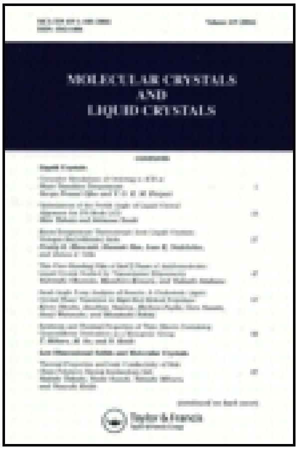

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Linear Electro-Optic Response in a Stretched Polymer Dispersed Ferroelectric Liquid Crystal Sponge System

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A linear electro-optic response in a stretched polymer dispersed ferroelectric liquid crystal (PDFLC) sponge system is presented. The composite material is prepared with the ferroelectric liquid crystal SCE10, which exhibits a SmC*-N* phase sequence, and polyvinylbutyral (PVB) using the solvent evaporation induced phase separation (SIPS) technique. The ferroelectric liquid crystal imbedded in the sponge system is aligned unidirectionally by mechanical stretching of the PDFLC material. The stretched PDFLC film exhibits a linear electro-optical response, a large induced tilt of the sample optic axis, and a constant response time with the applied electric field in a broad temperature range covering both the SmC* and N* phase. Surprisingly, the field-induced tilt in the N* phase is found to be larger than in the SmC*.

Keywords: linear electro-optic response; stretched polymer dispersed ferroelectric liquid crystal sponge system

INTRODUCTION

Liquid crystals in combination with polymers have during the last decades been developed into several new classes of liquid crystal composite materials. In the case of low concentration of the polymer (usually in the range of 1-10%), one talk about polymer stabilized liquid crystals, PSLCs or gel systems, and in the case of high concentration, 60-80%, about polymer dispersed liquid crystals, PDLCs[1]. In what we usually refer to as PDLC systems - small droplets of nematic or cholesteric liquid crystals dispersed into a self-supporting polymer matrix through a phase separation of the liquid crystal and the polymer. By introducing a ferroelectric liquid crystal into the polymer matrix instead of nematic, a new composite material, polymer dispersed ferroelectric liquid crystals (PDFLC), is created. The most frequently used electro-optic effect in PDFLC systems is the field-induced reorientation of the optic axis as the material is placed between crossed polarizers. In order to utilize this effect it is essential to obtain a uniform optic axis distribution in the PDFLC film. That can be possible only if there is a uniform orientation of the liquid crystal material within the droplets. The linear coupling between an applied electric field and the spontaneous or induced polarization in the chiral liquid crystal material will then allow the film to work as a birefringent plate with field-controlled optic axis[2,3]. Most work on these systems have been done on samples prepared with UV-curable polymers like NOA65[4], where the ferroelectric liquid crystal within the droplets are oriented by applying a shear flow on the polymer-liquid crystal mixture during the polymerization process. Alignment of the UV-curable polymer matrix, and thus also of the liquid crystal, accomplished by unidirectionally rubbed poly(1,4-butylene terephalate) of one of the glass plates in a sandwich cell has also been reported[5]. For thermoplastic polymers warm or cold stretching of the PDFLC films results in elongated droplets with uniform liquid crystal alignment[2,3].

Linear electro-optic effects reported in PDFLC materials, so far, have as an origin the deformed helix ferroelectric mode (DHF) [3-5], the electroclinic effect in SmA*[2-4] or the flexoelectric effect in the cholesteric phase[6], respectively. In the DHF mode the deformation of the helical structure of the SmC* phase causes a deviation of the optic axis in the plane of the PDFLC film. For small fields this effect is linear but saturates at higher fields, i.e. when the helix is completely unwound. The electroclinic effect in the SmA* phase of the liquid crystal material in the PDFLC film causes a deviation of the optic axis linear with the applied electric field and thus gives rise to a linear electro-optic response. Polymer dispersed short pitch chiral nematics, PDCN utilizing the flexoelectro-optic effect in cholesterics with uniformly lying helix (UHL) texture, have been reported recently[6]. In this case, the linear electro-optic response is caused by the coupling of the applied electric field to the field-induced flexoelectric polarization.

