Study of the Structure and Electrostrictive Property of Proton-irradiated P(VDF-TrFE) 56/44 mol% Copolymer

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ABSTRACT

High-energy proton (3 MeV) irradiation with dosages ranging from 43 to 200 Mrad have been carried out to investigate the potential for modifying both the structure and property of vinylidene fluoride-trifluoroethylene 56/44 mol% copolymer. The structural and transitional behavior of the irradiated copolymer was studied by X-ray diffraction and differential scanning calorimetry. The polarization hysteresis, relative permittivity properties and electrostrictive strain response of these copolymers were also measured. It was found that the ferroelectric copolymer could be successfully converted to a relaxor at a low proton dosage of about 75 Mrad at ambient temperature. A slim polarization hysteresis loop and a frequency dispersion of the relative permittivity observed in the irradiated copolymer imply that the high-energy protons break up the coherent polarization domains in the ferroelectric copolymer into nano-sized regions. In addition, the irradiation leads to a significant change in the ferroelectric-to-paraelectric phase transition behavior. X-ray diffraction measurements show that the crystalline region in the copolymer is converted into a nonpolar phase upon irradiation, and the lattice spacing increases significantly. The electric field induced phase transformation of the nano-sized regions between the nonpolar and polar phase leads to a high electrostrictive strain observed in the irradiated copolymer.

Index Terms — **P(VDF-TrFE), irradiation, relaxor, phase transition, electrostriction, copolymer, polarization, permittivity, ferroelectric.**

1 INTRODUCTION

IN recent years, considerable interest has been focused on ferroelectric polymers, as they offer several advantages over ferroelectric ceramics, e.g. low acoustic impedance, low density and high degree of flexibility. Among various functional polymers, polyvinylidene fluoride (PVDF) and the copolymers of vinylidene fluoride and trifluoroethylene (P(VDF-TrFE)) have attracted high interest due to their remarkable electroactive properties, and their potential applications in a variety of devices, including transducers, actuators, sensors and optical-phase modulators [1−6].

The piezoelectricity of PVDF was first studied by Kawai [7]. This polymer crystallizes into a nonpolar α phase. By mechanical drawing to several times the original length, the α phase can be transformed to a polar β phase. Poling treatment provides a film having considerable piezoelectric activity, but the activity is unstable above 100°C [8]. P(VDF-TrFE) copolymers containing 50-80 mol% of VDF are particularly interesting because the Curie transition between the ferroelectric and paraelectric state occurs at a temperature below the melting point. These copolymers also exhibit higher piezoelectric and electromechanical coupling coefficients than those of PVDF [9,10]. To improve the efficiency of polymeric transducers and actuators, the copolymer has been subjected to various treatments, e.g. annealing at high temperature and poling at high electric field [11,12].

Recent works on P(VDF-TrFE) copolymers have shown that both the structure and properties of these materials can be modified significantly by exposing them to various irradiation sources such as X-ray, gamma ray and electron beams [13−17]. Lovinger [13] exposed a series of ultrathin P(VDF-TrFE) copolymer films (10−20 nm thick) with 52, 65, 73 and 78 mol% VDF to 100 keV electron irradiation, and found that a polymorphic transformation of the ferroelectric phase to paraelectric phase was induced. Similar

phenomena were observed by Odajima et al. [14] in thick films (20−40 μm) of P(VDF-TrFE) 65/35 mol% copolymer after irradiation with ^{60}Co γ-rays. Cunha and co-workers [15] have performed a similar study involving X-ray irradiation of P(VDF-TrFE) 60/40 mol% copolymer. More recently, Zhang and co-workers [18,19] found that P(VDF-TrFE) copolymers at a composition of 65/35 mol% exhibited ultrahigh electrostrictive strain responses after high-energy (2.5−3.0 MeV) electron irradiation, namely 4% longitudinal strain and about 3% transverse strain. Moreover, by applying a biased dc electric field, high effective piezoelectric coefficients (d_{33} of about −350 pm/V and d_{31} of about 260 pm/V) comparable to those of ceramics can be achieved [20]. These results suggest that irradiation may be an effective method for improving the performance of copolymer-based transducers and actuators. Another important finding is that the irradiated P(VDF-TrFE) copolymers exhibit many features similar to those observed in relaxor ferroelectrics, including frequency dispersion of the relative permittivity [14,16,17].

Zhang and co-workers [17,19] also found that it was more difficult to transform P(VDF-TrFE) copolymers with higher VDF content into relaxor ferroelectrics. For example, they were not able to convert copolymers with 70 or higher mol % of VDF into relaxors by irradiation with 2.55 MeV electrons even at elevated temperatures (up to 120°C). One possible reason is that copolymers with higher VDF content exhibit stronger ferroelectricity because the VDF unit has a larger dipole moment than the TrFE unit. Thus a higher irradiation fluence (number of electrons injected on a unit area of the target) would be required to convert a normal ferroelectric copolymer into a relaxor ferroelectric.

