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Mechanical and Electromechanical Properties of Vinylidene Fluoride Terpolymers

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Electromechanical, mechanical, and volumetric measurements on vinylidene fluoride terpolymers with trifluoroethylene and trichlorofluoroethylene are reported. One purpose of the investigation was to assess the contribution of an electric field-induced crystal phase transformation to the large electrostrictive coefficient (43 $\mathrm{nm}^2\ \mathrm{V}^{-2}$ at 1 Hz, parallel to the field). Such a crystal transformation is evidenced by the change in the Curie transition enthalpy after application of an electric field. Using the volume change at the Curie transition, along with X-ray diffraction data, we quantify the amount of the ferroelectric and paraelectric crystalline forms. From this, we conclude that, for electric fields up to 10 MV/m, the strain resulting from the field-induced crystal phase change is too small to account for the large electrostriction observed in the terpolymer. The transition from the α to the β-crystalline form is also induced by hydrostatic pressure, with the β-crystals formed at elevated pressures stable at ambient pressure. The Curie transition in the terpolymer, similar to the behavior of the copolymer, is accompanied by changes in both the shear and bulk moduli. The Curie transition exhibits significant hysteresis during thermal cycling, implying that both the electrostriction and the mechanical properties will be sensitive to processing.

Introduction

Poly(vinylidene fluoride) (PVDF) and related polymers exhibit significant electromechanical coupling, whereby electrical energy can be converted to mechanical work, with higher efficiencies than electromagnetic motors. Electroactive polymers have attracted widespread interest for applications such as sensors, transducers, actuators, artificial muscles, and robotics. Recently, various groups have focused on vinylidene fluoride−trifluoroethylene copolymers and terpolymers.[1−9] Unlike the homopolymer, the copolymers and terpolymers crystallize spontaneously into the polar, all-trans β crystalline phase, with Curie transitions below their melting points. When subjected to a strong electric field, they exhibit electrostriction, which refers to strains varying quadratically and at double the frequency of the applied electric field.

The existence of five different crystalline forms (polymorphs) in vinylidene fluoride polymers[10,11] suggests the possibility of field-induced crystal transformations. The most important crystal phases are the polar β phase (which is only stable below the Curie point), the antipolar α phase, and the polar δ structure.[12,13] The δ crystal has the same unit cell as the α form, but with the dipoles of adjacent chains rotated 180° about the *c*-axis, to yield a net dipole moment. Although the α crystals have no net dipole moment due to antiparallel chain packing, there is a moment normal to the chain which allows strong interaction with applied fields.[14] This suggests the possibility of conversion by a strong electric field of the antipolar α crystal phase to the polar β phase. The resulting electrostriction can be significant since the β unit cell has a 2.5% smaller volume and is 10% smaller transverse to the *c*-axis in comparison to the α crystals.[15] Piezoelectricity and pyroelectricity in PVDF homopolymer have been shown to result from

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such a phase-conversion mechanism.[14,16] It is also well-known that mechanical drawing converts the α crystallites of PVDF to the *β* form.[17] Production of the different crystalline forms is also affected by hydrostatic pressure.[18,19] The compressibilities of both the α and *β* forms are highly anisotropic (least compressible in the chain direction) and are a decreasing function of pressure. The *β* form, having the denser unit cell, is less compressible.[20] Recently, we reported that the temperature dependence of the shear modulus of VDF−TrFE−chlorotrifluoroethylene terpolymers changes at the Curie temperature.[5] Herein, we explore further the changes in mechanical properties accompanying the *β* to α transition, both for the terpolymer and VDF−TrFE copolymer. We have also carried out various measurements intended to quantify the contribution of field-induced crystal phase transformation to the electrostriction measured in the terpolymer.