In the present work, the electro-optic response in PDFLC film with a sponge like structure studied over a wide temperature range, is reported. The investigations are done on PDFLC films prepared with the polymer PVB and the ferroelectric liquid crystal mixture SCE10 in two different polymer dispersed liquid crystal structures - sponge- and droplet-like. The electro-optic response of the sponge PDFLCs is compared with the one possessing a droplet structure. In the sponge system, the polymer matrix created in the phase separation process is expected to have a structure consisting of interconnected channels and pockets of different size with much smaller dimensions than those of the liquid crystal droplets in the PDLCs with the droplet structure. A strong dependence of the electro-optic response on the restricted geometry and the uncompleted phase separation can be expected.

EXPERIMENTAL

Sample preparation

Two different kinds of stretched PDFLC film were produced; one with droplet structure and one with sponge-like structure. The PDFLCs with imbedded liquid crystal droplets were prepared by dissolving the ferroelectric liquid crystal mixture SCE10 (BDH) and a small amount of lecithin, 0.1 wt. %, in chloroform or ethanol together with the non-mesogenic polymer PVB (PVB is known to give planar anchoring conditions for most liquid crystals). The lecithin is added to the liquid crystal/polymer mixture to give a homeotropic anchoring of the liquid crystal molecules. The presence of lecithin in the mixture also favors the liquid crystal droplet formation in the composite material. In the preparation process the optimum ratio liquid crystal/polymer/solvent was experimentally obtained. The mixture was then pored onto a flat glass substrate and utilizing the SIPS process (Solvent Evaporation Induced Phase Separation) at room temperature thin membranes (40-50μm) were prepared. The time for complete evaporation of the solvent and the rate of its evaporation, which depends on the ratio liquid crystal/polymer/solvent and temperature, have a strong effect on the PDFLC structure and on the liquid crystal droplet size. This process was not fully optimized and the droplets formed in the samples after phase separation showed rather small diameters, about 0.5 μm. Since PVB is also suitable for preparation of PDLC by means of TIPS (Thermally Induced Phase Separation) larger droplets could be produced by this method. According to this method, the thin PDFLC film was kept at a sufficiently high temperature (80°C) for several hours and then allowed to cool down with a cooling rate of 0.07 dpm to room temperature which resulted in larger liquid crystal droplets. Unidirectional alignment of the liquid crystal molecules in the droplets, and thus a unidirectional orientation of the sample optic axis, was obtained by gently heating the PDFLC film to the N* temperature range of the liquid crystal and thereafter stretching it (so called warm stretching). When cooling down to the SmC* phase the anisotropic shape, ellipsoidal in the case of droplet formation in the matrix, gives a preferable orientation of the smectic layers. Finally, the stretched PDFLC was glued in between two ITO covered glass plates with a very thin layer of Araldit, epoxy glue from Casco. After soldering the electric contacts, the samples were ready for electro-optical investigations.

By leaving the lecithin out from the preparation process described above, a sponge like polymer system without distinct liquid crystal droplet nucleation was created during the phase separation. In this case, the phase separation process resulted in a PDFLC material in which the structure of the polymer matrix seems to look more or less like an interconnected tunnel system with pockets of different size, like in a sponge (structural investigations of the polymer matrix are under way). TIPS on these samples did not favor a droplet formation instead the pores in the sponge system became larger.

