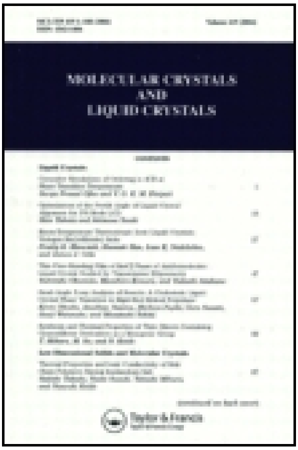

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Ferroelectric Polarization Hysteresis in a Liquid Crystal Polymer by Means of LIMM

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We present pyroelectric measurements of the electric field hysteresis in a ferroelectric liquid crystalline polymer. Different electrode arrangements were used to study the pyroelectric response for different directions of the applied electric field with respect to the film geometry and the direction of the incident heat wave. The results demonstrate that in a sandwich cell electrode/foil/FLCP/foil/electrode charge accumulation in the polyester foils leads to a reverse hysteresis loop while conventional hysteresis behavior is observed when the electrodes are in direct contact with the FLCP. In addition we have measured the pyroelectric current in the plane of the film and observed ferroelectric switching and hysteresis in this configuration as well. The LIMM-spectrum shifts significantly toward lower frequencies in this configuration, which is assumed to be mainly due to a heat flow perpendicular to the Laser beam.

Keywords: Ferroelectric liquid crystal polymer; spontaneous polarization; pyroelectric measurements; LIMM; Hysteresis; Bistable switching

I. INTRODUCTION

Pyroelectricity is one of the fundamental properties of ferroelectric liquid crystalline materials.[1] It probes the presence and the direction of permanent molecular dipole moments by measuring the change in the spontaneous polarization with temperature. The effect is based on the change of the molecular tilt angle with temperature, which in systems of uniformly oriented molecules, i.e. in the SmC* liquid

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crystalline phase, leads to establishing of macroscopic surface charges. These charges can be detected as a pyroelectric current across the sample.

The great interest on ferroelectric liquid crystalline materials with respect to fast display devices is based on their capability to reorient the molecular axis upon application of an external electric field and thus to flip the spontaneous polarization between opposite directions.[2,3] In a surface stabilized FLC cell[4] the significant difference in the macroscopic (optical) properties between the two switching states is achieved because of the uniform alignment of the molecules in a bookshelf geometry. Of special interest is therefore the investigation of the polarization and its distribution in different cell geometry's under the influence of an externally applied electric field. The Laser Intensity Modulation Method (LIMM) has been established as a useful tool to study the polarization and polarization distribution of ferroelectric materials.[5,6] In this work we report LIMM-measurements on a ferroelectric liquid crystalline polymer (FLCP) in the presence of an electric field. We present ferroelectric hysteresis loops for different directions of the applied electric field with respect to the polymer film and to the incident Laser beam.

II. EXPERIMENTAL SECTION

The experimental setup is depicted schematically in Figure 1. The sample is mounted on a heat sink in a shielded, temperature controlled holder connected to a capacitive coupling that allows the application of comparably large DC electric fields while measuring low AC currents. An acousto-optical modulator (AOM) driven by a frequency generator is used to modulate the light of a 632,5 nm He-Ne-Laser with a frequency f. The modulated light hits the sample and leads to periodical heating and relaxing, which in a pyroelectric material induces an AC current with a frequency f. This current is converted into a voltage using a current-to-voltage-converter (CVC) and recorded by a lock-in amplifier with the reference frequency f supplied by the frequency generator. The operation and data recording of the lock-in amplifier and the frequency generator is controlled by PC.

The ferroelectric liquid crystalline polymer was P8*S, a chiral side chain polymer with polysiloxane main chain.[7] The material shows the following phase transitions:[8] gl. 31–35 °C $S_C{}^*$ 44 °C S_A 47 °C is. Two different types of cells were fabricated with respect to the direction of the applied electric field. First, the conventional sandwich cell with the electric field perpendicular to the film plane (parallel to the laser beam) was constructed (Figure 2a and 2b). Second, we created a cell with planar electrode arrangement where the field is applied *in* the plane of the film (Figure 2c).

