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## The intermediate temperature $T^*$ revealed in relaxor polymers

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The temperature dependence of the dielectric and optical properties, crystal structure, and infrared spectra of the relaxor poly(vinylidene fluoride-trifluoroethylene-chloro-fluoroethylene) terpolymer films obtained from Langmuir-Blodgett method have been comprehensively investigated. All the results suggest that there exists a peculiar point at  $\sim 370$  K, which is attributed to the intermediate temperature  $T^*$  recently discovered in inorganic relaxors. Here,  $T^*$  results from the change in the growth rate of the trans gauche  $T_3GT_3G'$  chain conformations with temperature, which is similar to the transformation from dynamic to static behavior of the so-called polar nano-regions in inorganic relaxors. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4881268>]

Outstanding piezoelectric, electrostrictive, and dielectric properties have been observed in various ferroelectric solid solutions based on relaxors such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN),  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZN),  $\text{Ba}(\text{Zr,Ti})\text{O}_3$  (BZT), and so on.<sup>1–6</sup> Interestingly, some polymers, e.g., the electron irradiated copolymer of vinylidene fluoride-trifluoroethylene [P(VDF-TrFE)] and terpolymer of VDF-TrFE-chloro-fluoroethylene [P(VDF-TrFE-CFE)] also demonstrate typical relaxor behavior with higher both dielectric permittivity and electromechanical responses than the pristine P(VDF-TrFE).<sup>7–10</sup> Comprehensive investigations have been conducted on the inorganic relaxor systems in order to understand the microscopic mechanisms at the origin of their outstanding properties. Both theoretical and experimental results suggest that the unusual features of the inorganic relaxors are related to the existence of polar clusters, i.e., the so-called polar nanoregions (PNRs).<sup>11–14</sup> The nature of PNRs—their morphology and dynamics—has been intensely studied and fairly scientific descriptions have been established. Among these descriptions, four characteristic temperatures describing the dynamics of relaxors have been made clear. From the highest to the lowest, these temperatures are (i) the Burns temperature  $T_B$ ,<sup>11</sup> (ii) the intermediate temperature  $T^*$ ,<sup>15–18</sup> (iii) the frequency-dependent temperature of the maximum of the dielectric permittivity peak  $T_m$ , and (iv) the ferroelectric phase transition temperature  $T_c$  (or the freezing temperature  $T_f$ ).<sup>12</sup> Above  $T_B$ , the phase is paraelectric without PNRs, and the structure is essentially the same as the paraelectric state of normal ferroelectrics. Below  $T_B$ , in the so-called ergodic relaxor phase, the frustration between electric and spatial instabilities induces PNRs.<sup>19</sup> It is thought that the fluctuating PNRs are dispersed between  $T_B$  and  $T^*$  and the static components of PNRs start to appear only below  $T^*$ .<sup>20</sup> In the relaxor polymers, it is believed that the dominant

trans-gauche ( $T_3GT_3G'$ ) chain conformation should be responsible for the relaxor feature, like the PNRs in the inorganic relaxors. Up to now, however, only two characteristic temperatures have been reported in relaxor polymers, i.e.,  $T_m$  and  $T_c$  or  $T_f$ .<sup>7,21</sup> While relaxor polymers and inorganic relaxors are sharing several similarities, the absence of  $T_B$  and  $T^*$  in polymers makes difficult the understanding of their dynamics in the light of the advanced descriptions already applied in the inorganic relaxors. Furthermore, a question arises, is there any universal definition existing for all relaxor systems or not? Thus, studying the dynamics of relaxor polymers is not only needed for understanding the micro-mechanisms behind relaxor features, but also may provide alternatives to explain the origin of the outstanding properties because of some unique features related to polymers, e.g., their low dimensional properties like for instance the one-dimensional domain-wall motion.<sup>22,23</sup>

In the present work, the temperature dependence of the structure and different physical properties of relaxor P(VDF-TrFE-CFE) terpolymer films obtained from Langmuir-Blodgett (LB) method have been investigated. All the results show that there exists a characteristic temperature at  $\sim 370$  K, which is attributed to the peculiar temperature  $T^*$  known in inorganic relaxors.

