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Ferroelectricity in a Langmuir-Blodgett Multilayer Film of a Liquid Crystalline Side-Chain Polymer

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Abstract:

The first observation of ferroelectric behavior in a Langmuir-Blodgett (LB) film of a liquid crystalline polymer is reported. It is established that a 30-layer film exhibits spontaneous polarization and electro-optic switching. The magnitude as well as temperature dependence of the polarization of the LB film is found to be similar to that of the bulk material. The polarization current in the LB film follows the applied triangular wave field to higher frequencies as compared to the same material in a surface stabilized (sandwich) cell.

Based on an elegant physical argument it was first shown by Meyer et al. [1] that the smectic-C phase of chiral molecules (SmC*) is a ferroelectric liquid crystal (FLC). This was followed by the demonstration of fast electro-optic switching (in the range of μs) and optical bistability in surface-stabilized ferroelectric liquid crystal (SSFLC) displays [2]. Since then other types of electro-optic effects have also been observed in FLCs [3-5] and in chiral smectic A liquid crystals[6-8]. In all these cases the geometry of the cell is such that the sample is contained between two conducting surfaces, the surface interactions at both surfaces leading to a planar alignment of the molecules. There has also been a report on the electro-optic effects of FLC in a homeotropic (molecules perpendicular to the surface) geometry[9].

In this work, we report the first observation of ferroelectric polarization and electro-optic switching in a Langmuir-Blodgett (LB) film of a liquid crystalline polymer. We show that a 30-layer LB film whose top surface is free, exhibits spontaneous polarization and electro-optic switching. We also show that the polarization current of the LB film follows the applied electric field to higher frequencies compared to the same material as a bulk sample in a sandwich cell.

The material used was 8PPB2-Co, a side-chain polysiloxane copolymer which exhibits the SmC* phase in the range from 128°C to subambient temperatures [10]. A computer-controlled film balance (KSV 5000 with alternate dipping capability) was used to prepare the multilayer LB films [11]. Stable multilayers with transfer ratios of 0.9 to 1.0 were produced by ...ical transfers of monolayers[12] onto a glass substrate containing interdigitated electrode arrays (Fig. 1). The electrode pattern consisted of 500 gold electrode fingers, each of them being 9 mm long, 8 μm wide, and about 200 nm thick. Spontaneous polarization (P_s) was measured using the triangular wave method [13]. The active cell area (.005 cm^2) for the calculation of P_s of the 30 layer LB film is given by this geometry and the thickness of the LB film (about 1200 Å). To compare the properties of the LB films with the bulk, experiments were also conducted using a thick (10 μm) sandwich cell in the SSFLC geometry. To study the electro-optic characteristics, the LB film sample was placed on a microscope stage in between the crossed polarizers and the transmission light intensity was monitored using a photodiode.

The polarization current traces of the LB film and of the sandwich (bulk) sample in the SSFLC geometry are shown in Fig. 2. Clear current peaks are observed for the LB film. Although the polarization current of the film samples is more than 30 times smaller than of the sandwiched sample due to the difference in the active areas, an unambiguous signal could be observed at all temperatures in the SmC* phase. <u>Thus it is clear that the LB film exhibits ferroelectric polarization.</u> By comparing the current traces obtained at different frequencies for the 30-layer film and the bulk sample (Fig. 2), it is seen that the switching process in the film follows the electric field to higher frequencies than the bulk sample. At 28 Hz, the switching process for both the LB film and the bulk material is completed before the applied voltage is reversed. On the other hand, there is a marked difference at 120 Hz -the signal from the LB film regains the base line level while that from the bulk is not able to do so. Thus <u>the switching process in the LB film is faster than in the bulk.</u> This striking difference is perhaps due to differences in the molecular anchoring at the substrate surface, the LB film is anchored only at one surface while there are two anchoring surfaces in the case of the sandwich cell.

The temperature variation of the polarization of the LB film has been studied. The magnitude as well as the temperature variation of P_s of the LB film are essentially similar to those of the bulk indicating no major structural differences in the smectic layering or in the degree of dipolar order between the bulk and the LB film samples. This is supported by the results of x-ray investigations showing the same temperature dependence of the layer spacing in the SmC* phase for both samples [14].

