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Contributions of distinctive dynamic processes to dielectric response of a relaxorlike reduced poly(vinylidene fluoride-trifluoroethylene) copolymer

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Dynamic processes in relaxorlike reduced poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer have been studied by measurements of the temperature and frequency-dependent linear and third-order nonlinear dielectric response. Dielectric analysis of relaxor polymers has, namely, been incomplete until now, i.e., data interpretation was complicated by the fact that two similar types of dynamics, relaxorlike behavior in the crystalline part of the system and glass-to-rubber transition in the amorphous matrix, take place in the same temperature range and thus superimpose in the detected response. On the other hand, here, in the P(VDF-TrFE) system, synthesized via reductive dechlorination from the poly(vinylidene fluoride-chlorotrifluoroethylene), relaxor peaks take place at much higher temperatures, thus both dynamics can be investigated separately. Analysis of the experimental data reveals that the relaxorlike dielectric dynamics in the reduced P(VDF-TrFE) copolymer, which is now not influenced by processes in the amorphous matrix, indeed is almost identical to that observed in classical relaxor systems and, furthermore, reminiscent of the dynamic behavior observed in various spin glasses. Also, a clear indication was obtained that all polar dynamic processes terminate down to ≈100 K and that below this temperature only nonpolar contributions govern the dielectric response of the reduced P(VDF-TrFE) copolymer.

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I. INTRODUCTION

Electroactive polymers based on poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer are of great interest for a broad range of applications, as they exhibit fast response speeds, and strain levels far above those of traditional piezoceramic materials.[1–4] For example, a giant electrostriction in electron-irradiated P(VDF-TrFE) copolymer[3] and in terpolymer with chlorofluoroethylene P(VDF-TrFE-CFE) (Ref. 4) has been detected. Furthermore, these systems exhibit typical relaxor behavior,[5] suggesting that electron irradiation or introduction of CFE converts the coherent polarization domain (all-trans chains) in normal ferroelectric P(VDF-TrFE) into nanopolar regions, thus transforming the material into a relaxorlike system. Concomitantly, an ultrahigh strain response in relaxorlike polymers is generated due to expansion of the polar regions under an external electric field, coupled with a large difference in the lattice strain between polar and nonpolar phases.[3] Ferroelectric and relaxorlike P(VDF-TrFE)-based polymer systems have in recent years also been suggested for various advanced applications, as they possess high electric energy density with fast discharge speed[6] and large electrocaloric effect near room temperature.[7]

Dielectric analysis of relaxor polymers has, however, been incomplete until now; data interpretation and understanding were complicated by the fact that two similar types of dynamics take place in the same temperature range. It is well known, from x-ray, heat capacity, and infrared investigations, that PVDF and its copolymers are semicrystalline systems comprising noncrystalline, i.e., amorphous regions, and crystalline regions with a spontaneous polarization associated with parallel packing of all-trans polymer chains.[1,8] On heating, the amorphous region undergoes a transition from glassy to a rubbery state below room temperature while the crystalline region adopted ferroelectric phase undergoes a transition into a paraelectric phase and finally melts.[8] Further manipulation (introduction of defect structure by electron irradiation or addition of CFE which breaks the long-range ordering of polymer chains) results in coexistence of polar and nonpolar phases within the same crystalline region[9] and, concomitantly, the paraelectric-to-ferroelectric peak in the dielectric constant transforms into a typical relaxor frequency-dependent dielectric maximum.[10] Similar as in inorganic relaxors, this peak is a consequence of polar nanoregions' dynamics and does not denote any phase transition, just as being the case in dipolar glasses.[11] In relaxorlike polymers, this broad maximum occurs, however, at slightly lower temperatures than the previous ferroelectric peak and almost completely overrides the dielectric anomaly due to the glassy transition in the amorphous matrix—the latter is almost not influenced by introduction of defects. This means that a typical dielectric maximum, up to now observed in relaxor polymers—an example is shown in Fig. 1—is in fact not only due to the relaxorlike dynamics in crystalline regions but comprises also the contribution of the glassy transition in the amorphous matrix.

