Determination of polarisation profiles in P(VDF-TrFE) films with LIMM and LITP

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Abstract
Vinylidenefluoride-trifluorethylene copolymer films were polarized under different conditions and then investigated with the laser intensity modulation method (LIMM) and the laser induced thermal pulse technique (LITP). For thick films with thick electrodes the results derived from LIMM and LITP experiments are identical. For thin films experimental and methodical constraints influence the applicability and resolution achieved with LITP.

1. Introduction

Thermal methods are useful for the investigation of the polarization profiles in pyroelectric materials. The sample under investigation is heated on one surface by the absorption of laser light. The incident radiation intensity is varied with time and the pyroelectric current is recorded. The laser intensity modulation method (LIMM) [1] uses sinusoidally modulated light, the laser induced thermal pulse technique (LITP) [2, 3] a short laser pulse. The thermal excitation generates a thermal wave which penetrates into the sample. For LIMM the penetration depth varies with the modulation frequency, while for LITP it is a function of time. From a fundamental point of view both techniques are equivalent as the input-output relation of a linear system can be either determined from the response to a sinusoidal input as a function of frequency or from the response to a short input pulse as a function of time. We report on investigations of thick and thin films of polyvinylidenefluoride-trifluoroethylene (PVDF-TrFE) with both methods.

2. Experimental

Thick films (≈ 0.8 mm) and thin films ($\approx 25\ \mu$m) of PVDF-TrFE in the composition 75/25 mol% were prepared for investigations with LIMM and LITP. Thin layers of silver paint ($5 \ldots 10\mu$m thickness) were deposited on the two surfaces of the thick samples to serve as electrodes and also as absorbing layer for the laser radiation. Three thick films (samples A, B, C) were polarized under different conditions. Sample A was poled under 16 kV for 2 hours at 115 °C , sample B under 22 kV at 110 °C . Sample C was poled under 18 kV for 2 hours at 90 °C and then reversely poled under 20.5 kV for 3 hours at 110 kV. On the two surfaces of the thin film (sample D) 100 nm thick gold electrodes were evaporated. The thin film was polarized at room temperature by the application of a half cycle of a sinusoidal voltage with an amplitude of 2.9 kV and a duration of 50 s.

In the LIMM experiments the output power of a laser diode with the wavelength 750 nm was modulated sinusoidally with an amplitude of 10 mW. The laser light was directed to one electrode of the sample. Pyroelectric current spectra were measured with a fast current-to-voltage converter (risetime 10^{-7}s) and a Lock-In amplifier as a function of modulation frequency. The frequency range was 0.1 Hz to 10 kHz for the thick samples and 1 Hz to 100 kHz for the thin sample. Ten data points were measured per frequency decade. With an integration time of 30 s, the total time required for the recording of a pyroelectric spectrum was about half an hour. The response

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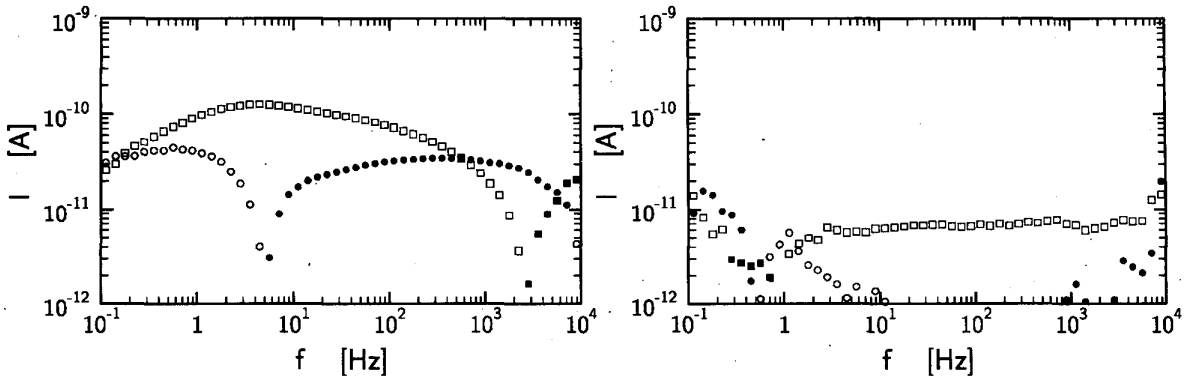

Figure 1 The pyroelectric current spectra measured on the thick sample A with illumination of the anode (left figure) and of the cathode (right figure). Symbols used: Real part $\Re I_\sim > 0$: □, $\Re I_\sim < 0$: ■. Imaginary part $\Im I_\sim > 0$: ○, $\Im I_\sim < 0$: ●.