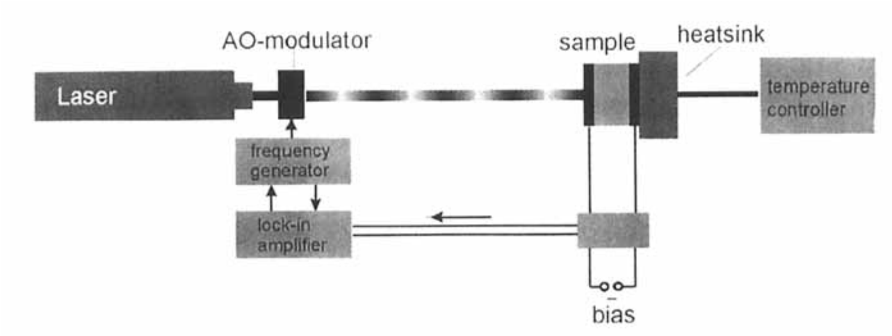

FIGURE 1 Experimental apparatus for LIMM measurements

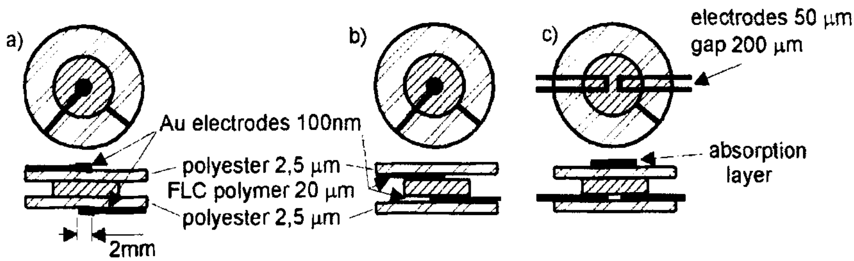

FIGURE 2 Different electrode configurations for FLCP pyroelectric cells: a) electrodes-outside-configuration, b) electrodes-inside-configuration, c) planar configuration

In the first arrangement (sandwich) we have investigated two different configurations: first, the 15 µm FLC polymer film is sandwiched between two 2,5 µm thin polyester foils that carry 100 nm evaporated gold electrodes on their outside, i.e. not in direct contact with the polymer (Figure 2a). This electrodes-outside-configuration is normally used for LIMM-measurements on ferroelectric liquid crystals and FLC-polymers[9,10] because of the better alignment of the liquid crystal at the polyester foils. In the electrodes-inside-configuration the polyester foils are arranged with the gold electrodes in direct contact to the FLCP (Figure 2b).

The second arrangement (electric field in the film plane) was realized by two ultra thin wires (50 µm), which were carefully fixed with a distance of 200 µm from each other and, again, placed between polyester foils (Figure 2c). One of the foils carried an gold layer on their outside to ensure the absorption of the laser light. All samples were filled with the FLCP in the isotropic phase (at ≈50 °C) and were slowly cooled down including several heating-cooling cycles around the phase transition point SmC*-SmA.

III. RESULTS AND DISCUSSION

We first consider the pyroelectric effect in the conventional LIMM cell, i.e. with the electric field perpendicular to the film plane and electrodes outside (Figure 2b). In this configuration the electric field is applied across the system of the two foils and the FLCP. The applied bias was varied in the range from −180 V to 180 V, the obtained hysteresis curve of the pyroelectric current is depicted in Figure 3. The direction of the bias sweep is denoted by arrows. A clear reverse hysteresis behavior can be observed: After applying a bias of +150 V the pyrocurrent decreases quickly with decreasing bias and vanishes at U_b=100 V. When after that the bias is shortened a negative remanence pyrocurrent of almost −18 pA is observed, which is comparable to the maximum signal of 22 pA at U_b=150 V. The effect recurs in reverse direction after applying a negative bias, i.e. a positive remanence of 8 pA is obtained.

