Effect of electron irradiation on poly(vinylidene fluoride-trifluoroethylene) copolymers

Yiwen Tang and Xing-Zhong Zhao[a]
Department of Physics, Wuhan University, Wuhan 430072, China

Helen L. W. Chan and C. L. Choy
Department of Applied Physics, Honk Kong Polytechnic University Hung Hom, Kowloon, Hong Kong, China

(Received 13 April 2000; accepted for publication 5 July 2000)

Electrical field-induced strain response of electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer has been studied by a Mach–Zehnder type heterodyne interferometer in the frequency range of 3–9 kHz. The electrostrictive constant is calculated from the strain results, which is of the same order of magnitude as those obtained at 1 Hz by a bimorph-based strain sensor but at much lower electrical field. Changes in the dielectric property, phase transition behavior and crystal structure of the same copolymer have also been studied. The reversible solid–state transition between the polar and nonpolar phase in the crystalline regions of the copolymer driven by the external electric field is suggested to be responsible for the significant high electrostrictive strain of the electron-irradiated copolymer. *© 2000 American Institute of Physics.* [S0003-6951(00)04235-2]

It is well known that high-energy particle irradiation is a very effective means for improving many performances of poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene [P(VDF-TrFE)].[1–3] More recently, it was found by Zhang *et al.* that the 2.55–3.00 MeV electron-irradiated P(VDF-TrFE) 65/35 and 50/50 mol. % copolymers exhibit exceptionally high electrostrictive responses (~4% longitudinal strain and ~3% transverse strain). The frequency range of bimorph-based strain sensor used in their strain measurement is from 0.1 to 10 Hz.[4–7] That is, the electromechanical performance of P(VDF-TrFE) copolymer in this frequency range can be effectively enhanced through high-energy irradiation. Clearly, materials with such high electrostrictive strain are attractive for actuator, sensor, and transducer applications. For an electrostrictive material, different application will need different working frequency range. In this letter, the electrostrictive coefficients have been determined on electron-irradiated P(VDF-TrFE) copolymer with 80 mol. % VDF in frequency range of 3–9 kHz. We have further investigated the influence of radiation on other properties, with special emphasis on the changes in the structure, which may be helpful for clarifying the microstructure-property relationship of high strain response observed in the irradiated copolymer.

The random copolymer of P(VDF-TrFE) used in this study, obtained from Piezotech in France, had a comonomer ratio, VDF/TrFE, of 80/20 mol. %. Thin films (about 100 μm thick) were made by solvent (dimethylformamide) casting method. To remove residual solvent and improve the crystallinity, films were directly annealed at 135 °C in oven for 2 h after casting. The electron irradiation was carried out at ambient temperature in vacuum with 3 MeV energy-level electrons. The dosage used was in the range of 70–145 Mrad. Al electrodes were evaporated on both surfaces of the film. We report results here obtained from films irradiated with 100 Mrad, for it generated the highest longitudinal strain observed in the present study. Since all results reported here were obtained from samples irradiated with same dosage, the thermal effect introduced during electron irradiation are considered to be the same. Strain was measured by a Mach–Zehnder type heterodyne interferometer[8] (SH-120 from B. M. Industries, France). All the strain measurements were performed in the frequency range of 3–9 kHz, and at room temperature. The dielectric constant was evaluated by HP multifrequency LCR meter equipped with a temperature chamber. X-ray diffraction patterns were recorded at room temperature, using Cu K α radiation, on a Shimadzu (XD-3A) diffractometer. Differential scanning calorimeter was performed using a PERKIN ELMER DSC7 at a heating rate of 10 °C/min.

Figure 1 shows the longitudinal strain versus the square of electric field at frequency of 5 kHz. Since the copolymer films thicker than one hundred micron were used in the strain measurement, the maximum electric field, which is limited by the present setup, is only 8 MV/m. The plot of unirradiated film is also presented in Fig. 1 for comparison. The strain is linearly proportional to the square of electric field due to the pure electrostrictive effect. The electrostrictive coefficient is defined as $S = ME^2$. Therefore, M constant obtained from Fig. 1 are $M_{100\mathrm{M}} = 2.83\times 10^{-18}\ \mathrm{m}^2/\mathrm{V}^2$, which is of the same order of magnitude as those obtained from 50/50 mol. % copolymer by a bimorph-based strain sensor,[9] and $M_{\mathrm{un}} = 3.26\times 10^{-19}\ \mathrm{m}^2/\mathrm{V}^2$, respectively. Apparently, electrostrictive coefficient is improved markedly through high-energy irradiation. Restricted by the mechanical resonance of the bimorph-based strain sensor, previous reported strain measurement was performed at very low frequency,[4–6] 1 Hz or even lower. So the present result is significant in that the electron-irradiated P(VDF-TrFE) copolymer is still a very competent candidate for actuator and transducer application in the frequency range lower than 10 kHz. It is also worthy to point out that this result was obtained at a relatively lower

