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Glassy dynamics in an electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer system

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The dynamic processes in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)], copolymer with a VDF content of 55 mol % have been studied by measurements of the temperature and frequency-dependent linear (ε_1) and third-order nonlinear (ε_3) dielectric constants. Analysis of the complex linear dielectric response by a temperature-frequency plot has revealed that the longest relaxation time diverges at $T = 277$ K, while the bulk of the relaxation times remains finite below this freezing temperature. Such an asymmetric behavior is, together with the temperature dependence of the static field-cooled dielectric constant, very similar to that observed in classical relaxor systems, such as lead magnesium niobate and lanthanum lead zirconate titanate, and is reminiscent of the dynamic behavior observed in various spin glasses. In addition, a paraelectric-to-glass crossover in the temperature dependence of the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_0^3\varepsilon_1^4$, typical for relaxors, has been observed.

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I. INTRODUCTION

Ever since high piezoelectric coefficients in polyvinylidene fluoride have been reported,[1] these polymers have played an important role in sensor and actuator applications. A high piezoelectric effect has also been found in a poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)], copolymer, which, after the ferroelectricity in this material was observed, attracted a great interest in its basic physical properties.[2–5] Recently, a giant electrostrictive response of an electron-irradiated P(VDF-TrFE) copolymer has been reported,[6] making it a promising material for numerous applications. After irradiation, the P(VDF-TrFE) copolymer exhibits typical relaxor behavior, suggesting that high-energy electrons break up all-trans chains in normal ferroelectric P(VDF-TrFE) into nanopolar regions. The expanding of these polar regions under external electric fields, coupled with a large difference in the lattice strain between polar and nonpolar phases, generates an ultrahigh strain response.[6]

Classical relaxor systems, such as lead magnesium niobate and lanthanum lead zirconate titanate ceramics, are characterized by a broad frequency dispersion in the complex dielectric constant, slowing dynamics, and logarithmic polarization decay.[7] These systems are believed to provide a conceptual link between ferroelectrics and dipolar glasses. Namely, in zero electric field no long-range ferroelectric state is established and relaxors undergo a freezing transition into nonergodic state.[7] On the other hand, by cooling the relaxor material in an electric field higher than the critical field, a long-range ferroelectric phase is formed.[8]

Intensive investigations of the electron-irradiated P(VDF-TrFE) copolymer, carried out in recent years,[9–12] indeed revealed some typical relaxor properties, such as a broad dispersive dielectric maximum and a slowing down of the characteristic relaxation time according to the Vogel-Fulcher law.[12] However, a breakthrough in understanding the dielectric properties of classical relaxor systems has been achieved only after static field-cooled dielectric polarization measurements[13,14] and the temperature-frequency plot analysis of the complex dielectric response had been carried out. The latter showed that, like in various spin glasses, the ergodicity is broken at the freezing transition temperature T_f due to the divergence of the longest relaxation time, while the bulk of the relaxation times remains finite even below T_f.[13,14] Furthermore, nonlinear dielectric spectroscopy also turned out to be a powerful tool for investigations of relaxor properties: the temperature dependence of the dielectric nonlinearity $a_3 = \varepsilon_3/\varepsilon_0^3\varepsilon_1^4$, where ε_1 and ε_3 are linear and third-order nonlinear dielectric constants, respectively, can in fact distinguish between ferroelectric and glass transitions, because a_3 should vanish at the ferroelectric transition or diverge at the glass transition.[15]

Therefore, in order to deepen our knowledge of relaxor-like properties of the electron-irradiated P(VDF-TrFE) copolymer, the dielectric dynamics in this system has been studied by detailed measurements of the temperature and frequency-dependent linear and third-order nonlinear dielectric constants. The P(VDF-TrFE) copolymer with a VDF content of 55 mol % has been used for investigations. While nonirradiated material undergoes a paraelectric-to-ferroelectric transition at $T_c \approx 320$ K,[12] analysis of the complex linear dielectric response by a temperature-frequency plot revealed that the longest relaxation time in the electron-irradiated system diverges at $T_f = 277$ K, while the bulk of the relaxation times remains finite below this freezing temperature—a behavior that is typical for classical relaxor systems. Furthermore, the temperature dependencies of the static field-cooled dielectric constant and dielectric nonlin-

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earity $a_3=\varepsilon_3/\varepsilon_0^3\varepsilon_1^4$ were found to be very similar to those observed in the classical relaxor systems.

