Structural evolution and dielectric relaxation behavior of electron-irradiated poly(vinylidene fluoride–trifluoroethylene) 80/20 mol% copolymers

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The effect of high-energy electron irradiation on poly(vinylidene fluoride-trifluoroethylene) 80/20 mol% copolymers has been studied in a broad dose ranging from 0 to 120 Mrad. It was found that the copolymers transformed from a normal ferroelectric to a relaxor ferroelectric phase (RFE) at high electron doses. For copolymers irradiated at the dose above 90 Mrad, they exhibited typical dielectric behavior of RFE, e.g., whose dielectric constant peaks show strong frequency dispersion. X-ray diffraction patterns showed that the irradiation induced a coexistence of the polar and nonpolar phase in the crystalline regions, leading to nanosized coherent regions in the irradiated copolymer films. Differential scanning calorimetery and polarization hysteresis loops also revealed the reduction in the crystallinity and stability of the ferroelectric state, reflecting significant changes in the ferroelectric-to-paraelectric phase transition due to the effect of high-energy electron irradiation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1606853]

I. INTRODUCTION

Copolymers of vinylidene fluoride–trifluoroethylene [P(VDF–TrFE)] are normal ferroelectrics which exhibit typical ferroelectric-to-paraelectric $(F-P)$ phase transitions below the melting point for the compositions with VDF content in between 50 and 82 mol%.[1] Recent research on P(VDF–TrFE) copolymers found that high-energy irradiation with proper dose can effectively modify the electromechanical properties of these copolymers.[2–5]

Lovinger found that electron irradiation could change the ferroelectric β phase to a paraelectric-like structure at room temperature in P(VDF–TrFE) copolymers in both intramolecular and intermolecular fashions.[6] For the copolymer with more VDF content, higher irradiation dose was required for this phase transformation. More recently, Zhang *et al.* found that after irradiated by 1.2–3.0 MeV electrons, P(VDF–TrFE) 50/50, 65/35, and 68/32 mol% copolymers exhibited exceptionally high electrostrictive responses, so it was of great interest in using these irradiated copolymers for high performance electromechanical devices.[7–10] In addition, the dielectric constant of irradiated copolymers exhibited strong frequency dispersion which can be fitted well by the Vogel–Fulcher (VF) law that holds for RFE.[11,12] The VF law

is an empirical relation that can describe temperature dependence of relaxation time observed in many glass systems and in relaxor ferroelectric (RFE) ceramics. This implied that the copolymers could be converted from normal ferroelectrics to RFE upon the irradiation process.[13–15]

From our previous report, we found that P(VDF–TrFE) 80/20 mol% copolymers can exhibit high strain response with a high electrostrictive constant under a proper electron irradiation.[16] In this article, we report that 80/20 copolymer can be completely converted from a normal ferroelectric to a RFF by means of varying the defect concentration introduced by 3.0 MeV electrons. The experimental results in this study were obtained by x-ray diffraction (XRD), differential scanning calorimetery (DSC), dielectric measurement, and polarization hysteresis measurement over a broad electron dose ranging from 0 to 120 Mrad.

II. EXPERIMENT

The random copolymers of P(VDF–TrFE) used in this study had a comonomer ratio, VDF/TrFE, of 80/20 mol%, which was supplied in powder form by Piezotech Co., France. The copolymer powder was first dissolved in dimethylformamide solvent by stirring at 50 °C. Thin copolymer films with thickness of about 20–30 μm were then fabricated by solution casting on a glass substrate. The copolymer films were annealed at 120 °C for 12 h to remove residual solvent.

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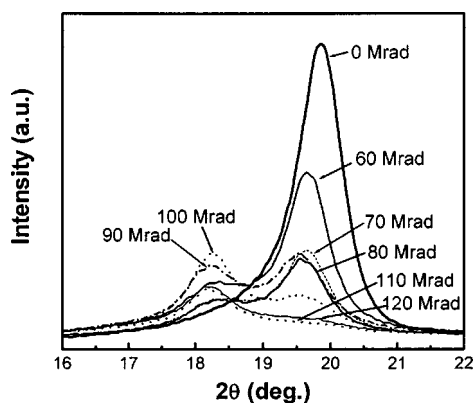
FIG. 1. The (110) and (200) x-ray diffraction peaks of P(VDF–TrFE) 80/20 mol % as a function of electron dose at room temperature. From bottom curve to top curve, the corresponding doses are 0, 60, 70, 80, 90, 100, 110, and 120 Mrad, respectively.

To further improve the crystallinity, the films were annealed at higher temperature (135 °C) for 2 h. The irradiation process was carried out in air ambient with 3 MeV electrons using a BF-5 electron-beam accelerator. The irradiation rate was set at $\sim 10^4$ rad/s. As the irradiation process proceeded, the sample temperature increased at a rate of about 20 °C/h due to the collision of electrons. The electron dose used in this work was set from 0 to 120 Mrad. After irradiation, a chromium/gold (Cr/Au) electrode with thickness of about 0.1 μm was sputtered on both surfaces of the film for subsequent electrical characterizations.