In order to investigate both, relaxor and glassy dynamics separately, we performed a high-resolution dielectric measurements in a new class of relaxor P(VDF-TrFE) copolymer, synthesized via reductive dechlorination from the poly(vinylidene fluoride-chlorotrifluoroethylene) [P(VDF-

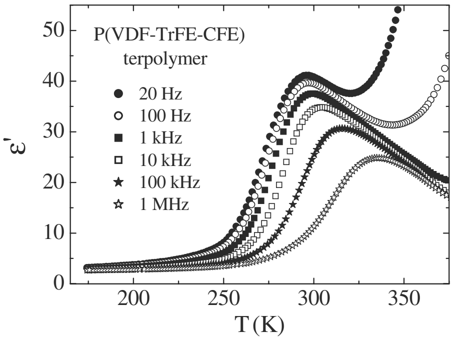

FIG. 1. Temperature dependence of the real part of the complex dielectric constant, measured at different frequencies in relaxorlike P(VDF-TrFE-CFE) terpolymer.

CTFE)]. In this system relaxor peaks take place at much higher temperatures than that of previous reported relaxorlike polymers (here they remain in the temperature region of a previous ferroelectric phase transition) and thus also much higher than is the temperature of the glass transition in the amorphous matrix.[12] Analysis of the experimental data reveals that the relaxorlike dielectric dynamic in the reduced P(VDF-TrFE) copolymer, i.e., the dynamics which is now not influenced by separate processes in the amorphous matrix, indeed is almost identical to that observed in classical relaxor systems, such as lead magnesium niobate and, furthermore, reminiscent of the dynamic behavior observed in various spin glasses.

II. EXPERIMENTAL PROCEDURES

Reduced P(VDF-TrFE) was prepared as follows: 1.0 g of P(VDF-CTFE) 66/34 copolymer and 88.6 mg of azobisisobutyronitrile in tetrahydrofuran was stirred at 333 K for 30 min, then tri(*n*-butyl)tin hydride (4.52 mmol) was added. The solution was kept stirring at 333 K for 24 h. P(VDF-TrFE) was then collected by precipitation and dried in vacuum. Finally, copolymer films were prepared by solution cast method, using dimethylformamide as the solvent, followed by further annealing at 413 K.

Due to different synthetic process, the reduced copolymer possesses different chain structure compared with that from the normal polymerized system. Infrared spectroscopy data clearly revealed head-to-head (H-H) and tail-to-tail (T-T) linkages in this system.[12] The reduced P(VDF-TrFE) copolymer thus possesses high degree of T-T and H-H defects, which are very different from the predominate H-T chain arrangement in the normal polymerized P(VDF-TrFE) copolymers. A large content of H-H and T-T defects in the copolymer breaks coherent ferroelectric domains and is most probably responsible for the observed high-temperature relaxor behavior.

For dielectric measurements, surfaces of the 20-μm-thick polymer films were covered by sputtered gold electrodes. Complex linear dielectric constant $\varepsilon^*(\omega,T)=\varepsilon'-i\varepsilon''$ was measured in the frequency range of 20 Hz–1 MHz by using HP4282 Precision LCR Meter. The amplitude of the probing ac electric signal was 0.1 V. The real part of the complex ac conductivity $\sigma^*=\sigma'+i\sigma''$ was calculated via $\sigma'=2\pi\nu\varepsilon_0\varepsilon''$, with ε_0 being the permittivity of free space. After heating the samples up to 420 K, the dielectric response was detected during cooling runs with the rate of ± 0.5 K/min. Similar heating/cooling procedure was used for the third-order nonlinear dielectric-response measurements, which were carried out at various frequencies by using HP35665A Dynamic Signal Analyzer. Here, the first and the third harmonic dielectric responses were measured simultaneously, which, in comparison to the separate measurement runs, reduces mistake in the subsequent computation of the ratio $a_3=\varepsilon_3/\varepsilon_0^3\varepsilon^4$. In this computation, the real part of the linear and the absolute value, ε_3, of the third-order nonlinear dielectric constant were used.