Experimental Section

The terpolymer, provided by T. C. Chung of the Pennsylvania State University, had a backbone composition of 61.1% VDF, 32.2% TrFE, and 6.2% CTFE. The method of synthesis has been described in the literature.[7,21] The random copolymer (65% VDF and 35% TrFE) was obtained from Solvay. Electrostrictive strains were measured on films cast from 5% dimethylformamide solutions. The films were air-dried followed by vacuum-drying for 48 h at 70 °C. An MTI 1000 Fotonic Sensor was used for the measurements, with details of the technique described elsewhere.[3,5] A triangular wave having an amplitude of 10 MV/m was applied, at frequencies in the range from 10^{-3} to 10^{3} Hz. The reported strains are the average of the response to the positive and negative fields, which in turn was averaged over several cycles. Dynamic mechanical measurements utilized a Bohlin VOR, with the sample in the form of disks (6 × 1.5 mm) molded at 160 °C in a vacuum. The temperature was cooled from above the melting point, with shear data taken at 1 Hz during both cooling and heating at 0.5 °C/min. Replicate runs were made to ensure an absence of crystallization. Pressure−volume−temperature (PVT) measurements used a Gnomix apparatus, with the sample (∼1 g) immersed in mercury.[22] Both isobaric and isothermal volume measurements were carried out during cooling at a rate of 0.5 °C/min, at hydrostatic pressures up to 200 MPa. Differential scanning calorimetry (DSC) employed a Perkin-Elmer 7, at 10 °C/min. For the X-ray diffraction measurements, films (220-μm thick) supported on an aluminum substrate were measured at 2 °C/min, with six scans averaged.

Results

In Figure 1 is shown the longitudinal (thickness) strain, ϵ, induced by an electric field, $E = 10$ MV/m electric field. These strains represent the steady-state peak amplitude of the response to an applied field having a triangular wave form. The response is almost purely electrostrictive,[7] with the sign of the strain (corresponding to compression) independent of the sign of the electric field. There is a marked decrease with frequency, the electrostrictive coefficient, ϵ/E^2, decreasing from 90 to 20 nm^2/V^2 for a 6 decade increase in frequency. The inset shows the dynamic response at 1 Hz. Note that there is a large offset after the initial cycle, having a magnitude equal to ca. one-half the dynamic amplitude. This residual 0.3% strain remains after removal of the field. DSC measurements indicate an increase in the magnitude of the Curie transition from 9.1 to 9.4 J/g after the exposure to $E = 10$ MV/m.[23] The indication is that there is a field-induced crystal transformation that is stable (at least in part) after removal of the electric field.

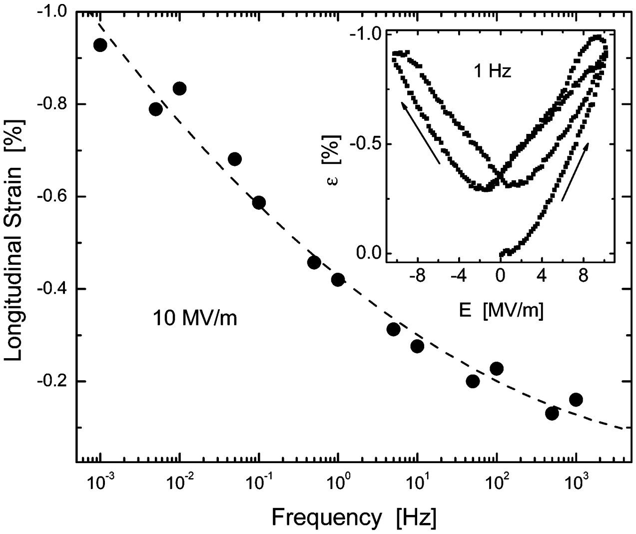

Figure 1. Frequency dependence of the thickness (longitudinal) strain in the terpolymer at room temperature. Inset shows the same strain measured as a function of the electric field. There is an offset after the initial cycle, equal to roughly one-third the maximum strain.

Quantifying the contribution of the α to *β* phase transition to the electrostrictive response requires determination of the concentration of the α crystals. To do this, we use pressure−volume−temperature (PVT) measurements. The terpolymer was heated above the Curie temperature at fixed pressure and then was isobarically cooled. Shown in Figure 2 are the measured changes in the specific volume, ΔV, for various pressures from 10 to 200 MPa. At the Curie transition, T_C, there is a discontinuity associated with the change in the crystal unit cell from the α to the *β* form. Pressure enhances the stability of the denser *β* crystals,[24] leading to a systematic increase in T_C with pressure (Figure 3). Below T_C, both forms coexist; however, the fraction of *β*-crystals also increases with pressure. This is reflected in the larger ΔV for higher pressure (Figure 3).

