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# Tunable electric-field-induced piezoelectricity in high strain relaxor ferroelectric P(VDF-TrFE) copolymer

Wenhui Ma<sup>1,3</sup> and L E Cross<sup>2</sup>

<sup>1</sup> Department of Physics, Shantou University, Shantou, Guangdong 515063, People's Republic of China

<sup>2</sup> Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802, USA

E-mail: mawenhui\_usa@yahoo.com

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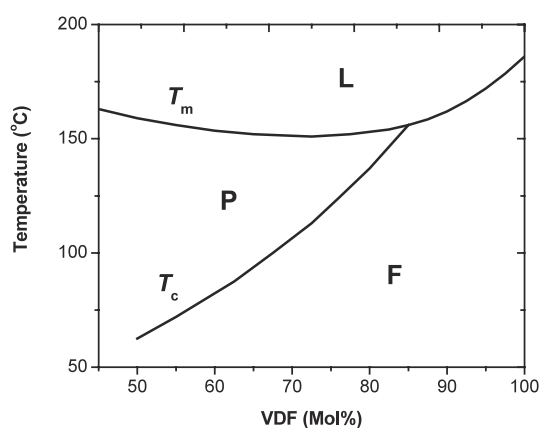
## Abstract

Ferroelectric poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer (50% of VDF) was transformed into the relaxor ferroelectric state by high-energy electron irradiation. The field-induced piezoelectric response in the relaxor P(VDF-TrFE) copolymer was obtained by measuring the electrostrain induced by a small ac voltage superimposed on a dc bias voltage. It was shown that the effective piezoelectric coefficient in the relaxor ferroelectric copolymer, which was enhanced as compared to the unirradiated ferroelectric copolymer, could be tuned by dc biasing field. The effective piezoelectric coefficient  $d_{31}$  initially increased with the dc biasing field and reached a value of 84 pm V<sup>-1</sup> at 30 MV m<sup>-1</sup>; afterwards,  $d_{31}$  began to decrease with the biasing field and had a value of 52 pm V<sup>-1</sup> at 50 MV m<sup>-1</sup>. The mechanism for the tunable field-induced piezoelectricity is discussed based on the high-field electromechanical coupling behaviour in the relaxor ferroelectric polymer.

## 1. Introduction

Materials with large electromechanical coupling have been exploited in the fields of stress or displacement sensing and actuating. Piezoelectricity is the linear coupling between mechanical strain and electric field (converse effect) or between mechanical stress and electric polarization (direct effect), while electrostriction is a nonlinear electromechanical coupling phenomenon in which the generated mechanical deformation is proportional to even powers of the electric field. Although most of the current commercial electromechanical systems are based on piezoelectric effect or linear mechanisms, nonlinear electromechanical coupling is of great interest in smart structures and systems with tunable properties [1, 2].

<sup>3</sup> Author to whom any correspondence should be addressed.



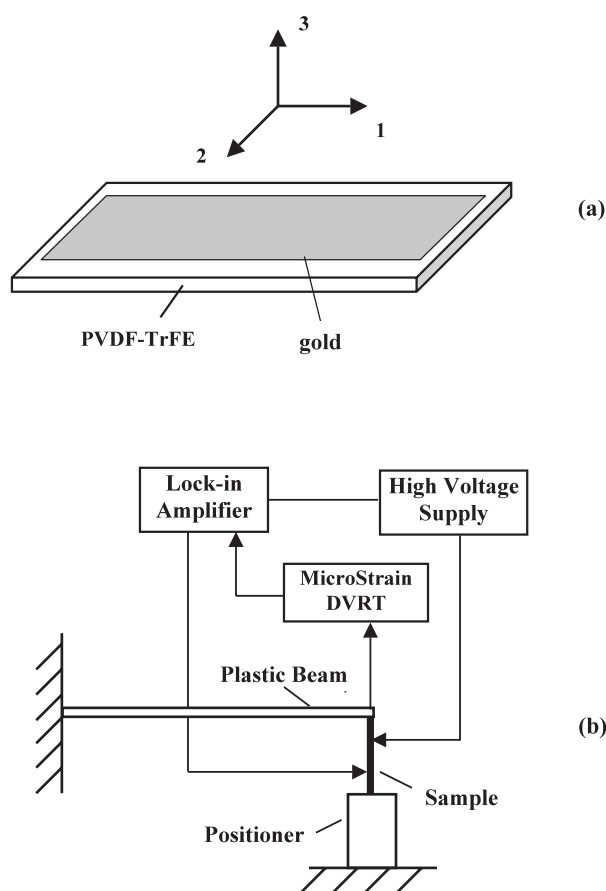
**Figure 1.** Phase diagram of P(VDF-TrFE) copolymers.  $T_m$ ,  $T_c$ ,  $L$ ,  $P$ , and  $F$  stand for the melting point, Curie point, liquid phase, paraelectric phase and ferroelectric phase, respectively.