II. EXPERIMENTAL PROCEDURES

A P(VDF-TrFE) 55-/45-mol % copolymer was supplied by Solvay and Cie. The *N*,*N*-dimethyl formamide solvent was used to cast unstretched films. Films, having the thickness of ≈10 μm, were annealed at 408 K for 10 h in order to improve their crystallinity. The electron irradiation was carried out in a nitrogen atmosphere at 373 K with 1.2-MeV electrons. While earlier investigations were carried out in copolymers irradiated with electrons of higher energies,[6,9,11,12] it was found recently that irradiation at a temperature above a paraelectric-to-ferroelectric transition reduces the electrons' energy and the irradiation dose needed to achieve a high electrostrictive response.[16] The irradiation dose of 55 Mrad was chosen, thus in the range of 40–100 Mrad, where the irradiated copolymer exhibits relaxor behavior.[12,16]

Samples having silver paste electrodes on both surfaces were used for dielectric measurements. It was found that sputtering of gold is not suitable for these samples, as will be shown in detail in the next section. A complex linear dielectric constant $\varepsilon_1^*(\omega,T)=\varepsilon_1'-i\varepsilon_1''$ was measured in the frequency range of 20 Hz–1 MHz using an HP4282 Precision LCR meter. The amplitude of the probing ac electric signal was 1 V. Samples were first heated up to 350 K and then the dielectric response was detected during cooling of the system with the rate of -0.5 K/min. Only a small amount of thermal hysteresis was observed in the dielectric data monitored during subsequent heating runs. The same procedure was used for the third-order nonlinear dielectric response measurements, which were carried out at several frequencies between 1 Hz and 10 kHz by using an HP35665A dynamic signal analyzer. Here, the first, ε_1, and the third, ε_3, harmonic dielectric responses were measured simultaneously, thus greatly reducing noise in the subsequent computation of the ratio $a_3=\varepsilon_3/\varepsilon_0^3\varepsilon_1^4$. The absolute value of the third-order nonlinear dielectric response ε_3 and the real part of the linear dielectric constant ε_1 were used in this computation.

The temperature dependence of the static dielectric polarization can be measured by using the corresponding method described in Ref. 17. After the external electric field E is applied at the highest temperature in the desired temperature range, the sample is cooled down in the same electric field, and the corresponding polarization P_{FC} (FC denotes field cooled) is monitored via a charge accumulation technique using a Keithley 617 programmable electrometer. The static dielectric constant ε_s can then be calculated directly from the dielectric polarization as $\varepsilon_s=1+P_{FC}(E,T)/\varepsilon_0E$. Here, the relatively high conductivity of the copolymer prevents charge measurements at higher temperatures, therefore a slightly modified method was adopted. The sample was first cooled in zero electric field to a fixed temperature, where the conductivity is sufficiently low, and then the external electric field was applied. After the measured charge reached its saturated value $[P_{FC}=P_{ZFC}(t\rightarrow\infty)]$, the temperature-dependent measurement commenced. The temperature of the samples was stabilized to within ±0.01 K by using a lock-in bridge technique with the platinum resistor Pt100 as a thermometer.

