

Highly electrostrictive poly(vinylidene fluoride–trifluoroethylene) networks

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We report greatly improved electromechanical performance from a poly(vinylidene fluoride–trifluoroethylene) copolymer by chemical cross linking. Curing with an organic peroxide in combination with a free-radical trap, followed by crystallization, yields a ferroelectric network exhibiting a high electrostrictive response. The electric-field-induced strains were measured at low frequency using an air gap capacitance method and by a noninterferometric optical technique. At electric fields as low as 9 MV/m, longitudinal strains of 12% are obtained. This is more than two orders of magnitude better than conventional vinylidene fluoride materials, and more than an order of magnitude larger than the best results reported to date on any fluoropolymer. Since the mechanical modulus of the network is high (~ 0.5 GPa), this work demonstrates the potential for extending the range of utility for polymer-based electromechanical materials. © 2001 American Institute of Physics. [DOI: 10.1063/1.1409595]

Electroactive materials convert electrical energy into mechanical displacements, with lower power consumption than electromagnetic motors. While piezoelectric strains are proportional to the applied electric field, E , the electrostrictive strain increases quadratically with the field. Thus, materials with substantial electrostrictive coefficients offer the possibility of obtaining very large deformations. Applications include sensors, transducers, actuators, and potentially robotics and artificial muscles.

Electromechanical polymers must, of course, be polar. However, macroscopic alignment of molecular dipoles is limited for polymers, since they are rarely ordered on the microscopic level. Even among highly crystalline polymers, whose orientation can be high, there are few cases in which the chains can both undergo conformational changes and adopt more than one stable configuration (in order to allow switching in response to an external field). As a consequence, only a few polymers are piezoelectric, and only polyvinylidene fluoride (PVDF) and its copolymers are commercially significant. The electromechanical coupling in PVDF is less than ceramics, which limits the range of applications. The development of better electromechanical properties, in particular electrostriction, is an active area of research,^{1,2} and recently advances with PVDF copolymers have been achieved.^{3,4}

In this letter, we report the electrostrictive properties of chemical networks of poly(vinylidene fluoride–trifluoroethylene) [P(VDF-TrFE)]. The copolymer, obtained from Solvay and having a 65/35 copolymer ratio, was cross linked with an organic peroxide in combination with a free-radical trap. The use a free-radical cross linker and coagent enables formation of a three-dimensional network of high cross-link density, without substantial side reactions.^{5,6} Films were cast from a solution of the polymer and cure reagents. The films were cured in a mold for 40 min at 453 K under

modest pressure, followed by air quenching. The typical film thickness was 75 μm .

As illustrated in Fig. 1, two methods were employed to measure electrostrictive strains (i.e., relative decrease in film thickness): In the first method, the plates of an air-gap capacitor are supported by the sample (two pieces, 1.3×3.0 cm, to avoid tilting). The separation of the plates, which is equal to sample thickness t is inversely proportional to capacitance C

$$t = \epsilon_0 A / C, \quad (1)$$

where ϵ_0 is the permittivity of free space ($= 8.85 \times 10^{-12}$ F/m) and A is the electrode area. Any change in film thickness displaces the top plate, thus changing the capacitance.⁷ The latter was measured with a HP 4192A impedance analyzer. In this method, a small error (estimated to be a couple percent) arises from neglect of stray capacitance.

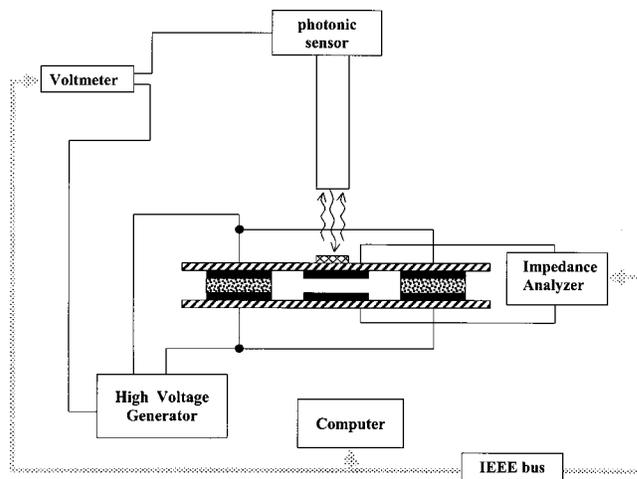


FIG. 1. Schematic of the experimental apparatus used to measure simultaneously the electrostrictive strain by the two methods.