The optical trace from the LB films is an average signal of the LB film samples in between at least 20 different electrode fingers. Fig. 3 shows the optical signal with the substrate positioned such that the electric field is parallel to the polarizer direction (dark state). When the field is reversed (point $t=t_0$ in Fig. 3), the optical trace shows a narrow maximum (bright state) followed by a second broad maximum of slightly lesser amplitude. The final state of the sample (on approaching $t=t_1$) has nearly the same optical transmittance as the initial state. On reversing the field again, essentially the same optical trace is generated. The characteristic switching time τ, defined as the time between field reversal and the second maximum, is found to be 150 ms for 40 V across the LB film. It decreases to 65 ms for 90 V, all data being taken at 30° C.

The optical trace of the switching process can be qualitatively explained by considering the molecular motion constituting the ferroelectric reorientation. On reversing the electric field applied to the monodomain LB film sample, the mesogenic side chains perform a 180° rotation around the cone coaxial with z (Fig. 1). Simultaneously, the projection of the optical axis n_p performs a 180° rotation in the substrate plane thereby passing different optical states. For n_p parallel to the polarizer, a transmittance minimum is seen while for n_p at a 45° angle to the polarizer, a maximum occurs. A quantitative description of the angular dependence of light transmittance through the LB film would have to take into account the distribution of angular velocities for different states of the switching and the fact that the experimental traces are the sum of different sample areas separated by the electrode fingers having opposite direction of the field and possibly different sense of rotation.

In summary, it is shown for the first time that a Langmuir-Blodgett deposited film of a liquid crystal is ferroelectric and exhibits electro-optic switching. A new electro-optic effect is described for the LB film. These properties of the LB film in combination with its thermal stability which allows for investigations of its dielectric and pyroelectric properties, are promising features for possible applications in the areas of electronic/ optical devices and thermal imaging.

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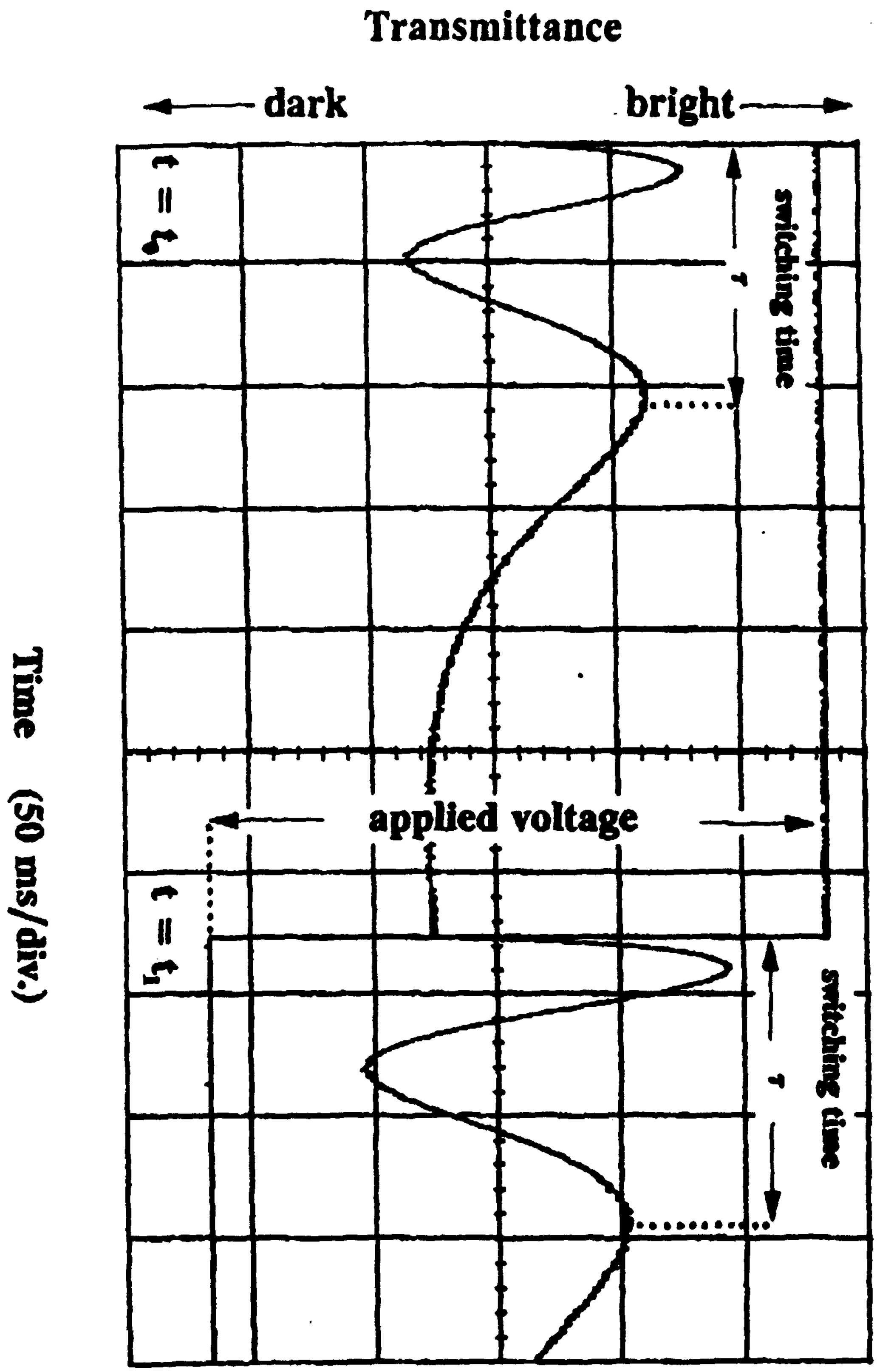
Figure Captions