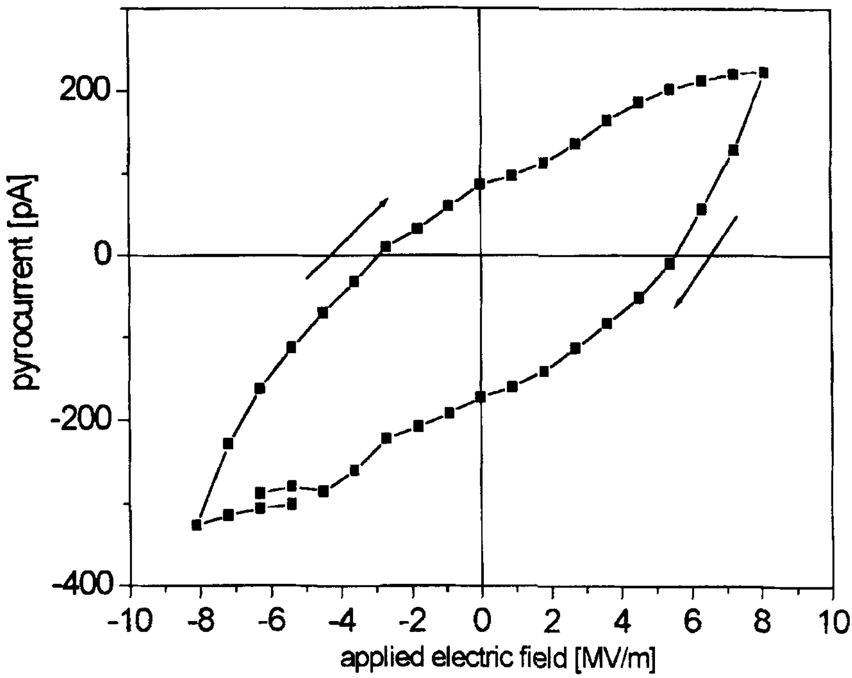

FIGURE 3 Electric field hysteresis of the pyroelectric current of 20 μm P8* between 2,5 μm polyester foils in electrodes-outside-configuration at 38°C with the applied electric field perpendicular to the film. Laser modulation frequency f was 80 Hz

"Reverse hysteresis loops" where also found for non-polymeric liquid crystals[11] and explained by an ions migration effect. We suggest a similar process to be responsible for the bias dependence of the pyrocurrent in P8*. At high bias voltage polarization charges are induced in the surface region of the polyester foils that oppose the external applied electric field. When the bias is reduced these charges remain in the foil and compensate the external field at the coercivity field. After decreasing the bias to zero the pyrosignal is solely induced by the electric field that is build up by the remaining polarization charges in the foils. If, afterwards, the bias is increased in opposite direction the polarization charges are relieved and charges of opposite sign are accumulated, which allow the process to recur in reverse direction. From the experimental results the remanence is determined to be 13 pA and the coercivity is 4.3 MV/m. Following our explanation this value represents the maximum field that can be established by polarization charges in the foils.

Another noteworthiness of Figure 3 is the shift of the whole hysteresis loop towards negative values for the pyrocurrent. An explanation for this finding might be a difference in the capability of charge storage between the upper foils that is in contact to air and the lower foil, which is attached to the heat sink.

In the configuration where the electrodes are in direct contact with the polymer, which means that the external field is not applied to the polyester foils the hysteresis behavior of the pyrocurrent is significantly different and is found to be in good agreement with results of Kozlovsky *et al.*,[8] which were obtained using P8*S between glass substrates (spaced 10 μm), coated with ITO and rubbed polyimid. The hysteresis curve (Figure 4) can now be recorded in conventional counter clockwise direction, it possess steep edges and pronounced saturation plateaus. The whole curve is now very centrosymmetric with respect to the point of origin with high reproducibility. As another important difference the coercivity and the saturation field are reduced by a factor 30 when compared to the values for the electrodes-outside-configuration. We now obtain a remanence of 26 pA, which is near the saturation signal and a coercivity of 0.11 MV/m. That means that in this configuration bistable ferroelectric switching is possible using a switching voltage of ±5V.

The pyroelectric current measured in planar electrode configuration, i.e. with the electric field and the signal detection in the plane of the FLCP film, is depicted in Figure 5. Again, the direction of the hysteresis loop is counterclockwise as expected for ferroelectric switching processes. The pyrosignal shows saturation behavior for absolute values of the applied field of about 0.1–0.2 MV/m, also it possesses a high ratio of remanence to saturation signal. When compared to the sandwich cell in electrodes-inside-configuration we find the same saturation field and coercivity of about 0.1 MV/m but with the pyrocurrent generally reduced by a factor 30.

