Influence of dc bias electric field on Vogel-Fulcher dynamics in relaxor ferroelectrics

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Changes in dynamic processes of relaxors due to a dc bias electric field have been studied in the reduced poly(vinylidene fluoride-trifluoroethylene), a copolymer system where relaxor-like behavior in the crystalline part can be separated from the glassy processes in the amorphous matrix. Strong electric field dependence of the Vogel-Fulcher temperature and the activation energy has been detected. Comparison of the results with those obtained in a classical inorganic relaxor, lanthanum-modified lead zirconate titanate ceramics, reveals that the nonlinear dielectric susceptibility dominantly influences the dielectric dynamics of relaxors in dc bias electric fields. We have additionally found that even low bias voltage effectively blocks the ac electrical conductivity of the studied copolymer.

Relaxor ferroelectrics are attracting considerable attention in view of their unique physical properties.[1] A key feature of relaxors is the absence of long-range ferroelectric order in zero electric field at any temperature; the relaxor state is usually described as a network of randomly interacting polar nanoregions (PNRs) which are embedded in a highly polarizable medium and on cooling undergo a freezing transition into a glassy nonergodic state.[2,3] Instead, a ferroelectric phase is formed by cooling the relaxor in an electric field higher than the critical field.[3,4] Relaxors exhibit a high dielectric constant and a giant piezoelectric effect[5] and are therefore very attractive for a variety of technological applications.

In inorganic systems, relaxor behavior is usually correlated with the cationic disorder in the same crystallographic site (in fact, only disordered ferroelectric systems show relaxor behavior) and has predominantly been detected in lead-containing ternary compounds and solid solutions.[2–7] Relaxors are characterized by a broad frequency dispersion in the complex dielectric constant, logarithmic polarization decay, and slowing dynamics which signals the onset of freezing.[2,6] At the freezing temperature T_f the longest relaxation time in the system diverges, while the bulk of the relaxation spectrum remains active.[6] The characteristic relaxation time diverges at a somewhat lower temperature T_0 according to the Vogel-Fulcher relation $\nu = \nu_0 \exp[-E/k(T - T_0)]$, where ν_0 is the attempt frequency and E the activation energy. Although this empirical law has experimentally been observed in a variety of systems, its derivation at the mesoscopic level has just recently been proposed.[8]

It has been argued not only that the external electric field induces a ferroelectric order, but also that dielectric relaxation time in relaxors is governed by the mechanism of growth and percolation of PNRs,[19] with an appropriate correction of the local electric field inside a PNR if bias field is applied. This correction has theoretically been determined by the anharmonic polarization term in the free energy functional;[20] the relaxation time then follows a modified Vogel-Fulcher law with T_0 depending on the applied field and nonlinear susceptibility.[20] In order to experimentally detect changes in dynamics of relaxors due to a dc bias electric field, we have performed measurements of the dielectric response of two systems: archetypal inorganic relaxor lanthanum-modified lead zirconate titanate ceramics $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ ($x = 0.09$, $y = 0.65$, denoted as 9/65/35 PLZT), and the polymeric relaxor, reduced poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer. The majority of the investigations were performed on the latter.

Relaxor polymers based on P(VDF-TrFE) are of great interest for a broad range of applications, as they exhibit fast response speeds, giant electrostriction,[9,10] high electric energy density,[11] and large electrocaloric effect.[12] Here the disorder is introduced into the ferroelectric polymer, either by high-energy electron irradiation[9] or introduction of an additional monomer, such as chlorofluoroethylene (CFE).[10] Relaxor polymers exhibit the same macroscopic dielectric properties as inorganic relaxors,[13] suggesting that introduction of defects converts the coherent polarization domain (all-trans chains) in the ferroelectric P(VDF-TrFE) into nanopolar regions.

A detailed dielectric analysis of relaxor polymers is, however, complicated by the fact that two similar dynamics take place in the same temperature range. It is known that P(VDF-TrFE)-based materials are semicrystalline systems comprising an amorphous region, which undergoes a transition from a glassy to a rubbery state below room temperature, and crystalline regions with a spontaneous polarization associated with parallel packing of all-trans polymer chains.[14,15] The introduction of defects results in the coexistence of polar and nonpolar phases within the same crystalline region,[16] and concomitantly, the ferroelectric peak transforms into a typical relaxor frequency-dependent dielectric maximum,[17] which usually completely overrides the dielectric anomaly due to the glassy transition in the amorphous matrix. This means that a typical dielectric maximum (upper frame in Fig. 1) is in fact not only due to the relaxor-like dynamics in crystalline regions, but comprises also the contribution of the transition in the matrix.