Such behavior is not unique to the terpolymer. In Figure 4 is shown the specific volume through the Curie transition for the copolymer. The *β* phase in the copolymer is also enhanced by pressure. Moreover, when

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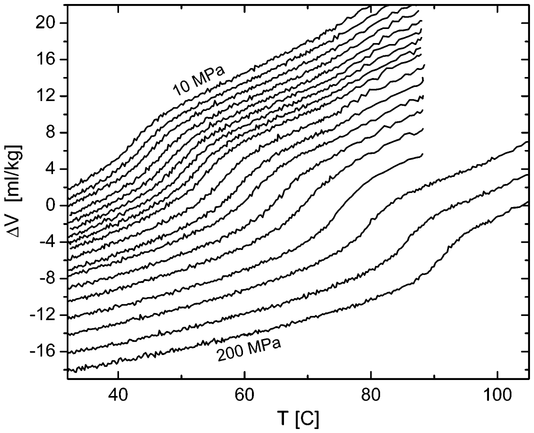

Figure 2. Change in specific volume of the terpolymer at (top to bottom) 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 95, 110, 130, 150, 175, and 200 MPa. The specific volume at ambient temperature and pressure was 0.547 mL/g.

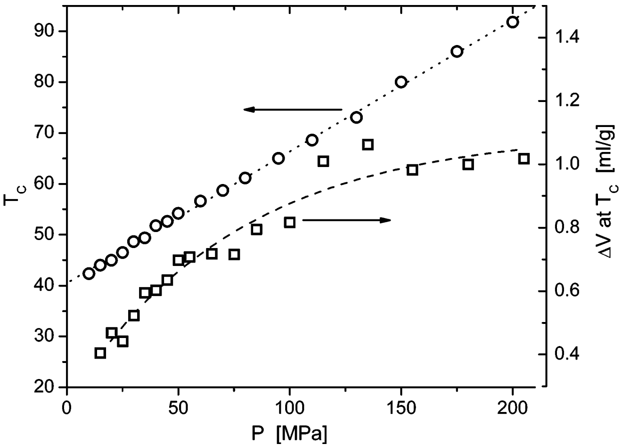

Figure 3. Temperature of the Curie transition (○) and volume change at T_c (□), from the data in Figure 2. The lines through the data are only to guide the eyes.

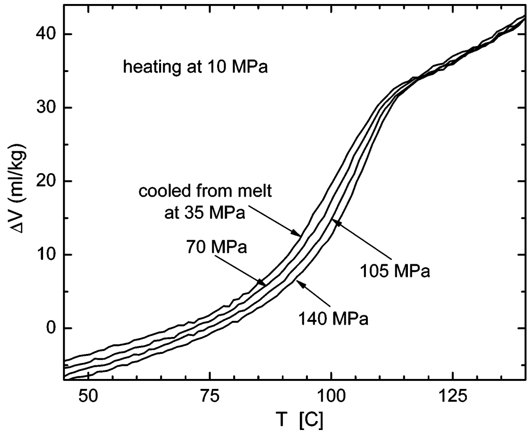

Figure 4. Change is specific volume of the copolymer measured during heating at 10 MPa, following cooling from above the melting point (>155 °C) at the indicated pressures.

measured at low pressure (10 MPa), the volume below T_C, the value of T_C, and the change in volume at T_C all systematically change with the magnitude of the pressure applied above T_C during cooling from the melt point. High pressure induces the transformation to β crystals, and these are stable below T_C, even at low pressure; that is, reversion to the α-form does not occur upon reduction of the pressure.

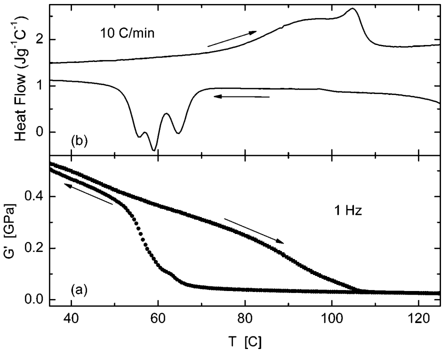

Figure 5. (a) Dynamic storage modulus of the copolymer measured in shear as a function of temperature. (b) DSC of the copolymer in the vicinity of the Curie transition.

The changes in volume at the Curie transition contribute to a change in the shear modulus at T_C, as reported previously for the terpolymer.[5] Data are shown for the copolymer in Figure 5a, wherein it can be seen that this behavior is sensitive to processing. The temperature coefficient of the shear modulus is −7 MPa/K below T_C, changing to −0.3 MPa/K above T_C. There is a large difference between the temperatures at which this change in T-dependence of the shear modulus is observed during heating versus cooling. This parallels the hysteresis in the Curie transition seen in thermal measurements (Figure 5b).