The dielectric constant and loss dependence of temperature ranging from -60 to 140 °C were evaluated using an impedance/gain-phase analyzer (HP 4194A), equipped with a temperature chamber (Delta 9023). The polarization hysteresis loops were acquired by a computer-controlled automatic system based on a modified Sawyer–Tower circuit and a sinusoidal wave with a frequency of 10 Hz was used. DSC was performed with a Perkin–Elmer DSC7 thermal analyzer at a heating rate of 10 °C/min from 0 to 170 °C. XRD measurement was carried out using an x-ray diffractometer with nickel filter Cu $K\alpha$ irradiation (D8 Advance, Bruker analytical x-ray system) at a scanning speed of 0.005° 2θ/s.

III. RESULTS AND DISCUSSION

A. X-ray results

It is well-known that P(VDF–TrFE) copolymer is a semicrystalline polymer, i.e., there are crystalline lamellae imbedded in an amorphous matrix.[17,18] The room temperature x-ray diffraction patterns of the copolymer films with the dose of irradiation from 0 to 120 Mrad are shown in Fig. 1. P(VDF–TrFE) have an orthorhombic unit cell in the crystalline phase in which the lattice a and b axes are perpendicular to the chain. Because the ratio of the lattice constants of the unit cell along the two axes is close to $\sqrt{3}$, the lattice has a quasihexagonal structure, resulting in the overlap of the (110) and (200) reflections.[19] For the unirradiated copolymer film, only a single narrow reflection peak at $2\theta=19.8°$ is observed, corresponding to the all-*trans* ferroelectric phase (polar phase). After irradiation, a broad peak at $2\theta=18.2°$

grows at the expense of the narrow peak of the polar phase, corresponding to the *trans–gauche* paraelectric phase (nonpolar phase). As can be seen, the relative intensity of the peak associated with the polar phase subsides and the one associated with the nonpolar phase increases with the dose. Furthermore, the peak position of polar phase moves to a slightly lower angle, indicating a continuous expansion in the lattice dimension occurred in the ferroelectric domain. After irradiated by a dose of 100 Mrad, the polar phase becomes a shoulder beside the nonpolar phase, indicating a strong intrachain coupling between the two phases. The data revealed that the polar and nonpolar phases coexisted in the same crystalline regions after irradiation. As will be seen later, the two-phase coexistence and the reduction of crystallinity will influence the dielectric behavior of the copolymer films significantly.

Presented in Fig. 2 are the typical x-ray diffraction spectra at different temperatures for copolymers irradiated with doses of 0, 60, 90, and 120 Mrad. As can be seen, the peak width of the paraelectric phase (nonpolar phase) becomes quite narrow as the temperature increases. The ferroelectric phase (polar phase) decreases showing that the nonpolar phase is dominant in the copolymer at high temperature. In an unirradiated copolymer sample, the polar phase was totally converted to nonpolar phase at a high temperature of 140 °C. However, for the irradiated samples with different irradiation doses (60 and 90 Mrad), the nonpolar phase increased at the expense of the polar phase in the whole temperature range, indicating two-phase coexistence in the irradiated copolymer as revealed by x-ray data at room temperature. Eventually, there is no obvious change of transition occurred in the sample with a high dose of 120 Mrad, because of more amorphous phase induced by the irradiation. It is interesting to note that the position of the x-ray diffraction data shifts slightly, indicating that both the interchain spacing and crystalline size are affected by the irradiation.

We can estimate the size of the coherent x-ray reflection region D_{hkl} by the Scherrer equation[20]