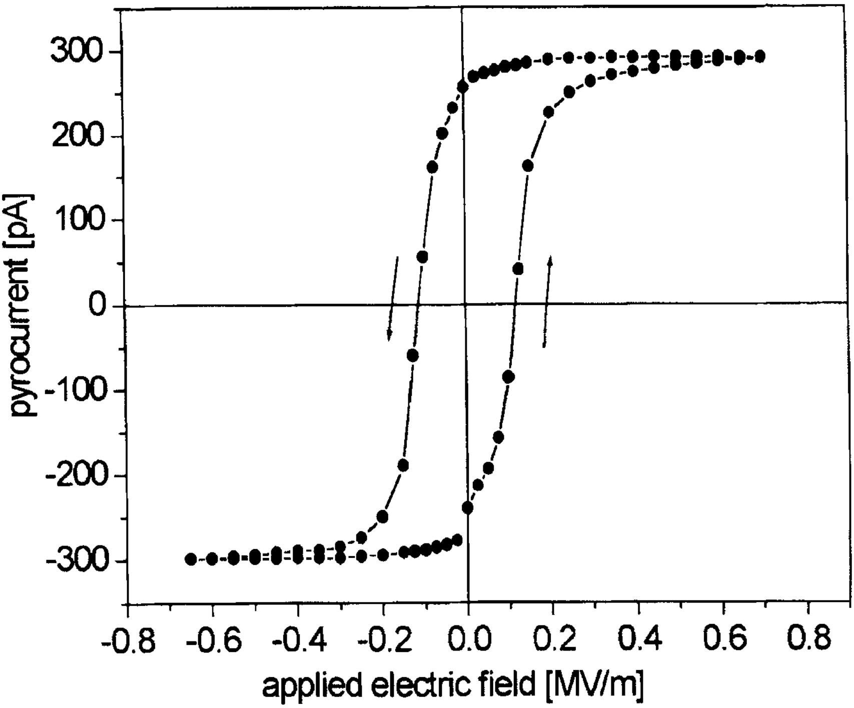

FIGURE 4 Electric field hysteresis of the pyroelectric current of 20 μm P8* between 2,5 μm polyester foils in electrodes-inside-configuration with the applied electric field perpendicular to the film and the electrodes in direct contact to the polymer. Laser modulation frequency f was 80 Hz, temperature was 38°C

The LIMM-spectra of the FLC-polymer showing the change of the pyrocurrent with the modulation frequency, are depicted in Figure 6 for the sandwich-configuration (Figure 6a) and for the planar-electrode-configuration (Figure 6b). It can be seen that the maximum of the spectrum shifts by about one order of magnitude towards lower frequencies when the planar configuration is used. This might be due to the dynamics of the heat flow. At high frequencies the heat wave penetrates a certain (frequency dependent) distance into the film and its path is approximately one-dimensional along the incident laser light. At low frequencies (f<10Hz) the diffusion of heat in the plane of the film has to be considered as well.[12] At the frequency of the maximum pyrocurrent in the planar configuration (about 3 Hz) the heat wave should have traversed the whole layer leading to homogeneous heating perpendicular to the film and inhomogeneous heating in the plane of the film, which results in the slow pyroelectric response.

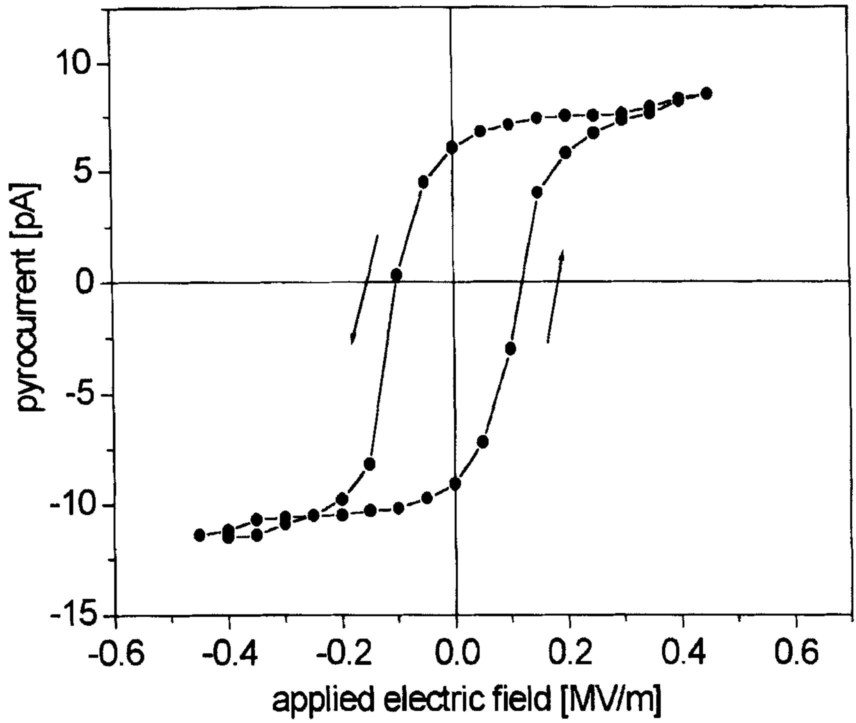

FIGURE 5 Electric field hysteresis of the pyroelectric current of a 50 μm film P8* in planar electrode configuration with the electric field in the plane of the film, perpendicular to the heat wave. Electrodes were in direct contact with the polymer, laser modulation frequency was 42.5 Hz, temperature 38 °C