Thin films of terpolymer of P(VDF-TrFE-CFE) (56.2/36.3/7.5 mol. %) (Piezotech, France) were deposited on Au-coated  $\text{SiO}_2/\text{Si}$  substrate using a horizontal LB technology (Nima 611) as described in Ref. 24. Samples with different transferred layers, from one layer up to 60 layers, were obtained. The as-grown films were annealed at 390 K for 2 h in air to improve the crystallinity. X-ray diffraction measurements were performed on a highly accurate two-axis diffractometer in a Bragg-Brentano geometry using Cu  $K\alpha$  wavelength issued from a 18 kW rotating anode generator with diffraction angles precision better than  $0.002^\circ$  (2 theta). Variable-angle spectroscopic ellipsometry with the wavelength from 500 nm to 800 nm was used to acquire the

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temperature dependent of the refractive index. A Nicolet 510 spectrometer with a  $2\text{ cm}^{-1}$  resolution and averaged over 16 scans was used to obtain the Fourier Transform Infrared (FTIR) spectra to analyze the evolution of the polymer chain conformation with temperature. Al was evaporated onto the films through a mask to form the Al-terpolymer-Au capacitor structure for characterizing the electric properties of the polymer films. The frequency dependence of dielectric properties was measured at various temperatures by an Agilent E4980A Precision LCR Meter. The temperature was varied at a rate of 1 K/min via a cryostat (MMR Tech., Inc.).

The temperature dependences of the dielectric constant  $\epsilon$  and dielectric losses ( $\tan \delta$ ) versus frequency are shown in Fig. 1(a). It can be seen that both  $\epsilon$  and  $\tan \delta$  demonstrate a dielectric anomaly on a broad temperature range with the temperature of its maximum  $T_m$ , which shifts to higher temperature with increased frequency. This frequency dispersion is a common feature of relaxor ferroelectrics. A more careful inspection of  $\epsilon(T)$  curve shows that the frequency dispersion basically ceases at  $\sim 370\text{ K}$  (see Fig. 1(b)). Simultaneously, the temperature dependence of the reciprocal of the dielectric constant, i.e.,  $1/\epsilon(T)$  starts to deviate from the linear behavior at  $\sim 370\text{ K}$  (see Fig. 1(c)). These two results indicate a characteristic and additional temperature actually exists in the relaxor P(VDF-TrFE-CFE) films besides already known  $T_m$  and  $T_c$  temperatures.  $T^*$  may reflect the evolution of the dominant chain conformation with temperature like the PNRs in inorganic relaxors.<sup>15</sup> In the present case, the temperature of  $\sim 370\text{ K}$  is supposed to be the intermediate temperature  $T^*$ , at which the dominant conformations in the relaxor polymer start to transform from dynamic to static. This deduction is mainly based on the change of the frequency dispersion in the dielectric constant.<sup>15</sup> Interestingly, 370 K is very close to the critical temperature of the ferroelectric phase transition occurring in P(VDF-TrFE) which indicates that  $T^*$  can be seen as the reminiscence of the phase transition of the ordered or normal state as suggested in Ref. 16.

Moreover as pointed out by Toulouse,  $T^*$  is the temperature at which the PNRs with finite lifetime polarization fluctuations transform into the polar nano-domains (PNDs) with

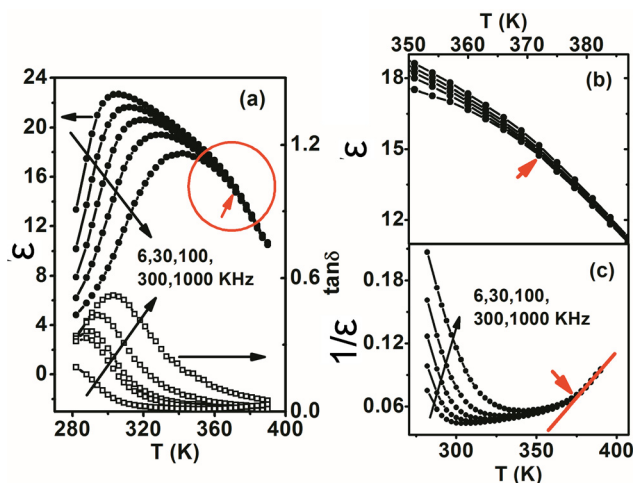


FIG. 1. Temperature dependence of (a) dielectric permittivity (left), loss (right), and (b) reciprocal of the dielectric permittivity of terpolymer P(VDF-TrFE-CFE) at various frequencies. The black straight line in (b) is a linear fit.

