High electrostriction and relaxor ferroelectric behavior in proton-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer

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Effect of proton irradiation on poly(vinylidene fluoride-trifluoroethylene) 56/44 mol % copolymer has been studied using a Mach–Zehnder heterodyne interferometer, polarization hysteresis loop and dielectric constant measurements. The electrical-field-induced strain response of the copolymer after proton bombardment follows a quadratic electrostriction relationship. The electrostrictive coefficient at 5 kHz is similar to that obtained with a bimorph-based strain sensor, but at a much lower electric field. The polarization hysteresis after proton irradiation is reduced considerably and the dielectric constant exhibits typical relaxor behavior, which is suggested as the cause of the observed results. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1715151]

High-performance materials capable of converting electrical energy to mechanical energy or vice versa are needed for a wide range of demanding applications. The search for new materials[1–4] and for new processes[5,6] capable of enhancing the performance of existing materials has attracted a great deal of attention. Electroactive polymers are of particular interest because of the low cost and easy processing, and the ability of polymers to be tailored to different applications. It was recently reported that under electron irradiation treatment, a massive longitudinal (parallel to the applied electric field) electrostrictive strain can be induced in poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymers.[7,8] Subsequent studies showed that the copolymers also possess other good features, which makes them a very competitive candidate for a wide range of electromechanical applications.[9,10] In this letter, we report the results of a preliminary study on proton irradiation of P(VDF-TrFE) 56/44 mol % copolymer. Electrostrictive strain, dielectric constant, and polarization hysteresis loop measurements show that proton irradiation also improves the electromechanical properties of the copolymers.

The random copolymer P(VDF-TrFE) used in this study, obtained from Piezotech, Saint Louis, France, has a monomer ratio of 56/44 mol %. Thin films (about 25 μm thick) were prepared by compression molding at 190 °C. The proton irradiation experiments were performed on a Tandetron 4120-LC accelerator (High Voltage Engineering Europa B.V., Netherlands). Since copolymer films irradiated with 40 and 100 Mrad electrons exhibited the best performance, proton dosages equivalent to these electron dosages were chosen.[6] Proton dose in ions/m^2 could be converted to rad by multiplying the electronic energy loss at the sample surface in eV/m/ion first, and then dividing by the density of the material in kg/m^3 and the factor of 6.24×10^{16} eV/kg (1 rad is equal to 6.24×10^{16} eV/kg).[11] The density of 1690 kg/m^3

of 56/44 P(VDF-TrFE) was used to roughly estimate the electronic energy loss of a 3-MeV proton in the copolymer as 1.54 eV/Å. The proton doses corresponding to 40 and 100 Mrad were calculated to be 2.58×10^{17} and 6.35×10^{17} ions/m^2 approximatively, and were used in the proton irradiation treatments of the P(VDF-TrFE) copolymers. Taking into the account the density of the copolymers and calculating the electronic energy loss of 3-MeV protons in the copolymer films, it was estimated that copolymer films with a thickness of about 200 μm can be penetrated by the 3-MeV protons. We report results obtained with a proton irradiation dose of 6.35×10^{17} ions/m^2. These films generated the highest longitudinal strain in present study.

After irradiation, a chromium/gold (Cr/Au) electrode with thickness of about 0.1 μm was sputtered on both surfaces of the film. The dielectric behavior of the copolymers was measured with an impedance analyzer (HP 4194) equipped with a temperature chamber (Delta 9023). The polarization hysteresis loops were measured with a modified Sawyer–Tower circuit at a frequency of 10 Hz. The electric-field-induced strain was measured with a Mach–Zehnder heterodyne interferometer (Model SH-120, B. M. Industries, France).[12] The low cutoff frequency for the strain measurement is around 3 kHz. The high-end frequency is 10 kHz, which is limited by the Trek 610D high-voltage amplifier (Trek Inc.). The strain measurement setup was first calibrated using a commercial lead zirconate titanate ceramic sample. Hence, all the strain measurements were performed accurately at a frequency of 5 kHz, and the driving electric field applied to the copolymer films was less than 40 MV/m.

