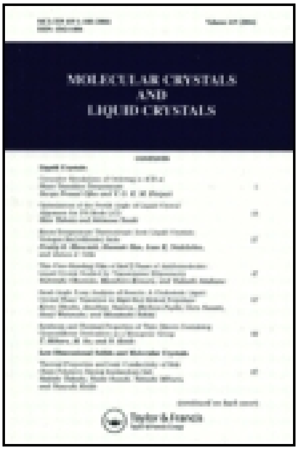

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: P. L. Almeida, M. H. Godinho, M. T. Cidade & J. L. Figueirinhas (2001): Electro-Optical Properties of Cellulose Based PDLC Type Cells: Dependence on the Type of Diisocyanate Cross-Linking Agent Used, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 368:1, 121-128

To link to this article: http://dx.doi.org/10.1080/10587250108029938

Mol. Cryst. and Liq. Cryst., 2001, Vol. 368, pp. 121-128
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Gordon and Breach Science Publishers imprint,
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Printed in the USA

Electro-Optical Properties of Cellulose Based PDLC Type Cells: Dependence on the Type of Diisocyanate Cross-Linking Agent Used

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We have studied the effect of different diisocyanate cross-linking agents on the electro-optical properties of cellulose derivative based PDLC type cells and on the dielectric properties of the films used on their preparation. Each optical cell was assembled with a cross-linked film produced with a different type of diisocyanate and with the nematic liquid crystal (E7). One was assembled with a non cross-linked film. The six different cells were then analysed by light transmission and the results were correlated with the dielectric properties of the cellulosic films used in each one of them. It was found that the cell with the higher contrast is the one prepared with the film cross-linked with 1,4-diisocyanatobutane (BDI) [6]. Based on the results obtained, we propose a mechanism to describe the electro-optical behaviour of these systems.

Keywords: cross-linked hydroxypropylcellulose films; liquid crystals; PDLC; electro-optical properties; dielectric properties; dielectric constant

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INTRODUCTION

Hydroxypropylcellulose (HPC) is readily available at low cost and exhibits a good stability toward UV light [1]. HPC can form solid films that act as barriers to air and moisture [2], therefore, it can be used in coatings that can impart gloss and do not become sticky, even at high humidities, because of their low equilibrium moisture content [2, 3]. HPC is biodegradable and can also be used as a packaging material [3-5]. Recently, it was found that solid films of HPC and HPC cross-linked with diisocyanates can be used as the matrix of a polymer/liquid crystal composite system with application in the production of electro-optical displays [6]. The electro-optical behaviour of such cells depends on the nature of the cellulose derivative used, the nematic liquid crystal, the kind of cross-linking agent used, the preparation conditions of the cells and the rugosity of the films' surface. It was pointed out that one advantage of this kind of systems over conventional PDLC type systems [7], is the possibility of preparing the polymer film in absence of the liquid crystal component [8].

In this work we have determined the frequency dependence of the dielectric constant in the solid films of HPC as a function of the type of cross-linking agent used in their preparation. A qualitative relationship between the type of cross-linking agent, the dielectric constant of the cross-linked HPC solid films and the electro-optical properties of the cells was investigated.

EXPERIMENTAL

Solid films were prepared from solutions of HPC (commercial reagent grade Aldrich Mw=100 000 g mol^{-1}) and acetone (Pronalab), cross-linked afterwards with an amount of 7.0 % w/w of cross-linking agent according to the procedure described previously [6].

The different cross-linking agents used were: 1,4-diisocyanatobutane (BDI) (Aldrich), 1,6 diisocyanatohexane (HDI) (Aldrich), 1,8 diisocyanatooctane (ODI) (Aldrich), 1,12 diisocyanatododecane (DDI) (Aldrich) and toluene diisocyanate (TDI)(Companhia Petroquímica do Barreiro – CPB, Portugal).

The complex dielectric constant of the films was determined with a HP 4284A bridge. The radius of the circular electric contacts used was 1.0 cm, and the measurements were made at room temperature (23 °C) at frequencies between 20 Hz and 1MHz.