---

[a] Author to whom correspondence should be addressed; electronic mail: xzzhao@whu.edu.cn

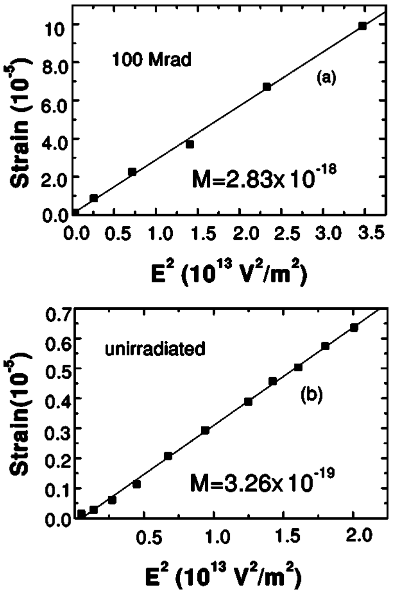

FIG. 1. The amplitude of longitudinal strain as a function of the square of electric field. (a) 100 Mrad irradiated film, $M = 2.83\,c(m/V)^2$. (b) Unirradiated film, $M = 3.26\times 10^{-19}\,(m/V)^2$.

electric field, one order of magnitude smaller than those reported previously,[4–6] on thicker P(VDF-TrFE) copolymer films (over 100 microns). It is shown that the performance of irradiated P(VDF-TrFE) copolymer films is still very good when the thickness of the films increased, which is also very useful from the view point of some transducer applications. The large increase of M constant in the irradiated materials compared with that of unirradiated ones could also be attributed to the difference in the polarization responses in the two materials. Figure 2 shows the electrostrictive coefficient versus the driving frequency of the applied field at 5 MV/m for the 100 Mrad irradiated film. The M value is gradually decreased with increasing frequency. The appearance of the frequency dispersion is characteristic of the relaxor ferroelectric material.

The dielectric constant (ϵ') of irradiated film were measured as a function of the temperature for various frequency at a heating rate 2 °C/min. It can be seen from Fig. 3 that a broad peak appears in the dielectric constant as a function of temperature. With increasing frequency, T_m (the temperature of the dielectric constant maximum) increases, while the magnitude of the peak decreases. These experiment results are the most typical feature of the relaxor ferroelectric.[10] Vogel–Folcher (V–F) relation,[11] $f = f_0 \exp[-U/k(T_m - T_f)]$, where U is a constant related to the activation energy, k is the Boltzmann constant, and T_f can be interpreted as the freezing temperature, can characterize the relation between the frequency f and the T_m of the relaxor ferroelectric behavior reasonably. Applying the V–F relation to fit the experimental results in Fig. 3 through least-square fitting, we get the results of $f_0 = 4.04\,\mathrm{MHz}$, $T_f = 332.7\,\mathrm{K}$, $U = 0.002\,04\,\mathrm{eV}$. The fitted results of the relation between the f and T_m for the irradiated film are shown in Fig. 4. It can be seen that the experimental results are well fitted by the V–F relation. It confirms again that the electron irradiation has changed the normal ferroelectric copolymer film to a ralxor ferroelectric one. It is widely accepted that the frequency dispersive dielectric characteristics of the relaxor ferroelectric ceramics are mainly due to the nanometer-size polar regions in the materials.[9] By analogy, it is supposed that the irradiated copolymer films contain polar regions of different size, and the distribution of both the size and polarization strength of these polar regions cause the diffuse dielectric response with frequency. It might also be the reason for the appearance of the large longitudinal strain in the irradiated film.