We have previously found that P(VDF-TrFE) copolymer with 80 mol % of VDF can be converted into a relaxor by irradiating with a 200 Mrad dosage of 3 MeV protons [21]. The reason why protons are more effective than electrons may be understood as follows. In the irradiation process, energetic charged particles enter and move through the polymer and transfer their kinetic energy to the surrounding atoms as they interact with the electrons and nuclei of the host polymer. These interactions and subsequent energy deposition result in various physical and chemical processes including electronic excitation, ionization, radical formation, molecular emission, unsaturated double and triple bond formation, crosslinking and chain scission [22]. Property changes of the polymer depend upon these physical and chemical processes, which are ultimately related to how a particle dissipates its energy. The term "linear energy transfer" (LET) is generally used to describe the energy deposition per unit path by a charged particle (eV/nm). We calculated the LET using the Monte Carlo simulation code *Transport of Ions in Matter* (TRIM) [23] and found a LET of about 19 eV/nm, which results predominantly from ionizing (elec-

tronic stopping) collisions. On the other hand, the LET for an electron with energy in the MeV range is 0.2−0.36 eV/nm [24], almost two orders of magnitude smaller than that of a 3 MeV proton. This may be the reason why, in the MeV range, protons are more effective than electrons in modifying the structure and properties of P(VDF-TrFE) copolymers.

As mentioned earlier, we have successfully transformed normal ferroelectric P(VDF-TrFE) with 80 mol% VDF into a relaxor ferroelectric possessing ultrahigh electrostrictive response by irradiating with 3 MeV protons at a dosage of 200 Mrad [21]. It is interesting to demonstrate the effectiveness of proton irradiation on P(VDF-TrFE) copolymers of other compositions. In this paper, we report the work on P(VDF-TrFE) 56/44 mol% copolymer irradiated with 3 MeV protons at dosages ranging from 43 to 200 Mrad. The effects of irradiation on the lattice spacing, phase transition behavior, polarization hysteresis, relative permittivity properties and electrostrictive strain response will be reported.

2 EXPERIMENTAL

Copolymers of vinylidene fluoride and trifluoroethylene [P(VDF-TrFE)] with the composition 56/44 mol% were studied in this work. P(VDF-TrFE) was supplied in pellet form by Piezotch Co., Saint Louis, France. Circular copolymer films with diameter of 25 mm were fabricated by compression molding at 210°C under a load of 3 metric tons. Copolymer films were then annealed at 120°C for 2h in order to improve the crystallinity.

The copolymer films were irradiated with 3 MeV protons (H^{+} ion) in a Tandetron 4120-LC accelerator (HV Engineering Europa B.V., Netherlands) at ambient temperature and at a pressure of 1.3×10^{-4} Pa. A low beam current at a level of about 0.01 mA/m^2 was used during the irradiation process in order to prevent excessive temperature increase in the films. The proton fluences were in the range of 2.58 to 11.91×10^{17} ions/m^2. The proton dosage was calculated to be in the range of 43 to 200 Mrad. Using the TIRM program the penetration depth was found to be about 90 μm. To ensure that the proton beam has passed through the copolymer films, the film thickness used in the present study was between 30 and 60 μm.

X-ray diffraction measurements were performed at room temperature using an X-ray diffractometer with nickel-filter CuKα irradiation (X'pert System, Philips Electronic Instruments). The thermal measurement was carried out using a differential scanning calorimeter (Perkin Elmer DSC 7) at a scanning rate of 10°C/min under nitrogen atmosphere. For the characterization of the polarization behavior, relative permittivity property and field-induced strain response, circular aluminum electrodes of 3 mm diameter and 150 nm thickness were evaporated on both surfaces of the copolymer film. The polar-

ization-electric field (P-E) hysteresis loop was obtained at room temperature using a Sawyer-Tower circuit [25] at a frequency of 10 Hz. The relative permittivity property was studied as a function of temperature using an impedance analyzer (HP4194A), and the measuring frequency ranged from 1 kHz to 10 MHz. The strain along the thickness direction induced by an electric field applied along the same direction was measured by a heterodyne laser interferometer [26] at a frequency of 10 kHz.