The ferroelectric liquid crystal used is a commercial mixture SCE10 from Merck (BDH) which shows the following phase sequence and characteristics:

SCE10:
I-109°C -N* 61°C -SmC* 20°C-SmI,
Spontaneous polarization P_s = 19.5 nC/cm^2 at 20°C,
helical pitch in the N* phase close to the SmC*-N* phase transition >146μm

A significant part of the investigations on the sponge system, was focused on examining if there was any change in the phase sequence of SCE10 after being dispersed into the polymer matrix. Such a study is necessary in order to understand the origin of the detected linear electro-optic response exhibited by the sponge system. In order to study the influence of the restricted geometry in our PDFLC films on the phase sequence of SCE10, conventional sandwich cells with substrates covered by PVB as alignment layer were prepared. The PVB was spin coated onto the clean glass plates and then unidirectionally rubbed. The thickness of the cells were controlled by adding polyballs of 2μm in the UV curable glue, NOA65, used for the assembling of the cells. Finally, the cells were filled with SCE10 in the isotropic phase by means of capillary forces. Cells without any spacers, thus with an expected cell gap below 1μm, were used in this study as well.

Measurements

Phase sequences and phase transition temperatures for the liquid crystal within the PDFLC film were studied by means of DSC and polarizing microscope. These parameters can be expected to change because of incomplete phase separation of the polymer and the liquid crystal or due to the restricted geometry of the composite material. Liquid crystal material squeezed out of the PDFLC film by heavily pressing it and, in addition, different mixtures of

SCE10 and polymer, where small concentrations of PVB were dissolved directly into the liquid crystal, were studied. The phase sequence of SCE10 was also studied in thin, 1-2μm sandwich cells, with PVB alignment layers, by means of polarizing microscope.

For determination of the phase transition temperatures and for texture observations, a Nikon polarizing microscope and an Instec hotstage in combination with a computerized image system were used. Measurements in a differential scanning calorimeter, Perkin Elmer DSC, could further confirm the results of the microscopy study.

Electro-optical measurements were made in a set-up containing: a Zeiss polarizing microscope, a Leader LFG-1300 function generator, a photo-detector and a Tektronix TDS 540 oscilloscope. The sample temperature was controlled by a Mettler FP52 hot stage.

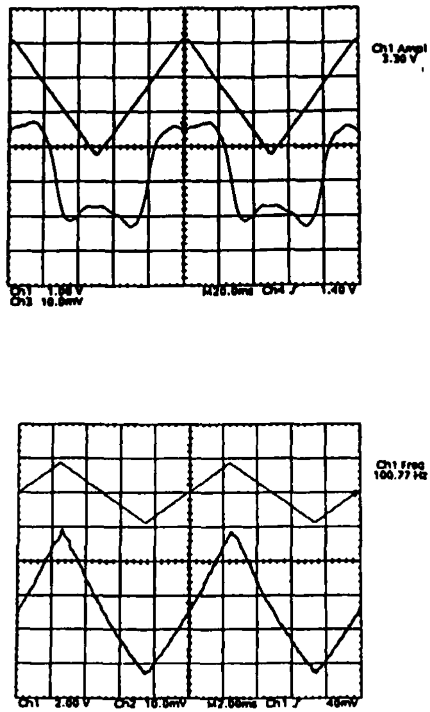
RESULTS

Phase transition temperature shift

The confined geometry in the polymer matrix and incomplete phase separation can be expected to cause a shift in the phase transition temperatures of the liquid crystal imbedded in the polymer material and also broadening and rounding of these transitions as well as induction of new phases into the initial phase sequence. In the DSC and microscope study both a shift and broadening of the phase transitions were observed. The main reasons for the shift in phase transition temperatures turned out to be caused mainly by two factors - the uncompleted phase separation in the PDFLC system and the restricted geometry in this system. Due to the uncompleted phase separation, a small amount of polymer material remains dissolved in the liquid crystal droplets. The phase transition temperatures measured for the liquid crystal material taken out from the PDFLC film show that the SmC* to N* phase transition temperature for SCE10 decreases approximately 5 - 6 degrees and the N* to Iso transition temperature increases by approximately 2-3 degrees. This gives a broadening of the N* phase of about 7-9 degrees which was further confirmed by the study of mixtures of SCE10 and small amount of PVB dissolved into it. Thin sandwich cells with PVB as surface treatment has been found to show only a slight increase in the temperature of N* to Iso phase transition (0.5 degrees) whereas the temperature of SmC* to N* transition has been lowered with about 5 degrees. No induction of a smectic A* phase could be detected. Hence, we can conclude that the phase sequence of the SCE10, after being incorporated into PVB matrix, does not change. Only the phase transition temperatures are somehow affected by the uncompleted phase separation and by the restricted geometry in the PDFLC film.