To quantify the contribution to the electromechanical properties from the crystal phase, it is necessary to determine the degree of crystallinity. To do this, we measure the X-ray diffraction over all 2θ and fit the data to the sum of peaks whose shape is described by the pseudo-Voight function[25]

$$I(2\theta) = A\frac{2\ln 2}{\pi^{3/2}}\frac{w_L}{w_G}\int_{-\infty}^{\infty}\frac{e^{-t^2}}{\left(\sqrt{\ln 2}\frac{w_L}{w_G}\right)^2 + (\sqrt{4\ln 2})\frac{2\theta - 2\theta_C}{w_G} - x}\,dx \tag{1}$$

where A, w_L, w_G, and θ_C are constants. Results for the terpolymer are shown in Figure 6, with the degree of crystallinity determined to be 38.4 (± 1.0)%. From DSC on the same sample (inset), we measured 20.5 J/g for the heat of fusion. This yields a value of 53.4 J/g for the perfect heat of fusion of this terpolymer. This is high in comparison to the value of 31 J/g reported by Kodama et al.[26] for VDF−TrFE copolymer.

Discussion

The Curie transition in these materials, associated with a conversion of the ferroelectric phase, comprised primarily of polar β crystals, to the paraelectric, α-crystalline phase, is accompanied by changes in both shear modulus and volume. For the terpolymer, this volume change is about 10-fold smaller than for the copolymer. The magnitude of this volume change is dependent on pressure, with the Curie temperature itself varying

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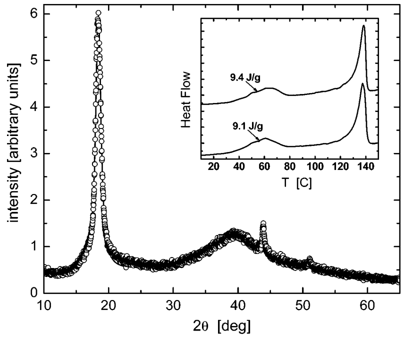

Figure 6. Wide-angle X-ray diffraction from the terpolymer. The integral of the crystalline peaks is 38.4% of the total diffracted intensity (neglecting the peaks, at 2θ ~44° and 51°, due to the sample holder). The inset shows the DSC data on the same sample, for which the melting enthalpy measured 20.5 J/g, yielding 53.4 J/g for the perfect heat of fusion.

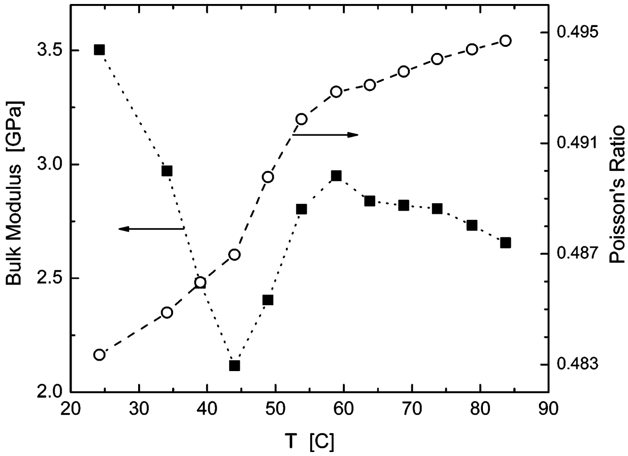

Figure 7. Bulk modulus and Poisson's ratio of the terpolymer.

linearly with pressure. The changes in volume reflect the presence of more β crystals at higher pressures. These changes can also be seen in the values of the bulk modulus, K, extracted from the PVT measurements (Figure 7). From the shear and bulk moduli, we can calculate Poisson's ratio, ν:

$$\nu = \frac{3K - 2G}{6K + 2G} \tag{2}$$

Note the change in temperature dependence of both K and ν at T_C.