Dielectric response in bias electric fields has thus been studied in a new class of relaxor P(VDF-TrFE), synthesized via reductive dechlorination (which introduces defects into
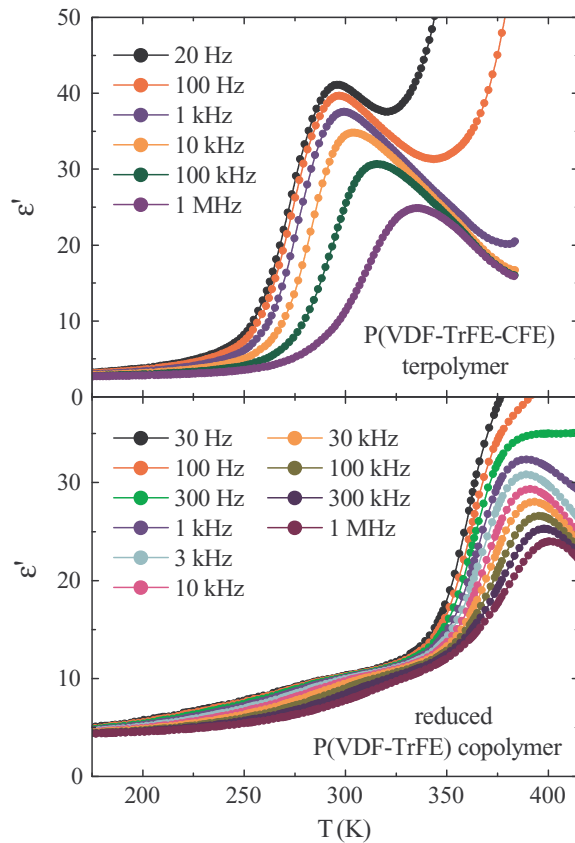
FIG. 1. (Color online) Temperature dependence of the real part, ε', of the complex dielectric constant, measured at different frequencies in zero dc bias field in the P(VDF-TrFE-CFE) terpolymer and in the reduced P(VDF-TrFE) copolymer.
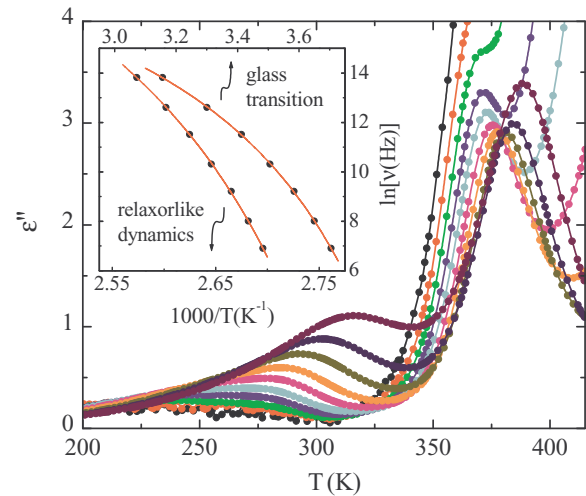

FIG. 2. (Color online) Imaginary part of the complex dielectric constant vs temperature, detected in the reduced P(VDF-TrFE) copolymer at the same frequencies as ε' in Fig. 1. The inset shows the Vogel-Fulcher dependence of the characteristic relaxation times for the (i) relaxor dynamics in the crystalline part and (ii) glass-to-rubber transition in the amorphous matrix.

ordered structure via head-to-head and tail-to-tail linkages) from P(VDF-CTFE).[18] Here, relaxor peaks occur in the temperature region that is much higher than the temperature of the glassy transition in the matrix (lower frame of Fig. 1). Thus, the relaxor-like dynamics in the crystalline regions can be studied separately from the processes in the amorphous matrix.