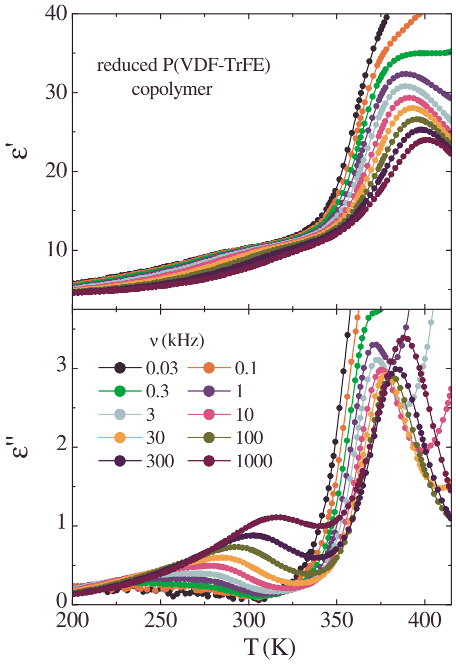

FIG. 2. (Color online) Temperature dependence of the real, ε', and imaginary, ε'', parts of the complex linear dielectric constant, detected at various frequencies in the reduced P(VDF-TrFE) copolymer.

III. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the real, ε', and imaginary, ε'', parts of the complex linear dielectric constant, measured at several different frequencies in the reduced P(VDF-TrFE) copolymer. Two dispersive dielectric anomalies, one in the temperature region of 350–400 K and the other in the temperature region of 275–335 K, can clearly be seen.

At this stage, typical features detected in the $\varepsilon^*(T)$ spectra of P(VDF-TrFE)-based systems should be stressed out: (i) in the ferroelectric P(VDF-TrFE) the most distinctive feature is a frequency-independent peak in both, ε' and ε'', at $T_c \approx 350-380$ K (depending on the VDF to TrFE ratio), which denotes the phase transition from the distorted trans-gauche paraelectric to all-trans ferroelectric phase, occurring in the crystalline region of the copolymer.[5,8,13,14] The second feature is a dielectric relaxation in the temperature region of 275–335 K,[8,13,14] the identical one as detected also in our samples (see Fig. 2). This so-called β process is without ambiguity associated with the dynamic manifestation of the glass transition in the amorphous phase of copolymer, i.e., a transition from the glassy to rubbery state.[13–15] Earlier studies have shown that the temperature dependence of the characteristic relaxation time of this β relaxation is of the Williams, Landel, and Ferry type, thus being clearly different than the Arrhenius-type relaxation process, which also occurs at low temperatures in the crystalline region of copolymer.[14]

(ii) In the relaxorlike P(VDF-TrFE)-based systems up to now only one, broad dispersive maximum has been observed, as shown in our Fig. 1. This typical relaxor feature is a result of the fact that, similar as in dipolar glasses and inorganic relaxor systems, ε' at a certain temperature which depends on the experimental time scale, i.e., frequency, starts to deviate from its static value (the static dielectric constant thus does not show any anomaly—as confirmed by measurements of the static dielectric constant via charge accumulation technique in the P(VDF-TrFE-CFE) terpolymer).[5] However, it can also clearly be seen that β relaxation is in the dielectric spectra of P(VDF-TrFE-CFE) terpolymer (Fig. 1) overlapped by a relaxorlike dielectric dispersion, which means that the measured response is in fact a superposition of two different types of dynamics.