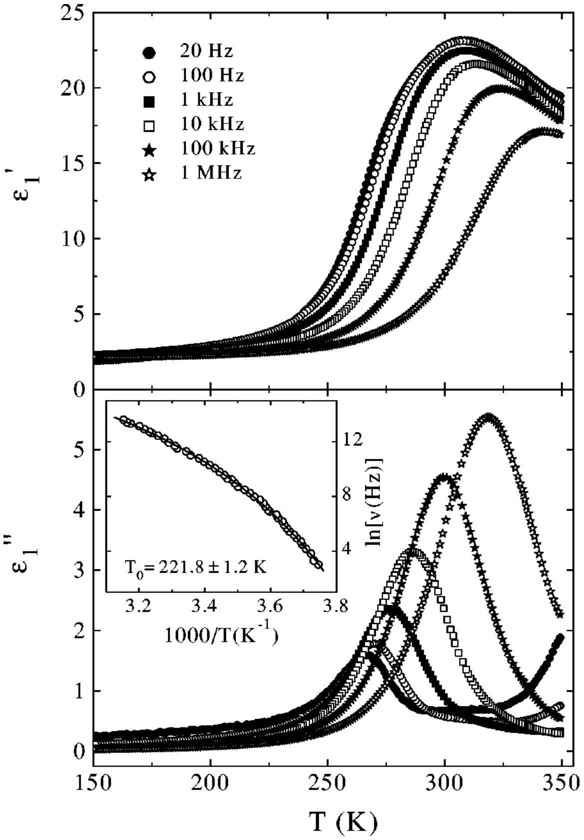

FIG. 1. Temperature dependence of the real, ε_1', and imaginary, ε_1'', parts of the complex linear dielectric constant, measured at several different frequencies. The inset shows that the characteristic relaxation time follows the Vogel-Fulcher law.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the real, ε_1', and imaginary, ε_1'', parts of the complex linear dielectric constant, measured at several different frequencies. A broad dispersive dielectric maximum can be observed, which is a result of the fact that, as in dipolar glass and relaxor systems, ε_1', at a certain temperature dependent on the experimental time scale, i.e., frequency, starts to deviate from its static value. Besides this broad dielectric maximum only a conductivity contribution in ε_1'' can be observed at the highest temperatures, while there is no additional anomaly at $T_c \approx 320$ K, which means that high-energy electrons completely transformed the ferroelectric material into a relaxor-like system. The inset to Fig. 1 shows that the characteristic relaxation frequency, determined from peaks in $\varepsilon_1''(T)$, follows the Vogel-Fulcher law $\nu=\nu_0\exp[-U/k(T-T_0)]$ with the Vogel-Fulcher temperature $T_0=221.8\pm1.2$ K.

Here it should be noted that two different relaxation processes, α and β, have been observed in the P(VDF-TrFE) copolymer.[2,4,12] The α-relaxation process is associated with the local dipolar motions in the crystalline region, while the β-relaxation process is attributed to the molecular motions in