Ferroelectric polymers have attracted much attention in electromechanical devices such as actuators and transducers due to their flexibility, easy processing and light weight [3]. Poly(vinylidene fluoride) (PVDF) and copolymers were reported to possess the highest piezoelectric activity among all the existing polymers. However, their piezoelectric coefficients ( $d_{31} = 15\text{--}30 \text{ pm V}^{-1}$ ) are at least one order of magnitude lower than those of traditional piezoelectric ceramics (for example,  $d_{31} = 100\text{--}300 \text{ pm V}^{-1}$  for lead zirconate titanate), which greatly limits their applications [4]. Recently, an ultrahigh electrostrictive response ( $\sim 4\%$ ) was observed in electron-irradiated P(VDF-TrFE) copolymers under high external electric field [5–9]. The irradiated copolymers exhibited typical relaxor ferroelectric behaviour [5–7], suggesting that electron irradiation transformed the normal ferroelectric copolymers into relaxor ferroelectrics [10].

Earlier studies in ferroelectric materials (either ceramics [11] or polymers [12]) have revealed that electrostriction is the origin of piezoelectricity and that it is the most fundamental mechanism for electromechanical coupling phenomena. In ferroelectric P(VDF-TrFE) copolymers, it was shown that piezoelectricity arises from the electrostriction coupled with the remnant polarization [12]. The origin of piezoelectricity in electrostriction enables us to control the piezoelectric coefficients by an external electric field. Hence, the giant electrostriction in the relaxor ferroelectric copolymers stimulated our interest in the investigation of electric-field-induced piezoelectric activity in the electron-irradiated P(VDF-TrFE) copolymer. In this paper, we report the investigation of piezoelectric response in a high-energy electron irradiation generated relaxor ferroelectric P(VDF-TrFE) copolymer under external dc biasing field. It is shown that the field-induced piezoelectricity in the relaxor ferroelectric P(VDF-TrFE) copolymer is enhanced in comparison to the normal ferroelectric copolymer and the effective piezoelectric coefficients can be tuned by the applied dc biasing field.

## 2. Experimental details

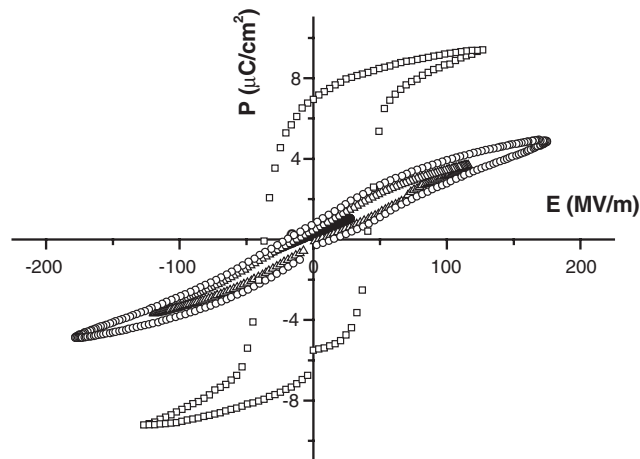
The phase diagram for P(VDF-TrFE) ferroelectric copolymer [3] is shown in figure 1. P(VDF-TrFE) copolymer with 50 mol% of VDF content was chosen for the current study. The preparation method for thin layers of the ferroelectric copolymer and the electron irradiation procedures were similar to those used before [13]. Briefly, copolymer films with



**Figure 2.** Measurement of the electric-field-induced transverse strain response in polymers: (a) sample geometry; (b) experimental setup.

thickness between 18 and 28  $\mu\text{m}$  were obtained by hot-pressing and subsequent stretching of commercially available copolymer powders followed by annealing treatment. High-energy electron irradiation was carried out at 95  $^{\circ}\text{C}$  under nitrogen ambient with 2.55 MeV electrons. For electric characterization, a thin layer of gold electrode was sputtered onto the film surfaces.

