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Dielectric nonlinearity of PVDF–TrFE copolymer

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Abstract

The experimental study of small signal dielectric nonlinearity is a powerful procedure for the investigation of complex ferroelectric materials. Dielectric nonlinearity of a copolymer of polyvinylidenefluoride with trifluoroethylene, in the compositions 70/30 and 56/44 mol%, has been measured by an analysis of the harmonic spectrum of the electric current in response to a sinusoidal voltage. The Landau parameters of the crystalline phase are determined from the experimental data, and the order of the phase transition is discussed. It is found that the values of the Landau parameter γ in the ferroelectric and in the paraelectric phase are different. In the ferroelectric phase γ is a function of the degree of poling. The experimental results are also compared with theoretical predictions derived from Odajima's microscopic model, which assumes a one-dimensional Ising model for the dipolar coupling along the polymer chains and a mean field theory for the interchain interaction. Copolymer film deposited from a solution that is poled before annealing shows a small second-order dielectric nonlinearity even in the paraelectric phase. The reason for this is a non-switchable polarization, which is stable above the Curie temperature. We attribute this polarization to the intermediate phase in between the crystallites and the amorphous regions.

Keywords: Poly(VDF–TrFE); Nonlinear dielectricity; Ferroelectric transitions

1. Introduction

The investigation of nonlinear dielectric permittivities gives valuable information on the ferroelectric properties of a material. The permittivities of odd order give direct access to the free energy (Landau parameters) [1–3] and the order of the phase transition [4,5]. The second-order permittivity provides information on the degree of poling [6] and the existence of fixed dipoles [7]. The method should, in particular, be suitable for describing complicated ferroelectric systems such as the semicrystalline polyvinylidenefluoride–trifluoroethylene, P(VDF–TrFE), copolymers, as it provides much more information than the linear permittivity alone. P(VDF–TrFE) copolymers consist of ferroelectric regions with crystalline order embedded in an amorphous matrix. They exhibit a diffuse phase transition from the ferroelectric to the paraelectric phase caused by a statistical variation of the VDF content of the crystallites [8]. The dielectric properties of the copolymers near the phase transition depend strongly on the composition of VDF and TrFE.

In this work the nonlinear dielectric properties of P(VDF–TrFE) copolymers are investigated and some interesting conclusions are obtained from the results. The data are compared with a detailed phenomenological description. A microscopical approach developed by Odajima [9] for describing the polarization of P(VDF–TrFE) copolymers is, for the first time, considered with respect to the nonlinear dielectric permittivities and compared with the experimental results.

2. Theory

2.1. Model for the nonlinear dielectric properties of a semicrystalline ferroelectric system

Fig. 1 illustrates the structure of a semicrystalline polymer (Fig. 1a) and its approximation by a brick like structure (Fig. 1b) as proposed for PVDF [10]. For this structure, the electric field in the whole sample is assumed to be in parallel to the external field, and the dielectric properties are described by a capacitor model (Fig. 1c). The ferroelectric crystalline system is characterized by nonlinear dielectric permittivities ε_{cn} defined by the expansion of the dielectric displacement D in powers of

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