For dielectric measurements, surfaces of 20 μm thick polymer films were covered by sputtered gold or silver paint electrodes. Complex dielectric constant $\varepsilon^*(\omega,T) = \varepsilon' - i\varepsilon''$ was measured in the frequency range of 20 Hz–1 MHz by using the HP4282 Precision LCR Meter. The amplitude of the probing ac electric signal was 0.1 V. After heating the samples up to 420 K, the dc bias electric field was applied and then the dielectric response was detected during cooling runs with the rate of -0.5 K/min. The temperature of the samples was stabilized within ± 0.01 K by using the lock-in bridge technique with a platinum resistor Pt100 as a thermometer. A similar experimental procedure was used for the polished platelet-shaped sample, cut from the hot pressed 9/65/35 PLZT ceramics.

Figure 2 shows that in the zero bias electric field, the characteristic relaxation frequencies, determined from peaks in $\varepsilon''(T)$, obey the Vogel-Fulcher law with temperatures of $T_{01} = 336 \pm 5$ K and $T_{02} = 225 \pm 4$ K for the relaxor dynamics in the crystalline parts of the reduced P(VDF-TrFE) and in the

glass transition in the amorphous matrix, respectively. The absence of any frequency-independent anomaly indicates that during preparation the precursor polymer has been completely transformed into a relaxor-like rather than a ferroelectric system.

The influence of the dc bias electric field on the dielectric response of the reduced P(VDF-TrFE) is depicted in Fig. 3 (for clarity only frequencies above 1 kHz are shown). For the relaxor contribution both ε' and ε'' decrease and the peaks occur at lower temperatures, while there is almost no influence of the bias field on the glassy processes in the matrix. The electrical conductivity astonishingly decreases in the dc bias electric field—a strong increase of $\varepsilon''(T)$ curves in the zero bias field at the highest temperatures, which is due to the increasing conductivity, is almost completely suppressed by the field.

This effect is thoroughly demonstrated in Fig. 4. The main frame shows decreasing of the electrical conductivity at 400 K when the dc bias field increases. The conductivity remains low after removal of the bias field; however, it can be restored to the initial value by applying ac voltage of the same level as the previously applied dc bias. Obviously, charge carriers, which are responsible for the ac electrical conductivity, migrate in a dc bias electric field and become pinned, probably mainly at the electrode-sample interface, while the ac electric field unpins them and restores the conductivity; a similar space charge blocking effect on ac electrical conductivity has already been found in various ionic conductors[21] and thin ceramic films.[22] This is throughout a dynamic process; thus determination of any blocking field (indicated by arrows in Fig. 4, which extends the initial linear dependence) is strongly influenced by the measurement rate. The inset to Fig. 4 shows that at high temperatures, even very low bias voltages in a few minutes effectively block the ac electrical conductivity of the reduced P(VDF-TrFE).

The decreasing of ε' values in a dc bias electric field as seen in Fig. 3 could thus be the result of either (i) the nonlinear
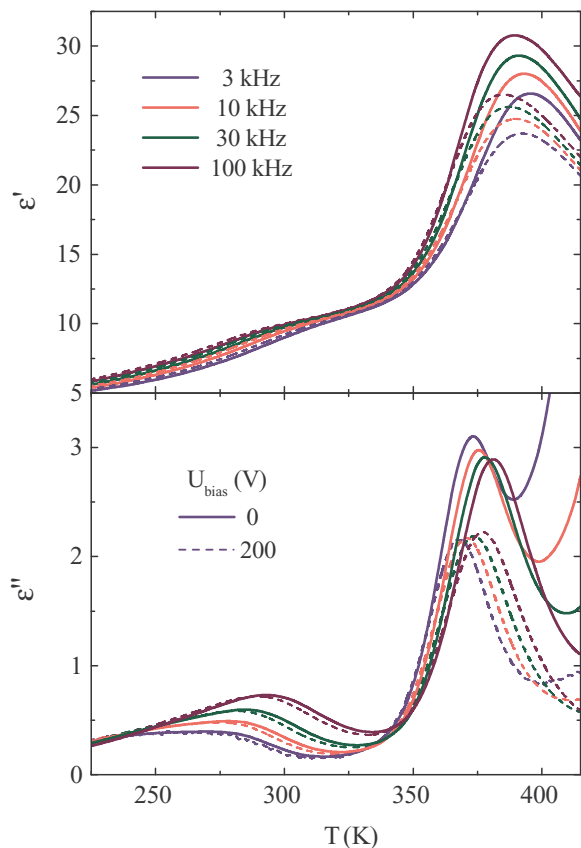
FIG. 3. (Color online) ε' and ε'' vs temperature at various frequencies in the reduced P(VDF-TrFE), without U_{bias} and under 200 V, corresponding to the dc bias electric field value of 10 MV/m.
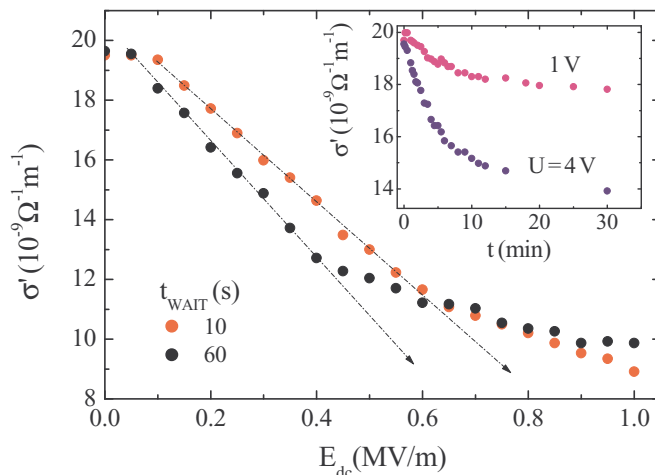

