

# Influence of Poling and Annealing on the Nonlinear Dielectric Permittivity of PVDF-TRFE Copolymers

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## ABSTRACT

The linear and second order permittivities of as-prepared and annealed, poled and unpoled PVDF-TRFE 56/44 mol% copolymer film are investigated as a function of temperature. In contrast to annealed PVDF-TRFE, the linear permittivity of unannealed PVDF-TRFE and its temperature dependence is not influenced by poling. This effect can be explained by the existence of domain walls in the crystalline regions of annealed samples, while the smaller crystallites in unannealed samples are always in a single domain state. Thus the poling degree dependence of the linear permittivity of annealed samples may therefore be an effect of domain wall motion. The second order permittivity is a measure of the remanent polarization. Samples poled before the first annealing exhibit a small persistent polarization that remains stable in the paraelectric phase, in contrast to samples which remain unpoled before annealing. This non-switchable polarization is unchanged after several heating cycles and even after poling in the opposite direction. An explanation for this fixed polarization are non-switchable dipoles which form an intermediate phase between the crystalline and the amorphous phase.

## 1. INTRODUCTION

COPOLYMERS PVDF (polyvinylidene fluoride)-TRFE (trifluoroethylene) consist of ferroelectric crystallites embedded in an amorphous matrix. During the first heating of spin coated copolymer films above the Curie temperature the crystallites grow and the crystallinity of the samples increases. In the higher crystalline annealed samples a higher polarization is achieved, what is important *e.g.* for pyroelectric and piezoelectric applications. Therefore, the copolymer usually is annealed before it is poled. In this paper, also the poling of unannealed material and its influence on the dielectric properties have been studied.

## 2. MEASUREMENT PRINCIPLE

To measure the linear permittivity  $\varepsilon_1$  and the second order permittivity  $\varepsilon_2$ , *i.e.* the coefficients in the series expansion of the dielectric displacement  $D$  in powers of the electric field  $E$

$$D = P_s + \varepsilon_0 \varepsilon_1 E + \varepsilon_0 \varepsilon_2 E^2 + \varepsilon_0 \varepsilon_3 E^3 + \dots \quad (1)$$

a sinusoidal electrical field with the frequency  $f_0 \approx 1$  kHz,  $\omega_0 = 2\pi f_0$ , and an amplitude  $E_{\sim}$  far below the coercive field is applied to the sample. A signal with a high spectral purity is generated by appropriate filtering of the output signal of a frequency synthesizer. The current through the sample is recorded by the voltage developed over a series resistor and digitized by a 16 bit AD (analog digital) converter at a sampling period of 20  $\mu$ s. Spectra of the current density  $j(t)$  are calculated

by Fourier transform

$$j(t) = \frac{dD(t)}{dt} = \sum_{l=0}^{\infty} (j_l' \cos l\omega_0 t + j_l'' \sin l\omega_0 t) \quad (2)$$

The nonlinear permittivities  $\varepsilon_n$  can be evaluated from a sum of Fourier coefficients  $j_l''$  [1]. If the excitation amplitude is chosen appropriately, *i.e.*, sufficiently small so that the coefficients  $j_n''$  decrease strongly with increasing order  $n$ , then  $\varepsilon_n$  can be calculated approximately from the component  $j_n''$ .

$$\varepsilon_0 \varepsilon_n \approx \frac{-1}{\omega_0} \frac{2^{n-1}}{n E_{\sim}^n} j_n'' \quad (3)$$

In the general case, the  $\varepsilon_n$  defined by Equation (3) form the real parts  $\varepsilon_n'$  of the complex nonlinear permittivities. Non-vanishing components  $j_n'$  can be described by the definition of imaginary parts  $\varepsilon_n''$  which are calculated from  $j_n'$  in analogy to Equation (3). Equation (1), however, explains only real permittivities.

If a crystalline ferroelectric material is described by a Landau free energy expansion [2]

$$F = F_0 + \frac{1}{2} \alpha D^2 + \frac{1}{4} \gamma D^4 + \frac{1}{6} \delta D^6 \quad (4)$$

the second order permittivity is given by the relation [3]

$$\varepsilon_0 \varepsilon_2 = -P_r (\varepsilon_0 \varepsilon_1)^3 (3\gamma + 10\delta P_s^2) \quad (5)$$

as a function of the remanent polarization  $P_r = X_P P_s$ , where  $X_P$  is the poling degree of the sample.  $X_P$  is zero for unpoled samples fallen into domains and reaches  $X_P = 1$  if all dipoles are aligned in parallel to the poling field.