Electrooptic properties of polymer dispersed liquid crystals

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An investigation of the electrooptic properties of polymer dispersed liquid crystals (PDLC) is presented. These materials are light modulating systems. They show a reversible optical response from an opaque state to a highly transmitting state under the action of an appropriate electric field which aligns the liquid crystal director. The switching voltage required to establish such an electric field has been monitored as a function of (i) the starting materials used for the preparation of the PDLCs, (ii) the ageing (curing time) of the PDLC cells. Other physical properties, such as the electrical resistivity and the dielectric constant of the materials, have been measured. The correlations between these properties have been studied. The PDLC switching voltage appears to be strongly correlated with the resistivity. Our data suggest that ionic impurities play a dominant role with respect to the electrooptic response of PDLC films.

1. Introduction

Polymer dispersed liquid crystals are composite materials constituted of liquid crystal droplets having a size of the order of microns, embedded in a transparent polymer matrix. It has been recently observed that such materials can be easily obtained through phase separation processes [1–5]. One of these processes involves the mixing of a liquid crystal with a low molecular weight, fluid and transparent pre-polymer. A fluid and optically transparent solution is obtained, which can be gradually cured by U.V. light or by adding a chemical curing agent. As the reaction proceeds, the liquid crystal gradually becomes less soluble in the forming polymer and eventually sub-micron droplets can be nucleated. At the end of the curing process the material consists of nematic droplets cast in a solid matrix, as shown schematically in figure 1. Similar materials can also be obtained by thermally induced phase separation processes [6]. PDLC films can be used as electrically controlled light valves. As shown in figure 1, when the liquid crystal director is randomly oriented, the film is in a white opaque state due to the light scattered from the droplets. When an electric field is applied across the film, the liquid crystal director is oriented in a direction parallel to the field, if the dielectric anisotropy, $\Delta\varepsilon$, is positive. In this case the PDLC becomes transparent if $n_{\perp}$, the liquid crystal refractive index for light polarized perpendicular to the nematic director, matches the refractive index of the polymer. The effect is completely reversible on removing the electric field, and the switching time can be of the order of milliseconds. PDLC materials are very promising for applications in display technology, especially for fabrication of large scale flexible displays. The use of PDLC films overcomes the two major problems normally encountered in display technology, that is to say the liquid crystal fluidity and the need for light polarizers.
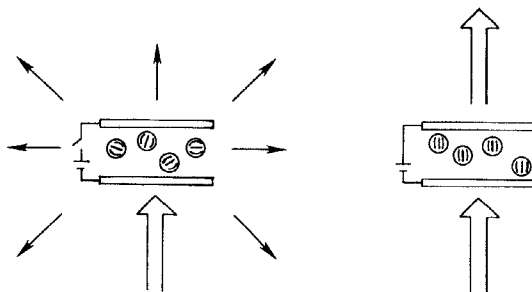
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Figure 1. Schematic representation of the use of PDLCs as a component of a display.

Since PDLCs are relatively new materials, very few studies concerning their chemical and physical properties are available in the literature. The optical transmission across PDLC films has recently been studied extensively [6–9], but other properties such as resistivity, dielectric constant, switching voltages and switching time still require an extensive investigation. The aim of this paper is to clarify the connections of the switching voltage of PDLC cells, that is to say the voltage needed to switch the cell from the opaque state to the clear state, with their resistivity and dielectric constant. The interest for these studies results from the fact that usually the switching voltage for PDLC cells is higher than that needed for other conventional displays, ranging between ~15 and more than one hundred volts as a function, among other things, of the polymeric resin and the curing process used in their preparation. It is then of great interest to understand the factors determining the switching voltage to be able to choose materials having suitable properties for specific PDLC technological applications.

2. Experimental

The procedures and methodology employed in our study can be summarized in the following steps.

(1) Many DPLC displays have been prepared by using different low molecular weight epoxy resins and different curing agents, and also by changing the relative quantities of these components.
(2) The switching voltages have been measured as a function of the aging of the PDLC cells (that is to say for different curing times).
(3) The resistivity and dielectric constant of the PDLC cells have been measured.
(4) The possible correlations between the different quantities measured have been established and explained in terms of a very simple model.