3   RESULTS AND DISCUSSION
3.1   XRD CHARACTERIZATION

P(VDF-TrFE) copolymer is semi-crystalline and consists of crystallites embedded in an amorphous matrix. Most ferroelectric-related properties, such as polarization and electromechanical response, observed in the copolymer arise from the crystalline regions. Therefore, it is interesting to monitor the structural change in the crystalline regions of the irradiated copolymer films with proton dosage in order to explain the outstanding behavior observed in these films. The X-ray diffraction patterns of the (200)/(110) reflection peak obtained from the unirradiated and irradiated P(VDF-TrFE) copolymers at room temperature are presented in Figure 1. The unirradiated 56/44 copolymer exhibits two partially overlapping peaks at 18.8° and 19.23° which are associated with lattice spacing d of 4.71×10^{-10} m (4.71 Å) and 4.60 Å, respectively. The peak at 18.8° is attributed to the hexagonal packing of the 3/1 helical conformations while the peak at 19.23° arises from the presence of disordered ferroelectric β phase (polar phase) [27]. Upon irradiation to a dosage of 43 Mrad, a single peak is observed at 18.46°; this is associated with a lattice spacing ($d = 4.80$ Å) close to that of the paraelectric (nonpolar) phase determined from the X-ray data obtained above the Curie temperature of the unirradiated copolymer [27,28]. With further increase in proton dosage, the diffraction peak shifts to a slightly lower angle and becomes sharper.
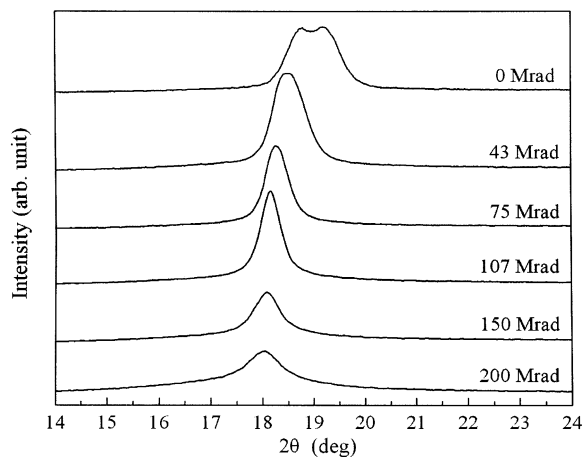
Figure 1. (200/110) X-ray diffraction peak of copolymer films irradiated with different proton dosages.
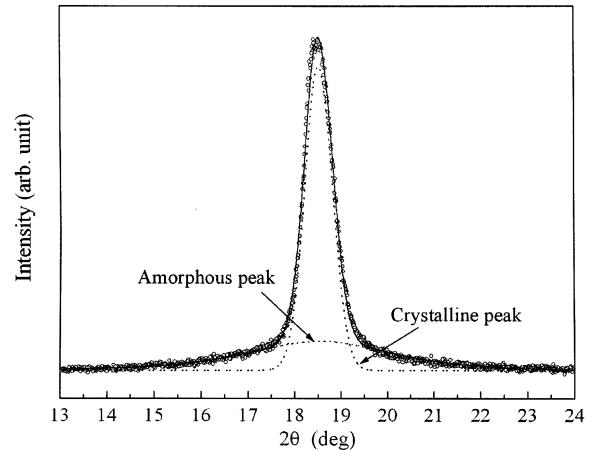
Figure 2. Separation of the observed X-ray diffraction pattern into crystalline and amorphous peaks for copolymer film irradiated with a dosage of 43 Mrad. The open circles are the experimental data and the solid line is the fitted curve.
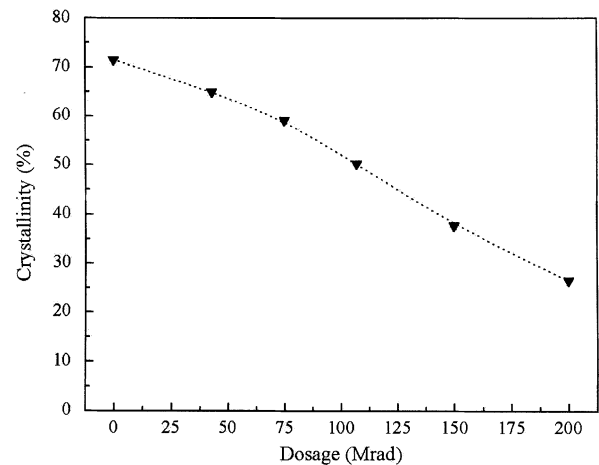
Figure 3. Change in the crystallinity with the proton dosage calculated from X-ray data.

To evaluate the degree of crystallinity X_c of the irradiated copolymers, the observed diffraction peak for the irradiated copolymers is separated into one amorphous peak and one crystalline peak, as exemplified in Figure 2. Each of the peaks is described by a Gaussian function and a least-square fit to the observed diffraction pattern is performed. X_c is then obtained by dividing the area under the corresponding crystalline peak by the total area under all the peaks. It should be noted that as the unirradiated copolymer exhibits two closely spaced peaks, the observed diffraction pattern is separated into one amorphous peak and two crystalline peaks [29]. As shown in Figure 3, the crystallinity X_c decreases steadily as the dosage increases, indicating that some of the crystalline regions are converted into amorphous regions.

3.2   DSC ANALYSIS

To study the effect of proton irradiation on the transition behavior of the copolymer, DSC measurements were carried out and the results are presented in Figure 4. The
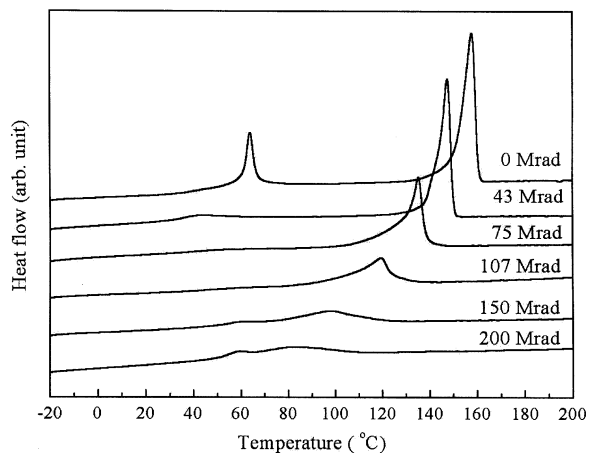
Figure 4. DSC thermograms in the first heating run for copolymer films irradiated with different proton dosages.

un-irradiated copolymer shows a typical DSC curve for copolymer of this composition. The endothermic peak at lower temperature (about 65°C) upon heating is attributed to a structural phase transition in the crystallites, at which the orthorhombic all-trans chain conformation of the ferroelectric phase transforms to the less ordered hexagonal paraelectric phase with TT, TG and TG′ sequence [30]. The other endothermic peak at 158°C corresponds to the melting of crystallites. After irradiation, both peaks shift to lower temperature and are reduced in amplitude. It is seen that the ferroelectric-paraelectric transition peak changes significantly with the proton dosage. At a dosage of 75 Mrad, the ferroelectric transition peak disappears but the melting peak can still be observed, indicating that the polar order is more seriously affected than the crystalline order.

