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Novel PDLC type display based on cellulose derivatives

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A novel type of PDLC display utilizing solid films obtained from the cellulose derivative hydroxypropylcellulose (HPC) with molecular weights of 60 000 (HPC60 000) and 100 000 (HPC100 000), cross-linked with two different di-isocyanates, 1,4-di-isocyanatobutane (BDI) and 1,6-di-isocyanatohexane (HDI), is presented. This kind of display (optical cell) is composed of a porous elastomeric film (20–60 μm thick) of HPC-BDI or HPC-HDI, impregnated with a nematic liquid crystal and contained between two transparent conducting substrates. The electro-optic behaviour of several optical cells is studied as a function of film thickness, the molecular weight of the polymer and the cross-linking agent. The preliminary studies presented in this work show that these systems present good contrast, high transmissivity in the on state and switching times in the range of some milliseconds to hundreds of milliseconds.

Cellulose and some cellulose derivatives have been widely investigated due to the chiral nematic behaviour they may exhibit. These systems appear to be ideally suited for optical applications, especially in laser systems [1], allowing the use of high intensity light sources without significant damage.

Earlier work was dedicated to studies of cross-linked hydroxypropylcellulose (HPC) films obtained by chemical cross-linking with dialdehydes [2–5] and with di-isocyanates (see, for example, [6]), by γ-irradiation [7] and by photoinitiation [8]. In some of the work performed previously, a catalyst was used and the films were made from anisotropic solutions in order to lock in the chiral nematic structure; some other elastomers were obtained from isotropic solutions [6].

Liquid crystals constrained by low concentrations of polymer networks are a new composite system with potential applications in electro-optic devices. This is one type of a polymer dispersed liquid crystal (PDLC) system [9], and PDLCs in general have been intensively studied in the last nine years [10]. The main applications for these materials range from large area displays and transparency controllable windows to projection displays [10].

In this work the polymer network used is a cellulose derivative, hydroxypropylcellulose (HPC) cross-linked with di-isocyanates.

To the best of our knowledge, we describe for the first time the electro-optical behaviour of a liquid crystal constrained in an elastomer of a cellulose derivative. The elastomeric film is obtained from an isotropic solution of HPC in acetone, in which a low level of networking is introduced by chemical cross-linking with di-isocyanates.

These new composite materials have similar performances to standard PDLCs with the advantages of an improved substrate and a high transmission coefficient in the on state.

Materials: Hydroxypropylcellulose (HPC) was of commercial reagent grade—Hercules, klucel E and klucel L, $M_w = 60\,000\,\mathrm{g\,mol^{-1}}$ (HPC60 000) and $M_w = 100\,000\,\mathrm{g\,mol^{-1}}$ (HPC100 000), respectively). Acetone (Aldrich) was used as received. 1,4-Di-isocyanatobutane (BDI) (Aldrich) and 1,6-di-isocyanatohexane (HDI) (Hüls), the cross-linking agents, were used without further purification.

The nematic liquid crystal mixture used was the commercially available E7 (Merck Ltd, UK).

Preparation of solid films: Isotropic solutions (10–20 % w/w) were prepared by mixing the HPC polymer with acetone; the mixture was then stored in a refrigerator ($T \approx 7$°C) for about one week. The solutions were then mixed, under a nitrogen atmosphere, with HDI or BDI (7 % w/w). Optimum conditions for cross-linking (content of di-isocyanate, reaction time before