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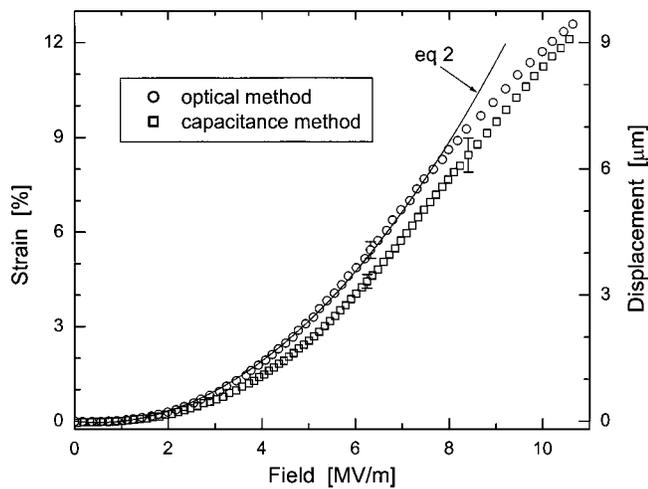


FIG. 2. Quasistatic, longitudinal response of the PVDF copolymer network as a function of the applied field. The capacitance (squares) and optical (circles) measures of the strain give comparable results. The solid line is the fit of the latter to Eq. (2). Note that the displacement is actually negative, since film thickness decreases upon application of the electric field.

The second method is based on a noninterferometric, optical technique (using an MTI 1000 Fotonic Sensor). Optical fibers illuminate the upper plate, and the light reflected from a small aluminum tab adhered to the plate surface is collected by parallel, receiving fibers. Over a range of roughly $25 \mu\text{m}$, the intensity of this reflected light is proportional to the distance separating the reflecting top surface of the plate from the optical fibers. The change in sample thickness is determined by calibration of the response using lead zirconate titanate (5500 type II from Channel Industries), a ceramic having a known piezoelectric constant (400 pm/V in the longitudinal direction). The principle source of error in this method is the initial film thickness, which was measured with a micrometer.

To ensure good contact of the sample with the electrodes, a pressure of $\sim 1.6 \text{ kPa}$ was applied by dead weighting. In a typical experiment a triangular wave (of frequency $5 \times 10^{-3} \text{ Hz}$) was generated by a Solartron 1254 and amplified with a Trek 410D to yield high voltage (10^3 V). The output from the voltage amplifier, as well as the signal from the photonic sensor, were measured with a voltmeter (HP1254). The digitized data, including the capacitance measurement from the impedance analyzer, were collected by a PC (Fig. 1).

The arrangement in Fig. 1 allowed two simultaneous measurements of the longitudinal electrostrictive strain. A comparison of typical results obtained at room temperature is shown in Fig. 2. The strains determined from the capacitance measurement are slightly lower, although the agreement between the two methods is within experimental error. The

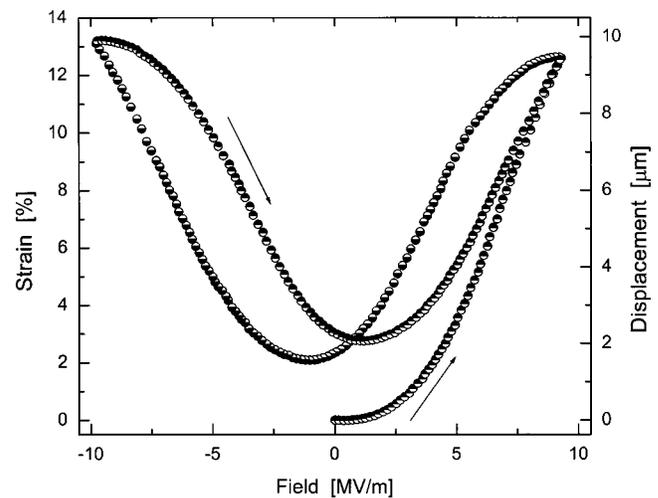


FIG. 3. Longitudinal strain of the PVDF copolymer network in response to an ac electric field. The offset after the initial cycle is due to polarization at the electrode interface.

latter, estimated to be $\sim 5\%$, reflects the presence of stray capacitance, as well as uncertainties in the film thickness and the calibration standard. The measured displacement was also invariant to changes in the lateral position of the optical probe, indicating that the film was uniform with respect to both its dimensions and its electrostrictive response.

The most significant aspect of the data in Fig. 2 is the enormous strain achieved at relatively low electric field, e.g., 12% at 9 MV/m . Compared at equal fields, these strains are 300 times higher than for conventional PVDF materials,⁸ and more than an order of magnitude larger than the best results reported to date on any fluoropolymer.^{3,4,9,10} Note that without cross linking, the P(VDF-TrFE) exhibits a much smaller response (Table I), roughly comparable to results reported by Lu *et al.*¹¹ for air-quenched poly(vinylidene-fluoride hexafluoropropylene) copolymer.

