Distinctive Contributions from Organic Filler and Relaxorlike Polymer Matrix to Dielectric Response of CuPc-P(VDF-TrFE-CFE) Composite

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The dielectric response of copper-phthalocyanine (CuPc) oligomers embedded in a poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymer matrix was studied. Although admixture of CuPc strongly increases the dielectric constant of the terpolymer at all temperatures, each of the two constituents determines the dielectric dynamics in a different temperature region—the relaxorlike matrix above and CuPc below the terpolymer's freezing temperature. Two relaxations, reflecting the charge carriers' response in CuPc, were detected. Results on ac conductivity reveal that the tunneling of polarons is the dominating charge transport mechanism.

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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) [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.

As a dielectric material, the input electric energy that can be converted into strain energy is directly proportional to the dielectric constant ε [6]. Therefore, a high electric field is required for the electromechanical operation of P(VDF-TrFE)-based polymers; as in most polymeric materials, ε is less then 100 [5], thus being far below values in inorganic piezoelectrics which reach several thousands. One attempt to increase ε was to develop composites of high-ε ceramic powder embedded in the polymer matrix [5]; however, a real enhancement has been obtained in composites of high-ε copper-phthalocyanine (CuPc) oligomers dispersed in the electrostrictive P(VDF-TrFE) copolymer matrix [7]. These composites exhibit high net dielectric constant while retaining almost the same elastic modulus as the copolymer as well as its flexibility [6,7].

It has originally been suggested that an ultrahigh strain response in relaxorlike polymers is generated due to the 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]. Just recently, another mechanism, the exchange coupling between CuPc and copolymer matrix, has been proposed that could lead to a dramatic enhancement of the electrostriction and dielectric constant of the CuPc-P(VDF-TrFE) composite [8]. However, as most of the application-oriented experiments were focused on the electromechanical properties of these materials around room temperature, theoretical predictions of the basic physical properties suffer from a lack of experimental data, especially dielectric data over a wide temperature range, to which they can be compared.

We therefore conducted high resolution measurements of the temperature and frequency-dependent dielectric constant in CuPc-P(VDF-TrFE-CFE) composite. The terpolymer matrix was chosen as it exhibits high electrostriction by itself, while electron irradiation is required in the case of P(VDF-TrFE) copolymer. Elimination of the irradiation process simplifies the processing and also removes undesirable side effects, such as the formation of radicals, chain scission, and cross-linking. The results show that this all-organic composite is unique in its dielectric behavior; although admixture of CuPc strongly increases ε of the terpolymer at all temperatures, the two constituents individually determine the dielectric response in different temperature regions. Namely, the dielectric dynamics is governed exclusively by the relaxorlike terpolymer matrix above its freezing temperature T_f, while below T_f the dielectric properties of CuPc become dominant. The latter are highly interesting, as two dielectric relaxations, both presumably reflecting the charge carriers' response, were detected. Furthermore, analysis of the ac conductivity data, following the universal dielectric response behavior, clearly demonstrates that tunneling of polarons is the dominating charge transport mechanism.

The CuPc-P(VDF-TrFE-CFE) composite with 40 wt % of CuPc was prepared by the solution casting method [6,7]. The complex dielectric constant $\varepsilon^*(\nu, T) = \varepsilon' - i\varepsilon''$ was measured between 10 and 350 K in the frequency range of 0.1 Hz to 3 MHz, using a Novocontrol Alpha High Resolution Dielectric Analyzer. The amplitude of the probing ac electric signal, applied to samples of 180 μm thickness, was 1 V. Temperature was stabilized within ±0.1 K using an Oxford Instruments continuous flow cryostat (10–300 K) or lock-in bridge technique with a Pt100 resistor as a thermometer (100–350 K). The real part of the complex ac conductivity $\sigma^*_{\mathrm{ac}} = \sigma'_{\mathrm{ac}} + i\sigma''_{\mathrm{ac}}$ was calculated via $\sigma'_{\mathrm{ac}} = 2\pi\nu\varepsilon_0\varepsilon''$, with ε_0 being the permittivity of vacuum.