function of the equipment was measured witn a fast photodiode as the reference element and used to correct the measured pyroelectric current spectra [4]. Two pyroelectric spectra were recorded for an irradiation of each electrode of the samples. The pyroelectric current spectra measured on the thick sample A with illumination of the anode and cathode, respectively, are shown in Fig. 1. In the LITP experiments one electrode of the samples was irradiated by the pulsed beam of a Nd/YAG laser with a pulse width of about 30 ns. The pyroelectric signal was measured with a charge amplifier (risetime 2×10^{-5}s) and recorded with two storage oscilloscopes to record the initial phase of the signal on a short time scale and to cover the total time range until the temperature distribution in the sample became homogeneous. Each oscilloscope recorded 8000 data points with a time raster of 10 μs and 1 ms, respectively. 256 equidistant data points were extracted from the total set of 16000 measured data points by averaging on a logarithmic time scale. The thermal pulse response signals of sample A when anode and cathode were illuminated by the laser pulse, respectively, are shown in Fig. 2.

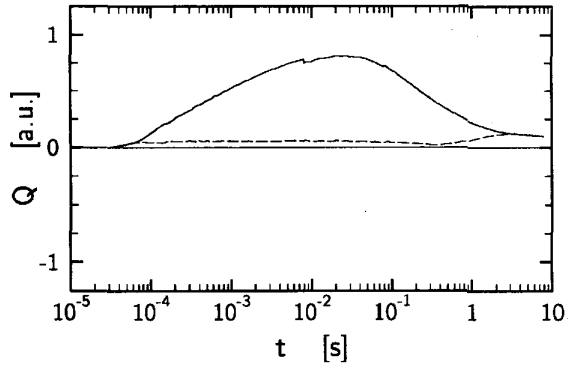

Figure 2 The thermal pulse response signals $Q(t)$ when the anode (———) and cathode (— — —) sides of sample A were irradiated by the pulsed laser.

