addressed display. These panels have great advantage that they do not use polarizers or require rubbed aligning layers.

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