$$D_{hkl}=\frac{0.9\lambda}{B\cos\theta}$$

where λ is the x-ray wavelength (Cu $K\alpha$, 1.5406 Å), B is the full width at half maximum of the reflection peak (hkl), and θ is the peak position. The D_{hkl} in the polar phase is determined by the polarization domain size while in the non-polar phase it corresponds to the crystallite size. Coherent size $D_{200,110}$ and interchain spacing $d_{200,110}$ dependence of temperature are shown in Figs. 3(a)–3(d) for different irradiation doses. The data show that both the polar and nonpolar $d_{200,110}$ ($2 d_{200,110}\sin\theta=\lambda$) exhibit a slight increase with temperature because the peaks shifted to lower reflection angles in the x-ray measurements. On the other hand, the crystallite size perpendicular to the polymer chain (nonpolar phase) has a trend to increase, especially for unirradiated sample (nearly four times larger than the polar $D_{200,110}$). Correspondingly, the polar $D_{200,110}$ shows a decrease with temperature for irradiated samples. For the irradiated copolymers with the dose of 90 Mrad, a continuous increase of nonpolar $D_{200,110}$ from 9.1 nm (25 °C) to 20.4 nm (100 °C)
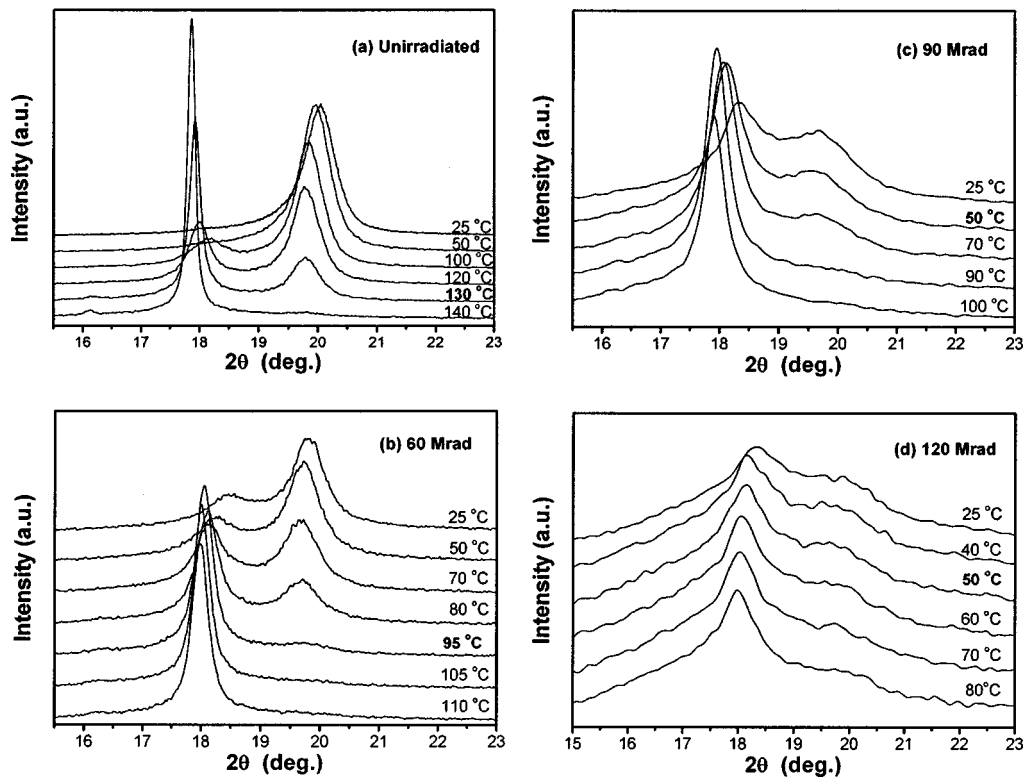
FIG. 2. Temperature dependence of (110) and (200) x-ray diffraction peaks for copolymers with different doses: (a) unirradiated film, (b) 60 Mrad, (c) 90 Mrad, and (d) 120 Mrad. The bold-typed temperature in each figure is the $F-P$ transition temperature found by DSC.

was observed comparing to the decrease in polar $D_{200,110}$ from 6.9 nm (25 °C) to 2.4 nm (100 °C). At high irradiation dose (120 Mrad), $D_{200,110}$ for polar domain has a value less than 5 nm, indicating a similar critical domain size for un-

stable ferroelectric phase. It should be noted that the results coincide with those obtained in P(VDF–TrFE) 68/32 mol % by Cheng *et al.*, which also show two-phase coexistence and a critical domain size of about 5 nm for unstable ferroelectric
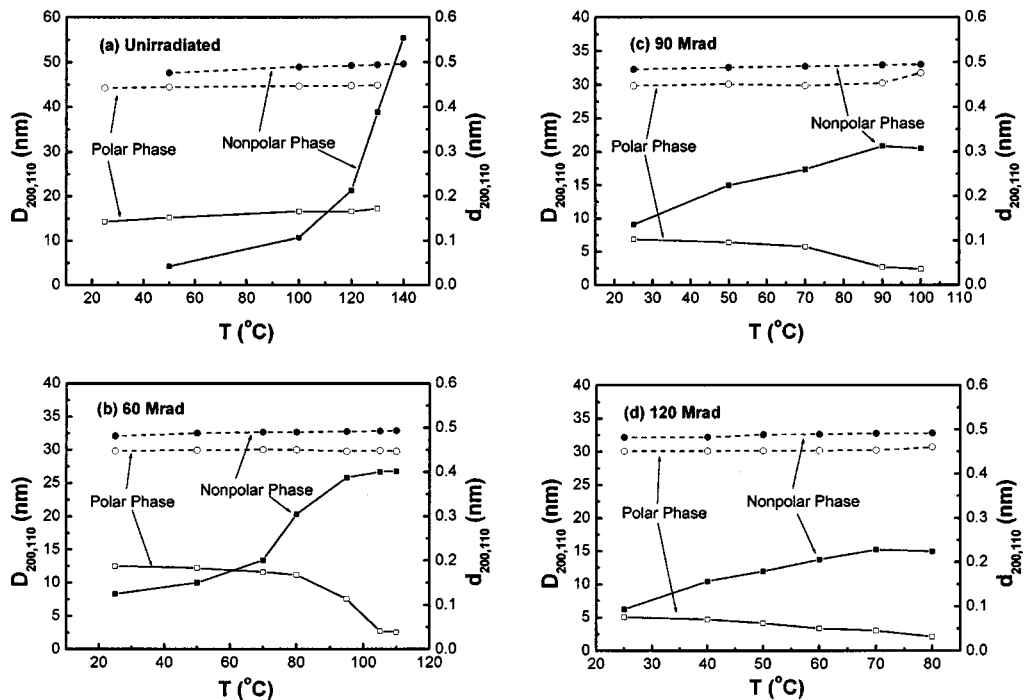