Polarization hysteresis loops were measured using a modified Sawyer–Tower circuit. Dielectric properties were measured using an HP 4158 multi-frequency LCR meter equipped with a temperature chamber. The electric-field-induced transverse strain response of the irradiated copolymer was measured using an experimental setup [13] as shown in figure 2. Typical samples used for the piezoelectric strain measurements have dimensions of 10 mm length and 4 mm width. The surface direction of the thin polymer layer in which the electric field was applied was denoted as direction 3, and the length direction was denoted as direction 1. Polymer stripes glued onto a cantilevered plastic beam were pulled down before the measurement, and the resilient force of the tensed plastic beam enables precise detection of the electrostrain in the polymer samples. The small ac driving field was supplied by an SR830 lock-in amplifier, and the dc bias was provided by a Trek high-voltage supply. The field-induced strain response was detected using a Microstrain<sup>TM</sup> DVRT (differential variable reluctance transducer).



**Figure 3.** Dielectric polarization hysteresis ( $P$  versus  $E$ ) loops from the normal P(VDF-TrFE) ferroelectric copolymer (50% of VDF) and slim  $P$  versus  $E$  loops (under various electric field levels) from the electron-irradiated copolymer.

### 3. Results and discussion

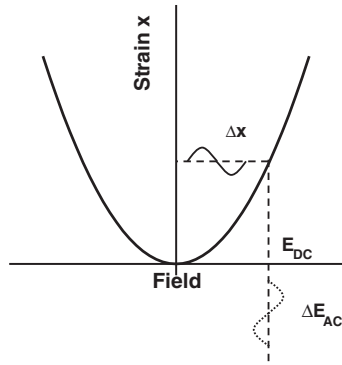
Figure 3 presents the dielectric polarization hysteresis ( $P$  versus  $E$ ) loops obtained in both the unirradiated and irradiated PVDF ferroelectric copolymers [13]. The polarization hysteresis in the loop for the unirradiated copolymer is characteristic of normal ferroelectrics with macroscopic polarization switching from the coherent domains. After high-energy electron irradiation with a total dosage of 60 Mrad at 95 °C, the spontaneous polarization was degraded and the polarization hysteresis significantly suppressed. The slim  $P$  versus  $E$  loops of the irradiated copolymer and strong frequency dispersion in the dielectric spectra [13] (not shown here) are analogous to the relaxor ferroelectric behaviour in ceramics [10], indicating that high-energy electron irradiation has broken up the coherent macropolar domains (all-trans chains) in the normal ferroelectric copolymer and turned the copolymer into relaxor ferroelectrics with polar microregions [13].

Without external electric field little piezoelectricity can be detected in the electron-irradiated copolymer. This is not unexpected, because on cooling from high processing temperature, although there may be local ordering at the nanoscale leading to the formation of polar microregions, there is no global paraelectric–ferroelectric phase transition as in the normal ferroelectric copolymer (figure 1), and macroscopically the electron-irradiation-induced relaxor ferroelectric copolymer is in a non-polar state. However, a material that normally has zero piezoelectric coefficients can have finite ones if a polarization is induced by applying a dc biasing field, as pointed out by Devonshire [14].

Following the Devonshire phenomenology, the strain caused by electromechanical coupling may be expressed as

$$x_{ij} = g_{mij}P_m + Q_{mnij}P_mP_n + W_{mnopij}P_mP_nP_oP_p, \quad (1)$$

where the first, second and third terms on the right-hand side correspond to piezoelectricity, quadratic electrostriction and high-order electrostriction [16], respectively. In the relaxor ferroelectric phase, the first term on the right-hand side of equation (1) vanishes due to the non-polar nature. Furthermore, by neglecting the high-order electrostriction terms, a quadratic relation (figure 4) can be established between the strain and the electric polarization. Using



**Figure 4.** Schematic illustration of the quadratic relation between the electrostrictive strain and the electric field in relaxor ferroelectrics. The field-induced piezoelectricity can be investigated by measuring the small ac field ( $\Delta E_3$ ) induced strain ( $\Delta x_1$ ) under a certain dc biasing field ( $E_{DC}$ ).

matrix notations, the transverse electrostrain induced by the longitudinal field ( $E_3$ ) is given by

$$x_1 = Q_{12}P_3^2, \quad (2)$$

where  $Q_{12}$  is the polarization-related electrostrictive coefficient and  $P_3$  the electric polarization.

For linear dielectrics, equation (2) may be approximated as

$$x_1 \approx Q_{12}\varepsilon_0^2(\varepsilon_3^T - 1)^2 E_3^2 = M_{12}E_3^2, \quad (3)$$

where  $M_{12}$  is the field-related electrostrictive coefficient,  $\varepsilon_0$  the vacuum dielectric permittivity, and  $\varepsilon_3^T$  the relative permittivity.