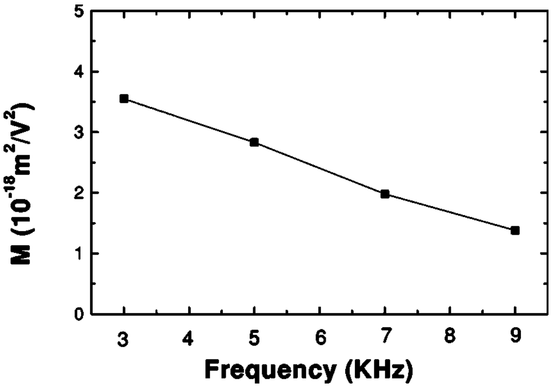

FIG. 2. The frequency dispersion of the electrostrictive coefficient of 100 Mrad irradiated film under 5 MV/m driving field.

It is well known that P(VDF-TrFE) copolymer is semicrystalline polymer, i.e., there are crystalline lamellae imbedded in amorphous matrix. The electromechanical activity of the copolymer mainly comes from the crystalline regions.[12,13] Therefore, the excellent electromechanical properties observed in the electron irradiated copolymers indicate that the irradiation have a strong influence on the structure of the crystalline region. X-ray diffraction patterns of the copolymer films unirradiated and irradiated with 100 Mrad dosage are shown in Fig. 5. The x-ray diffraction peak in Fig. 5 represents Bragg diffractions of (110) and (200). For the unirradiated film only a single narrow reflection at $2\theta = 19.7°$ is observed, corresponding to the polar phase. After irradiation, a broad reflection of nonpolar phase centered at $2\theta = 18.3°$ grows at the expense of the narrow reflection of polar phase at $2\theta = 19.7°$, which become a shoulder after 100 Mrad irradiation. This means that the polar phase and nonpolar phase are coexisted in the crystalline regions after irradiation. The x-ray peak of the irradiated film in Fig. 5 is fitted to two Gaussian function. It is estimated from the fitting results that the intensity ratio of the polar phase and

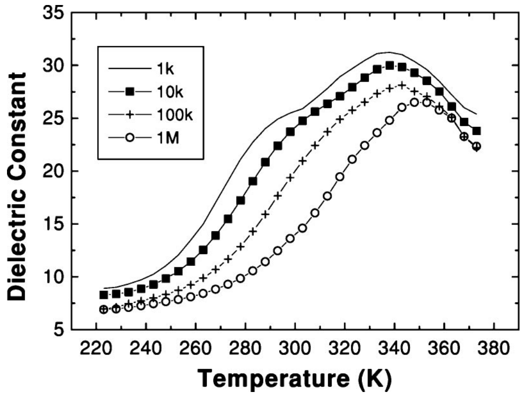

FIG. 3. The dielectric constant as a function of temperature for 100 Mrad irradiated film.

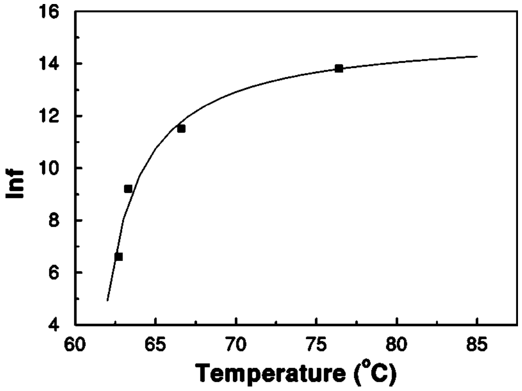

FIG. 4. The fitted results of the relation between f and T_m for 100 Mrad irradiated film. The dots are the experimental results and the solid curve is fitted curve.

nonpolar phase is about 1:4.08. Considering the polarization and Lorenze effect, the correct ratio of polar phase versus nonpolar phase is 1.14. So the volume ratio of polar phase and nonpolar phase is about 1:3.579. It is also noticed from the x-ray diffraction result that the full width at half maximum of the polar phase peak increased with the irradiation dosage while the integrated peak intensity decreased. This indicates the decrease of both the lamella crystalline phase volume fraction and the average size of the polar crystalline phase in the irradiated copolymer films. The later factor is believed to be helpful to reduce the energy barrier between polar and nonpolar phase in the crystalline regions of the copolymer films and facilitate the reversible solid–state phase transition between these two phases driven by externally applied electric field. It seems reasonable to suppose that if the lattice parameter of the crystal regions in polar phase is a constant, the larger the lattice parameter of the nonpolar phase in the crystal region, the larger the electric field induced strain response. It was proposed earlier that the large strain response observed in the irradiated copolymer is related to the electric field induced phase transition of the crystal regions between the nonpolar and polar phases.[5] Based on the x-ray diffraction results mentioned above and the large lattice parameter difference between the polar β phase and nonpolar α phase of the P(VDF-TrFE) copolymer, it is suggested here that the lattice expansion and contraction resulted from the reversible solid–state transition between polar and nonpolar phases in the crystalline regions of the irradiated copolymer driven by the externally applied electrical field is responsible for the microscopic mechanism of the high strain response observed in the irradiated copolymers.

