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Liquid Crystals

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Surface anchoring, polarization fields and memory states in polymer dispersed liquid crystals

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Online publication date: 06 August 2010

To cite this Article Cupelli, Daniela , MacChione, Marialuigia , Nicoletta, Fiore P. , De Filpo, Giovanni and Chidichimo, Giuseppe(2001) 'Surface anchoring, polarization fields and memory states in polymer dispersed liquid crystals', Liquid Crystals, 28: 2, 287 — 290

To link to this Article: DOI: 10.1080/02678290010008197

URL: http://dx.doi.org/10.1080/02678290010008197

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Liquid Crystals, 2001, Vol. 28, No. 2, 287–290

Surface anchoring, polarization fields and memory states in polymer dispersed liquid crystals

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(*Received 21 May 2000; in final form 2 August 2000; accepted 28 August 2000*)

We have investigated the formation and development of memory states in polymer dispersed liquid crystals induced by the application of a strong electric field. Both the optical transmittance and polarization field have been followed as functions of time. We have been able to distinguish between the contributions to the memory states arising from the surface anchoring of the liquid crystal at the droplet interface and from the electrical reorientation of the mesogenic molecules. The dependence of both residual transmittance and polarization field on temperature is reported and a simple model is proposed.

1. Introduction

A memory state in polymer dispersed liquid crystals (PDLCs) is characterized by a zero-field transmittance larger than the transmittance in the original OFF state. Memory effects in nematic-based PDLCs were first reported by Yamagishi *et al.* [1], and then widely investigated by Sato and co-workers [2–7]. Their films showed a reverse morphology, i.e. micron-sized polymer balls formed an irregular network where the liquid crystal filled the voids and crevices. This particular morphology accounted for the observed strong memory effects. In fact, it was expected that the many degenerate alignments, present on a local scale at the polymer interfaces, could stop the relaxation of the liquid crystal molecules in a more transparent state [1]. More recently, memory effects have been reported also in thermoplastic PDLCs, which in contrast are characterized by a droplet morphology [8–10]. The memory states in such films are supposed to arise from a change in polymer/liquid crystal coupling at the droplet boundary [11] or the onset of an internal polarization [9, 10].

In this paper we have investigated the time dependence of both the optical transmittance and depolarization field in thermoplastic PDLCs which were 'charged' by means of a strong d.c. electric field. We have observed that it is possible to distinguish between the residual transmittance arising from a polymer/liquid crystal coupling and the transparency due to the internal polarization field.

2. Experimental

PDLC films were prepared by thermally induced phase separation. Poly(methyl methacrylate) (Aldrich) and the nematic liquid crystal mixture E7 (Merck) were dissolved in a common solvent (dichloromethane) in the weight ratio 1 : 1. After solvent evaporation, a small amount of the mixture, heated to about 120°C, was placed between two conductive glass plates with a gap of 40 μm. Cells were then cooled to room temperature in order to obtain phase separation of liquid crystal droplets with an average radius of about 1 μm. Such samples were charged by applying an external d.c. electric field ($\approx 10\ \mathrm{V\ \mu m^{-1}}$) at a controlled temperature ($T_{\mathrm{charge}} = 20, 30, 40, 50$°C) for 15 min. The d.c. field was removed only after having cooled the cells to room temperature (20°C). The electro-optical properties were investigated with the optical set-up described in previous work [12]. The light intensity with no sample in place was taken as the full-scale intensity. The decay of the internal polarization was monitored over time with the experimental set-up described in [9] after external field removal. Morphology analysis was performed on cross sections with a Leica LEO420 scanning electron microscope.

3. Results and discussion

Figure 1 shows the time dependent transmittance of PDLC films for different charge temperatures.