Comparison of the maximum values of the pyrocurrent in both configuration shows that the response in the sandwich configuration is one to two orders of magnitude higher than in the planar configuration. Although a direct quantitative correlation is difficult because of the different heat flow mechanisms it seems sensible to conclude from the results that the FLC polymer exists as a domain structure of oriented domains each with the spontaneous polarization in a certain direction. The majority of the domains accomplish a bookshelf geometry with the polarization vector perpendicular to the film and can be probed using the sandwich configuration, while the planar electrode configuration detects residual domains that have components of the polarization in plane of the polymer film. The consistency in the minimal switching field of about 0.1 MV/m in both configurations suggests that the energetic surrounding for molecules of both orientations is comparable, which supports the domain picture.

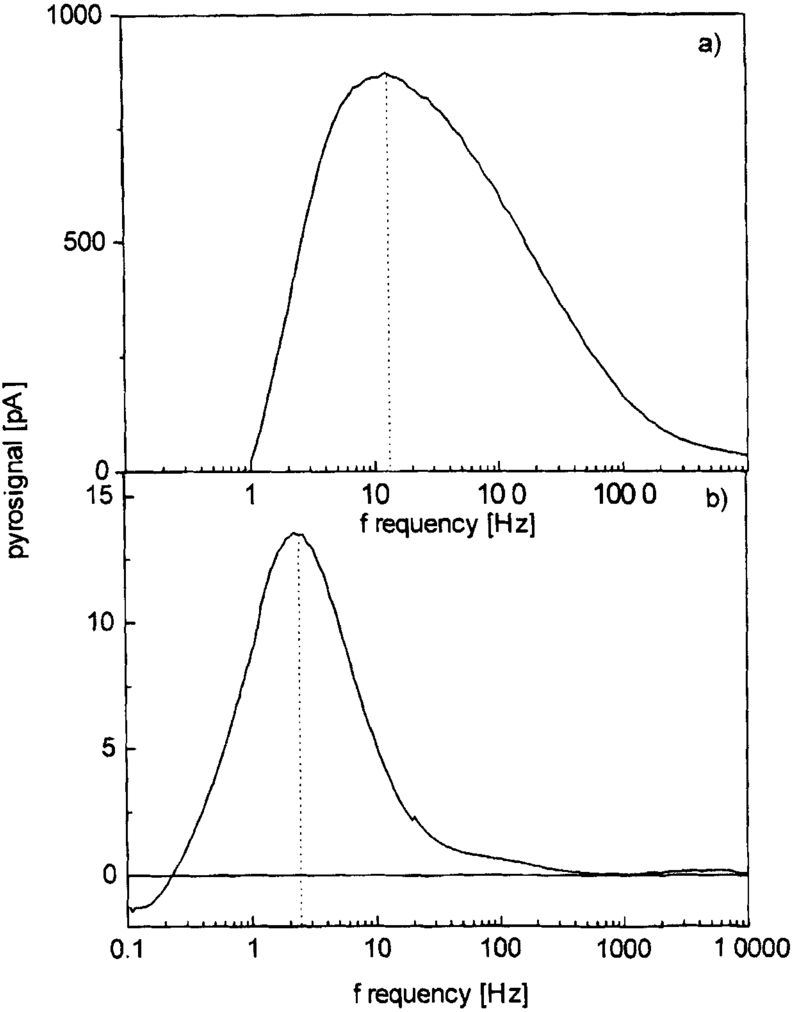

FIGURE 6 a/b LIMM-spectrum for the pyroelectric current in a) sandwich (electrodes-inside) configuration and b) in planar electrode-configuration measured at zero bias (after poling) and at a temperature of 38°C

IV. CONLUSIONS

We have presented the results of pyroelectric measurements of the electric field ferroelectric hysteresis in a ferroelectric liquid crystalline polymer using different electrode arrangements. We have found that the application of the electric field across the sandwich foil/FLCP/foil (electrodes-outside-configuration) leads to charge accumulation in the polyester foils establishing an internal electric field that opposes the externally applied field and that persists after switching off the external field. This results in a reverse hysteresis loop in contrast to a configuration where the electrodes are in direct contact with the FLCP and conventional hysteresis behavior is observed with low switching field.

We have also found that in-plane-diffusion of the heat can be used to probe the bistable ferroelectric switching in the direction parallel to the film. This is assigned to be due to a domain-like structure of the FLCP with some domains having components of the spontaneous polarization parallel to the film but most of the domains obeying a bookshelf geometry.

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