FIG. 3. Temperature dependence of crystalline size $D_{200,110}$ (solid line) and interchain spacing $d_{200,110}$ (dotted line) with a dose of: (a) 0 Mrad, (b) 60 Mrad, (c) 90 Mrad, and (d) 120 Mrad.
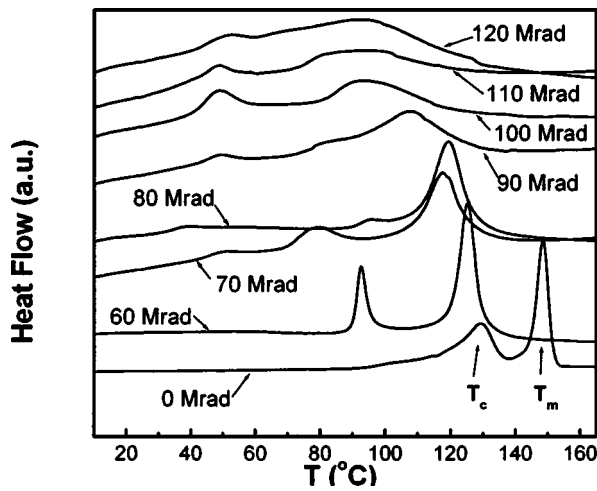
FIG. 4. DSC thermograms of unirradiated and irradiated P(VDF–TrFE) 80/20 mol % copolymers during the heating process.
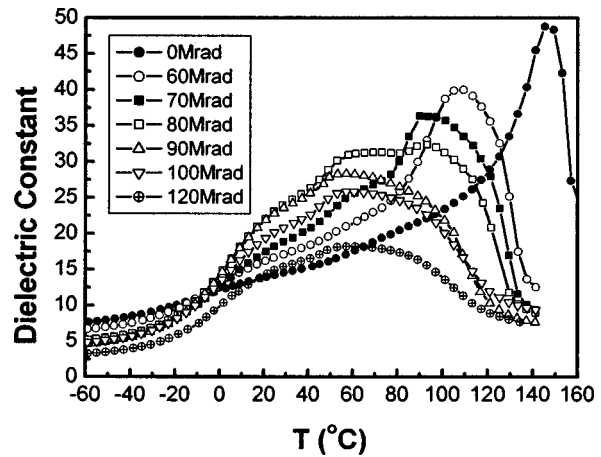

FIG. 5. Dielectric constant measured at 10 kHz as a function of temperature during the heating process for P(VDF–TrFE) 80/20 mol % copolymer films with the dose of 0, 60, 70, 80, 90, 100, and 120 Mrad.

phase after electron irradiation.[21] The change of D_{hkl} contributes to a lattice expansion perpendicular to the chain and contraction along the chain, respectively. It is reasonable to believe that the changes of lattice may contribute to the large electrostrictive response observed in these irradiated copolymers.

B. Differential scanning calorimetery (DSC) results

Figure 4 and Table I are the DSC results for copolymers with various electron irradiation doses in the heating run. Two endothermic peaks are associated with the ferro–paraelectric ($F-P$) phase transition temperature T_c and melting temperature T_m of the crystalline region with the values of 129.2 and 148.4 °C, respectively.[22] After irradiation, both T_c and T_m shift to lower temperatures with the increase in dose. The original $F-P$ transition nearly disappears beyond 120 Mrad, indicating the elimination of the crystalline phase in the samples due to electron irradiation.

Irradiation can cause lattice defects and crosslinking in the copolymer films, while the lattice defects and the reduction of the crystallinity due to the conversion of crystallites to amorphous phase can lead to the decrease of crystal ordering in the irradiated films.[15] Furthermore, the decrease of the enthalpy (Table I) at the melting temperature indicates the reduction of the crystallinity and the reduction of the

TABLE I. DSC data of melting temperature T_m, $F-P$ transition temperature T_c, melting enthalpy ΔH_m, and phase transition enthalpy ΔH_c dependence of dose for P(VDF–TrFE) of 80/20 mol % copolymers during the heating process.