The potential contribution to electrostriction from the α to β phase transformation depends on the quantity and stability of the two crystalline forms. Since pressure induces conversion to β crystals (Figure 3), it can potentially modify the electrostrictive properties. Note that the modification of the crystal structure at high pressure remains stable at lower pressure (Figure 4). That is, the higher T_C and larger ΔV seen at elevated pressures are retained at low pressure. For the lowest pressures in Figure 2, $\Delta V = 0.4\%$ at T_C. This represents the volume change resulting from conversion of the ferroelectric β phase to the paraelectric α phase. Since the crystal unit cell increases in volume by 2.5% in going from the β to the α form, the 0.4% ΔV at T_C implies the terpolymer has a β phase crystallinity equal to 16%. Since the sample is ~38% crystalline, the α crystallinity is then 22%. If 16% β crystallinity transforming to the α form yields a 0.4% volume change, the (hypothetical) 22% β crystallinity (the most that could be produced by an applied field) would yield a maximum $\Delta V = 0.55\%$. Assuming isotropy, a 0.55% volume change corresponds to a 0.16% change in the linear dimensions of the sample. This is an order of magnitude smaller than the longitudinal strain measured for $E = 10$ MV/m (Figure 1). The crystal unit cell dimension transverse to the c-axis (i.e., parallel to the dipole moment of the β phase) is 10% smaller for the β crystal than the for the α form. Assuming complete alignment of the (hypothetical) field-induced crystals with the field, the change in dimensions parallel to the field would equal 22% × 0.1 ~ 2%. This is an upper bound to the strain, obtainable by complete conversion of all α crystals into perfectly oriented β crystals.

We can make a second, independent estimate of the contribution of the α → β transition to the electrostriction. Prior to exposure to the field, the terpolymer exhibits an enthalpy change at the Curie transition enthalpy, $\Delta H_C = 9.1$ J/g (Figure 6). Thus, ΔH_C for the pure β phase would be 57 J/g (which is close to the magnitude of the perfect heat of fusion). Upon removal of the electric field, a strain of ~0.3% remains (Figure 1 inset), and the Curie transition enthalpy has increased by 0.3 J/g. This corresponds to a 0.5% increase (0.3 divided by 57) in the β crystalline form due to the electric field. Since the crystal unit cell dimension is reduced by 10% for conversion from α to β crystals, a field-induced conversion to 0.5% β crystals would yield a longitudinal strain of only 0.05%. This is 6-fold smaller than the residual strain, as shown in the inset to Figure 1.

From these two analyses, we conclude that crystal phase changes altering the unit cell dimensions cannot be the dominant mechanism underlying the terpolymer's electromechanical properties. Due to the high modulus of the copolymers and terpolymers, the Maxwell strain (Coulombic attraction of the electrodes) is negligible below the Curie point for these materials.[4,5] Other mechanisms can give rise to electrostriction. One possibility is an increase in crystallinity due to exposure to the electric field. Since the volume change accompanying the amorphous to crystalline phase transformation is 2-fold larger than that for the Curie transition, even a small increase in the degree of crystallinity could yield measurable changes in dimensions. However, the limited data available to date give no indication of such a contribution. Another mechanism for electrostriction is reorientation of internal dipoles, involving motion of the chain twist boundaries.[27] The orientation of polar crystal domains was, in fact, suggested as the mechanism for the large electrostrictive strains seen in cross-linked VDF−TrFE copolymers.[4] This possibility remains to be investigated.

Summary

Our main findings herein are as follows:

1. P(VDF−TrFE−CTFE) terpolymers exhibit large electrostrictive coefficients, which vary from ca. 90 nm^2 V^{-2} at 10^{-3} Hz to 20 nm^2 V^{-2} at 1 kHz.

2. The strain response to alternating fields is accompanied by a dc component, which is stable after

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removal of the electric field. The magnitude of this residual strain is about one-half the amplitude of the dynamic response.

3. The origin of the large electrostriction in the terpolymers is presently unknown, but for fields up to 10 MV/m, it cannot be accounted for by field-induced transitions between different crystalline unit cells. An alternate possibility is rotation of the polar crystals domains (motion of the chain twist boundaries); however, more work is needed to explore this possibility.

4. Hydrostatic pressure induces a transition from the α to the β crystalline form, thereby reducing the volume, and also increasing the Curie temperature. The newly formed β crystals are stable at lower pressures.

5. The shear and bulk moduli, as well as Poisson's ratio, of the copolymer and terpolymer change at T_C. Since the Curie transition is sensitive to processing, exhibiting a large hysteresis, this means the mechanical properties of the materials likewise vary with processing.

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