

## Electrostrictive behavior of poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene)

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(Received 25 February 2003; accepted 11 June 2003)

The mechanism underlying the large electric-field-induced strains in terpolymers of vinylidene fluoride, trifluoroethylene, and chlorotrifluoroethylene was investigated. The electrostrictive strain increased by an order of magnitude with increasing temperature, up to the Curie transition, and was essentially invariant to temperature thereafter. Infrared absorption spectra, obtained as a function of both temperature and electric field strength, revealed no change in the crystal phase structure for electric fields sufficient to induce longitudinal strains of  $\sim 1\%$ . Thus, the electrostriction observed herein is not due to crystal phase conversion. The Maxwell strain was also negligible under all conditions, because of the terpolymer's high mechanical modulus (10 to 100 MPa). The mechanical properties exhibit an anomalous change in behavior near the Curie transition, whose origin is unclear. © 2003 American Institute of Physics. [DOI: 10.1063/1.1600515]

Electrostriction refers to an electric-field-induced mechanical strain, quadratic in the applied field strength (for linear dielectrics up to fields at which the polarization begins to saturate<sup>1</sup>). Electroactive polymers show promise in various commercial and military applications, such as sensors, actuators, and transducers, where advantage can be taken of their ability to convert electrical energy into mechanical work. The two forms of energy are related via the polarization and the mechanical modulus of the material; however, the process by which this energy transformation takes place is not completely understood.

The most widely used and studied electroactive polymers are based on poly(vinylidene fluoride) (PVDF). PVDF can crystallize into five crystal phases,<sup>2</sup> the most prominent being the nonpolar  $\alpha$  phase and the polar  $\beta$  phase. The latter confers ferroelectric behavior to the material, and is necessary to achieve electromechanical properties. Conversion of the  $\beta$  crystals to the nonpolar  $\alpha$  form takes place thermally at the Curie temperature ( $T_C$ ), which accordingly defines the upper use temperature. While the PVDF homopolymer must be mechanically oriented or poled in a field to achieve the polar  $\beta$  phase, copolymers of VDF and trifluoroethylene (TrFE) spontaneously crystallize into an I phase (all *trans*, similar to  $\beta$  phase in PVDF). Even without mechanical or electrical processing, VDF-TrFE copolymers having approximately 75% of phase I crystallinity can be obtained below  $T_C$ . Thus, these materials are of substantial interest for applications.

Recent efforts have focused on reducing the size of the crystalline domains in VDF copolymers. The operating assumption is that small domains respond faster and more efficiently to an applied electric field, thus yielding large strains. Various methods have been used to reduce the crystalline domain size, including electron irradiation,<sup>3</sup> chemical crosslinking,<sup>4</sup> blending,<sup>5,6</sup> and through the incorporation of a

bulky third monomer. The latter approach has shown particular promise with terpolymers of VDF, TrFE, and either chlorotrifluoroethylene (CTFE)<sup>7</sup> or hexafluoropropylene.<sup>8</sup>

A quantitative understanding of the contribution from various molecular level mechanisms to electrostriction in VDF materials is lacking. One hypothesis, advanced for both VDF-TrFE copolymers<sup>3</sup> and terpolymers,<sup>9</sup> is that an applied field induces a crystal phase change from the nonpolar II phase to the polar I phase. This phase conversion would change the *c* lattice dimension of the unit cell by  $\sim 10\%$ , which in principle alters the macroscopic dimensions as well. Such a field-induced change from the nonpolar to the polar crystal form is a well-known mechanism for electrostriction,<sup>10</sup> and has been observed in infrared<sup>11</sup> and x-ray diffraction measurements<sup>12</sup> on VDF-TrFE copolymers. Note that reversible changes in the degree of crystallinity have also been described in polyvinylidene fluoride, and are believed to contribute to its pyroelectric behavior.<sup>13</sup> Another potential source of electromechanical transduction, active in all materials, is the Maxwell response, arising from Coulombic attraction of the electrodes. The Maxwell strain is given by  $S_m = PE/2K$ , where *P* is the polarization, *E* the applied field, and *K* the longitudinal Young's modulus. This effect is significant only for soft materials.