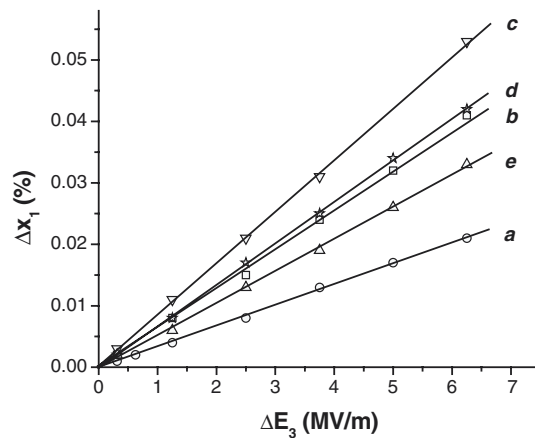
Based on the simple quadratic relation of equation (3), the field-induced piezoelectricity can be readily illustrated by figure 4. As shown in figure 4, the effective piezoelectric coefficients  $d_{31}$  at a certain dc biasing field ( $E_{DC}$ ) is equal to the ratio of the induced electrostrain ( $\Delta x_1$ ) to the small ac driving field ( $\Delta E_3$ ). A similar approach was used by Zhenyi *et al* [17] in the studies of polyurethane soft elastomers. Theoretically, the effective  $d_{31}$  can be deduced from equation (3) as follows:

$$d_{31} = \frac{\partial x_1}{\partial E_3} = 2M_{12}E_{DC}, \quad (4)$$

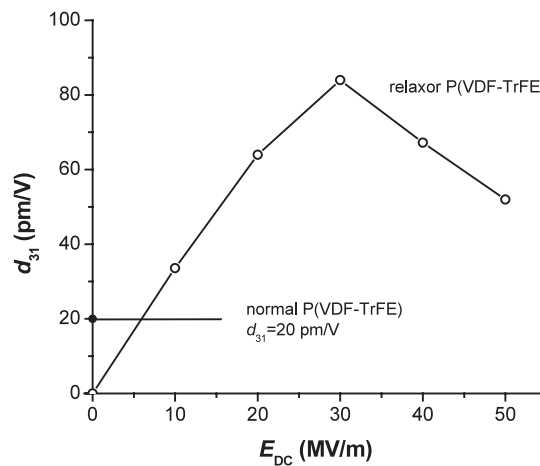
where  $\varepsilon_0$  is the vacuum permittivity and  $\varepsilon_3^T$  the relative permittivity.

Figure 5 displays the piezoelectric strain response induced by a small ac electric field measured at 10 Hz under various  $E_{DC}$  levels in the relaxor ferroelectric P(VDF-TrFE) copolymer. The lines in figure 5 are the linear fit of the experimental data, and the value of  $d_{31}$  is calculated to be 34, 64, 84, 67 and 52  $\text{pm V}^{-1}$ , respectively. The observed piezoelectric response can be associated with the field-induced micropolar to macropolar phase transition in the electron-irradiated copolymer. The electron-irradiation-generated phase can also be regarded as a metastable paraelectric-like phase, and the field-induced micropolar–macropolar phase transition was found to be reversible [15], i.e., the generated macropolar domains degenerate back to polar microregions upon removal of the external dc biasing field.

The measured  $d_{31}$  versus  $E_{DC}$  is displayed in figure 6. It can be seen that  $d_{31}$  in the electron-irradiation-induced relaxor ferroelectric copolymer was enhanced compared to the normal ferroelectric copolymer ( $d_{31} \sim 20 \text{ pm V}^{-1}$  for the unirradiated P(VDF-TrFE) copolymer with 50 mol% content of VDF). It can also be seen that  $d_{31}$  in the relaxor ferroelectric copolymer

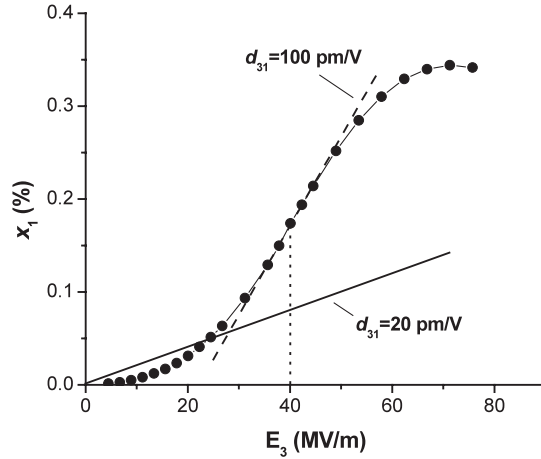


**Figure 5.** The transverse piezoelectric strain  $\Delta x_1$  induced in electron-irradiated P(VDF-TrFE) copolymer by a small longitudinal ac electric field ( $\Delta E_3$ ) measured at 10 Hz under various  $E_{DC}$  ( $\text{MV m}^{-1}$ ): (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50.