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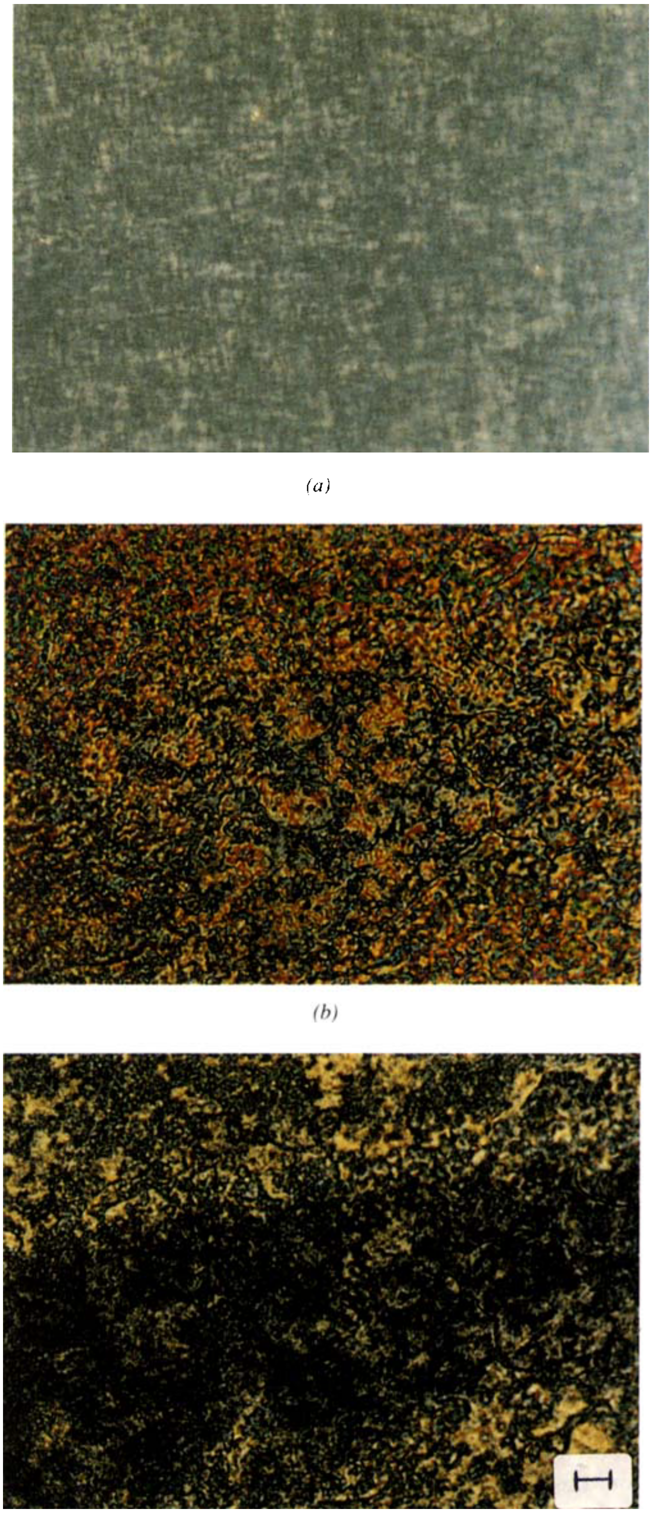
spreading the film and catalyst type) and film characterization are not discussed here [11]. HPC elastomeric films were cast from the isotropic solutions containing BDI or HDI; these solutions were spread on a flat Teflon film, and the solvent was allowed to evaporate for about 4 d in a laboratory atmosphere ($T \approx 20°C$). The solid HPC films obtained (20–60 μm thickness) were transparent and had a refractive index between 1·48(5) and 1·49(0). These films were then placed between two conductively coated glass plates previously covered with a layer of liquid crystal. The polymer/liquid crystal (E7) weight ratio used in our samples was 1 : 1. A percentage around 10 per cent (estimated by separate weighing experiments) of the liquid crystal used is absorbed into the polymer pores, the remainder forming a film between each electrode and the polymer film.

Optical microphotographs were taken using an Olympus microscope equipped with a camera and cross-polarizers.

Electro-optic response: The light transmission analyses were performed using an optical bench equipped with a 7 mW He–Ne laser and a photodiode detector connected to a digital storage oscilloscope. The driving a.c. voltage was obtained from a voltage amplifier connected to a function generator. The frequency of the a.c. electric signal was 4·5 kHz. The voltage dependence of the transmission coefficient was measured using a constant amplitude a.c. signal. To measure the sample switching times, a.c. voltage pulses were used. The amplitude and duration of the a.c. pulses was set in accordance with the sample characteristics. All results were obtained for normal sample incidence.

The optical anisotropy of the cells prepared can be detected by placing them between crossed polarizers. A representative image obtained from polarized light transmission microscopy is presented in figure 1 (*b*). We observed the presence of several multidomains that at the instant that the electric field ($\approx 1{\cdot}1\ \mathrm{V\,\mu m^{-1}}$) was applied changed to the pattern shown in figure 1 (*c*). In figure 1 (*a*) we present the picture obtained for the initial elastomeric solid film of HPC100 000/BDI, containing no liquid crystal.

The table shows the electro-optical results obtained for the five different cells studied. The cells denoted by # were prepared under the same conditions, i.e. without spacers. For these cells prepared without spacers, the effects of molecular weight of the polymer and length of the cross-linking agent on the electro-optical properties can be observed for some pairs of samples with the same thickness. As the molecular weight of the polymer increases (60 000 (#4) to 100 000 (#3)) and the length of the cross-link increases (BDI (#4) to HDI (#1)), the contrast coefficient increases (for film thickness ≈ 20 μm).


(*a*)

(*b*)

(*c*)

Figure 1. (*a*) Initial HPC100 000(#3)/BDI solid film without liquid crystal. (*b*) Microdomains at room temperature of cell HPC100 000(#3)/BDI containing the liquid crystal before electric field is applied. (*c*) As for (b) at the time electric field ($1{\cdot}1\ \mathrm{V\,\mu m^{-1}}$, 50 Hz) was applied. All with crossed polarizers. Bar indicates 20 μm.

Summary of the electro-optical results obtained for the five different cells analysed. The contrast of the cells was obtained from the ratio (maximum transmission)/(minimum transmission). V_{on} was calculated from the voltage dependence of the transmission coefficient and represents the applied rms voltage necessary to reach 95 per cent of the maximum transmission of the sample. t_{on} and t_{off} were calculated from the time dependence of the transmission coefficient. t_{on} is the time required to go from 10 per cent to 90 per cent of the maximum transmission when the sample is subjected to an a.c. electric pulse of amplitude V_{on}. t_{off} is the time required to go from 90 per cent to 10 per cent of the maximum transmission of the sample after removal of the a.c. electric pulse.