Herein, we describe a study of the electromechanical response of terpolymers having  $\sim 60\%$  VDF, 32% TrFE, and 8% CTFE backbone composition. These were synthesized using an organoborane-initiated bulk polymerization, described in detail elsewhere.<sup>7,14</sup> The backbone composition was determined by chlorine analysis and <sup>1</sup>H and <sup>19</sup>F nuclear magnetic resonance (NMR). Films were prepared from 5% solutions in dimethylformamide. For the Fourier transform infrared (FTIR) experiments,  $\sim 5\text{-}\mu\text{m}$ -thick films were cast on an (infrared transparent) germanium electrode. Scans were signal averaged at a resolution of  $2\text{ cm}^{-1}$ , with all absorbances within the limits of Beer's law. For electrostriction and polarization measurements, a 10-MV/m alternating elec-

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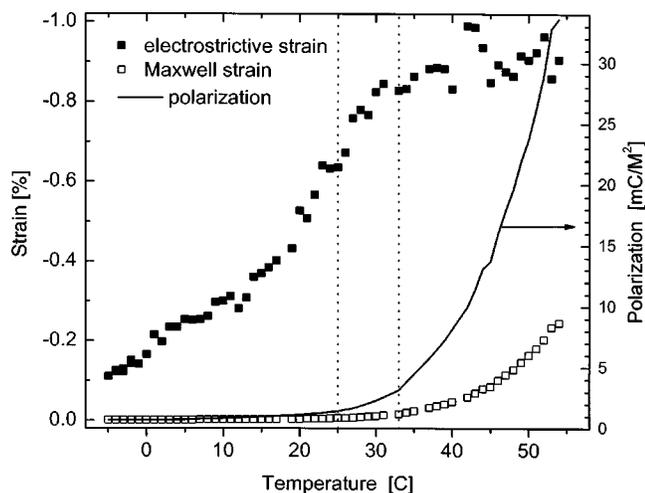


FIG. 1. Longitudinal compressive strain (■) and polarization (—) measured at  $E=10$  MV/m and 0.01 Hz for terpolymer with 7.6% CTFE, along with the calculated Maxwell strain (□). The onset and peak of the Curie transition are denoted by the vertical dotted lines.

tric field was supplied by a Solartron 1254, amplified using a Trek 610-D. Electrostrictive strains were measured with a MTI 1000 Fotonic™ Sensor, with the polarization simultaneously determined using a Sawyer–Tower circuit.<sup>15</sup> Dynamic mechanical measurements employed an IMass Dynastat spectrometer and a Bohlin spectrometer VOR for tension and shear deformation experiments, respectively. Mechanical test specimens, typically 1.5 mm thick, were prepared by molding at 160 °C in vacuum. Differential scanning calorimetry (DSC) was carried out at 10°/min using a Perkin-Elmer 7.

The longitudinal strain (change in film thickness parallel to the field) is shown in Fig. 1 as a function of temperature. The strain is compression, and independent of the field direction, consistent with electrostriction. The data in Fig. 1 were obtained at 0.010 Hz. Although the response is qualitatively similar, the magnitude of the strain decreases substantially with increasing frequency. For example at 50 °C, strain on the order of 1% is achieved at 10 mHz, whereas at 1 kHz it is less than 0.2%. The response to temperature increases monotonically up to the Curie transition, and levels off thereafter. For an electric field of only 10 MV/m, strains approaching 1% are obtained, corresponding to an electrostrictive coefficient of 100 nm<sup>2</sup>/V<sup>2</sup>. This rivals some of the best reported results for these type materials,<sup>3,16–18</sup> and is significantly larger than obtained for VDF terpolymers polymerized in bulk.<sup>19</sup>

After initial application of the field (first cycle), the material exhibits a “set,” having a recovery time of at least several hours. This initial strain is about one-third larger in magnitude than the response to subsequent application of the electric field. Thus, for a field of 12 MV/m at room temperature, the first cycle strain is 0.75%, while the steady-state response is 0.5%. DSC measurements on the poled sample prior to its recovery revealed a 3% increase in the magnitude of the Curie transition (from 9.1 to 9.4 J/g). This is too small to account for the observed strain. Thus, while the field-induced phase change mechanism is evidently present, the indication is that the effect is almost negligible in the terpolymer.

