Structural Changes and Transitional Behavior Studied from Both Micro- and Macroscale in the High-Energy Electron-Irradiated Poly(vinylidene fluoride−trifluoroethylene) Copolymer

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ABSTRACT: The microstructural changes in high-energy electron-irradiated poly(vinylidene fluoride−trifluoroethylene) 68/32 mol % copolymer have been studied by X-ray diffraction, FTIR spectroscopy, and differential scanning calorimetry. The macroscopic polarization response in these materials was investigated by examining the dielectric and polarization behavior in a broad temperature and frequency range. It was found that besides reducing crystallinity in the copolymer film, irradiation produces significant changes in the ferroelectric-to-paraelectric phase transition behavior. The irradiation leads to a reduction in the polar domain size to below a critical size (a few nanometers), resulting in the instability of the macroscopic ferroelectric state and transforming the structure of the crystalline region in the copolymer from a polar all-trans ferroelectric to a nonpolar state represented by a trans−gauche conformation. However, a reentrant polarization hysteresis was observed in the copolymers irradiated with higher doses (>75 Mrad). Therefore, there is an optimized dose that generates a copolymer with a nonpolar structure but relatively high crystallinity whose electromechanical performance is the best. In the copolymers in this optimum dose range, FT-IR data revealed that there is not much change in the molecular conformation with temperature, even as the temperature passes through the dielectric peak, indicating that there is no symmetry breaking in both the macroscale and local level. Although the lattice spacing of the crystalline region along the molecular chain direction discontinuously changes between two special cases, the interchain spacing continuously changes with the irradiation dose, reflecting a strong intrachain coupling between the nonpolar and polar regions. On the other hand, the X-ray data reveal that the crystalline size perpendicular to the polymer chain does not change with irradiation until at doses exceeding 85 Mrad.

I. Introduction

High-energy irradiation has been practiced widely to modify the properties of polymeric materials.[1,2] The effect of high-energy irradiation on the piezoelectric properties, crystal structures, and polymer morphology of poly(vinylidene fluoride−trifluoroethylene) (P(VDF−TrFE)) copolymers has been investigated quite extensively.[2] For instance, Lovinger observed the polymorphic transformation in P(VDF−TrFE) copolymers under high-energy electron irradiation, where the ferroelectric β-phase is converted to a paraelectric-like structure.[3] In addition, he found that the dosage required for this transformation increases with the VDF content in the copolymer, which was interpreted as arising from the increased close packing between the polymer chains in the copolymers with increased VDF content. In addition to the polymorphic transformation, irradiation also causes the conversion from the crystalline to amorphous phase due to cross-linking. At very high doses, the copolymer becomes totally amorphous. Macchi et al. also observed the disappearance of the ferroelectric phase in the copolymer due to irradiation and the transformation of the dielectric behavior from a strong first-order ferroelectric−paraelectric (F−P) transition peak to a broad dielectric peak at ambient temperatures much below the original F−P transition temperature in unirradiated copolymers.[4,5] The observed broad dielectric behavior in the irradiated copolymers was suggested to be an indication of a ferroelectric spin glass state.[6]

More recently, we reported that P(VDF−TrFE) copolymers with VDF contents below 70 mol % exhibit a slim polarization hysteresis loop at room temperature, following high-energy electron irradiation. Furthermore, because of the large magnitudes of conformational motions accompanying the interconversion between the all-trans (polar-phase) and trans−gauche (nonpolar phase) states, the electric-field-induced reversible polarization change results in a very high electrostrictive strain (∼5%, Figure 1a) and a high strain energy density, as well as a much improved electromechanical efficiency.[7−9]

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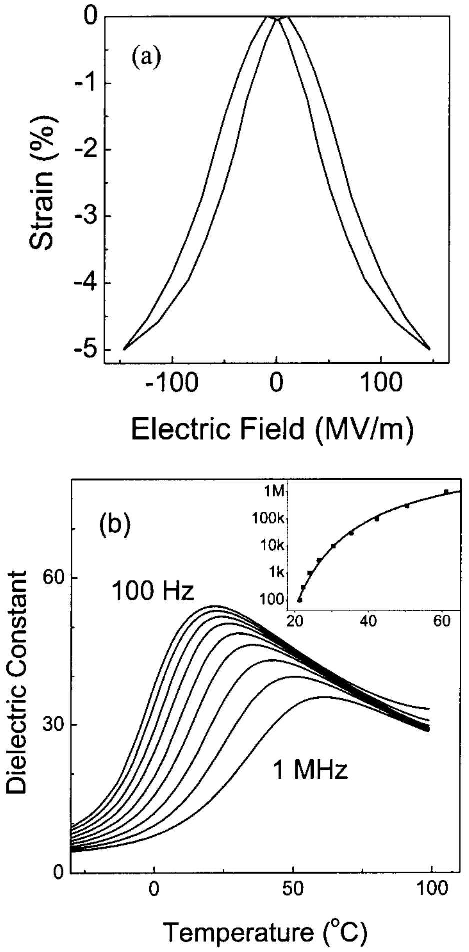

Figure 1. (a) Longitudinal strain response vs electric field (1 Hz) observed in electron-irradiated 68/32 copolymer films at room temperature. (b) Temperature dependence of the dielectric constant at frequencies of 100, 300, 1K, 3K, 10K, 30K, 100K, 300K, and 1 MHz for stretched 68/32 film irradiated at 100 °C with 75 Mrad dose. Inset is the measured relationship (square) between the frequency and dielectric constant peak temperature and the fitting results (solid line) using the Vogel−Fulcher relationship.