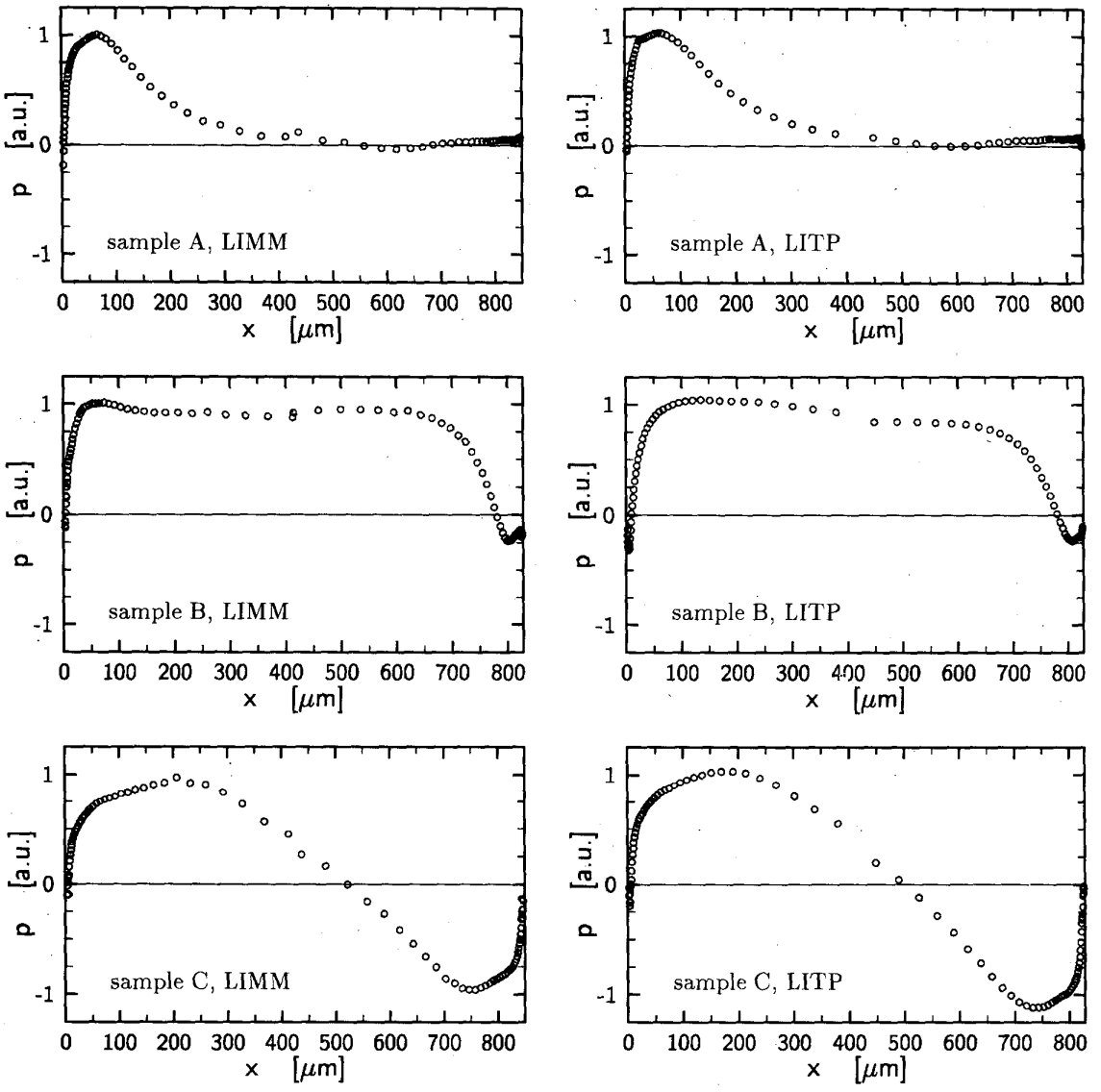

Figure 3 The polarization profiles of samples A, B and C obtained from the LIMM experiments (left figures) and from the LITP experiment (right figures).

3. Results and Discussion

The measured LIMM spectra of the samples have been evaluated with the thermal scanning function (TSF) technique [5, 6]. The LITP response signals have been analyzed with the procedure given in [7] using a Fourier transform of the response measured in the time domain to the frequency domain and a subsequent TSF analysis. The results for the thick samples A, B and C are shown in Fig. 3. The pyroelectric profiles obtained from LIMM and LITP are nearly identical. The situation is different for thin samples as shown in Fig. 4. The reason is the slow risetime of the charge amplifier used in the LITP experiments. To overcome this experimental limitation we have also used the fast current-to-voltage converter (like in LIMM) for the LITP measurements. With this setup, however, on thin film samples always only one strong pulse with the risetime of

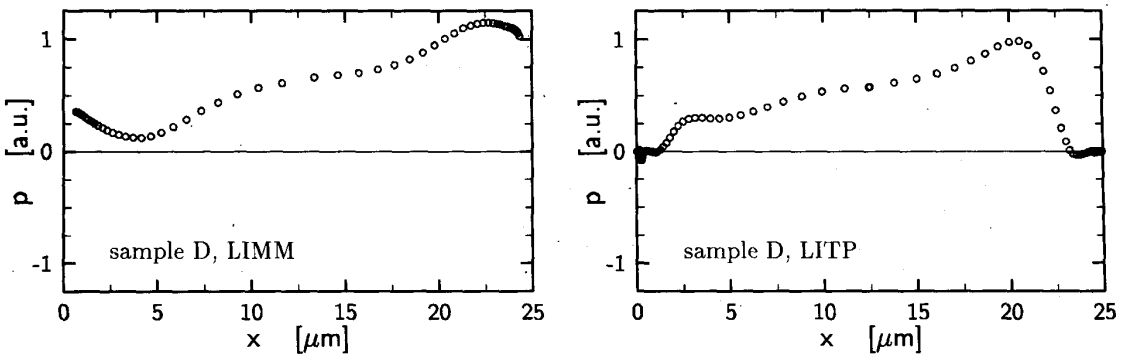

Figure 4 The polarization profiles of the thin sample D obtained from the LIMM experiments (left figure) and from the LITP experiment (right figure). The deviations are due to the limited response time of the charge amplifier used in the LITP setup.

the current-to-voltage converter was observed, even if their polarization profile was different. This signal results from the thermoelastic expansion of the illuminated electrode which induces a combined shear and tensile stress in the sample. Although the charge generated by the piezoelectric response of the sample is much smaller than the pyroelectrically generated charge, this short pulse dominates the current signal and makes a measurement of the pyroelectric signal impossible.

4. Conclusion

The identical pyroelectric profiles obtained with LIMM and LITP on thick PVDF-TrFE film with thick electrodes show that, as expected, both techniques are appropriate to determine the input-output relation of a pyroelectric film. An advantage of LITP is the short measurement time, in the case of the thick films 10 s compared to 30 min for LIMM. The intensity of the laser pulse in a LITP experiment, however, is substantially higher than with LIMM. When thin electrodes are used, which is necessary when a high surface near resolution is required, the thermoelastic expansion of the thin electrode generates substantial stress in the sample and therefore a piezoelectric signal. Although the piezoelectric charge signal is much smaller than the pyroelectric charge signal in a LITP experiment with PVDF-TrFE film, the amplitude of the piezoelectric current is so large that the pyroelectric signal is not detectable with a current-to-voltage converter.

References

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