The composite material was obtained by covering both surfaces of the solid film (≈ 25 μm thick) with a 10 μm thick layer of the nematic liquid crystal E7 (commercially available from Merck, UK).

Six samples were produced, five with films cross-linked with different diisocyanate cross-linking agents, and one with a non cross-linked film.

The voltage dependence of the transmission coefficient of the optical cells was measured using Helium-Neon laser light and an AC generator operating at the frequency of 1kHz. All the electro-optical results were obtained for normal sample incidence at room temperature (23 °C).

RESULTS AND DISCUSSION

Figure 1 and table I display the electro-optical results obtained for the six different cells studied. The effect of the use of different types of diisocyanate on the electro-optical properties can be observed. These results suggest that the type of diisocyanate used has a strong influence on the cell's minimum transmission and therefor on the cell's contrast. The cell prepared with the film cross-linked with BDI shows the lowest minimum transmission (0.012), while the cell made with the film cross-linked with TDI shows the highest maximum transmission (0.818). Although the BDI cell has a lower maximum transmission (0.762), it shows a much higher contrast (61.28) than the cell with the TDI film (4,16) (Table I).

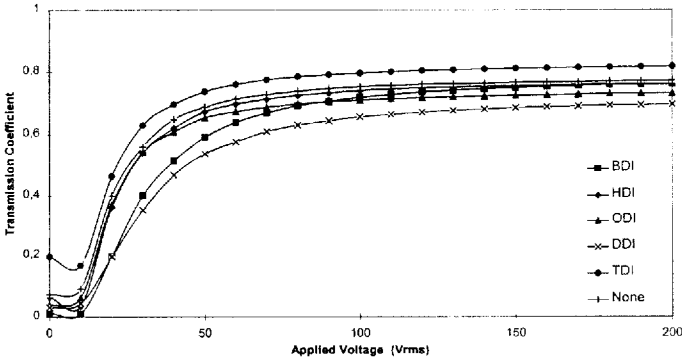

FIGURE 1 Voltage dependence of the light intensity transmission coefficient obtained for the six samples analysed (see Table I).

TABLE I Summary of the electro-optical characteristics of the samples referred to in Fig. 1. The contrast is defined as the ratio of the maximum transmission in the transparent state to the transmission for V=0 in the opaque state. V_{on} was calculated from the voltage dependence of the transmission coefficient and represents the applied rms voltage necessary to reach 90% of the maximum transmission of the sample.

Type of C.L.A.[a]	Minimum Transmission	Maximum Transmission	Contrast	Von (Vrms)
None	0.074	0.7726	10.44	55
BDI	0.012	0.7621	63.51	80
HDI	0.065	0.7631	11.74	65
ODI	0.038	0.7333	19.29	65
DDI	0.031	0.6979	22.51	80
TDI	0.197	0.8180	4.160	50

[a] C.L.A. ⇔ Cross-Linking Agent

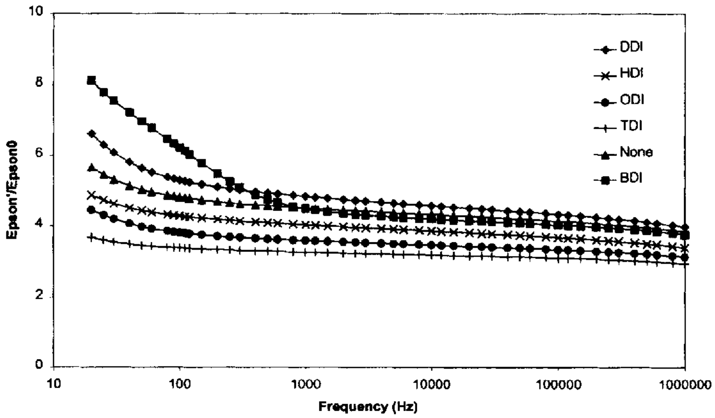

FIGURE 2 Frequency dependence of the real permittivity ($\varepsilon'/\varepsilon_0$) obtained for the six samples analysed (see Table II).

Figure 2 and table II display the real part of the complex dielectric constant results obtained for the six different cells studied.

The effect of the use of different types of diisocyanate on the dielectric properties can be observed.