The field-induced strain can be expressed as a power series

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

in which d and a are the piezoelectric and electrostrictive constants, respectively. The fit of Eq. (2) to the optically measured strains is shown in Fig. 2. The agreement is good, except at higher fields ($> 8 \text{ MV/m}$), where the film is evidently saturating. We obtain $d = 1.6 \times 10^{-9} \text{ m/V}$ and $a = -1.6 \times 10^{-15} \text{ m}^2/\text{V}^2$, indicating that electrostriction begins to dominate for fields greater than about 1 MV/m .

This predominance of electrostriction is seen in Fig. 3, which displays the strains obtained during cycling of the electric field (for clarity, we only show measurements by the

TABLE I. Properties of poly(vinylidene fluoride-trifluoroethylene) copolymers.

	v (mol/L)	Curie transition		Crystal melting		Strain (at field E)
		T (C)	ΔH (J/g)	T (C)	ΔH (J/g)	
Precursor	0	106	21	152	28	0.70% (20MV/m)
Network	0.26	102	9.4	135	12.8	12% (9 MV/m)

optical method). The direction of the film displacement (longitudinal compression) is invariant to the polarity of the field.

In Fig. 3 an offset is observed after the initial strain, which we ascribe to electrode polarization (i.e., charge accumulation at the electrode surfaces). Note that the chemical cross linking yields ionic species as by-products, which we have not attempted to remove. It was found that the original (first cycle) response was recovered after about an hour if the voltage were removed and the electrodes short circuited.

Differential scanning calorimetry of the network reveals a substantial degree of crystallinity (Table I). This crystallization transpires subsequent to the cross linking. Previously, it was reported that enhancement of the electrostrictive response can be obtained by exposure of semicrystalline P(VDF-TrFE) films to electron irradiation.³ This produces a network, similar to herein.⁵ However, ionizing radiation introduces defects into the crystalline phase, as well as reducing the crystallinity. The radiation-cross-linked PVDF copolymers exhibit substantially lower electrostrictive strains than herein. They are also paraelectric,³ which is distinctly different from the present networks. After chemical cross linking, the ferroelectric character of the precursor copolymer is retained, with a barely diminished Curie transition at 102 °C (Table I).

It is evident that the use of an organic peroxide in combination with a coagent free-radical trap enables formation of a three-dimensional network without substantial side reactions (degradation, cyclization, and other chemical changes¹²). The consequence is a high proportion of backbone units having the highly polar, β (all-trans) conformation, and thus crystals with large dipole moments. These ferroelectric domains enable large electric polarizations. However, the cross-linking process reduces the coherence length of the crystal phase (smaller β crystallites), presumably facilitating rotation (motion of the chain twist boundaries¹³) in response to an applied field. The chemical cross linking occurs while the material is wholly amorphous, enabling subsequent formation of a relatively defect-free crystalline phase.

We can compare the measured strains to the Maxwell strain, which refers to displacement resulting from Coulombic attraction of the electrodes. Since the modulus of the material is quite high (static compressive modulus, $Y \approx 0.5$ GPa), this effect is relatively small. The Maxwell strain can be calculated as

$$s_M = E^2 \epsilon_0 \epsilon / Y, \quad (3)$$

where ϵ the relative dielectric constant of the film. For ϵ measured at low fields (≤ 1 MV/m) to be in the range 10^2 , Eq. (3) indicates the Maxwell strain to be about three orders of magnitude smaller than strains measured herein for the copolymer network. However, since the dielectric properties of ferroelectric polymers are expected to be strongly nonlinear,¹⁴ the value of ϵ prevailing at the high fields in Figs. 2 and 3 is presently unknown.

High modulus *per se* is desirable in an electroactive material because it is a measure of the capacity to do work. A common practice is to calculate the conversion efficiency, defined as the fraction of input electrical energy converted to mechanical energy. For a homogenous material, the mechanical energy corresponding to the electric field-induced strain is simply $\frac{1}{2} Ks$.² The modulus, however, is measured from the macroscopic load/displacement response of the film, which is governed by the resistance to deformation of the amorphous phase. The molecular processes underlying the electrostrictive strain—rotation about twist boundaries of atoms within the crystal lattice—are completely distinct from those associated with mechanical deformation of the film. The mechanical resistance to these crystal motions is unknown, and thus likewise is the appropriate “modulus” for calculation of the conversion efficiency.

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