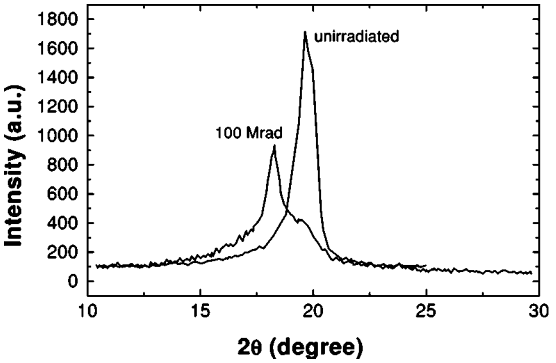

FIG. 5. X-ray diffraction diagrams of P(VDV$_{0.80}$-TrFE$_{0.20}$) copolymer before and after irradiation.

TABLE I. Differential scanning calorimeter experiment results of P(VDF$_{0.80}$-TrFE$_{0.20}$).

Sample	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)
Unirradiated	113.59	151.36	10.44	14.327
100 Mrad	55.94	101.2	2.95	7.53

Differential scanning calorimeter experiments show significant change of both the phase transition and crystallization behaviors in the copolymer films. The results are summarized in Table I. Both T_c (the temperature of phase transition between nonpolar and polar phases in the crystal regions) and T_m (the melting temperature) decrease after radiation. The enthalpies associated with both the melting of sample and the solid state phase transition decrease as well. The decrease of the enthalpy at the melting temperature indicates the reduction of the crystallinity. And the reduction of the enthalpy at T_c indicates the decrease of the average size of the polar crystalline phase in the irradiated copolymer films. This result is in consistent with the x-ray diffraction results mentioned above. It is believed that the crystal regions with small and distributed size of polar and nonpolar phases in the irradiated copolymer are responsible for the relaxor ferroelectric behavior and high strain response observed in the irradiated P(VDF-TrFE) copolymer films.

A large electrostrictive coefficient is obtained at the frequency range between 3 and 9 kHz in the electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer. Dielectric measurement shows that the material exhibits the characteristic of a relaxor ferroelectric. From x-ray diffraction result and differential scanning calorimetry (DSC) thermal analysis, it is found that both the volume fraction of crystalline phase and the sizes of the polar phase in the crystalline regions of the copolymer decrease after electron irradiation. It is suggested that the reversible solid–state phase transition driven by the external electrical field of polar and nonpolar phases is responsible for the excellent electromechanical properties observed in the irradiated copolymer.

This work was supported by the National Natural Science Foundation of China under Grant Nos. 59943001 and 59973015.

[1] A. J. Lovinger, Macromolecules **18**, 910 (1985).
[2] A. Odajima, Y. Takase, T. Ishibashi, and K. Yusa, Jpn. J. Appl. Phys., Suppl. **24**, 881 (1985).
[3] B. Daudin, M. Dubus, and J. F. Legrand, J. Appl. Phys. **62**, 994 (1987).
[4] Q. M. Zhang, V. Bharti, and X. Zhao, Science **280**, 2101 (1998).
[5] X-Z. Zhao, V. Bharti, and Q. M. Zhang, Appl. Phys. Lett. **73**, 2054 (1998).
[6] V. Bharti, X-Z Zhao, and Q. M. Zhang, Mater. Res. Innovations **2**, 57 (1998).
[7] Z.-Y. Cheng, T.-B. Xu, V. Bharti, S. Wang, and Q. M. Zhang, Appl. Phys. Lett. **74**, 1901 (1999).
[8] Z. Zhao, H. L. W. Chan, and C. L. Choy, Ferroelectrics **195**, 35 (1997).
[9] X.-Z. Zhao and Q. M. Zhang (unpublished results).
[10] L. E. Cross, Ferroelectrics **76**, 241 (1987).
[11] Z.-Y. Cheng, R. S. Katiyar, X. Yao, and A. Bhalla, Phys. Rev. B **57**, 8166 (1998).
[12] A. J. Lovinger, Science **220**, 1115 (1983).
[13] H. Ohigashi, K. Koga, M. Suzuki, T. Nakanishi, K. Kimura, and N. Hashimoto, Ferroelectrics **60**, 263 (1984).