Dose (Mrad)	T_c (°C)		T_m (°C)	ΔH_c (J/g)		ΔH_m (J/g)
0	129.19		148.39	25.17		29.37
60	92.47		125.02	5.56		18.59
70	78.42	50.22	117.55	1.02	3.49	13.66
80	94.91	39.23	119.37	1.19	0.17	13.88
90	81.8	48.62	108.4	1.67	0.04	6.84
100	48.2		94.66	2.48		6.11
110	48.12		94.45	2.3		7.09
120	51.16		95.09	0.75		7.66

enthalpy at T_c indicates the decrease of the average size of the polar crystalline phase. So the DSC data show a broad distribution in the crystallite size and reduction in the crystal ordering after high-energy electron irradiation. 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 peak and enthalpy dispersion, which may explain the apparent lowering and broadening of the melting and $F-P$ transition peaks. It is noted that two small T_c peaks were observed in the DSC curves of the samples irradiated with 70–90 Mrad.

C. Dielectric behaviors

The dielectric constants of P(VDF–TrFE) 80/20 mol % copolymer films were measured as a function of temperature at a rate of 4 °C/min. All the data were taken as the films were heated up from −60 °C. Figure 5 presents the dielectric constants of unirradiated and irradiated copolymer films at 10 kHz. It can be seen that the dielectric constant peak becomes broadened and decreases with the electron dose. Just as expected, the temperature of the dielectric constant maximum T_p shifts to lower temperature after irradiation at various doses. These are typical characters for the irradiated P(VDF–TrFE) copolymers with a low VDF content and the results observed here also corresponds to first-order transitions.[23] It is suggested that the P(VDF–TrFE) 80/20 mol % copolymer films have the possibility of transition from normal ferroelectric to a relaxor ferroelectric if they are subjected to a proper high-energy irradiation.

In order to study the transition from normal ferroelectric to relaxor ferroelectric phases, dielectric data of different irradiated copolymer films were measured. Figures 6(a)–6(f) show the dielectric constant of films with different irradiation doses at different frequencies. With increasing frequency, the peak related to the $F-P$ transition also becomes broader and decreases with the dose. The changes of dielectric constant peak were contributed by the coexistence of polar and nonpolar phase discussed above. It is interesting to point out that there is no obvious shifting in T_p for the irradiated copoly-
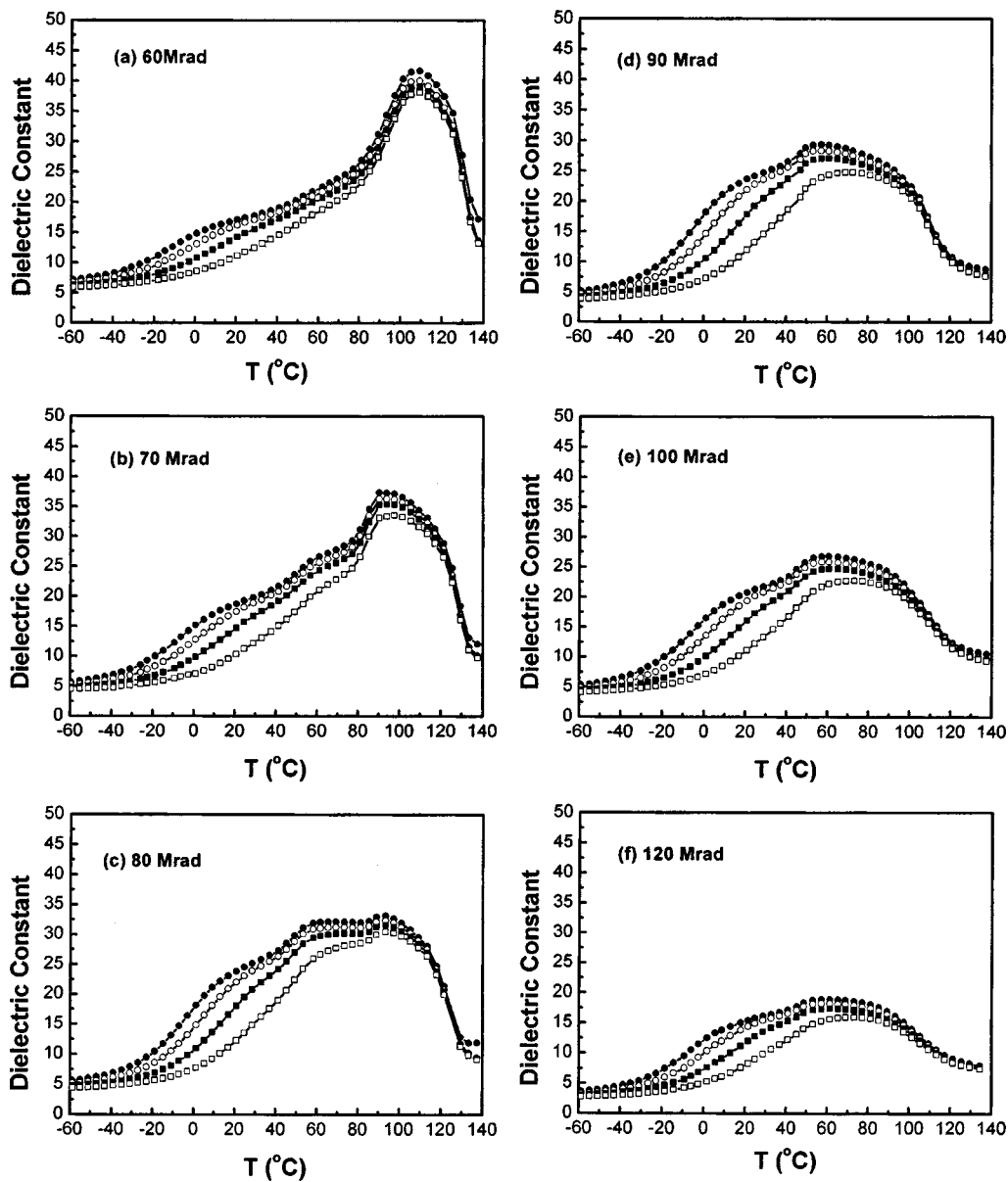
FIG. 6. Dielectric constant at different frequencies vs temperature for irradiated copolymer films during the heating process. The electron doses are: (a) 60 Mrad, (b) 70 Mrad, (c) 80 Mrad, (d) 90 Mrad, (e) 100 Mrad, and (f) 120 Mrad. From top to bottom, the frequencies are 1 kHz (-●-); 10 kHz (-○-); 100 kHz (-■-), and 1 MHz (-□-).