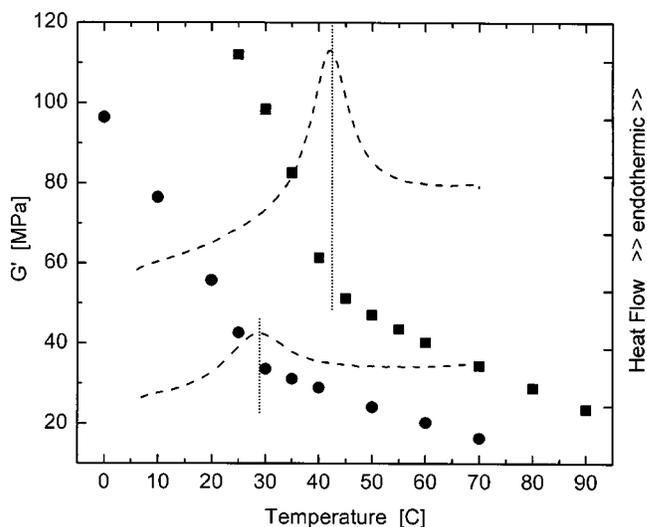


FIG. 2. Dynamic storage modulus measured in shear for terpolymers having 6.2% (■) and 4.0% (●) CTFE, with superimposed DSC curves for each. The vertical lines denote the temperature of the inflection point of the modulus data. The loss modulus over this range was less than 4 MPa.

The RT stress/strain response of the terpolymers is linear through at least 3% strain, with a yield stress  $\approx 5$  MPa.<sup>7</sup> For the 6.2% CTFE material, we measure a Young’s modulus equal to 270 MPa at RT. To determine the temperature dependence, we use the variation with temperature of the dynamic shear modulus (Fig. 2).

The temperature dependence of the shear modulus exhibits a discontinuity in the vicinity of the Curie transition. A similar effect has been seen in PVDF<sup>20</sup> and its copolymer with TrFE.<sup>21</sup> Since the modulus of the crystallites is much larger than that of the amorphous regions, the measured modulus essentially depends only on the latter and the volume degree of crystallinity.<sup>22</sup> This implies that any change in crystal modulus due to the crystal phase change at  $T_C$  should have negligible effect on the measured modulus. Thus, the effect seen in Fig. 1 must arise from changes in the interaction between the amorphous and crystalline regions; that is, the phase boundary. It has been shown that the ferro- to paraelectric phase change in VDF polymers originates at the outer periphery of the crystallites.<sup>23</sup> This aspect of the terpolymer behavior requires further investigation.

Figure 3 (lower panel) shows two regions of interest in the infrared spectra, measured at temperatures encompassing the Curie transition. As  $T_C$  is traversed from above, the absorption peak at 1290 wave numbers (symmetric CF<sub>2</sub> stretching vibration involving sequences of four or more *trans* units), which is almost absent at the highest temperature, grows in intensity. Similar increases are seen in the absorptions near 848 cm<sup>-1</sup> (CF<sub>2</sub> symmetric stretch) and 884 cm<sup>-1</sup> (CH<sub>2</sub> rocking and CF<sub>2</sub> asymmetric stretching).<sup>24</sup> These three peaks are all assigned to the I (all *trans*) phase.<sup>25,26</sup> In contrast, the weak shoulder at 865 cm<sup>-1</sup>, associated with the II (paraelectric) phase, decreases with decreasing temperature, reflecting development of the ferroelectric crystalline domains. Thus, the changes in crystal phase brought about by temperature are readily discernible in the FTIR spectra.