3.3 RELATIVE PERMITTIVITY BEHAVIOR

The temperature dependence of the relative permittivity ϵ_r at 1 kHz for the copolymer as a function of proton dosage is shown in Figure 5. For the un-irradiated copoly-
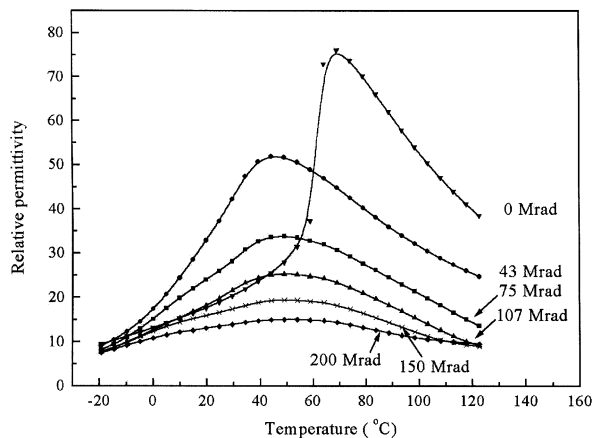

Figure 5. Relative permittivity ϵ_r measured at 1 kHz as a function of temperature for copolymer films irradiated with different proton dosages.

mer, the relative permittivity exhibits a peak at about 70°C, which is associated with the ferroelectric-paraelectric phase transition. After irradiation to 43 Mrad, the peak shifts to a lower temperature (about 45°C). As the proton dosage further increases, the peak temperature remains unchanged but the peak broadens and its amplitude is reduced progressively, indicating the disappearance of the
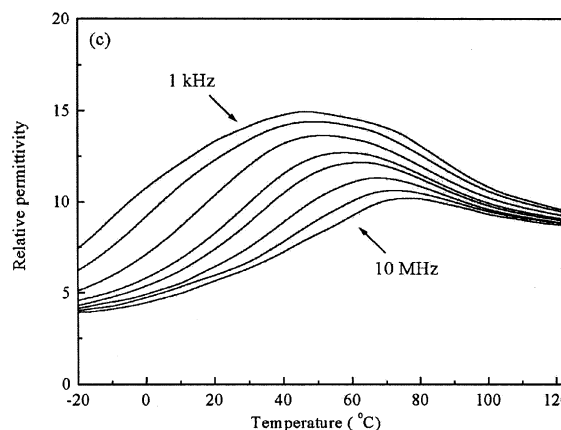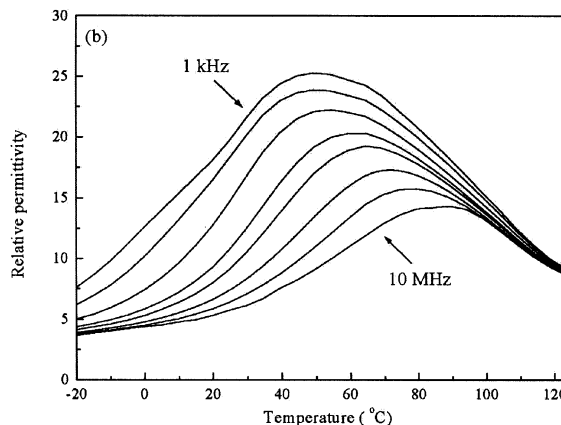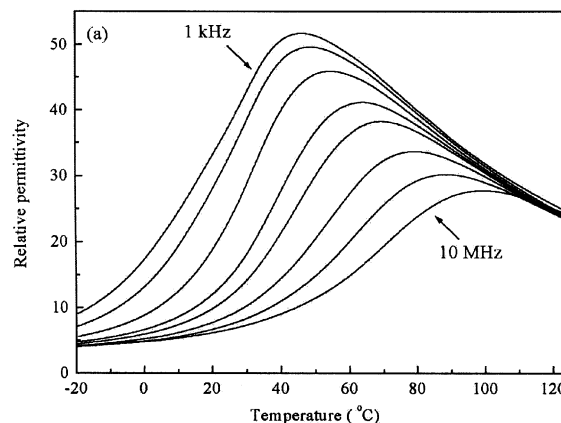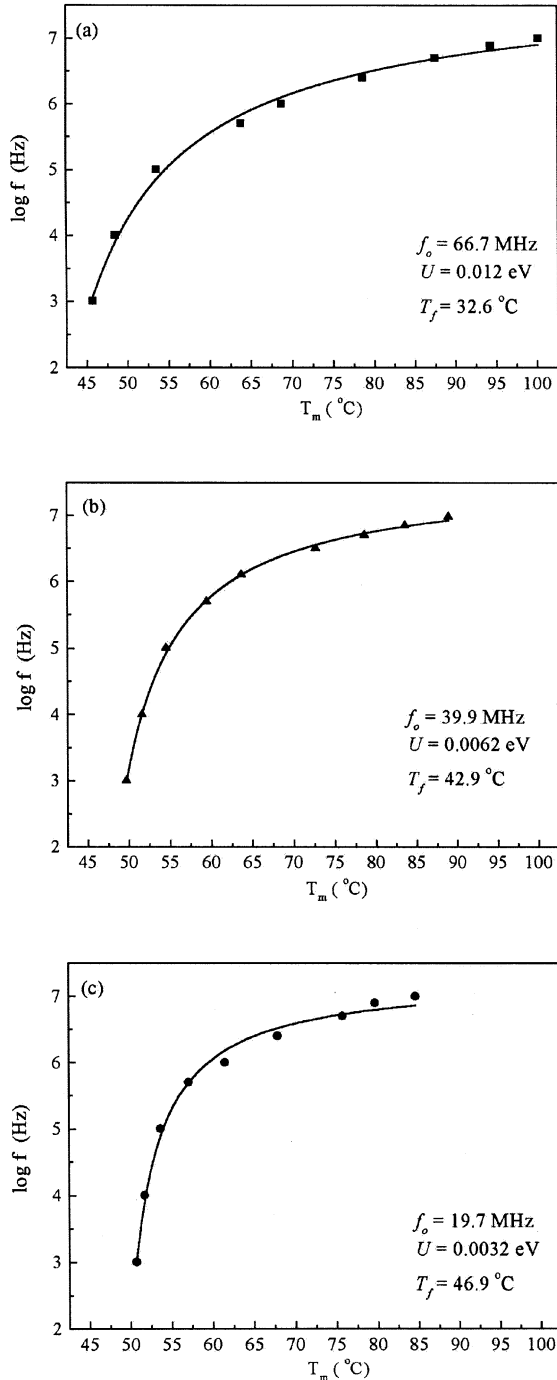