In addition, in a detailed study of dielectric and polarization behavior, it was shown that the irradiated copolymer exhibits a Vogel−Fulcher type dielectric relaxation as shown in Figure 1b,

$$f = f_0 \exp\left[\frac{-T_0}{T_m(f) - T_f}\right]$$

where f is the measuring frequency, $T_m(f)$ is the corresponding dielectric peak temperature, T_0 and f_0 are constants, and T_f is often regarded as the freezing temperature of a dipolar system (if the system is a dipolar glass). At temperatures below T_f, a ferroelectric state can be induced by a high electric field, while the remanent polarization increases gradually as the temperature is lowered. These features are very similar to those observed in inorganic relaxor ferroelectrics, and hence, the irradiated copolymer can be regarded as a polymeric relaxor ferroelectric, a “polar glass” system.[7,10,11]

In this paper, we will discuss in detail the microstructural changes occurring in this class of materials and the effects of irradiation-induced defects on the polar domains and crystallite sizes. As reported recently, the copolymer with a VDF/TrFE ratio of 68/32 mol % exhibits the best electromechanical performance at room temperature after irradiation.[8,9] Thus, we devote the current paper to a discussion of the macroscopic polarization responses and thermodynamic behavior of this composition in light of our analysis of its polarization, dielectric properties, and DSC data. It must be pointed out that although the macroscopic properties of the irradiated 68/32 copolymer were observed to exhibit similar trends to those of the 50/50 copolymer studied earlier, a detailed study the 68/32 mol % composition was considered desirable to compare the material and microstructural properties of these two compositions and to provide a conceptually improved picture of relaxor behavior in polymers.

With regard to the structural characterization, in an X-ray diffraction study to be described in this paper, a (110, 200) peak was observed at room temperature and at a temperature exceeding the Curie temperature. (Previously in the irradiated 50/50 copolymer this peak was recorded only at room temperature.[13]) These data lead to (1) a clearer picture of the microchanges in crystalline sizes and lattice spacings perpendicular to the chain direction and to (2) an improved understanding of the effects of irradiation-induced defects. More importantly, an X-ray diffraction (001) peak in the present study was analyzed to delineate the irradiation effect on the crystal size along the molecular chain direction and on the molecular conformations. The conformational changes were further confirmed by means of a Fourier transform infrared spectroscopic (FT-IR) study. When the results of the structural analysis are considered along with the macroscopic properties, a more refined picture emerges that describes the nature and role of the irradiation-induced defects.

II. Experimental Section

P(VDF−TrFE) copolymer at the composition 68/32 mol % was chosen for this investigation. Among all the compositions investigated, this composition exhibits the highest room temperature electrostrictive responses. This is a result of the competition between the strain achievable in the copolymer due to conformational changes, which become large with VDF content, and the electron dose required to convert the copolymer into an electrostrictive material, which also increases with VDF content.[12] Increased electron dose will cause a large reduction in the crystallinity and as well as an increase in cross-linking density. These structural changes are detrimental to the electrostrictive strain.

The copolymer films used in this investigation were fabricated by solution casting and then uniaxially stretched at room temperature to 5 times of the original length. The thickness of films was in the range between 15 and 30 μm. The films were annealed before irradiation to improve the crystallinity. The irradiation was carried out in a nitrogen atmosphere at 100 °C with an electron energy of 1.2 MeV. It was found that irradiation at a temperature higher than the F−P transition reduces the doses needed to eliminate the room temperature polarization hysteresis and to achieve high electrostrictive strain. This could be due to increased chain mobility in the paraelectric phase, facilitating the polymorphic transformations. The irradiation was carried out in a dose range from 0 to 1.75×10^6 Gy. To stay consistent with our previous publications, the unit of dose used here is rad and Mrad (1 Mrad = 10^6 rad and 1 Gy = 100 rad).

The X-ray experiments were performed at the National Synchrotron Light Source beam line X18A of the Brookhaven National Laboratory (the X-ray wavelength was 1.2399 Å). The (200, 110) peak reported here was obtained using the reflection scan, while the (00*l*) peak was obtained using the transmission scan. The FT-IR spectra at room temperature were obtained using a BIO-RAD WIN Fourier transform IR spectrophotometer in the spectral region 4000−400 cm^{-1}. The high-temperature FT-IR spectra were measured using a high-temperature optical cell. The DSC data were taken with a scan rate of 10 or 20 °C/min using (TA Instruments, DSC2920). Gold-sputtered electrodes were used on films used for the characterization of the polarization responses. The dielectric properties as a function of the temperature of the films were measured with a LCR meter (HP 4284A) equipped with a temperature chamber with a scan rate of 2 °C/min. The polarization hysteresis loops were acquired by a computer-controlled automatic system based on the Sawyer−Tower circuit.

III. Results and Discussion

3.1. Polarization Responses and Transitional Behavior in Copolymers with Different Doses. The polarization hysteresis loops measured at room temperature at 1 Hz for the copolymer films treated with different doses are presented in Figure 2a. The maximum induced polarization under 150 MV/m field P_s, the remanent polarization P_r, and coercive field E_c extracted from the polarization loops are summarized in Figure 2b. The data show a slow and continuous decrease of P_s with irradiation dose, a trend related to the conversion of the normal ferroelectric state into a nonpolar state and the reduction of the crystallinity in the polymer, as has been discussed in an earlier publication.[8] In contrast, a large drop in both E_c and P_r with dose is prominent, especially in the dose range between 35 and 70 Mrads. As a result, the sample irradiated with 75 Mrad exhibits the highest electrostrictive strain yet it displays only minor hysteresis. Interestingly, beyond 75 Mrad, there is an increased polarization hysteresis (reentrant hysteresis). In some of the samples irradiated with 100 Mrad dose, this reentrant hysteresis can be quite large as illustrated in Figure 2c. One possible cause for the observed reentrant hysteresis (ferroelectricity) is the high cross-linking density in the polymer irradiated with high doses.[13−15] Two cross-linking points located in close positions along the chains force a closer packing of the polymer chains in between, favoring the all-trans conformation and formation of small polar pockets. This reentrant behavior is also observed in X-ray data presented below.

