

## Tuning the Relaxor–Ferroelectric Properties of Poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) Terpolymer Films by Means of Thermally Induced Micro- and Nanostructures

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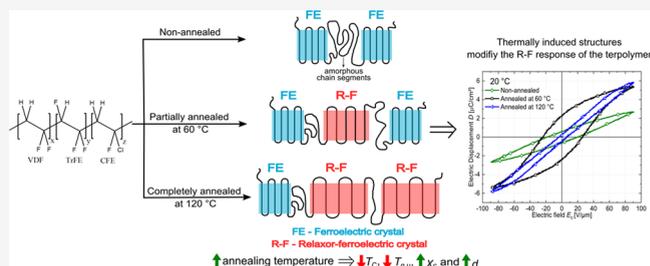
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**ABSTRACT:** The effects of thermal processing on the micro- and nanostructural features and thus also on the relaxor–ferroelectric properties of a P(VDF–TrFE–CFE) terpolymer were investigated in detail by means of dielectric experiments, such as dielectric relaxation spectroscopy (DRS), dielectric hysteresis loops, and thermally stimulated depolarization currents (TSDCs). The results were correlated with those obtained from differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and Fourier-transform infrared spectroscopy (FTIR). The results from DRS and DSC show that annealing reduces the Curie transition temperature of the terpolymer, whereas the results from WAXD scans and FTIR spectra help to understand the shift in the Curie transition temperatures as a result of reducing the ferroelectric phase fraction, which by default exists even in terpolymers with relatively high CFE contents. In addition, the TSDC traces reveal that annealing has a similar effect on the midtemperature transition by altering the fraction of constrained amorphous phase at the interphase between the crystalline and the amorphous regions. Changes in the transition temperatures are in turn related to the behavior of the hysteresis curves on differently heat-treated samples. During heating, evolution of the hysteresis curves from ferroelectric to relaxor–ferroelectric, first exhibiting single hysteresis loops and then double hysteresis loops near the Curie transition of the sample, is observed. When comparing the dielectric–hysteresis loops obtained at various temperatures, we find that annealed terpolymer films show higher electric-displacement values and lower coercive fields than the nonannealed sample, irrespective of the measurement temperature, and also exhibit ideal relaxor–ferroelectric behavior at ambient temperatures, which makes them excellent candidates for applications at or near room temperature. By tailoring the annealing conditions, it has been shown that the application temperature could be increased by fine tuning the induced micro- and nanostructures.



### INTRODUCTION

Terpolymers based on a copolymer of vinylidene fluoride (VDF or VF<sub>2</sub>) and trifluoroethylene (TrFE) and an additional fluorine-containing monomer represent a rather unique class of fluoropolymers as they often show strong relaxor–ferroelectric (R–F) behavior.<sup>1</sup> Although the structure of such terpolymers closely resembles that of the most often used PVDF variant, the family of P(VDF–TrFE) copolymers, they can exhibit superior dielectric and electromechanical properties depending on the requirements of a particular device application as a consequence of the introduction of the third fluorine-containing monomer into the copolymer macromolecules, which breaks the long-range interaction within the ferroelectric dipolar regions and reduces them to nanodomains.<sup>2,3</sup> Ultimately, the terpolymers have lower coercive fields ( $E_c$ ) and higher saturation polarizations  $P_s$  with slim hysteresis loops and thus exhibit higher electrostrictive coefficients,<sup>2,4</sup> which make them very attractive for applications such as energy-storage devices or soft actuators.

Furthermore, insertion of the monomer units forces the majority of the chains in the P(VDF–TrFE) copolymer with an original polar all-trans conformation to adopt  $TG^+TG^-$  and  $T_3G^+T_3G^-$  conformations that usually crystallize into the nonpolar  $\alpha$  and weakly polar/nonpolar  $\gamma$  phases.<sup>5,6</sup> Consequently, the ferroelectric-to-paraelectric (F–P) or Curie transition temperature ( $T_C$ ) is lowered and thus closer to room temperature (RT).<sup>2,7</sup> R–F terpolymers also exhibit unusually high dielectric permittivities at RT. Their features combined with the suitability for solution or melt casting into

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