Figure 1(a) shows the temperature dependence of the real part of the complex dielectric constant in the CuPc-P(VDF-TrFE-CFE) composite. As in pure P(VDF-TrFE-CFE) terpolymer of the same 68/32/9 composition [Fig. 1(b) [5]], a broad relaxorlike dispersive dielectric maximum is observed, which is a result of the fact that ε', at a certain temperature which depends on the experimental time scale, starts to deviate from its static value. Indeed, the frequency dispersion of ε' in the composite is enhanced due to the long-range electron delocalization in CuPc oligomers, which causes a strong space charge response [9] and also results in higher dielectric losses. However, values of ε' are significantly higher in the composite than in pure terpolymer, as is required for high-efficiency actuator material.

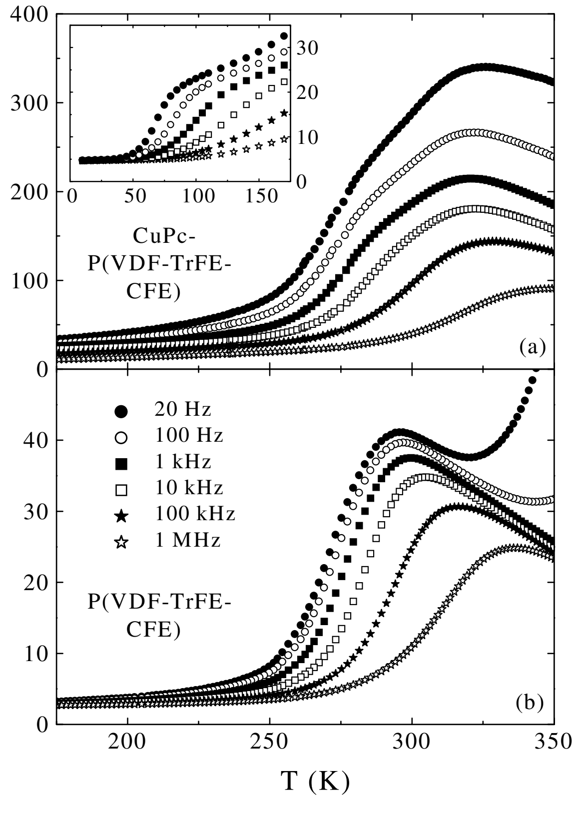

FIG. 1. Temperature dependence of the real part of the complex dielectric constant, ε', measured at several frequencies in CuPc-P(VDF-TrFE-CFE) composite (a) and in pure P(VDF-TrFE-CFE) terpolymer of the same composition [5] (b). The inset shows $\varepsilon'(T)$ in the composite at lower temperatures, indicating a dielectric relaxation, which has not been detected in pure terpolymer.

In spite of the fact that admixture of CuPc strongly increases values of ε', the composite retains the flexibility of the polymer matrix [6,7]. Furthermore, at temperatures above 270 K, the dielectric dynamics of the composite is governed exclusively by relaxation processes in the relaxorlike polymer matrix, as shown in Fig. 2. Here, the temperature-frequency plot for CuPc-P(VDF-TrFE-CFE) composite is shown. An extended description of this powerful analysis of $\varepsilon'(\nu, T)$ data is given in Ref. [10]. The essential point is that, by varying the reduced dielectric constant $\delta = [\varepsilon'(\nu, T) - \varepsilon_\infty]/[\varepsilon_s - \varepsilon_\infty]$ between the values 1 and 0, different segments of the relaxation spectrum are probed. Here, ε_s is the static dielectric constant and ε_∞ is the dielectric constant at high frequencies; the latter takes into account the ionic and electronic polarizability of the system. This method has already been successfully applied to various glassy and relaxor systems, including P(VDF-TrFE-CFE) terpolymer [5]. Determination of ε_s and ε_∞ in a relaxorlike polymer system has also been described in Ref. [5]. Solid lines in Fig. 2 are fits to the Vogel-Fulcher law, $\nu = \nu_0 \exp[-U/k(T - T_0)]$, demonstrating the diverging behavior of relaxation times. The inset of Fig. 2 shows the dependence of the Vogel-Fulcher temperature T_0 on δ, including data obtained in pure terpolymer [5]. Evidently, CuPc oligomers do not influence the dielectric dynamics