The liquid crystal employed in the PDLC preparation was the E7 mixture from Merck. The following commercially available epoxy resins purchased from Shell Chemical Co., Huston USA, have been used:

(1) EPON 828, with chemical structure:
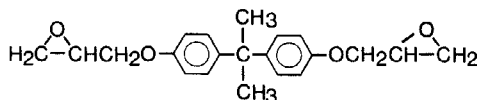
(2) EPON 165, having a chemical structure identical to that of EPON 828, except for the substitution of the phenyl rings with cyclohexane rings:

$$\text{H}_2\text{C}-\text{CHCH}_2\text{O}-\langle\text{H}\rangle-\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CH}_3}{|}}{\text{C}}}-\langle\text{H}\rangle-\text{OCH}_2\text{CH}-\text{CH}_2$$
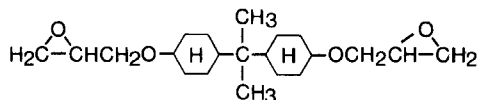
(3) EPON 185. In our study the curing process has been always achieved by means of chemical agents such as:
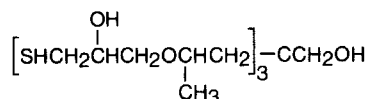
Capcure 3-800 (from Diamond Shamrock USA), having the structure

$$\left[\text{SHCH}_2\overset{\overset{\text{OH}}{|}}{\text{CHCH}_2\text{O}}\overset{}{\underset{\underset{\text{CH}_3}{|}}{\text{CHCH}_2}}\right]_3-\text{CCH}_2\text{OH}$$

A polyaminic mixture from Bostik, Italy.

In some cases the Capcure 3-800 curing agent has been used together with small quantities of the curing catalizer 2,4,6,-tris (N,N-dimethylaminomethy)phenol.

PDLC materials have been prepared by mixing appropriate amounts of the resin, curing agent and liquid crystal in small vials. The mixtures have been centrifuged to remove air bubbles. Samples for electrooptic measurements have been obtained by sandwitching the originally fluid mixtures between conductive glass. A uniform cell thickness of $30\,\mu\text{m}$ has been ensured by using mylar spacers placed between the conductive glass. The switching voltage has been determined by measuring the light transmitted across the PDLC cell under the application of A.C. fields: the voltage needed to ensure 90% of the maximum transmitted light across the device has been taken as the switching voltage. The error in the measurements has been estimated to be $\sim 2\,\text{V}$.

The resistivity and dielectric constant of the materials have been measured by inserting the cells in an automatic precision bridge (Wayne Kerr B 905 A), using an A.C. signal with a frequency of 1 kHz. PDLC materials have resistivity ranging from $0\cdot1$ to $1000\,\text{M}\Omega\text{m}$. It is then necessary to consider a PDLC device as a capacitance in parallel with a resistor. The resistivity, ϱ, and dielectric constant, ε, have been calculated from the value of the capacitance, C, and resistance, R, measured by the bridge using the relations

$$\varepsilon = \frac{Cd}{A\varepsilon_0}, \quad \varrho = \frac{RA}{d}, \tag{1}$$

Here A and d are the area and thickness of the cell, respectively. The PDLC cells were observed under a polarizing microscope, in order to check roughly the size of the liquid-crystalline droplets. In our samples the diameter of the droplets has been kept constant at about 1–$2\,\mu\text{m}$.

3. Results and discussion

In the following discussion, as well as in the table and the figures, PDLC samples are identified by a symbol, indicating the materials used for their preparation. The first part of the symbol is a number which identifies the type of epoxy resin used as

Resistivities and dielectric constants of the single components used for the preparation of PDLC's.