mer films up to 90 Mrad irradiation as shown in Figs. 6(a)–6(c), which indicates that it is more difficult to convert the normal ferroelectric to the relaxor ferroelectric phase in P(VDF–TrFE) with a high VDF content like 80 mol % copolymers. However, with further increase of irradiation doses, as illustrated in Figs. 6(d)–6(f) for films irradiated with 90 Mrad or above, T_p gradually moves to higher temperatures as the frequency increases. These experimental results are typical features of relaxor ferroelectrics.[24] Therefore, it is reasonable to believe that P(VDF–TrFE) 80/20 mol % copolymer films can be transformed from a normal ferroelectric to a RFE with the high-energy electron irradiation dose of 90 Mrad or above. However, at the higher dose of 120 Mrad, the copolymer films will lose most of the crystallinity and show a very low dielectric constant, indicating that more contribution comes from the amorphous phase in

the whole temperature range. In addition, the reduced crystallite size as revealed by x-ray data in the irradiated copolymer films also can reduce the range of the dipolar coupling.[23] So they exhibit a weaker VF relaxation during the ferroelectric to RFE transition as the dose increases.

The VF law can be used to describe the relaxor behavior in these irradiated P(VDF–TrFE) 80/20 mol % copolymer films. The relation between the frequency f and T_p of the relaxor ferroelectric is given by[25]

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

where U is a constant related to the activation energy, k is the Boltzmann constant, f_0 is a constant associated with the relaxation frequency, and T_f can be interpreted as the freezing
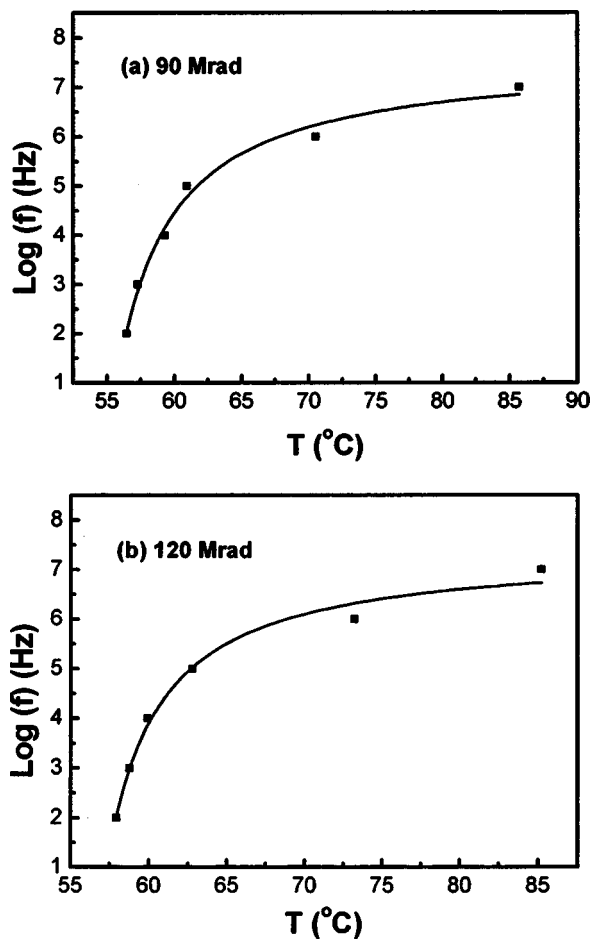
FIG. 7. The fitted results of the relation between f and T_p for P(VDF–TrFE) 80/20 mol % copolymer films irradiated at: (a) 90 Mrad and (b) 120 Mrad. The solid symbols are the experimental results and the solid line is the fitted one.