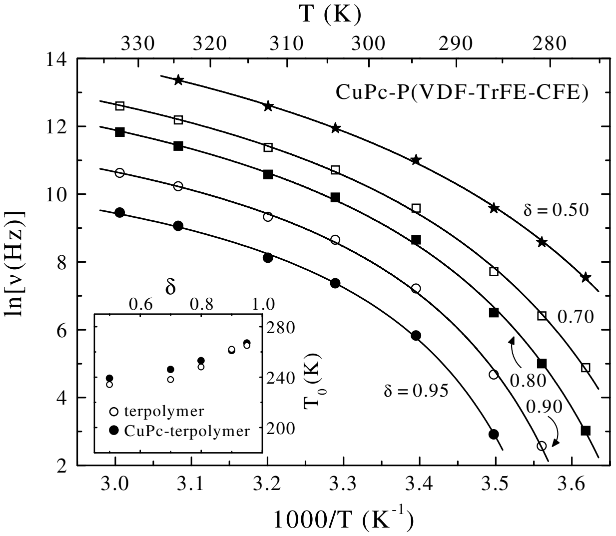

FIG. 2. Temperature-frequency plot for several fixed values of the reduced dielectric constant δ in CuPc-P(VDF-TrFE-CFE) composite. Solid lines are fits obtained with the Vogel-Fulcher expression. The inset shows the dependence of the Vogel-Fulcher temperature T_0 on δ, compared to data obtained in the pure terpolymer [5].

of the composite at temperatures above 270 K, as the temperature evolution of the relaxation spectrum is the same for the composite and terpolymer. The freezing temperature, where the longest-relaxation time diverges, was determined in both systems as $T_f = T_0(\delta \rightarrow 1) = 269 \pm 2$ K.

Below T_f the dielectric dynamics of a relaxor system becomes extremely slow, which is indicated by the very small values of $\varepsilon' \approx 3$ in P(VDF-TrFE-CFE) terpolymer at temperatures below 200 K [Fig. 1(b)]. Thus, below 200 K, the dielectric properties of CuPc start to govern the overall response. The inset of Fig. 1(a) shows $\varepsilon'(T)$ in CuPc-P(VDF-TrFE-CFE) composite below 175 K, indicating a dielectric relaxation which has not been detected in pure terpolymer. This relaxation is noticeable also in Fig. 3, where the imaginary part of the complex dielectric constant in CuPc-P(VDF-TrFE-CFE) composite is shown at several temperatures as a function of frequency. The temperature dependence of its characteristic frequency (denoted by circles) follows the Arrhenius law, $\nu = \nu_0 \exp[-U/kT]$. Dielectric relaxation in this frequency range has already been observed in CuPc structures on silicon [11], and since the CuPc molecule does not contain polar groups, it was ascribed to a so-called nomadic polarization [12]: In the external ac electric field, delocalized π electrons move over the entire CuPc molecule, thus acting very much like dipoles. Although the multiring CuPc oligomers in our composite contain polar carboxyl groups, the nomadic polarization mechanism appears to be even more realistic; here, completely delocalized π electrons can move over the relatively large distance of several molecules forming the oligomer.

Characteristic frequencies of relaxation processes occurring in the terpolymer matrix are denoted by squares in Fig. 3. As is typical for relaxors, the relaxation spectrum becomes extremely polydispersive at temperatures close to T_f (curve at 270 K). Furthermore, diamonds denote characteristic frequencies of another relaxation process, detected at temperatures below 80 K. Not only is the intensity of this relaxation extremely small (dielectric strength is $\varepsilon_s - \varepsilon_\infty \approx 0.5$), but its characteristic frequency is almost independent of temperature—a fact which suggests [13] that this relaxation is connected to a phonon assisted tunneling process in CuPc.