Materials	ϱ/Ωm	ε
828	$1{\cdot}82 \times 10^8$	$7{\cdot}14$
815	$6{\cdot}60 \times 10^6$	$8{\cdot}03$
165	$7{\cdot}07 \times 10^4$	$8{\cdot}48$
CC1%	$4{\cdot}20 \times 10^5$	$10{\cdot}26$
CC2%	$4{\cdot}06 \times 10^5$	$7{\cdot}02$
C	$3{\cdot}83 \times 10^5$	$10{\cdot}67$
B	$6{\cdot}60 \times 10^5$	$10{\cdot}75$
E7	$\begin{bmatrix} 2{\cdot}44 \times 10^7 \\ 1{\cdot}99\dagger \times 10^7 \end{bmatrix}$	$\begin{matrix} 6{\cdot}49 \\ 11{\cdot}27\dagger \end{matrix}$

†Measured with an applied electric field

starting polymer. This number corresponds to that used in the commercial name of the compounds (828 for the Epon 828, 165 for the Epon 165 and so on). The other letters and number follow to identify the type of curing agent: C and B are used to identify the Capcure 3-800 and the polyaminic mixture from Bostik, respectively; CCn indicates the Capcure 3-800 containing n% of 2,4,6,-tris(N,N-dimethylamino-methyl)phenol; BC is a B and C mixture. The liquid crystal has been indicated with its commercial name used by Merk (E7). As an example the symbol 828 B E7 indicates a PDLC material made from Epon 828 plus the polyaminic curing mixture from Bostik and the E7 liquid crystal. It is shown in the following that it was necessary to study the electrical properties of the cured polymer itself. In this case the identification symbol obviously lacks the E7 extension.

Samples were prepared by mixing known amounts of epoxide resin (W_{res}), curing agent (W_{cur}) and liquid crystal (W_{lc}). The amount of liquid crystal contained in the analysed mixtures was always 1/3 of the total weight: $W_{lc} = (W_{res} + W_{cur})/2$. As a consequence only one parameter is needed to identify the composition of the PDLC mixtures, that is to say the weight ratio between the curing agent and the eposide resin: $r = W_{cur}/W_{res}$. In figure 2 the switching voltages of the PDLC materials measured at three different curing times are reported as a function of composition. A first comment is that the switching voltage increases with increasing curing time. The effect is particularly large for the 828 B E7 and 815 CC1 E7 systems. The switching voltage is initially below 10 V for values of r of about 0·7. Unfortunately it can be seen that with the ageing of the materials it can increase by more than one order of magnitude. The explanation of this effect is the principal aim of our investigation.

The variation of the switching voltage with the curing time is not a consequence of a large variation in the sizes of the liquid crystal droplets, which were found to be constant by polarizing microscopy. On the other hand the effect is too large to be associated with a variation in the surface interaction between the polymeric matrix and the liquid crystal molecules. To understand the reasons of such behaviour we decided to undertake an extensive investigation of other electrical properties such as the resistivity and the dielectric constant of the PDLCs, of the starting materials and of the polymers cured without liquid crystal. The resistivities and dielectric constants of the starting materials are shown in the table. It must be noticed that while the dielectric constants of the different materials vary within a limited range, the resistivities fall in a very large range between 7×10^4 and 2×10^8 Ωm, approximately. For example Epon 828 is highly resistive ($1{\cdot}82 \times 10^8$ Ωm), while the analogous Epon 165
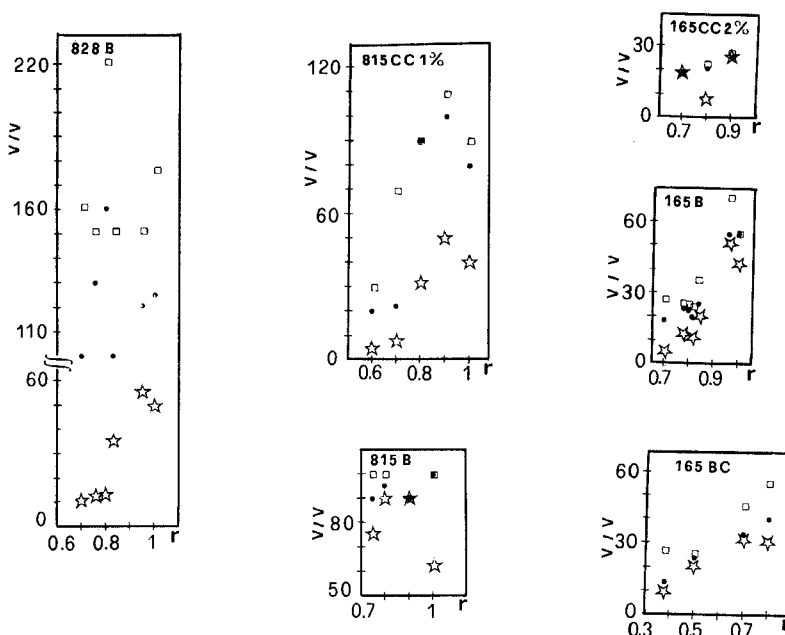
Figure 2. Switching voltages of PDLC systems (the meaning of the identification symbols is explained in the text) as a function of composition (r) and curing time (☆, 1 day; ●, 2 months, □, 4 months).