It may be noted that:

(1) The higher the charge temperature, the larger is the ON transmittance due, in our opinion, to a

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010008197

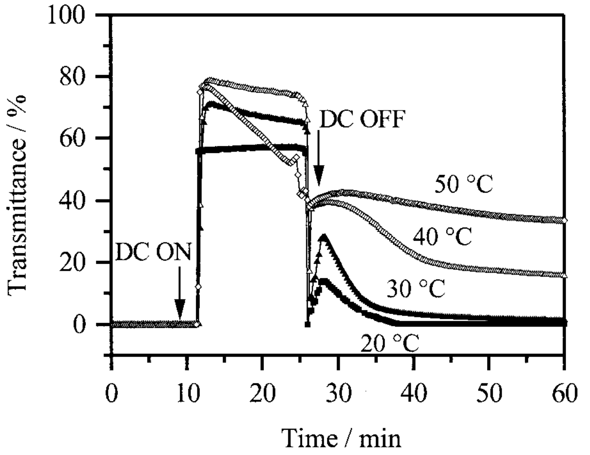
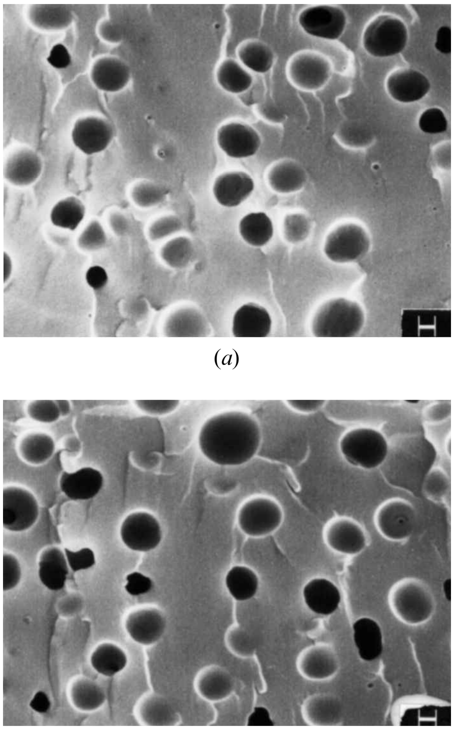


Figure 1. Time dependent transmittance of PDLC films for different charge temperatures. The first points of each curve are referred to the initial OFF state of PDLCs at their charge temperature. Then the d.c. field is applied for 15 min and turned off after fast cooling of the samples to room temperature.

better matching between the refractive indices of the polymer matrix and the liquid crystal with temperature.

(2) Some samples, especially at higher charge temperatures, show a gradual decrease of transmittance during the charge process. This is due to an increase of the internal polarization field originating from ion accumulation at the droplet interface (see later). This field opposes the external field and consequently reduces the degree of alignment of the liquid crystal molecules in the ON state.
(3) The optical transmittance first decreases, and then increases when the external field is slowly decreased to zero. The minimum value is reached when the external field is equal to the polarization field, i.e. when the effective field acting on the liquid crystal droplets is zero. If the external field is further reduced, the effective electric field changes direction, but increases in strength. Consequently, the transmittance increases, the PDLCs being unaffected by field polarity.
(4) After external field removal, the optical transmittance continues increasing slightly as the PDLC electro-optical response is delayed in the case of d.c. excitation [13] and then relaxes either to a finite value or to zero.

The memory state could be justified by assuming a change in the droplet average radius induced by the charge process. Figure 2 shows a comparison of the morphology between the two halves into which a larger PDLC was cut. The first half was left uncharged and the second was charged at 40°C.


(*a*)

(*b*)

Figure 2. SEM photographs of the films investigated: (*a*) uncharged and (*b*) charged PDLC. Samples were obtained by cutting a single larger cell into two parts. One part was left uncharged and the second was charged at 40°C with a d.c. electric field of strength 10 V μm^{-1}. The bar is equal to 1 μm.

It is evident from a statistical analysis that the charge process does not induce any appreciable change in the droplet average radius and number density. As a consequence, our results may be explained by hypothesizing a residual optical transparency arising from a change in the polymer/liquid crystal coupling at the droplet interfaces. In fact, the polymer chains at the droplet interface of thermoplastic PDLCs are heavily plasticized with liquid crystal and can be easily affected by liquid crystal alignment due to the charge field. The degree of ordering of polymer chains is expected to be enhanced if the charge process is performed at higher temperatures. Such an alignment can be stored during the cooling process in the presence of the external field. Consequently, polymer chains can keep the first liquid crystal layers at the droplet boundaries more or less aligned along a direction close to that of the applied field (memory state). The existence of a polarization field obviously contributes to the residual transparency.