Sample	Film thickness /μm	Maximum transmission/per cent	Maximum contrast	V_{on}/V_{rms}	t_{on}/ms	t_{off}/ms
HDI 60 000 (#1)	15	57	63	63	24	18
HDI 100 000 (#2)	64	67	16	120	133	6
BDI 100 000 (#3)	21	79	54	64	76	8
BDI 60 000 (#4)	18	81	22	69	48	13
BDI 100 000 (5)	21	78	470	59	12	6

The effect of these two parameters upon the maximum transmission coefficient seems to be the opposite, i.e. as the molecular weight and the length of the cross-link agent decreases the maximum transmission coefficient has a tendency to increase.

Cell (5) prepared with BDI 100 000 was mounted with 21 μm spacers and the results obtained were improved relative to cell (#3) prepared with the same film thickness, but without spacers (BDI 100 000 (#3) maximum contrast = 54 and BDI 100 000 (5) maximum contrast = 470). It is also seen that cells (#1 to #4) have in general larger t_{on} and t_{off} times than cell (5); this may be due to the fact that these cells were mounted without spacers and the switching on and switching off processes of the cells are perturbed by oscillations of the conducting glass plates.

In figure 2 is presented the voltage dependence of the light transmission coefficient for the 5 samples analysed; it is clearly seen that the samples prepared with the shortest cross-link agent (BDI) show the largest transmission coefficients in the on state. In figure 3 we present the time evolution of the transmission coefficient in cell (5) for different applied electric a.c. pulse intensities.

It is seen that these systems present high transmission coefficients in the on state and can be switched on with electric fields around 3 V μm^{-1}. We also observed that the switching-on process is slower than the fast part of the switching-off process for cells #1 to #4, but a very slow process can also be seen in the switching-off regime. However, this large discrepancy can be reduced if spacers are used (see the table—sample 5).

These materials open up new possibilities to PDLCs, taking advantage of their excellent optical properties. Much work has yet to be done to characterize and optimize these systems, because several parameters can be changed. However, some tendencies can be observed, i.e. the optical properties of the cells are very sensitive to cell thickness, molecular weight of the polymer and the cross-linking agent used.

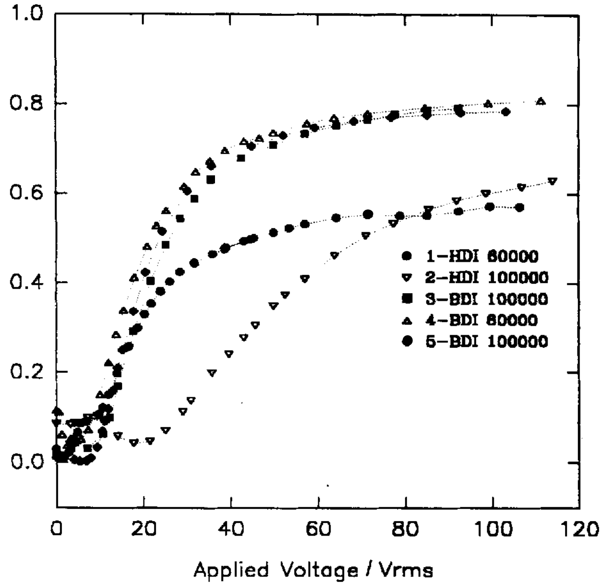


Figure 2. Voltage dependence of the light intensity transmission coefficient obtained for the five samples analysed.

Systems of this type may present, for some applications, advantages over conventional PDLC type systems. The possibility of preparing the polymer in the absence of the liquid crystal component and the high transmission coefficient registered in the on state are two of the main advantages of these types of PDLC system. Systematic studies of the influence of the different parameters that we have here started to study are under way.

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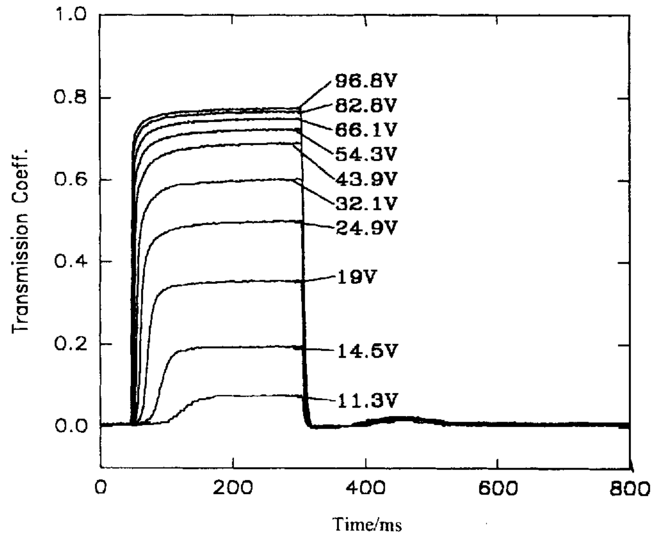

Figure 3. Time dependence of the light intensity transmission coefficient obtained for sample (5) for different values of the a.c. pulse voltage.

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