Figure 6. Relative permittivity as a function of temperature for copolymer films irradiated with different dosages. a, 43 Mrad; b; 107 Mrad; c, 200 Mrad. The measuring frequency is (from top to bottom) 1 kHz, 10 kHz, 100 kHz, 500 kHz, 1 MHz, 2.5 MHz, 5 MHz and 10 MHz.

phase transition. The relative permittivities of the irradiated copolymer films at various frequencies are shown in Figure 6. The irradiated 56/44 copolymer exhibits a strong dispersion in the relative permittivity. The peak temperature T_m of the relative permittivity shifts to a higher temperature when the measuring frequency increases. As shown in Figure 7, the dispersion of T_m with frequency f

can be described by the Vogel-Fulcher (V-F) law which holds for relaxor ferroelectric materials [31,32]

$$f = f_o \exp \left(\frac{-U}{k \left(T_m - T_f \right)} \right) \qquad (1)$$

where k is the Boltzmann constant, f_o is the Debye frequency, U is the activation energy and T_f is the freezing temperature. It is seen that the parameters (especially the activation energy U) vary significantly with the dosage. The observed changes in U may arise from the changes in the nano-sized regions and the pinning of these regions by defects in the irradiated copolymers.

3.4 POLARIZATION HYSTERESIS

To further evaluate the effect of irradiation on the ferroelectric behavior of the copolymer films, the polarization hysteresis loops for the copolymer films were measured at 10 Hz at room temperature, and the results are presented in Figure 8. The unirradiated copolymer film shows a typical hysteresis loop with a coercive field E_c of about 50 MV/m and remanent polarization P_r of about $6.4\,\mu C/cm^2$. After irradiation, the hysteresis loop becomes slimmer and the polarization level is reduced. Compared to 80/20 copolymer [21], E_c and P_r of 56/44 copolymer decrease much more drastically with the proton dosage. The values of E_c and P_r at an applied field of 100 MV/m are shown in Figure 9. It can be seen that E_c and P_r drop significantly upon irradiation and are close to zero as the dosage increases to 150 Mrad. Both the relative permittivity and polarization data show that the proton irradiation destroys the ferroelectric ordering and breaks the coherent polarization domains into nanopolar regions, thereby converting the normal ferroelectric copolymer into a relaxor ferroelectric at a relatively low dosage (about 75 Mrad). The decrease in the polarization at high proton dosage is due to the reduction in the fraction of crystalline regions in the copolymer films.

Figure 7. Fitting of the Vogel-Fulcher law to the relative permittivity data for copolymer films irradiated with different dosages. a, 43 Mrad; b, 107 Mrad; c, 200 Mrad. The symbols are the experimental data and the solid line is the fitted curve.
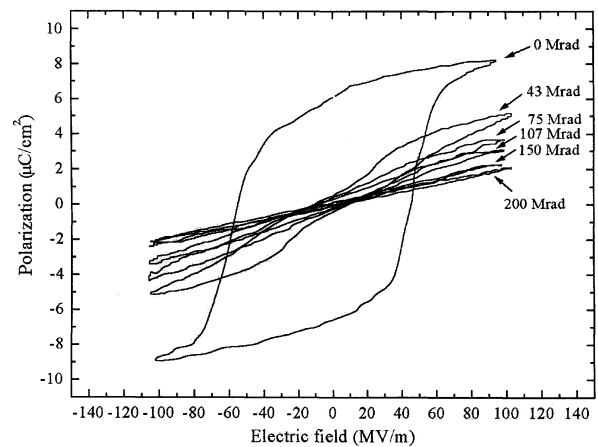