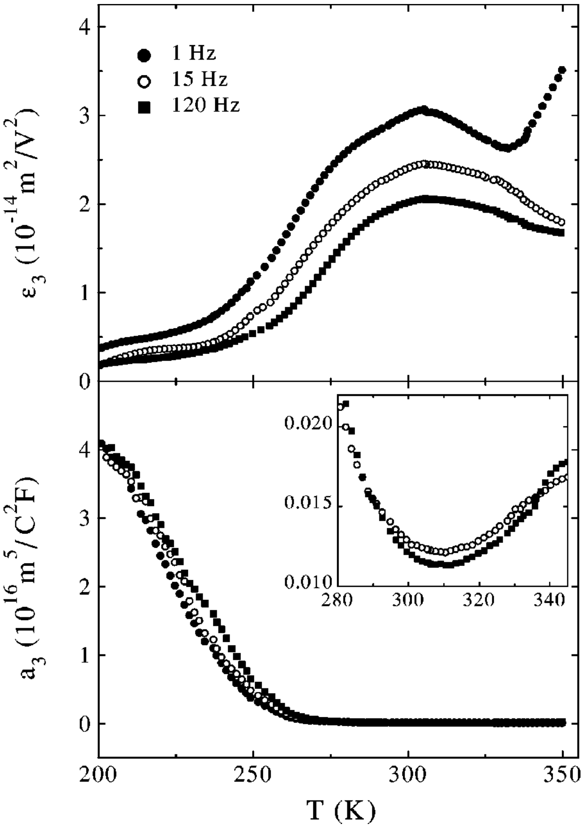

FIG. 2. The temperature dependencies of the third-order nonlinear dielectric constant ε_3 and dielectric nonlinearity a_3, measured at three different frequencies. The inset shows the paraelectric-to-glass crossover in the temperature dependence of a_3.

the amorphous region of the copolymer. The latter are only weakly polar in nature, therefore ε_1' does not show any significant anomaly connected to the β process. This process can be detected in $\varepsilon_1''(\omega,T)$, however, at lower frequencies than in the α process. We chose a frequency measurement range such that dominantly the α-relaxation process was detected. Thus, all the data in this paper describe relaxation processes in the crystalline region of the electron-irradiated P(VDF-TrFE) copolymer.

Figure 2 shows the temperature dependencies of the third-order nonlinear dielectric constant ε_3 and dielectric nonlinearity $a_3=\varepsilon_3/\varepsilon_0^3\varepsilon_1^4$, measured at three different frequencies. The inset to Fig. 2 shows that a_3, when approaching the freezing transition from above, undergoes a crossover from decreasing paraelectriclike to increasing glasslike temperature behavior. While a_3 should vanish at the paraelectric-to-ferroelectric phase transition[18] or diverge at the freezing transition in dipolar glasses,[19] such behavior is typical for relaxors. The paraelectric-to-glass crossover in a_3 has been detected in several relaxor systems[15,20,21] and is in fact in accordance with the predictions of the spherical random-bond–random-field model of relaxor ferroelectrics.[15]

The complex linear dielectric constant data, shown in Fig. 1, are shown again in Fig. 3 in the ε_1'' vs ε_1' representation. One standard way to analyze these experimental data is fit to the Cole-Cole expression

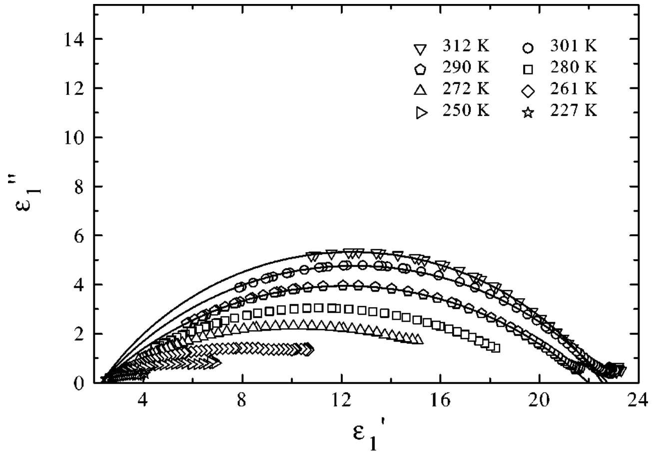

FIG. 3. Measured values of ε_1'' plotted vs ε_1' at several different temperatures. Solid lines through the experimental data, obtained at high temperatures, represent fits to the Cole-Cole expression [Eq. (1)].

$$\varepsilon_1^*=\varepsilon_\infty+\frac{\Delta\varepsilon_1}{1+(i\omega\tau)^{1-h}}, \tag{1}$$