has a resistivity three orders of magnitudes lower (7·07 × $10^4 \Omega$m). We believe that such a difference cannot be attributed to an intrinsic property of the resins themselves, since their chemical structures are very similar. A possible explanation for the observed difference can be a different impurity content, such as ions or humidity, in the two materials.

In order to gain further information on the electrical behaviour of PDLC materials we have studied the resistivity of the polymers without liquid crystal for different curing times. The results of such investigations are summarized in figure 3. For the 815 CC1, 165 CC2 and 165 BC materials, the resistivity increases with curing time, while it remains almost constant for the 828 system. This must be attributed to the gradual hardening of the materials with the evolution of the curing process. It seems obvious that the growth of branches among the linear polymer chains reduces the ion mobility. For the 828 system the curing process is very fast and this may be the reason for the constant resistivity observed with the ageing of the materials.

Taking into account the resistivity of the cured polymers as a function of the composition it can be seen that systems obtained from EPON 828 and EPON 815 show a gradual decrease of resistivity with increase of the percentage of curing agent. This may be due to the fact that the resistivities of the curing agents are always much lower than those of the epoxy resins, suggesting that the increment of r corresponds to an increment in the number of ions in the cured polymers. This interpretation is confirmed when resistivity data obtained for EPON 165 polymers are taken into account. In this case the resistivity tends to increase when the amount of curing agent increases, because of the lower resistivity of the EPON 165 with respect to the resistivity of the curing agents.
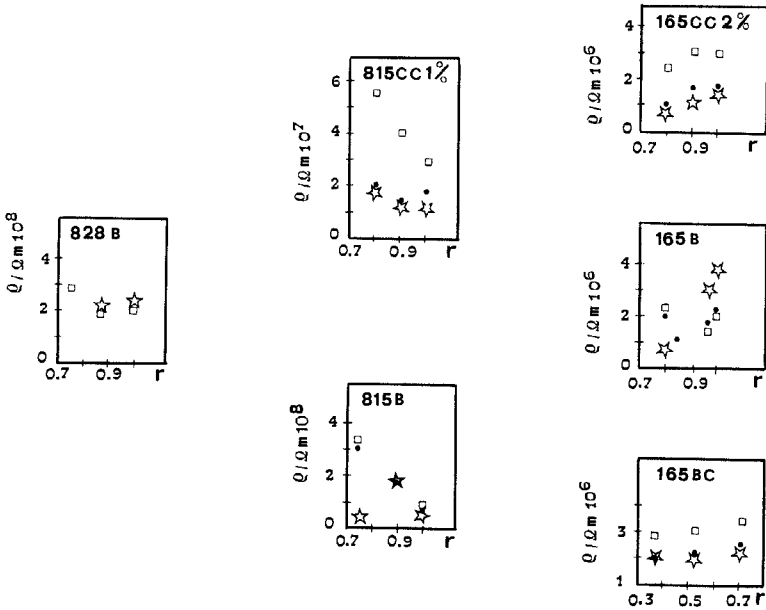
Figure 3.   Electrical resistivity of the polymers used for the preparation of the PDLCs as a function of the weight ratio between the curing agent and the epoxy resin (r) and of the curing time (☆, 1 day; ●, 2 months; □, 4 months).
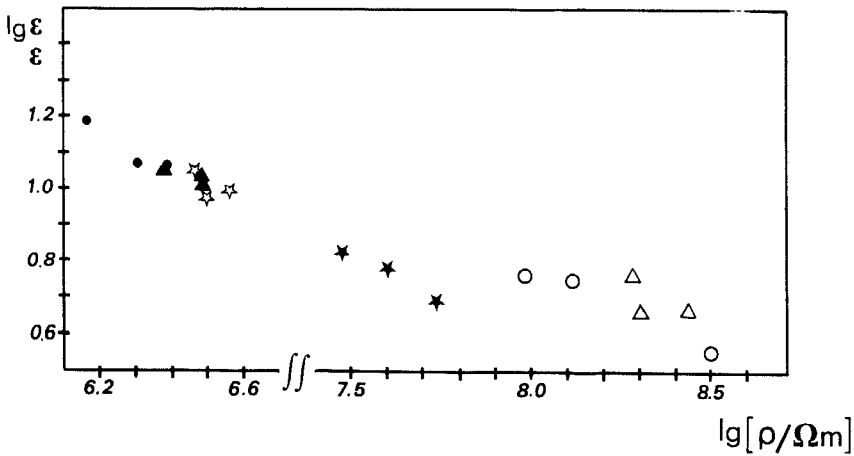