Fig. 1: Schematic representation of the geometry of the glass substrate containing the gold electrode patterns used for studying the LB film. Top: Cross-sectional view of the LB layers deposited between a pair of gold electrodes. Bottom: Oblique view of a section of the surface with patterned electrodes. **E** is the field direction parallel to the layers, **z** the smectic layer normal, **n** the tilt director, $\mathbf{n}_P$ the projection of **n** onto the substrate plane and $\mathbf{P}_s$ the spontaneous polarization. The angle between director and layer normal is the tilt angle θ.

Fig. 2: Oscilloscope traces of the polarization current in a 30-layer LB film (right) and in the bulk material in a sandwich cell (left) on applying a triangular wave electric field of different frequencies. All traces are obtained at 70°C with a field of 10 V/μm. The polarization current follows the field to higher frequencies than the bulk (see text). The vertical arrows indicate minimum and maximum of the applied voltage.

Fig. 3: Optical trace of the LB film sample in between crossed polarizers on applying a square wave electric field (U = ± 50 V, f = 1.5 Hz, T = 30°C). The direction of the electric field is parallel to the polarizer. On reversing the field, a narrow maximum (bright state) followed by a second broader maximum is observed.


Transmittance
dark
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t = t0
switching time
τ
applied voltage
t = t1
switching time
τ
Time (50 ms/div.)

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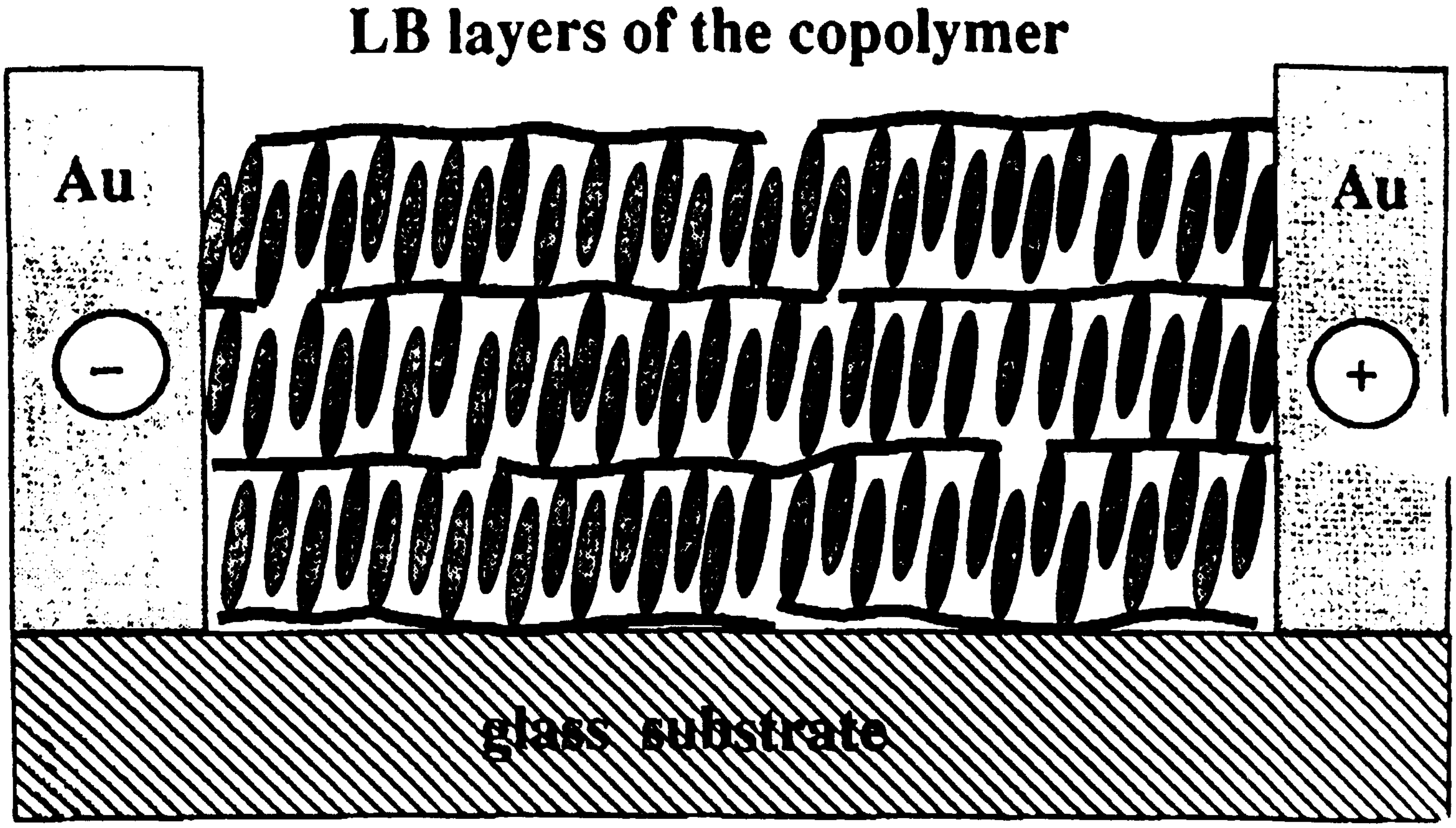