**Figure 6.** Effective piezoelectric coefficient  $d_{31}$  versus  $E_{DC}$  in the electron-irradiated P(VDF-TrFE) copolymer. The typical  $d_{31}$  value ( $20 \text{ pm V}^{-1}$ ) for the normal ferroelectric copolymer (50% of VDF) is shown for comparison.

can be tuned by the biasing field. From equation (4), it is clear that for simple dielectrics  $d_{31}$  increases linearly with  $E_{DC}$ . In the relaxor ferroelectric copolymer it is shown that, despite the initial increase with  $E_{DC}$ ,  $d_{31}$  started to drop after reaching  $84 \text{ pm V}^{-1}$  at  $30 \text{ MV m}^{-1}$ , and it had a value of only  $52 \text{ pm V}^{-1}$  at  $50 \text{ MV m}^{-1}$ . In lead magnesium niobate (PMN), a typical relaxor ferroelectric ceramic, a similar maximum was found in the  $d_{31}$  versus  $E_{DC}$  curve [18], whereas a linear relation was observed between  $d_{31}$  versus  $P_3$  over the whole range of measurement. It is noted that in the PMN relaxor ferroelectric ceramic, the maximum applied field was just  $3 \text{ MV m}^{-1}$ , much lower than that used in the current investigation of relaxor ferroelectric polymer. Polymers generally can withstand much higher electric field due to the much larger breakdown strength. The relaxor ferroelectric polymer behaves like a linear dielectric at relatively low field level. However, the linear  $d_{31}$  versus  $E_{DC}$  relation does



**Figure 7.** Large ac-field-induced electrostrictive strain response in the electron-irradiated P(VDF-TrFE) copolymer (50% of VDF). The slope of the dashed line represents the largest predicted piezoelectric coefficient obtained around  $40 \text{ MV m}^{-1}$  in the electron-irradiated copolymer. The solid line represents the piezoelectric effect in the normal ferroelectric copolymer.

not apply at higher field since nonlinear coupling essentially exists between the polarization and the field in ferroelectrics, and  $d_{31}$  should be deduced from equation (2) as follows:

$$d_{31} = \frac{\partial x_1}{\partial E_3} = 2Q_{12} (\partial P_3 / \partial E_3)_E P_3. \quad (5)$$

The electric polarization tends to saturate at higher field levels, while in the meantime the weak-field dielectric permittivity [13] decreases with the increase of dc biasing field. These two factors can explain the drop of  $d_{31}$  at higher  $E_{DC}$ .

As indicated by equations (4), (5) and figure 4, the slopes of the curve of electrostriction versus field at any points can give estimates of the effective piezoelectric coefficients [19]. In order to analyse the field-induced piezoelectricity in the relaxor ferroelectric PVDF-TrFE copolymer, we measured the large ac electric-field-induced transverse electrostrictive strain response over a broad field range (figure 7). As shown in figure 7, the effective piezoelectric coefficient  $d_{31}$  in the irradiated copolymer increased with dc biasing field, and reached a maximum of  $\sim 100 \text{ pm V}^{-1}$  at a field around  $40 \text{ MV m}^{-1}$ ; afterwards  $d_{31}$  gradually decreased with the increase of the biasing field. The slope of the dashed line in figure 7 represents the largest effective piezoelectric coefficient predictable for the relaxor ferroelectric copolymer. By comparing the slopes at various field levels in figure 7 with the data shown in figure 6, it is seen that the measured  $d_{31}$  is generally lower than the predicted one, and the  $d_{31}$  peak shifts to lower biasing field. That the measured  $d_{31}$  differs from the values predicted with the quadratic  $x_1 - P_3$  relation suggests that the high-order electrostriction term as shown in equation (1) should probably not be neglected for the electron-irradiated copolymer.

#### 4. Conclusion

Field-induced piezoelectric responses were investigated in the electron-irradiation-generated relaxor ferroelectric state of the P(VDF-TrFE) copolymer. Enhanced effective piezoelectric coefficients were found in the relaxor ferroelectric copolymer as compared with the normal ferroelectric copolymer. The piezoelectricity in the relaxor ferroelectric copolymer can be



tuned by the dc bias, and an enhanced piezoelectric response was observed. Such tunable piezoelectricity may provide useful technological applications in smart structures.

### Acknowledgment

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