Figure 4.   Correlation between resistivities and dielectric constants of cured polymers (curing time of 4 months). ▲ = 165 CC2 per cent; ☆ = 165 BC; ● = 165 B; ★ = 815 CC1; ○ = 815 BC; △ = 815 B.

The dielectric constant data for the different polymers show a composition and curing time dependence always opposite to that of the resistivities. For brevity we do now show them here. The dielectric constant-resistivity correlation is shown in figure 4, where the logarithm of ε is reported as a function of $\log \varrho$ for every analysed cured polymer and for a curing time of 4 months. It can be seen that there is an inverse proportionality between ε and ϱ. This is an indication of ion polarizability as the main mechanism determining the dielectric constant of the polymers. In this case, in fact,

a reduced ion mobility leads both to an increase in the resistivity and to a reduced polarizability of the materials. Similar considerations can be made when examining the resistivities measured from the PDLC materials; these are shown in figure 5. It is again observed that the resistivities increase with the curing of the materials, because of the decreased ion mobility. The dependence on the composition is less regular than that observed for cured polymers, even if the general trend of the data remains analogous.
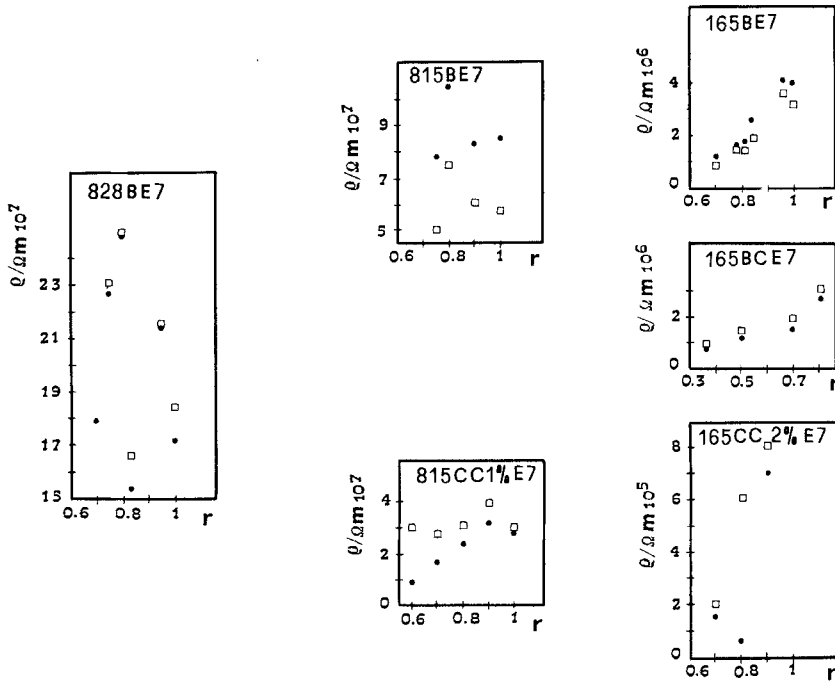
Figure 5. Resistivity of PDLCs as a function of polymer composition, r, and curing time ($\star$, 1 day; $\bullet$, 2 months, $\square$, 4 months).