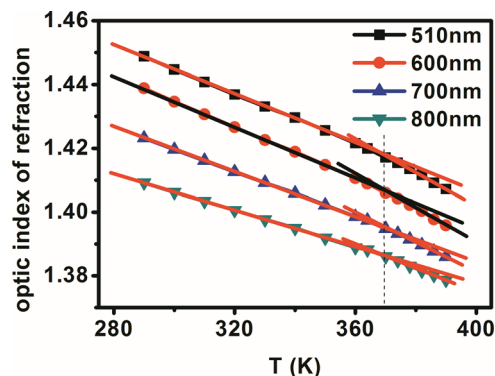


FIG. 2. The optic index of refraction ( $n$ ) as a function of temperature from 260 to 390 K with 510 nm, 600 nm, 700 nm, and 800 nm wave lengths for terpolymer P(VDF-TrFE-CFE) films. The solid lines are linear fits.

permanent polarization fluctuations.<sup>26</sup> This transformation can manifest through the change of the optical properties, such as refractive index and absorption coefficient, which are associated with the features of the PNRs or PNDs, e.g., the inhomogeneity of strain and polarization effect.<sup>27,28</sup> The temperature dependence of the optical refractive index with various wavelengths of the P(VDF-TrFE-CFE) films is shown in Fig. 2. For all the data derived from different wavelengths, there is a transition point at nearly the same temperature, i.e., 370 K. This temperature point is coincident with that observed in the temperature dependence of the dielectric constant and thus optical index measurements provide a further support to the existence of such peculiar 370 K temperature.

The appearance of static-like PNRs should be associated to appearance of strains<sup>16</sup> and thus should be reflected in the temperature dependence of the lattice parameter. The temperature dependence of the interplanar distance extracted from the Bragg peak located at  $2\theta \sim 18^\circ$  (which remains unique whatever the temperature<sup>25</sup>) is shown in Fig. 3 and illustrates the change in the interchain spacing of the terpolymer crystallines with temperature on cooling process. It can be seen that as expected the interchain spacing decreases with decreasing temperature. Nevertheless, a distinct change of slope can be obviously evidenced at  $\sim 370\text{ K}$ . This change may be then related to the dynamics of the chain conformations with temperature and especially with the occurrence of static strains as reported for  $T^*$  in inorganic relaxors.<sup>16</sup>

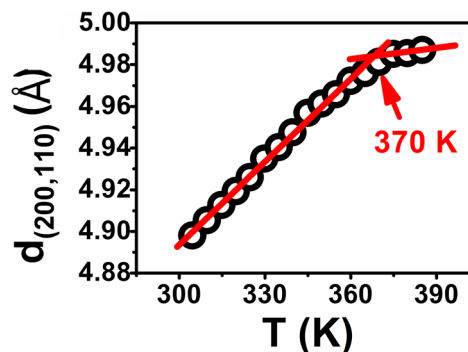


FIG. 3. Interplanar distance extracted from the Bragg peak located at  $2\theta \sim 18^\circ$  position as a function of temperature from 300 to 390 K for terpolymer P(VDF-TrFE-CFE) films.

Zhang *et al.* pointed out that the dominant  $T_3GT_3G'$  chain conformations in relaxor polymers play a role similar to that of PNRs in the inorganic relaxors.<sup>21</sup> Thus, studying the evolution of the  $T_3GT_3G'$  entities with temperature may bring essential information to better understand the dynamics of relaxor polymers. The FTIR infrared spectroscopy is a powerful method to reveal the information of organic chain conformations. Previous studies have shown that the different chain conformations in PVDF-based polymers, i.e.,  $T_{m>4}$ ,  $T_3GT_3G'$ , and  $TGTG'$ , have well-separated characteristic IR absorbance bands.<sup>29–31</sup> Xu *et al.* point out that the  $T_3GT_3G'$  conformation has a typical absorption peak in the IR absorbance spectrum, i.e.,  $\sim 510\text{ cm}^{-1}$  in the P(VDF-TrFE-CFE) terpolymers.<sup>9</sup> In the present case, the temperature dependence of the IR absorbance spectra for the P(VDF-TrFE-CFE) films is shown in Fig. 4. The absorbance peaks at  $510\text{ cm}^{-1}$ ,  $612\text{ cm}^{-1}$ , and  $1290\text{ cm}^{-1}$  are attributed to  $T_3GT_3G'$ ,  $TGTG'$ , and  $T_{m>4}$  conformations, respectively. Since the typical peak of the polar all-trans ( $T_{m>4}$ ) conformation (at  $1290\text{ cm}^{-1}$ ) is too weak to be properly extracted in the all temperature range, only two conformations, i.e.,  $T_3GT_3G'$  and  $TGTG'$  in the P(VDF-TrFE-CFE) films have been considered.  $TGTG'$  is the non-polar chain conformation, which represent the paraelectric  $\alpha$ -phase. The fraction of the conformations can be calculated by the model proposed by Osaki,<sup>32,33</sup>