We have monitored over time the polarization field induced during the charge process. The behaviour of the polarization field after external field removal is reported in figure 3 for different charge temperatures.

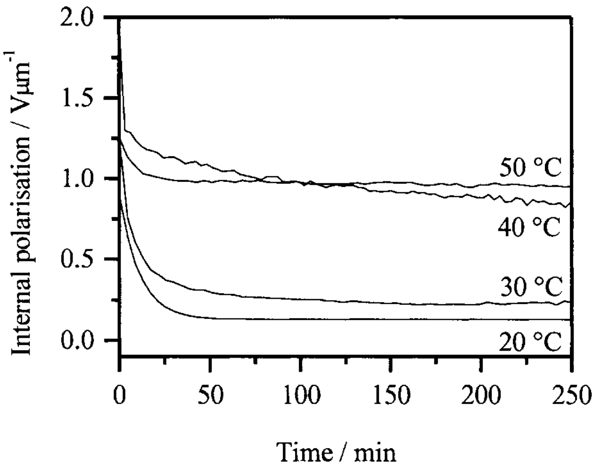


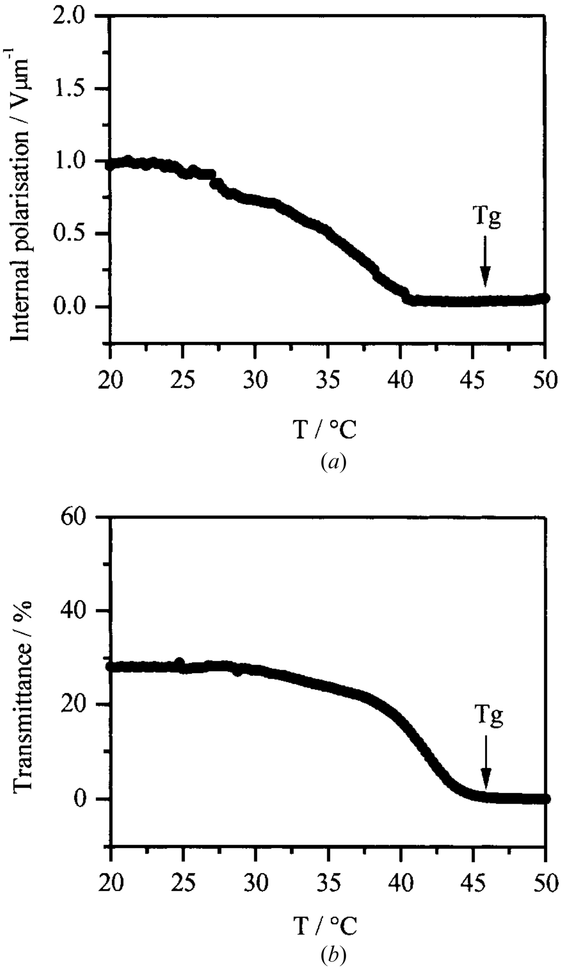
Figure 3. Time dependent internal polarization field after switching off the external d.c. electric field.

The internal polarization field can originate from various phenomena: charge separation due to the microscopic displacement and trapping of ions, electric dipole alignment, space charge injected from the electrodes, and space charge due to migration of ions over macroscopic distances. Only the first two mechanisms can give a uniform polarization [14]. In addition, dipole alignment can be excluded as we never observed any residual polarization for charge frequencies larger than 1 kHz, i.e. when ionic motions are frozen out. As no polarization field appears in samples without phase separation (E7 < 30 wt %), the phenomenon can be associated with the presence of liquid crystal doplets. In particular, it can be related with ionic accumulation at the polymer/liquid crystal interface, because no similar effect has been ever observed in liquid crystals.