TABLE II Summary of the real permittivity and conductivity values for a frequency of 1 kHz referred in Figure 2.

Type of C.L.A. [a]	$\varepsilon'/\varepsilon_0\ (\varepsilon_r)^b$	$\sigma\ (\Omega^{-1}\ m^{-1})^c$
None	4.5089	1,1533E-08
BDI	4.4924	3.8945E-08
HDI	4.0309	9,1878E-09
ODI	3.5921	7,5902E-09
DDI	4.8384	1,5604E-08
TDI	3.2626	4,3541E-09

[a] C.L.A.⇔ Cross-Linking Agent. [b] $\varepsilon_r = \varepsilon' / \varepsilon_0$, [c] Conductivity

Figure 3 displays the real permittivity results obtained, as a function of the voltage V_{on}, for the six different cells studied. A tendency of increase of V_{on} with increase in the real permittivity seems to dominate the electric behaviour of the samples.

The V_{on} voltages obtained for the different cells correspond to switching electric fields substantially higher than those normally required to reorient nematic layers of 10 µm thickness as those found for instance in twist nematic cells. One is then faced with the question why such relatively high fields are required for switching these systems. The first hypothesis would be to have the majority of the applied voltage falling on the cellulosic film due to a low value of its dielectric constant, comparatively with the values for E7 ($\varepsilon_{//}/\varepsilon_0=19$, $\varepsilon_{\perp}/\varepsilon_0=5.2$)[10], since the optical cell is approximately a capacitors series circuit. If this was the case, an increase in the dielectric constant of the cellulosic film should produce a lower switching voltage, contrary to what is seen experimentally. Other explanation that seems much more plausible has to do with the process of reorientation of the nematic layers in between the polymeric film and the glass substrate. Looking at the Figure 1, we observe that the voltage dependencies of the transmission coefficients, for the majority of the cells studied, show a minimum value for applied voltages below 10 V, the corresponding fields are compatible with the switching fields for 40 μm thick oriented nematic layers [11]. We propose then the following scenario to explain the high voltages required by these kind of cells:

Up to the voltage when the transmission shows an absolute minimum V_{min}, only the director in the core of the nematic layers reorients under the external field action, the director near the rough polymeric surface does not change its orientation. The largest optical mismatch between the liquid crystal in the surface and in the core of the nematic layer is then obtained at V_{min}. For voltages above V_{min}, the director near the surface begins to reorient and the optical mismatch between the surface and the core of the nematic layers begins to decrease, increasing the overall light transmission coefficient. This hypothesis is in agreement with the light scattering results obtained recently in these kind of systems [12], where it was concluded that the most important contribution for the transmission coefficient comes from refractive index mismatches between the core and the surface of the nematic layers. In this scenario V_{on} will be mostly determined by the surface interaction between the nematic and the polymeric film leaving to second plane the influence of the films dielectric constant on V_{on}.

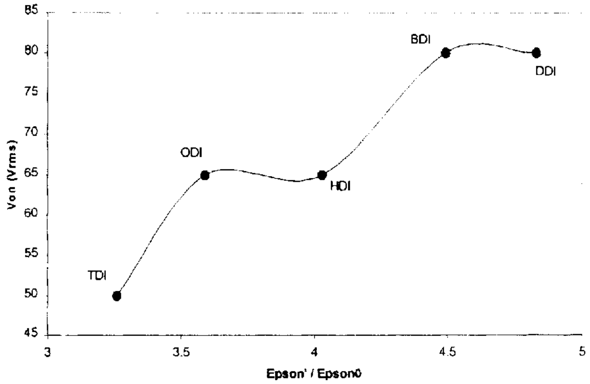

FIGURE 3 Relation between the Voltage V_{on} and the real permittivity ($\varepsilon'/\varepsilon_0$) for 1 kHz.

Acknowledgements

This work was supported by PRAXIS XXI, Portugal, under research contract 3/3.1/CEG/2620/95. P.L. Almeida wishes to thank partial support from the PRAXIS programme grant no. PRAXIS XXI BD 17071/98.

The Authors thank M. Dionísio for making possible the dielectric measurements and for critically reading the manuscript.

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