

Influence of Crystallization Conditions on the Microstructure and Electromechanical Properties of Poly(Vinylidene Fluoride-Trifluoroethylene-Chlorofluoroethylene) Terpolymers

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The crystallization process and its influence on the microstructure, ferroelectric, and electromechanical properties of a poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (PVDF-TrFE-CFE) terpolymer were investigated. By varying the isothermal crystallization temperature T_x of this terpolymer, the ratio of ferroelectric crystal concentration to the concentration of relaxor ferroelectric crystal (a defect-modified class of ferroelectrics exhibiting strong electrostrictive behavior) can be determined. The higher T_x samples show an increased polarization hysteresis and reduced electric field-induced strain response. In addition, the experimental results, in combination with other reported results, indicate that CFE units are included in the crystalline lattice. Consequently, the influence of CFE on the ferroelectric behavior of the polymer is through the defects it induces in the crystal lattice.

Polymers for electromechanical applications offer many unique and inherent advantages when compared with other materials, being lightweight, flexible, and relatively easy to process and form into complicated shapes or large areas. We have examined one of these terpolymers, P(VDF-TrFE-CFE), and investigated how its ferroelectric and electromechanical responses are influenced by polymer crystallization processes in tandem with corresponding microstructure changes. We found that, by varying the crystallization temperature T_x , we can selectively vary the fraction of polar and non-polar crystallites in the crystalline phase. Crystallites formed during long periods of time at T_x exhibit less polar behavior. Crystallites formed during the rapid cooling process between T_x and room temperature exhibit stronger polar behavior. This is established most quantitatively by wide-angle x-ray diffraction (WAXD) and reinforced by Fourier transform infrared (FT-IR) spectroscopy, polarization loop, and electromechanical strain measurements. As will be shown, crystallizing the terpolymer at higher T_x values has an adverse effect on its electromechanical strain response.

X-ray data were collected in order to interrogate interchain spacing and, via x-ray peak width, the crystalline order perpendicular to the chain direction. For PVDF-TrFE copolymers in the ferroelectric phase, this peak corresponds to the (110, 200) reflection. The data were acquired at selected temperatures between room temperature and T_x (taken on heating)

in order to follow the evolution of the microstructure. The x-ray data in the 2θ range of the (110, 200) reflection acquired at room temperature for ter-



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BEAMLINE X8A

Funding

The Office of Naval Research

Publication

R.J. Klein, J. Runt, and Q.M. Zhang, "Influence of Crystallization Conditions on the Microstructure and Electromechanical Properties of Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) Terpolymers," *Macromolecules*, **36**, 7220-7226 (2003).

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polymer films with different T_x are shown in **Figure 1a**.

For the terpolymer films with T_x at 112, 122, and 127°C, the x-ray data are relatively well characterized by a single peak at 14.7°, which represents the non-polar phase. The data fitting can be improved, however, by including a small peak at 15.3°, which is close to the position of the diffraction peak expected for the polar phase of the terpolymer's corresponding copolymer, PVDF-TrFE. As T_x is raised to 132 °C, this higher angle shoulder increases quite markedly, and the best fitting to the data is achieved by including two peaks, one near 15° and the other at 15.4°. **Figure 1b** summarizes the evolution of the x-ray peak positions as T_x is raised from 112 to 142°C. In comparison with the x-ray data for PVDF-TrFE, we deduced that the peak at the lower angle arises from the non-polar phase while the peaks at 15° and 15.4° indicate the presence of the polar phase component in the crystallites.

The importance of these x-ray peak assignments is seen in the electromechanical strain data for samples at the extremes of the T_x range. As shown in **Figure 2**, the terpolymer sample with a T_x of 112°C exhibits a field-induced strain of -5.9% at 133 MV/m (megavolts per meter), while for the sample with T_x of 142°C, the strain is reduced to -4.2% under the same field. The lower field-induced strain is due to existing ferroelectric domains that do not undergo the local conformation change upon application of the electric field. Thus, for better performance, a sample should be annealed near 112°C.

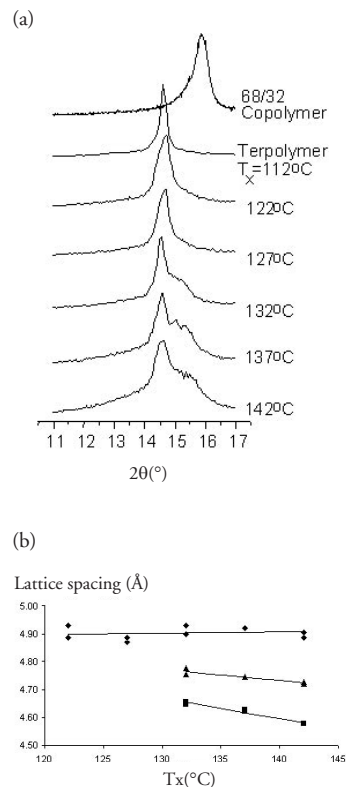


Figure 1. (a) X-ray data in the angular range of the (110, 200) reflection taken at room temperature for the terpolymers with different T_x , from which lattice constants are determined. (b) Lattice constants for the non-polar (4.9 Å) and polar (triangles and squares) components of the (110, 200) reflection measured at room temperature as a function of T_x . The data for the copolymer of similar composition are also shown. The x-ray wavelength is 1.2399 Å.

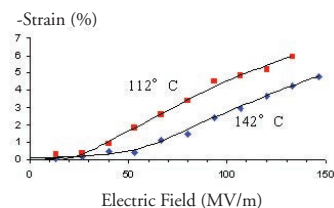


Figure 2. Thickness strain of the terpolymer as a function of the applied field for the terpolymer samples with $T_x = 112$ and 142 °C. The data were acquired at room temperature and 1 Hz AC field.