In contrast to the effect of temperature on the absorption spectrum, the application of an electric field to the sample

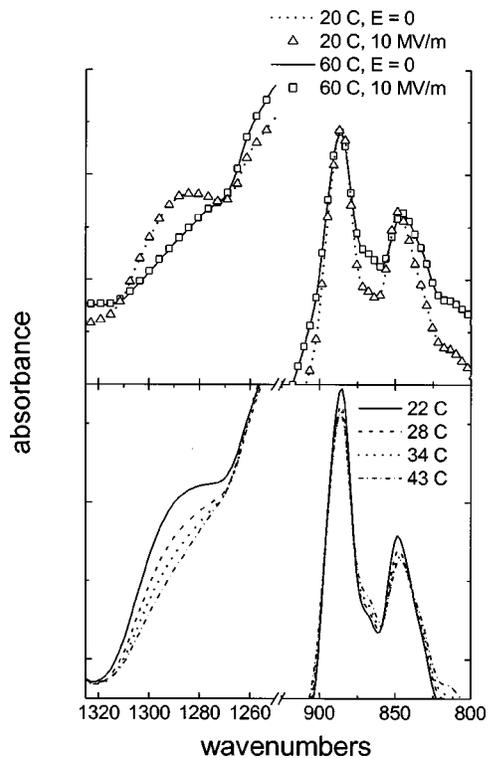


FIG. 3. Infrared spectra of terpolymer (7.6% CTFE) at the indicated temperatures. The Curie transition onsets at 25 °C, with the peak at 33 °C. Lower panel: The sample was heated above the  $T_C$  and allowed to cool slowly back to room temperature, with no electric field present. Upper panel: Two scans below  $T_C$  and two above the  $T_C$ , in each case with and without an applied electric field.

has no significant effect. As illustrated in Fig. 3 (upper panel), at temperatures from RT to 60 °C, there is no difference between the absorption spectra with and without a 10 MV/m field (aside from the trivial decrease due to orientation induced parallel to the applied field). Thus, a field sufficient to yield large electrostrictive strains does not measurably affect the relative population of the type I and II crystal phases.

There are other problems with the idea that the large electrostrictive strains observed in PVDF materials arises from the conversion of the nonpolar II phase to the polar I phase. From calorimetry, the crystallinity of the 7.6% CTFE terpolymer is roughly 30%. Moreover, below the Curie transition, only approximately 25% of the crystals are in the II phase.<sup>1</sup> Even assuming perfect orientation of the crystallites and 100% conversion from phase II to their phase I crystal form (notwithstanding the results in Fig. 3), a 10% change in unit cell dimensions due to such a phase conversion could effect a macroscopic strain below  $T_C$  of only  $\sim 0.7\%$ . Since the film is essential isotropic, the actual value would be smaller, and thus less than the measured strain (Fig. 2). Although these results do not rule out the possibility of a contribution from crystal phase change at higher electric fields (the nonpolar to polar phase conversion in VDF homopolymer, responsible for large piezoelectricity, is only observed at large fields<sup>27,28</sup>), this mechanism cannot be the dominant source of the electrostrictive strains reported herein. Our conclusion is also consistent with neutron diffraction experiments,<sup>29,30</sup> which found no change in lattice spacing upon application of an electric field to PVDF copolymers.

Included in Fig. 1 is the Maxwell strain, calculated from

the measured values of  $G'$  and  $\nu$ . Up through  $T_C$ ,  $S_m < 2 \times 10^{-4}$ , which is negligible compared to the obtained electrostrictive response. Thus, the source of the large electrostriction remains to be determined. We speculate that entire (albeit small) crystallites may underlie the electromechanical response. As the temperature is raised, the local viscosity (modulus) impeding motion is reduced; thus, more facile reorientation of these nanodomains causes the polarization to increase, with concomitant increase in electrostrictive strain. The implication is that movement, rather than phase conversion, of crystals may underlie the measured electrostrictive strains. This putative crystal motion would obviously be limited at higher frequencies, consistent with the reduction of the electrostriction at higher frequencies.

The authors thank R. Casalini and G. Kavarnos for insightful discussions. One of the authors (J.T.G.) thanks the American Society for Engineering Education for a postdoctoral fellowship. This work was supported by the Office of Naval Research.

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