$$F_i = \frac{A_i}{A_I + A_{II} + A_{III}}, \quad (1)$$

where  $i = I, II, III$ , and  $A_I, A_{II}$ , and  $A_{III}$  are the absorbances of crystal forms  $I, II$ , and  $III$ , i.e., with all-trans ( $T_{m>4}$ ),  $T_3GT_3G'$ , and  $TGTG'$  sequences, respectively.  $F_i$  is the fraction of chain conformation  $i$ .  $A_I, A_{II}$ , and  $A_{III}$  are extracted from the data in Figure 4. In the extraction process, each absorbance peak was fitted with a Lorentzian shape. Since the  $A_I$  representing the polar  $T_{m>4}$  conformation is nearly zero in the measured temperature range, Eq. (1) can be simplified as:  $F_i = A_i/(A_I + A_{II})$ . In the present study, the attention is paid on the  $T_3GT_3G'$  conformation. The temperature dependence of the fraction of  $T_3GT_3G'$  entities is shown in Fig. 4 inset. It can be seen that the  $T_3GT_3G'$  conformation exists in the whole temperature range of measurement and thus suggests that the characteristic temperature at 370 K is not  $T_B$  as in inorganic relaxors, i.e., the temperature above which

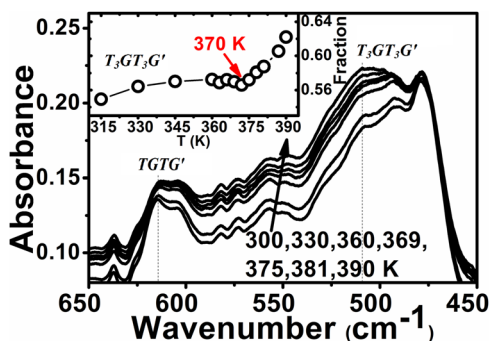


FIG. 4. FTIR spectra of P(VDF-TrFE-CFE) at various temperatures in the low wavenumber region, the absorption peak nearby  $510\text{ cm}^{-1}$ , and  $612\text{ cm}^{-1}$  are attributed to  $T_3GT_3G'$  and  $TGTG'$  conformations, respectively. The inset shows the evolution of the fraction of  $T_3GT_3G'$  conformations as a function of temperature.

PNRs vanishes. A reason for the absence of  $T_B$  in our present study is that  $T_B$  for P(VDF-TrFE-CFE), if it exists, is probably higher than the melting point. The fraction of the  $T_3GT_3G'$  decreases with decreasing temperature in the all measurement range. However, an obvious inflexion point is also observed at  $\sim 370\text{ K}$ . Cooling from high temperature, the fraction of  $T_3GT_3G'$  conformations decreases rapidly until  $370\text{ K}$ , while it decreases more slowly below this peculiar temperature. It is assumed that the decrease of the fraction of  $T_3GT_3G'$  conformations may be correlated to the increase of size of the  $T_3GT_3G'$  regions. Indeed, it is known that the size of the  $T_3GT_3G'$  clusters is not constant with external fields, e.g., electric field or temperature.<sup>34</sup> In the present study, as expected the size of the  $T_3GT_3G'$  clusters increases with decreasing temperature, but the growth rate changes at  $\sim 370\text{ K}$ . Therefore, the temperature  $370\text{ K}$  can be considered as the intermediate temperature  $T^*$ , above which the growth rate of  $T_3GT_3G'$  is rapid while it is roughly suppressed below  $T^*$ . This is similar to the observation in PZN relaxor single crystals.<sup>15</sup> More evidences should be further explored to investigate the mechanisms of the dynamics of relaxor polymers. The unique features of ferroelectric polymers, such as the one-dimensional domain-wall motion, may provide an experimental way to prove the new model for the relaxor ferroelectrics.<sup>35</sup>

In summary, relaxor P(VDF-TrFE-CFE) terpolymer films grown by Langmuir-Blodgett technique were investigated as a function of temperature using dielectric, optical, diffraction, and infrared measurements. All the experimental results demonstrate there exists a change of behavior for all the properties at  $\sim 370\text{ K}$ . This peculiar temperature which is ascribed to the intermediate temperature  $T^*$  similarly to inorganic relaxor,<sup>16</sup> reflects the evolution of the dominant chain conformation  $T_3GT_3G'$  with temperature.

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