

Electrostrictive Properties of Poly(vinylidene fluoride–trifluoroethylene–chlorotrifluoroethylene)

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Terpolymers of vinylidene fluoride (VDF), trifluoroethylene (TrFE), and chlorotrifluoroethylene (CTFE) were synthesized as potential materials for electromechanical transduction. These terpolymers had relatively high molecular weights (~30 kg/mol) and CTFE levels in the range of 5–10 mol %. The presence of the bulky CTFE units disrupts the sequence length of the crystal, which lowers both the melting and Curie transitions; however, the degree of crystallinity remains high. The formation of smaller, more mobile polar domains gives rise to good electromechanical response. At low electric fields (7 MV/m), longitudinal strains as high as 0.5% are attained. This is significantly higher than the strains achieved with the same terpolymer obtained by bulk polymerization. The present materials exhibit a low mechanical modulus (ca. 0.2 GPa) relative to other VDF–TrFE copolymers. This might limit their use, depending on the application.

Introduction

Piezoelectric and electrostrictive materials convert electrical energy into mechanical energy and have important advantages (e.g., low power consumption and fast response) over electromagnetic motors. Although electroactive ceramics are widely used in piezoelectric devices, polymeric materials are lower in weight, have greater toughness and better processability. Thus, substantial efforts have been made to develop electroactive polymers. The only commercially significant polymer is polyvinylidene fluoride (PVDF) and its copolymer with trifluoroethylene [P(VDF–TrFE)], and most work has focused on them.

A common feature of various approaches for improving the electrostrictive properties of PVDF is reduction of the crystallite size through the introduction of defects. This can be accomplished through the formation of a network structure, either by radiation^{1,2} or by chemical cross-linking,^{3,4} or through quenching of the polymer from the amorphous state.⁵ Smaller ferroelectric domains are more effectively oriented by an applied field, potentially yielding better electromechanical properties.

Another method for achieving the same objective is incorporation of a disparate monomer into the polymer

backbone. If this monomer is poorly accommodated within the unit cell, the crystal sequence length is reduced, yielding smaller, more easily oriented crystalline structures. Some promising results have been obtained with terpolymers of hexafluoropropylene with VDF and TrFE.^{5–7}

An interesting variation is terpolymers of VDF and TrFE with chlorotrifluoroethylene (CTFE). The presence of the chlorine atom imposes a large steric hindrance, which favors the (ferroelectric) trans conformation of the polymer backbone (to alleviate steric repulsions between the chlorine and fluorine atoms).^{8,9} This is important because, in the trans conformation, the dipoles all add, enabling a higher polarization to be achieved. The electrical energy that can be stored in the material is directly proportional to this polarization and thus determines, in combination with the transduction efficiency, the electromechanical performance. At the same time, the random placement of the CTFE units disrupts the polar coupling, resulting in more easily oriented domains.

Recently, promising results were reported for bulk polymerized P(VDF–TrFE–CTFE) terpolymer.¹⁰ In this paper, we describe characterization of the electromechanical properties of similar terpolymers synthesized using a novel borane/oxygen initiator. This process affords control over the monomer addition, yielding compositionally homogeneous (nonblocky) materials.

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Table 1. Terpolymers

sample	VDF (mol %)	TrFE (mol %)	CTFE (mol %)	M_w^a (kg/mol)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
T58	61.2	33.0	5.8	30.7	143.9	27.9	43	7.7
T72	58.5	34.3	7.2	26.3	131.0	22.4	31	2.3
T76	58.2	34.2	7.6	37.4	131.9	22.6	32	2.0
T86	59.4	32.0	8.6	14.8	123.9	16.1	24	1.5
T97	63.2	27.1	9.7	—	113.2	20.9	23	2.7
T103	59.8	29.9	10.3	39.5	119.6	20.1	18	1.9

^a From GPC calibrated using polystyrene.