Figure 8. Polarization hysteresis loops for P(VDF-TrFE) 56/44 copolymer film irradiated with different proton dosages.
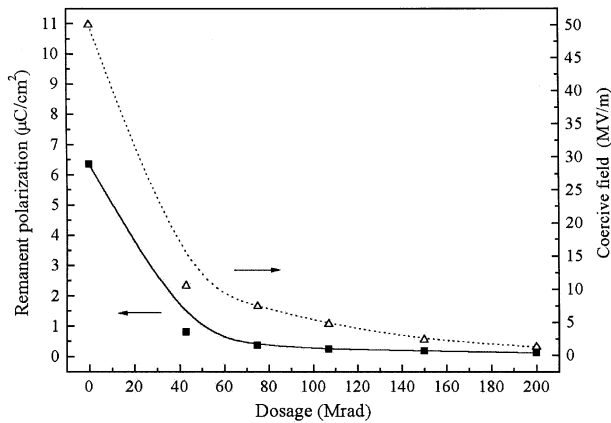
Figure 9. Variation of remanent polarization P_r and coercive field E_c under electric field of 100 MV/m with different proton dosages.

3.5   ELECTROSTRICTIVE STRAIN RESPONSE

The electrostrictive strain S under an electric field E_3 is given by [33]

$$S = M_{33}E_3^2 \qquad (2)$$

where M_{33} is the electrostrive coefficient and the displacement is in the same direction (3 direction) as the electric field. If an ac field is applied,

$$E = E_o\cos(\omega t) \qquad (3)$$

$$E^2 = \frac{1}{2}E_o^2(1 + cos\, 2\,\omega t) \qquad (4)$$

Therefore, the relation $S = ME^2$ can be rewritten as

$$S = \frac{1}{2}ME_o^2 + \frac{1}{2}ME_o^2(\cos 2\,\omega t) \qquad (5)$$

The first term on the right of equation (5) represents a steady strain. In the present study, the field-induced strain was measured using an interferometer in which the steady strain is compensated by a feedback arrangement, and hence only the varying strain (the second term in equation (5)) was measured. The field-induced longitudinal strain S for the unirradiated and irradiated copolymer was measured at 10 kHz and plotted as a function of the square of the applied field E^2 (Figure 10). The M_{33} coefficient can then be determined from the slope of the curves shown in Figure 10. The change in the M_{33} coefficient of the copolymer film is shown as a function of proton dosage in Figure 11. Upon irradiation, the M_{33} coefficient increases and attains a maximum value of 1.5×10^{-18} m²/V² at a dosage of 75 Mrad. Comparing with the M_{33} coefficient of the unirradiated copolymer, M_{33} is improved by a factor of five through the irradiation process. Based on the X-ray diffraction results mentioned above, the nano-sized crystalline regions of the irradiated copolymer are in the nonpolar phase. As the lattice constant of nonpolar phase is much larger than that of the polar phase, the electric field
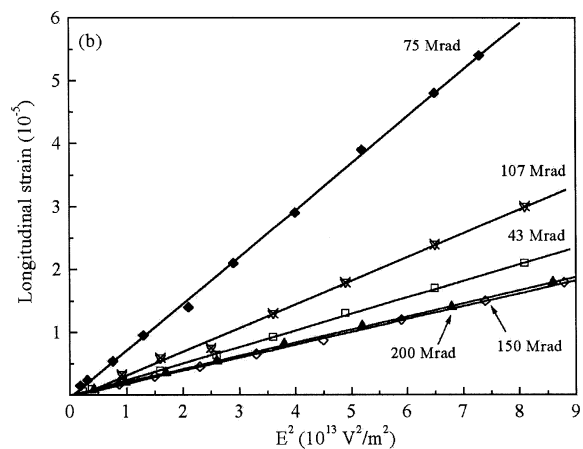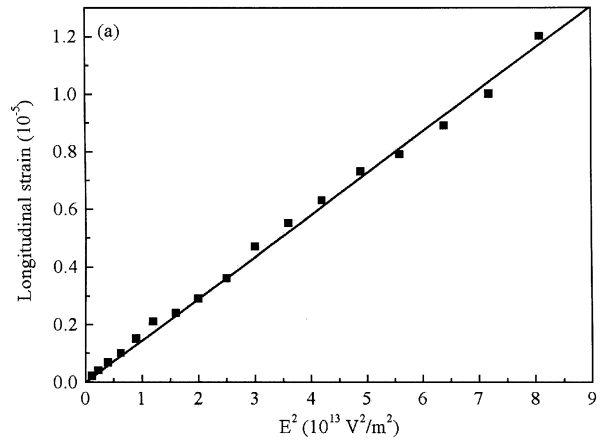

Figure 10. Field-induced strain measured at 10 kHz as a function of the square of the applied field. a, unirradiated copolymer; b, unirradiated copolymers irradiated with different proton dosages.
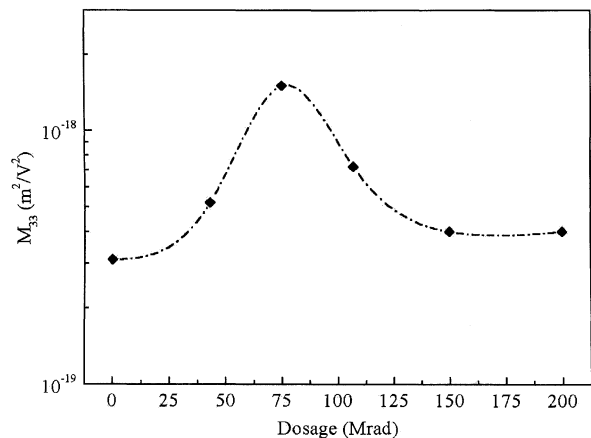

Figure 11. Change in the electrostrictive coefficient M_{33} with proton dosages for P(VDF-TrFE) 56/44 copolymer films.

induced transformation between the nonpolar and polar phase leads to the greatly increased M_{33} observed in the irradiated copolymer. However, M_{33} decreases at the dosages above 75 Mrad. This may arise because the volume fraction of crystalline regions decreases as a result of increasing number of irradiation-induced defects.