Figure 1 shows the field-induced strain at room temperature. The electrostrictive strain is about 0.15% at a field of 35 MV/m, comparable to the electron-irradiated P(VDF-TrFE) copolymers films at similar field levels. The strain versus electric field for the fresh copolymer films is presented in Fig. 1(b). As can be seen, the field-induced strain without proton irradiation is more than one order of magnitude smaller than that with proton irradiation. This result demon-

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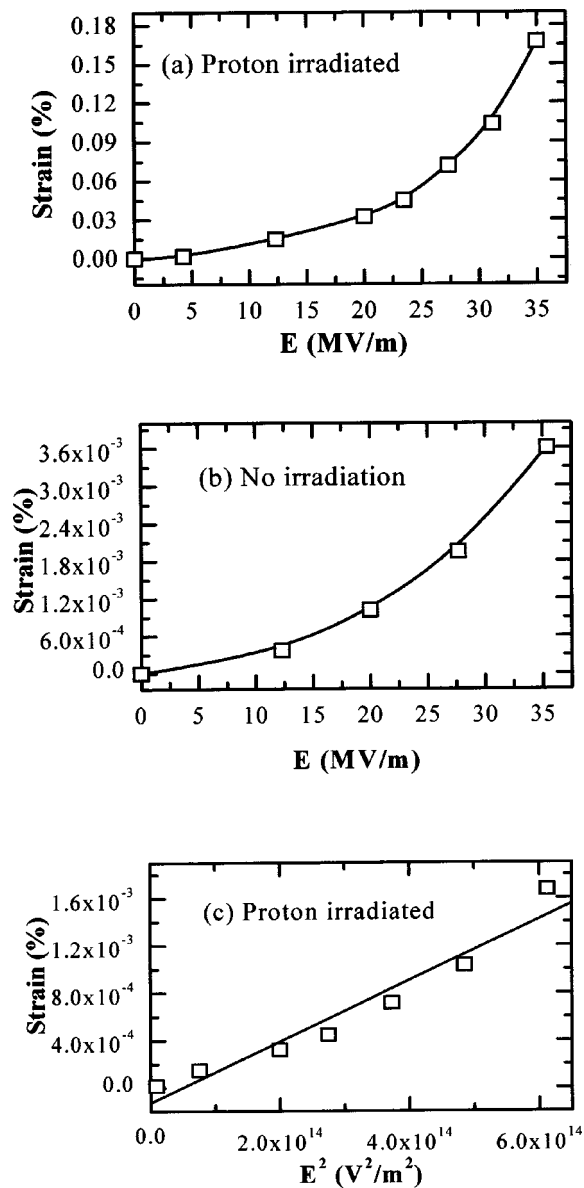
FIG. 1. Strain versus electric field curves for (a) nonirradiated, (b) proton-irradiated, and (c) strain versus square of electric field for proton-irradiated P(VDF-TrFE) 56/44 mol % copolymer samples.

FIG. 2. Polarization hysteresis loops for (a) nonirradiated and (b) proton-irradiated P(VDF-TrFE) 56/44 mol % copolymer samples.