Experimental Section

A P(VDF-TrFE) copolymer (65/35 mole ratio) was obtained from Solvay. P(VDF-TrFE-CTFE) terpolymers were synthesized at ambient temperature using a combination of bulk polymerization and oxygen-activated free-radical initiation, based on oxidation adducts of the organoborane molecule.^{11,12} In a typical reaction, the tributylboron initiator was introduced into the autoclave under an argon atmosphere. The reactor was cooled with liquid nitrogen prior to distillation of the monomers into the reactor, followed by addition of oxygen (2:1 mole ratio of oxygen to boron). The reactor was then allowed to warm to room temperature, with bulk polymerization proceeding for 5 h. Unreacted monomers were then removed by vacuum distillation. Typically, 6.5 g of the terpolymer was obtained, which was washed with methanol to remove impurities (e.g., boric acid and butanol). Control of monomer addition results in relatively narrow polydispersities ($1.2 \leq M_w/M_n \leq 1.7$) and compositionally homogeneous structures.

The compositions of the terpolymers, as determined by chlorine analysis and ¹H and ¹⁹F NMR spectroscopies, are listed in Table 1. Also included are approximate molecular weights, determined by GPC using polystyrene for calibration.

Differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 instrument was carried out by heating at 10 °C/min, after cooling at the same rate from above the melting temperature, T_m . For mechanical testing, samples were molded at 20–30 °C above the melting point. Some minor discoloration accompanied this thermal treatment. Room-temperature mechanical measurements were acquired using a modified Dynastat instrument. Tensile specimens (15 mm × 5 mm × 0.5 mm) were deformed at a rate of 0.5%/s to a strain beyond the yield point.

Electromechanical measurements were made on thin films prepared by casting from DMF, followed by vacuum-drying at 50 °C. Strains were measured with an MTI 1000 Fotonic Sensor. In this technique, optical fibers illuminate a plate resting on the top surface of the sample. The light reflected from a small aluminum tab adhered to the plate surface is collected by parallel receiving fibers. Over a range of roughly 25 μm, the intensity of this reflected light is proportional to the distance separating the reflecting top surface of the plate from the optical fibers. The voltage output of the Fotonic Sensor is converted to distance using an empirically determined calibration constant. Polarization data were obtained with a Sawyer-Tower circuit, using a 10-Hz triangular waveform with a 100 MV/m amplitude.

Results

Thermal Properties. Melting temperatures, T_m , and enthalpies, ΔH_m , obtained from DSC are listed in Table 1. A monotonic decrease in T_m is observed with increasing content of the third monomer; however, the degree of crystallinity is relatively constant for CTFE levels beyond 6 mol %. Figure 1 shows representative DSC traces for samples that were cooled at 10 °C/min from above T_m . Sample T97 exhibits a weak, secondary

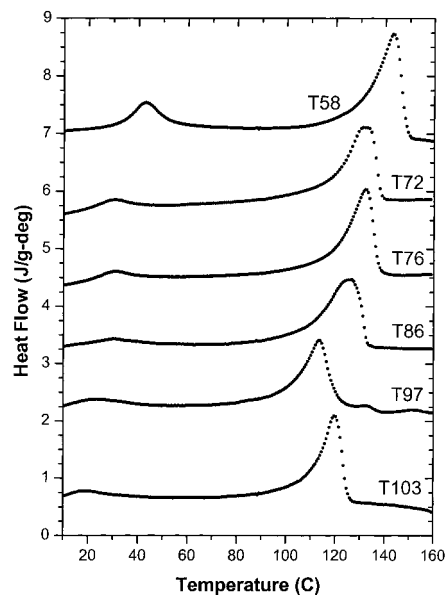


Figure 1. DSC traces for the P(VDF-TrFE-VDF) terpolymers whose compositions are given in Table 1. These data were obtained during heating at 10 °C/min, after annealing for 15 min at 160 °C, followed by cooling at 10 °C/min.