4   CONCLUSIONS

THE structure and property changes in high energy (3 MeV) proton-irradiated P(VDF-TrFE) 56/44 mol% copolymers have been investigated. The irradiated copolymers exhibit a slim polarization hysteresis loop with a much reduced polarization level. In addition, a strong dispersion is observed in the relative permittivity of the irradiated copolymer with frequency, which follows the Vogel-Fulcher law. These are the characteristic features of relaxor ferroelectrics, suggesting that the proton irradiation breaks up the coherent polarization domains into nano-sized regions and transforms a normal ferroelectric copolymer into a relaxor. From our previous reports, higher proton dosage (200 Mrad) is required to convert 80/20 mol% copolymer into a relaxor. However, for 56/44 mol% copolymer, the conversion to relaxor is almost complete at a low dosage of 75 Mrad. XRD measurements indicate that nano-size regions are in the nonpolar phase. By applying an external field, a local phase transformation between nonpolar and polar phase is induced and this gives rise to a slim hysteresis loop. Since the lattice spacing of the nonpolar phase is greater than that of the polar phase, this phase transformation also leads to a high electrostrictive response. At 75 Mrad, the irradiated copolymer shows the highest M_{33} coefficient of 1.5×10^{-18} m^2/V^2. However, if the proton dosage is further increased, the volume fraction of crystalline regions in the irradiated copolymer decreases, resulting in a lower strain response.

ACKNOWLEDGMENTS

REFERENCES

[1] P. A. Lewin and M. E. Schafer, "Wide-band Piezoelectric Polymer Acoustic Sources", IEEE Trans. Ultrason., Ferroelec., Freq. Contr., Vol. 35, pp. 175−184, 1988.

[2] G. Gao, Z. Wang and R. Gao, "A PVDF Film Sensor for Material Identification", Sensors and Actuators A: Physical, Vol. 23, pp. 886−889, 1990.

[3] K. W. Kwok, H. L. W. Chan, Y. Zhang and C. L. Choy, "Dual-frequency Transducers Fabricated Using Partially Poled Vinylidene-trifluoroethylene Copolymer", J. Korean Phys. Soc., Vol. 32, pp. S1757−S1759, 1998.

[4] S. Tsuchiya, T. Sato, K. Koyama, S. Ikeda and Y. Wada, "Application of Piezoelectric Film of Vinylidene Fluoride-trifluoroethylene Copolymer to a Sensitive Miniature Hydrophone", Jpn. J. Appl. Phys., Vol. 26 (Suppl. 1), pp. 103−105, 1987.

[5] H. L. W. Chan, A. H. Ramelan, I. L. Guy and D. C. Price, "Piezoelectric Copolymer Hydrophones for Ultrasonic Field Characterization", Rev. Sci. Instrum., Vol. 62, pp. 203−207, 1991.

[6] M. Imai, H. Tanizawa, Y. Ohtsuka, Y. Takase and A. Odajima, "Piezoelectric Copolymer Jacketed Single-mode Fibers for Electric-field Sensor Application", J. Appl. Phys., Vol. 60, pp. 1916−1918, 1986.

[7] H. Kawai, "The Piezoelectricity of Polyvinylidene Fluoride", Jpn. J. Appl. Phys., Vol. 8, pp. 975−976, 1969.

[8] M. Tamura, S. Hagiwara, S. Matsyniti and N. Ono, "Some Aspects of Piezoelectricity and Pyroelectricity in Uniaxially Stretched Poly(vinylidene fluoride)", J. Appl. Phys., Vol. 48, pp. 513−521, 1977.

[9] K. Koga and H. Ohigashi, "Piezoelectricity and Related Properties of Vinylidene Fluoride and Trifluoroethylene Copolymers", J. Appl. Phys., Vol. 59, pp. 2142−2150, 1986.

[10] T. Furukawa, "Structure and Functional Properties of Ferroelectric Polymers", Adv. Colloid Interface Sci., Vol. 71, pp. 183−208, 1997.

[11] J. S. Green, B. L. Farmer and J. F. Rabolt, "Effect of Thermal and Solution History on the Curie Point of VF$_2$-TrFE Random Copolymers", J. Appl. Phys., Vol. 60, pp. 2690−2693, 1986.

[12] G. M. Sessler, "Poling and Properties of Polarization of Ferroelectric Polymers and Composites", Ferroelectric Polymers and Ceramic/Polymer Composite (D.K. Das-Gupta, Ed.), Trans Tech Publications, Switzerland, pp. 249−274, 1994.

[13] A. J. Lovinger, "Polymorphic Transformations in Ferroelectric Copolymers of Vinylidene Fluoride Induced by Electron Irradiation", Macromolecules, Vol. 18, pp. 910−918, 1985.