where $\Delta\varepsilon_1=\varepsilon_s-\varepsilon_\infty$ is the dielectric relaxation strength, with ε_s the static dielectric constant and ε_∞ the dielectric constant at high frequencies, which takes into account the ionic and electronic polarizability of the system; τ is the characteristic relaxation time; and h is the parameter describing the distribution of the relaxation times. $h=0$ describes monodispersive relaxation, while $0<h<1$ indicates the broad distribution of the relaxation times in the system. This procedure can provide information about parameters ε_s, ε_∞, τ, and h, however, Cole-Cole plots cannot provide direct and independent information about the actual relaxation spectrum under investigation. Furthermore, since the relaxation spectrum becomes extremely polydispersive with decreasing temperature, as can clearly be seen in Fig. 3, even this standard analysis can be performed only at higher temperatures. On the other hand, information on the relaxation spectrum behavior and thus on dynamic processes can directly be extracted using the so-called temperature-frequency plot. This method has already been successfully applied to various glassy[22–24] and relaxor systems.[13,14] Its extended description is given in Ref. 22. The essential point is that by varying the reduced dielectric constant

$$\delta\equiv\frac{\varepsilon_1'(\omega,T)-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty}=\int_{z_1}^{z_2}\frac{g(z)dz}{1+(\omega/\omega_a)^2\exp(2z)} \tag{2}$$

between the values 1 and 0 different segments of the relaxation spectrum $g(z)$ can be probed ($\delta=1$ probes the upper limit of the relaxation spectrum, i.e., the longest relaxation time). The distribution of relaxation times is limited by the lower and upper cutoffs z_1 and z_2.

Obviously, the knowledge of ε_s and ε_∞ is necessary to this procedure. Due to rapidly increasing polydispersivity with decreasing temperature, analysis of Cole-Cole plots, presented in Fig. 3, provided values of ε_s only at temperatures above 290 K. Indeed, it can be deduced from Fig. 3 that

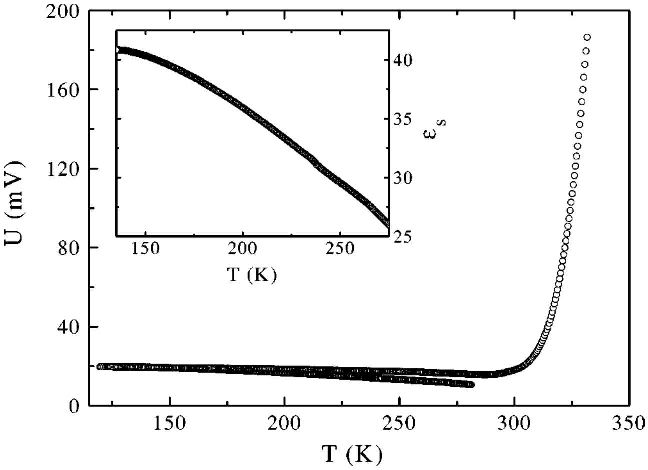

FIG. 4. Determination of the temperature dependence of ε_s. Main frame: measured voltage, corresponding to the dielectric polarization. Inset: temperature dependence of ε_s, determined from data shown in the main frame after subtraction of the conductivity effect. At higher temperatures rapidly increasing conductivity prevents determination of ε_s.

ε_∞ is almost independent of temperature, having the value of 2.3. But still, independent measurement of ε_s at lower temperatures is necessary for temperature-frequency plot analysis.

Figure 4 thus shows determination of the temperature dependence of ε_s in a broad temperature range by using a charge accumulation technique. First the sample was cooled in zero electric field to the temperature of 280 K, where conductivity is sufficiently low. Then the external electric field was applied, and after the measured charge reached its saturated value, temperature-dependent measurement commenced. The main frame of Fig. 4 shows voltage measured by an electrometer. Here, the effect of the conductivity can clearly be seen, causing measured values during cooling and subsequent heating runs to be slightly different. Also, high conductivity of the copolymer at temperatures above 300 K is very noticeable. The inset to Fig. 4 shows the temperature dependence of ε_s, calculated from values presented in the main frame, after the effect of conductivity had been subtracted. Obviously, at higher temperatures, rapidly increasing conductivity prevents this determination, but fortunately in this temperature range the values of ε_s were successfully extracted from Cole-Cole plots. Using these values of ε_s and the value of $\varepsilon_\infty = 2.3$, the temperature-frequency plot was determined and is shown in Fig. 5. In practice, this procedure requires that within the set of dielectric data at a given temperature T a frequency ν be found at which the prescribed value of δ can be reached. Solid lines through the $\delta = 0.95, 0.8, \ldots, 0.05$ data in Fig. 5 are fits to the Vogel-Fulcher law, which demonstrate the diverging behavior of relaxation times. The inset to Fig. 5 shows dependence of the Vogel-Fulcher temperature T_0 on δ. Freezing temperature, where the longest relaxation diverges, was determined as $T_f = T_0(\delta \rightarrow 1) = 277 \pm 2$ K. Its value is considerably higher than the Vogel-Fulcher temperature $T_0 = 221.8$ K of the characteristic relaxation time (see inset to Fig. 1), because the