strates that, similar to electron irradiation, proton irradiation also improves the electromechanical behavior of P(VDF-TrFE) copolymers. Since polarization P versus strain S measurement at high frequencies is very difficult, if not impossible, we were unable to calculate the electrostrictive Q constant ($S=QP^2$), but we did calculate the electrostrictive M constant ($S=ME^2$) based on strain measurements. As can be seen in Fig. 1(c), the strain is almost linearly proportional to the square of electric field, indicating a roughly electrostrictive effect. Therefore, the M constant obtained from Fig. 1(d) is $M_{5K}=1.83\times10^{-18}$ m^2/V^2 for the proton-irradiated sample, which is comparable to $M=2.83\times10^{-18}$ m^2/V^2 of the electron-irradiated sample,[10] and is significantly higher than the M value ($M_{un}=3.26\times10^{-19}$ m^2/V^2) for an unirradiated copolymer film. Apparently, the electrostrictive strain response of the P(VDF-TrFE) copolymers is enhanced markedly through high-energy proton irradiation. Restricted by the mechanical resonance of the bimorph based strain sensor, previously reported strain measurements were performed at
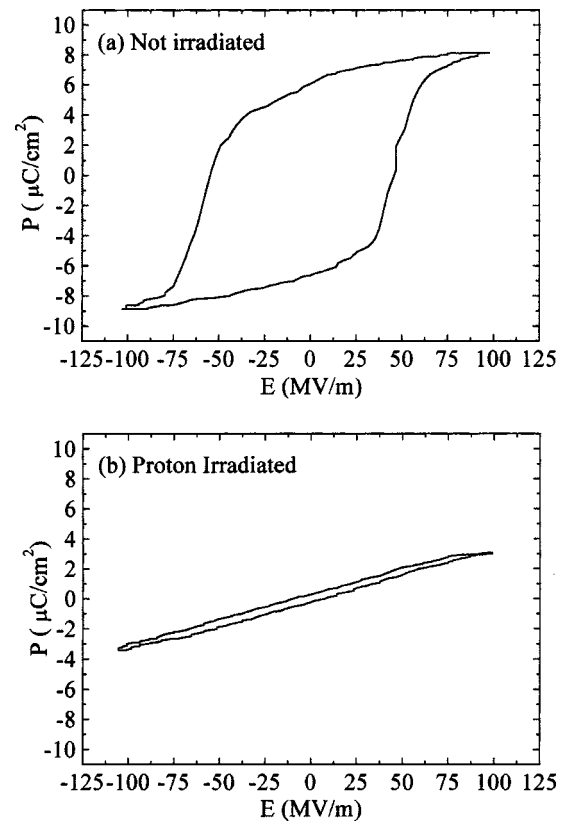
low frequency, 1 Hz or lower.[6–9] A similar electrostrictive strain response is also found in the proton-irradiated P(VDF-TrFE) copolymer films with a proton dose of 2.58×10^{17} ions/m^2, equivalent to 40 Mrad. Thus, the present results are also significant in that the proton-irradiated P(VDF-TrFE) copolymer is a viable candidate for actuator and transducer applications up to 10 kHz.

The polarization hysteresis loops of P(VDF-TrFE) 56/44 mol % copolymer films measured at room temperature before and after ion bombardment are shown in Fig. 2. As can be seen in Fig. 2(a), the copolymer film before proton irradiation exhibits a well-defined ferroelectric polarization hysteresis loop with a coercive field of 50 MV/m and a remanent polarization of 6.3 μC/cm^2. On the other hand, the copolymer film irradiated with a dose of 6.35×10^{17} ions/m^2 shows a narrower hysteresis loop and a much lower remanent polarization. This indicates a transition from more crystalline to amorphous phase. The defects induced by high-energy electron irradiation in the irradiation process such as the dangling bonds and crosslinkings can reduce the stability of the ferroelectric state.[13] Thus, the decrease of the crystal ordering can be interpreted by the lattice defects and reduction of the crystallinity in irradiated copolymer films.

Although many authors studied the radiation chemistry of fluoropolymers, most research has been conducted on the effects of radiation on the mechanical and sol/gel behavior of fluoropolymers, with very few papers providing a detailed mechanism for the reactions.[14,15] To emphasize the effect of proton irradiation, we further focused the study on ferroelectric characteristics of the irradiated copolymers using weak-field dielectric constant measurements. The dielectric con-

