PERSISTENT NON-SWITCHABLE POLARIZATION IN P(VDF–TrFE) FILMS

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Abstract

Poling experiments were performed on as-prepared and on annealed polyvinylidene fluoride/trifluoroethylene (P(VDF-TrFE)) copolymer films. The polarization of the samples was recorded as a function of temperature by the measurement of the second order dielectric permittivity. The polarization of samples annealed before the first poling completely vanishes in the paraelectric phase. However, in samples poled before the first annealing a persistent polarization is detected that remains stable in the paraelectric phase. It is unchanged after several heating and cooling cycles and even after poling the sample in the opposite direction. This constant polarization can be explained by non–switchable dipoles which form an intermediate phase between the crystalline and the amorphous phase. The polarization state of the film before the first annealing is permanently stored in this intermediate phase.

1. Introduction

P(VDF-TrFE) copolymers 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. Thus usually the copolymer is annealed before it is poled. In this paper we show how poling before annealing influences the sample properties after the annealing process.

2. Determination of the polarization from the second order permittivity

The second order permittivity, i.e., the coefficient ε_2 in the series expansion of the dielectric displacement D in powers of the electric field E

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

is a measure for the polarization. The Landau free energy expansion (e.g. [1])

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