Electro-optic characteristics

The electro-optic response in PDFLCs with droplet and sponge system, respectively, was characterized. As it can be seen in Figure 1, the electro-optic response detected in these two PDFLC systems at room temperature, i.e. in the SmC* phase of the liquid crystal material, is different. The response in the PDFLC with droplet structure is a typical ferroelectric response, while the sponge system exhibits a linear response. Such a linear response was detected in the sponge system for a wide temperature range. The field-induced deviation of the optic axis θ_{ind} of PDFLC film with sponge structure measured as a function of temperature for different voltages (see Figure 2 and Figure 3, respectively) show that the electro-optic response is a linear function of the applied field in both SmC* and N* phases. The measured values of θ_{ind} in the N* phase are much larger than the ones measured in the pure liquid crystal material. Very surprising result is the linear electro-optic response in the SmC* phase which can be followed deep in this phase. The temperature dependence of θ_{ind} in Figure 3 shows that the induced tilt diverges as the N*-SmC* phase transition is approached from the N* phase. This behavior is typical for the electroclinic effect in the N* phase. On both sides of the N*-SmC* phase transition θ_{ind} decreases almost symmetrically. The response time in the PDFLC film with sponge structure is of the same order as the one measured in SCE10. It is slowly increased on decreasing the temperature. The response time seems to be almost constant with the applied electric field for both SmC* and N* phases of the liquid crystal material in the sponge PDFLC film.



a)

b)

FIGURE 1. The electro-optic response of two PDFLC samples at room temperature for a triangular voltage. The upper curve is the applied voltage and the lower one is the optical response. The response is detected in PDFLC samples with SCE10(28%) imbedded in a PVB matrix with a) a droplet structuresand with b) a sponge structure.

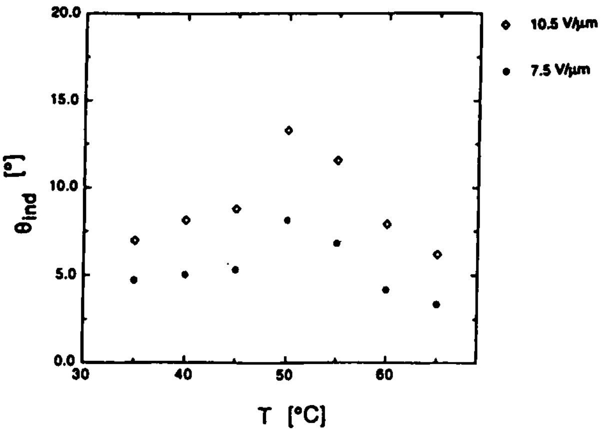


FIGURE 2. Induced tilt θ in PDFLC sponge sample, containing SCE10 (28%) and PVB, as a function of temperature for two different field strengths.

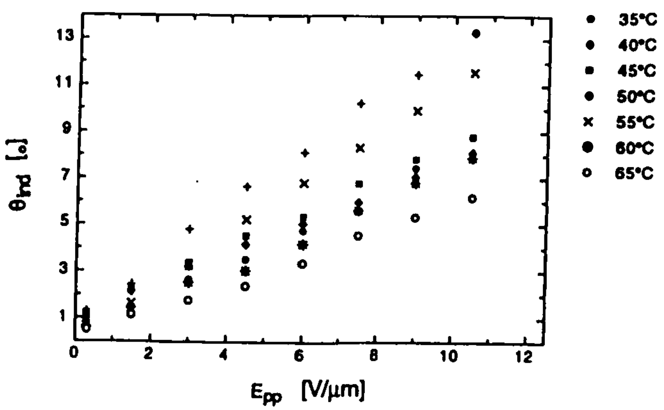


FIGURE 3. Induced tilt θ in PDFLC sponge sample as a function of the applied electric field in both smectic C* and N* phase. Notice, the maximum amplitude of the response at temperature close to the N* - SmC* phase transition.