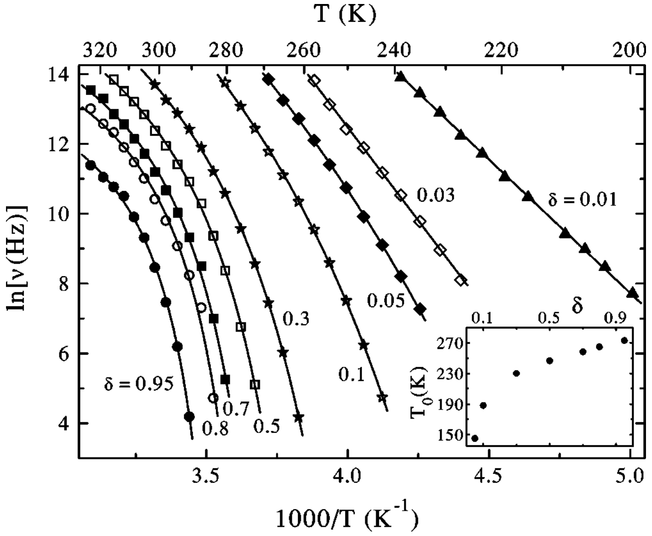

FIG. 5. Temperature-frequency plot for several fixed values of the reduced dielectric constant δ. Solid lines are fits obtained with Vogel-Fulcher ($\delta = 0.95, 0.8, \ldots, 0.05$) or Arrhenius ($\delta = 0.03, 0.01$) expressions. The inset shows dependence of the Vogel-Fulcher temperature T_0 on δ.

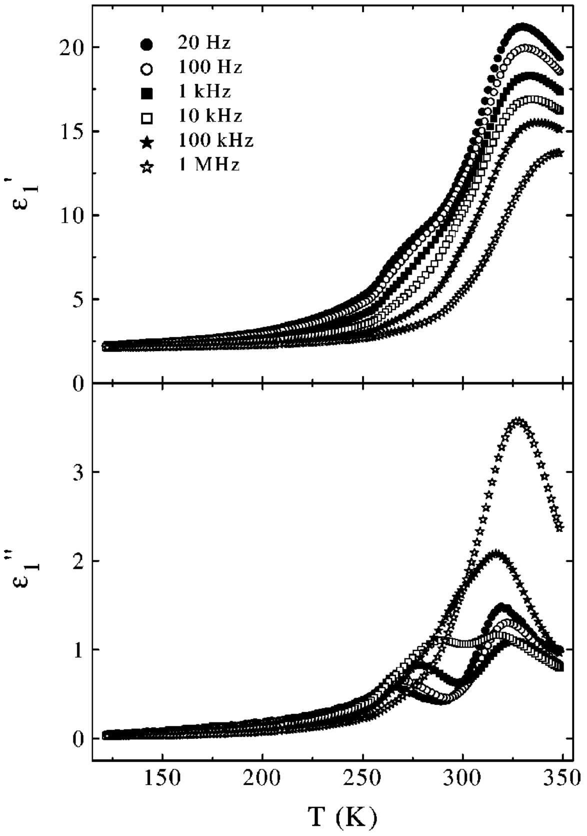

FIG. 6. Temperature dependence of the real, ε_1', and imaginary, ε_1'', parts of the complex linear dielectric constant, measured at several different frequencies on the sample having sputtered gold electrodes. Anomalies at $T_c \approx 320$ K indicate the existence of the ferroelectric phase.