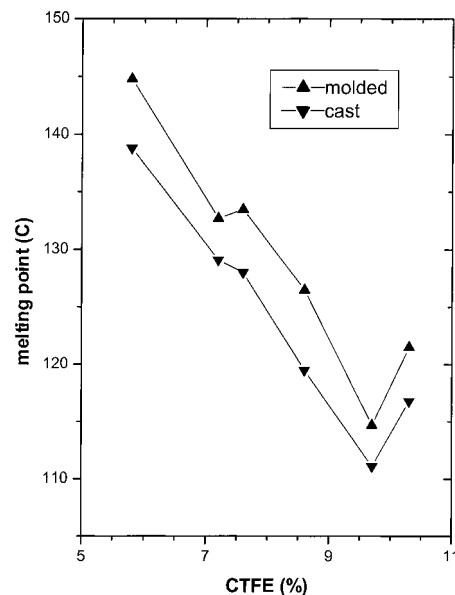


Figure 2. Melting point of the terpolymers as a function of chlorotrifluoroethylene monomer content.

melting peak, which might indicate some compositional inhomogeneity of the backbone. This terpolymer differs from the others in that it has a very low TrFE content and, consequently, a lower melting point.

The thermal data in Table 1 were obtained on samples molded above T_m and then cooled in air. As shown in Figures 2 and 3, this thermal treatment, in comparison to solvent casting followed by drying at 50 °C, increases both the melting point and the degree of crystallinity (where the latter was calculated from the melting enthalpy using a value for the perfect heat of fusion of 102.5 J/g).¹³ Generally, higher crystallization temperatures yield higher values of T_m .^{14,15} The solvent-cast

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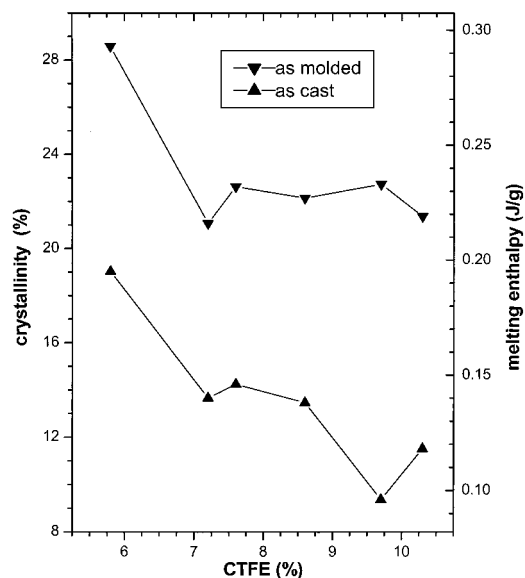


Figure 3. Degree of crystallinity, calculated from the melting enthalpy, for the terpolymers. The upper curve is for samples molded above the melting point, followed by cooling in air. The lower curve is for samples cast from DMF, followed by vacuum-drying at 50 °C.

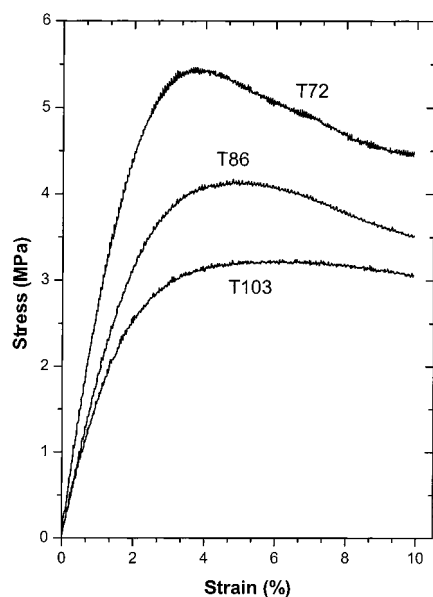


Figure 4. Representative room-temperature stress/strain curves for the terpolymers stretched at a rate of 0.005 s^{-1} . The Young's modulus is obtained from the slope of the initial response, with the yield stress defined as the maximum.

films also have substantial higher Curie transition temperatures, T_c . This is consistent with previous work, showing that annealing P(VDF-TrFE) copolymers above T_c increases the Curie temperature.^{16,17}

Mechanical Properties. Representative stress/strain measurements for the terpolymers are shown in Figure 4. The behavior is typical for a thermoplastic: an elastic, linear response through a few percent strain, followed by yielding. Beyond the yield point, the deformation was irreversible.