On the other hand, here, in the reduced P(VDF-TrFE) copolymer both, relaxorlike behavior in the crystalline part of the system and glass-to-rubber transition in the amorphous matrix, obviously take place at different temperatures. This is due to the fact that here the disorder (H-H and T-T defects), which breaks coherent ferroelectric domains, does not shift the relaxorlike dynamics to lower temperatures but this remains in the temperature region of a previous ferroelectric phase transition (350–380 K). Investigations of relaxorlike dynamics is thus in this P(VDF-TrFE)-based system not influenced by processes in the amorphous matrix. Furthermore, this system is very attractive for high-temperature applications—not only that relatively high dielectric constants (for a polymer system) are obtained around 375 K, it also exhibits a high melting point of ≈475 K.[12]

It should be stressed here that relaxorlike polymers are usually obtained by introducing disorder into ferroelectric systems. First attempts by using high-energy electron irradiation[3] or γ irradiation[16] indeed successfully transformed the long-range all-trans ferroelectric ordering into trans sequences of shorter correlation length and moreover, nonpolar trans-gauche conformation has been induced. This scission of ferroelectric ordering occurred mainly due to double C=C bonds and consequently, a typical relaxor structure, polar nanoregions in the nonpolar matrix, was formed. Unfortunately, the radiation induced also several other defects, for example, by breaking of C—H and C—F bonds different free radicals were formed.[17] Thus further processing of relaxor polymers involved introduction of monomers with large chlorine atoms,[4] which, due to the size, prevent formation of long-range ordered all-trans chains and favor trans-gauche conformation. This noninvasive procedure is almost free of other undesirable defects and thus resulted in an almost ideal relaxor dielectric response (see Fig. 1). A similar response has also been detected here, in the reduced P(VDF-TrFE) system, which means that processing most probably did not introduce additional defects to H-H and T-T linkages, which are in fact responsible for the relaxorlike structure and thus for the observed dielectric response. Indeed, the electrical conductivity is higher than in relaxorlike terpolymers [$\varepsilon''(T)$ curves in Fig. 2 increase at higher temperatures even when measured at 30 kHz] but this can also be due to the fact that the relaxorlike response is here obtained at much higher temperatures than in terpolymers, which certainly imply higher electrical conductivity.

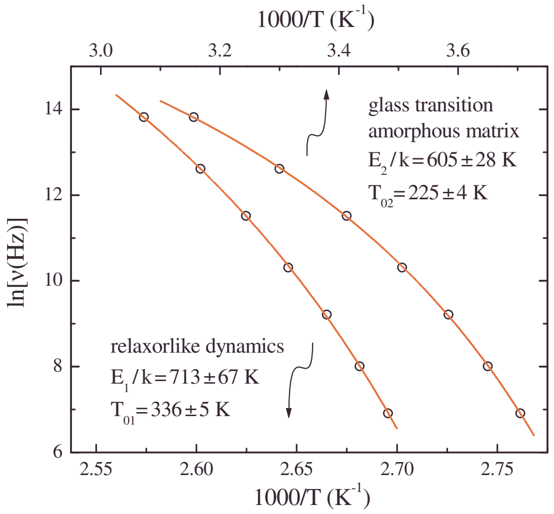

FIG. 3. (Color online) The Vogel-Fulcher dependence of the characteristic relaxation times for the (i) relaxorlike dynamics in the crystalline part of the system and (ii) glass-to-rubber transition in the amorphous matrix.

Characteristic relaxation frequencies, determined from peaks in $\varepsilon''(T)$ (Fig. 3), for both processes follow the Vogel-Fulcher law $\nu=\nu_0\exp[-E/k(T-T_0)]$ with the Vogel-Fulcher temperatures of $T_{01}=336\pm5$ K and $T_{02}=225\pm4$ K for relaxorlike dynamics in the crystalline regions and glass-to-rubber transition in the amorphous matrix, respectively. Such a dependence is typical for relaxor (and glassy) systems, and as there is also no sign of any frequency-independent anomaly, we can conclude that during preparation P(VDF-TrFE) has been completely transformed from the ferroelectric into a relaxorlike system.