The evolution of the dielectric behavior with irradiation dose is shown in Figure 3, which exhibits trends similar to those observed in Figure 2. For instance, the peak temperature associated with the original F−P transition decreases with dose, indicating the weakening of the F−P transition; above 75 Mrad, it moves up slightly. For doses below 35 Mrad, the transition peak is still relatively sharp and exhibits thermal hysteresis. That is, the peak position measured during a heating scan is different from that during a cooling scan, an indication of a first-order transition. For samples irradiated with doses above 35 Mrad, the dielectric peak broadens and thermal hysteresis disappears. As will be shown from the FT-IR data, in samples irradiated with doses near 70 Mrad, the broad dielectric peak actually does not correspond to a phase transition, but the polymer remains in a nonpolar phase even at temperatures far below the dielectric peak, reminiscent of the relaxor ferroelectric behavior in ceramics.

Interestingly, using the dielectric data, we found that the Vogel−Fulcher law can, in fact, be used to fit the change of the dielectric peak temperature with frequency, even for the unirradiated copolymer, which is a typical normal ferroelectric. This observation supports an early theoretical result by Tagantsev that the Vogel−Fulcher dielectric behavior can also be observed in a dielectric system with a broad dielectric relaxation distribution that broadens gradually with decreasing

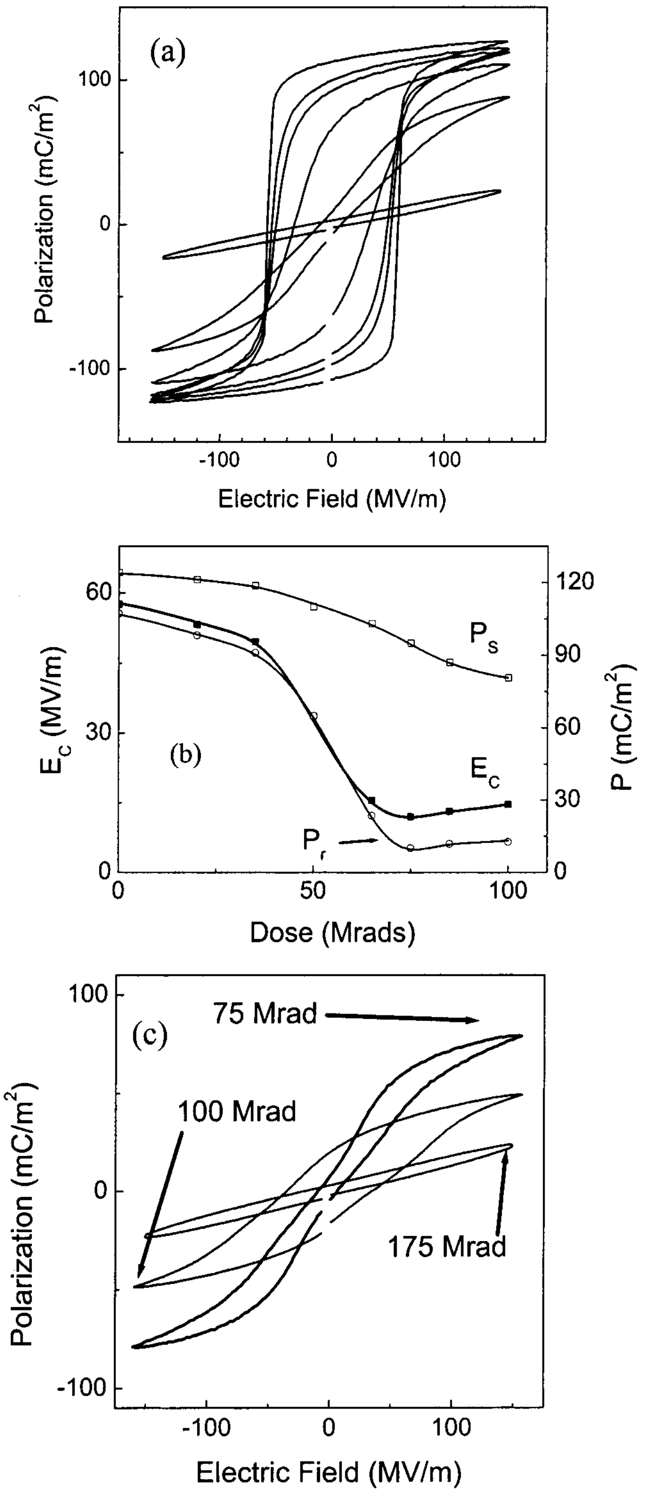

Figure 2. (a) Polarization hysteresis loops measured at room temperature and 1 Hz for copolymer films irradiated with different doses. For the polarization level from high to low, the corresponding dose is 0, 20, 35, 50, 75, and 175 Mrad, respectively. (b) Spontaneous polarization P_s, permanent polarization P_r, and coercive field E_c vs irradiation dose, where P_s, P_r, and E_c were measured at room temperature and 1 Hz using an electric field with an amplitude of 150 MV/m. (c) Polarization hysteresis loops for films irradiated with 75, 100, and 175 Mrad.