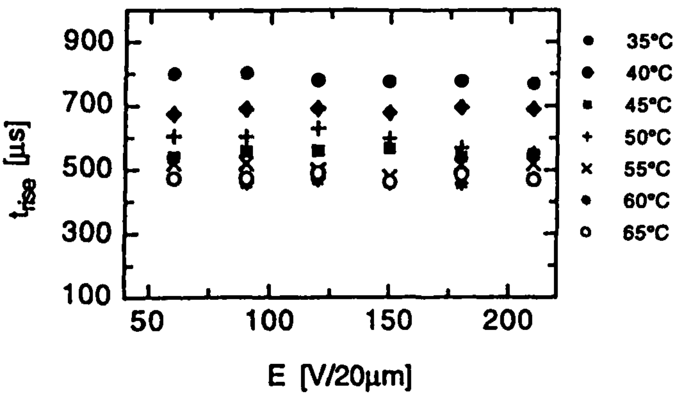


FIGURE 4. The response time of the PDFLC sponge system. The response is constant with the electric field for a wide temperature range. The shortest response is obtained around the N*-SmC* phase transition.

DISCUSSION

The electro-optic effects in very complex liquid crystal composite systems similar to the sponge PDFLCs are not sufficiently studied. We are still far from fully understanding the importance of all factors affecting the electro-optic response in such systems. In the present study we intended to investigate the electro-optic response in stretched PDFLCs with two different structures, namely sponge-like and droplets-like. We found that the structure of the PDFLC is of major importance for the character of the detected electro-optic response. Whereas the PDFLC film with sponge structure exhibits a linear electro-optic response in a wide temperature range, covering both SmC* and N* phases, the one exhibited by the PDFLC with droplet structure has been found to be similar to the response of the embedded ferroelectric liquid crystal. The complexity of the sponge like structures makes it difficult to interpret the obtained results. However, some assumptions about the origin of the linear electro-optic response detected in this sponge system can be made. It seems that the linear response detected in the sponge system, when the imbedded liquid crystal is in the SmC* phase, arise from the fact that this system contains a variety of interconnected pockets and channels with different size. These structural units possess different threshold voltages for the ferroelectric switching of the liquid crystal. As consequence, the number of the switched units will be proportional to the amplitude of the applied field. Thus, the higher the field the larger is the number of the switched units. Hence, the integrated electro-optic response of all structural units in the sponge PDFLC film appears to a great extent to be linear with the applied electric field. The large induced tilt of the optic axis in the sponge system when the imbedded liquid crystal is in the N* phase, is the most surprising result of this study. It is linear with the field and it has the electroclinic effect as an origin. The large amplitude of the field-induced deviation of the sample optic axis in this case might be attributed to the presence of dense anisotropic polymer network (complex system of interconnected pockets and channels). This network is rigid and supplies with a large internal surface area interacting with the liquid crystal material. These interactions in turn result in an enhancement of the electroclinic response in the N* phase as it has been reported by us recently on volume stabilised N* phase of the same material. Remarkably, the field-induced tilt in the sponge system, at temperatures corresponding to the N* phase of the imbedded liquid crystal material, is almost an order of magnitude higher than the tilt induced in the N* of the same liquid crystal material in a sandwich cell.

CONCLUSION

Linear electro-optic response has been detected in a stretched PDFLC system with sponge structure in both SmC* and N* phases. Such a behavior is quite different from the one obtained in the PDFLC with droplet structure. Moreover, a linear electro-optic response corresponding to a large field-induced tilt of the optic axis has been detected in the N* phase. The large amplitude of the induced tilt in this case make feasible some implementations of the electroclinic effect in the N* phase. However, a lot has to be done in order to understand the physics behind these observations.

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