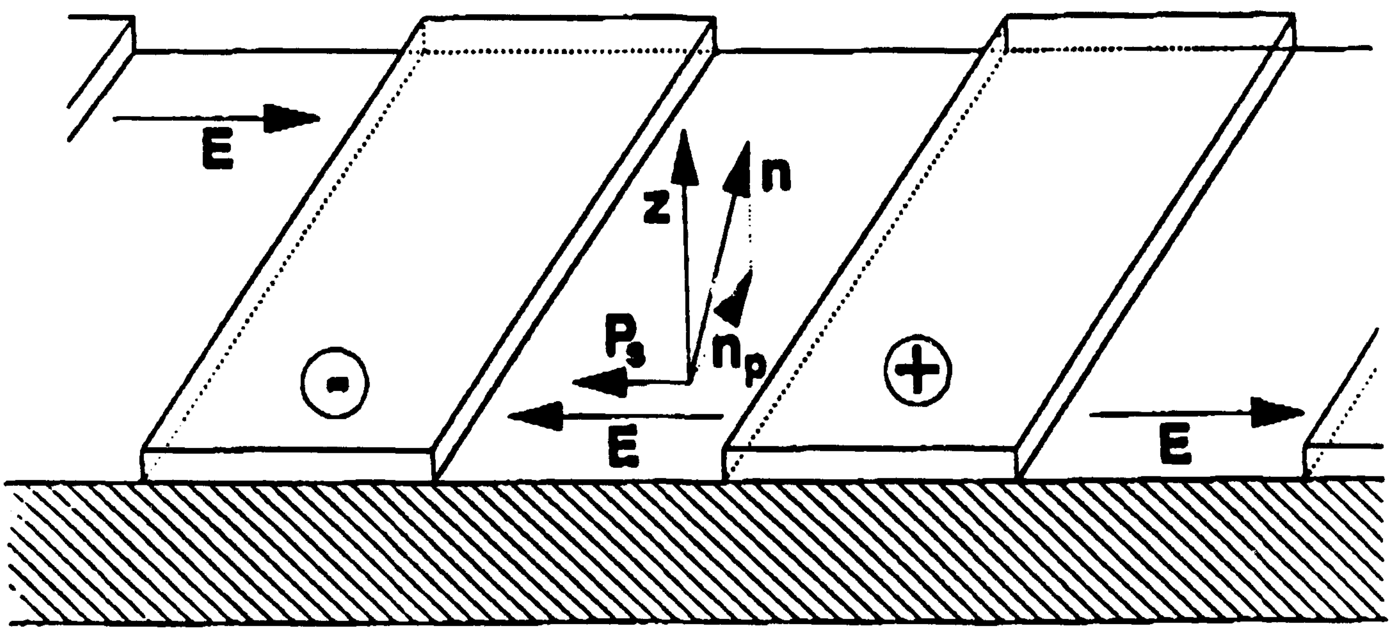

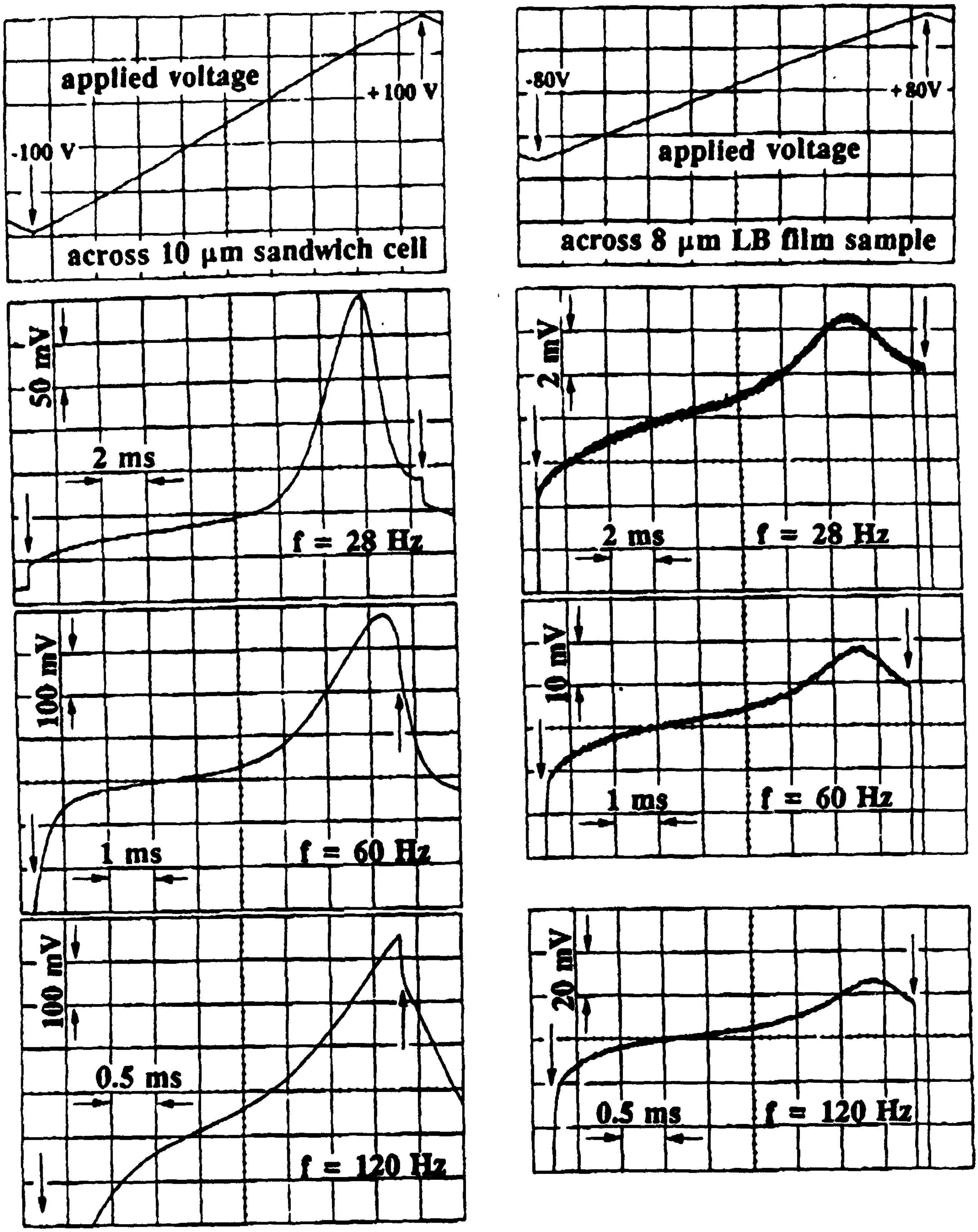
applied voltage
+100 V
-100 V
across 10 μm sandwich cell
-80V
+80V
applied voltage
across 8 μm LB film sample
50 mV
2 ms
f = 28 Hz
2 mV
2 ms
f = 28 Hz
100 mV
1 ms
f = 60 Hz
10 mV
1 ms
f = 60 Hz
100 mV
0.5 ms
f = 120 Hz
20 mV
0.5 ms
f = 120 Hz

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