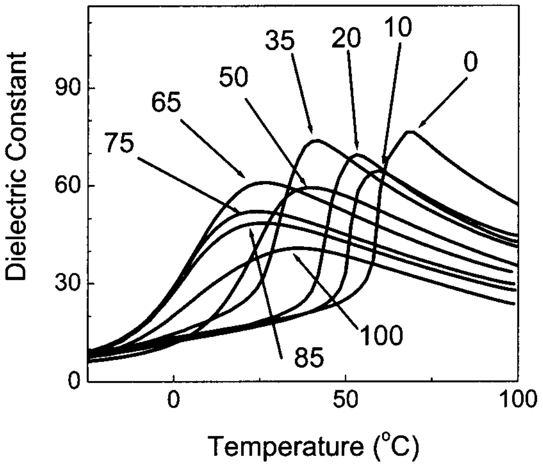

Figure 3. Temperature dependence of dielectric constant at 1 kHz measured during cooling of irradiated copolymers. The irradiation doses in Mrad are indicated in the figure.

temperature.[16] The gradual freezing of a dipolar system with temperature is not a necessary condition for the presence of Vogel−Fulcher dielectric behavior.

DSC data for the irradiated copolymers are summarized in Figure 4 (acquired during heating of the samples). The data show that in general both the peak temperature and the enthalpy of the melt decrease with dose, due to the decrease in crystallinity and reduced crystalline ordering in the polymer, except for the samples irradiated at 10 Mrad. The melt enthalpy of the copolymer irradiated with the 10 Mrad dose is actually higher than that without irradiation, implying an increase in the crystallinity. Such an increase in crystallinity with irradiation had been observed earlier and is probably caused by chain scission in the copolymer allowing for an increase in the chain mobility and hence the crystallinity.[17] At higher doses, the cross-linking becomes dominant with a reduction in crystallinity.[13−15]

The peak associated with the original F−P transition of the unirradiated sample changes with dose quite remarkably, which is in sharp contrast with the behavior of the melt transition. For samples irradiated with doses above 50 Mrad, the F−P transition peak almost disappears, and the temperature of the very weak F−P transition changes only to a minor extent with dose (Figure 4b,c). In addition, the peak temperature from DSC data (~45 °C) for the copolymers irradiated in this dose range is higher than the temperature of the broad dielectric maximum (~20 °C), suggesting that the two are associated with different phenomena. It is likely that the weak DSC peak observed here originates from the small residual polar regions in the copolymer, while the dielectric maximum results from the collective dipole responses and thus involves relatively long-range dipolar motions.

3.2. Structure Changes on the Micro- and Mesoscales. 3.2.1. Evolution of Crystal with Dose As Revealed by Room Temperature X-ray Data. X-ray data were obtained for copolymers irradiated with different doses, including diffraction peaks perpendicular and parallel to the polymer chains, to follow structural changes in both directions. The data from the (110, 200) diffraction peak, which are due to changes in polymer interchain spacing and ordering perpendicular to the chains in the crystalline regions, are presented in Figure 5. The corresponding data for the (00*l*) diffraction peak, which arise from the dimensional changes of unit cell along the polymer chain, are presented in Figure 6. Both data sets were acquired at room temperature.

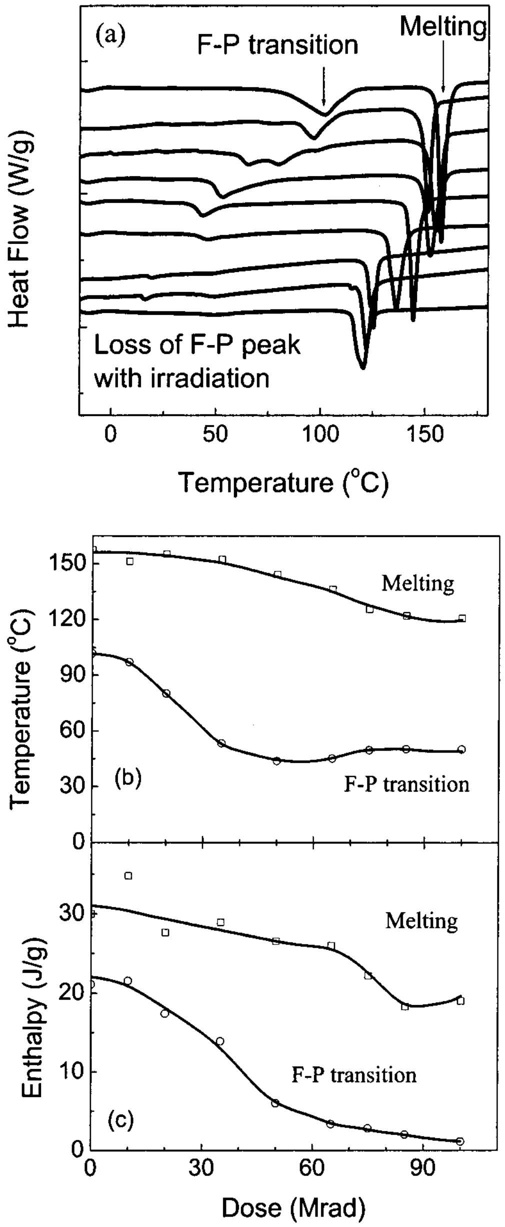

Figure 4. (a) DSC data collected by heating irradiated copolymer from −40 to 200 °C. From top curve to bottom curve, the corresponding doses are 0, 10, 20, 35, 50, 65, 75, 85, and 100 Mrad, respectively. (b) Melt temperature and F−P transition temperature. (c) Melting enthalpy and phase transition enthalpy for copolymer irradiated with different doses.

The crystalline phase of P(VDF−TrFE) copolymers has an orthorhombic unit cell in which the *c*-axis is parallel to the polymer chain.[18] Because the ratio of the lattice constants of the unit cell along the "*a*" and "*b*" axes (perpendicular to the chains) is close to $\sqrt{3}$, the lattice has a quasi-hexagonal structure, resulting in the overlap of the (110) and (200) reflections.