The frequency dependence of ε' and σ', measured at various temperatures, is shown in Fig. 4. The ε' data are presented in a logarithmic scale. Indeed, such a representation does not reveal different contributions to the measured response so clearly as the linear one. However, main contributions to the measured response have already been revealed from the temperature-dependent data—relaxorlike dynamics in the crystalline regions and glass-to-rubber transition in the amorphous matrix. On the other hand, this representation clearly shows that already at ≈100 K the measured value is only $\varepsilon'\approx4$. Furthermore, this value is independent of the measuring frequency and the same applies to the measured ε'' data at this temperature—to demonstrate this the solid line in the lower frame of Fig. 4, representing constant dielectric

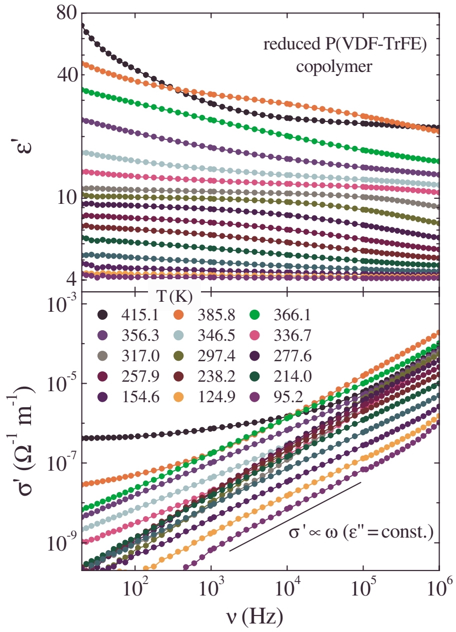

FIG. 4. (Color online) Frequency dependence of ε' and σ', measured at various temperatures in the reduced P(VDF-TrFE) copolymer. The solid line in the lower frame demonstrates the constant dielectric losses dependence.

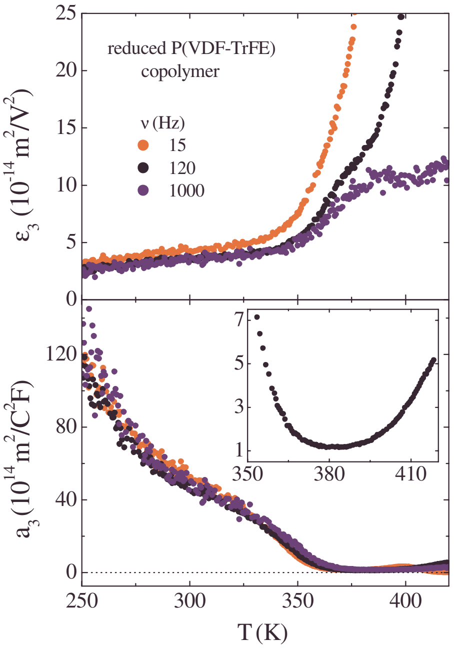

FIG. 6. (Color online) Temperature dependence of the third-order nonlinear dielectric constant ε_3 and dielectric nonlinearity a_3, measured at three different frequencies. The inset shows a paraelectric-to-glass crossover in the $a_3(T)$ in the temperature region, where relaxorlike dynamics dominates the dielectric response.

losses dependence, is plotted. This result—very low, frequency-independent ε^* data—indicates that all major polar processes, connected with the above mentioned relaxorlike and glassy dynamics, are already terminated, and that at temperatures below 100 K only high-frequency nonpolar processes contribute to the dielectric response. This is further supported in Fig. 5, which shows the frequency-dependent data, obtained in the temperature range of 228–288 K, in $\varepsilon''(\varepsilon')$ representation. In this temperature range there still is a strong polar contribution (the one originating from the glassy transition in the amorphous matrix) to the measured dielectric response. Solid lines through the experimental data in Fig. 5 are fits to the Cole-Cole expression

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

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric relaxation strength, τ is the characteristic relaxation time, and h is the parameter describing the distribution of relaxation times ($h=0$ describes monodispersive relaxation while $0<h<1$ indicates a distribution of relaxation times in the system). The inset of Fig. 5 shows that the polydispersivity of the relaxation spectrum increases on decreasing temperature. More important, on the other hand, is the fact that this analysis even here, in the temperature range where polar processes govern the dielectric response, provides almost temperature-independent value of $\varepsilon_\infty \approx 4$—so the same value as measured at all frequencies at ≈ 100 K. As ε_∞ takes into account only high-frequency nonpolar processes, this result thus confirms the conclusion, brought already from Fig. 4, that all polar processes in this system terminate down to $T \approx 100$ K.

