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Persistence Effects and Memory States in Charged Polymer Dispersed Liquid Crystals

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Abstract Polymer dispersed liquid crystals (PDLC) can be affected by either persistence or memory states after the application of a strong electric field (charge process). We have investigated the post-charge states of PDLCs as a function of liquid crystal loading and found that the appearance of either a persistence or memory state depends on the polymer matrix glass transition temperature.

Keywords Memory State; Glass Transition; PDLC; Liquid Crystals.

INTRODUCTION

Polymer dispersed liquid crystals (PDLC) are composite materials formed by liquid crystal droplets dispersed in a polymer matrix. Their importance is due to the diffuse scattering in the OFF state and the transparency in the ON state because of the electrically controlled refractive index matching. [1,2] PDLCs can be characterized by either persistence or memory states. A memory state shows a zero field transmittance larger than the transmittance in the original OFF state, while a persistence state requires some time to reach the zero field transmittance. [3] Memory effects were first reported by Yamagishi et al. [4], and then investigated by Sato and coworkers in reverse morphology PDLCs, i.e. films characterized by the presence of a micron-sized polymer network [5-7] where the liquid crystal fills the crevices. More recently, memory states have been obtained in droplet PDLCs by means of a change of polymer-liquid crystal coupling at the droplet boundaries and the onset of an internal polarization field. [8,9] In particular, it was found that if a memory state was induced it could

be accompanied or not by a long-term stable polarization field, which disappeared at the polymer matrix glass transition temperature.

In this paper we have investigated the states (memory or persistence) of PDLCs after the application of a strong electric field and the polymer matrix glass transition temperature values as a function of liquid crystal loading. We will show that the appearance of either a persistence or memory state is strictly related to the polymer matrix glass transition temperature.

EXPERIMENTAL

PDLC films were prepared by thermally induced phase separation from homogeneous mixtures of polymethylmethacrylate (PMMA, Aldrich) and E7 nematic liquid crystal (Merck). PMMA and liquid crystal were dissolved in a common solvent (dichloromethane) in the appropriate weight ratio. After solvent evaporation, a small amount of mixtures was sandwiched in homemade cells, whose thickness was set to be about 40 μm by glass spheres. Then, samples were heated to about 120 °C and cooled to room temperature (20 °C) at a controlled rate (2 °C min^{-1}) in order to induce phase separation. Samples were charged by applying a dc electric field (10 $V\mu m^{-1}$) at a controlled temperature (50.0±0.1 °C) for 10 minutes. The field was removed only after the films were cooled to room temperature. The electro-optical properties were investigated with the optical line described in a previous work. [10] The light intensity, transmitted without any cell, was assumed to be full-scale intensity. The polarization fields were measured with the experimental set up described in ref. 8. The polymer matrix glass transition temperatures were determined by measuring the decay times of transmittance as a function of temperature. [11]

RESULTS AND DISCUSSION

Figure 1 shows the behavior of optical transmittances as a function of time for two different samples, which will reach or not a memory state after the charge process. The transmittance of both samples slightly increases after the charge process as the electro-optical response of a PDLC is delayed in the case of a dc excitation. [12] Then, the optical transmittance decreases either to zero (persistence) or to a lower value (memory state).

We have followed the behavior of the internal polarization field in both previous cases and obtained the results reported in figure 2.

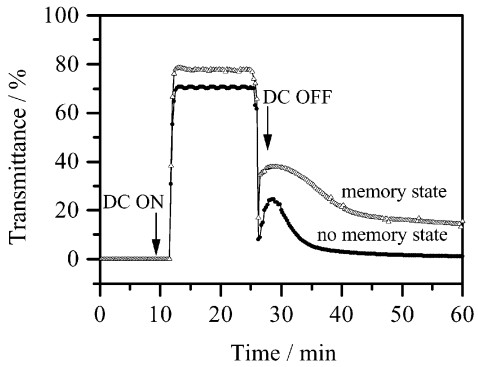

FIGURE 1 Time dependent transmittances before, during and after the charge process for two samples (40 % E7, and 75 % E7), which will reach a memory state or not.

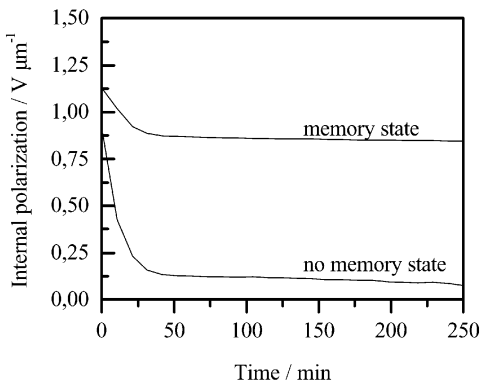

FIGURE 2 Time dependent polarization fields for two samples (40 % E7, and 75 % E7), which will reach a memory state or not.

Both polarizations decrease according to a bi-exponential law either to zero (persistence) or to a lower value (memory state). [9] One could conclude that memory states are due to the presence of such internal polarization fields, which align the liquid crystal molecules. Nevertheless, we observed, under different experimental conditions, that memory states can be induced without the onset of an internal field. As a consequence, the memory state in a charged PDLC can be generally attributed both to the onset of the polarization field and the alignment of polymer chains. In fact, polymer chains at droplet interface are heavily plasticised and can be easily aligned by the liquid crystal reorientation. Such alignment is more effective at higher temperature and can be stored if samples are cooled to room temperature in the presence of the external field.