We first discuss the X-ray data from the (00*l*) reflection. Clearly, there are two peaks at $2\theta = 28.29°$ and $2\theta = 31.53°$. The peak at $2\theta = 28.29°$ (corresponding to a lattice space of 0.2537 nm) originates from the (001) reflection in the ferroelectric (F) phase, while the peak at $2\theta = 31.53°$ (corresponding to a lattice space of 0.4564

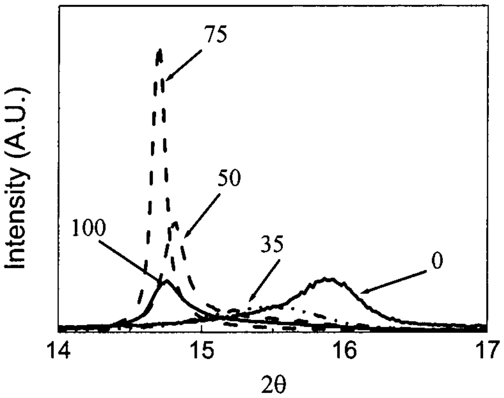

Figure 5. The (200, 110) diffraction peak observed at room temperature using the reflection scan for copolymer films irradiated with different dose. The number in the figure expresses the dose in Mrad.

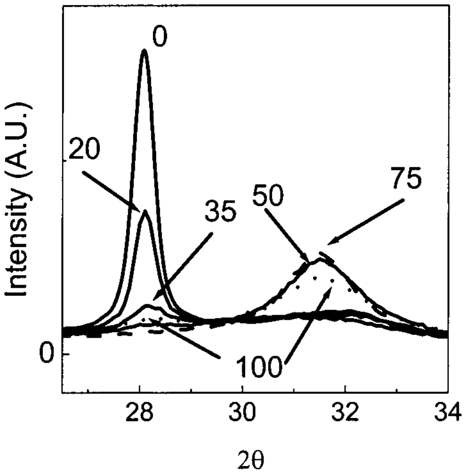

Figure 6. The (001) diffraction peak observed at room temperature using the transmission scan for copolymer films irradiated with 0, 20, 35, 75, and 100 Mrad.

nm) originates from the (002) reflection in the nonpolar (NP) phase, i.e., the paraelectric α-phase or δ-phase.[18,29] The data from the (00*l*) reflection (Figure 6) demonstrate quite clearly that the polymorphic transformation caused by irradiation is a first-order process between the F and NP phases. That is, the intensity of the (001) peak in the F phase decreases while the intensity of the (002) peak in NP phase increases with dose. There are two features that should be noted here: (i) Although there is a large variation in the peak intensity for the F and NP phases as the dose changes, the peak position remains nearly the same for all the doses. (ii) The evolution of the F phase peak with dose also displays a reentrant behavior. Initially, as the dose increases, the peak intensity decreases until a dose of 75 Mrad is reached, at which point the sample shows very little sign of the presence of a F phase peak. Beyond 75 Mrad, there is a gradual increase in the peak intensity for the F phase. This reentrant behavior is consistent with observations from polarization loops and dielectric data for the same doses.

By employing the Scherrer equation, the size of the coherent X-ray reflection region D_{hkl} can be estimated,[19]

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

where λ is the X-ray wavelength, B is the full width at half-maximum (fwhm) of the reflection peak (*hkl*), and θ is the peak position. In the F phase, the coherent X-ray reflection region is determined by the polarization domain size; in the NP phase, it corresponds to the crystallite size. In Figure 7a, we plot D_{001} for the F phase and NP phase measured for samples treated with different doses. Before irradiation, the polar domain size of the F phase along the *c*-axis is about 15 nm. This value decreases with dose, due to the defects introduced by the irradiation, which break up the polarization coherence. In samples irradiated with a dose of 35 Mrad, D_{001} for the F phase is reduced to 10 nm; for samples treated with doses beyond that, the peak intensity of the F phase drops precipitously. The NP phase peak is visible even in samples irradiated with very low doses, a result that can be attributed to the domain boundary region and can account for its broad appearance. In samples treated with doses higher than 50 Mrad, the NP phase peak dominates; the coherent crystallite size along the polymer chain for this phase is about 5 nm, which is much smaller than that in the F phase.

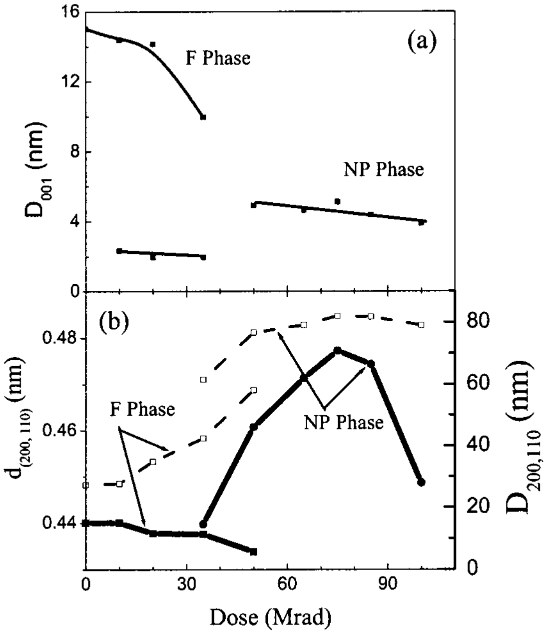

Figure 7. (a) Irradiation dose dependence of crystallite size D_{001} parallel to the molecular chain at room temperature. (b) Dose dependence of crystalline size $D_{200,110}$ (solid line) and interchain spacing $d_{(200\ 110)}$ (dotted line) measured at room temperature. The data indicate a lattice expansion perpendicular to the chain and contraction along the chain, respectively, in the dose range from 0 to 50 Mrad.