FIG. 4. (Color online) The electrical conductivity (at 110 Hz) of the reduced P(VDF-TrFE) as a function of the dc bias electric field, detected with two different field change rates—the waiting time between two subsequent points was either 10 s or 60 s. The arrows point toward anticipated ac conductivity blocking field. The inset shows the time-decreasing of the ac conductivity under applied bias voltages of 1 V and 4 V, corresponding to the dc bias fields of 0.05 MV/m and 0.2 MV/m, respectively.

$E = (\varepsilon_0 \chi_1)^{-1} P + b_e P^3 + \cdots$ and thus, as $b_e = \chi_3/(\varepsilon_0 \chi_1)^4$, also to χ_3.[20]

This result has been further confirmed by dielectric investigations of the relaxor 9/65/35 PLZT ceramics in dc bias electric fields and analysis of the characteristic relaxation time behavior. It is namely known that the nonlinear dielectric response in this system increases the static polarization [the limiting value is $-\chi_3 = 6.4 \times 10^{-19}$ AsmV^{-3} (Ref. 25)]. Indeed, as can be seen in Fig. 6, the Vogel-Fulcher temperature in PLZT, contrary to the reduced P(VDF-TrFE) copolymer,

dielectric contribution—the third-order nonlinear dielectric susceptibility χ_3 affects polarization and thus the detected linear dielectric constant via $P = \chi_1 E - \chi_3 E^3 + \cdots$ (here the linear susceptibility is $\chi_1 = \varepsilon - 1$)—or (ii) decreasing electrical conductivity, which also affects the real part of the complex linear dielectric constant via Kramers-Kronig relations. The data in Fig. 5, however, clearly reveal that this occurs due to the nonlinear dielectric contribution. The dielectric response (as shown in Fig. 3 in two bias fields) has been measured in the reduced P(VDF-TrFE) in several dc bias electric fields and Fig. 5 shows the Vogel-Fulcher analysis of the characteristic relaxation time behavior for the relaxor dynamics. Here it should be stressed that relaxation times can only be unambiguously determined from frequency dependencies of permittivity, while determination from $\varepsilon''(T)$ peaks can give either equal [as in the Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ relaxor] or different results.[23,24] We have thus checked the frequency dependencies of ε' and ε'' in dc bias electric fields, and relaxation times are, within the experimental error, identical to those determined from peaks in $\varepsilon''(T)$. The upper inset to Fig. 5 shows that the activation energy strongly increases on increasing dc bias field, while the lower inset shows that the Vogel-Fulcher temperature strongly decreases. This suggests a negative nonlinear dielectric contribution, as variation of T_0 in dc bias electric fields is directly proportional to the value of parameter b_e from the inverted $P(E)$ relation
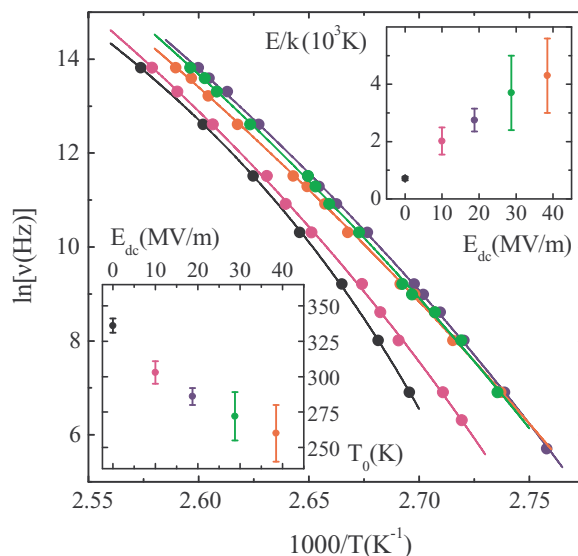