bulk of the relaxation times remains finite below T_f. The high-frequency part of the relaxation spectrum even remains active down to the lowest temperatures. Namely, solid lines through the $\delta = 0.03$ and 0.01 data in Fig. 5 represent fits to the Arrhenius law $\tau = \tau_0 \exp(E/kT)$. Such an asymmetric behavior of the relaxation spectrum has already been detected in many glassy[22–24] and relaxor systems.[13,14] The activation energy of 0.63 eV, resulting from the $\delta = 0.01$ data fit, seems relatively high. However, as has already been reported,[12] activation energies for the irradiated copolymers are higher than that of the noniradiated ones due to random trans-gauche chain conformation (instead of all-trans conformation) in the nonpolar phase, induced by irradiation process.

Irradiation of the P(VDF-TrFE) 55-/45-mol % copolymer with 1.2-MeV electrons, with the dose of 55 Mrad, completely transformed the ferroelectric material into a relaxor system. However, several observations of the coexistence of the relaxor and ferroelectric phases in electron-irradiated P(VDF-TrFE), either using x-ray[16] or dielectric spectroscopy investigations,[25] have been reported. It is very interesting that both phases coexist not only if small doses of irradiation are used, but also after irradiation with high doses. Namely, in the 68-/32-mol %, copolymer reentrant polarization hysteresis was observed after irradiation with doses >75 Mrad,[16] suggesting that there exists an optimized dose that generates a copolymer with a nonpolar structure whose electromechanical performance is the best. It should be pointed out that we also have detected both phases in our samples, but only after gold electrodes had been sputtered to the surfaces. Figure 6 shows the temperature dependence of the real and imaginary parts of the complex linear dielectric constant, measured at several different frequencies on the sample having sputtered gold electrodes. Besides dispersion, typical for relaxors, also frequency-independent peaks in ε_1'' at $T_c \approx 320$ K were detected, demonstrating that the ferroelectric phase coexists in the system together with the relaxor phase. It seems that higher temperatures during the sputtering process caused partial transformation of nonpolar trans-gauche conformation back into the polar all-trans ferroelectric state. Therefore, it is very important to manipulate irradiated samples carefully, since presence of the polar phase highly reduces giant electrostriction of the irradiated, relaxorlike P(VDF-TrFE) copolymer.

IV. SUMMARY

Using linear and third-order nonlinear dielectric spectroscopy measurements we showed that high-energy electron irradiation with the dose of 55 Mrad transformed a ferroelectric P(VDF-TrFE) 55-/45-mol % copolymer into nanopolar regions. A temperature-frequency plot analysis of the complex linear susceptibility revealed typical glassy (relaxor) asymmetric behavior of the relaxation spectrum: While ergodicity of the system is effectively broken due to divergence of the longest relaxation time at a freezing temperature $T_f = 277 \pm 2$ K, the bulk of the relaxation times remain active below T_f, the low-frequency part, obeying the Arrhenius law, even to the lowest temperatures. The temperature dependence of ε_s, reaching almost a constant value at lower temperatures, is by itself reminiscent of the dynamic behavior observed in various glassy systems. Also, the dielectric nonlinearity a_3 undergoes a crossover from decreasingly paraelectriclike to increasingly glasslike temperature behavior when approaching the freezing transition from above, which is a typical behavior for relaxor systems. It can therefore be concluded that an electron-irradiated P(VDF-TrFE) copolymer system is an organic system in which dielectric dynamics in fact shows the same characteristics as in dipolar glasses and relaxor ferroelectrics.

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