FIG. 8. Dielectric loss (tan δ) vs temperature for irradiated copolymer films of: (a) 90 Mrad and (b) 120 Mrad at 1 kHz, 10 kHz, 100 kHz, and 1 MHz. The arrow in figure indicates the broad transition above the peak temperature T_p of the real part of the dielectric constant.

temperature. Applying the VF law to fit the experimental data of 90 Mrad in Fig. 6(d), we obtain the results of $T_f = 51.86\,°C$, $f_0 = 40.78\,MHz$, and $U = 0.00507\,eV$, as shown in Fig. 7(a). And the fitting data for 120 Mrad are $T_f = 54.08\,°C$, $f_0 = 25.12\,MHz$, and $U = 0.00409\,eV$, which are shown in Fig. 7(b). It can be seen that the experimental results are well fitted by the VF law. As the dose increases, the freezing temperature T_f increases, while the f_0 and U decrease.

In P(VDF–TrFE) copolymers, electron irradiation can induce several types of defects in the crystalline region, some of which act as random fields to the dipoles in the crystalline regions[26,27] and there are irregular changes in the interchain and intrachain spacings due to the presence of those defects, resulting in a random interaction between dipoles and limiting of the growth of the polar region. Therefore, the system can be regarded as a dipolar glass.[23,28] The observed VF behavior for copolymers in the dose range from 90 to 120 Mrad can be interpreted as a direct consequence of freezing of the system into the polar glass state. It is believed that a broad distribution in the crystallite size and reduction in the crystal ordering are responsible for the relaxor ferroelectric behavior observed in the irradiated P(VDF–TrFE) copolymer films, which are caused by the lattice defects, crosslink-
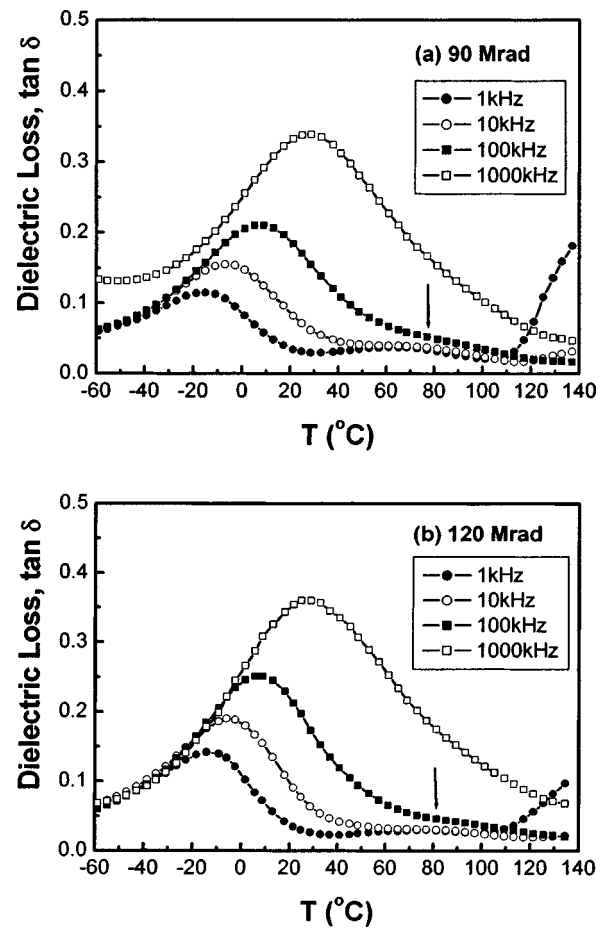
ing within the crystalline regions and at the crystalline–amorphous interface. It is also widely accepted that the frequency dispersive dielectric characteristics of the relaxor ferroelectric ceramics are mainly due to the nanometer-size polar regions. By analogy, it is supposed that the irradiated copolymer films contain polar regions of different sizes, and the distribution of both the size and polarization strength of these polar regions cause the diffuse dielectric response with frequency. The influence of small polar region plays an important role in the RFE transition. It might also be the reason for the high electrostrictive constant response observed in the irradiated films.