An attempt has been made to reproduce the resistivities of the PDLC materials by averaging the resistivities of the cured polymer and of the liquid crystal, according to

$$\varrho_{PDLC} = x\varrho_{LC} + (1 - x)\varrho_{POL}, \tag{2}$$

where ϱ_{PDLC}, ϱ_{LC} and ϱ_{POL} are the resistivities of PDLC, liquid crystal and cured polymer respectively, and x is the volume fraction of the liquid crystal, which can be approximated by the weight ratio. The data reported in figures 3 and 5 do not always satisfy equation (2). It only holds, in some cases in particular for $r \sim 1$ (815 CCl E7, 165 BC E7). For $r < 1$ the calculated value for ϱ_{PDLC} is much higher than the experimental resistivities of the PDLC materials.

Equation (2) is based on the hypothesis that both the number of ions and their mobilities in the liquid crystal and polymer, mixed in a PDLC system, remain equal to those of the separated materials. The failure of equation (2) for $r < 1$ can probably be attributed to the fact that the polymer part of the PDLC systems, at a given curing time, may be less cured with respect to polymers not containing liquid crystals. It is also possible that the ion content in the droplets and in the polymer changes drastically

due to diffusive processes. The dielectric constants of PDLC materials are correlated with their resistivities in a way similar to that already discussed for the cured polymers. Such a correlation is shown in figure 6.

The most interesting information can be obtained when the PDLC resistivities are correlated with the switching voltages. We do not show any plot of the switching voltages against the dielectric constants since ϱ and ε are linked by an inverse proportionality and no further independent physical effect would be discovered by such a correlation. From figure 7 it can be seen that, at least in four of the systems (828 B E7, 165 BC E7, 165 B E7, 815 CC1 E7), the switching voltages increase linearly as a function of the resistivities. In the other cases (815 B E7, 165 CC2 E7) the switching voltage does not appear to be correlated with the resistivity.
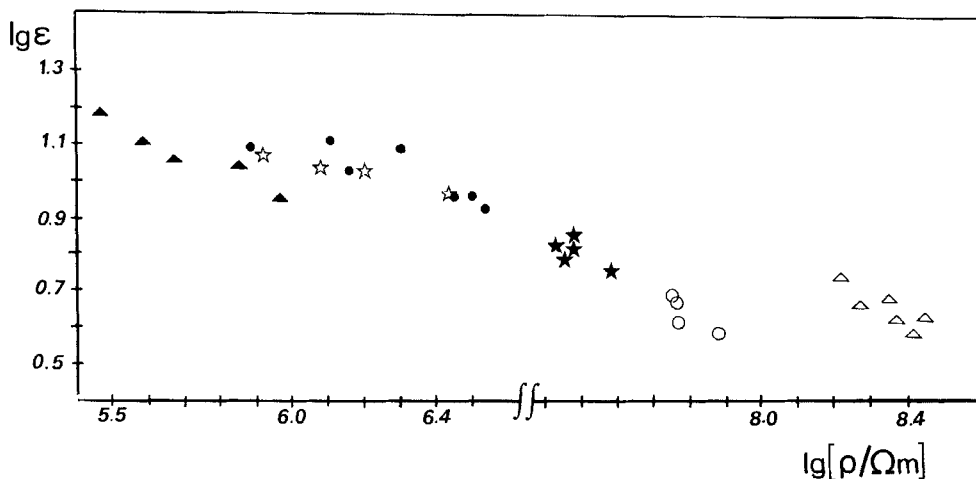

Figure 6. Correlation between resistivities and dielectric constants in PDLCs. The curing time is 4 months. ▲ represents 165 CC2 per cent E7; ☆, 165 BC E7; ●, 165 B E7; ★, 815 CC1 per cent E7; O, 815 BC E7; and △, 815 B E7.

These apparently contradictory results can be explained on the basis of a very simple model. We assume, as we did with equation (2), that the PDLC real impedance can be considered as an average due to two resistors connected in series. Considering the geometry of the PDLCs this is only a rough approximation but it allows a simple interpretation of our experiments. In this case, if V is the voltage needed to orient the nematic director in the droplets, the effective voltage, V_{eff}, which must be applied to the PDLC cell is

$$V_{\text{eff}} = \frac{R}{R_{\text{lc}}} V, \tag{3}$$

where R is the total resistance of the PDLC cell and R_{lc} is the resistance of the liquid crystal. Equation (3) can be rewritten as