Each experimental curve of figure 4 can be well fitted by the following bi-exponential function:

$$E(t) = E_\infty + E_1 \exp(-t/\tau_1) + E_2 \exp(-t/\tau_2). \qquad (1)$$

The table shows the fitting parameters of the curves reported in figure 3. E_∞ is the value of the polarization field present across the samples some hours after the charge process. It is interesting to note that E_∞ increases with charge temperature, and higher residual polarizations can be obtained with larger charge temperatures. The time dependent polarizations, E_1 and E_2, are characterized by two different decay times, τ_1 and τ_2, whose values are some tens and hundreds of minutes, respectively. These decays are, in our opinion, due to thermally activated ion diffusion and relaxation motion of polymer chains.



(*a*)

(*b*)

Figure 4. Internal polarization field (*a*) and residual transmittance (*b*) as functions of temperature. Measurements were made several hours after the charge process at a rate of 0.2°C min^{-1}. The arrows indicate the glass transition temperature of the polymer matrix.

The data in the table allow us to propose an onion-like model for the liquid crystal/polymer interface. We can distinguish three different shells. The first is that

Table. Fitting parameters of the time dependent internal polarization field after switching off the external d.c. electric field: fitting to equation (1).

T_{charge}/°C	E_∞/10^{-3} V μm^{-1}	E_1/10^{-3} V μm^{-1}	E_2/10^{-3} V μm^{-1}	τ_1/min	τ_2/min
20	70 ± 2	57 ± 2	760 ± 5	423 ± 2	10.9 ± 0.2
30	227 ± 2	327 ± 10	690 ± 10	33 ± 2	4.6 ± 0.2
40	570 ± 2	557 ± 2	210 ± 5	334 ± 2	17.8 ± 0.5
50	920 ± 2	80 ± 10	90 ± 10	253 ± 2	16.3 ± 0.5

nearest to the liquid crystal droplet and accounts for the E_1 polarization field characterized by a fast decay time, τ_1, as the liquid crystal concentration is large. The ions in the intermediate shell generate the E_2 polarization field and can remix over a longer relaxation time. The third shell is the furthest from the liquid crystal droplet and accounts for E_∞. Ions cannot leave this shell at room temperature, due to the reduced mobility of the polymer matrix, and give rise to the long term stable polarization. Such a residual polarization field decreases on increasing the temperature and reaches a zero value at the glass transition temperature of the polymer matrix, as shown in figure 4 (*a*).

A similar thermal behaviour is shown by the residual optical transmittance, figure 4 (*b*). In agreement with the above shell model, both decreases (polarization field and optical transmittance) can be attributed to an increased polymer chain mobility, which softens the polymer's mechanical action on both ions (decrease of polarization field) and liquid crystal molecules (decrease of optical transmittance).

In order to evaluate the contribution of surface anchoring and polarization field to the residual transparency, we have measured the optical transmittance in the presence of an external d.c. electric field. The field strength was exactly equal to the residual polarization, but with the opposite direction. The optical transmittance in the case of such an 'electric erasure' of the residual polarization field (data not shown) is lowered less than 10% for each charge temperature (e.g. 34% instead of 37% for $T_{\mathrm{charge}} = 50°\mathrm{C}$). Such a result supports the idea that surface anchoring is the major cause of the residual transmittance. Nevertheless, a large polarization field could be important in the fabrication of polarity sensitive devices. In fact, PDLCs with a built-in d.c. field are expected to show quasi-linear electro-optical properties, i.e. they should follow the driving electric field [15].

4. Conclusions

In this paper we report the memory states induced in thermoplastic polymer dispersed liquid crystals by application of strong electric fields. The liquid crystal molecules in the presence of the external field imprint the polymer surface. Such imprinting is stored during the cooling process and the liquid crystal molecules are kept in a more aligned state. At the same time a long term stable polarization can be built in. We have been able to distinguish between the residual transmittance arising from a mechanical anchoring of liquid crystal molecules at the droplet interface and the transparency due to the presence of a polarization field. Optical transmittance decreases to zero with temperature as the increase in the interface mobility allows a remixing of ions and a random distribution of liquid crystal directors.

MURST, the Italian Ministry for Universities, is acknowledged for financial support (project 'VARILUX' #1262/153).

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