The bi-exponential decay of polarization fields suggests the existence in the droplet boundaries of three different shells of ions, which generate the polarization field. The shells originate during the charge process as a consequence of the separation at the droplet interface of ion impurities (present in the mixture components). The two shells, which are near to liquid crystal droplets, can justify the fast and long-term decay times of polarization as the interface is softer and allows the remix of ions. The third shell is the furthest from the liquid crystal droplets and accounts for the onset of a stable polarization field, being the ions mechanically trapped in this shell.

We expect that both the alignment of polymer chains and the ion freezing be strongly related to the polymer matrix glass transition temperature, Tg, of samples. Consequently, we have investigated the behavior of Tg as a function of liquid crystal content by measuring the decay times of transmittance as a function of temperature. It is known that the decay time of transmittance, i.e. the time required for the transmittance to drop to 10 % of its maximum value after the external field is removed, shows a sharp increase if the temperature is larger than Tg. [11] An example of Tg measurement is reported in figure 3.

Figure 4 shows the behavior of Tg for different liquid crystal contents and we experimentally found that it is not possible to achieve a memory state for samples whose polymer glass transition temperature is around room temperature (E7 > 60 %). Nevertheless it is possible to obtaine a stable memory state in such samples by cooling them (during the charge process) to 0 °C, i.e. by increasing the difference between Tg and room temperature. Such result confirms the hypothesis of a deep relationship between memory states and polymer glass transition temperatures. It allows to propose the simple structure model reported in figure 5 for samples exhibiting a memory state after the charge

process. According to this model, a temperature value, which is around or larger than Tg, will determine an increase in the motion of polymer chains present at droplet interface. Polymer chains will "shake" the liquid crystal molecules, which will loose the preferential alignment achieved during the charge process. At the same time ions are allowed to remix and, consequently, no residual polarization field is stored in the PDLC film.

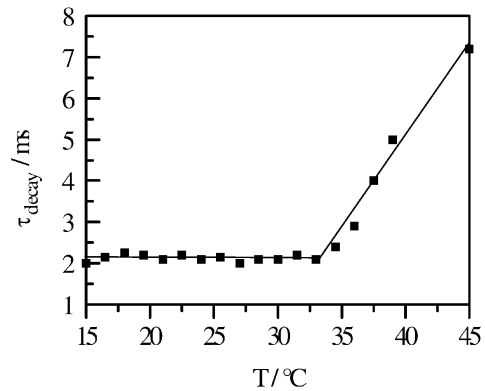

FIGURE 3 Example of Tg measurements.

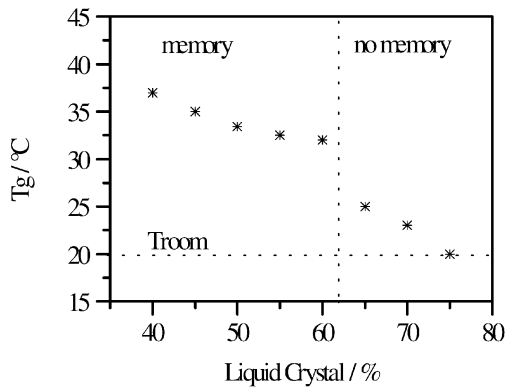

FIGURE 4 Behavior of polymer glass transition of PDLC samples as a function of liquid crystal content.

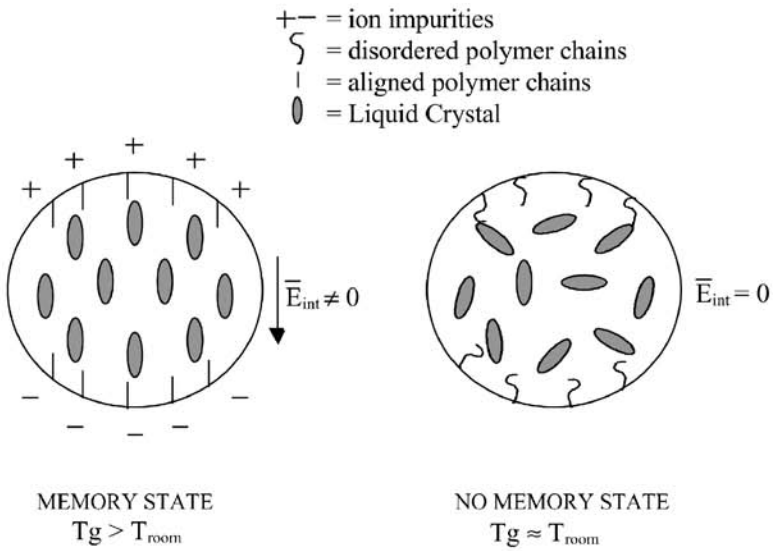

FIGURE 5 A simple model for the droplet interface in the presence and absence of a memory state.

CONCLUSIONS

We have investigated the relationship between polymer matrix glass transition temperatures of PDLC samples, charged by means of a dc electric field, and the onset of a memory state. We found that a memory state can be built in a thermoplastic PDLC only if its polymer matrix glass transition temperature is higher enough than room temperature. In this condition an internal polarization field can be also obtained and will contribute to the increase of the memory level gained by the mechanical action of aligned polymer chains on mesogenic molecules. On the contrary, only persistence effects can be observed.

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