$$V_{\text{eff}} = \frac{\varrho_{\text{lc}} + \varrho_{\text{p}}(x_{\text{p}}/x_{\text{lc}})}{\varrho_{\text{lc}}} V, \tag{4}$$

where x_{p} and x_{lc} are the volume fractions of the polymer and nematic respectively, while ϱ_{p} and ϱ_{lc} are the resistivities assumed by the two materials once they are mixed in the PDLC system (These are in principle different from the resistivities of the two
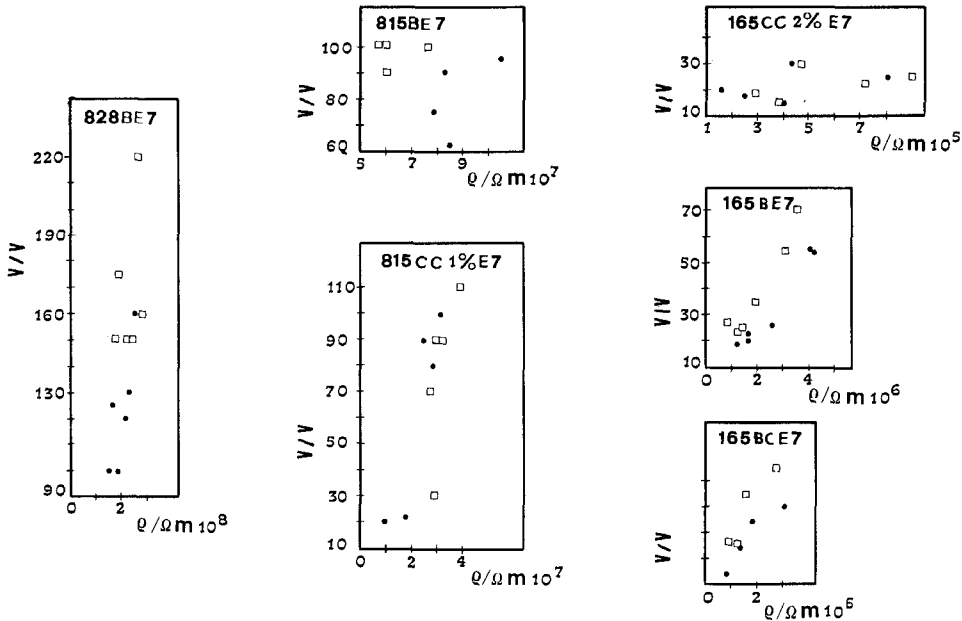
Figure 7. The switching voltage for PDLCs as a function of the measured resistivities and curing time (●, 2 months; □, 4 months).

separate components). The ratio x_p/x_{lc} can be approximated by the polymer to liquid crystal weight ratio, which for our samples is always equal to 2. On the other hand $(\varrho_{lc} + 2\varrho_p)/3$ is the average resistivity of PDLC materials and as a consequence it is possible to write

$$V_{eff} \simeq \frac{3\varrho}{\varrho_{lc}} V. \tag{5}$$

On the basis of this result the following considerations can be made. If the resistivity of the liquid-crystalline droplets remains constant in the set of PDLC materials obtained by gradually changing the composition (the factor r), the switching voltage V_{eff} will depend linearly on the resistivity of the cell. On the other hand for some PDLC materials it can happen that both ϱ and ϱ_{lc} vary as a function of r in such a way that their ratio remains nearly constant. In this second case the switching voltage will apparently not be correlated with the resistivity of the material. This simple model provides then an explanation of the observed dependence of the switching voltages on the resistivities.

4. Concluding remarks

Even if these problems require further attention, by analysing samples containing well-defined amounts of ions we have shown that the primary controlling factor determining the switching voltage is represented by ionic currents across the PDLC components. The indication that V_{eff} depends on ϱ/ϱ_{lc} must be taken at the moment as useful information for the development of materials having very high resistivity and a low switching voltage. This can obviously be achieved by using liquid crystals and polymers such that ϱ turns out to be very high while the ratio ϱ/ϱ_{lc} remains very low.

Further work on this subject is in progress. In particular, the assumption that the droplets and the polymer matrix can be considered as resistors in series is certainly too crude. A more refined model taking into account the fact that the polymer matrix is interconnected while the droplets are not is already being considered.

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