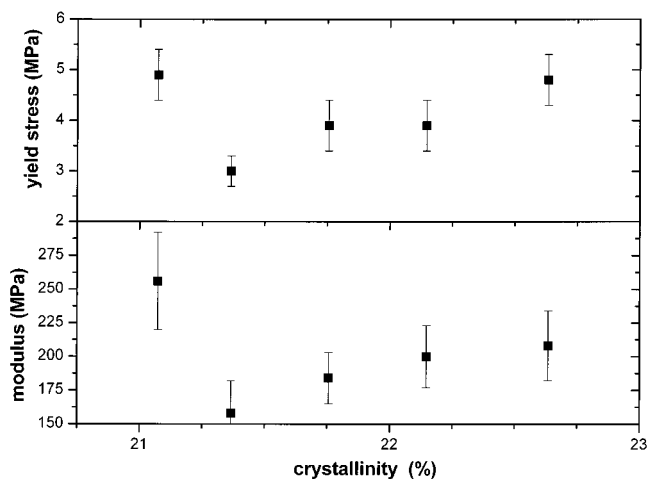


Figure 5. Young's modulus and yield stress of the terpolymers expressed as a function of the degree of crystallinity.

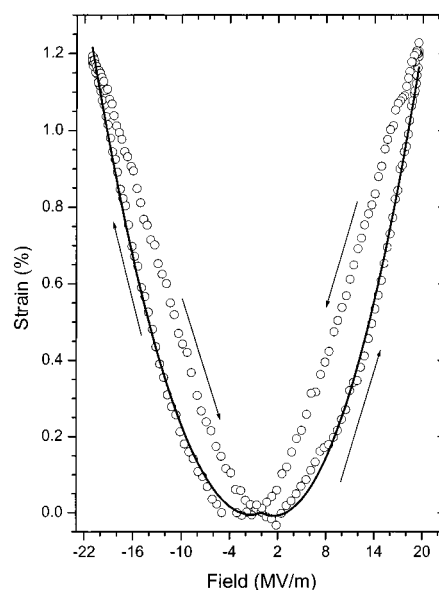


Figure 6. Longitudinal strain of T72 in response to a 2-mHz alternating electric field. The solid line is the fit to eq 1.

In Figure 5, the Young's modulus, K , and yield stress for the copolymers are plotted as a function of the degree of crystallinity. In general, one expects a correlation of the mechanical properties with crystallinity, and except for sample T72, that is true here. However, T72 is relatively low in crystallinity, yet it has the highest modulus and yield stress.

All terpolymers exhibit lower mechanical properties than P(VDF-TrFE). When processed under the same conditions, the degree of crystallinity of the copolymer, 27%, is of the same magnitude as that of the terpolymers. However, for P(VDF-TrFE), we measure a modulus and yield stress equal to 1580 and 21 MPa, respectively. These values are substantially higher than the results reported in Figure 5.