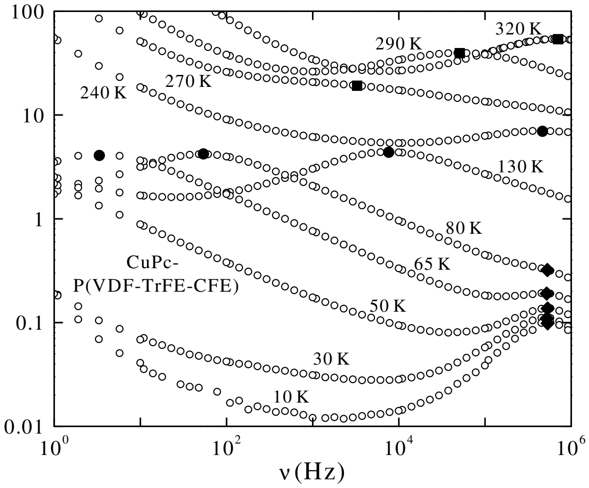

FIG. 3. Imaginary part of the complex dielectric constant, ε'', measured in CuPc-P(VDF-TrFE-CFE) composite as a function of frequency at several temperatures. Characteristic frequencies of three different relaxation processes are denoted by squares, circles, and diamonds.

Previous studies of charge transport in CuPc structures on silicon [11] and in cobalt-Pc thin films [14] revealed that ac conductivity in specific temperature and frequency ranges varies as $\sigma'_{\mathrm{ac}} \propto \nu^s$. These results were interpreted in terms of charge carriers hopping through a band of localized states. We will show that, besides a relaxation which suggests a tunneling process in the system, ac conductivity data clearly reveal that tunneling of polarons is the dominant charge transport mechanism in CuPc-P(VDF-TrFE-CFE) composite.

Figure 4(a) shows the frequency dependence of the real part of the complex conductivity in CuPc-P(VDF-TrFE-CFE) composite at several temperatures. Three different contributions were detected. While in the frequency range shown in the inset to Fig. 4(a) σ' varies as $\sigma'_{\mathrm{ac}} \propto \nu^s$, at lower and higher frequencies results deviate from this relation. At lower frequencies, σ' data tend towards the dc conductivity value σ_{dc}, while at higher frequencies a dielectric relaxation contribution (the one ascribed to the nomadic polarization, denoted by circles in Fig. 3) becomes significant.

Thus, omitting the relaxation contribution, the frequency dependence of the real part of conductivity can be described by the so-called universal dielectric response (UDR) with the addition of a dc conductivity [15]

$$\sigma' = \sigma_{\mathrm{dc}} + \sigma_0 \nu^s. \tag{1}$$

Several theoretical approaches deduce such behavior from the microscopic transport properties, including tunneling of the charge carriers through an energy barrier separating different localized states [16]. The temperature dependence of the UDR exponent s, extracted from data presented in the inset to Fig. 4(a), is shown in Fig. 4(b). Below 140 K the relaxation contribution—its characteristic frequency decreases with decreasing temperature according to the Arrhenius law—overcomes the UDR behavior in the examined frequency window. The solid line in Fig. 4(b) is the fit to a model for polaron tunneling (originally this model was developed for overlapping large polarons [16], but it was argued in [17] that it is in fact applicable to small polarons) which yields the temperature dependence of s as [16]

$$s = 1 - \frac{4 + 6W_\infty r_0'/kTR'^2(W_\infty, r_0', \tau_0)}{R'(W_\infty, r_0', \tau_0)[1 + W_\infty r_0'/kTR'^2(W_\infty, r_0', \tau_0)]^2}. \tag{2}$$