In contrast, the X-ray data from the (110, 200) reflection, which results from changes of the lattice parameters with doses perpendicular to the polymer chains, show a markedly different evolution behavior. First, the data do not display a clearly defined two-peak pattern. Furthermore, the X-ray peak position changes continuously with the irradiation dose. For instance, from 0 to 35 Mrad, the peak at the original F phase moves to a lower angle, indicating a continuous expansion in the interchain dimension as shown in Figure 7b. Concomitantly, there is a reduction of the ferroelectric domain size from 15 to 7.5 nm. The expansion in the interchain dimension and the reduction of the ferroelectric domain size with the dose in this range indicate that the surface of ferroelectric domain changes to a NP phase. At 35 Mrad, the existence of the NP phase can be observed in the X-ray data as shown in Figures 5 and 7b. As the dose increases from 35 to 50 Mrad, the peak position moves to that of the NP phase, indicating that the crystal now is predominantly nonpolar. Consistent with this shift in the peak position, the (110, 200) peak width also shows a large reduction, because of the disappearance of the ferroelectric domains. In any case, at 50 Mrad, there are still some ferroelectric domains with very small sizes as shown in Figure 7b. For doses beyond 50 Mrad, there is only a negligible variation in the peak position. Meanwhile, in the same dose range, the peak width of the (110, 200) reflection decreases continuously until near 75 Mrad, where $D_{110,200}$ reaches 70 nm, which is close to the crystallite size measured in the paraelectric phase, as will be shown in the next section. Increasing the dose to 100 Mrad causes a further reduction of $D_{110,200}$ to about 26 nm, caused by the reduction of the crystallite size due to increased cross-linking density.

The results show unequivocably that the ferroelectric domain size in unirradiated samples is nearly isotropic (~15 nm). In P(VDF−TrFE) copolymers, the lattice symmetry dictates the polarization direction between neighboring domains in angles of 60°, 120°, and 180°.[20] For a ferroelectric material in equilibrium, the domain size is determined by the domain wall energy, coupling between domain walls, and crystallite size.[21,22] In the polymers investigated here, because of the high nucleation barriers and the high defect concentrations, we believe that the domain size is controlled mainly by defects in the crystallites and the crystallite−amorphous boundary conditions, which can also be regarded as defects. Therefore, with increased doses, the concentration of defects (such as chain ends and pendant groups generated by chain scission) in the crystallites also increases, resulting in the observed reduction of the polarization domain size. Eventually, as the domain size is reduced to a value below a certain critical size, the macroscopic polarization state becomes unstable with respect to the nonpolar phase, leading to the disappearance of the macroscopic polarization. From the data here, it is not clear that the domain size, whether along or perpendicular to the polymer chain, or both, determines this critical size. From the strong intrachain coupling as well as the recent experimental results on the presence of a two-dimensional ferroelectric state in P(VDF−TrFE) films of a few molecular layers thick,[23] it seems reasonable to assume that the polar domain size along the polymer chain may play a more important role.

3.2.2. Temperature Dependence of X-ray Data for Copolymers with Different Doses.

Presented in Figure 8 are typical X-ray data taken from the (110, 200) reflections as a function of temperature for copolymers irradiated with different doses (0, 35, 50, and 75 Mrad). The data from samples irradiated with a 0−35 Mrad dose show a first-order F−P transition with temperature (two-phase coexistence region). In the nonpolar phase, the X-ray peak width, which becomes quite narrow, is determined by the coherent X-ray scattering region or approximately by the crystallite size along the ⟨110, 200⟩ direction. It is interesting to note that the peak width of the paraelectric phase (nonpolar phase) is nearly the same as that measured at room temperature in copolymers irradiated with 65−85 Mrad doses. This is consistent with the fact that the NP phase is dominant in polymers in that dose range. In samples irradiated at 50 Mrad or higher doses, a transition is not observed, and the lattice constant exhibits a typical thermal expansion curve of the nonpolar phase.

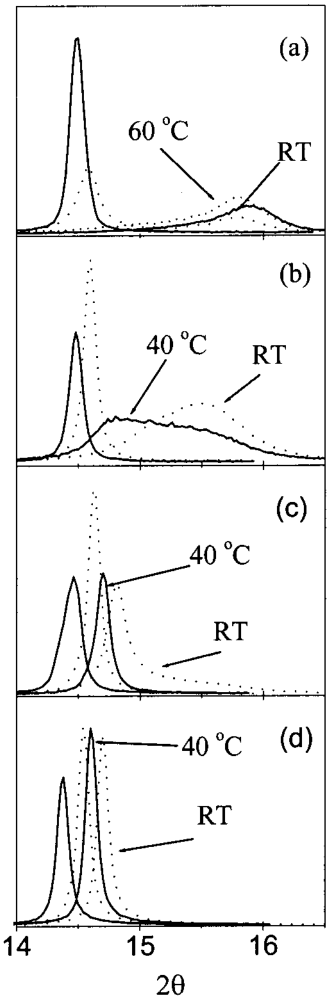

Figure 8. The (200, 110) diffraction peak observed at different temperatures using the reflection scan for unirradiated film (a) (solid line, 110 °C; dotted line, 90 °C; 60 °C and RT data are indicated) and irradiated films with different doses (solid line, 90 °C; dotted line, 60 °C; RT and 40 °C data are indicated in the figure): (b) 35 Mrad dose, (c) 50 Mrad dose, and (d) 75 Mrad dose. "RT" is room temperature.