Finally, Fig. 6 shows the temperature dependence of the third-order nonlinear dielectric constant ε_3 and dielectric nonlinearity $a_3 = \varepsilon_3 / \varepsilon_0^3 \varepsilon^4$. While a_3 should vanish at the paraelectric-to-ferroelectric phase transition[18] or diverge at the freezing transition in dipolar glasses,[19] it has been shown that in relaxors this quantity undergoes a crossover from decreasing paraelectriclike to increasing glasslike temperature behavior when approaching the freezing transition from above[20–23] (such a dependence is also in accordance with the predictions of the spherical random-bond-random-field model of relaxor ferroelectrics).[20] The inset of Fig. 6 shows

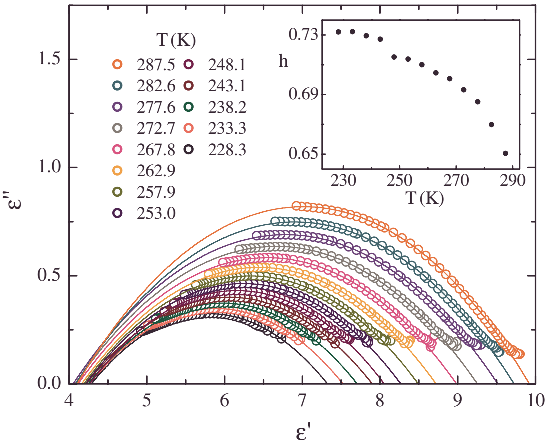

FIG. 5. (Color online) Measured values of ε'' plotted vs ε' at various temperatures in the range, where dynamics in the amorphous matrix dominates the dielectric response. Solid lines through the experimental data are fits to the Cole-Cole expression [Eq. (1)]. The inset shows the temperature dependence of the polydispersivity of the relaxation spectrum.

exactly such a crossover in the $a_3(T)$ in the temperature region, where relaxorlike dynamics dominates the dielectric response, which confirms the absence of the long-range order and a relaxorlike structure of reduced P(VDF-TrFE) copolymer system.

IV. SUMMARY

In summary, we have investigated the dielectric response of relaxorlike P(VDF-TrFE)-based system, synthesized via reductive dechlorination from the P(VDF-CTFE) copolymer. In this system the disorder introduced during preparation (H-H and T-T defects), which breaks coherent ferroelectric domains, does not shift the relaxorlike dynamics to lower temperatures but this remains in the temperature region of a previous ferroelectric phase transition. Not only that for this reason this system is very attractive for high-temperature applications but investigations of relaxorlike dynamics are here not influenced by processes in the amorphous matrix; up to now, the measured response in relaxorlike polymers was is in fact a superposition of two types of dynamics, relaxorlike behavior in the crystalline part of the system and glass-to-rubber transition in the amorphous matrix.

Measurements of the temperature and frequency-dependent linear and third-order nonlinear dielectric response revealed for the high-temperature dynamic process in the crystalline regions of reduced P(VDF-TrFE) copolymer: (i) a broad frequency dispersion in the temperature dependence of the linear and nonlinear dielectric constants, (ii) a Vogel-Fulcher temperature dependence of the characteristic relaxation time, and (iii) a paraelectric-to-glass crossover in the temperature dependence of the dielectric nonlinearity a_3. All these properties are very similar to those observed in the classical relaxor systems and are reminiscent of the dynamic behavior observed in various spin glasses. Thus, finally a conformation that macroscopic dielectric response is almost identical to the response of inorganic relaxors has been obtained for a relaxor polymer system, where dynamic processes occurring in the crystalline regions can be studied separately from processes taking place in the amorphous matrix.

An additional analysis of the experimental data also revealed that polar dynamic processes, taking place in both, the crystalline regions and amorphous matrix, terminate down to ≈ 100 K and that below this temperature only nonpolar processes contribute to the dielectric response of the reduced P(VDF-TrFE) copolymer system.

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