Chapter 5

PYROELECTRIC AND NONLINEAR DIELECTRIC PROPERTIES OF COPOLYMERS OF VINYLIDENE FLUORIDE AND TRIFLUOROETHYLENE*

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Polymer ferroelectrics like poly(vinylidene fluoride) and its copolymers with trifluoroethylene are intrinsically two-phase systems consisting of crystalline regions surrounded by amorphous material. Connected by covalent bondings, the coupling of dipoles along a polymer chain is much stronger than in an anorganic ferroelectric crystal. The interest in these materials is motivated by fundamental interest and by a high potential for applications.

The main topics in this chapter concern the ferroelectric phase transition and the interaction of charge in the amorphous phase with polar crystallites. The experimental investigations are based on a detailed analysis of pyroelectric response and dielectric nonlinearities.

Injection of charge from the electrodes and migration of charge in the amorphous phase can cause complicated profiles of the electric field during the poling of the material. The result is spatially inhomogeneous profiles of the polarization. The laser intensity modulation method (LIMM) introduced by Lang is an experimental technique for the nondestructive scanning of pyroelectric profiles. It is based on the generation of thermal waves by the absorption of intensity-modulated laser light at the surface of the material. The decay length of the thermal waves propagating into the material is a function of frequency. A pyroelectric response is generated in the heated part of the material. Therefore, the information on the spatial pyroelectric profile is contained in a measured frequency spectrum of the pyroelectric current. However, the extraction of the profile from measured data has been a major difficulty, because it means the solution of an ill-posed inversion problem. We have introduced an evaluation technique based on the fact that a particular component of the pyroelectric current is directly connected to a thermal scanning function. It is shown that an extension of this thermal scanning function technique by partial deconvolution allows the extraction of a maximum of information on the pyroelectric profile from a measured pyroelectric spectrum. Our experimental realization of the LIMM technique achieves a near surface resolution of $\approx$100 nm, unrivaled by other techniques. The extension to a pyroelectric tomography procedure allows three-dimensional imaging of pyroelectric distributions.

To study the charge injection in poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) during poling, the resulting pyroelectric profiles in the vicinity of the electrodes have been investigated. At the cathode side an unpolarized region is detected that grows with increasing poling duration, while the shape of the pyroelectric profile at the anode side is not influenced. This effect can be understood as follows. During the poling process negative charge is injected into the polymer. This negative space–charge shields the external electric field and prevents the coercive field from being reached. In addition, approximately 150 nm wide unpolarized regions are detected at both electrodes, independently of the poling procedure.

Pyroelectric profiles measured with the LIMM technique on a variety of specimens with different polarization profiles are compared with the piezoelectric profiles recorded with the piezoelectric pressure step (PPS) method. For each sample the observed spatial structures are identical, indicating that pyroelectricity and piezoelectricity in these materials have the same underlying mechanism. Whereas the resolution of pyroelectric and piezo-

electric profiling techniques is constant on a logarithmic and on a linear scale, respectively, both techniques are highly competitive. Near the surface the LIMM technique provides higher resolution; in the bulk the PPS method does.

Pyroelectric investigations performed at very low frequencies show a significant contribution from the movement of compensating charge in the amorphous region. At higher frequencies the pyroelectric response arises only from the dipoles; that is, from the change of dipolar orientation and dipolar density in the crystallites. The magnitude of this low frequency contribution indicates neutralization; that is, the electric field of the polarized crystallites is locally compensated by charge at the interface to the amorphous phase. If the polarization is varied by a temperature change, the excess in compensating charge becomes mobile. Even small variations of the polarization are compensated by an appropriate rearrangement of charge within a time scale of some seconds.

In a semicrystalline ferroelectric there are two possibilities to realize a state with zero remanent polarization. The directions of the polar axes of the single crystallites may be randomly oriented in the material or the single crystallites may fall into ferroelectric domains analogous to a single crystalline ferroelectric. Dielectric investigations indicate that both cases are realized in PVDF-TrFE. A domain contribution to the permittivity is detected in annealed material with larger crystallites, but not in unannealed material in which the crystallites are smaller. This shows that the crystallites in PVDF-TrFE can fall into domains if their size exceeds a critical value.

In PVDF-TrFE that is polarized before the first annealing, a persistent polarization is found that remains stable in the paraelectric phase. During the annealing of PVDF-TrFE, chain links near the surfaces of the crystallites become ordered and the crystalline regions grow. The observed persistent polarization is explained by nonswitchable dipoles, which form an intermediate phase between the crystalline and the amorphous phase in annealed samples. The polarization state of the material before the first annealing is permanently stored in this intermediate phase.

To study the ferroelectric phase-transition behavior of PVDF-TrFE, dielectric nonlinearities have been investigated. The experimental technique is based on the analysis of harmonics in the electric current while a sinusoidal voltage is applied to the material. The results obtained on PVDF-TrFE in the 56/44 and 70/30 mol% compositions allow the test of theoretical predictions. The semicrystalline structure of the material and the distribution of Curie temperatures of the crystallites are taken into account. For a phenomenological description, the Landau parameters of the crystalline system are determined. Odajima has proposed a microscopic model that is based on an Ising model for the intrachain interaction and a mean field approximation for the interchain interaction of the dipoles. For the first detailed experimental test of Odajima's theory, the dielectric nonlinearities are derived from the theory and compared with experimental findings. The intrachain and interchain interaction energies are determined. With respect to the strong approximations involved in Odajima's theory, the agreement with experimental findings is reasonable.

For many applications of ferroelectric polymers it is important to prepare them in a state with a high macroscopic polarization. A problem in the poling of polymers is caused by the fact that the coercive field strength required for the orientation of the polar groups is only slightly lower than the electrical breakdown field strength. A new technique has been developed. The unmetallized polymer film is poled in a sandwich between ferroelectric crystals. The interfaces between the ferroelectric crystals and the polymer form well defined sources for a high dielectric displacement. In this way the intensive quantity polarization rather than the extensive quantity electric field, is fixed in the polymer. With this technique a high polarization is achieved, while destructive electrical breakdown is completely prevented.

A promising application of PVDF-TrFE is use as detector material in integrated pyroelectric sensor arrays for infrared radiation. Examples for a realized and a projected sensor are given.