



Non-linear dielectric spectroscopy for detecting and evaluating structure-property relations in a P(VDF-TrFE-CFE) relaxor-ferroelectric terpolymer

Thulasinath Raman Venkatesan^{1,2} · David Smykalla³ · Bernd Ploss³ · Michael Wübbenhorst² · Reimund Gerhard¹

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Abstract

Non-linear dielectric spectroscopy (NLDS) is employed as an effective tool to study relaxation processes and phase transitions of a poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) relaxor-ferroelectric (R-F) terpolymer in detail. Measurements of the non-linear dielectric permittivity ϵ_2' reveal peaks at 30 and 80°C that cannot be identified in conventional dielectric spectroscopy. By combining the results from NLDS experiments with those from other techniques such as thermally stimulated depolarization and dielectric-hysteresis studies, it is possible to explain the processes behind the additional peaks. The former peak, which is associated with the mid-temperature transition, is found in all other vinylidene fluoride-based polymers and may help to understand the non-zero ϵ_2' values that are detected on the paraelectric phase of the terpolymer. The latter peak can also be observed during cooling of P(VDF-TrFE) copolymer samples at 100°C and is due to conduction and space-charge polarization as a result of the accumulation of real charges at the electrode-sample interface.

Keywords Non-linear dielectric spectroscopy · P(VDF-TrFE-CFE) · Relaxor-ferroelectric polymer · Dielectric hysteresis · Curie-transition · Mid-temperature transition

1 Introduction

In recent years, terpolymers that are based on vinylidene fluoride (VDF) and tri-fluoroethylene (TrFE), but that have an additional fluorine-containing monomer, receive more and more attention due to their unique properties. In contrast to their ferroelectric counterparts such as the homopolymer polyvinylidene fluoride (PVDF) or its well-known copolymers with tri-fluoroethylene (P(VDF-TrFE)), tetrafluoroethylene (P(VDF-TFE)), and hexa-fluoropropylene (P(VDF-HFP)), the terpolymers exhibit relaxor-ferroelectric (R-F) behavior which leads to a significantly wider spectrum of useful properties. In R-F terpolymers, a slim polarization

versus electric-field hysteresis curve and a very large electrostriction coefficient are often available [1, 2]. A narrow hysteresis loop with a low coercive field E_c and a high saturation polarization P_s leads to advantages, e.g. in energy-storage devices [2]. In addition, a lower coercive field E_c yields lower switching voltages, which is very useful for memory applications [3]. The ability to be cast into very thin films makes R-F terpolymers very attractive for use in flexible and stretchable electronics [4, 5].

Addition of a third fluorine-containing co-monomer such as chlorofluoroethylene (CFE) or chlorotrifluoroethylene (CTFE) into P(VDF-TrFE) copolymer chains can break the long-range interaction within the ferroelectric dipolar regions and may reduce them to nano-domains [1, 6]. Such a nano-structure forces the majority of the copolymer units to adopt gauche-containing TG^+TG^- and $T_3G^+T_3G^-$ conformations [7, 8]. As a result, the ferroelectric-to-paraelectric (F-P) or Curie transition temperature (T_C) of the terpolymer is found close to room temperature (RT) [1, 9]. The reduced interactions between the dipoles allow them to be more easily oriented in an applied electric field, which results in a characteristic reduction of the coercive field E_c and also in a high saturation polarization P_s . The dielectric permittivity of

✉ Thulasinath Raman Venkatesan
thulasinath.raman.venkatesan@uni-potsdam.de

¹ Institute of Physics and Astronomy, University of Potsdam, Karl-Liebknecht-Strasse 24-25, 14476 Potsdam, Germany

² Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

³ Department of SciTec, University of Applied Sciences Jena, Carl-Zeiss-Promenade 2, 07745 Jena, Germany