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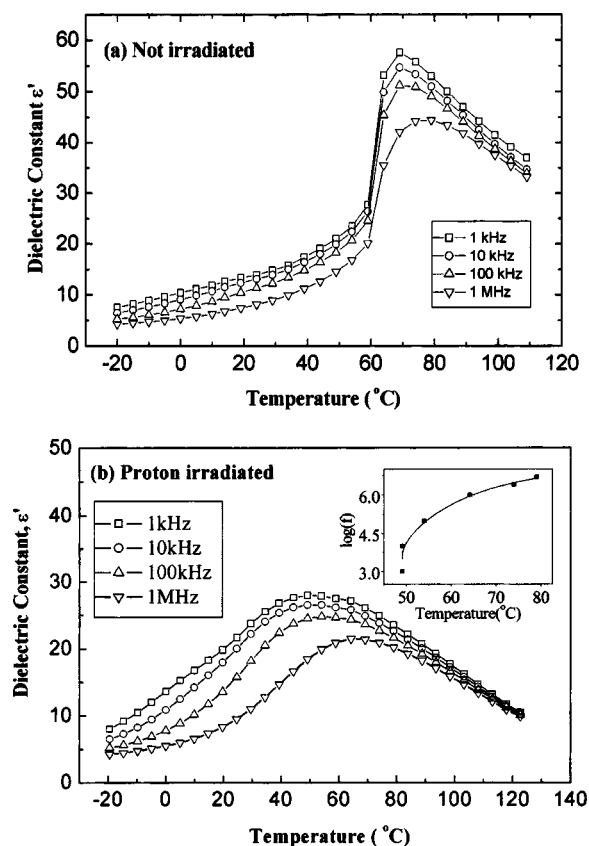
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FIG. 3. Dielectric constant as a function of temperature for (a) nonirradiated and (b) proton-irradiated P(VDF-TrFE) 56/44 mol % copolymer samples. The relation between the frequency f and T_m applying the V–F law is plotted in the inset figure.

$$f = f_0 \exp \frac{-U}{k(T_m - T_f)}, \tag{1}$$

where U is a constant related to the activation energy, k is the Boltzmann constant, T_m is the dielectric constant peak temperature, and T_f is interpreted as the freezing temperature where the activation energy of the process approach infinity. The inset in Fig. 3(b) shows the relation between the frequency f and T_m applying the V–F law. Least squares fitting yields $f_0 = 32.6$ MHz, $U = 6.9 \times 10^{-3}$ eV, and $T_f = 313$ K (40 °C). The fitted T_f and f_0 values are higher than those reported previously for electron-irradiated P(VDF-TrFE) 56/44 mol %, and considerable deviation between the experimental T_m and fitted curve is noted at lower frequencies. The polarization hysteresis remaining in the proton-irradiated sample may be responsible for such a deviation.

In conclusion, a relatively high strain response is obtained in a proton-irradiated P(VDF-TrFE) 56/44 mol % copolymer at 5 kHz under a lower electric field. Dielectric measurement shows that the material exhibits the characteristics of a relaxor ferroelectric and that the polarization hysteresis is reduced considerably after proton irradiation. All the results give clear evidence that proton irradiation is another effective way to improve the electromechanical performance of the P(VDF-TrFE) copolymers similar to electrons.

stants of P(VDF-TrFE) 56/44 mol % films measured in a heating run before and after proton irradiation are shown in Fig. 3. As shown in Fig. 3(a), the copolymer film before proton irradiation displays a typical normal ferroelectric behavior. It has a clearly defined Curie point with a ferroelectric-to-paraelectric phase transition temperature near 64 °C at different frequencies, although the temperatures corresponding to the dielectric constant maximum (T_m) are varied slightly at different frequencies. In contrast, the copolymer film after irradiation exhibits a typical relaxor ferroelectric behavior, as shown in Fig. 3(b). The dielectric constant versus temperature curve exhibits very broad peak at a temperature substantially lower than that for the unirradiated sample. The dielectric properties of the irradiated copolymer strongly depend on the electric field, and considerable remnant polarization still exists in the irradiated film, as shown in Fig. 2(b). These are the possible reasons the strain versus square of electric field curve might not strictly follow the linear relation, even when the strain versus square of polarization curve is linear.[16] It demonstrates that proton irradiation is another effective means of transforming a normal ferroelectric P(VDF-TrFE) 56/44 mol % copolymer to a relaxor ferroelectric.

The frequency dispersion of the dielectric behavior of the films after proton irradiation roughly follows the Vogel–Fulcher (V–F) law, an empirical relation that holds for many spin-glass systems and relaxor ferroelectrics, given by[17,18]

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