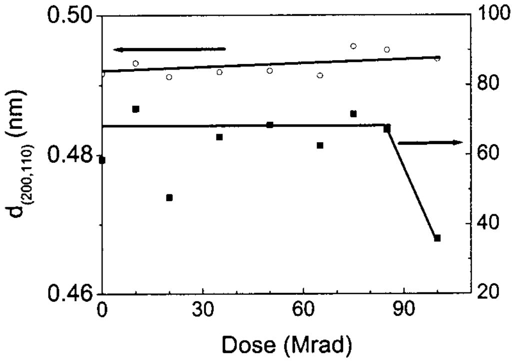

Figure 9. Dose dependence of crystalline size $D_{200,110}$ and interchain spacing $d_{(200,110)}$ measured at high temperature (nonpolar phase).

The data also show that the crystallite size perpendicular to the polymer chain is not affected by the irradiation until above 85 Mrad (Figure 9). On the other hand, the crystallite size parallel to the chain is reduced by the irradiation even at doses far below. For example,

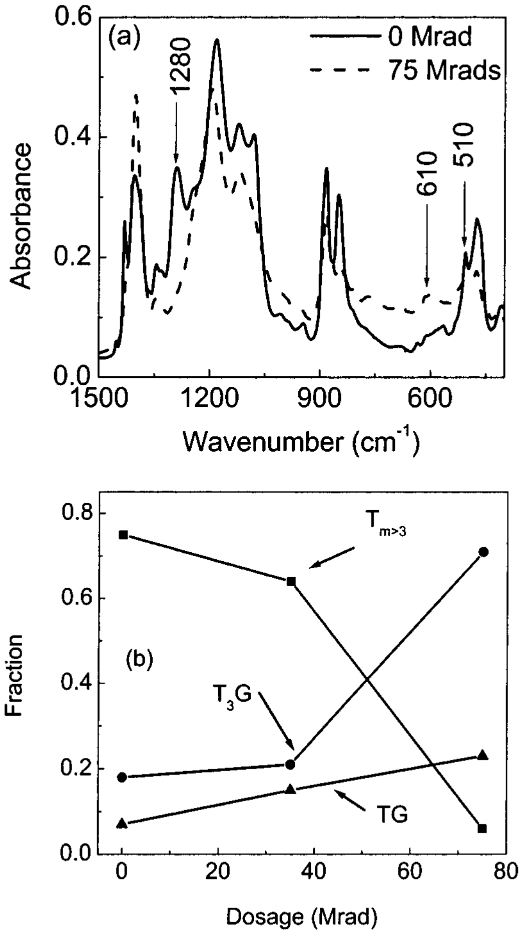

Figure 10. FTIR data of P(VDF−TrFE) 68/32 copolymer film at room temperature. (a) Spectrum for stretched film before irradiation and stretched film irradiated at 100 °C with 75 Mrad using 1.2 MeV electrons. (b) Fraction of different conformations in film vs irradiation dose.

above 75 Mrad and at room temperature, the copolymer is in the nonpolar phase; therefore, the X-ray peak width should be that defined by the crystallite size. This is exemplified in Figure 7 where D_{001}, which is the crystallite size along the ⟨001⟩ direction, is about 5 nm. This is much smaller than that of the ferroelectric domain size in the copolymer before irradiation.

3.2.3. Conformational Changes with Dose and Temperature. The FT-IR spectra obtained on copolymers irradiated at different doses measured at room temperature are shown in Figure 10a (dose = 0, 35, and 75 Mrad). To quantify the conformational change with dose, we focus on three absorbance peaks at 1288 cm^{-1} for the long trans sequence ($T_{m>3}$), 614 cm^{-1} for the trans−gauche (TG), and 510 cm^{-1} for the T_3G conformations, which are due to the vibration of the CF_2 group.[24] Before irradiation, the spectrum is characterized by a strong absorbance peak at 1288 cm^{-1}, which diminishes with irradiation dose. In Figure 10b, we present a summary of the change of the three conformations with dose, extracted from the data in Figure 10a. In the extraction process, each absorbance peak was fitted to a Lorentzian shape. To account for possible variations in the sample thickness and therefore the absorbance, an internal standard (at 3022 cm^{-1}, which is the asymmetric stretching vibration of C−H bond) was used to calibrate those absorbance peaks of interest.[25] The fraction of each conformation can be calculated (data in Figure 10b) following the method of Osaki et al.,[26]

$$F_i = \frac{A_i}{A_{\mathrm{I}} + A_{\mathrm{II}} + A_{\mathrm{III}}}$$

where i = I, II, III, and A_{I}, A_{II}, and A_{III} are the absorbances of crystal forms I, II, and III, i.e., with all-trans ($T_{m>3}$), T_3GT_3G', and $TGTG'$ sequences, respectively. F_i is the fraction of chain conformation i. Prior to irradiation, the conformation of the samples is predominantly all-trans because of the ferroelectric nature of the material. The absorption bands are due to small concentrations of TG and T_3G conformations in the domain boundary regions and as well as in the interphase regions between the crystallite and amorphous phases, as has been observed in the X-ray data. The trends in the conformational changes with dose are very similar to those observed in the X-ray data. All three conformations exhibit slow changes with doses below 35 Mrad, but at higher doses, large changes occur. For example, at 75 Mrad, the all-trans conformation disappears and is replaced by T_3G conformations randomly mixed with TG conformations, consistent with the X-ray results that demonstrate that the crystallite is in the NP phase.

