Journal of the Korean Physical Society, Vol. 32, February 1998, pp. S1084~S1086

Phenomenological and Microscopical Description of the Nonlinear Dielectric Permittivities of P(VDF–TrFE)

Beatrix PLOSS and Bernd PLOSS
Institut für angewandte Physik der Universität Karlsruhe, D-76128 Karlsruhe, Germany

Nonlinear dielectric permittivities up to the third order are investigated on P(VDF–TrFE) copolymers in the compositions 56/44 mol% and 70/30 mol% as a function of temperature and poling degree. The experimental results are described both phenomenologically and microscopically, while the semicrystalline structure of the copolymers and a distribution of Curie temperatures of the crystallites are taken into account. From the phenomenological description the Landau parameters of the crystalline phase are estimated, and the observed dependence of the phase transition temperature on the degree of poling is explained. Furthermore, the nonlinear dielectric permittivities are calculated following the microscopic theory derived by Odajima. The interaction of the dipoles in a polymer chain is described by a one-dimensional Ising model, while the interaction of dipoles in different chains is taken into account by a mean field approximation. The interchain and the intrachain interaction energies are determined from experimental results.

I. INTRODUCTION

P(VDF–TrFE) copolymers consist of ferroelectric crystals embedded in an amorphous matrix. Caused by the statistical variation of their VDF content the crystallites show a distribution of Curie temperatures, and as a consequence the materials exhibit a diffuse phase transition. Due to this complicated semicrystalline structure, experimental results of linear dielectric investigations are usually not sufficient for a detailed comparison with the predictions of theoretical models [1]. More valuable information on ferroelectric copolymers can be obtained by the investigation of nonlinear dielectric permittivities [2,3].

II. THEORY

1. Model for the Nonlinear Dielectric Properties of a Semicrystalline Ferroelectric System

Fig. 1 illustrates a semicrystalline polymer (a) and its approximation by a brick like structure (b) as proposed for PVDF [4]. 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 (c). The ferroelectric crystalline system is characterized by nonlinear dielectric permittivities ε_{Kn} defined by the expansion of the dielectric displacement D in powers of the electric field E:

$$D = P_{Ks} + \varepsilon_0\varepsilon_{K1}\,E + \varepsilon_0\varepsilon_{K2}\,E^2 + \varepsilon_0\varepsilon_{K3}\,E^3 + \cdots. \quad (1)$$

The amorphous system is described by the linear permittivity ε_A. The calculation of the nonlinear dielectric permittivities of the whole system ε_n yields

$$\varepsilon_1 = \frac{X_c}{h}\,\frac{\varepsilon_{K1}}{h+(1-h)\varepsilon_{K1}/\varepsilon_A} + (1-\frac{X_c}{h})\varepsilon_A, \quad (2)$$

$$\varepsilon_n = X_c\,\frac{\varepsilon_{Kn}}{(h+(1-h)\varepsilon_{K1}/\varepsilon_A)^{n+1}}, \quad \text{for} \quad n>1. \quad (3)$$

$X_c = V_K/V$ is the volume fraction of the crystalline part *i.e.*, the crystallinity of the sample. The quotient $h = d_K/d$ of the thicknesses of the crystalline region and the sample depends on the shape of the crystallites. For cubic crystallites h is equal to $\sqrt[3]{X_c}$.

2. Phenomenological and Microscopical Theory for the Crystalline System

Ferroelectrics near the phase transition are usually described phenomenologically by the Landau free energy

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

Using the nonlinear relation between the electric field $E = \partial F/\partial D$ and the dielectric displacement the nonlinear dielectric permittivities ε_{Kn} can be calculated as a function of the Landau parameters α, γ and δ. In the paraelectric phase where $P_s = 0$ the permittivities of even order vanish and the first two of odd order are $\varepsilon_0\varepsilon_{K1} = 1/\alpha$ and $\varepsilon_0\varepsilon_{K3} = -\gamma/\alpha^4$.

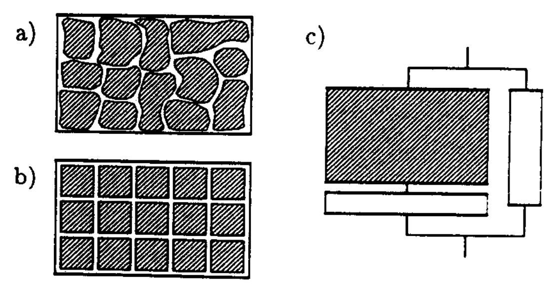

Fig. 1. Model for the dielectric properties of the semicrystalline copolymers. (a) ferroelectric crystallites embedded in an amorphous matrix, (b) simplification: brick like structure, (c) capacitor model.