[14] A. Odajima, Y. Takase, T. Ishibashi and K. Yuasa, "Diffuse Phase Transition in Ferroelectric Polymers and its Irradiation Effect", Jpn. J. Appl. Phys., Vol. 24 (Suppl. 2), pp. 881−883, 1985.

[15] H. N. da Cunha, L.H.C. Mattoso and R. M. Faria, "Effect of X-ray Radiation on the Structure of P(VDF-TrFE) Copolymers", J. Polym. Sci.: Polym. Phys., Vol. 35, pp. 1201−1205, 1997.

[16] B. Daudin, M. Dubus, F. Macchi and J. F. Legrand, "Modification of the Ferrroelectric Properties of Vinylidene Fluoride Trifluoro-ethylene Copolymers Induced by Electron Irradiation", Nuclear Instrum. Methods in Phys. Research B, Vol. 32, pp. 177−181, 1988.

[17] Q. M. Zhang, V. Bharti and X. Zhao, "Giant Electrostriction and Relaxor Ferroelectric Behavior in Electron-irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer", Science, Vol. 280, pp. 2101−2104, 1998.

[18] Z. Y. Cheng, T. B. Xu, V. Bharti, S. X. Wang and Q. M. Zhang, "Transverse Strain Response in the Electrostrictive Poly(vinylidene fluoride-trifluoroethylene) Copolymer", Appl. Phys. Lett., Vol. 74, pp. 1901−1903, 1999.

[19] Z. Y. Cheng, V. Bharti, T. Mai, T. B. Xu, Q. M. Zhang, T. Ramotowski, K. A. Wright and R. Ting, "Effect of High Energy Electron Irradiation on the Electromechanical Properties of Poly(vinylidene fluoride-trifluorethylene) 50/50 and 65/35 Copolymers", IEEE Trans. Ultrason., Ferroelect., Freq. Contr., Vol. 47, pp. 1296−1307, 2000.

[20] Z. Y. Cheng, V. Bharti, X. Zhao, Shexi Wang, T. B. Xu, Q. M. Zhang, "Relaxor Ferroelectric Polymers for Actuators and Transducers", IEEE Ultrasonics Sympos., pp. 581−584, 1998.

[21] S. T. Lau, K. Y. Leung, H. L. W. Chan, C. L. Choy, B. Sundaravel and I. Wilson, "Effects of Proton Irradiation on the Structure and Properties of Poly(vinylidene-trifluoroethylene) 80/20 mol% Copolymer", Ferroelectrics, Vol. 273, pp. 9−14, 2002.

[22] J. L. Magee and A. Chatterjee, Radiation Chemistry: Principles and Applications (Farhataziz and Micheal, A. J. Rogers, Eds), VCH Publishers, Inc., pp. 173−199, 1987.

[23] J. F. Ziegler, J. P. Biersack and U. Littmark, The Stopping and Range of Ions in Solids, New York, Pergamon Press Inc., 1985.

[24] E. H. Lee, G. R. Rao and L. K. Mansur, "Super-hard-surfaced Polymers by High-energy ion-beam Irradiation", Trends in Polymer Science, Vol. 4, pp. 229−237, 1996.

[25] C. B. Sawyer and C. H. Tower, "Rochelle Salt as a Dielectric", Phys. Rev., Vol. 35, pp. 269−273, 1930.

[26] C. M. Leung, H. L. W. Chan, C. Surya, W. K. Fong, C. L. Choy, P. Chow and M. Rosamond, "Piezoelectric Coefficient of GaN Measured by Laser Interferometry", J. Non-crystalline Solids, Vol. 254, pp. 123−127, 1999.

[27] A. J. Lovinger, G. T. Davis, T. Furukawa and M. G. Broadhurst, "Crystalline Forms in a Copolymer of Vinylidene Fluoride and Trifluoroethylene (52/48 mol%)", Macromolecules, Vol. 15, pp. 323−328, 1982.

[28] T. Yamada, T. Ueda and T. Kitayama, "Ferroelectric-to-para-electric Phase Transition of Vinylidene Fluoride Trifluoroethylene Copolymer", J. Appl. Phys., Vol. 52, pp. 948−952, 1981.

[29] M. V. Fernandez, A. Suzuki and A. Chiba, "Study of Annealing Effects on the Structure of Vinylidene Fluoride-trifluoroethylene Copolymers Using WAXS and SAXS", Macromolecules, Vol. 20, pp. 1806−1811, 1987.

[30] A. J. Lovinger, T. Furukawa, G. T. Davis and M. G. Broadhurst, "Crystallographic Changes Characterizing the Curie Transition in Three Ferroelectric Copolymers of Vinylidene Fluoride and Trifluoroethylene: 1. As-crystallized Samples", Polymer, Vol. 24, pp. 1225−1232, 1983.

[31] D. Viehland, M. Wuttig and L. E. Cross, "The Glassy Behavior of Relaxor Ferroelectrics", Ferroelectrics, Vol. 120, pp. 71−77, 1991.

[32] A. K. Tagantsev, "Vogel-Fulcher Relationship for the Dielectric Permittivity of Relaxor Ferroelectrics", Phys. Rev. Letts., Vol. 72, pp. 1100−1103, 1994.

[33] J. F. Nye, *Physical Properties of Crystal: Their Representation by Tensors and Matrices*, London, England: Oxford University Press, pp. 78−189, 1957.

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