It is interesting to note that a broad transition was observed at a temperature above the peak temperature T_p of the real part of the dielectric constant, as indicated by an arrow in Fig. 8 for copolymer films with the doses of 90 and 120 Mrad, respectively. As the frequency increases, this small transition disappears at high frequency (>1 MHz). Such behavior was also experimentally observed in electron-irradiated P(VDF–TrFE) 68/32 mol % with lower doses, which is quite similar to what is observed in inorganic materials in which a spontaneous RFE to ferroelectric transition was observed.[23,29] It can be interpreted that this broad transition above T_p is another typical characteristic of the tran-
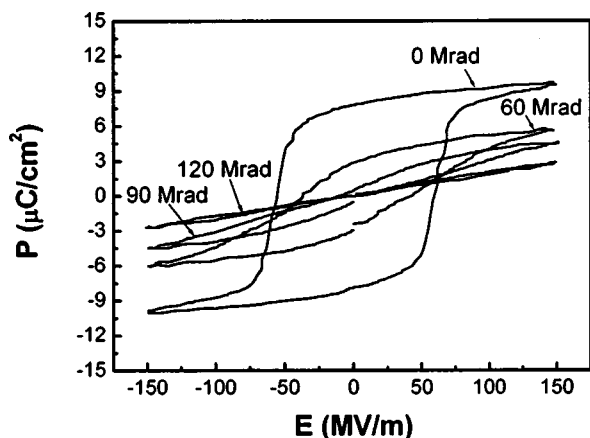
FIG. 9. Polarization hysteresis loops measured at room temperature for copolymer films with different doses of 0, 60, 90, and 120 Mrad. The electric field is a sinusoidal wave with amplitude of 150 MV/m at 10 Hz.

sition between RFE and normal ferroelectric observed in these irradiated P(VDF–TrFE) copolymers with a high VDF content. For P(VDF–TrFE) 80 mol % copolymers in this study, a higher defect concentration will be needed to transform them from the normal ferroelectric to a RFE.

D. Polarization hysteresis loop

The polarization hysteresis loop was measured at room temperature for copolymer films irradiated with different doses as shown in Fig. 9. A square shaped hysteresis loop was obtained in unirradiated films with a relative large remanent polarization P_r and coercive filed E_c. The defects induced by high-energy electron irradiation in the irradiation process such as the pedant groups and crosslinkings also reduce the stability of the ferroelectric state.[30] In comparison to unirradiated film, the irradiated ones exhibit hysteresis with a reduced remanent polarization and coercive field. It can be seen that a relatively slim hysteresis loop was observed in the irradiated copolymer films with the dose of 90 Mrad, indicating the features resembling RFE behavior obtained in a low VDF content of vinylidene fluoride and trifluoroethylene copolymers. At a high dose (120 Mrad), the hysteresis loop becomes nearly a line with zero P_r and E_c. Because of the conversion of the crystallites to amorphous phase, the decrease of the crystal ordering can be interpreted by the lattice defects and reduction of the crystallinity in irradiated copolymer films. It can be explained that the reduction of the size of polarization regions leads to the reduction of the energy barrier associated with the slim polarization hysteresis loops.

IV. SUMMARY

It is found that the high-energy electron irradiated poly-(vinylidene fluoride–trifluoroethylene) 80/20 mol % copolymers change from a typical ferroelectric to a RFE as the irradiation dose increases. The x-ray data show that the irradiation induced a two-phase coexistence between the polar and nonpolar phase in the crystalline regions, leading to a nanosized coherent region in the irradiated copolymer films. The results of DSC show that both the ferroelectric-to-

paraelectric ($F-P$) and melting temperatures decrease after irradiation, associating with the reduction of enthalpy with the increased dose, which reflects significant changes in $F-P$ phase transition due to the effect of high-energy electron irradiation. The polarization hysteresis loops revealed the reduction of remanent polarization P_r and coercive electric field E_c due to the reduction of crystallinity and stability of ferroelectric state. In a lower electron dose below 90 Mrad, no obvious RFE behavior was found due to the high VDF content (80 mol %). However, copolymers irradiated with dose between 90 and 120 Mrad show a typical relaxor ferroelectric response, whose shift in the dielectric constant peaks obey the VF law. As the dose increases, the freezing temperature T_f increased while the activation energy U and relaxation frequency f_0 decreased assuming in this dipole glass system.

Data presented in this work can be used in the design of electromechanical devices employing these irradiated P(VDF–TrFE) 80/20 mol % copolymers. Giant strain response could be obtained and a tunable piezoelectric constant can be induced in these copolymers under different dc electric bias fields. Further investigations in using the irradiated P(VDF–TrFE) 80/20 mol % copolymers in various applications such as ultrasonic transducers and actuators are in progress and will be reported in the future.

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