Prior to irradiation, there is a large and relatively sharp change in the chain conformation in P(VDF−TrFE) copolymer due to the phase transition from a nonpolar phase to a polar phase as the temperature is lowered through the F−P transition. However, for relaxor ferroelectrics, extensive investigations such as Raman scattering experiments carried out on inorganic materials have shown that there is a gradual increase of the population of micropolar regions as the temperature is reduced.[27] In other words, there is a local symmetry breaking from the nonpolar to polar ordering even though macroscopically the sample remains nonpolar.[28] Now the question is whether a similar explanation applies to the irradiated copolymer. To examine this question, we consider the data showing the conformational changes as the temperature is varied for the three samples under different dose treatments (Figure 11). In the unirradiated samples, the absorbance peak intensity remains nearly constant at temperatures below 70 °C. The data point at 100 °C suggests a transition to the nonpolar phase, as indicated by the drop of the peak intensity due to the all-trans conformation and the increase in peak intensities attributed to the T_3G and TG conformations.[29] In samples irradiated with a 35 Mrad dose at 100 °C, the chain conformation is mainly T_3G, and there is very little indication of the all-trans conformation (the polar conformation). As the temperature is reduced, the all-trans conformation increases nearly linearly until 30 °C. This can be compared with the dielectric data where a weakly first-order transition was observed to begin at about 30 °C.

In contrast, in the sample irradiated with 75 Mrad at temperatures above 30 °C, there is no suggestion of the all-trans conformation, although a small increase of the all-trans chain conformation is seen at lower temperatures, coinciding with the Vogel−Fulcher temperature, T_f. This behavior contrasts sharply with that observed in samples not exposed to irradiation as well as samples irradiated with 35 Mrad, demonstrating that the broad dielectric peak does not correspond to a broad phase transition between a polar and nonpolar phase.

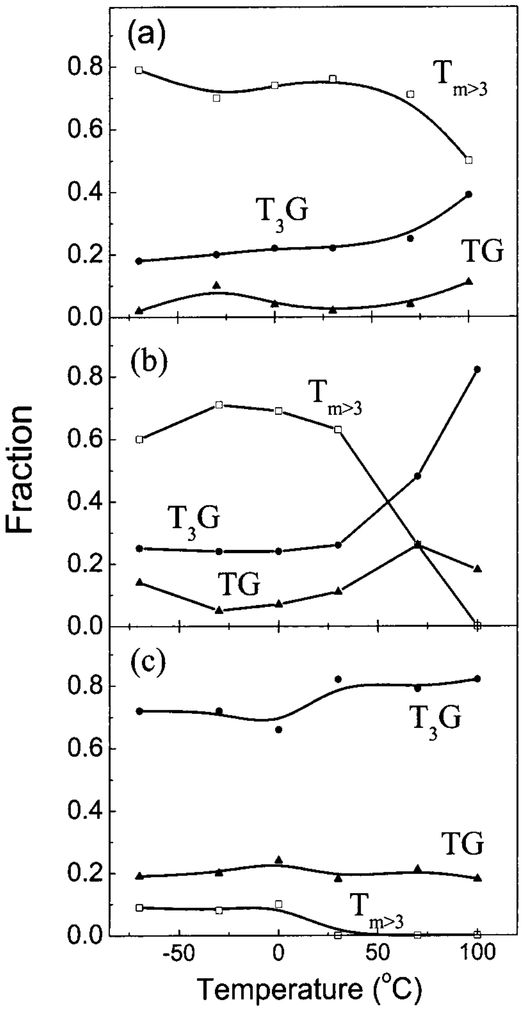

Figure 11. Temperature dependence of fractions of different conformations in stretched 68/32 copolymer films: (a) unirradiated, (b) irradiated with 35 Mrad dose, (c) irradiated with 75 Mrad dose.

Furthermore, the absence of the all-trans conformation and only minor changes in chain conformations at temperatures above the broad dielectric peak are indicative of behavior that differs from that observed in relaxor ferroelectrics in inorganic relaxor ferroelectrics, in which there is a large increase in the population of local polar regions with reduced temperature, even at temperatures far above the broad dielectric constant peak.[28]

IV. Summary

High-energy electron irradiation was carried out at 100 °C on previously solution cast and subsequently stretched P(VDF−TrFE) 68/32 mol % copolymer films, with doses from 0 to 175 Mrad using 1.2 MeV electrons. The polarization behavior of the irradiated copolymer indicates that there is an optimized dose (i.e., 75 Mrad) required to generate a slim P−E loop with relatively high polarization levels at room temperature, which describes a copolymer exhibiting the best electromechanical performance. The structural causes of this phenomenon were explored by means of X-ray diffraction, FT-IR, and DSC measurements. It was found that irradiation lowers the ferroelectric-to-paraelectric phase transition temperature and leads to the disappearance of this transition. More importantly, the irradiation transforms the structure of the crystalline regions from polar, characterized by an all-trans configuration in the molecular chains, to a nonpolar state, represented by the trans−gauche conformations in the molecular chains. However, in copolymers irradiated with higher doses (exceeding 75 Mrad), a reentrant polarization hysteresis is observed in the material, and at very high doses (∼150 Mrad), the copolymer is completely transformed into an amorphous phase, as characterized by a linear dielectric response.

The X-ray data indicate that as the dose increases, there is a gradual increase of the interchain spacing with doses from 0 to 50 Mrad, and on the other hand, the lattice constant along the chain exhibits a first-order transition process with dose (a discontinuous change between two phases), a reflection of strong intrachain coupling between the polar and nonpolar regions, and weak interchain coupling between them. Concomitant with this process, the ferroelectric domain size decreases with dose, and as the polar domain size is reduced to below a critical size (a few nanometers), the ferroelectric state becomes unstable and the crystalline region transforms into a nonpolar state (at doses above 50 Mrad). For the irradiated copolymers exhibiting slim polarization loops at room temperature (dose > 50 Mrad), the FT-IR data reveal that there is no significant change in the polymer chain conformations as the temperature passes through the dielectric maximum, consistent with the DSC data showing the disappearance of the regular F−P transition. Interestingly, the Vogel−Fulcher relationship was observed for the dielectric data even for the copolymers without much irradiation, indicating that Vogel−Fulcher dielectric behavior is not necessarily associated with the gradual freezing of a polar system.

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