FIG. 5. (Color online) The Vogel-Fulcher dependence of the characteristic relaxation time for the relaxor-like dynamics in the reduced P(VDF-TrFE) in different dc bias electric fields. Insets show the dc bias field dependence of the activation energy (upper inset) and Vogel-Fulcher temperature (lower inset).
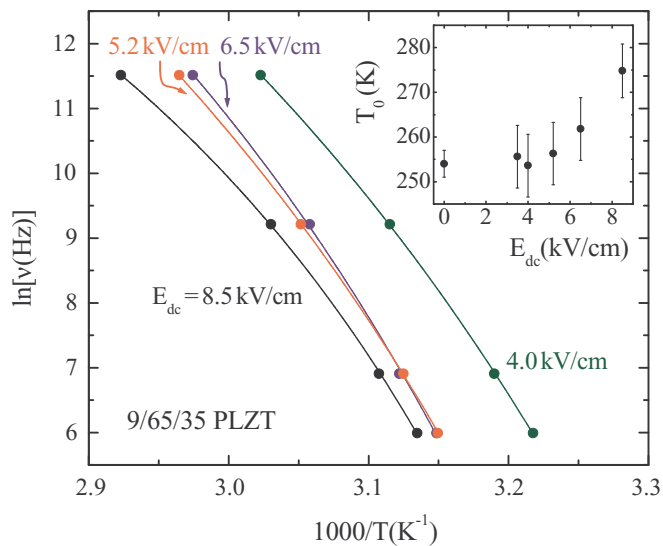
FIG. 6. (Color online) The Vogel-Fulcher dependence of the characteristic relaxation time for the relaxor 9/65/35 PLZT ceramics in different dc bias electric fields. The inset shows the dc bias field dependence of the Vogel-Fulcher temperature.

increases with increasing dc bias electric field. Furthermore, the activation energy systematically decreases from $E/k \approx$ 1400 K without dc bias field to $E/k \approx 700$ K in the dc bias field of 8.5 kV/cm. It should be stressed that, although there exists a critical dc bias field of ≈ 5 kV/cm which induces long-range ferroelectric order in this system, the relaxor dynamic peaks can still be studied using Vogel-Fulcher analysis, as they occur at temperatures around 350 K while the ferroelectric state appears below ≈ 250 K[3].

In summary, dielectric response of organic and inorganic relaxor systems has been investigated in different dc bias electric fields. For relaxor polymer, the reduced P(VDF-TrFE) copolymer has been chosen, as in this system, contrary to most other polymers, relaxor behavior in the crystalline part can be separated from the glassy processes in the amorphous matrix. We have found that even low bias voltage effectively blocks the ac electrical conductivity of this system. Decreasing conductivity could also be the reason for smaller values of the real part of the complex linear dielectric constant in dc bias electric fields. However, the Vogel-Fulcher analysis of the characteristic dynamic behavior revealed that this occurs due to the nonlinear dielectric contribution. We have found that in the reduced P(VDF-TrFE) system the Vogel-Fulcher temperature T_0 strongly decreases with increasing dc bias electric field. On the other hand, in relaxor PLZT ceramics T_0 increases in dc bias electric fields. This is in accordance with predictions that T_0 in dc bias electric fields varies proportionally to nonlinear dielectric susceptibility χ_3, which is in PLZT known to increase the static polarization and thus detected linear dielectric constant.

The experimental data thus revealed that the nonlinear dielectric response dominantly influences the dielectric dynamics of relaxors in dc bias electric fields: While in inorganic PLZT ceramics the nonlinear dielectric response increases the electric polarization and, concomitantly, the Vogel-Fulcher temperature, in organic reduced P(VDF-TrFE) copolymer this contribution is negative; it decreases the linear dielectric constant and the Vogel-Fulcher freezing temperature.

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