Here, W_∞ and r_0' denote the energy barrier and reduced

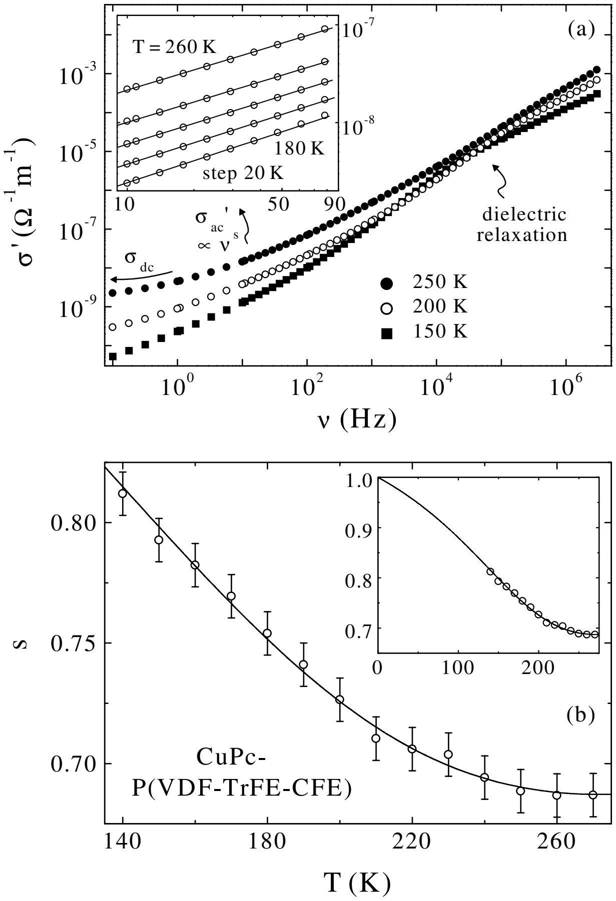

FIG. 4. (a) Frequency dependence of the real part of the complex conductivity, σ', measured in CuPc-P(VDF-TrFE-CFE) composite at several temperatures. The inset shows the frequency interval where data follow the universal dielectric response $\sigma'_{\mathrm{ac}} \propto \nu^s$. (b) Temperature dependence of the UDR exponent s, with the solid line being a fit to a model for polaron tunneling [Eq. (2)]. The inset shows the simulation of $s(T)$ at lower temperatures, using obtained fit parameters.

polaron radius, respectively, while R' is the reduced tunneling distance, also being a function of W_∞ and r'_0 and additionally, of the inverse attempt frequency τ_0 [16]. We are aware that the model predicts a frequency dependence of s and therefore Eq. (1) should no longer be valid in a strong sense, i.e., with $s = \mathrm{const}$. However, in the present data a pure ν^s contribution is seen only over a relatively small frequency range and it can be assumed that the rather weak $\ln(\nu)$ dependence of R' [16] leads to only small deviations from Eq. (1). The inset to Fig. 4(b) shows the simulation of $s(T)$ [Eq. (2)] at lower temperatures, using obtained fit parameters $W_\infty = 0.59$ eV, $\tau_0 = 10^{-13}$ s, and $r'_0 = 2.43$.

In summary, we have shown that the two constituents individually determine the dielectric response of the CuPc-P(VDF-TrFE-CFE) composite in different temperature regions. Although admixture of CuPc strongly increases ε' values of P(VDF-TrFE-CFE) terpolymer at all temperatures, the dielectric dynamics of the composite is governed exclusively by the relaxorlike terpolymer matrix above its freezing temperature $T_f = 269$ K. In this temperature range the composite also exhibits almost the same elastic modulus as the terpolymer and retains its flexibility [6,7]. On the other hand, below T_f the dielectric properties of CuPc become dominant. Two dielectric relaxations, both presumably reflecting the charge carriers' response, were detected; one was ascribed to the nomadic polarization phenomenon, completely delocalized π electrons in oligomers act very much like dipoles, and the other to a phonon assisted tunneling in CuPc. The existence of the tunneling process was revealed by the UDR behavior $\sigma'_{\mathrm{ac}} \propto \nu^s$. In particular, the temperature dependence of the UDR parameter s demonstrates that tunneling of polarons is the dominating charge transport mechanism in CuPc-P(VDF-TrFE-CFE) composite.

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