# Nonlinear Dielectric Spectroscopy of P(VDF-TrFE-CFE) Films for Non-Volatile Memory Applications

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***Abstract*- The potential suitability of P(VDF-TrFE-CFE) relaxor-ferroelectric terpolymer films for non-volatile memory devices is assessed from the $\varepsilon_2/(3\varepsilon_0^2\varepsilon_1^3)$ ratio that is directly proportional to the remanent polarization. Non-linear dielectric spectroscopy was employed to obtain $\varepsilon_2/(3\varepsilon_0^2\varepsilon_1^3)$ ratios *vs.* time or temperature. For comparison, dielectric hysteresis loops were measured in a Sawyer-Tower circuit. Optimum poling temperatures and polarization stabilities of non-annealed and annealed terpolymer samples were also determined. The results indicate that annealed samples show definite polarization values only when poled at low temperatures close to their respective glass transition. On the other hand, non-annealed samples allow poling at ambient temperature due to their higher content of the ferroelectric crystalline phase. Both, non-annealed and annealed terpolymer films show stable polarization values for several minutes after field removal – indicating their possible use at least in short-term memory devices.**

## I. INTRODUCTION

The rapid increase in the market of organic electronic devices [1] has led to a demand for applications with better performance, higher reliability and easier fabrication. Poly(vinylidene fluoride – trifluoroethylene) (P(VDF-TrFE)) **co**polymers have been the workhorse materials for such devices that can be used for non-volatile memory applications [2]–[6] and as ferroelectric field-effect transistors [7], [8]. This is due to their excellent polarization stability and the large remanent polarization they can exhibit. However, they suffer from the drawback that a high activation energy is required for polarization switching, thus requiring high operating voltages [9], [10]. In addition, relatively longer times are necessary for the polarization switching in P(VDF-TrFE) [11], [12].

On the other hand, the more recently developed P(VDF-TrFE)-based **ter**polymers offer lower switching voltages on account of their lower coercive field ($E_c$) and high electrical energy density with faster discharge rates [13], which makes them very attractive for ferroelectric random-access memory (FeRAM) devices with low operating voltages and high reading/writing speeds [14]. P(VDF-TrFE)-based terpolymers contain a bulky termonomer such as chlorofluoroethylene (CFE) that reduces the interaction between ferroelectric VDF-TrFE segments, making the material relaxor-ferroelectric (R-F) in nature [15]. In addition, their Curie transition ($T_C$) lies within ambient temperature ranges where the permittivity reaches a maximum [16]. The polarization of a P(VDF-TrFE-CFE) terpolymer depends on the annealing conditions and on the temperature at which the polarization is measured [17].

In addition to dielectric-hysteresis measurements, the polarization behavior of electro-active materials can also be assessed from non-linear permittivity measurements by evaluating the $\varepsilon_2/(3\varepsilon_0^2\varepsilon_1^3)$ ratio that is proportional to the remanent polarization ($P_r$) in the respective sample [18]. The state of polarization can be known by reading the sign of the second-order permittivity [19], where the unpoled and poled states would correspond to '0' and '1' in a binary memory device, respectively. After poling, we may assess polarization stability and retention in the samples non-destructively by means of non-linear dielectric spectroscopy (NLDS). In addition, though PVDF-based terpolymers show a broad Curie-transition, the phase change is of second-order as clearly observed from the change of sign of $\varepsilon_3$ from positive to negative at $T_C$ [20]. Hence, NLDS was employed to study the polarization behavior and the polarization stability in differently heat-treated P(VDF-TrFE-CFE) terpolymers to determine the optimum poling conditions. Dielectric hysteresis loops were also measured to compare and correlate the results obtained from NLDS.

## II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

### *A. Sample Preparation*

A P(VDF-TrFE-CFE) terpolymer resin from Piezotech-Arkema with a 62.2/29.4/8.4 molar ratio of VDF/TrFE/CFE, respectively, was used. For the NLDS experiments, P(VDF-TrFE-CFE) films with thicknesses between 1.7 and 3.6 µm were prepared by means of spin-coating. The heat-treated samples were annealed at a temperature of 120 °C (4 hrs) either immediately after spin-coating or before the NLDS runs (1 hr). Before spin-coating, the glass slides were first coated (vacuum evaporation) with a protective layer of chromium (10 nm) and then with a layer of aluminum (60 nm), which served together as the bottom electrode. After spin-coating of the polymer solution, a top aluminum electrode (60 nm) was deposited. A non-electroded portion of the terpolymer film was removed to establish electrical contact with the bottom electrode.

### *B. Non-Linear Dielectric Measurement principle*

For the non-linear dielectric measurements, a sinusoidal electric field with an amplitude $E_\sim$ = 5 V/µm (*i.e.*, below the $E_c$

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