Electrostrictive Response. As shown in Figure 3, films cast from solution had lower crystallinities than molded samples; nevertheless, casting was used to obtain films for electromechanical measurements to optimize the uniformity of the test specimens. Figure 6 shows the response of T72 to an alternating field (frequency = 2 mHz). The direction of the dimensional change is invariant to the polarity of the field; that is,

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Table 2. Electrostrictive Response of VDF Materials

material	a (eq 1) (nm ² /V ²)	reference
electron beam irradiated P(VDF-TrFE)	5	2
chemically cross-linked P(VDF-TrFE)	46	4
P(VDF-TrFE-HFP)	10	
quenched P(VDF-HFP)	140	5
bulk polymerized P(VDF-TrFE-CTFE)	8	10
P(VDF-TrFE-CTFE)	44	this work

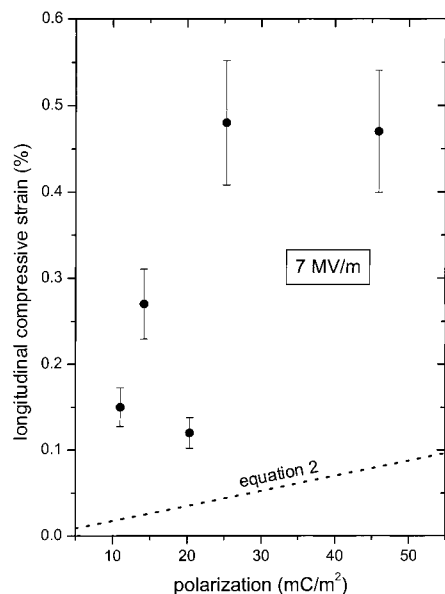


Figure 7. Strain at $E = 7$ MV/m as a function of the polarization induced at the same value of the field. The estimated contribution from the Maxwell strain (eq 2) is indicated by the dotted line.

the film thickness always decreases. This means that the dominant response is electrostriction. The field-induced strain can be expressed as a power series

$$s = dE + aE^2 + \dots \quad (1)$$

in which d and a are the piezoelectric and electrostrictive constants, respectively. Included in Figure 6 is the fit of eq 1, yielding for the electrostrictive coefficient $a = 44$ nm²/V². This response is in the range of values reported for other VDF-type polymers (Table 2). Moreover, no attempt was made to optimize the electromechanical properties, for example, by thermal processing.⁵

Displayed in Figure 7 is the electromechanical strain measured for the terpolymers at $E = 7$ MV/m as a function of the polarization, P , measured for the same field. All terpolymers exhibit substantial strains. At this

value of E , the electrostrictive response dominates the piezoelectric contribution. An electrostrictive coefficient can be defined as the ratio of the strain to the square of the polarization, $Q = s/P^2$. From the data in Figure 7, Q is in the range from -2 to -13 C²/m⁴ (the values are negative because the deformation is compression).

The Maxwell strain, because of Coulombic attraction of the electrodes, contributes to the electrostrictive response of all materials. Its magnitude, which is proportional to the polarization

$$s_M = \frac{PE}{2K} \quad (2)$$

is included in Figure 7. It can be seen that the Maxwell strain is quite small, the dominant electromechanical response being due to direct coupling between the mechanical displacement and the polarization.

Conclusions

Terpolymers of vinylidene fluoride, trifluoroethylene, and chlorotrifluoroethylene having different compositions were synthesized using bulk polymerization in combination with oxygen-activated free-radical initiation. By control of monomer addition, terpolymers of low polydispersity could be obtained with molecular weights of ca. 30 kg/mol. CTFE levels were in the range of 5–10 mol %. The presence of the bulky CTFE units disrupts the sequence length of the crystals, lowering both the melting and Curie transitions; nevertheless, the degree of crystallinity remains high.

The formation of smaller, more mobile polar domains enhances the electromechanical response. At relatively low electric fields (7 MV/m), longitudinal strains as high as 0.5% are attained. This is significantly higher than the strains achieved with the same terpolymer obtained by bulk polymerization. However, relative to other VDF-TrFE copolymers, the mechanical modulus of the present materials is low (~ 0.2 GPa). This might limit their use, depending on the application. Future efforts need to be directed toward improving the mechanical properties by increasing the molecular weight or by processing.

The results presented herein demonstrate that improvement in electromechanical properties can be achieved by synthetic control of the composition, confirming the validity of the approach of incorporating a third monomer into the PVDF-TrFE backbone. This method offers many possibilities for further modifications.

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